Machine learning and data-driven techniques are quickly being adopted to accelerate materials research in a variety of ways. In this tutorial, we introduce material scientists to a wide variety of machine learning topics which have found utility in real-world materials research. We will review fundamental topics in machine learning, including supervised and unsupervised learning, reinforcement learning, and Bayesian techniques and optimization. We will also cover practical tools and techniques for handling experimental data, in addition to extracting the relevant information from such data to make the applications of machine learning methods possible. After the tutorial, participants will have a broad understanding of machine learning in general, as well as concrete example applications of the topics to material science problems. No previous knowledge of machine learning will be required.

10:15 AM
Supervised Learning  Daniel V. Samarov; National Institute of Standards and Technology

Regression and classification models and techniques including: regularized least squares, support vector machines, neural networks, ensemble learning, gaussian processes.

1:30 PM
Unsupervised Learning  Aaron Gilad Kusne; National Institute of Standards and Technology

Clustering, similarity measures, latent variable analysis, spectral unmixing, matrix factorization.

2:45 PM BREAK

3:15 PM
Sequential Experimental Design and Reinforcement Learning  Kristofer Reyes; University at Buffalo, The State University of New York

Bayesian optimization and experimental design, belief models, decision policies, Markov decision processes.
demonstrate the attempt towards building an inverse design problem capable of designing a poly(oxazoline) architecture based on a required cloud point. We will demonstrate how the algorithm was trained using polymers synthesized at varying levels of precision. Finally we will demonstrate the use of modern machine learning techniques which are able to correlate the various parameters describing polymer architecture, to importantly, the 3D curve does not cover all the parameters and is incapable of identifying the feature importance of the design parameters. In this paper, we show that these pathways help to bridge the gap between fundamental materials properties and structure and materials performance. This presentation will focus on how data science methods can discover new pathways for the chemical design of glasses/ ceramics as well as uncover hidden information in molecular scale structure of amorphous solids.

9:00 AM *GI01.01.02
Predicting Colloidal Crystals from Shapes via Inverse Design and Machine Learning Yina Geng, Greg v. Anders and Sharon C. Glotzer; University of Michigan, Ann Arbor, Michigan, United States.

A fundamental challenge in materials design is linking building block attributes to crystal structure. Addressing this challenge is particularly difficult for systems that exhibit emergent order, such as entropy-stabilized colloidal crystals. We combine recently developed techniques in inverse design with machine learning to construct a model that correctly classifies the crystals of more than ten thousand polyhedral shapes into 13 different structures with a predictive accuracy of 96% using only two geometric shape measures. With three measures, 98% accuracy is achieved. We test our model on previously reported colloidal crystal structures for 71 symmetric polyhedra and obtain 92% accuracy. Our findings (1) demonstrate that entropic colloidal crystals are controlled by surprisingly few parameters, (2) provide a quantitative model to predict these crystals solely from the geometry of their building blocks, and (3) suggest a prediction paradigm that easily generalizes to other self-assembled materials.

9:15 AM GI01.01.03
Machine Learning Augmented Polymer Design—Mapping the Size and Composition of Poly(Oxazolines) to Cloud Points Jatin Kumar1, Karen Tang1, Qianxiao Li2, Amibal Gonzalez Oyarce2 and Jun Ye2; 1Institute of Materials Research & Engineer, Singapore, Singapore; 2Institute of High Performance Computing, Singapore, Singapore.

It has been long suggested that present synthetic techniques of polymers afford an excessive strain on resources, and efforts should be undertaken to devise new methods to predictively design polymers based on their desired properties.[1] One of such properties include phase behavior. Phase behavior is a unique characteristic of polymers which afford interesting assemblies and microstructure of polymer solutions, blends and films,[2] which are in turn influenced by the four key fundamentals of polymer architecture: (a) topology; (b) molecular weight; (c) composition; (d) functionality. Efforts were made by Hoogenboom and co-workers[3],[4] to systematically vary composition and molecular weight for poly(oxazoline)s so as to ascertain their relationship with cloud points – a temperature dependent phase behavior. A 3D curve of best fit was obtained correlating 2 of the numerous design parameters to cloud point. However, a 3D curve is an inaccurate correlation as there is no model that suitably fits the data, resulting in a poor fit with a loss of detail. Most importantly, the 3D curve does not cover all the parameters and is incapable of identifying the feature importance of the design parameters. In this paper, we will demonstrate the use of modern machine learning techniques which are able to correlate the various parameters describing polymer architecture, to its associated cloud point. We will demonstrate how the algorithm was trained using polymers synthesized at varying levels of precision. Finally we will demonstrate the attempt towards building an inverse design problem capable of designing a poly(oxazoline) architecture based on a required cloud point.


9:30 AM *GI01.01.04

The true potential of additive manufacturing (AM) as a next-generation production technology will only be realized by synergy of automated machinery with predictive models of process and material performance. I will discuss our recent efforts to improve the performance of extrusion AM technology, including the design of a desktop system that achieves ~10X greater build rate than commercial benchmarks, implementation of feed-forward motion control algorithms to mitigate trajectory errors, and development of graph-based toolpath planning algorithms enabling continuous printing of lattice structures. In-process thermal imaging is used to calibrate toolpath planning algorithms for large-scale extrusion AM, mitigating deformation and strength loss due to local thermal gradients during printing. I will close with commentary on the opportunities and challenges toward autonomous manufacturing systems wherein AM is a cornerstone, and machine learning is an essential, yet currently primitive, component.
Toyota Research Institute (TRI) was founded in order to develop technology for a new world of mobility - with an overall mission to use artificial intelligence (AI) to improve the quality of human life. In the coming decades, our society will continually need better and more environmentally sustainable sources of energy storage for mobility and transportation. At TRI, the Accelerated Materials Design and Discovery (AMDD) program will accelerate discovery of energy materials through new tools, technologies, and methodologies that leverage advances in AI. The research program consists of efforts to 1) create extensive and dynamic databases of materials knowledge via high-throughput computing, high-throughput experimentation, and mining of existing literature data, 2) develop software tools to aid the human expert in extracting knowledge from large databases and 3) develop novel automated materials discovery systems by integrating simulation, machine learning, artificial intelligence, and robotics. The AMDD program is comprised of our research scientists, software engineers, and an extensive network of funded collaborators at a number of universities and research institutions. This talk will describe the vision of our research program, progress to date, challenges and early successes in applying AI to materials research for the discovery of catalysts and battery materials, and future opportunities at the intersection of materials and computer science.

11:00 AM  GI01.01.05
Accelerating the Discovery of New Energy Materials Brian Storey; Toyota Research Institute, Cambridge, Massachusetts, United States.

Toyota Research Institute (TRI) is conducting research on developing technology for a new world of mobility, leveraging artificial intelligence (AI) to improve the quality of human life. Within the coming decades, society will continually need sources of environmentally sustainable energy storage for mobility and transportation. The Accelerated Materials Design and Discovery (AMDD) program at TRI aims to accelerate energy materials discovery through innovative tools, technologies, and methodologies that harness advances in AI. The program's efforts include creating extensive and dynamic databases of materials knowledge via high-throughput experimentation and simulation, developing software tools to facilitate human expertise in extracting knowledge from large databases, and building automated materials discovery systems by integrating simulation, machine learning, artificial intelligence, and robotics. The presentation will outline the research program's vision, progress, and early successes in applying AI to materials research for the discovery of catalysts and battery materials, identifying future opportunities at the intersection of materials and computer science.

11:00 AM  GI01.01.06
Damage Nucleation and Growth Prediction from Microstructure Spatial Characteristics Benjamin Cameron1 and C. Cam Tasan2; 1Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The vast compositional space of metallic materials provides ample opportunity to design stronger, more ductile and cheaper alloys. However, the substantial complexity surrounding microstructural deformation makes simulating new microstructures exceedingly difficult. Instead, tedious experiments are conducted to optimize properties without tools to predict how microstructures will perform. Here, we exploit recent developments in data collection capabilities and develop a purely empirical model to forecast microstructural performance in advance, entirely bypassing the challenges associated with physics based simulations. In-situ experiments are conducted using a scanning electron microscope in order obtain detailed microstructural information. 6400 12.5 μm square microstructural regions are tracked using a quasi digital image correlation algorithm and imaged throughout deformation in order to obtain sufficient data to train the model. Detailed analysis is conducted on three experimental datasets, two of dual-phase steel and one of bearing steel. The models are trained to predict crack nucleation and crack growth, a complex process with an intricate relationship to microstructural geometry. Multiple machine learning approaches are compared and contrasted including a n-point statistics and principle component analysis algorithm based on grain boundaries, a support vector machine approach, and a convolutional neural network. Using this approach, significant predictive ability is achieved and the model can accurately predict crack nucleation and crack size on a new microstructure. For example, 84.8% of microstructures predicted to crack, actually crack. Artificial microstructures with idealized properties are constructed and fed into the model in order to understand how it makes its prediction. For example, there is a major difference in cracking probability for grain boundaries aligned with the loading direction (12%) and inclined at 45° to the loading direction (72%). These results demonstrate the success of this approach and paves the pathway for use of this framework in alloy design to predict a range of behaviors.

11:15 AM  GI01.01.07
Extraction of Capacitance Variance Mechanisms via a Neural-Net Accelerated Genetic Algorithm Venkatesh Meenakshisundaram1,2, David Yoo1,2, Andrew Gilman3, Clare Mahoney3, James R. Deneau3,1, Nicholas Glavin1 and Phil Buskohl1; 1Air Force Research Laboratory, WPAFB, Ohio, United States; 2UES, Inc., Dayton, Ohio, United States; 3UTC, Dayton, Ohio, United States.

Microscale spatial and material heterogeneities in 3D printed electrical devices present significant challenges to predictable electrical performance and device reliability. High permittivity particles are often added to dielectric inks to tailor the macro level permittivity of printed dielectric substrates and coatings. However the combined role of particle morphology, discrete spatial arrangement and material properties on variance is difficult to distinguish experimentally, due to the large parameter space of processing variables and electrical sensitivity to local heterogeneities. To address this challenge, we developed a 3D, high-fidelity finite element model of an interdigitated capacitor (IDC) with a dielectric coating of distinct spatial distributions of discrete dielectric particles. The volume fraction, particle size and permittivity distributions for each IDC was then encoded into the genome of a genetic algorithm (GA) with the objective of identifying combinations of these properties that generate high variance in the capacitance of the IDC. In addition, the genetic algorithm was guided by an artificial neural network (ANN) that recursively trains on the data produced by GA and sends suggestions back to the GA to accelerate the identification of optimized properties. This autonomous and robust optimization approach allows us to build a database with strong likelihood of high variance mechanisms, while saving on computational costs. Preliminary results indicate that large particles in dilute volume fractions generate high variability in capacitance, due to heighten influence these particles positions on excluding the electric field. Classification-based machine learning techniques were also applied to the spatial distributions of the dielectric particles to determine whether a critical spacing parameter or local clustering was a component in driving up the variance. Collectively, the study provides a useful framework to correlate electrical performance with both macro- and microstructural variation sources, which is key to accelerating the development of 3D printing materials.

11:30 AM  GI01.01.08
Machine Learned Defect Level Predictor for Semiconductors—The Example of Hybrid Perovskites Arun Kumar Mannodi Kanakkithodi, Michael Davis and Maria K. Chan; Argonne National Laboratory, Lemont, Illinois, United States.

Electronic levels introduced by impurities and defects in the middle of the band gap are critically important in semiconductors for optoelectronic, photovoltaic (PV) and quantum sensing applications. While “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination, impurity levels in the band gap could also be exploited for quantum sensing or lead to increased absorption of sub-gap photons which can enhance efficiencies. Predicting formation energies and charge transition levels for defects in semiconductors is thus paramount; density functional theory (DFT) calculations have been widely applied for such studies to overcome experimental bottlenecks. However, the requirement of large supercells and inclusion of charged states make these computations very expensive, and trends and knowledge from previous calculations are not exploited in subsequent ones. In this work, we use DFT to generate a substantial computational dataset of the formation energies and transition levels of vacancy, interstitial and substitutional point defects in many lead-based pure and mixed halide hybrid perovskites (MAPbX3, where MA = methylammonium and X = Cl/Br/I). These computations help determine the dominant intrinsic defects in any perovskite, the equilibrium Fermi level (and thus the nature of conductivity) for different chemical potential conditions, and the stable extrinsic substituents (atoms selected by screening across the periodic table). That
compensate for intrinsic defects and change the equilibrium Fermi level. Further, we apply machine learning to extract crucial design rules and predictive models of the emitters. As a result, we present a data set of small molecule donor-acceptor pairs gathered from the literature (between 2013 and 2017), for which equilibrium geometries and electronic properties have been computed at DFT level. We used electronic data in combination with Scharber’s model to calculate photovoltaic parameters of the organic solar cells. Comparison with experimental data reveals a disappointing performance of DFT. It has been shown that DFT data can be refined through Machine Learning to improve the performance of Scharber’s model to predict experimental photovoltaic parameters.

In this contribution, we present an approach to predict Organic Solar Cells Efficiency based on Machine Learning. We present a data set of small molecule donor-acceptor pairs gathered from the literature (between 2013 and 2017), for which equilibrium geometries and electronic properties have been computed at DFT level. We used electronic data in combination with Scharber’s model to calculate photovoltaic parameters of the organic solar cells. Comparison with experimental data reveals a disappointing performance of DFT. It has been shown that DFT data can be refined through Machine Learning to improve the performance of Scharber’s model to predict experimental photovoltaic parameters.

Finally, with a similar approach, we obtain direct predictions of solar cell efficiencies. We show that considering only electronic or structural parameters leads again to similar results, while considering both parameters at the same time results in improved predictions, allowing to obtain direct predictions of solar cells efficiency with a reasonable level of accuracy.

Finally, we critically assess the usefulness of the proposed approach for the discovery of new materials that have not been synthesized yet.

REFERENCES
Metal-organic frameworks (MOFs) are promising solid-state adsorbents thanks to their high gravimetric capacities. However, realizing a high volumetric $H_2$ adsorption capacity, balanced with a high gravimetric density, is one of the main barriers of the successful application of MOFs as solid-state adsorbents. A large database of half-a-million MOFs consisting of real and hypothetical compounds was compiled and screened using semi-empirical and atomistic (grand canonical Monte Carlo) techniques. Several machine learning (ML) algorithms were benchmarked for their ability to predict hydrogen storage in MOFs at multiple conditions. The top performing algorithm, extremely randomized trees, was applied to rapidly identify MOFs with high usable $H_2$ storage capacities across the entire database. A combinatorial approach was then used to understand the importance of crystallographic properties and training set size. This approach identifies the number and combination of crystallographic features needed to achieve the most accurate predictions. Finally, we assess multilinear regression models for their ability to out-perform the well-known Chaline rule for predicting $H_2$ uptake.

3:00 PM BREAK

3:30 PM GI01.02.05

**Functional Defects by Design—A High-Throughput Approach to Energy Materials Discovery**

Janakiraman Balachandran, Jiuli Ding, Xiaohan Sung, Wei Guo, Shreyas Muralidharan, Jonathan Anchell, Gabriel Veith, Craig Bridges, Yongqiang Cheng, Christopher Rouleau, Jonathan Anchell; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2University of California, Berkeley, California, United States.

Defects and impurities introduce localized heterogeneities in solids and decisively control the behavior of a wide range of energy technologies. Fuel cell materials, especially proton conducting fuel cells, are a quintessential example in this regard. Designing and developing solid oxide materials that can selectively transport protons will enable us to develop the next generation proton conducting solid oxide fuel cells. Protons require less activation energy compared to oxygen ions which results in a lower operating temperature, higher operating efficiency and better material reliability. In this work [1,2,3,4] we focus obtaining fundamental insights on how properties of host material structure along with dopants, disorder and strain influences proton transport properties in solid oxides by coupling high-throughput computations with functional imaging, neutron spectroscopy and transport measurements.

We initially focus on the perovskite family of compounds (such as doped BaZrO$_3$). We benchmark our calculations against a wide range of experimental measurements such as kelvin probe force microscopy (KPFM), inelastic neutron scattering (INS) and atom probe tomography (APT). To obtain better insights on why certain cubic perovskite/dopant combinations are better at conducting protons compared to others, we developed a high-throughput framework to perform $ab$ _initio_ calculations. The high-throughput framework can scale massively to tens of thousands of nodes to fully exploit the computational capability of Titan at OLCF supercomputing facility. We employ this approach to calculate proton transport properties in several cubic perovskite materials with different host atoms and dopants. The results obtained from these calculations enables us to obtain better insights on how material structure – such as atomic properties (electronegativity, ionic radius) and lattice properties (sub-lattice distortion) influences proton transport. The results obtained from this high-throughput analysis is being employed to develop a machine learning framework to predict structure-property correlations on a larger set of perovskites materials. Finally, we explore the role of disorder on proton transport by studying for example fluorite based lanthanum tungstate materials.


3:45 PM GI01.02.06

**Polymer Genome—A Data-Powered Polymer Informatics Platform for Property Predictions**

Chinho Kim, Anand Chandrasekaran, Huan Tran, Deya Das, and Rampi Ramprasad; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2University of Connecticut, Storrs, Connecticut, United States.

The recent successes of the Materials Genome Initiative has opened up new opportunities for data-centric informatics approaches in several subfields of materials research, including in polymer science and engineering. Polymers, being inexpensive and possessing a broad range of tunable properties, are widespread in many technologically applications. The vast chemical and morphological complexity of polymers though gives rise to challenges in the rational discovery of new materials for specific applications. The nascent field of polymer informatics seeks to provide tools and pathways for accelerated property prediction (and materials design) via surrogate machine learning models built on reliable past data. We have carefully accumulated a dataset of organic polymers whose properties were obtained either computationally (bandgap, dielectric constant, refractive index and atomization energy) or experimentally (glass transition temperature, solubility parameter and density). A fingerprinting scheme that captures atomistic to morphological structural features was developed to numerically represent the polymers. Machine learning models were then trained by mapping the fingerprints (or features) to properties. Once developed, these models can rapidly predict properties of new polymers (within the same chemical class as the parent dataset) and can also provide uncertainties underlying the predictions. Since different properties depend on different length-scale features, the prediction models were built...
on an optimized set of features for each individual property. Furthermore, these models are incorporated in a user friendly online platform named Polymer Genome (www.polymergenome.org). Systematic and progressive expansion of both chemical and property spaces are planned to extend the applicability of Polymer Genome to a wide range of technological domains.

4:00 PM GI01.02.07
High-Throughput Materials Discovery and Development—Breakthroughs and Challenges in the Mapping of the Materials Genome
Marco Buongiorno Nardelli and Jeria Silva; University of North Texas, Denton, Texas, United States.

High-Throughput Quantum-Mechanics computation of materials properties by ab initio methods has become the foundation of an effective approach to materials design, discovery and characterization. This data driven approach to materials science currently presents the most promising path to the development of advanced technological materials that could solve or mitigate important social and economic challenges of the 21st century. In particular, the rapid proliferation of computational data on materials properties presents the possibility to complement and extend materials property databases where the experimental data is lacking and difficult to obtain. Enhanced repositories such as AFLOWLIB open novel opportunities for structure discovery and optimization, including uncovering of unsuspected compounds, metastable structures and correlations between various properties. The practical realization of these opportunities depends almost exclusively on the the design of efficient algorithms for electronic structure simulations of realistic material systems beyond the limitations of the current standard theories. In this talk, I will review recent progress in theoretical and computational tools for data generation and advanced characterization, and in particular, discuss the development and validation of novel functionalities within Density Functional Theory and of local basis representations for effective ab-initio tight-binding schemes.

4:30 PM GI01.02.08
Feature-Based Data Analysis for Localized Characterization of Electroactive Materials
Nikolay Borodinov1, Anton V. Ievlev1, Jan-Michael Carrillo1, Andrea Calamari2, Marc Mamak2, John Mulcahy2, GiCommunication, Joshua Agar1, Lane W. Martin1, Bobby G. Sumpter1, Sergei V. Kalinin1, Olga Ovchinnikova1 and Petro Makaryovych1; 1Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Research and Development, Procter & Gamble, Cincinnati, Ohio, United States; 1University of California Berkeley, Berkeley, California, United States.

Effective research and development efforts in the field of electroactive materials are critically dependent on the characterization methods that can generate information about the physical properties at the relevant scale. When the scope of these efforts includes engineering materials, fundamentally new challenges arise as the intrinsic complexity of industrial-grade samples requires decoupling of the observed phenomena. The characterization of the materials response in this case is impossible to be directly reflected using a single parameter. In order to tackle this challenge, we adopted a different strategy which included expanded representation of the analyzed materials with subsequent multivariate analysis. Its results were used to extract relevant features that may be intrinsic to a specific composition or instead may span across the sample library. We demonstrate this feature-centric approach for the rapid identification of the materials ability to develop triboelectric charge, observation of the electric charge migration on industrial-grade polyethylene terephthalate (PET) samples and property-driven analysis of effective piezoelectric coefficients observed across PZT-PZO (lead zirconate titanate - lead zirconate) phase diagram. We have employed multivariate adaptive regression splines, principal component analysis, large-scale molecular dynamics simulations, finite element analysis, multivariate Naïve Bayes classifier as parts of our method. Resulting insights allow for the isolation of the common features of the dataset reflecting specific piezoelectric and electrostatic phenomena as well as identification of the samples satisfying certain criteria. We believe that feature-base analytics demonstrated in this work can be successfully applied in other materials science fields where the nanoscale behavior of the relevant materials needs to the understood.

References:
1) Nikolay Borodinov et al, Probing static discharge of polymer surfaces with nanoscale resolution, available at arxiv.org/abs/1806.05169
This research was carried out at the Center for Nanophase Materials Sciences, a U.S Department of Energy Office of Science User Facility. The scope of the work was under a CRADA between Proctor & Gamble Co. and Oak Ridge National Laboratory. This research also used resources of the Oak Ridge Leadership Computing Facility at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

4:45 PM GI01.02.09
The Search for P-Type Transparent Conducting Chalcogenides
Rachel Woods-Robinson, Shyam Dwarknath and Kristin A. Persson; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Despite our increasing demand for renewable energy materials over the past decade, as well as recent advances in photovoltaics and transparent electronics, progress in the field of high-performing p-type transparent conductors (TCs) has been relatively slow. All TCs used in industry are still n-type, since state-of-the-art n-type TCs have figures of merit orders of magnitude higher than p-type analogues due to the localized, 2p character of valence bands and doping difficulties in wide-gap oxides. Both n-type and p-type TCs are conventionally oxides but, due to energetics of the chalcogen 2p orbitals, chalcogenide (S, Se, Te) semiconductors have shown promise of higher hole transport and greater p-type doping propensity than oxides (in exchange for a decreased band gap).

Here, we use high throughput computation to screen a large database of over 10,000 chalcogenide compounds for binary, ternary, and quaternary chalcogenides likely to have a high hole conductivity and high optical transparency. The first round of screening uses GGA and GGA+U functionals from the Materials Project database to calculate band gaps and hole effective mass derived from the BoltzTraP code. Refined screenings use additional transport and HSE calculations. Our ultimate goal is to synthesize promising compounds in the laboratory for use in stable devices, so we also apply a proxy for structural thermodynamic stability.

From these criteria, we discover a large set of computationally stable multi-anionic compounds. Several compounds studied previously as TCs emerge from our screening, including ZnS and sulfanitites TaCu3X4 (X = S, Se, Te). We further pare down this list for synthesis by selecting only single anionic compounds, removing compounds with toxic and highly reactive elements, and estimating p-type dopability. A refined list of ten top experimentally-favorable candidates emerges and includes spinal ZnAl2S4, distorted rocksalt BaS3Sn2S2, and several other rocksalt structures.

We delve deeper into the bonding characteristics of the valence band that give each predicted candidate its low calculated effective mass, and discuss these computed structures and our screening metrics in the context of state-of-the-art p-type and n-type transparent conductors. Additionally, we discuss defect calculations and dopant selection for the most promising structures, present our initial attempts to combinatorially synthesize and characterize a few of the candidates, and lay out a roadmap for a future high-throughput screening, synthesis, characterization, and device paradigm for new p-type transparent conducting chalcogenides.
The Role of Theoretical Prediction in Data-Driven Materials Development

Ruth Pachter; Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States.

Development of two-dimensional materials, including graphene and 2D transition metal dichalcogenides (TMDs), has greatly advanced. For example, engineered defective structures are of interest, where graphene meshes were used for sensing, while defective monolayer TMDs exhibited single-photon emission, potentially useful for quantum information processing. Here, we first discuss the theoretical prediction of defect-induced Raman signatures in graphene by a combined first principles-tight binding approach, to be integrated within a data-driven experimental system for defect engineering. Our predictions of D and D’ Raman band intensities demonstrated that it is possible to distinguish between defect types, which also assists in characterization of realistic materials. Next, we note that to overcome limitations in photon-extraction efficiency and integration within photonic circuits when using bulk solid-state materials, the 2D geometry emerged as potentially useful as a single-photon source. In aiming to achieve localized excitons in monolayer WS2 due to defects, we found theoretically that calculated defect excitons red-shift significantly for experimentally observed patterns. However, although development of databases of 2D materials beyond graphene is progressing, so far the focus is on discovery of materials with low excitation energies. We provide a perspective on database development and machine learning for 2D materials with defects.

Rapid Screening of Potential Inorganic Scintillator Chemistries Using Physics-Informed Machine Learning

Ghanshyam Pilania, Kenneth McClellan, Chris Stanek and Blas P. Uberuaga; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Applications of inorganic scintillators—activated with lanthanide dopants, such as Ce—are found in diverse fields. As a strict requirement to exhibit scintillation, the 4f ground state (with the electronic configuration of [Xe]4f^{n}5d^{0}) and 5d_{1} lowest excited state (with the electronic configuration of [Xe]4f^{n-1}5d^{1}) levels induced by the activator must lie within the host bandgap. This talk will discuss a new machine learning (ML) based screening strategy that relies on a high throughput prediction of the lanthanide dopants’ ground and excited state energy levels with respect to the host valance and conduction band edges for efficient chemical space explorations to discover novel inorganic scintillators [1]. Building upon well-known physics-based chemical trends for the host dependent electron binding energies within the 4f and 5d energy levels of lanthanide ions and available experimental data [2,3], the developed ML model can rapidly and reliably estimate the relative positions of the activator's energy levels relative to the valance and conduction band edges of any given host chemistry. Using a set of perovskite oxides and elpasolites (a class of double perovskite halides) as examples, it will be demonstrated that the developed approach is able to (i) capture systematic chemical trends across host chemistries and (ii) effectively screen promising compounds in a high-throughput manner. While a number of other application-specific performance requirements need to be considered for a viable scintillator, the present scheme can be a practically useful tool to systematically down-select the most promising candidate materials in a first line of screening for a subsequent in-depth investigation.

Prediction of Glass Dissolution Kinetics Using Physics-Informed Machine Learning

Mathieu Bauchy; 1University of California, Los Angeles, Los Angeles, California, United States; 2Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi, India.

Predicting the dissolution kinetics of silicate glasses is of paramount importance to ensure the long-term integrity of vitrified nuclear wasteform. However, this is a complex task as the underlying corrosion mechanism(s) are poorly understood and the dissolution kinetics can depend on a large number of intrinsic and extrinsic factors. Here, we assess the potential of data-driven models based on machine learning to predict the dissolution rates of various aluminosilicate glasses exposed to a wide range of solution pH values, from acidic to caustic conditions. We show that, although “blind” machine learning yield promising results, the incorporation of physical space explorations into the machine learning framework greatly enhance the accuracy of the model, both in terms of interpolating and prediction far from the training set. This demonstrates how “physics-informed” machine learning can overcome the limitations of informatics approaches based on limited datasets.

Machine Learning vs Physical Insight in the Discovery of Molecular Materials for Organic Photo-Voltaics

Alessandro Troisi; Department of Chemistry, University of Liverpool, Liverpool, United Kingdom.

A number of proposals have been put forward to describe the properties required to improve the efficiency in organic solar cell. The number of experimental data available allow an evaluation of these proposal in a strict statistical sense, e.g. a good sampling of the space of the experiment can provide support to a given physical hypothesis. Alternatively, one can abandon any hope of physical insight and use a battery of machine learning approaches trying to correlate descriptor and photovoltaic efficiency. This lecture compares the two approaches and consider two specific problems (i) identification of high efficiency electron-acceptor and (ii) identification of high efficiency electron-donors.

References:
Design and Innovation, University at Buffalo, The State University of New York, Buffalo, New York, United States; 2Department of Computer Science

In this work, we focused specifically on solid state synthesis of materials and used various natural-language processing [Collobert et al. J. Mach. Learn. Res. 2011] techniques to a) find relevant synthesis paragraphs, b) resolve materials entities referring to starting compounds, environment and final products, yet to c) obtain synthesis operations and firing temperatures. As a preliminary result of our work, we extracted 17,500 papers describing solid state synthesis procedure and obtained ~16,000 unique codified recipes. We analyzed these recipes using deep learning algorithms to relate materials features and their synthesis conditions. Our results present a first step toward predictive synthesis theory, and provide insights into further development.

Automated Extraction of Phase Diagram Features for Identifying Candidate Binary Alloy Systems for Metallic Glasses Aparnita Dasgupta1, Connor Mack1, Bhargava U. Kota2, Ramachandran Subramanian2, Scott Broderick1, S. Setlur2, Venugopal Govindaraju2 and Krishna Rajan1; 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The use of machine learning techniques to expedite the discovery and development of new materials is an essential step towards the acceleration of a new generation of domain-specific highly functional material systems. In this paper, we use the test case of bulk metallic glasses to highlight the key issues in the field of high throughput predictions and propose a new probabilistic analysis of rules for glass forming ability using rough set theory. We demonstrate the use of automated machine learning methods that go far beyond text recognition approaches by also being able to interpret phase diagrams. When combined with structural descriptors, this approach provides the foundations to develop a hierarchical probabilistic prediction tool that can rank the feasibility of glass formation.

Machine Learning of “Codified Synthesis Recipes”—Making Steps Toward Predictive Synthesis of New Materials Olga Kononova1, Haoyan Huo1, Tanjin He1, Ziqin Rong2, Tiago Botari1, Vahe Tshitoyan2 and Gerbrand Ceder1, 2; 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

In the past decade, first-principles methods for high-throughput computational screening and design of new materials have proven to be effective and indispensable for various applications [Curtarolo et al. Nature, 2013; Curtarolo et al. Phys. Rev. Lett. 2003]. Moreover, the design and optimization of novel materials has been transformed by the emergence of genomic approaches, where materials properties of many tens of thousands of materials can be modeled, catalogued in searchable databases, and analyzed for trends. However, knowing the structure and properties of a novel material is not enough for its successful production. Often, even knowing what material to make, an obstacle emerges how to make it, which results in the slow and tedious experimental process of trials and errors due to high complexity of materials synthesis procedure. Therefore, predicting conditions under which a specific experimental compound or crystal structure can be synthesized is an unresolved and fundamental problem in materials science, which imposes significant constrains on facile design and production of novel advanced materials. Yet, no any universal theory of synthesis exists which would relate synthesizability of materials and their obtained and computable parameters.

In our work, we approach the predictive synthesis problem by trying to answer the question how well synthesis can be learned from existing data. To address it, we developed a data mining pipeline which extracts information about synthesis of inorganic compounds from available scientific publications using machine learning techniques. The most important steps of pipeline include: i) collecting of research articles available on-line, ii) extraction of experimental sections and identification of paragraphs describing ceramics synthesis, iii) extraction of so-called “codified recipes” of the synthesis procedures, iv) accumulating all recipes in the database and their mining.

In this work, we focused specifically on solid state synthesis of materials and used various natural-language processing [Collobert et al. J. Mach. Learn. Res. 2011] techniques to a) find relevant synthesis paragraphs, b) resolve materials entities referring to starting compounds, environment and final products, yet to c) obtain synthesis operations and firing temperatures. As a preliminary result of our work, we extracted 17,500 papers describing solid state synthesis procedure and obtained ~16,000 unique codified recipes. We analyzed these recipes using deep learning algorithms to relate materials features and their synthesis conditions. Our results present a first step toward predictive synthesis theory, and provide insights into further development.
Polymer nanocomposites have great advantages in achieving improved performance with relative low cost compared with traditional materials. By integrating material science, informatics and information technology, efforts on Material Genome Initiative (MGI) have produced different database infrastructures, material data schemas and ontologies as well as material design tools across different material fields including polymer nanocomposite materials. Under the concept of MGI, we have developed a nanocomposite data resource: NanoMine, which consists an online material database, data-driven analysis tools and physics-based simulation tools for polymer nanocomposite data sharing, analysis and design. To appropriately capture the full suite of possible data for nanocomposites, a nanocomposite schema is designed and served as the templates to ingest data from scientific literatures and in-house experiments. The data schema consists six major sections: data source, materials, processing, characterization, property and microstructure. The current database population and curation mainly relies on the manual data abstraction from scientific literatures by humans with expert knowledge, which is an expensive, labor-intensive and error-prone process.

In order to accelerate the data curation, reduce the possible errors and provide more insights on nanocomposite material synthesis, we take a step toward fully automated data extraction by applying recent machine learning and natural language processing methods and develop an end-to-end framework to extract material processing and synthesis information from full-length journal articles. Our method starts from building a paragraph classifier which is able to select the relevant paragraphs containing the material processing information from the whole paper. Then, individual sentences from those relevant paragraphs are further classified into different categories (e.g., material characteristics, experimental action, irrelevant information etc.) using a hierarchical attention neural network based on their semantic meanings. The network is trained on a set of over one hundred human annotated literatures created by material scientist while reading through the material synthesis sections. Lastly, the learning from the attention network is combined with the outputs from grammar parser and different heuristic rules are applied in order to extract the material processing actions and parameters. The extracted material processing steps and parameters are then postprocessed in order to create a machine readable and compatible data structure (XML in our case) so that the data is ready to be populated to the database.

11:45 AM *GI01.03.10*
**Natural Language Processing for Materials Discovery**
John Dasgupta1, 2, Leigh Weston2, Vahe Tshitoyan2, Gerbrand Ceder1, 2, Kristin A. Persson1, 2 and Anubhav Jain2; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The majority of all materials data is currently scattered across the text, tables and figures of millions of scientific publications. We present recently developed natural language processing and machine learning techniques to extract materials knowledge by textual analysis of the abstracts of several million journal articles. We describe our use of Word2Vec to map words in our corpus to vector representations, which we then use as inputs to named entity recognition (NER) classifiers to extract materials, structures, properties, applications, synthesis methods, and characterization techniques from the abstracts in our database. With this information, we have created new tools for materials literature review such as: searching within chemical systems, filtering articles by experiment/theory, summarizing the known attributes of a material, or finding similar materials to a target. Furthermore, we report how these techniques can be used not only to automatically summarize existing knowledge, but enable new ways of discovering novel materials such as thermoelectrics or ion-conductors by revealing previously undiscovered relationships between materials and their properties.

1:30 PM *GI01.04.01*
**Autonomous Science Using Robot Scientists**
Ross D. King1, 2; 1University of Manchester, Manchester, United Kingdom; 2Artificial Intelligence, The National Institute of Advanced Industrial Science and Technology, Tokyo, Japan.

A Robot Scientist is a physically implemented robotic system that applies techniques from artificial intelligence to execute cycles of automated scientific experimentation. A Robot Scientist can automatically execute cycles of hypothesis formation, selection of efficient experiments to discriminate between hypotheses, execution of experiments using laboratory automation equipment, and analysis of results. The motivation for developing Robot Scientists is to better understand the scientific method, and to make scientific research more efficient. The Robot Scientist ‘Adam’ was the first machine to autonomously discover scientific knowledge: it formed and experimentally confirmed novel hypotheses. Adam worked in the domain of yeast functional genomics. The Robot Scientist ‘Eve’ was originally developed to automate early-stage drug development, with specific application to neglected tropical disease such as malaria, African sleeping sickness, etc. More recently we have adapted Eve to work on yeast systems biology, and cancer. We are also teaching Eve to autonomously extract information from the scientific literature.

2:00 PM *GI01.04.02*
**Autonomous Experimentation Applied to Carbon Nanotube Synthesis**
Benji Maruyama1, Pavel Nikolaev2, Daylond Hooper3, Fred Webber4, Kevin Decker5, Jason Poleski1, Michael Krein1, Richard Barto5, Ahmad Islam5, Rahul Rao1 and Abigail Juhl1; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States; 3US Inc., Dayton, Ohio, United States; 4InfoSext, Inc., Dayton, Ohio, United States; 5Lockheed Martin Corp., Cherry Hill, New Jersey, United States.

We have developed a first-of-its-kind Autonomous Research System, ARES, capable of designing, executing, and analyzing its own experiments autonomously using artificial intelligence (AI) and Machine Learning (ML). The closed loop, iterative method enables ARES to design new experiments based on prior results dynamically, after each experiment; a first for materials research.

We are applying this method to understand and control the synthesis of single wall carbon nanotubes, in this case optimizing growth rate in (7) - dimensional parameter space. We use automated in situ Raman spectroscopy characterization of growth rate for CVD synthesis of carbon nanotubes as a metric for a target objective used by our AI planner. We use a random forest learning approach which models experimental results, and a genetic algorithm planner to propose new experiments expected to achieve the targeted growth rate.
We expect ARES to be a disruptive advance in the near future, combining advances in robotics, AI, data sciences and operando methods to enable us to attack high dimensional research problems that were previously intractable by current research processes. We are applying the ARES method to multiple problems, including Additive Manufacturing and defect engineering in graphene. Human-robot research teams have to potential to redefine the research process and lead to a Moore’s Law for the speed of research.

2:30 PM GI01.04.03
Experimental Bayesian Optimization of a 3D Printed Mechanical Structure Aldair E. Gongora1, Bowen Xu1, Wyatt C. Perry1, Chika S. Okoye2, Kristofer Reyes3, Elise F. Morgan1 and Keith A. Brown1; 1Department of Mechanical Engineering, Boston University, Boston, Massachusetts, United States; 2Department of Materials Design and Innovation, University at Buffalo, Buffalo, New York, United States.

Additive manufacturing presents numerous possibilities for design due to the high level of control afforded by the 3D fabrication processes. However, each new design choice introduced by the flexibility of the processing represents a decision that could have important implications on performance. While structures can be optimized for many types of mechanical performance, improving failure properties is particularly challenging due to the stochastic nature of failure and the difficulty in reliably predicting the influence of the microstructure introduced by processing. Here, we explore the degree to which machine learning can guide physical experimentation to produce tough 3D-printed structures in as few experiments as possible. Specifically, we present an experimental optimization of a parametric structure to maximize specific toughness as a model figure of merit that is central to the realization of energy-absorbing structures. Utilizing Bayesian optimization with Gaussian process regression, the mechanical performance of each new design is predicted based on previous experiments in order to continuously predict the optimal design with all available data. Of particular importance, we study the influence of the decision policy, or the algorithm by which subsequent experiments are selected, on convergence to an optimum design. We investigate the effectiveness of policies such as pure exploration, expected improvement, maximum variance, and Bayesian D-optimality in optimizing specific toughness. These approaches are benchmarked against classical design of experiments. The application of these machine learning approaches to an experimental system forces the accommodation of real-world artifacts such as defects introduced through printing, variability between printers, and the stochastic nature of failure. In addition to aiding in the development of high-performance materials and structures, the lessons described will assist in the selection of decision policies for broader classes of experimental optimizations in a manner that facilitates the convergence of machine learning, physical experimentation, and design.

2:45 PM GI01.04.04
Machine Learning Based Monitoring of Advanced Manufacturing Brian Gieria1, Bo Li2, Albert Chu3, Philip DePond4, Gabe Guss2, Du Nguyen1, Congwang Ye1, William Smith1, Nikolai Dudukovic1, Sara McMains1 and Manyalibso Matthews1; 1Lawrence Livermore National Lab, Livermore, California, United States; 2Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States.

As with most advanced manufacturing (AM) systems, analysis of AM sensor data currently occurs post-build, rendering process monitoring and rectification impossible. Supervised machine learning offers a route to convert sensor data into real-time assessments; however, this requires a wealth of labeled sensor data that traditionally is too time-consuming and/or expensive to assemble. In this work, we solve this critical issue in a variety of AM systems. We develop and implement machine learning (ML) algorithms for the purposes of automated quality assessment and, in some cases, rectification. We discuss ML-based algorithms capable of automated detection in a host of AM technologies such as Laser Powder Bed Fusion and Direct Ink Write and also microfluidic platforms that are used for feedstock production. The common thread within these systems is that routinely collected sensor data (e.g. high-speed video, pressure gauges, etc.) contains pertinent information about the state of the system that can be converted into actionable information in real-time via ML. Successful implementation of these machine learning algorithms will reduce time and cost during process by automating quality assessment and lead to process control.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

3:00 PM BREAK

3:30 PM GI01.04.05
Autonomous Integration of Materials Theory, Experiment and Computation—SARA R. Bruce van Dover1, John M. Gregoire2, Carla P. Gomes1, Bart Selman1, Christopher M. Woverton3 and Alex Zunger4; 1Cornell University, Ithaca, New York, United States; 2California Institute of Technology, Pasadena, California, United States; 3Northwestern University, Evanston, Illinois, United States; 4University of Colorado Boulder, Boulder, Colorado, United States.

Many new materials have been suggested, either by first principles theory or by heuristic inference, as having critical enabling properties for technologies such as Li-ion batteries, transparent conductors, and photochemical energy capture. Yet theory has not provided adequate guidance regarding the conditions, if any, under which they can be synthesized. Traditional synthesis of novel compounds often involves laborious and slow manual iterative exploration of composition and processing space. We are radically transforming the ability to identify and synthesize new materials using innovative AI-based strategies for reasoning and conducting science, including the representation, planning, optimization, and learning of materials knowledge. The logical structure of our approach, SARA (Scientific Autonomous Reasoning Agent), is based on a community of software agents that cooperatively generate hypotheses and autonomously test them through autonomous execution of the materials discovery/development process, and is enabled through concomitant development of robotic processing and characterization tools, on-the-fly DFT calculations, and AI-based algorithms. Our approach is further augmented with human insights so that the artificial intelligence leverages the human intelligence of expert scientists, creating an unprecedented platform for human-machine collaboration. SARA includes methods and methodologies for the rational design of functional materials and for discovering the requisite synthesis parameters for both stable and metastable materials.

4:00 PM GI01.04.06
Autonomous Research System for Biology (ARES-B)—A Machine Learning Approach to Optimizing Materials Synthesis Using Synthetic Biology Maria Torres1, Colleen Reynolds1, David Coar1, Jeffrey Stuart1, Michael Jewett2, Ashby Karim2 and Michael Krein1; 1Lockheed Martin, Cherry Hill, New Jersey, United States; 2Northwestern University, Evanston, Illinois, United States.

Synthetic biology is an emerging manufacturing method of materials and precursors, such as those typically derived from fossil fuels. However, controlling synthesis pathways to optimize product yield remains a significant challenge in process maturation and scale up. Current strategies rely on laboratory experimentation. Depending on the design of experiments, this can be time and resource intensive, and results are not guaranteed. A metabolic synthesis pathway is typically a multistep process with dozens of degrees of freedom, such as cofactor concentrations and homologue variants. This describes a
parameter space intractable to exhaustively explore through experiments. Machine learning provides a means to intelligently and efficiently explore this parameter space by building and optimizing models which describe the synthesis process and guide state-of-the-art cell-free experiments. We adapted principles from our previous work on the Autonomous REsearch System (ARES) in which an autonomous system iteratively performed experiments, analyzed results, and applied machine learning models to automatically design and execute a new set of experiments, drastically reducing the experimental time needed to optimize a chemical synthesis process. Here, we applied our approach to synthetic biology pathway modeling and optimization. We used two machine learning approaches – neural networks and parameter-fit ordinary differential equations (ODEs) – to build models of a 5-step metabolic process for butanol production. These models were used to inform a series of cell free experiments, resulting in a 3-fold improvement in butanol yield over prior trial-and-error experimentation. We found a trade between model interpretability and optimization ability: The ODEs required very little initial information and were interpretable, but fell short of the neural networks’ ability to suggest optimized conditions.

SESSION GI01.06: Machine Learning for Imaging, Characterization and Inverse Problems
Session Chairs: Noa Marom and Olga Wodo
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 110

8:30 AM GI01.06.01
Helium Ion Microscopy for Imaging and Quantifying Porosity at the Nanoscale
Alex Belianinov, Matthew J. Burch, Kyle T. Mahady, Holland Hysmith, Philip D. Rack and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanoporous materials play a key role as components in a vast number of applications from energy to drug delivery and to agriculture. However, a comprehensive analysis to analytically measure and quantify salient features e.g.: surface structure, pore shape, and size, remain limited, or prohibitively expensive. The most common approach is gas absorption, where volumetric gas absorption and desorption are measured. The gas absorption approach has a few fundamental drawbacks such as low sample throughput and a lack of direct surface visualization. In this work, we demonstrate Helium Ion Microscopy (HIM) for imaging and quantification of pores in industrially relevant SiO2 catalyst supports. We start with the fundamental principles of ion-sample interaction, and expand to experiment; where we observe and quantify pores on the surface of the catalyst support by using the HIM, and image data analytics. We contrast our experimental results to gas absorption and demonstrate full statistical agreement between two techniques. The principles behind the theoretical, experimental, and analytical framework presented herein offer an automated framework for visualization and quantification of pore structures in a wide variety of materials, and offer data processing solutions to automate these types of imaging workflows.

Acknowledgements
The HIM imaging, image analytics, and simulations portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. This research was funded by the Center for Nanophase Materials Sciences, which is a U.S. Department of Energy Office of Science User Facility (H.H., A.V.I., P.D.R., O.S.O.), part of the data analytics work was supported by the Laboratory Directed Research and Development Program (A.B.), and the ExxonMobil Chemical Company (M.J.B.). The authors acknowledge Robert Colby, David Abmayr, Sergey Yakovlev, Lubin Luo, and Bill Lambert from the ExxonMobil Corporation for much appreciated input and helpful discussions.

8:45 AM *GI01.06.02
Thoughts on Automated Electron Microscopy
Mark Ruemmler1, 2; 1SIEMIS, Suzhou, China; 2CMPW, Zabzre, Poland.

The use of materials in society cannot be underestimated. Indeed, it is often said that our ability to use materials has developed civilizations throughout human history and this is even reflected in how we name historical ages, for example the stone age and the bronze age. As we have developed ever better scientific understanding so has our knowledge base on materials and ways to use them increased. We are now at an age where we are beginning to deal with materials in terms of their processing and properties at the atomic scale. At the same time there is an important drive to discover complex materials and be able to manipulate their properties with an ever greater efficiency. This is leading to an immense drive for instrument automation, data interpretation, and the development of new ways to do this both with existing and novel instrument and equipment. In our quest to achieve these goals, particularly at the atomic level, it is clear one of the more important techniques will be microscopy, with electron microscopy based techniques probably playing key roles. The automation and interpretation of data from electron microscopy is enormously challenging. That said, approaches toward these goals are being developed and are expected to grow rapidly in the next decades. In this presentation some of the advances in automation and data interpretation are presented. Numerous challenges in achieving automation, data interpretation, sample preparation and measurement are discussed. The importance of this for new materials discovery (viz. synthesis (including combinatorial materials science) and structure-property relationships at the atomic scale) are also discussed and early ideas and approaches, such as the development of ins situ/in operando electron microscopy are presented.

9:15 AM GI01.06.03
Real-Time Tomography with Interactive 3D Visualization Using tomviz
Robert Hovden1, Jonathan Schwartz2, Chris Harris3, Cory Quammen2, Shawn Waldon1, Yi Jiang1, Peter Ercius4 and Marcus Hanwell2; 1University of Michigan, Ann Arbor, Michigan, United States; 2Kitware Inc., Clifton Park, New York, United States; 3Argonne National Laboratory, Lemont, Illinois, United States; 4Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Three-dimensional (3D) characterization at the nano- and meso-scale using scanning / transmission electron microscope (S/TEM) is now possible[1,2] but high-throughput tomography still requires innovative tools for reconstruction and visualization of large datasets. Currently, the best tomographic reconstructions are obtained from algorithms that are slow and iterative and will run from hours to days depending upon the size of the data set and the algorithm(s) employed. Thus, it has been a longstanding desire to see a reconstruction and begin 3D analysis before it completes. Continuous feedback provides high-throughput and early diagnoses for 3D structure or opportunity to optimize experimental parameters for maximal reconstruction quality. Here we demonstrate interactive 3D visualization displayed in real-time as tomographic reconstructions proceed and as new data arrives using the open-source tool, tomviz. In the actual software, the 3D visualizations are dynamically updated throughout the computation. This means that scientists need not wait for a reconstruction to complete, or all data to be collected before beginning the interpretation of results. The iterative nature of tomographic methods
allows tomviz to show intermediate results with minimal impact on performance. This enables interactive 3D analysis of the current reconstruction state while the reconstruction proceeds on a separate thread. A robust graphical interface allows objects to be rendered as shaded contours or volumetric projections and these objects can be rotated, cropped, or sliced[3]. Experimental nanomaterial datasets were made public and used to validate live reconstruction[4]. Additionally, tomviz visualizes new data as it arrives. As aligned projections are provided from each new specimen tilt, the tomographic reconstruction quality improves in real-time. tomviz accomplishes this by monitoring data / directories for change, and upon arrival of new data, the data is imported and all associated 3D data visualizations are dynamically updated. If data processing routines are present in the pipeline—such as alignment, preprocessing, and reconstruction—all steps will automatically rerun. This capability opens radically new possibilities for developing high-throughput, real-time tomographic reconstruction algorithms. Ultimately, interactive real-time visualization will allow researchers to make early judgments to best answer scientific questions or guide experimental design.

tomviz is publicly available for download at www.tomviz.org

[5] tomviz is supported from DOE Office of Science contract DE-SC0011385.
Machine Learning Clustering Technique Applied to X-Ray Diffraction Patterns to Distinguish Alloy Substitutions

Rutchopon Hunkao1, Keishu Utimula3, Masao Yano3, Hiroyuki Kimoto3, Shogo Kawaguchi3, Sujiin Suwanna3, Kentaro Hongo3 and Ryo Maccione3; 1School of Information Science, JAIST, Nomi, Japan; 3Department of Physics, Mahidol University, Bangkok, Thailand; 3School of Materials Science, JAIST, Nomi, Japan; 3Research Center for Advanced Computing Infrastructure, JAIST, Nomi, Japan; 3Advanced Material Engineering Div., Toyota Motor Corporation, Toyota, Japan; 3FASRI, Sayo-gun, Japan.

SmFe12 is one of the candidate of the main phase in rare-earth permanent magnets[1]. The origin of intrinsic properties emerging at high temperature as well as that of the phase stability has not yet been clarified well. Introducing Tl and Zr to substitute Fe and Sm is found to improve the magnetic properties and the phase stability. To clarify the mechanism how the substitutions improve the properties, it is desired to identify substituted sites and its amount quantitatively, preferably with high throughput efficiency for accelerating the 'materials tuning'. Motivated by the above, we have developed a machine learning clustering technique to distinguish powder XRD patterns to get such microscopic identifications about the atomic substitutions.

Ab initio calculations are used to generate supervising references for the machine learning of XRD patterns: We prepared several possible model structures with substituents located on each different sites over a range of substitution fractions. Geometrical optimizations for each model give slight different structures each other. Then we generated many XRD patterns calculated from each structure. We found that the DTW (dynamic time wrapping) analysis can capture slight shifts in XRD peak positions corresponding to the differences of each relaxed structure, distinguishing the fractions and positions of substituents. We have established such a clustering technique using Ward's analysis on top of the DTW, being capable to sort out simulated XRD patterns based on the distinction.

The established technique can hence learn the correspondence between XRD peak shifts and microscopic structures with substitutions over many supervising simulated data. Since the ab initio simulation can also give several properties such as magnetization for each structure, the correspondence in the machine learning can further predict functional properties of materials when it is applied to the experimental XRD patterns, not only being capable to distinguish the atomic substitutions. The machine learning technique for XRD patterns developed here has therefore the wider range of applications not limited only on magnets, but further on those materials which properties are tuned by the atomic substitutions.


Deep Learning for Inverse Imaging Problems

Rama K. Vasudevan, Noumane Laaait, Ondrej Dyck, Maxim Ziatdinov, Stephen Jesse, Andrew Lupini, Junqi Yin, Mark Osley and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Inverse problems in imaging constitute some of the most interesting and challenging tasks, with examples ranging from tomographic reconstruction to protein structure determination. Here, we present an approach to tackling the inverse problem in imaging via large-scale forward modeling of many physically realizable examples, and then using these simulations to train deep neural networks to learn the inverse mapping. We show this method with two test cases: in the first, we introduce a deep convolutional neural network trained on simulated 2D diffraction patterns, to perform a classification task to sort each diffraction pattern into one of the five possible Bravais lattice types. The DCNN is tested on experimental imaging data from both scanning transmission electron microscopy and scanning tunneling microscopy, and is found to be robust, providing advantages over more traditional threshold-based methods and is largely insensitive to both scale and rotations of the lattice. By using Monte-Carlo dropout on the predictions, a confidence estimate is obtained for each symmetry classification.

In the second example, we train a 3D convolutional neural network on hundreds of gigabytes of simulated convergent beam electron diffraction patterns of the LaAlO3-SrTiO3 interface. The network is trained on simulated data to classify whether the interface is diffuse or stepped in nature and shows extremely high accuracy on a simulated validation set. The approach outlined here is general to any situation where forward simulations exist, but wherein the inverse is difficult to obtain using traditional means.

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which also provided support and is a US DOE Office of Science User Facility. This research used resources of the Compute and Data Environment for Science (CADES) at the Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

Accelerating Materials Development Through Rapid Analysis of Experimental Data Using Machine Learning Based Tools

Marcus Schwarting1, Caleb Phillips1, Andriy Zakutayevey2, Robert White2, Kristin Munch3, Magali Ferrandon2, Deborah Myers2 and John D. Perkins1; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

To effectively use high-throughput experiments (HTE) as envisioned in the Materials Genome Initiative (MGI) requires not only rapid experiments but also the ability to efficiently transform the resultant large sets into usable knowledge. To address this issue, we are developing machine learning based tools to address the specific challenge of rapid analysis of large amounts of x-ray diffraction (XRD) data including factoring and clustering analysis along with custom data visualizations. These capabilities will be demonstrated by application to both combinatorially grown Co-Zn-Ni-O thin film and bulk powdered Fe-N-C catalyst materials. The composition-gradient thin-film libraries were grown on glass substrates using off-axis co-sputtering and the powdered Fe-N-C materials were synthesized by pyrolysis of Fe substituted ZIFs. XRD patterns were measured using a commercial (Bruker D8 Discover diffractometer equipped with either a 2D detector (thin film libraries) or a point detector (bulk powder samples). The developed tools are built in Python and leverage the machine learning algorithms available in scikit-learn (scikit-learn.org). After testing a variety of algorithms, we are currently using Orthogonal Matching Pursuit (OMP) for factoring analysis and Spectral Clustering for clustering analysis. Reference XRD patterns for factoring are pulled from the ICSD for known materials as well as from MatDB (materials.nrel.gov) and the Materials Project (materialsproject.org) for unknown or unmeasured materials. Experimental data can be pulled from HTEM-DB (htem.nrel.gov), a recently-launched public-facing database of experimental synthesis and property data for inorganic thin film materials with more than 50,000 entries. Select data visualization and machine learning based tools have been implemented in unmix_xrd, our custom Python package which combines the analysis and visualization into simple single line command calls to facilitate use. For deployment, we are testing locally hosted and cloud hosted Jupiter notebooks with the latter aimed at creating free standing analysis tools intended for deployment on the Energy Materials Network (EMN) such as via the Electr0CAT database (databhub.electrocat.org). In addition, this analytics package can be run from within program capable of issuing a system command which we will demonstrate using Igor Pro, a commercial analysis program widely used at NREL. The overall result is a scientist-friendly extensible analysis environment with project specific machine learning analysis and
In the traditional materials optimization paradigm, a material system is characterized by forming many different samples across different compositions and measuring their properties as a function of e.g. temperature or pressure to produce a phase diagram. As such, each measurement represents a single point in chemical space, and spanning the phase diagram requires many samples and measurements which are time-consuming and expensive. At the same time, small fluctuations in the samples are considered a hindrance and limiting factor to the interpretation of the results. Here, we present an alternative approach that instead exploits this fact, leveraging statistical physics to take atomic observations of structural and chemical fluctuations to map them into generative lattice models that have predictive power. We use a newly developed statistical distance framework to perform model optimization based on imaging data, and then use the model to produce configurations for a range of compositions and temperatures. We apply the method to understand segregation in FeSexTe1-x single crystal, attempting to identify the segregation tendency of the chalcogen atom, as well as the divalent cation segregation in a manganite thin film. The generative model produces configurations that well approximate those observed, and further are run for different temperatures and compositions. A variational autoencoder is then applied on the simulated configurations to map the observations to a single latent parameter, allowing easy visualization of any anomalies in the phase diagram. In this way, a measurement of a single point in chemical space is turned into a prediction across a finite range of chemical space. This method is general and can be used to add to the current materials design paradigms, providing more information on microscopic driving forces, and reducing the need to finely sample the chemical space.

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division (R. K. V., S. V. K., L.V). Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

SESSION GI01.05: Poster Session: Machine Learning and Data-Driven Materials Development and Design
Session Chairs: Keith A. Brown, Kristofer Reyes and Kristofer Reyes
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

GI01.05.01
Database-Driven Materials-Selection Framework for Semiconductor Heterojunction Design Ethan Shapera and Andre Schleife; University of Illinois at Urbana-Champ, Urbana, Illinois, United States.

At the interface of two semiconductors, where bulk band structures merge into each other, an electronic transition region forms, with band-edge discontinuities that are confined to not more than a few atomic layers near the interface. These discontinuities, also known as valence- and conduction-band offsets, naturally occur at the interface of materials with different band gaps. While the sign of an interface as a barrier or conductor for electrons or holes, their magnitudes determine how good of a barrier/conductor the interface is. Such heterojunctions are at the heart of many modern semiconductor devices with tremendous societal impact: Light-emitting diodes shape the future of energy-efficient lighting, solar cells are promising for renewable energy, and photo-electrochemistry seeks to optimize efficiency of the water-splitting reaction.

Unfortunately, design of heterojunctions, e.g. to find optimal electron- and hole-transport layers for new active-component materials, is difficult due to the limited number of materials for which band alignment is known and the experimental as well as computational difficulties associated with obtaining this data. At the same time, the dependence of band alignment on intrinsic properties of the involved materials turns the design of heterojunctions with specific alignment into an interesting materials-design or materials-selection optimization problem. In order to tackle this problem, we show that band alignment based on branch-point energies is a good and efficient approximation that can be obtained exclusively using data from existing electronic-structure databases. To this end, we shows that errors associated with this approach are comparable to those of expensive first-principles computational techniques as well as experiment.

We then incorporate branch-point energy alignment into a framework that is capable of rapidly screening existing online databases to design semiconductor heterojunctions. We showcase our technique for different prototype cases, including successful predictions of electron- and hole transport layers for CdSe- and InP-based LEDs as well as for novel CH3NH3PbI3- and nanoparticle PbS-based solar absorbers. From our results we show that our framework addresses the challenge of accomplishing fast materials selection for heterostructure design by tying together first-principles calculations and existing online materials databases. We show that it can be used to directly design desired semiconductor heterostructures, or, at least, to reduce the vast candidate search space.

GI01.05.02

The study of gas adsorption in microporous solids is vitally important for addressing the crises facing modern society including climate change (carbon dioxide capture) and energy production (hydrogen storage). Whilst databases of possible materials[1] and software for performing Grand Canonical Monte Carlo (GCMC) simulation of these[2] have been created, to date there is no framework for performing the fully autonomous computational screening of these materials.

In this contribution we present a freely available software package, GCMCWorkflow[3], which allows fully autonomous computational modeling of materials in a reliable, repeatable and reproducible way. The package is built upon the Fireworks[4] package and acts as a controller of existing GCMC tools, in this case Raspa[5].

Building upon previous work into the quantification of uncertainty of these simulations and what constitutes “enough” sampling[6], the package is able to adaptively start more simulations as required to achieve the defined sampling. Other features such as restarting simulations after crashes and the massively parallel scale enabled by Fireworks allows GCMCWorkflow to make performing large scale screening on high performance computing clusters far less
user intensive.

Finally we show how the abstraction layer this automation provides allows multiple GCMC simulations to be programmed into larger machine learning pipelines. In the first example we show how genetic algorithms can be used to derive force field parameters in a top down approach to match data gathered from experiments. In another example, we show how we can search for adsorption capacities of materials where the exploration of sampling space is automated through data-driven algorithms.

References:


G101.05.03

The huge demand for new materials, rapid change in technology, and limitation associated with long-term and costly experiments encouraged the scientific community to predict material properties using various scientific simulation tools. In order to discover new materials, simulation tools such as density functional theories, force field modeling, finite difference time domain methods, and other ab-initio methods are available to predict the band-structures, atomic arrangement, and other physical properties. Undoubtedly these methods have been used in many aspects, however, most of these methods are highly computationally expensive and do not much incorporate inputs from previous outcomes and past results. In contrast, a relatively new method, machine learning, can also be used to predict the performance of material and can be used as a screening tool prior to DFT simulations. In this piece of research, data have been selected from the database and literature that are divided into test sets, cross-validation tests, and training sets. The mathematical models have been made using standard machine learning tools such as logistic regression, support vector machine, and artificial neural network. Using these models, band gap, electronic properties, and crystal structures can be predicted and accuracy can also be measured by performing actual DFT calculations for some of them. Note that machine learning outcomes depend mainly on the size of the training set, hence, performance graphs will also be presented for selected results.

G101.05.04
Dodecahedral Inorganic Cage Discovery Assisted by Machine Learning Algorithms Kai Ma1, 3, Yunye Gong2, Tangi Aubert1, 3, Melik Z. Turker4, Teresa Kao1, Peter C. Doeschuk2, 4 and Ulrich Wiesner1, 3 Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2School of Electrical and Computer Engineering, Cornell University, Ithaca, New York, United States; 3Department of Chemistry, Ghent University, Ghent, Belgium; 4Nancy E. and Peter C. Meinig School of Biomedical Engineering, Cornell University, Ithaca, New York, United States; *Current Affiliation: Elucida Oncology, New York, New York, United States.

Artificial intelligence (AI) is beginning to show significant potential for accelerating research in materials science and engineering. In particular, single-particle three-dimensional (3D) reconstruction of cryo-electron microscopy (cryo-EM) images using machine learning computer algorithms has recently emerged as a powerful tool in structural biology for revealing high-resolution information of biological structures, including virus, protein, and DNA assemblies. However, to the best of our knowledge such AI-based approaches have not yet been successfully applied to synthetic materials discovery. In this contribution, we describe how such machine learning approaches resulted in the discovery of an ultrasmall (~10 nm diameter) dodecahedral silica nanocage, or ‘silicage’ [1].

In the study, tens of thousands of single-particle cryo-EM images were collected on early formation stages of surfactant self-assembly directed silica nanostuctures. However, the well-defined structures could not be identified from regular TEM and cryo-EM observations. In contrast, feeding the cryo-EM images into machine learning algorithms for single-particle 3D reconstruction revealed a previously unidentified dodecahedral silica cage. The dodecahedron is the highest symmetry structure of the five Platonic solids known since antiquity and extensively studied by the ancient Greeks. Details of the reconstruction provided insights into possible formation mechanism of these cages around self-assembled surfactant micelles. Cage structures were not limited to silica, but were also observed from other materials including metals and transition metal oxides. Such materials may find a plethora of applications in areas including catalysis and nanomedicine. This discovery, facilitated by artificial intelligence, not only provides novel insights into the fundamental understanding of molecular self-assembly, but also paves the way for the search of related structures with different symmetry and from different materials.


G101.05.05
Software Tools, Methods and Applications of Machine Learning in Functional Materials Design Anubhav Jain; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

In this talk, I will describe our group’s efforts to build a general framework for performing data mining on materials properties based on structure and composition. I will introduce matminer (https://hackingmaterials.github.io/matminer/), an open-source code capable of extracting materials data, generating thousands of crystal structure and compositional descriptors, and quickly reproducing and extending existing machine learning studies. I will demonstrate
how new structural features implemented in matminer based on local environment can be used for machine learning and classification. I will also describe our group’s effort to create a “black-box” machine learning model that can be applied to any property and that can be used as a benchmark comparison for machine learning efforts. Finally, I will describe multiple applications, including the prediction of electronic properties, bulk metallic glass behavior, and an effort to learn the properties of materials from unstructured text.

**GI01.05.06**

Data Analytics for Mapping of Catalytic Performance Form High Throughput Cyclic Voltammetry Experiments Kiran Vaddi, Surya V. Devaguptapu, Tianmu Zhang, Xiaozhou Shen, Scott Broderick, E. Bruce Pitman, Fei Yao, Olga Wodo and Krishna Rajan; Material Design and Innovation, University at Buffalo, The State University of New York, Buffalo, New York, United States.

The high throughput exploration of materials space has been recognized as a new paradigm in materials design and discovery. However, typical high throughput exploration methods deliver high dimensional datasets that pose the challenge of extracting the key features and trends that could guide the discovery process. To address this challenge, we develop data analytics tools to extract irreducible representation of the high throughput exploration data.

We develop computational tools to perform feature extraction from high throughput electro-chemistry experiments. We leverage non-linear dimensionality reduction techniques to project a high dimensional set of cyclic voltammetry (CV) experiments into a lower dimensional space. The main advantage of our approach is the mathematically rigorous extraction of the inherent dimensionality of a given data set. This is in contrast to the traditional Engineering Figure of Merit used to interpret CV curves. To demonstrate the performance of our approach, we analyze CV curves for a compositional library of perovskites devices subjected to a series of various electrochemical tests. Each device’s current response to cyclic voltammetry test is recorded over several time points (considered as dimensions from here on). In all these cases, we discovered the inherent dimensionality to be as low as 3 (comparing to input 4200 dimensions) with over 90% variance explained. Moreover, we observed a strong compositional dependency of the current responses. Finally, we unraveled the dominant structure hidden in the data as belonging to two types of manifolds regardless of the noise present in the data.

Our method has capability to inform the iterative design process of linking theory, modeling, and experiments for improvement and acceleration of materials design.

**GI01.05.07**

Automated Bayesian Optimization of the CANDLE Implicit Solvation Model Yuxi Chen, Henry C. Herbol and Paullette Clancy; 1Chemical Engineering, Cornell University, Ithaca, New York, United States; 2Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

The creation of hybrid organic-inorganic perovskite thin films is frequently made in solution to promote energy-inexpensive sustainable processing. Unfortunately, the inclusion of solvent molecules greatly increases the computational expense during simulations of the solubilization and subsequent crystallization of said thin films. Implicit solvation models represent a solvent as a continuous medium instead of individual atomically “explicit” solvent molecules, and are commonly used in order to allow for larger-scale studies of solvent-solute interactions in DFT. The Joint Density Functional Theory (JDFTx) is a Density Functional Theory (DFT) software written by Prof. Tomás Arias (Physics, Cornell). JDFTx specializes in its implementation of solvation models, such as the charge-asymmetric nonlocally-determined local-electric solvation model (CANDLE), which has been shown to be particularly efficient and accurate [R. Sundararaman et al., 2014].

Despite the efficiency and accuracy of the model, the solvent parametrization process is tedious. We are working to apply an automated Bayesian Optimization algorithm towards parametrization of CANDLE Models on other organic solvents. This novel approach, as applied to molecular simulations, will make the parametrization process more readily accessible to the scientific community at large. Bayesian Optimization searches for the best combination of the parameter set to maximize an objective function, which is set to be the mean absolute error (MAE) between the experimental solvation energy and the calculated solvation energy of a set of solute molecules. To allow for robustness, solute molecules studied include neutral, anionic, and cationic species.

**GI01.05.08**

Semiconducting Materials from Analogy and Chemical Theory (SMACT) Daniel W. Davies, Keith Butler, Adam J. Jackson, Jonathan Skelton and Aron Walsh; 1University of Bath, Bath, United Kingdom; 2ISIS Facility, Oxford, United Kingdom; 3Chemistry, University College London, London, United Kingdom; 4Materials, Imperial College London, London, United Kingdom.

We present an open-source code SMOCT [1] to perform rapid screening of known and hypothetical materials. It combines elemental descriptors and chemical heuristics to navigate large numbers of compounds, which can be fed into machine learning procedures or other materials design workflows.

Forming a four-component compound from the first 103 elements of the periodic table results in more than $10^{12}$ combinations. Such a materials space is intractable to high-throughput experiment or first-principles computation. We introduce a framework to address this problem and quantify how many materials can exist. We apply principles of valency and electronegativity to filter chemically implausible compositions, which reduces the inorganic quaternary space to $10^{10}$ combinations [2]. We demonstrate that estimates of bandgaps and absolute electron energies can be made simply based on the chemical composition and apply this to search for new semiconducting materials to support the photoelectrochemical splitting of water [3].

The applicability to crystal structure prediction by analogy with known compounds is shown, including exploration of the phase space for ternary combinations that form a perovskite lattice. Computer screening reproduces known perovskite materials and predicts the feasibility of thousands more. Due to the simplicity of the approach, large-scale searches can be performed on a single workstation. For example, we have been able to assign likely crystal structures to all hypothetical quaternary oxide compositions produced by SMOCT, constituting a database of over 2 million compounds. The stability and properties of these compounds are then assessed methodically using high-throughput workflows for first-principles calculations.

1. https://github.com/WMD-group/SMACT

**GI01.05.09**

Predicting the Glass Forming Ability of Bulk Metallic Glasses Using Random Forests Vanessa Nilsen, Michael Hibbard, Logan Ward and Dane Morgan; 1University of Wisconsin - Madison, Madison, Wisconsin, United States; 2Computation Institute, The University of Chicago, Chicago, Illinois, United States.
Predicting the glass forming ability of metallic alloys is an active area of research due to the many existing and potential uses of metallic glasses. Many descriptors accounting for the thermodynamics and kinetics of the vitrification process have been proposed to quantify the likelihood of glass formation for an alloy. A particularly widely used class of descriptors involve simple functions of the glass transition temperature ($T_g$), the liquidus temperature ($T_l$), and the crystallization temperature ($T_c$). The descriptors we focus on in this work include $Tr_g = T_g/T_l$, $\gamma = T_c/(T_g + T_l)$, and $\omega = T_g/T_c - 2T_g/(T_g + T_l)$. It is of interest to predict these descriptors quickly for new alloy systems. We note that these transition temperatures are also of interest in their own right, separate from their ability to predict glass forming ability, as they control important design properties of alloys. Accurately predicting these transition temperatures could also prevent the need to first make a glass to calculate the value of any of the descriptors. In this work we have used a random forest machine learning method to model these descriptors as a function of simple elemental properties. We used two approaches to model the value of the glass forming descriptors. First, we modeled $Tr_g$, $\gamma$, and $\omega$ directly. Second, we modeled the transition temperatures and used the resulting predictions to calculate the glass forming descriptors. Interestingly, the latter approach was significantly more accurate. In addition to predicting the glass forming descriptors, we assessed the applicability of the model in various compositional domains by examining the error and uncertainty on predictions of alloys with varying degrees of representation in the training data set.

GI01.05.10
Extending Bayesian Inference to Infer Thermal Transport Characteristics in Thermoelastic Materials


We report on a single-step experimental diagnostic tool, which applies Bayesian inference to infer electronic and thermal transport characteristics of thermoelastic materials from simple power-load curve data. By using Boltzmann transport equation as the forward model and by feeding experimental data from our in-house built single-leg thermoelastic measurement setup, our tool is able to extract intrinsic thermoelastic properties. Employing only three experimental input parameters (base temperature, temperature across the device - $\Delta T$, and external load resistance) and the output power from the thermoelastic setup as constraint parameters, we are able to extract the electronic transport parameters of thermoelastic material. In addition to electronic material descriptors, a good thermoelastic behaves like an ‘electron-crystal-phonon-glass’, where optimally tuned electronic transport has to be coupled with reduced thermal conductivity. Measurement of thermal conductivity is typically an independent experiment, which requires careful domain expertise and detailed analysis. In this work, we extend our work to inferring thermal conductivity by replacing the $\Delta T$ by heat current as the input, incorporated into a Bayesian Inference algorithm. This is done by taking into account both the radiative and conductive heat loss using the Stefan-Boltzmann law in the guiding forward model. Remarkably, we are able to also extract the heat loss which serves as a valuable guide for further experimental optimization. Our Machine learning based technique allows, from a single step experiment, to provide all transport properties of the thermoelastic material of interest.

GI01.05.11
A Data Driven Analysis of Volcano Plots and Prediction of New Binary Catalysts

Aparajita Dasgupta, Yingjie Gao, Thaicia Stona de Almeida, Scott Broderick, E. Bruce Pitman and Krishna Rajan, Material Design and Innovation, University at Buffalo, The State University of New York, Buffalo, New York, United States.

In this study, we describe a computational approach where we ingrain the underlying theoretical constructs behind these and subsequently use the underlying physical descriptors to expand and extend the database of known catalytic reactions. To this end, we use spectral clustering methods to identify key physical regimes underlying volcano plots by using the volcano plot for ammonia synthesis rate as a function of nitrogen adsorption energy as our case study. The application of dimensionality reduction techniques and graph networks to these catalytic systems is illustrated by applying to elemental and binary transition metal alloys to predict the positions of these systems on volcano plots.

GI01.05.12
Pycroscopy—A Community-Driven Approach for Analyzing and Storing Materials Imaging Data

Suhas Somnath, Christopher R. Smith, Rama K. Vasudevan and Stephen Jesse, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Materials science is undergoing profound changes, driven by continual improvements to instrumentation that have resulted in an explosion in the data volume, dimensionality, complexity, and variety, in addition to increased accessibility to high-performance computing (HPC) resources, and more sophisticated computer algorithms. These changes are especially prominent in the functional imaging of materials. However, the current software typically do not provide access to advanced or user-defined data analysis routines, and store measurement data in proprietary file formats. These proprietary software and file formats not only impede data analysis but also hinder continued research and instrument development, especially in the era of “big data.” Therefore, moving to the forefront of data-intensive materials research requires general and unified data curation and analysis platforms that are HPC-ready and open source.

We have developed a free and open-source python package called Pycroscopy for analyzing, visualizing and storing data. Pycroscopy is freely available via popular software repositories, and therefore lifts any financial burden for interrogating data. Pycroscopy describes data in an instrument-agnostic structure that allows it to represent data of any size, dimensionality, or complexity acquired on a regular grid of positions or random positions as in compressed sensing. This data model is stored in open hierarchical data format files (HDF5) that can be interrogated using any programming language, scale well from kilobyte to terabyte sized datasets, and can readily be used in HPC environments unlike proprietary data formats. As a consequence, Pycroscopy-formatted data files are curation-ready and therefore both meet the guidelines for data sharing issued to federally funded agencies and satisfy the implementation of digital data management as outlined by the United States Department of Energy. The generalized data format allows data processing and analysis algorithms to be generalized in turn allowing a single version of the algorithm to be applied to data collected from instruments from different brands or even modalities. The simple structure and comprehensive documentation in pycroscopy enable even novice programmers to easily translate physical or chemical problems into computational problems. Unlike many other open-source packages that focus on analytical or processing routines specific to an instrument, the general definition of the Pycroscopy data format can be readily adopted for different microscopy techniques. Furthermore, the generality of Pycroscopy provides a natural step towards a vast and growing library of community-driven data processing and analysis routines that far exceed those provided by instrument manufacturers and are desperately needed in the age of big data. This research was conducted at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility.

GI01.05.13
Theoretical Classification for Softmagnetic Compounds Applying Regression-Based Model Selection

Masakuni Okamoto, 1 Research & Development Group, Hitachi Ltd., Hatoyama, Japan; 2Department of Data Science, Yokohama City University, Yokohama, Japan.

Materials science is undergoing profound changes, driven by continual improvements to instrumentation that have resulted in an explosion in the data volume, dimensionality, complexity, and variety, in addition to increased accessibility to high-performance computing (HPC) resources, and more sophisticated computer algorithms. These changes are especially prominent in the functional imaging of materials. However, the current software typically do not provide access to advanced or user-defined data analysis routines, and store measurement data in proprietary file formats. These proprietary software and file formats not only impede data analysis but also hinder continued research and instrument development, especially in the era of “big data.” Therefore, moving to the forefront of data-intensive materials research requires general and unified data curation and analysis platforms that are HPC-ready and open source.

We have developed a free and open-source python package called Pycroscopy for analyzing, visualizing and storing data. Pycroscopy is freely available via popular software repositories, and therefore lifts any financial burden for interrogating data. Pycroscopy describes data in an instrument-agnostic structure that allows it to represent data of any size, dimensionality, or complexity acquired on a regular grid of positions or random positions as in compressed sensing. This data model is stored in open hierarchical data format files (HDF5) that can be interrogated using any programming language, scale well from kilobyte to terabyte sized datasets, and can readily be used in HPC environments unlike proprietary data formats. As a consequence, Pycroscopy-formatted data files are curation-ready and therefore both meet the guidelines for data sharing issued to federally funded agencies and satisfy the implementation of digital data management as outlined by the United States Department of Energy. The generalized data format allows data processing and analysis algorithms to be generalized in turn allowing a single version of the algorithm to be applied to data collected from instruments from different brands or even modalities. The simple structure and comprehensive documentation in pycroscopy enable even novice programmers to easily translate physical or chemical problems into computational problems. Unlike many other open-source packages that focus on analytical or processing routines specific to an instrument, the general definition of the Pycroscopy data format can be readily adopted for different microscopy techniques. Furthermore, the generality of Pycroscopy provides a natural step towards a vast and growing library of community-driven data processing and analysis routines that far exceed those provided by instrument manufacturers and are desperately needed in the age of big data. This research was conducted at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility.
In order to improve the magnetic properties of the compounds forming the main phase of the soft magnetic materials, we study the magnetization ($M_H$) and the magnetostriction constant ($\lambda_{001}$) of ternary alloy compounds consisting of 3d transition-metal elements by using the first principles calculation and the machine learning technique. First we prepare totally 1393 training data using first-principles calculation for bcc/fcc-(Fe,Co,Ni)-based ternary compounds. We obtain 36 promising compounds after manual screening of 1393 compounds under several conditions such as $|\lambda_{001}| > 2 \times 10^{-5}$. We expect magnetic permeability ($\mu$) of these compounds is large due to a correlation between $\mu$ and $\lambda_{001}$. Next we classify the calculated 1393 data by using the machine learning technique. We use new descriptors based on the Voronoi-polygons, in addition to the common descriptors for materials informatics, such as lattice constants, ionization energy, atomic angular momentum $L$, $S$, $J$. Nonlinear regression with a Gaussian kernel and sparse modelling accurately reproduces the values $M$, of 1393 compounds. The relevant descriptors for prediction of $M$, are $L$, $S$, $J$ and Voronoi volumes. On the other hand, prediction of $\lambda_{001}$ is poor at present, some new descriptors may be necessary.

We demonstrate how the first-principles calculation and the regression-based model selection technique can be utilized for classifying new materials.

GI01.05.14 Predicting the Charge Density of Organic Molecules and Polymers Using Deep Learning Deepak Karnal, Anand Chandrasekaran and Rampi Ramprasad, Georgia Institute of Technology, Atlanta, Georgia, United States.

Over the past few decades, the Kohn-Sham scheme of density functional theory (KS-DFT) has become the customary method to probe solid-state properties of materials. Despite its preeminence, the computational cost of this methodology renders it intractable for large-scale calculations involving thousands/millions of atoms. The simulation of mesoscale properties of polymers is one such example where this limitation is most apparent. Here we propose a method to accurately predict charge densities of organic systems (both molecules and polymers) by learning from pre-calculated examples of smaller systems. We start with creating a database of organic compounds which cover a wide range of configurational and bonding environments. Further, we introduce a novel fingerprinting scheme which maps the charge density to the local atomic environment using deep neural networks. The model thus obtained is systematically improved (both in terms of accuracy and transferability) by selectively training on poorly predicted local environments encountered in new configurations. Following the proposed methodology, we develop a robust model that can rapidly predict the charge density of large organic systems. This charge density can then be used as input to orbital free density functional theory scheme to swiftly access a broad range of materials properties, thus bypassing the need to explicitly solve the Kohn-Sham equation.

GI01.05.15 Accelerated Informatics Base Design of Multi-Component Systems Xiaozhou Shen, Tianmu Zhang, Scott Broderick, E. Bruce Pitman and Krishna Rajan, Material Design and Innovation, University at Buffalo, The State University of New York, Buffalo, New York, United States.

We introduce an integrated computational chemistry/ informatics approach to accelerate the design and discovery of new complex materials. Our approach involves coupling topological data (TDA) analysis classification methods with Hirshfeld Surface Analysis (HSA). 3-dimensional Hirshfeld surfaces, encode both chemical bonding and molecular geometry information; while TDA captures the “shape” of data in a multiscale manner to probe for hidden correlations between crystallographic structure and electronic structures. When applied collectively, we show how new classifications and insights into crystal chemistry can be revealed.

GI01.05.16 Fast Evaluation of Microstructure-Property Relation in Duplex Alloys Using SEM Images Thantip S. Krasienapibal, Yasuhiro Shirasaki, Momoyo Enyama, Akiko Kagatsume, Minseok Park and Sayaka Tanimoto, Research and Development Group, Hitachi Ltd., Tokyo, Japan.

Recently, fast material development and design is highly in-demand due to the needs of high performance materials. Microstructure-property relation, a key in material development, has long been investigated qualitatively. For example, controlling crystal structure and crystal size can manipulate material strength and anti-corrosion properties in alloys. To achieve highly-efficient experimental planning such as process tuning and controlling trade-off of multiple properties, the quantitative and large volume of datasets of microstructure-property relation is required. However, a method that accurately and automatically provide microstructure features in a short time is still a challenge.

For alloys, the microstructure i.e. crystal phase and orientation, is usually evaluated by electron back-scattered diffraction (EBSD) measurement [1]. The measurement needs highly-skilled technicians and long time limiting the automation for lots of samples. Backscattered electron (BSE) images acquired from scanning electron microscope (SEM) also provide crystal information. Using Z-contrast in BSE images, crystal phase information can be simply obtained due to different average atomic density [2]. In comparison to EBSD, using BSE images is promising since it can be acquired within few minutes and easy to operate. Hence, an approach to realize microstructure-property using BSE images should be considered.

In this research, we propose a method to utilize microstructure features in alloy from BSE images. By applying machine learning i.e. DNN-based segmentation, microstructure features, such as the amount of each phase present are extracted and are used for evaluation of microstructure-property relation. We evaluated the relation of microstructure and mechanical properties in Cr-duplex alloy. In addition, we study the detail of preparation of training data for the DNN-based segmentation under different measurement conditions of BSE images. The result suggested that by applying DNN-based segmentation on BSE images of Cr-duplex alloy, accurate phase distinction was performed with 90% accuracy in average resulting in reliable extraction of microstructure features i.e. the amount of each phase. The extracted amount of each phase is well-agreed with the result of EBSD measurement. The relation of the microstructure features and mechanical properties such as Vickers hardness, abrasion loss, and 0.2% yield strength of Cr-based duplex alloy was evaluated using regression model. Using the relation, prediction of the mechanical properties was performed and the error was less than 10%. From these results, we have demonstrated a method to utilize microstructure features from BSE images leading to fast and easy evaluation of microstructure-property relation in duplex alloy.

References

GI01.05.17 Elastic Strain Engineering Reaches Six Dimensions via Machine Learning Zhe Shi1, Evgeni Tsymbalov2, Alexander Shapecree2 and Ju Li3; 1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Center for Computational and Data-Intensive Science and Engineering, Skolkovo Institute of Science and Technology, Moscow, Russian Federation; 3Nuclear Science Engineering and Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The controllable incorporation of strain on materials merits unfold scientific and technological potential, yet poses a challenge of exploring the vast six-
dimensional space of admissible elastic strains. Here we demonstrate that systematic machine learning can make the problem of representing electronic structure as a function of six-dimensional strain computationally tractable. Specifically, we develop a number of general methods for surrogate modeling of elastic strain engineering which, relying on a limited amount of data from ab initio calculations, can be used to fit the required properties with sufficient accuracy. In particular, an artificial neural network predicts the band structure within the accuracy of 19 meV in case of three-dimensional strain.

**GI01.05.18**

**Oxygen Removal from Ce₀.75Zr₀.25O₂ Solid Solution Under Reducing Condition Using Genetic Algorithm**

Ki-Yung Kim¹, Yurie Kim², Jason Kim³, Dong-Gang Shin¹, Jun-Yeong Jo¹ and Yeong-Cheol Kim¹; ¹School of Energy Materials and Chemical Engineering, KoreaTech, Cheonan, Korea (the Republic of); ²Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Mean field approach has been employed to consider random distribution of atoms in solid solutions [1]. The mean field approach, however, shows averaged characteristics of the solid solutions, and, therefore, cannot represent energetically favorable solid solutions. We studied Ce₀.75Zr₀.25O₂ solid solutions using genetic algorithm and density functional theory (DFT) [2]. Initial population, fitness function, selection, crossover, and mutation were varied in genetic algorithm to find an energetically favorable solid solution. In this study, we employed lattice dynamics to increase the calculation speed and to consider temperature effect. The increased calculation speed also allowed us to consider bigger systems. The bond strengths of the oxygen atoms in the favorable solid solution structure should vary because each oxygen atom is surrounded by Ce and/or Zr atoms differently; the oxygen atom with weak bond strength would be removed first under reducing conditions. We employed genetic algorithm again to find easily removable oxygen atoms in the solid solution under reducing conditions.

References

**GI01.05.19**

**Machine Learning Approach to Discover the Correlation Between Core-Loss Spectra and Materials Information via Clustering and Decision Trees**

Shin Kiyohara and Teruyasu Mizoguchi; University of Tokyo, Tokyo, Japan.

Spectroscopy is one of the most promising techniques to reveal atomic and electronic structures of material inside and surface. Among a variety of spectroscopy, core-loss spectroscopy using electron (ELNES) and X-ray (XANES) has nano- or sub nano-scaled spatial resolution and nano- or femto-scaled temporal resolution, enabling to analyze lattice defects and chemical reaction. However, interpreting ELNES/XANES spectra is not straightforward, and therefore comparing experimental spectra with those in databases, namely, “experimental fingerprint”, has been generally used. While such a large database has been constructed, we often come across an unknown spectrum which isn’t contained by the database. To overcome the infeasibility of interpreting an unknown spectrum, theoretical calculation must be effective. Devoting a lot of effort enabled to calculate ELNES/XANES spectra of most of elements and atomic configurations, whereas calculating just single spectrum requires much computation time. Since the spatial and temporal resolutions of ELNES/XANES can generate a thousand of spectra in an experiment, such one by one “theoretical fingerprint” is impracticable. In that situation, utilizing the correlations between the spectra and atomic information discovered from the database can be an alternative method.

Here, we developed a new interpretation approach based on machine learning which can deal with a big data and be implemented without the theoretical calculation. First, a spectra database was constructed by the theoretical calculation. Then, hierarchical clustering was performed on the database, resulting in categorizing similar spectra into clusters. Spectral similarity was measured by cosine distance. Cutting the hierarchical tree at an arbitrary threshold makes some clusters of the spectra. We successively lowered the cutting threshold to each branch point, resulting in making two clusters at every branch point. At those branch points, we repeatedly implemented decision tree analysis considering the newly generated two clusters of the spectra as the training label and their structure information as the descriptors.

The queries of the constructed decision trees can provide the best (most characteristic) features for distinguishing each of the clusters. These features are also believed to be physically important, and detailed comparison of the two types of spectra in the clusters can endow the origins of the differences between these two types of spectra.

We applied this approach to approximately a lot of O-K edge ELNES spectra of SiO₂ polymorphs. The results will be discussed in my presentation.

**GI01.05.20**

**Analytic Continuation via “Domain-Knowledge Free” Machine Learning**

Hongkee Yoon, Jae-Hoon Sim and Myung Joon Han; KAIST, Daejeon, Korea (the Republic of).

We present a machine-learning approach to a long-standing issue in quantum many-body physics, namely, analytic continuation. This notorious ill-conditioned problem of obtaining spectral function from imaginary time Green’s function has been a focus of new method developments for past decades including many numerical approaches; such as maximum entropy method [1,2], stochastic method [3], Padé approximation [4]. Here we demonstrate the usefulness of modern machine-learning techniques including convolutional neural networks and the variants of stochastic gradient descent optimizer. Machine-learning continuation kernel is successfully realized without any ‘physical domain knowledge’ and the outstanding performance is achieved for both insulating and metallic band structure [5]. Unlike other methods, our method is additional parameter free fully automatic approach with no further human intervention. Our machine-learning-based approach not only provides the more accurate spectrum than the conventional methods in terms of peak positions and heights but is also more robust against the noise which is the required key feature for any continuation technique to be successful. Furthermore, the ML-based kernel is 10³-10⁴ faster than conventional analytic continuation algorithms and more robust to noise from Green’s function. Our approach to tackling ill-posed problems by statistical data-based ML shows the applicability of ML in other ill-posed physical problems.

References

**GI01.05.21**

**First-Principles Theory Based Machine Learning Force Fields for 2D Materials**

Yang Yang¹,², Hongxiang Zong², Hua Wang¹, Xiandong
Molecular dynamics simulation is a powerful tool to understand the underlying physics of dynamic behavior of materials. However, its application is greatly limited by the availability of accurate force fields. Here we demonstrate machine learning as a strong tool to combine the accuracy of first-principles density functional theory and low-cost MD simulations. By learning the database generated from density functional theory calculations, we are able to generate accurate and effective force fields. We will show a few interesting examples of our method for elemental materials and 2D materials where the generated force fields can capture both energetic and structural properties.

**G101.05.23**

**Machine Learning Induction of Parameters in Numerical Models of Capacity-Voltage Curve in Lithium-Ion Batteries**

Takuya Hiramoto, Masahiro Soeno, Misato Nakamura, Takashi Kusachi, and Hiromitsu Takaba; Graduate School of Applied Chemistry and Chemical Engineering, Kogakuin University, Tokyo, Japan; School of Advanced Engineering, Kogakuin University, Tokyo, Japan.

Numerical model of battery performance is indispensable for developing and optimizing battery materials and structures. Since Newman-model built one-dimensional model based on electrochemical reactions and ion transport, a numerical simulation to evaluate a charge/discharge characteristics as well as a capacity-voltage curve of lithium ion batteries have been widely applied in the field of battery research. It is difficult to know, however, all needed parameters in the model only from the experiments. Moreover, the induction of unknown parameters mostly depends on the experience of expert researchers. We have studied a numerical model for describing a charge/discharge characteristics of lithium air battery where the precipitation of discharged compound, lithium peroxide, on the surface of carbon is modeled in which the deposition rate and distribution on the carbon surface are considered as the parameters [1]. There are more than 20 parameters in this numerical model. It would take a lot of time to obtain all of them only from the experiments. In this study, we conducted the parameters needed for the numerical model for describing the charge and discharge or capacity voltage curves of lithium ion and lithium air batteries using a machine-learning. Used learning method is the neural network (NN) that shows remarkable progress in the field machine learning. NN has a layered structure, and between layers are formed by multiply-add operation with a weighting factor. In this research, NN learning is carried out to induce parameters used in the numerical model. Training-data (capacity-voltage or discharge-capacity curves) are generated by employing the numerical model calculation with various different input parameters. For instance, we constructed a deduction model using 24 charge using NN and discharge curves as a training set and confirmed the reasonable accuracy. In addition, we also check the accuracy for the induction of multiple parameters such as the reaction rate and temperature, etc. The accuracy of induction tends to depend on the number of kind of unknown parameters, the accuracy and their dependency on the detailed algorithm of NN will be presented and discussed. Consequently, machine learning is useful tool for quickly determination of unknown parameters in the numerical model that are sometimes difficult to measure directly.


**G101.05.24**

**Bayesian Inference Enabled Experimental Determination of Materials and Transport Descriptors in ThermoElectric**

D V M. Repaka, Ady Suwardi, Zekun Ren, Tonyo Buonassisi, and Kedar Hippalgaonkar; IMRE A-STAR, Singapore, Singapore; Singapore-MIT Alliance for Research and Technology, Singapore, Singapore; Massachusetts Institute of Technology, Cambridge, Boston, Massachusetts, United States.

ThermoElectric, which can convert heat into electrical power based on the Seebeck effect and vice-versa based on the Peltier effect can be a very useful alternative source of both electrical and thermal power. So far, machine learning approaches have only been used to predict promising new thermoelectric compositions from density functional theory calculations, building upon open-source databases towards the discovery of high performance materials. Further, high-throughput materials screening approaches are still rudimentary, limited by the lack of universally defined material and thermoelectric transport descriptors. Finally, rapid and accurate materials characterization that can directly measure these descriptors are arduous (for example, method of four coefficients) or do not exist. Our work discloses a rapid and accurate way to determine the material and transport descriptors of thermoelectric performance by feeding simple single-leg power/load experimental data to a Bayesian machine learning algorithm using Boltzmann transport theory. The accurate generalized forward model we have developed allows the use of Bayesian inference demonstrating its utility as an ideal machine-learning (ML) tool for material diagnostics. Employing only two input parameters (temperature gradient and external load resistance) and the observed power output, the Bayesian inference algorithm is able to extract thermoelectric parameters ranging from material-layer properties (Seebeck coefficient, electrical resistivity) to transport-layer characteristics (energy-dependent scattering parameter, band gap offset, etc.) as well as extrinsic contributions such as parasitic contact resistance. In addition, systematic error from measurement can also be identified and corrected. This is made possible since we have devised an experimental setup developed in-house that can generate temperature-dependent data for ML-enabled characterization. Hence, we are able to predict band and transport descriptors that can be measured directly using experiments for the first time. While these reveal the complex dynamics of scattering in thermoElectric materials, we envision that they will also provide universal screening criteria for high performance thermoelectrics in the near future.

**G101.05.25**

**Accelerating Molecular Dynamics with On-the-Fly Machine Learning**

Jonathan Vandermause, Steven Torrisi, Simon Batzner, Alexie Kolpak, and Boris Koziynsky; Harvard University, Cambridge, Massachusetts, United States; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Ab initio molecular dynamics (MD) is a powerful tool for accurately probing the dynamics of molecules and solids, but it is limited to system sizes on the order of 1000 atoms and times scales on the order of 10 ps. We present a scheme for rapidly training a machine learning (ML) model of the interatomic force field that approaches the accuracy of ab initio force calculations but can be applied to larger systems over longer time scales. Gaussian Process (GP) models are trained “on-the-fly”, with density-functional theory (DFT) calculations of the atomic forces performed whenever the model encounters atomic configurations sufficiently far outside of the training set. This active learning scheme includes a principled means of deciding when to run additional DFT calculations, accelerating the model's exploration of parameter space while reducing the time spent training the model. Furthermore, we demonstrate that additional ML models can be trained in parallel to predict other quantities of interest, including the ground state energy and charge density, making it possible to efficiently capture with ML the wealth of information provided by full DFT calculations. We demonstrate the flexibility of our approach by testing it on a range of single- and multi-component molecular and solid-state systems, including benzene, silicon, and silicon carbide.

**G101.05.26**

**Prediction of Repeat Unit of Optimal Polymer by Bayesian Optimization**

Tokuya Minami, Masaki Kawata, Toshio Fujita, Katsumi Murofushi, Hiroshi Uchida, Kazuhiro Omori, Yoshishige Okuno; Showa Denko K. K., Tokyo, Japan; National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan; Research Association of High-Throughput Design and Development for Advanced Functional Materials, Tokyo, Japan.

In recent years, an inverse analysis that can predict materials with desired physical properties has attracted attention as a method that enables rapid design of materials [1].
Bayesian optimization is one of the approaches which efficiently design optimal materials [2]. For examples, numerous successful studies have been reported on Bayesian optimization in inorganic material design [3] and automatic laboratory robots [4]. However, although it is important for industries, there are only a few reports on Bayesian optimization in polymer design. In this study, to confirm the effectiveness of Bayesian optimization for polymer design, we performed the case study on the prediction of repeat unit of polymer with optimal glass transition temperature. To evaluate the number of trial and error for achieving optimal physical properties, a trial and error test was conducted using a known data set. Here, the prediction model was constructed by a part of prepared dataset, and the optimal polymer was explored for the rest dataset. The prediction model was made from the features of structural formulas [5] and the glass transition temperatures of polymers, by using Gaussian process regression. As the result, we found that the Bayesian optimization could significantly reduce the number of trial and error in the prediction of repeat unit of polymer, compared to the random search.


GI01.05.27
Feature-Based Data Analysis Methods in Alloy Systems
Zhiting Guo1, Tao Xu1, Hongqing Hu1, Gaofeng Zhou1, Shengzhou Li1, Xin Wang1, Dongbo Dai1, Xiao Wei1, Huiran Zhang1 and Guangxi Ding1; 1School of Computer Engineering and Science, Shanghai University, Shanghai, China; 2Materials Genome Institute, Shanghai University, Shanghai, China.

This paper proposes a dynamic model, which is built by machine learning methods, used for predicting the property in metal alloy systems. The model is trained by adding features of 64 sets of the data. It is found that the process of phase transformation is related with its properties and can accurately predict the property like solid solution ability. The result of the experiment shows that if the optimal features are chosen, the model has a better predicting performance than traditional methods using all the features.

GI01.05.28
Realizing Real-Time Crystallographic and Materials-Based Analysis Using Deep Learning Tools
Jeffery A. Aguiar1, 3, Matthew Gong2, 1 and Tolga Tasdizen2; 1Nuclear Materials Department, Idaho National Laboratory, Idaho Falls, Idaho, United States; 2Scientific Computing and Imaging Institute, The University of Utah, Salt lake city, Utah, United States; 3Materials Science and Engineering Department, The University of Utah, Salt Lake City, Utah, United States.

Extending from the micron to the atomic scale transmission electron microscopy is a powerful research tool for structural and chemical analysis for materials research. The breadth of data collected simultaneously in the latest generation of scanning transmission electron microscopes presents challenges and opportunities for advancements in microscopy, multi-modal data analytics, image-based forensics, and materials research. Recent advancements in deep learning have made it possible to analyze these massive data sets and perform complex imaging tasks. However, deep learning and augmented analysis have not yet disrupted the microscopy and microanalysis community like they have the computer vision community. Breakthroughs in automating and augmenting microscopy data collection and analysis could more than halve research cycle times in fields that rely on microscopy including materials and biological research.

The goal of recent technological developments and research is to create a suite of tools to expand the real-time analytic capabilities of microscopy as well as post-hoc analysis for diffraction-based tools. By applying cutting edge deep learning, computer vision, and signal processing techniques, our team aims to make real-time event tracking and automation of imaging, diffraction, and spectroscopy acquisition a reality in the future. This suite of computational tools and analytical packages is being developed in collaboration with commercial partners, national laboratories, and universities/academia. The software has now been publicly released and designed to draw from standard materials libraries including the Materials Project database and the Open Crystallography database, but also can be further enhanced by research and experimental data from the greater materials community.

In this late breaking poster, we will present our developments and look to the community to further evaluate our emerging real-time augmented feedback framework for materials prediction. This includes pending developments that utilize hybridized first principal and deep learning models for augmented analysis of material properties, spectroscopy, and diffraction patterns. We further look forward to discussing the growing potential of automating data collection from materials-centric data feeds for real-time event tracking and potentially prediction.

GI01.05.29
Application of Deep Learning Methods to the Analysis of Mass Spectra in Atom Probe Tomography
Arpan Mukherjee, Scott Broderick and Krishna Rajan; Materials Design and Innovation, University at Buffalo, The State University of New York, Buffalo, New York, United States.

We present the use of deep learning methods to develop automated methods for the deconvolution of time of flight spectra in atom probe tomography. This work describes the nature of the algorithms underlying the deep learning methods. This new automated process of labeling of atoms replaces the manual process of ranging and shows high accuracy.

GI01.05.30
Statistical Learning and Prediction of Electronic Transport in Multilayered Non-Ideal Semiconductor Architectures
Sanhmitra Neogi and Artem K. Pimachev; University of Colorado Boulder, Boulder, Colorado, United States.

Computing components are being aggressively inserted into electronic, optical, sensing, robotic, bio-system or energy transport devices, to perform multitudes of data-centric operations at high rates. Modern fabrication techniques have reached the sizes of quantum confinement regime, therefore making it possible to model electronic properties of device components with first principle calculations. The contact interfaces between these components dictate the device performance, especially as the device dimension approaches nanoscale. These interfaces are often marked by point defects, dislocations and additional strains due to lattice mismatch between the components. Ab initio methods become expensive and infeasible to predict electronic properties of integrated architectures with such a great number of compositional and configurational degrees of freedom. In recent years, there has been a large effort in the materials science community to employ data driven methods to accelerate materials discovery or to develop new understanding of materials behavior. However, the number of efforts, employing first-principle based data-driven methods to predict device performance incorporating processing variability, is almost non-existent.

In this study, we employ machine learning (ML) algorithms to predict electronic structure and transport properties of non-ideally fabricated multilayered thin film Si/Ge nanostructures. The ML model is trained on inexpensive ~200 DFT calculations of Si/SiGe alloys: the training data set is populated exploiting the relationship between geometrical features or local atomic environments in these systems and their electronic structure properties. The predictor variables are obtained with Voronoi tessellation approach and the response variables are calculated with the decision tree regression algorithm. [1] This approach has successfully predicted formation energies to expedite materials discovery, [2] Our ML model trained on random alloys, has shown remarkable ability to predict electronic band structures and Onsager electronic transport coefficients of large non-ideal thin film Si/Ge superlattices. We show the predictive power of our model by comparing the predicted band structures learned from small 16-atom alloy unitcells with the electronic states of large Si/Ge superlattices unfolded to 4x4 monolayer superlattice Brillouin zones [3]. The ML framework has been especially effective in capturing crucial trends in electronic properties for a range of multilayered structures. Our ML framework will facilitate the development of inverse design approach to engineer interface profiles of integrated semiconductor architectures, to accomplish desired device performance and functionalities.


G01.05.31
Machine Learning for Perovskite Solar Cells
John M. Howard and Marina S. Leite; University of Maryland, College Park, Maryland, United States.

Perovskite solar cells have recently reached power conversion efficiency > 22%, representing a promising option for high-performance and low-cost photovoltaic (PV) devices [1]. Yet, their performance is dynamic, varying as a function of time under intrinsic (bias, temperature, and light) and extrinsic (water and oxygen) parameters [2,3]. Because the influence of each stressor on device response depends on the perovskite chemical composition (>9000 options with potential application in PV) and on the order of exposure and the value range of each parameter, an extremely large number of possible combinations is expected. Therefore, we propose a machine learning (ML) paradigm based on an artificial neural network (ANN) to determine the optimal conditions for the perovskites operation, including their ‘reap’, ‘rest’ and ‘recovery’ phases [3]. ‘Reap’ is required for harvesting energy (PV device operation), while both ‘rest’ and ‘recovery’ stages are needed for assuring that the changes in the optical and electrical responses are reversible, preventing material/device degradation and maximizing long-term performance [4]. The successful implementation of the ANN routine for ultimate unsupervised learning relies on our suggested ‘knowledge-shared’ tactic, where researchers from academia, national laboratories and companies will gather positive and negative experimental results in a shared data repository. We highlight that while most ML efforts applied to perovskites focus on screening thermodynamically stable options, our artificial intelligence approach targets the dynamic response of this promising class of material, never exploited before. Our ML strategy will accelerate monitoring and controlling of device performance recovery, paving the way for the fast development of stable perovskites and its commercialization.

Coordination environments (e.g., tetrahedra and octahedra) are powerful descriptors of the structure of a solid. An automatic and robust detection of these environment is an important step towards the data mining of the large databases (experimental or theoretical) currently available to materials scientists. In this work, we present a tool to automatically determine coordination environments in a given structure. The identification is performed based on the sole consideration of the geometrical knowledge of the structure. Distortions are taken into account and we allow the description of an environment as a mixture of several environments. After outlining our algorithm, we will illustrate the approach by presenting a statistical analysis of coordination environments for all oxides from the Inorganic Crystal Structure database (ICSD). We will discuss the implication of our study and how this tool can be used to accelerate the materials design process.

2:15 PM GI01.07.03 Materials Discovery for Thermal Energy Storage—A High Throughput Computational and Machine Learning Approach Steven G. Kiyabu, Alaudin Ahmed, Jeffrey S. Lowe and Donald Siegel; University of Michigan, Ann Arbor, Michigan, United States.

Salt hydration reactions show great promise for thermal energy storage (TES) due to their high energy densities, cost effectiveness, and potential for reversible operation at moderate temperatures. While a number of salt hydrate compositions have been investigated previously for TES, many have yet to be explored. The goal of this work is to identify hypothetical salt hydrate structures that are thermodynamically stable and can out-perform known materials. All 25 distinct crystal structures of the form M\textsuperscript{n+}\textsubscript{m}nH\textsubscript{2}O (where M\textsuperscript{n+} is a metal cation, X\textsuperscript{2} is a halide, and n \geq 6) found in the Inorganic Crystal Structure Database were used as structural templates. A total of 1,824 hydrate structures were generated from systematic cation and anion substitution and were characterized by Density Functional Theory calculations according to their energy densities and operating temperature range. A variety of classification and regression machine learning (ML) algorithms were trained on the data to predict stability as well as TES performance. Thousands of mathematical combinations of the basic ionic and structural properties were generated and the most promising features were selected from this list to be used in the ML algorithms. In addition to identifying new, promising materials for TES, our study identified which features are relevant to TES performance as well as predictive models that can be used to further accelerate our screening of hypothetical salt hydrate structures for TES.

2:30 PM BREAK

3:30 PM *GI01.07.04 Accelerated Search for Materials with Targeted Properties Turab Lookman; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Finding new materials with targeted properties with as few experiments as possible has been a goal of the materials genome initiative. The enormous complexity due to the interplay of structural, chemical and microstructural degrees of freedom in materials makes the rational design of new materials rather difficult. Machine learning and optimization, used in industry for solving complex problems, are increasingly being adapted for the design of new materials by learning from past data and making smart decisions about what the test next. However, the number of well characterized samples available as sources of data to learn from is often relatively small. I will review how we have utilized Bayesian Global Optimization to iteratively guide experiments to discover new alloys and ceramics.

4:00 PM GI01.07.05 Accelerated Search for Ultra-Incompressible, Superhard Materials Through Machine Learning Aria Mansouri Tehrani and Jakoah Brgoch; University of Houston, Houston, Texas, United States.

In the search for materials with exceptional mechanical properties, we have developed a machine-learning model to predict the elastic moduli of inorganic materials, which act as a proxy for hardness. Materials project database of elastic moduli has been used as the training set and the machine learning model is developed using support vector regression method implementing 150 compositional and structural variables. Further, a genetic algorithm-based variable selection is performed using partial least square regression method resulting in a cross-validated root mean square error (RMSE) of 17.2 GPa and 16.5 GPa for bulk and shear modulus. Subsequently, 118,287 compounds from crystalline databases are screened regardless of their chemical composition and atomic disorder for compounds with high bulk and shear moduli having potential for superhardness. We then identified compounds of two interest, a ternary rhenium tungsten carbide and a quaternary molybdenum tungsten borocarbide for experimental investigation. These materials were synthesized using arc melting and characterized with high-pressure diamond anvil cell measurements to confirm the machine learning predictions with <10% error. Vickers hardness measurements revealed the extremely high hardness nature of these compounds making these the hardest transition metal carbide and borocarbide reported. The successful identification of these superhard materials using state-of-art machine learning and materials screening techniques emphasizes the effectiveness of these methods in materials discovery and development.

4:15 PM GI01.07.06 Machine Learning for Searching the Stable Structure of Crystal Interface Teruyasu Mizoguchi and Shin Kiyohara; The University of Tokyo, Tokyo, Japan.

Interfaces are a lattice defect inside materials, and influence the overall material properties. For instance, interfaces in polycrystalline materials, i.e., grain boundaries (GB), determine ion transportation properties and high-temperature mechanical properties. The fact that interfaces have different properties from the bulk is a consequence of the fact that they have different atomic configurations from that inside the bulk. Thus, for a comprehensive understanding of the interface properties, determination of the atomic structure of the interface is crucial. However, extensive calculations are necessary to determine even one interface structure because of the geometrical freedom of the interface. The number of atomic configurations to be considered often reaches 10,000 in even the simplified coincidence site lattice grain boundary, namely Σ grain boundaries. To accelerate interface structure searching, very efficient methods based on machine learning techniques, including virtual screening and Bayesian optimization have been proposed by the present authors.

We applied the virtual screening method to [001] symmetric tilt GB of Cu. The predictor was constructed using two Σ5 and two Σ17 GBs, and totally 83 descriptors related to the geometrical data, such as bond length and atom density, were used. The constructed predictor successfully determined other 12 GBs of Cu, Σ13 ~ Σ125 [1].

In addition to the virtual screening, we have developed an alternative and powerful method with the aid of a geostatistics approach called kriging[2]. Kriging is an effective interpolation method based on a Bayesian optimization and Gaussian process governed by prior covariance. The kriging method has been applied and demonstrated to determine the grain boundaries of fcc-Cu, bcc-Fe, MgO, rutile-TiO2, and CeO2 GBs [3-4].

The details of those studies will be shown in my presentation.

Fast charging protocols for lithium-ion batteries are critical for widespread adaptation of electric vehicles. However, a limited understanding of battery degradation modes during fast charging and the large manufacturing variability of commercial lithium-ion batteries are major challenges to the development of high-performance fast charging protocols. In this work, we optimize a three-step charging protocol for commercial 18650 lithium-ion batteries that achieves 80% state of charge in ten minutes. We employ two key elements to reduce the optimization cost: early prediction of failure, which uses cycling data from the first 100 cycles to predict cycle lives that reach up to 1200 cycles, and adaptive Bayesian optimal experimental design, which significantly reduces the number of experiments required. We identify promising fast charging protocols with identical charging times but lifetimes that exceed the baseline charging protocol out of a candidate pool of nearly 180 protocols. This method can be extended to accelerate development of other tasks in battery manufacturing and deployment, such as formation cycling and state-of-health estimation.

References:

SESSION GI01.08: Machine Learning Enhanced Computational Materials
Session Chairs: Keith A. Brown and Patrick Riley
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 110

8:00 AM *GI01.08.01

The advent of innovative molecular modeling algorithms, optimization strategies, and machine learning techniques is ushering in a new era of materials science and engineering in which computational tools are routinely used to probe, design, and interrogate matter and functional materials systems. In this presentation I will illustrate some of these ideas in the context of a variety of examples taken from chemical engineering, physics, biology and materials science. In the first, I will discuss the simultaneous interpretation of scattering data from multiple sources by relying on molecular models. In the second I will present models of biological systems that use machine learning to integrate experimental and computational information form a wide range of sources, and to discover collective variables that can be used to enhance sampling. In a third demonstration, I will explain how machine learning can by itself be used to improve and accelerate enhanced sampling algorithms. In a fourth example, I will discuss how evolutionary optimization and machine learning can be used to create new mechanical metamaterials, and to predict electronic transport in organic conductors.
Emerging machine learning (ML)-based atomic force fields provide a powerful tool to accurately model a variety of large-scale (length-scale > nm and time-scale > ns) physical and chemical processes, which remain outside the realm of quantum mechanical methods—such as density functional theory (DFT)—owing to their computational cost [1,3,4]. In the past, we proposed one such approach to construct a ML-based force field, where only the vectorial force on an atom is “learned” directly from its atomic environment [1]. The capability and transferability of this approach was demonstrated by accurately reproducing the structural, mechanical, transport and vibrational properties of elemental Al [1,2], and correctly modeling atomic forces for diverse elemental solids such as Cu, Ti, W, Si and C [5]. In this contribution, we showcase the true power of such ML-based force fields, the capability to systematically improve by actively learning from “failed” cases. The general strategy is based on the idea of repeated augmentation of poorly predicted configurations to the reference dataset, and re-training the model in a cyclic manner. Such a pathway for the iterative improvement of these force fields is straightforward, efficient, and universal. Here, we demonstrate this approach for Cu, Al and Pt using actively trained ML-based force fields that capture an array of phenomena such as surface diffusion mechanisms, stacking fault energies, divacancy behaviors and screw dislocation core structure. We conclude that this simple strategy can be adopted to construct targeted, application-specific ML force fields, extending our ability to capture materials phenomena which lie beyond the current reach of classical and/or quantum mechanical methods.


The scale of typical polymer molecular dynamics (MD) simulation usually involves at least several thousand atoms, which is necessary because the motion and dynamics of polymer chains strongly depends on the length of the polymer chains. This in turn makes it impossible to use ab-initio MD on systems which are representative of real polymer system, making it necessary to fit ab-initio data from separate fragments of organic functional groups in gas phase to classical force field with complex functional forms (such as the OPLS force field, for example). These functional forms typically do not describe chemical reactions due to its definition of explicit unbreakable atomic bonds. In addition, they do not accurately describe ionic interactions and other properties which involve electronic polarizability and charge transfer of atoms which only shows up under quantum mechanics in real bulk atomic systems.

In this work, we develop a multi-element neural network force field fitting procedure suitable for simulating randomly large bulk atomic systems such as polymers. We show that atomic snapshots under a certain radius of the central atom contains sufficient information to describe quantum mechanical atomic force accurately. Consequently, small atomic cluster snapshots can be simulated within quantum mechanical simulations in reasonable time scale to generate the training set (in the order of several tens of thousands of small atomic snapshots). Force vector projection on internal structural axes in combination with Behler-Parrinello style fingerprinting scheme enables direct training of atomic force vectors of individual atom elements, as opposed to training on the aggregate scalar energy of the entire ab-initio ensemble in the original Behler-Parrinello scheme. The neural network force field fitting algorithm will be presented, as well as accuracy results for polyethylene oxide (PEO) polymer typically used in Lithium battery polymer electrolytes.

The evaluation of atomic forces and total energy is a key challenge for large-scale atomistic simulations of materials. Ab-initio molecular dynamics (AIMD) is a successful approach but it becomes computationally too expensive for large systems. In this work, we demonstrate a direct and local Deep Learning (DL) model for atomic forces. We demonstrate this model for bulk aluminum, silicon and sodium and show that the model errors are comparable to other state of the art algorithms. Our model allows the calculation of forces in large cells using a training data that we built from smaller cells that were calculated with Density Functional Theory (DFT). In addition, we examine the question of temperature transferability of the mode and show that we can train the model with data that was produced at a high temperature and then test it on data that was produced at lower temperatures. Finally, we show that the physical properties of the system (e.g. number of nearest neighbors) is manifested in the model convergence with respect to some of its parameters.
Molecular crystals are bound by dispersion interactions, whose weak nature produces potential energy landscapes with many local minima. Hence, molecular crystals often exhibit polymorphism, whereby the same molecule crystalizes in several structures. Polymorphs may exhibit markedly different physical and chemical properties. Crystal structure prediction is challenging due to the high accuracy required for the small energy differences between polymorphs and the high dimensionality of the configuration space. We present the genetic algorithm (GA) code, GAtor [J. Chem. Theory Comput., 14, 2246 (2018)], and its associated structure generation package, Genarris [J. Chem. Phys., 148, 241701 (2018)]. Both rely on dispersion-inclusive density functional theory (DFT) for geometry relaxations and energy evaluations.

Genarris generates random structures with physical constraints and uses a Harris approximation to construct the electron density of a molecular crystal by superposition of single molecule densities. The DFT energy is then evaluated for the Harris density without performing a self-consistent cycle, enabling fast screening of initial structures with an unbiased first-principles approach. Genarris creates a maximally diverse initial pool of structures by using machine learning for clustering based on structural similarity with respect to a relative coordinate descriptor (RCD) designed for molecular crystals. GAs rely on the evolutionary principle of survival of the fittest to perform global optimization. GAtor offers a variety of crossover and mutation operators, designed for molecular crystals, to create offspring by combining/modifying the structural genes of parent structures. GAtor achieves massive parallelization by spawning several GA replicas that run in parallel and read/write to a common pool of structures. GAtor performs evolutionary niching [Faraday Discussions, DOI: 10.1039/C8FD00067K (2018)] by using machine learning for dynamic clustering on the fly. A cluster-based fitness function is then used to steer the GA to under-sampled low-energy regions of the potential energy landscape. This helps overcome initial pool biases and selection biases.

Transition metal dichalcogenide (TMD) are novel nanomaterials that can behave like conductors, semiconductors, or insulators depending on the type of transition metal used. With a thickness as small as 3 atoms and size dependent properties, TMDs have a great potential in applications such as flexible and wearable electronics. Despite the early discovery of TMDs and their synthesis via vapor deposition, fundamental understanding on their growth mechanisms remains largely unknown, which hindered the preparation of these materials on a larger scale. Molecular simulations can be used to address this problem, but the lack of accurate interatomic potentials and the large effort required to develop them presents a major barrier. Here, we demonstrate the use of a machine learning based framework in the development of a reactive force field model for tungsten diselenide. Our data-driven procedure led to a model that accurately captures various properties, including structures, dynamical stability, phonon, and various energetics, which is obtained without the need to rely heavily on human intuitions or lengthy development time. With the model, we perform molecular dynamics simulations to investigate the growth of 2D tungsten diselenide under different vapor deposition conditions as well as to study their mechanical properties.

DNA-stabilized silver clusters (Ag-DNAs) are composed of ~10-30 silver atoms wrapped in short strands of DNA [1]. Ag-DNAs can be highly fluorescent and are finding use for chemical sensing and DNA detection [2]. The nucleobase sequence that stabilizes a cluster controls silver cluster size, leading to well-known yet little-understood sequence-tuned Ag-DNA fluorescence colors. The large space of possible stabilizing sequences challenges the understanding of how sequence selects Ag-DNA properties, limiting the design of new applications for Ag-DNA. Are there subsequences, akin to genes, that are important for stabilization of products with desired properties? Can these subsequences be used for predictive Ag-DNA design? To answer these questions, we develop a closed-loop framework combining machine learning and experimentation. We determine the fluorescence spectra
of Ag-DNAs stabilized by over 1000 distinct DNA oligomers of fixed length using high-throughput synthesis and fluorimetry. Then, we mine for DNA subsequences, or motifs, that are discriminative of fluorescence brightness and color. As a result, each DNA template is represented by a feature vector encoding the inclusion/exclusion of discriminative motifs. We train classification models based on the above training data and further employ those to generate and screen new sequences, improving both fluorescence brightness [3] and the selectivity for a desired Ag-DNA color [4]. Our methodology improves color selectivity by 330% for Ag-DNAs with peak emission beyond 660 nm. The discovered motifs also provide physical insights into how DNA sequence controls silver cluster size and color. This data-driven design approach for color of DNA-stabilized silver clusters demonstrates the potential of machine learning and data mining to increase precision and efficiency of nanomaterials design.

In our ongoing work, we extend these methods to varying-length templates and Ag-DNAs emissive at unobserved wavelengths. Are the motifs detected in a training set of fixed-length DNA template predictive when templating with DNAs of different length? Furthermore, is it possible to employ our data-driven framework to predict and design for unobserved Ag-DNA colors in the near-infrared? Strong evidence for the utility of motifs in the above tasks will support the hypothesis of “motifs serving as genes” for Ag-DNAs and further direct the study of these important materials.


11:30 AM GI01.08.12
Data Generated Formula for Creep and Stress Relaxation Sheng Sun and Tong-Yi Zhang; Materials Genome Institute, Shanghai University, Shanghai, China.

Analytic formula is the best and ideal means in the clear description of time-, stress-, and temperature-dependent deformation behavior and in the understanding of the deformation mechanism. To have such a formula for creep and stress relaxation, multi-temperature creep, stress-relaxation, and indentation creep tests were conducted on nanograined copper and nanotwinned copper under various loading levels to generate sufficiently large number of data, which allows one to develop an analytic formula of plastic strain rate versus temperature and stress (or hardness in indentation creep) by using symbolic regression with domain knowledge. The analytic formula explicitly involves the athermal stress (or hardness) exponent, activation energy, and activation volume, which values are determined reliably from the experimental data from the multi-temperature tests.

SESSION GI01.09: Deep Learning and Neural Networks for Materials
Session Chairs: John J. Boeckl and Kristofer Reyes
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 110

1:30 PM *GI01.09.01
Promise and Perils of Machine Learning in the Sciences Patrick F. Riley; Google Research, Google, Mountain View, California, United States.

All around we see excitement about machine learning to make a meaningful change in a variety of scientific disciplines. Sometimes lost in this discussion is a clear understanding and discussion of the risks, expected utility, and proper application of these powerful techniques. Through vignettes of real applications of machine learning to scientific problems by the Google Accelerated Science group, this talk will illustrate important lessons for scientists who want to make machine learning part of their toolkit.

2:00 PM GI01.09.02
Automatic Classification of Hypothetical Zeolites with Unsupervised Machine Learning Daniel Schwalbe-Koda and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Zeolites are inorganic nanoporous materials with wide industrial applications for their catalytic, adsorbent and ion-exchange properties. Because of their broad applications, selectivity, robustness and cost-effectiveness, intense basic and applied research is devoted to the discovery new zeolitic materials. Whereas hundreds of thousands of hypothetical zeolite-like frameworks are theoretically possible, only ~235 different known geometries have been synthesized to date [1]. The virtual space of possible zeolites has been explored by algorithmic generation and later filtered by physics-based simulations of thermodynamic driving force [2]. Several hand-made criteria based on geometrical or thermodynamic analysis have been proposed to differentiate synthetically accessible zeolites, but the underlying aspects that define zeolite feasibility remain unknown.

Aiming to accelerate the discovery and design of realizable zeolites, we have applied unsupervised machine learning methods to explore the topological and geometrical degrees of freedom responsible for the synthetic accessibility of zeolitic frameworks. Similar deep learning models have been successfully applied to map molecules onto a continuous space [3]. A generative model comprised of a Wasserstein autoencoder [4] was coupled to graph convolutional neural networks customized for crystalline solids [5]. Using a large dataset of hypothetical zeolites, the model was trained to reconstruct the original unit cells from a low dimensional representation. Going through this information bottleneck allows to automatically identify the key collective variables that describe zeolitic frameworks. In addition, the model was jointly trained to predict physics-based labels in a semisupervised fashion using existing simulations, thus contributing to create a smooth and robust latent representation. In a last step, hypothetical and known feasible zeolites were projected onto the latent space. By exploring common patterns, the deep learning toolset allows to single out hypothetical zeolite frameworks that are likely to be feasible.

Emerging machine learning (ML) based methods provide powerful tools to extract structure-property relations from the ever-growing materials simulation and experimental databases. However, most existing ML methods depend on feature vectors to represent different materials, which are limited to specific material groups and some computationally expensive features. In this talk, we present a crystal graph convolutional neural networks (CGCNN) framework [1] that represents an arbitrary periodic structure with an arbitrary number and type of atoms in a unit cell. We achieve state-of-the-art prediction performance for 8 different material properties using only the crystal structure information. We also extract materials design knowledge from the neural networks which can help accelerate the screening of materials. Finally, we show several examples of how the method can be applied to the design of Li metal battery electrolytes [2] and other material systems.


2:30 PM GI01.09.04
Deep Transfer Learning for Active Optimization of Functional Materials Properties in the Data-Limited Regime Brian DeCost and Gilad Kusne; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The recent development of learned representations for molecules and crystals via variants of graph convolutional neural networks (GCNs) has enabled significant improvements in the performance of data-driven models of chemical and physical properties of materials. This class of neural networks learns complex hierarchical representations of molecules and crystals using only a small number of elemental properties and the topology of the molecule or crystal. The representations learned by GCNs are built up by sequentially performing graph convolutions (i.e. local weighted sums) over the bonding network, where the graph convolution weights are optimized by stochastic gradient descent via backpropagation. We explore a deep transfer learning approach to leverage this representational power in solid state systems for which available data is limited and especially where additional data is expensive to acquire. In this proof of concept study, we hold out entire classes of functional materials (e.g. perovskite photovoltaic candidates, Heusler and Heusler-related compounds) during the GCN training process, using large density functional theory (DFT) calculation datasets for both training and active learning test sets. We then perform de novo active learning using GCN-derived features to optimize the relevant functional materials properties for each held out materials system. We compare the computational efficiency of the active learning process using GCN features to that using competitive engineered features, such as the Magpie feature set. Future efforts will focus on directly driving experimental efforts and DFT calculations using this deep transfer learning strategy.

2:45 PM BREAK

3:15 PM #GI01.09.05
Applying Deep Learning to Proteins and Small Molecules Lucy Colwell; Department of Chemistry, University of Cambridge, Cambridge, United Kingdom.

The evolutionary trajectory of a protein through sequence space is constrained by its function. Collections of sequence homologs record the outcomes of millions of evolutionary experiments in which the protein evolves according to these constraints. The explosive growth in the number of available protein sequences raises the possibility of using machine learning and artificial intelligence to exploit the natural variation present in homologous protein sequences to infer these constraints and thus identify sequences with different protein phenotypes.

Because in many cases phenotypic changes are controlled by more than one amino acid, the mutations that separate one phenotype from another may not be independent, requiring us to understand the higher order structure of the data. We show that models learned from data are capable of predicting key aspects of protein function. These include (i) the inference of residue pair interactions that are accurate enough to predict all atom 3D structural models; and predictions of (ii) binding interactions between different proteins and (iii) binding between protein receptors and their target ligands. Finally, I will discuss current efforts to search the space of possible sequences for those that correspond to proteins with specific functional properties that exploit recent advances in deep learning.

3:45 PM GI01.09.06
Design of Bioinspired Hierarchical Systems Using Machine Learning, Additive Manufacturing and Experiment Grace Gu, Chun-Teh Chen, Deon Richmond and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Developments in the materials science community are tending more and more to a materials-by-design approach, no longer accepting the status quo with the insight that we can tailor-make materials with desired properties for specific applications. Biological materials, such as bone, wood, and seashells, have multifunctional properties that often surpass that of their synthetic counterparts. Composed of a limited set of building blocks, nature intelligently organizes these building blocks into hierarchical architectures, allowing them to overcome the limitations of their constituents while combining their best attributes. These complex architectures pose a challenge for traditional manufacturing techniques due to their multi-material construction, hierarchy, and potential voids. Additive manufacturing is a new tool that can overcome these limitations. In this work, we use convolutional neural networks (CNN) to cast the natural process of evolution into a computational framework to study bioinspired hierarchical structures. With an integrated approach of simulation, machine learning, additive manufacturing, and experimental testing, we investigate the optimal microstructural patterns that lead to tougher and stronger materials. In the future, this bioinspired machine learning approach will enable materials-by-design of complex architectures to tackle demanding engineering challenges.
Deep Learning Bandgaps of Topologically Doped Graphene

Yuan Dong, Chuhan Wu, Chi Zhang, Jianlin Cheng and Jian Lin; University of Missouri-Columbia, Columbia, Missouri, United States.

Manipulation of physical and chemical properties of materials via precise doping has afforded an extensive range of tunable phenomena to explore. Recent advance shows that in the atomic and nano scales topological states of dopants play crucial roles in determining their properties. However, such determination is largely unknown due to the incredible size of topological states, which makes it almost impractical to search by experiments or ab initio calculations. Here, we present a case study of using deep learning algorithms to predict bandgaps of boron-nitrogen pair doped graphene with random dopant topologies. In the study, the bandgaps are calculated by the accurate first-principle calculations, and together with the structure information they are fed as datasets to train three types of convolutional neuron networks (CNNs), including VGG16 convolutional network (VCN), residual convolutional network (RCN), and concatenate convolutional network (CCN). All of these CNNs afford good prediction accuracy, outperforming non-convolutional support vector machine (SVM). We further perform the transfer learning by leveraging data generated from smaller systems to improve the prediction for large supercell systems. The success of this work provides a cornerstone for future investigation of topological doping in graphene and other 2D materials beyond graphene. Furthermore, it will stimulate widespread interests in applying materials property data into actionable knowledge, and more recently it has been used to assist in experiment design. In this talk we present the next step in machine learning for materials research - autonomous materials research systems. We first demonstrate autonomous measurement systems for phase mapping, followed by a discussion of ongoing work in building fully autonomous systems. For the autonomous measurement systems, machine learning

SESSION GI01.10: Autonomous Research II
Session Chairs: Keith A. Brown and Kristofer Reyes
Friday Morning, November 30, 2018
Hynes, Level 1, Room 110

8:30 AM *GI01.10.01
Autonomous Materials Research Systems—Phase Mapping Gilad Kusne1, 2, Brian DeCost1, Jason Hattrick-Simpers1 and Ichiro Takeuchi2; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2University of Maryland, College Park, Maryland, United States.

The last few decades have seen significant advancements in materials research tools, allowing researchers to rapidly synthesize and characterize large numbers of samples - a major step toward high-throughput materials discovery. Machine learning has been tasked to aid in converting the collected materials property data into actionable knowledge, and more recently it has been used to assist in experiment design. In this talk we present the next step in machine learning for materials research - autonomous materials research systems. We first demonstrate autonomous measurement systems for phase mapping, followed by a discussion of ongoing work in building fully autonomous systems. For the autonomous measurement systems, machine learning
controls X-ray diffraction measurement equipment both in the lab and at the beamline to identify phase maps from composition spreads with a minimum number of measurements. The algorithm also capitalizes on prior knowledge in the form of physics theory and external databases, both theory-based and experiment-based, to more rapidly hone in on the optimal results. Materials of interest include Fe-Ga-Pd, TiO2-StrO2-ZnO, and Mn-Ni-Gic.

9:00 AM GI01.10.02 Streaming Data Analysis Software Taking Us Towards Autonomous Experimentation—SHED and Streamz
Christopher J. Wright1, Jason Hattrick-Simpers2 and Simon J. Billinge3, 4; 1Columbia University, New York, New York, United States; 2Materiel Energy and Sustainable Development Group, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 3Condensed Matter Physics & Materials Science, Brookhaven National Laboratory, Upton, New York, United States.

Autonomous experiments have three major parts, data acquisition, data analysis, and feedback. While all three are crucial to performing the experiment, the data analysis portion may be the most challenging. The data analysis must take raw data, produce meaningful quantities of interest, and translate them into actionable experimental parameters. Importantly all of this must be done live. In this talk I will discuss our approach to streaming data analysis for x-ray total scattering measurements, using analysis pipelining programs we have written, streamz and SHED. Streamz and SHED provide a simple, powerful, and easy to use way to build streaming data processing protocols in python. The SHED system also provides seamless data provenance with minimal user input. Finally we'll discuss the application of these pipelines to kriging driven autonomous experimentation for discovering novel glass forming alloys via atomic pair distribution function analysis.

9:15 AM *GI01.10.03 Industrial Waste Gas Mixture as a Feedstock in Efficient Carbon Nanotube Growth—Using an Autonomous Research System to Probe Growth Kinetics and Mechanisms
Brian Everhart1, Pavel Nikolaev2, 3, Rahul Rao2, 3, Benji Maruyama2 and Placidus B. Amama1; 1Tim Taylor Department of Chemical Engineering, Kansas State University, Manhattan, Kansas, United States; 2Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio, United States; 3UES Inc., Dayton, Ohio, United States.

Fischer–Tropsch synthesis (FTS) is an environmentally friendly process used in industry for the conversion of syngas (CO and H2) – usually obtained from low-value biomass, natural gas, and coal – to high-value hydrocarbon liquid fuels over transition metal catalysts (typically Fe or Co). The gaseous product mixture (FTS-GP) usually consists of C1-C4 hydrocarbons and unconverted CO and H2, which we use as a feedstock for the chemical vapor deposition (CVD) growth of carbon nanotubes (CNTs). A comparison of the growth curve of FTS-GP CVD using an Fe catalyst with other conventional CVD processes for CNT forest growth, reveals growth behavior (in terms of catalyst lifetime and growth rate) superior to existing CVD approaches. The objective of this study is to develop the fundamental understanding required to couple catalytic CVD for CNT growth to the waste-gas stream of FTS (FTS-GP) for scalable, continuous, and controlled growth of CNT arrays. Due to the breadth of parameters that affect CVD growth of CNTs, rapid experimentation is necessary for effective growth condition optimization and detailed understanding of the role of FTS-GP. Here we employ an autonomous research system (ARES), equipped with in situ Raman spectroscopy, to probe the growth kinetics of CNTs and elucidate the secret role of FTS-GP in enhancing catalyst lifetime and growth efficiency. ARES allows for both rapid, automated experimentation as well as autonomous growth, in which the system self-generates experiments to maximize growth rate based on previous results. Our study reveals the dependence of growth temperature, catalyst properties, feedstock composition, and partial pressure of FTS-GP on activity and lifetime of catalysts. As examples, the optimal growth temperature and FTS-GP partial pressure for CNT growth on an Fe catalyst were determined to be approximately 850 °C and 20 Torr, respectively. We have also studied the effects of continual water generation on the surface of a catalyst, and its capability of enhancing growth by prolonging catalyst lifetimes. This study is expected to illuminate the complex interdependence of catalysts and carbon feedstock and facilitate rational design of catalysts and growth recipes for efficient and controlled CNT growth.

9:45 AM GI01.10.04 The Odds of Synthesis—Predictions from Network Analysis and Phase Diagrams
Muratathan Avkoli; Toyota Research Institute, Los Alisos, California, United States.

Synthesis of new materials is a complex, multi-faceted process driven not only by thermodynamics or kinetics but also by the availability of precursors and techniques, expertise, intuition and many other circumstantial factors. With this complexity, predictive synthesis is emerging as the new grand challenge in materials discovery. In this talk, we will present a tractable information approach to predicting the likelihood of successful experimental synthesis of hypothetical materials, such as those identified via high-throughput (HT) density functional theory (DFT), prototype searches or various other modeling techniques. The method combines network interpretation of the free energy-composition space obtained from HT-DFT, i.e. the convex-hull, and the discovery timeline of materials extracted from publications, to build accurate machine-learning models that forecast probability of successful synthesis in the laboratory. *This work was done in collaboration with Santosh Suram, Patrick Herring, Linda Hung, Vinay Hegde, Jens Hummelsheim and Chris Wolverton.

10:00 AM BREAK

10:30 AM *GI01.10.05 Cold Spray from Coatings to Additive Manufacturing
Leonardo Ajdehazian; GE Global Research, US, Niskayuna, New York, United States.

This work describes the fundamentals of cold spray and explore its use beyond just a coating process. The use of cold spray as an additive technology shows promising due to the unique solid-state characteristics of the process and the low thermal input to the material. This enable us to produce microstructures that are not possible with traditional manufacturing techniques, and properties that can exceed current commercially available alloys with the same chemistry. Nevertheless, to transform a coatings process into a 3D additive modality, a significant effort must be placed on how to design and build complex shapes using cold spray. The implementation of machine learning techniques to produce complex geometries using cold spray, and its advantages over other approaches, will also be discussed.

11:00 AM GI01.10.06 A Bayesian Framework for Selection, Calibration and Uncertainty Quantification of Thermodynamic Property Models
Noah H. Paulson, Elise Jennings and Marius Stan; Argonne National Laboratory, Chicago, Illinois, United States.

Thermodynamic property models form the basis of numerous technologically important applications including the calculation of equilibrium phase diagrams and the simulation of microstructure evolution. Traditionally, the selection of models, weighting of data and removal of outliers are informed by the intuition of the researcher. Furthermore, model calibration is deterministic, rarely resulting in uncertainty intervals for the model predictions. In this work, we present a framework for the selection, calibration and uncertainty quantification (UQ) of thermodynamic property models. Enabled by recent developments in the field of machine learning and Bayesian inference, we present a methodology for applying a Bayesian framework to the above problems. The method combines network interpretation of the free energy-composition space obtained from high-throughput density functional theory (DFT), prototype searches or various other modeling techniques. The method combines network interpretation of the free energy-composition space obtained from high-throughput density functional theory (DFT), prototype searches or various other modeling techniques.
On Converting Material Phase Dynamic Transformation Problem into Material Video Frame Variation Problem

2:15 PM

advances in numerical sampling algorithms, we employ fully Bayesian methods to address each of these tasks in addition to common issues seen in thermodynamic data including outliers, inaccurately reported or missing error bars and systematic errors. In addition, the framework enforces consistency between the thermodynamic quantities while optimally leveraging data from all available sources. The framework is demonstrated through the construction of thermodynamic property models for the alpha, beta and liquid phases of Hafnium metal for specific heat, enthalpy, entropy and Gibbs free energy.

SESSION GI01.11: Late News—Machine Learning and Data-Driven Materials Development and Design
Session Chairs: John J. Boeckl and Keith A. Brown
Friday Afternoon, November 30, 2018
Hynes, Level 1, Room 110

1:45 PM GI01.11.02
Learning UV-Vis Spectroscopy from Images on the World's Largest Experimental Materials Database Helge S. Stein, Dan Guevarra, Paul Newhouse, Edwin Soedarmadji and John M. Gregoire; Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California, United States.

UV-Vis spectroscopy is the first step in assessing light absorbers for solar fuels generation, but the community lacks sufficiently large experimental datasets and predictive models for experimental optical properties. Based on the largest and most diverse experimental materials science dataset of 180,902 distinct materials, including 45 elements, and more than 80,000 unique quinary oxide and 67,000 unique quaternary oxide compositions we trained different deep neural nets that enable us to predict complete UV-Vis absorption spectra from a materials sample image. The models learn how to spectrally hyperscale from a low energy but high spatial resolution input. Extracting direct bandgaps from predicted spectra yields an accuracy of bandgap prediction of 0.2 eV RMSE, which is well within the uncertainty of traditional extraction of bandgaps. Building upon these models we will present a one million experimental materials sample image dataset with complete data lineage and UV-Vis characterization. We will discuss methods and challenges in predicting optical properties from composition featurizers and chart pathways to autonomous experiment planning using state of the art visualization tools.

2:00 PM GI01.11.03
Material Image Segmentation with Machine Learning Method and Complex Network Method Chuabin Lai, Leilei Song, Yueying Han, Qian Li and Hui Gu; Shanghai University, Shanghai, China.

The study of the relationship among the manufacturing process, the structure and the property of materials can help to develop the new materials. Material images contain the microstructures of materials, therefore, the quantitative analysis for material images is the important means to study the characteristics of material structures. Generally, the quantitative analysis for material microstructures is based on the exact segmentation of the materials images.

However, most material microstructures are shown with various shapes and complex textures in images, and they seriously hinder the exact segmentation of the component elements. In this research, machine learning method and complex networks method are adopted to the challenge of automatic material image segmentation. Two segmentation tasks are completed: one, images of titanium alloy are segmented based on pixel-level classification through feature extraction and machine learning algorithm; the other, ceramic images are segmented with complex networks theory. In the first task, texture and shape features near each pixel in titanium alloy image are calculated, such as Gabor filters, Hu moments and GLCM (Gray-Level Co-occurrence Matrix) etc. Feature vector for the pixel may be obtained by arraying these features. Then, classification is performed with the random forest model. Once each pixel is classified, the image segmentation is also completed. In the second task, a complex network structure is built for the ceramic image, by using K-mean algorithm and gridding method. Then, a clustering algorithm of complex network is used to obtain network connection area. Finally, the clustered network structure is mapped back to the image and getting the contours among the component elements.

The experimental results demonstrate that these methods can accurately segment materials images. The segmentation methods can provide the data foundation for further quantitative analysis of the materials microstructures.

2:15 PM GI01.11.04
On Converting Material Phase Dynamic Transformation Problem into Material Video Frame Variation Problem Guangti Ding1,2, Jianxun Fu1,3, Huiran Zhang12,1, Tong-Yi Zhang1 and Quan Qian1; 1School of Material Science & Engineering, Shanghai University, Shanghai, China; 2School of Computer Engineering and Science, Shanghai University, Shanghai, China; 3Materials Genome Institute of Shanghai University, Shanghai, China.

In this paper, based on dynamic image analysis technique, material videos or image sequences captured by high temperature laser scanning confocal microscope are analyzed so as to reveal or interpret some facts of martensitic transformation, etc. The main goal of the research is to establish the quantitative relationship between the micro-structural features of the materials, especially their two-dimensional spatial and one-dimensional temporal characteristics, and their video image features. Dynamic image analysis theory and algorithms oriented to martensitic phase transformation problem will be mainly discussed. The method and algorithms in this paper can be applied and generalized to austenite, ferrite, pearlite and other metal phase transformation analysis and applications.

2:30 PM BREAK

3:00 PM GI01.11.05

Recent development of nickel superalloys for additive manufacturing has shown to be challenging due to the susceptibility to micro cracking in as build microstructure. Significant effort has gone into optimizing build parameters for these hard to process alloys. A new protocol was developed by leveraging machine learning algorithm to accelerated the development cycles. In this paper, example of the use of machine learning method to guide parameter development for hard to weld alloys will be presented.

3:15 PM GI01.11.06
Development of a Machine Learning-Based Approach for Diffusion Studies in Crystals—Application to Diffusion in III-V Semiconductors Mardochee Reveil1 and Paulette Clancy1; 1Cornell University, Ithaca, New York, United States; 2Corning Incorporated, Corning, New York, United States.
Recent developments in machine learning have created unprecedented opportunities for incorporation of artificial intelligence techniques in scientific research in a variety of fields including medicine, astronomy, robotics, etc. Application of such advanced techniques in molecular design of materials is still in its infancy and, indeed, lags behind the fields mentioned above. Here, we explore and develop a novel approach whereby recent advances in machine learning techniques are used to study diffusion in crystals, which is critically important for the semiconductor industries. We show that this method offers a viable alternative to traditional techniques used to quantitatively (i.e., gain mechanistic insights) and qualitatively uncover how different species diffuse in a crystal lattice. We explain how this method can be applied to the study of defect diffusion in III-V semiconductors. III-V materials, like GaAs or InGaAs, are promising classes of materials for use in next-generation computing devices for their combination of high performance and better heat management characteristics. But the combinatorial nature of this design space makes it challenging to efficiently explore potential candidates. By providing enhanced screening capabilities, this new approach represents a significant step in the right direction for faster design of next-generation materials. Finally, we explain why Machine Learning could be a powerful tool to help tackle other traditional chemical engineering problems.

3:30 PM GI01.11.07
Combined Data-Driven Identification and Physically-Based Understanding to Materials Development—Building a Solid Process-Structure-Property Link in Ga-Doped ZnO Films Yuyun Chen and Feng Huang; Ningbo Institute of Materials Technology and Engineering, Ningbo, China.

Building a solid process-structure-property link to improve electrical properties effectively is difficult, especially in the vapor-deposited functional films with hierarchical structures. Here, we have introduced a semi-empirical method combined top-down data-driven identification and bottom-up physically-based understanding to build such a link for the magnetron sputtered Ga-doped ZnO (GZO) films. Artificial neural network (ANN) was utilized to identify the most correlative inverse structure-property and process-structure relationships. Moreover, a physically-based understanding of ANN results was to examine the rationality of the identified inverse relationships and capture the dominant mechanism for further materials design. It has been demonstrated that this combined method can identify the feasible process space to tailor the structures at a "correct length scale" and thus significantly improve the conductivity of our GZO films. Our semi-empirical method is probably valid for effective enhancement in physical properties of other vapor-deposited thin films.

3:45 PM GI01.11.08
Exploring Large Scale ToF-SIMS Data Matrices Using Artificial Neural Networks—Polymers and Biointerfaces Paul Pigram1, Robert Madiona1, Nicholas Welch2, David Winkle3,2,3 and Benjamin Muir2; 1La Trobe University, Melbourne, Victoria, Australia; 2CSIRO Manufacturing, Melbourne, Victoria, Australia; 3Monash University, Melbourne, Victoria, Australia.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is continuously advancing. The data sets now being generated are growing dramatically in complexity and size. More sophisticated data analytical tools are required urgently for the efficient and effective analysis of these large, rich data sets. Standard approaches to multivariate analysis are being customised to decrease the human and computational resources required and provide a user-friendly identification of trends and features in large ToF-SIMS data sets. We demonstrate the generation of very large ToF-SIMS data matrices using mass segmentation of spectral data in the range 0 – 500 m/z in intervals ranging from 0.01 m/z to 1 m/z. No peaks are selected and no peak overlaps are resolved. Sets of spectra are calibrated and normalized then segmented and assembled into data matrices. Manual processing is greatly reduced and the segmentation process is universal, avoiding the need to tailor or refine peak lists for difficult sample types or variants. ToF-SIMS data for standard polymers (PET, PTFE, PMMA and LDPE) and for a group of polyamides are used to demonstrate the efficacy of this approach. The polymer types of differing composition are discriminated to a moderate extent using PCA. PCA fails for polymers of similar composition and for data sets incorporating significant random variance.

In contrast, artificial neural networks, in the form of self-organising maps (SOMs) deliver an excellent outcome in classifying and clustering different and similar polymer types and for spectra from a single polymer type generated using different primary ions. This method offers great promise for the investigation of more complex bio-oriented systems.

We compare the analysis of large scale mass segmented matrices with those formed using conventional selection of ToF-SIMS peak lists. SOMs are used to cluster and discriminate antibody fragments bound at surfaces and to demonstrate antibody orientation in optimised ELISA format assays.

4:00 PM GI01.11.09
Machine Learning with Force-Field-Inspired Descriptors for Materials—Fast Screening and Mapping Energy Landscape Kamal Choudhary; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

We present a complete set of chemo-structural descriptors to significantly extend the applicability of machine learning (ML) in material screening and mapping the energy landscape for multicomponent systems. These descriptors allow differentiation between structural prototypes, which is not possible using the commonly used chemical-only descriptors. Specifically, we demonstrate that the combination of pairwise radial, nearest-neighbor, bond-angle, dihedral-angle, and core-charge distributions plays an important role in predicting formation energies, band gaps, static refractive indices, magnetic properties, and modulus of elasticity for three-dimensional materials as well as exfoliation energies of two-dimensional (2D)-layered materials. The training data consist of 24549 bulk and 616 monolayer materials taken from the JARVIS-DFT database. We obtained very accurate ML models using a gradient-boosting algorithm. Then we use the trained models to discover exfoliable 2D-layered materials satisfying specific property requirements. Additionally, we integrate our formation-energy ML model with a genetic algorithm for structure search to verify if the ML model reproduces the density-functional-theory convex hull. This verification establishes a more stringent evaluation metric for the ML model than what is commonly used in data sciences. Our learned model is publicly available on the JARVIS-ML website (https://www.ctcms.nist.gov/jarvisml), property predictions of generalized materials.

4:15 PM GI01.11.10
Crystal Site Feature Embedding Enables Deep Image Recognition Based Exploration of Chemical Spaces Exceeding One Billion Compounds Mikhail Askerka1, Kevin Ryczko2, Oleksandr Voznyy1, Kyle Mills2, Isaac Tamblyn3, 2 and Edward H. Sargent1; 1University of Toronto, Toronto, Ontario, Canada; 2University of Ottawa, Ottawa, Ontario, Canada; 3National Research Council, Ottawa, Ontario, Canada.

Recent years have seen rapid advancements in artificial intelligence, with computer vision methods achieving >96% accuracy on image classification problems. Mapping materials science problems onto computational frameworks that can leverage advances in image recognition could accelerate the discovery of new materials for applications ranging from energy storage to efficient photon capture. Here we translate the
problem of ordering atoms in crystals into an image recognition problem. In Crystal Site Feature Embedding (CSFE), we partition the crystalline lattice into sites according to their spatial arrangement and map it onto a 4D feature vector. This volumetric vector is analogous to a 3D color image, where the first three dimensions reflect the sites’ arrangement, and the fourth dimension corresponds to the sites’ physical properties. We show that this new compact, position-agnostic representation carries sufficient physical insight to machine learn materials properties predicted by complex and time-consuming electronic structure methods such as Density Functional Theory (DFT). Only by using CSFE to leverage image recognition techniques such as Convolutional and Extensive Deep Neural Networks, do we achieve an impressively low mean absolute test error of 3.5 meV/atom on DFT total energies and 0.07 eV on DFT bandgaps of mixed halide perovskites. This enables us to capture nontrivial property trends, such as the U-shape of the bandgap of MAPbSn(1-x)I3 even though the learned algorithm was not explicitly trained in any of the intermediate compositions that make up this nonmonotonic bandgap vs. composition behavior. The method provides an unprecedented >10¹⁰ times acceleration factor compared to DFT alone. Additionally, we use CSFE to explore chemical spaces beyond those used for training, taking advantage of Brillouin zone folding and nature of deep image recognition methods.

4:30 PM GI01.11.11
Data-Driven Equation Discovery—Peak Current of Cyclic Voltammetry Simulations Sheng Sun and Tong-Yi Zhang; Materials Genome Institute, Shanghai University, Shanghai, China.

Cyclic voltammetry test is popular in electrochemical field to study the redox reaction kinetics at the electrode/electrolyte interface. Cyclic voltammogram (CV) can be plotted showing the current as a function of periodic linear swept potential. The current peak ($I_p$) in a CV under different experiment setup and reaction condition is a significant indicator of the underneath reaction kinetics. However, the explicit expression of $I_p$ cannot be derived theoretically. Here, we demonstrate the success of data-driven model discovery by using symbolic regression (SyR) combining with sparse regression (SpR) for $I_p$. At first, SyR and SpR were shown to be able to produce exactly the widely used expressions of $I_p$ as a function of diffusion constant, potential scan rate, reaction constant and initial concentration of the oxide for reversible and irreversible reactions. Then, a very accurate expression of $I_p$ across all reaction regions, including reversible, quasi-reversible and irreversible reactions, was obtained by SyR, when a few expert knowledge was introduced. This preliminary work indicates that SyR should be a powerful tool to find expressions of $I_p$ for more complex reactions with other influence factors, such as stress field and electrode shape.

SYMPOSIUM GI02

Materials for Next-Generation Robotics
November 26 - November 28, 2018

Symposium Organizers
Donglei (Emma) Fan, University of Texas at Austin
Peer Fischer, Max Planck Institute for Intelligent Systems
Rebecca Kramer-Bottiglio, Yale University
Bradley Nelson, ETH Zürich

Symposium Support
Science Robotics | AAAS

8:30 AM *GI02.01.01
Unleashing your Inner Maker Daniela Rus; EECS, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The digitization of practically everything coupled with the mobile Internet, the automation of knowledge work, and advanced robotics promises a future with democratized use of machines and wide-spread use of robots and customization. While the last 60 years have defined the field of industrial robots, and empowered hard bodied robots to execute complex assembly tasks in constrained industrial settings, the next 60 years will be ushering in our time with Pervasive robots that come in a diversity of forms and materials, helping people with physical tasks. However, pervasive use of robots remains a hard problem. How can we accelerate the creation of robots customized to specific tasks? Where are the gaps that we need to address in order to advance toward a future where robots are common in the world and they help reliably with physical tasks? In this talk I will discuss recent developments toward pervasive robots the role of computation in (1) on demand creation of robots, (2) making robots more capable of reasoning in the world, and (3) making more intuitive interfaces between robots and people.

9:00 AM *GI02.01.02
Developments in materials promise to help improve the skin and muscle of robots and protheses - in both hard and soft machines. Here the potential of supercoiled polymer fibres is explored as a 'muscle'. Elastomer and gel-based sensors are proposed as the 'skin' that can actively or passively detect pressure, stretch, bend, proximity and - possibly - shear.

Coiled nylon and polyethylene actuators make use of anisotropies in thermal expansion coefficients in order to generate strains that are similar to or larger than those of muscle. They can operate under much larger loading conditions. Low cost and ready availability makes these interesting for robotics. Challenges are speed, efficiency and shape memory effects. In comparing requirements of various robotic actuators with the specifications of this artificial muscle, some application areas are identified, along with a path for further materials and device development.

In order for robots and prosthetic limbs to be dexterous, sensation is essential. Thin sheets of eactomers can be combined with gels and other conducting materials to simultaneously sense multiple inputs. One approach uses capacitive sensing, similar to that on a touch screen - but in a stretchable format. Some challenges include distinguishing between the touch of a finger, the stretch or bend of the sensor, and forces - normal or shear. Early work shows an ability to discriminate between these modes, while detecting finger proximity within about 1 cm, and very light touch. Another sensor type, which is loosely dubbed piezoionic, makes use of the voltages and currents generated by differences in ion mobilities produced by the deformation of ionically conductive materials. These can be slow, but sensitivity is similar to piezoelectrics. Fast response is obtained by ionic double layer sensors, where changes in contact area between gels and metals lead to 0.5 V amplitude responses with no input electrical energy. Combining these two modes of sensing could provide a mix of fast and slow 'receptors' that require no electrical power input to run.

Looking ahead, how do we integrate actuators and sensors into complex robots - or even make the electrical & mechanical connections between soft and hard materials? And will we need to replace or regenerate materials? Muscle can undergo billions of cycles- while artificial muscle reaches 1/10th that at its very best. Successful approaches will need to combine materials, processing, design, manufacturing and cycle life considerations.

9:30 AM *GI02.01.03 Reprogrammable Shape-Memory Polymer Actuators for Robotics Andreas Lendlein1, 2; 1Institute of Biomaterial Science, Helmholtz-Zentrum Geestacht GmbH, Teltow, Germany; 2Institute of Chemistry, University of Potsdam, Potsdam, Germany.

The classical shape-memory effect in polymers has so far been limited to its one way character, one time shape change. This limitation was overcome with the realization of shape-memory polymer actuators, which can repetitively change their shape under stress-free conditions [1]. A conceptual novelty in this soft actuator class is the re-programmability of the shape changing geometry and the switching temperature. The reversible actuation can occur many times upon heating and cooling within a suitable temperature interval. Besides the geometry of movement, the switching temperature could be made programmable in temperature-memory polymer actuators [2]. Interestingly, semi-interpenetrating polymer networks, obtained by incomplete crosslinking, additionally exhibited a pronounced self-heating capability [3].

With the availability of such shape-memory polymer actuators (SMPA) being able to bend, twist or contract fully reversibly upon cyclic temperature changes, the next generation of reprogrammable, adapting robots seems to be approachable [4]. A prospect, of what can be achieved, is given by a demonstration of a twisted, non-continuously responding SMPA, which reversibly turns an arrow sign between three different positions in the hand of a manikin [5].


10:00 AM BREAK

10:30 AM *GI02.01.04 HASEL Artificial Muscles—Versatile High-Performance Actuators for Next-Generation Robotics Christoph Keplinger; University of Colorado-Boulder, Boulder, Colorado, United States.

Actuators are key components of robotic systems. Robots today predominantly rely on rigid components and electric motors based on metal and magnets. The limited choice of materials and actuators restrains the capabilities of robots, which are heavy, complicated, expensive, often unsafe near humans, and ill-suited for unpredictable environments. Nature, in contrast, makes extensive use of soft materials and has produced living systems that drastically outperform robots in terms of agility, dexterity, and adaptability. Biological muscle is a masterpiece of evolution, featuring astonishing all-around actuation performance, the ability to self-heal after damage, and seamless integration with sensing in a soft matter based system. Advances in materials science and actuation mechanism are necessary to overcome limitations of traditional robotic hardware and enable a new generation of bio-inspired robots which replicate the vast capabilities of biological systems.

This talk gives an overview of a new class of self-sensing, high-performance artificial muscles, termed Hydraulically Amplified Self-healing Electrostatic (HASEL) transducers. HASEL actuators are electrically driven and harness a mechanism that couples electrostatic and hydraulic forces to achieve a wide variety of actuation modes. Several different designs and fabrication strategies, as well as prototypical applications are introduced. Using only off-the-shelf materials, current designs of HASEL are capable of exceeding actuation stress of 0.3 MPa, linear strain of 100%, specific power of 800W/kg, full-cycle electromechanical efficiency of 30% and bandwidth of 50Hz. All these metrics match or exceed the performance of biological muscle. Additionally, HASEL actuators can repeatedly and autonomously self-heal after electric breakdown, thereby enabling lifetimes of a few million cycles at muscle-like levels of strain. Further, this talk introduces a facile fabrication technique that uses an inexpensive CNC heat sealing device to rapidly prototype HASELs. New designs of HASEL incorporate mechanisms to greatly reduce operating voltages, enabling the use of lightweight and portable electronics packages to drive untethered soft robotic devices powered by HASELs. Finally, a model of linearly contracting Peano-HASEL actuators predicts the behavior and scaling laws of these actuators, laying out a roadmap towards future HASEL actuators with drastically improved performance. These results highlight opportunities for the materials science community to further develop HASEL artificial muscles for wide use in next-generation robotic devices.

11:00 AM GI02.01.05 Rapid Prototyping of HASEL Actuators for Versatile and High-Speed Artificial Muscles Shane K. Mitchell1; Xingruo Wang1, 2; Eric Acome, Trent Martin1; Khoo Ly1; Nicholas A. Kellaris1, 3 and Christoph Keplinger1, 4; 1Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 2Tongji University, Shanghai, China; 3Electrical, Computer & Energy Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 4Materials Science and Engineering, University of Colorado Boulder, Boulder, Colorado, United States.
Soft robots with outstanding agility and dexterity require versatile and high-speed artificial muscles. Recently developed hydraulically amplified self-healing electrostatic (HASEL) actuators open new opportunities to create high-performance muscle mimetic actuators that are electrically driven, energy efficient, and capable of self-sensing their deformation. Initial prototypes of HASELs utilized fabrication techniques not easily modified to iterate designs and required bulky high voltage driving electronics. Here, we describe a facile fabrication technique that uses an inexpensive CNC heat sealing device to rapidly prototype complex designs of HASEL actuators using only off-the-shelf materials. We fabricate HASELs which feature linear and out-of-plane deformations and harness electrostatic zipper mechanisms to reduce operating voltages, thereby allowing us to demonstrate a lightweight and portable electronics package for untethered operation of these soft robotic devices. We show designs of HASEL which features linear strains up to 118 %, strain rates of 13,000 %/s, and power densities greater than 800 W/kg. These metrics enable actuators that are fast and powerful enough to jump, while rapid design iteration allows us to create continuum actuators with three-dimensional mobility. We further prototype designs for HASEL actuators to create bio-inspired curling actuators which mimic the high-speed strike of a scorpion tail. We show that these curling actuators can also operate as multifunctional grippers and shape-morphing structures. This presentation will highlight opportunities to further develop HASEL actuators tailored towards a variety of applications in robotics.

11:15 AM GI02.01.06
Dielectric Elastomer Actuators as Soft, Energy Dense, Artificial Muscles
Mihai Duduta, Ehsan Hajesmaili, Huichan Zhao, Robert Wood and David Clarke; Harvard University, Cambridge, Massachusetts, United States.

Soft robots require a new set of technologies aimed at operating in natural environments, including near, or inside the human body. To move within and interact with their environment, soft robots require artificial muscles to actuate movement. These artificial muscles need to be as strong, fast, and robust as their natural counterparts. Dielectric elastomer actuators (DEAs) constitute a highly promising class of materials, but typically exhibit low output forces and low energy densities, when used without rigid supports. Here we report a soft composite material made of strain stiffening elastomers and carbon nanotube electrodes, which actuates under an applied electric field and demonstrates a peak energy density of 19.8 J/kg. The result is close to the upper limit for natural muscle (40 J/kg) making these DEAs the highest performance electrical driven artificial muscles. To obtain high forces and displacements, we used low density, ultra-thin carbon nanotube electrodes which can sustain applied electric fields upwards of 100 V/micron, without suffering from dielectric breakdown. The fabrication process described herein is fast, scalable, and uses relatively low cost components and equipment. Potential future applications include biomedical uses, such as prosthetics, surgical robots, and wearable devices, as well as more capable soft robots capable of locomotion and manipulation in natural or human-centric environments.

11:30 AM GI02.01.07
Hybrid Soft Dielectric Elastomer Robots Exploiting Pneumatics to Generate Large Actuation
Ernst-Friedrich M. Henke1,2,3, Sascha Pfeil1,3 and Andreas Richter1; 1Solid State Electronics Lab, TU Dresden, Dresden, Germany; 2Auckland Bioengineering Institute, The University of Auckland, Auckland, New Zealand; 3Institute of Semiconductors and Microsystems, TU Dresden, Dresden, Germany.

Multifunctional Dielectric Elastomer (DE) devices are well established as actuators, sensors and energy harvesters. Since the invention of the DE Switch (DES), a piezoresistive electrode that can directly switch charge on and off, it became possible to expand the wide functionality of dielectric elastomer structures even more.

It is possible to couple arrays of actuator/switch units so that they switch charge between themselves on and off. One can then build DE devices that operate as self-controlled oscillators. With an oscillator one can produce a periodic signal that controls a soft DE robot. Now one has a DE device with its own DE nervous system.

We have demonstrated a variety of components for autonomous soft robots without conventional electronics. The combination of digital logic structures for basic signal processing, data storage in dielectric elastomer flip-flops and digital and analogue clocks with adjustable frequencies, made of dielectric elastomer oscillators (DEOs), puts us in the position to design self-controlled and electronics-free robotic structures.

The last remaining stiff structures in DE robotic structures were stiff PMMA frames to maintain necessary pre-strains to enable sufficient actuation of dielectric elastomer actuators (DEAs). Here we present a design and production technology for a first robotic structure consisting only of soft silicones and carbon black. We present different promising designs for entirely soft DE-driven robots.

We present the design of the hybrid, soft DE robots exploiting pneumatics for pre-stretching their muscles. It combines the advantages of pneumatic pre-stretching DE membranes with the electronic control of DE muscles. This approach reduces the complexity of the necessary pneumatic control system needed for driving the robot, it only needs a constant internal pressure. We present a circular crawling robot that is designed in such a way that an internal pneumatic pressure only leads to an elongation in longitudinal direction, but not in radial direction. This design prevents an inflation of the DE muscles, and, thus keeps the diameter of the structure constant. The actuation is generated by pulsing electric signals applied to the robot’s muscles. The elongation of the individual muscle segments is then transformed into an actuation by directional friction structures. We present the design of the robot an analytical and a FEA model and the first experimental results.

11:45 AM GI02.01.08
Brilliantly Structured Light-Weight Twisted-Coiled Fiber Actuators Using Polymer Threads and Twisted Dry Spun Carbon Nanotube Yarns
Brilliantly Structured Light-Weight Twisted-Coiled Fiber Actuators Using Polymer Threads and Twisted Dry Spun Carbon Nanotube Yarns
Yasuhiko Hasyashi1,2, Takayuki Yoshiyama1, Hirota Inoue1, Masaki Hada1,2, Daiki Chujo1, Yoshitaka Saito1, Kaito Paneer Selvam1, Wataru Takarada1 and Hideoshi Matsumoto1; 1Graduate School of Natural Science and Technology, Okayama University, Okayama, Japan; 2Institute of Innovative Research, Tokyo Institute of Technology, Tokyo, Japan; 3Department of Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Fiber actuators have attracted considerable attention as they are not only lightweight but also can generate a large strain, they realize human mimetic motions that are strongly demanded in the field of soft robotics. One of the crucial challenges presented by self-contained electrically heated carbon cloth-shaped fiber actuators resides in their thermal absorption and contraction units. So far, coil-shaped polymer actuators wrapped with copper wire or silver paste as heating sources were reported. However, the use of metals increases the weight of the fiber actuators and effect their flexibility. Also, the difference in the thermal expansion coefficients between the polymer thread and accompanying metal frame may degrade the performance of actuation motions.

Fiber actuators and shape-morphing structures. This presentation will highlight opportunities to further develop HASEL actuators tailored towards a variety of applications in robotics.

Hear, three types of coil-shaped polymer fiber actuators were fabricated from polyethylene terephthalate (PET) threads as actuators and high thermal conducting twisted dry spun carbon nanotube (CNT) yarns as heating wires. We analyzed the thermal absorb desorb effects on their performance concerning their mechanical force.

The diameter of a PET fiber was approximately 20 μm. The lengths of PET threads and CNT yarns were 15 cm. The “MultiF-A” is composed of the PET threads and CNT yarns homogeneously. These fibers contain randomly in their cross section profile and they were rotated until it changes to coil-shaped structure. The “MultiF-B” is composed of few fine coil-shaped threads. At first, two CNT yarns and four PET threads are bundled and rotated. And then, a
certain number of fine coil-shaped PET/CNT fibers are bundled. The "MonoF" is fabricated from a bundle of PET threads and a bundle of CNT yarns, similar to the reported fiber actuator made from one polymer fiber and one heating wire.

The applied electric power to CNT yarns was maintained constant at 50 mW (5 mW per CNT yarn). The mechanical force linearly increases as the number of PET threads are increased in all types of fiber actuators. The mechanical force generated in MultiF-A and -B is 1.6 times higher than that generated in the MonoF. The responsivities (heating and cooling processes) of the fiber actuator strongly depends on the time constant of the deformation of PET threads, and therefore the response behaviors of the three types of fiber actuators are identical. The amount of displacement of MultiF-A and -B is 1.4–1.8 times higher than the MonoF at 50 mW. This is in good agreement with the result obtained by the measurements of mechanical force.

A more in-depth analysis of the thermal effects on the fiber actuator was performed by constructing a model including both MultiF-A and MonoF. The MultiF-A is homogeneously thermalized with the input energy, however, the MonoF shows inhomogeneous thermal distribution.

Based on our results, homogenous thermal distribution in the fiber actuators realized by brilliant structure is key factor for the highest actuation performance.

SESSION GI02.02: Responsive Materials
Session Chair: Peer Fischer
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 111

1:30 PM *GI02.02.01
Materials for Next Generation Robotics Soft Materials and Soft Robotics for Future Robot Abilities and Applications Cecilia Laschi and Matteo Cianchetti; The BioRobotics Institute, Scuola Superiore Sant’Anna, Pisa, Pisa, Italy.

Though a young discipline, robotics progressed rapidly and pervaded our lives more than we perceive, becoming a tool we cannot do without in manufacturing. Futuristic scenarios have been proposing robots in daily life of citizens and professionals for decades, creating expectations that have not yet been matched. What is the real status of development of robotics today and what are the realistic scenarios that robotics technologies enable today? What are the abilities that robots still miss to match expectations for extensive application and healthier and safer human life?

Largely inspired by the observation of the role of soft tissues in living organisms, the use of soft matter for building robots is recognized as one of the current challenges for pushing the boundaries of robotics technologies and building robotic systems for service tasks in natural environments. The study of living organisms sheds light on principles that can be fruitfully adopted to develop additional robot abilities or to facilitate more efficient accomplishment of tasks, because living organisms exploit soft tissues and compliant structures to move effectively in complex natural environments. The compliance and the elasticity of soft body parts, and especially a tunable stiffness, allow purposive reactions to interaction forces. So-called Soft Robotics is the use of soft materials or deformable structures in robotics. The wide spreading of soft robotics research worldwide has brought significant achievements in terms of principles, models, technologies and prototypes.

The main characteristic of compliance makes soft robotics technologies particularly well suited for biomedical applications, where robots have to interact effectively and safely with a patient. Soft robots are well suited when used in direct contact with a patient, like in surgery in rehabilitation and assistance. A soft manipulator can move safely inside the human body and act as an endoscope or change its stiffness to perform surgical procedures. A soft arm can help elderly people in bathing activities by becoming a robotic shower, able to approach and interact safely yet effectively with the user. In addition to this, soft robotics technologies are useful for building simulators of body parts, for medical studies and training, like the vocal cords or the minute lungs of pre-term babies. Explorations are also a terrific field of applications for soft robots, that can reach remote inaccessible areas, including and especially underwater. Advances in soft materials, smart materials and energy harvest represent today the main line of robotics progress.

2:00 PM GI02.02.02
Multi-Responsive Tactile Hydrogels as Soft Robotic Materials Xinmin He, Yixuan Xu, Yusen Zhao and Mo Sun; University of California, Los Angeles, Los Angeles, California, United States.

Stimuli-response hydrogels have found tremendous applications as adaptive lenses, artificial muscles, vehicles for drug deliveries, scaffolds or matrices for tissue engineering, as well as sensors and actuators for soft robots and soft machines. Here we report a tough, conductive, multi-responsive hydrogel, which is designed and synthesized by one-step polymerization with double network made of conductive polymer and chemically nano-crosslinked hydrogels. This hydrogel possesses a highly mechano-electrically sensitive that can change shape rapidly at large ratios upon local sensing of the approaching of an arbitrary object in contact with the hydrogel. This smart hydrogel can change its volume in response to subtle mechanical force and electric signals like the neural commands and acute tactility of octopus or human skin when it is in contact with an object. This presents a novel capability of force-induced shape changing, achieved through the force-electro-mechanical energy transduction within the gel material. Overall, the important novel characteristic of this force-sensitive tactile hydrogel is the capability of detecting the geometry or rigidity of the environment and adaptively changing its own shape to adapt to the shape of the environment. For example, such gel can behave as a fully automatic gripper without external control, which can grasp an object in arbitrary shape that is poking the gel. Additionally, this hydrogel is highly strong mechanically. Unlike previously developed pneumatic or hydraulic soft robotic arms and manipulators, our tactile hydrogel-based robotic materials will be self-contained and capable of continuous "sense-diagnose-response" to perform adaptive configuration changes without incurring damage.

2:15 PM GI02.02.03
Fabric Reinforced Hydrogel/Elastomer Composites for Stimuli-Responsive Actuators Daniel R. King1, 2, Amber M. Hubbard1, Wei Cui1, Yiwan Huang1, Michael Dickey2, Jan Gretzer1, 2 and Jian Ping Gong1, 2; 1Faculty of Advanced Life Science, Hokkaido University, Sapporo, Japan; 2Global Station for Soft Matter Research, Sapporo, Japan; 3Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States; 4Graduate School of Life Science, Hokkaido University, Sapporo, Japan.

Hydrogels are useful in biomaterials applications, but often lack the robust mechanical properties seen in nature. Natural materials rarely consist of discrete independent materials, rather utilizing composite structures to achieve significant mechanical properties. Here, we report the use of fabrics as a reinforcing phase within hydrogel matrices. The use of fabric results in many preferential properties. During tearing, we observe a synergistic increase in fracture strength due to a dramatically enlarged process zone in the composite structure. Furthermore, the hydrogel composites possess high stiffness in plane, while
Advantageous in these scenarios if the robot is padded. This led to our exploration of stretchable tactile sensing skins, which can accommodate the large energy harvesters and actuator devices. New azo liquid crystal materials and polymers to optimize this effect will be presented, and some simple mechanically to permit visible light to be converted directly to mechanical work. Reversible changes in surface energy are also inducible as a result, for a variety of reversible surface energy switching applications via light. Irradiation with light in the solar spectrum at sun-like intensities will be shown to lead to a measurable reversible photo-expansion of these coatings, of up to a few %, allowing the materials to function as photo-mechanical switches or light energy harvesters and actuator devices. New azo liquid crystal materials and polymers to optimize this effect will be presented, and some simple macroscopic devices will be demonstrated that take mechanical advantage of this effect for larger scale motion driven by sunlight.

The mechanism for this effect will be discussed from studies using ellipsometry, light-bending of AFM cantilevers, high-pressure raman spectroscopy, and neutron reflectometry. In particular, recent materials prepared from pseudostilbene-type azo molecules exhibit unusually fast, and reversible photomechanical motion under visible-light irradiation, with the extremely rapid switching using just one wavelength of light by shortening the lifetime of the ciss-form. This results in a bending motion in the microsecond regime. The influence of density, thickness, and molecular orientation on optimization of the photomechanical effect will be discussed. Lastly, some simple soft-robotic proof-of-principle devices will be presented, that upon visible irradiation, can bend and wiggle; crawl, walk, and roll.

3:00 PM BREAK

SESSION GI02.03: Robots
Session Chair: Rebecca Kramer-Bottiglio
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 111

3:30 PM *GI02.03.01
Bio-Inspired Tactile Sensing Skins for Robots Elisabeth Smela, Ying Chen, Miao Yu and Hugh Bruck; Department of Mechanical Engineering, University of Maryland, College Park, Maryland, United States.

Robots working in unstructured situations, particularly around humans, need to detect the occurrence and location of physical contacts with objects or people, not only for safety but also to enable touch-based communication. Care-giving and factory floor environments are two examples. It is also advantageous in these scenarios if the robot is padded. This led to our exploration of stretchable tactile sensing skins, which can accommodate the large deformations experienced during contact and which can be produced at whole-body scales. In fact, the response of piezoresistive strain sensors is amplified by localized deformation in the foam. The advantages of soft materials are, however, tempered by their concomitant time and history-dependent mechanical responses. The behavior of the foam, in particular, can dominate the response from the sensor. The readings from the skin may be useful nonetheless because a robot may only need to determine the nature, magnitude, and location of contacts rather than exact force values for operational success. The use of multilayered or geometrically restricted architectures can aid the interpretation of data obtained during contact, as can the use of techniques such as electrical impedance tomography (EIT) for distributed sensing, particularly for interpreting human touches such as multi-point finger...
presses and sliding. For example, while information from a single sensing layer on foam can reasonably distinguish forces applied by a machine, two stretchable sensing skin mimics with two foam layers are superior for interpreting highly variable human touch. Use of multiple layers also permits higher sensitivity readings at low force coupled with an extended high force range. To move forward in this effort, it is critical to address integration issues, particularly the formation of good electromechanical connections between the soft materials and the rest of the platform. Another challenge is improving the stability and robustness of the soft sensors.

4:00 PM GI02.03.02
Towards Damage Resilient Soft-Matter Robotics and Electronics
Eric Markvicka1, Michael D. Bartlett2, Xiaolan Huang1, Ravi Tutika3 and Carmel Majidi1; 1Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Iowa State University of Science and Technology, Ames, Iowa, United States.

Emerging applications in soft robotics, human-machine interaction, and wearable robotics will increasingly rely on new soft-matter technologies that are considered inherently safe as they are primarily composed of intrinsically soft materials—elastomers, gels, and fluids. These materials provide a method for creating soft-matter counterparts to traditionally rigid devices that exhibit the mechanical compliance of natural, biological systems. However, these soft-mimics are increasingly susceptible (as compared to their rigid counterparts) to varying forms of mechanical damage such as cutting, tearing, or puncture. These can result in operational failure. Here, a new material architecture will be presented for creating soft and highly deformable circuit interconnects. The traces are electromechanically stable under typical loading conditions, and exhibit uncompromising resilience to mechanical damage—cutting, tearing, or puncture. The material is composed of micron-scale droplets suspended in a soft elastomer, when damaged, the droplets rupture to form new connections with neighbors and re-route electrical signals without interruption. Since self-healing occurs spontaneously, these materials do not require manual repair or external heat. We demonstrate this unprecedented electrical robustness using a self-healing soft robotic quadrapod that continues to function after significant damage. We will also present a recently developed method for actively sensing and localizing damage (compression, cutting, and puncture) within a thin elastomer film. When coupled with processing, actuation, and communication, this soft and highly deformable composite presents new opportunities to identify and respond to mechanical damage in soft-matter robotic systems.

4:15 PM GI02.03.03
Biodegradable Soft Robots with Electronic Skins
Florian Hartmann, Melanie Baumgartner, Michael Drack, David Preninger, Stephan Demchysyn, Robert Gerstmayr, Daniela Wirthl, Lukas Lehner, Siegfried Bauer and Martin Kaltenbrunner; Johannes Kepler University, Linz, Austria.

Cephalopods, caterpillars and other soft creatures inspired a broad spectrum of bio-mimetic actuators -- enhanced with perceptive electronic skins -- capable of sensing and adapting to their complex erratic environments. Yet, they are missing a feature of nature’s designs: biodegradability. Soft robots that degrade at the end of their life cycle reduce electronic waste and are paramount for a sustainable future. At the same time, medical (robotic) technologies have to address hygiene requirements. We therefore develop biodegradable hydrogels for single-use wearable electronics and transient soft robots that are reversibly stretchable, are able to heal and are resistant to dehydration. Soft machines and robots -- built from hydrogels with tuned mechanical properties - are designed to be operated in ambient conditions and degrade after use. An equally compostable electronic skin provides our soft actuators tactile feedback and temperature sensing, directly processed with a recyclable on-board computation unit. Besides progressing stand-alone soft machines, our advances in the synthesis of biodegradable hydrogels bring bionic soft robots a step closer to nature.

4:30 PM GI02.03.04
Electronic Epidermis That Activates Soft Robots Wirelessly
Junghwan Byun1,2, Yoontaek Lee1,3, Jaeyoung Yoon1,3, Yongtaek Hong1,3 and Kyu-Jin Cho1,2; 1Seoul National University, Seoul, Korea (the Republic of); 2Soft Robotics Research Center, Seoul, Korea (the Republic of); 3Inter-university Semiconductor Research Center, Seoul, Korea (the Republic of).

A recent stream of research on robotics, called “Soft Robotics”, aims for designing softness into each robot part on the basis of soft materials and body architectures. Reducing rigid boundaries of robots greatly improves robotic compliance to dynamic, unstructured environments in terms of adaptiveness. In this regard, several studies have reported fabrication and integration methodologies for soft body architectures in which soft actuators or actuating frames are integrated into a soft body frame. Despite the body’s softness, however, existing models mostly carry inherent hardness and bulkiness in their driving parts, such as pressure-regulating components and rigid circuit boards. This compliance gap can frequently interfere with the robot motion and makes soft robotic design dependent on rigid assembly of each robot component. In this work, we report a class of electronic systems that can be softly and reversibly integrated as a “robotic epidermis” into soft robot frames and then can activate (and control) them wirelessly. The proposed electronic epidermis (e-epidermis) is soft (~30% stretchable), thin (~1 mm), lightweight (~1 g), and involves driving capability on the basis of controlled Joule heating. The electronic functionality with skin-like mechanical property is designed by stretchable hybrid electronics (SHE) layouts. A large number of surface mountable devices (SMDs) are directly assembled onto a soft substrate and bridged by inkjet-printed stretchable interconnection networks (silver thin films with wrinkled geometry) to achieve adequate circuit architectures for wireless robot control. In particular, the size of the assembled SMDs is regulated (≤1.5×1.5×0.6 mm²) for the e-epidermis to share the large local bending curvature which can be the deformation profile of soft robots. The resulting e-epidermis can not only mechanically conform to dynamic surfaces like soft robot frames but also activate soft actuators through controlled current driving. Benefits of this design enable compact integration of fully soft robots. We demonstrate a thin (total thickness: 2 mm), compact, soft robotic hand whose body dimension in itself cannot possibly equip any other types of conventional driving systems. This fully soft robot can be actuated and mechanically deformed in ways not previously possible: a body architecture and embedded e-epidermis can equally share the sequential deformation profiles. Furthermore, this e-epidermis concept provides universality for robotic actuation based on reversible assembly.

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (MSIP) (No. NRF-2016R1A5A1938472).

4:45 PM GI02.03.05
Self-Healable Stretchable Light Sources
Benjamin C. Tee1,2, Yu Jun Tan1 and Hareesh Godabai1; 1Materials Science and Engineering, National University of Singapore, Singapore, Singapore; 2Biomedical Institute for Global Health Research and Technology, National University of Singapore, Singapore, Singapore; 3Institute of Materials Research and Engineering (IMRE), Agency for Science Technology and Research, Singapore, Singapore.

Most human-machine interfaces rely on some form of visible light sources such as light emitting displays. In flexible and stretchable electronics, exciting progress has been made via the use of strain robust electronic devices for advanced soft robotics1, wearable biomedical devices2 and flexible touch interfaces3. On the other hand, self-healing and self-repairable materials and devices are gaining tremendous interest due to the possibility of reducing technological waste4,5. Hence, it is useful to investigate stretchable light sources that could have self-repair functions for such applications. In this talk, I will describe a stretchable and self-healable electroluminescent (EL) material that can stretch elastically. The material processing is facile, and the devices
can withstand multiple mechanically inflicted ‘wounds’ and recover functionality. Such materials can be integrated into devices for emerging wearable soft robotics and human-machine interactions.


---

**SESSION GI02.04: Structures**

**Session Chair: Donglei (Emma) Fan**

**Tuesday Morning, November 27, 2018**

**Hynes, Level 1, Room 111**

**8:00 AM *GI02.04.01**

**Navigable Soft Robotic Microcatheter for Endovascular Treatment of Cerebral Aneurysms**

*James Friend*; University of California, San Diego, La Jolla, California, United States.

We report a unique solution of an unmet clinical need in vascular microsurgery using a combination of novel 10-100-µm scale soft polymer cast-and-print fabrication techniques, simple microhydraulics, hyperelastic media with tailored nonlinear elasticity properties, and carefully designed, complex cross-sectioned microstructures. The third most common cause of death in the United States, strokes present a tremendous sociological and economic burden. While rapid, minimally invasive surgical intervention is sometimes beneficial, the crude tools available today are completely inadequate. We focus upon the most serious problem in stroke intervention: intracranial aneurysms. Nearly one-fourth of neurointerventions fail due to the difficulty in navigating the microcatheter to the aneurysm location through tortuous vasculature and in orienting the microcatheter tip in the aneurysm dome to an optimal position for coil deployment to close off the aneurysm.

Our approach produces a completely steerable microcatheter at the small (~100 µm) scales necessary for endovascular neurosurgery via direct hydraulic microactuation and a hand controller simple enough for a neurointerventionist to use. With data from ex-vivo and in-vivo animal trials, we show the technology quantifiably produces better outcomes, fewer mistakes, speeds treatment, and enables greater treatment capabilities than current state-of-the-art devices. Our ex-vivo testing furthermore employs new MRI-to-in-silico models printed from anonymized angiograms of patients with aneurysms. The models include accurate blood flow and neurovascular elasticity, and such minor but important details as the surgical bed and the extended vasculature from the groin through the aorta, heart and chest to the neurovasculature. Beyond the neurovasculature and steering, ideas on the next generation of facile, distal microactuation for biopsy, suturing, drug delivery, and many other applications via our technology will be proffered to result in improved patient outcomes and reduced healthcare costs for all.

**8:30 AM *GI02.04.02**

**Photoalignment Control and Mechanical Analysis of Polymer Films for Soft Robotics**

*Atsushi Shishido*; Tokyo Institute of Technology, Yokohama, Japan.

Macroscopic alignment control of liquid crystal (LC) films is key to the development of next-generation high-performance soft robot materials. Current methods achieve such large-area alignment of LCs, having intrinsic structural ordering over various length scales from nanometer to micrometer, by applying uniform external fields along one direction, such as mechanical stress, surface rubbing treatment, and electromagnetic or light fields. Among these more advanced 2D techniques, light-driven alignment control (photoalignment) might provide the greatest potential for fine control over molecular orientation, because of its remote and precise influence, and suitability for micro- or nanofabrication, which can enable many applications that require more complex alignment patterns. With conventional photoalignment methods, one typically irradiates an LC film containing added photoreactive molecules with spatiotemporally uniform polarized light. We report here a new concept of scanning wave photopolymerization (SWaP) using spatiotemporal scanning of UV light to start photopolymerization and create a mass flow in the film, which results in LC alignment coincident with the incident UV light patterns. Furthermore, we introduce mechanical analysis of such flexible polymer films to quantitatively understand a new mechanics for soft robotics.

---


**9:00 AM *GI02.04.03**

**Self-Growing Adaptable Soft Robots**

*Barbara Mazzolai*, Ali Sadeghi, Emanuela Del Dottore and Alessio Mondini; Istituto Italiano di Tecnologia, PONENTE, Italy.

Growth is a very interesting feature of living beings that can inspire a generation of robots endowed with new and unprecedented abilities of movement. Growth involves the cellular activity of both animals and plants, yet the evolution of organisms in these two kingdoms is completely different. Animals grow until maturity, while plants grow indefinitely, mostly for their entire life. Animal growth is also known as “determinate” growth, since trajectory and asymptotic size are usually genetically defined and environmental influence has a limited impact. Plant growth, on the other hand, is “indeterminate”, since it extends throughout life. Growth allows a strong adaptation of body morphology to environmental conditions, also called plasticity, which characterizes the plant kingdom. Differently from animals, plants grow to move, in search for nutrients and light and for protection from harmful agents. Noteworthy,
plants represent an alternative model of movement in robotics, which is not animal-like and muscle-based.

For the first time in robotics, we proposed a growing robot inspired by movements and behaviors of plant roots. The robot is able to create in real-time its own body structure exploiting a 3D printer-like system integrated in its tip for the deposition of a thermoplastic material, thus imitating the indeterminate axial growth and bending root abilities.

Passive and active movements in plants can also be exploited for developing multifunctional materials and energy-efficient actuators based on osmosis. Starting from the investigation of nutrient uptake phenomena, movements and communication strategies adopted by plant roots, we developed uptake–kinetics feedback control and self-organization ability for exploitation tasks. Based on these plants’ features, we can generate new, unexplored abilities in bioinspired robots, which can better adapt to external, unstructured environments, move purposively, effectively and efficiently.

9:30 AM GI02.04.04
Polymer Hydrogels for Artificial Transpiration in Biomimetic Plant Robots

Doruk S. Cezan1, Hasan T. Baytekin2 and Bilge Baytekin1, 2; 1Chemistry Department, Bilkent University, Ankara, Turkey; 2 National Nanotechnology Research Center (UNAM), Bilkent University, Ankara, Turkey.

Bio-inspired materials – using the strategies of nature to design materials – has many implications in fields extending from energy to medicine to robotics. In robotics, biological systems have been a great inspiration source owing to their fascinating abilities developed in the course of evolution. Plants, in particular, have interesting abilities like adaptability, sensing, self-regulation, self-healing, and unique surfaces structures that have great possibilities to feed ideas for new materials production. Especially interesting are heliotropism (solar tracking of plants), and nyctinasty (opening and closing leaves) in plants, used for achieving high-energy efficiency in photosynthesis. Previously, using shape memory alloys or liquid crystal structures, it was shown that plant robots, too, can possess these features but none of these robots were truly biomimetic. In this study, we demonstrate biomimetic robot plants, which display heliotropism and nyctinasty by artificial transpiration (water transport in plants) – the exact strategy used in nature. Several thermo-responsive hydrogels (PNIPAM, PDEAAM, and PNVCL) were used on a cellulose plant body to achieve the targeted biomimicry. The systems are assessed for the transpiration efficiency, actuation speed and its relevance to the sensory motion, as well as for their heliotropic efficiencies. The bioinspired approach used in this study for the plant robots and structures designed by using them could be of interest for autonomous soft robotic systems in which the motion solely controlled by materials.

9:45 AM GI02.04.05
Memory and Learning in Biomolecular Soft Matter for Low-Power Brain-Like Computing

Joseph S. Najem1, 2, Md Sakib Hasan1, Ryan Weiss1, Catherine Schuman2, Alex Belianinov2, Graham Taylor1, 2, Garrett Rose1, Stephen A. Sarles1 and Charles P. Collier2; 1The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The capacity of robots to learn, operate autonomously, and support other cognitive tasks independently and in complex and dynamic environments will require approaches to computation that are inherently brain-like. Neuroromorph computing systems co-locate information processing and memory at levels approaching the density, complexity, and energy efficiency of the brain needed for the next generation of robotics. Reproducing these features using traditional electronic circuit elements is virtually impossible, requiring the design and fabrication of new hardware elements that can adapt to incoming signals and remember processed information. We refer to these elements as mem-elements (short for memory elements), which are passive, two-terminal devices whose resistance, capacitance, or inductance remembers the past electrical activity of the device. These elements should be scalable, biomimetic, and preferably ionic to achieve energy consumption levels approaching those in the brain. Here we describe two-terminal, biomolecular memcapacitors and memristors, consisting of highly insulating 5 nm-thick lipid bilayers assembled between two water droplets in oil. These devices exhibit memcapacitance that is nonlinearly dependent on the applied voltage, and hysteresis in the charge due to reversible changes in the area and thickness of the bilayer membrane in response to voltage. This is the first demonstration of a memcapacitor in which capacitive memory results from geometrical changes in a lipid bilayer membrane. We also show that the incorporation of voltage-activated alamethicin peptides in these devices results in variable ionic conductance across the membrane and memristive behavior.

We discuss how these devices exhibit learning through synaptic plasticity, and how to implement them in online learning applications. These results serve as a foundation for a new class of low-cost, low-power, soft mem-elements based on lipid interfaces and other biomolecules for applications in neuromorphic computing which could have major implications on the robotics field.

10:00 AM BREAK

SESSION GI02.05: Electronics, Memory and Perception

Session Chair: Peer Fischer
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 111

10:30 AM *GI02.05.01
The Mechanical Side of AI
Robert Wood; Wyss Institute for Biologically Inspired Engineering and John A Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Artificial Intelligence typically focuses on perception, learning, and control methods to enable autonomous robots to make and act on decisions in real environments. On the contrary, our research is focused on the design, mechanics, materials, and manufacturing of novel robot platforms that make the perception, control, or action easier or more robust for natural, unstructured, and often unpredictable environments. Key principles in this pursuit include bioinspired designs, smart materials for novel sensors and actuators, and the development of multi-scale, multi-material manufacturing methods. This talk will illustrate this philosophy by highlighting the creation of several classes of soft-bodied robots.

11:00 AM GI02.05.02
3D-Printable Shape-Morphing Architectures via Programmable Stress
Quanduan Han and Victor Ugaz; Texas A&M University, College Station, Texas, United States.

Significant advancements in soft robotics have been achieved through the use of polymeric materials that actively respond to external stimuli via shape memory or physico-chemical interactions with their surroundings. And recent excitement has been generated by application of these responsive properties to produce shape-shifting 2D structures capable of morphing into complex 3D topologies. But manufacturing these active components generally requires
specialized chemical formulations and sophisticated multi-material patterning capabilities that are not widely available outside research laboratory settings, significantly limiting their impact. Here we show how this barrier can be overcome by using 3D printing to embed prescribed internal stresses within a planar2D substrate. These stresses are controllably released in response to an external trigger, deforming the material into a desired 3D shape.

We apply this capability to construct active components relevant to soft robotics in three ways. First, we produce a library of building blocks embedding programmed internal stresses that can be assembled to enable 3D deformation with controllable local curvature. We then show how these elements can be combined to spatially distribute strain across multiple length scales, replicating hierarchical structures found in living systems. Finally, we apply these design principles to produce a self-assembled metal/air battery capable of functioning either as a stand-alone power source or as part of a self-powered electrochromic glucose sensor for use as a diagnostic tool in resource-limited settings. Notably, all of these components can be manufactured using standard 3D printers and materials, significantly broadening access to soft robotics technology.

11:15 AM GI02.05.03 Actively Perceiving and Responsive Soft Robots Enabled by Self-Powered, Highly Extensible, and Highly Sensitive Triboelectric Proximity- and Pressure-Sensing Skins Ying-Chih Lai¹ and Zhong Lin Wang‡; ¹Materials Science and Engineering, National Chung Hsing University, Taichung City, Taiwan; ²Georgia Institute of Technology, Atlanta, Georgia, United States.

We will propose the first demonstrations of using triboelectric effect to realize various actively sensing and responsive capabilities in soft robots. Robots that can move, feel, and respond like organisms will bring revolutionary impact to today’s technologies. Soft robots with organism-like bodies have shown great potential in vast robot-human and robot-environment applications. Developing skin-like sensory devices allows them to naturally sense and interact with environment. It would be better if the capabilities to sense can be active like real skin. However, challenges in complicated structures, incompatible moduli, poor stretchability and sensitivity, large driving-voltage, and power dissipation hinder applicability of conventional technologies.

Here, for the first time, various actively perceivable and responsive soft robots are enabled by using self-powered active triboelectric robotic skins that simultaneously possess excellent stretchability and excellent sensitivity in low-pressure regime. The robots’ skins can actively sense proximity, contact, and pressure to external stimuli via self-generating electricity. The driving-energy of its sensing ability comes from natural triboelectrification effect. Various kinds of perceiving soft robots will be demonstrated to use triboelectric effect to complete different actively sensing and responding tasks. For a conscious gripper, it can actively be aware of different actions in moving an object including approaching, grabbing, lifting, lowering, and even the accident of dropping off the objects. A perceivable robot-finger can check a baby’s diaper condition. A conscious robotic crawler enable to perceive its muscle motions during undulating gaits and detect very subtle human physiological signals, showing their potential in palpation. Such robots with large-area skins have been demonstrated for actively multiplexing sensing uses. Moreover, the actively responding signals can directly drive optoelectronic components for intuitive communication and be further processed for more sophisticated uses such as answering with sound, light, phrases, and so on. We believe the presented robotic skins that are self-powered, highly-sensitive, highly-stretchable can meet applications where soft interfaces are needed. And, the first achievements in the actively perceiving and responsive soft robots can push the boundaries of artificial intelligences, soft robotics, as well as their vast related applications.

11:30 AM GI02.05.04 Enhanced Material Stiffness Change Using Low-Melting-Point Metallic Alloy Particle Additives Trevor L. Buckner¹, Rebecca Kramer-Bottiglio¹, Michelle C. Yuen² and Sangyup Kim¹; ¹Yale University, East Hartford, Connecticut, United States; ²Purdue University, West Lafayette, Indiana, United States.

Soft robots made from flexible and conformable materials face a major challenge resisting structural collapse or properly transferring forces when interacting with external loads. Without a permanent rigid support structure, soft robot design often turns to variable stiffness techniques that allow a robot to selectively generate rigid bones or soft joints as needed, thereby retaining the desirable properties of a soft robotic system while adding the ability to adapt to external obstacles and tasks as required. Many such solutions utilize stiffness-changing materials that soften or undergo a phase change with increasing temperature. In this talk we present a method of enhancing the range of stiffness change in these materials by introducing low-melting-point metallic alloy particles as an additive into the host material, specifically Field’s metal embedded in an epoxy matrix. This method can drastically increase the stiffness of the rigid state, enhance the stiffness change of the host material phase transition due to particle jamming effects, and further decrease the final stiffness of the softened state by taking advantage of the solid-to-liquid transition of the particle inclusions. We will present a facile method for fabricating low-melting-point metal particles which improves upon existing techniques by scaling up batch size while maintaining control of particle size distribution. These particles will then be demonstrated as an additive in a conductive thermoset epoxy composite to enhance the stiffness change of that material. The effects of this additive on thermal and electrical material properties will also be presented. Finally, we will demonstrate the application of this variable stiffness material towards a soft robotic platform that can be continuously varied between compliant and load-bearing states.

11:45 AM GI02.05.05 Lightweight Multifunctional Structures for Next-Generation Robotics Monica Jung de Andrade; The University of Texas at Dallas, Richardson, Texas, United States.

Flexible, lightweight, multifunctional structures have a significant impact towards morphing technologies. In this work, we discuss some of the main techniques to fabricate fiber-like materials towards robotics. For instance, both infiltration and conformal deposition routes demonstrated the versatility of nanostructured nanotube based nanocomposites towards yarn-like actuators and flexible woven energy harvester. We demonstrated our silent, flexible, and tunable and scalable actuators can perform over thousands of cycles with negligible hysteresis. Finally, we demonstrated that fiber-like actuators have great potential towards lightweight and inexpensive orthotics, prosthetics and other tensegrity structures.
Variable Elasticity Silicone—Multifunctional Elastomeric Systems Enabled by Modulus Switching

Michelle C. Yuan1, 2, Trevor L. Buckner2 and Rebecca Kramer-Bottiglio1; 1Purdue University, West Lafayette, Indiana, United States; 2Yale University, New Haven, Connecticut, United States.

Composite materials are greater than the sum of their parts—constituent materials work symbiotically to enhance the overall functionality of the composite. In this work, we create a new kind of silicone elastomer composite that can vary in its modulus of elasticity on demand. Our composite is made by embedding low melting point alloy (Field’s Metal - FM) particles in a silicone elastomer matrix creating Field’s Metal Silicone (FMSi). By applying heat to transition the FM particles between solid and liquid states, the composite can embody two different moduli of elasticity on-demand. In all cases, the composite remains “soft”—with a very low modulus (<10MPa)—but by changing its modulus, the silicone can fulfill different functions. Furthermore, by melting the FM particles, straining the bulk composite and then chilling the system, the shape of the deformed inclusions is fixed, holding the composite in a stretched state and adding anisotropy to the elastic modulus of the composite. This form of variable stiffness, (i.e. variable elasticity) has yet to be shown as a functional quasi-homogeneous material, rather than a functional system constructed of discrete materials. We will present the fabrication of the FM particles and the composite; characterization of the FMSi over a range of particle loading fractions, temperatures, and deformations; and finally applications of the FMSi composite material in soft robotics.

A Stretchable Ionic Diode from Interpenetrating Polyelectrolyte Hydrogels

Hae-Ryung Lee and Jeong-Yun Sun; Seoul National University, Seoul, Korea (the Republic of).

As the demand for soft and flexible devices steadily increases, the ionic applications demonstrated with gel materials have come under the spotlight. Here, stretchable ionic diodes (SIDs) made from polyelectrolyte hydrogels are introduced. Polyelectrolyte hydrogels were mechanically modified by methacrylated polysaccharides, forming interpenetrating networks (IPN) while preserving the ion-selectivity of poly(sulfopropyl acrylate) potassium salt (PSPA) and poly[(acrylamidopropyl)trimethylammonium chloride] (PDMAPAA-Q). Then, SIDs composed of interpenetrating polyelectrolyte gels were fabricated in VHB® substrates engraved by a laser. The SIDs showed rectifying behaviours under a maximum stretch of 3 and preserved their rectifications over hundreds of cycles. A wearable ionic circuit with LEDs operating during finger movements was also demonstrated as a corollary application of SIDs.

3D Printing of Liquid Crystal Elastomeric Actuators with Spatially Programmed Nematic Order

Arda Kotikian1, Ryan L. Truby1, John W. Boley4, Timothy J. White2 and Jennifer Lewis5; 1Harvard University, Cambridge, Massachusetts, United States; 2Yale University, New Haven, Connecticut, United States.

Applications ranging from soft robotics to deployable devices would benefit from shape-morphing architectures that exhibit reversible, programmable actuation. Liquid crystal elastomers (LCEs) are of particular interest due to their intrinsic contractility, large deformations and high energy density. Here, we present a 3D printing method that enables one to pattern LCE inks with programmed director alignment in arbitrary form factors for use as artificial muscles. Specifically, we use high operating temperature direct ink writing (HOT-DIW) to align their mesogen domains along the direction of the print path. We then characterize their order parameter, actuation strain, and specific work. Using this process, we create shape-morphing LCE actuator (LCEA) architectures that undergo reversible planar-to-3D and 3D-to-3D transformations on demand as well as 3D LCEAs (~1 mm thick) capable of lifting 233% more weight than other LCE actuators reported to date.

Zwitterions with Distinctive Stimuli-Responsive Behaviors to Construct Deformable Sensory Systems in Soft Robots

Zhouyue Lei1 and Peiyi Wu1, 2; 1Department of Macromolecular Science, Fudan University, Shanghai, China; 2Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China.

With growing interests in the fields of soft robots, it is crucial yet rather challenging to construct deformable sensory systems with customizable functionalities and human tissue-compatible mechanical properties. Herein, we design a type of zwitterions combining distinctive stimuli-responsive behaviors, i.e., both UCST (Upper Critical Solution Temperature) and LCST (Lower Critical Solution Temperature) by simply manipulating nano-level molecular dynamic interactions. It also integrates ultra-stretchability, high strength, impressive toughness, fatigue resistance, self-healability (at room temperature within 12 h) and facile processability (3D printing et al.), along with ionic conductivity for information transport. This material provides intelligent skins for soft robots and shows many advantages such as multiple sensations, tunable sensitivity, distinct visual effect (UCST and LCST) and adaptable mechanical properties. We believe this presentation is inspiring for the regulation of mechanical properties and stimuli-responsive behaviors in soft robots and we will also discuss the material design of artificial neuromuscular systems from the prospective of molecular dynamic interactions.
Liquid Metals for Soft Robotics

Michael Dickey; North Carolina State University, Raleigh, North Carolina, United States.

This talk will discuss recent progress in utilizing liquid metals as conductors for stretchable, soft, and reconfigurable components for soft robotics. Alloys of gallium are noted for their low viscosity, low toxicity, and near-zero vapor pressure. Despite the large surface tension of the metal, it can be patterned into non-spherical 2D and 3D shapes due to the presence of an ultra-thin oxide skin that forms on its surface. Because it is a liquid, the metal is extremely soft and flows in response to stress to retain electrical continuity under extreme deformation. By embedding the metal into elastomeric or gel substrates, it is possible to form soft, flexible, and conformal electrical components, stretchable antennas, and ultra-stretchable wires that maintain metallic conductivity up to ~800% strain. Thus, these materials are well-suited for soft robotics because they decouple electrical conductivity and mechanical properties. In addition to introducing the advantages of these materials for soft robotics, this talk will focus on recent work to utilize liquid metal for (1) soft energy harvesting that converts mechanical motion to electrical energy, (2) tough energy absorbing materials, and (3) color changing materials for camouflage, strain sensing, and materials logic. These advances have implications for soft machines and robots that have ultra-soft mechanical properties.

Jet Based Electrochemical 3D Printing for Micromechanical Systems Realization

Marco Stefancich1, Harry Apostoleris2,3, Matteo Chiesa2,3 and Wael Othman1; 1Dubai Electricity and Water Authority, Dubai, United Arab Emirates; 2Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates; 3Fluid Metal 3D, Skien, Norway.

While laser based metal 3D printing is having a strong impact on the manufacturing sector, the lack of a low cost approach for this class of materials limits its further diffusion due to the high investment cost of the printer and the adjoining post-treatment equipment. The realization of small scale mechanical systems, to enable next generation robotics, calls for different approaches capable of operating in the 10 to 1000 microns scale. Multiple approaches are currently being proposed, among which we identify direct metal 3D printing by jet assisted localized electrochemical deposition as a particularly promising one. In its simplest form this approach is based on the use of a high speed electrolyte jet impacting on the intended deposition surface where a current, flowing through the jet, leads to the reduction of the metal ions to solid metal at the jet impact point. The specific hydrodynamic properties of the jet ensure that the reduction is highly localized, potentially down to the microns scale, and its limited solely by the jet diameter. The deposition rate, moreover, largely exceeds those of conventional electrodeposition processes. This approach allows metal deposition at room temperature without the need for controlled atmosphere and employing common water based electrolytic solutions with the use of simple hardware in a well understood process. Due to the properties of the process, the deposition is also not limited to conductive substrates but can be extended to plastics without any pre-treatment as long as sufficient metal-plastic adhesion is achieved. Here we discuss the fundamental physics and chemistry underlying the process and present the most current results on 3 dimensional structures in the mm scale realized in copper and nickel on conductive and non-conductive substrates. Deposition rates of several microns/second are demonstrated and complex structures like micro-gears and free standing spindles are realized without the need for supporting structures.

This approach can be applied to the realization of complex mechanical micro devices to be used as platform for mm scale robotics systems.

Programmable Elasticity of Soft Materials Overcomes the Gauge Limit of Capacitive-Type Strain Sensor

Young-Joo Lee, Seung-Min Lim, Jeong-Ho Lee, Sung-gyu Kang, Heung Nam Han, Jeong-Yun Sun, In-suk Choi and Young-chang Joo; Seoul National University, Seoul, Korea (the Republic of).

Soft and smart materials have been highlighted for providing intelligence to devices, i.e., soft robots, stretchable electronics, self-healing materials, camouflaging materials and so on. In this presentation, we will introduce a new soft material named ‘auxetic elastomer’, having unique elastic properties beyond the theoretical limit, by incorporating an auxetic frame within soft materials. Auxetic is known to be an open cell structure that can show negative Poisson’s ratio. The elastic property of our auxetic elastomer can be predictively modulated by considering the auxetic geometry design and proper material selection. The experimental and simulation results proved that our continuum-solid auxetic elastomers can be designed to have negative in-plane and high positive out-of-plane Poisson’s ratios, that cannot be achieved by conventional elastomers. Incorporating the mechanical characteristics of the auxetic elastomer, we successfully overcome the electrical performance limit of a capacitive-type stretchable strain sensor in terms of sensitivity. Our sensor can show a gauge factor improved by 3.2-fold even maintaining the linear response. The sensor can be stretched up to 100 %, and show great cyclic durability. Our research has an originality in mechanical metamaterial research because it provides mechano-electric developments beyond conventional structural applications.

3D Fabrication of Fully Metallic Magnetic Microrobots

Carlos C. Alcantara, Sangwon Kim, Bumjin Jang, Prakash Thakolkaran, Bradley Nelson and Salvador Pané; ETH Zurich, Zurich, Switzerland.

Small-scale robots have been proposed for a variety of medical applications, such as minimally invasive surgery, drug delivery, biopsy and diagnosis1. To transfer micro- and nanorobotics technologies to real clinical applications, approaches enabling the batch fabrication of micro- and nanoswimmers with biocompatible and biodegradable characteristics are necessary. Here, we present a process to manufacture arrays of fully metallic iron-based microrobots with complex features such as helices, double helices and spherical microscaffolds. The devices are fabricated by means of template-assisted electrodeposition (TAE) in 3D printed molds. The molds are obtained by two-photon polymerization (2PP). Compared to previous works with TAE and 2PP, our method is not restricted to the use of transparent conductive oxides (TCO) such as indium-tin-oxide2-4. While this substrate has been widely used in 3D printed molds. The molds are obtained by two-photon polymerization (2PP). Compared to previous works with TAE and 2PP, our method is not restricted to the use of transparent conductive oxides (TCO) such as indium-tin-oxide2-4. While this substrate has been widely used for 4:30 PM *GI02.07.01

Incorporating the mechanical characteristics of the auxetic elastomer, we successfully overcome the electrical performance limit of a capacitive-type strain sensor having unique elastic properties beyond the theoretical limit, by incorporating an auxetic frame within soft materials. Auxetic is known to be an open cell structure that can show negative Poisson’s ratio. The elastic property of our auxetic elastomer can be predictively modulated by considering the auxetic geometry design and proper material selection. The experimental and simulation results proved that our continuum-solid auxetic elastomers can be designed to have negative in-plane and high positive out-of-plane Poisson’s ratios, that cannot be achieved by conventional elastomers. Incorporating the mechanical characteristics of the auxetic elastomer, we successfully overcome the electrical performance limit of a capacitive-type stretchable strain sensor in terms of sensitivity. Our sensor can show a gauge factor improved by 3.2-fold even maintaining the linear response. The sensor can be stretched up to ~800% strain. Thus, these materials are well-suited for soft robotics because they decouple electrical conductivity and mechanical properties. In addition to introducing the advantages of these materials for soft robotics, this talk will focus on recent work to utilize liquid metal for (1) soft energy harvesting that converts mechanical motion to electrical energy, (2) tough energy absorbing materials, and (3) color changing materials for camouflage, strain sensing, and materials logic. These advances have implications for soft machines and robots that have ultra-soft mechanical properties.

Jet Based Electrochemical 3D Printing for Micromechanical Systems Realization

Marco Stefancich1, Harry Apostoleris2,3, Matteo Chiesa2,3 and Wael Othman1; 1Dubai Electricity and Water Authority, Dubai, United Arab Emirates; 2Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates; 3Fluid Metal 3D, Skien, Norway.

While laser based metal 3D printing is having a strong impact on the manufacturing sector, the lack of a low cost approach for this class of materials limits its further diffusion due to the high investment cost of the printer and the adjoining post-treatment equipment. The realization of small scale mechanical systems, to enable next generation robotics, calls for different approaches capable of operating in the 10 to 1000 microns scale. Multiple approaches are currently being proposed, among which we identify direct metal 3D printing by jet assisted localized electrochemical deposition as a particularly promising one. In its simplest form this approach is based on the use of a high speed electrolyte jet impacting on the intended deposition surface where a current, flowing through the jet, leads to the reduction of the metal ions to solid metal at the jet impact point. The specific hydrodynamic properties of the jet ensure that the reduction is highly localized, potentially down to the microns scale, and its limited solely by the jet diameter. The deposition rate, moreover, largely exceeds those of conventional electrodeposition processes. This approach allows metal deposition at room temperature without the need for controlled atmosphere and employing common water based electrolytic solutions with the use of simple hardware in a well understood process. Due to the properties of the process, the deposition is also not limited to conductive substrates but can be extended to plastics without any pre-treatment as long as sufficient metal-plastic adhesion is achieved. Here we discuss the fundamental physics and chemistry underlying the process and present the most current results on 3 dimensional structures in the mm scale realized in copper and nickel on conductive and non-conductive substrates. Deposition rates of several microns/second are demonstrated and complex structures like micro-gears and free standing spindles are realized without the need for supporting structures.

This approach can be applied to the realization of complex mechanical micro devices to be used as platform for mm scale robotics systems.

Programmable Elasticity of Soft Materials Overcomes the Gauge Limit of Capacitive-Type Strain Sensor

Young-Joo Lee, Seung-Min Lim, Jeong-Ho Lee, Sung-gyu Kang, Heung Nam Han, Jeong-Yun Sun, In-suk Choi and Young-chang Joo; Seoul National University, Seoul, Korea (the Republic of).

Soft and smart materials have been highlighted for providing intelligence to devices, i.e., soft robots, stretchable electronics, self-healing materials, camouflaging materials and so on. In this presentation, we will introduce a new soft material named ‘auxetic elastomer’, having unique elastic properties beyond the theoretical limit, by incorporating an auxetic frame within soft materials. Auxetic is known to be an open cell structure that can show negative Poisson’s ratio. The elastic property of our auxetic elastomer can be predictively modulated by considering the auxetic geometry design and proper material selection. The experimental and simulation results proved that our continuum-solid auxetic elastomers can be designed to have negative in-plane and high positive out-of-plane Poisson’s ratios, that cannot be achieved by conventional elastomers. Incorporating the mechanical characteristics of the auxetic elastomer, we successfully overcome the electrical performance limit of a capacitive-type stretchable strain sensor in terms of sensitivity. Our sensor can show a gauge factor improved by 3.2-fold even maintaining the linear response. The sensor can be stretched up to ~800% strain. Thus, these materials are well-suited for soft robotics because they decouple electrical conductivity and mechanical properties. In addition to introducing the advantages of these materials for soft robotics, this talk will focus on recent work to utilize liquid metal for (1) soft energy harvesting that converts mechanical motion to electrical energy, (2) tough energy absorbing materials, and (3) color changing materials for camouflage, strain sensing, and materials logic. These advances have implications for soft machines and robots that have ultra-soft mechanical properties.

3D Fabrication of Fully Metallic Magnetic Microrobots

Carlos C. Alcantara, Sangwon Kim, Bumjin Jang, Prakash Thakolkaran, Bradley Nelson and Salvador Pané; ETH Zurich, Zurich, Switzerland.

Small-scale robots have been proposed for a variety of medical applications, such as minimally invasive surgery, drug delivery, biopsy and diagnosis1. To transfer micro- and nanorobotics technologies to real clinical applications, approaches enabling the batch fabrication of micro- and nanoswimmers with biocompatible and biodegradable characteristics are necessary. Here, we present a process to manufacture arrays of fully metallic iron-based microrobots with complex features such as helices, double helices and spherical microscaffolds. The devices are fabricated by means of template-assisted electrodeposition (TAE) in 3D printed molds. The molds are obtained by two-photon polymerization (2PP). Compared to previous works with TAE and 2PP, our method is not restricted to the use of transparent conductive oxides (TCO) such as indium-tin-oxide2-4. While this substrate has been widely used for
terms of locomotion with weak rotating magnetic fields (<10mT) and in different fluids. Iron microhelices can perform corkscrew motion, while spherical microscaffolds can roll on surfaces. Interestingly, our microrobots exhibit a relatively high maximum forward velocity \((v_{max})\) of approximately 500 \(\mu m/s\) when manipulated in isopropyl alcohol. In silicone oil, the spherical rollers and the helices exhibit \(v_{max}\) values of 25 \(\mu m/s\) and 42 \(\mu m/s\), respectively. Additionally, we demonstrate that the iron microhelices can swim against gravity and in three dimensions. Finally, preliminary degradation tests in simulated gastric acid at pH 1.7 show partial degradation of the helical structures.


4:45 PM GI02.07.05
3D Printed Biodegradable Microrobots for Theranostic Delivery Hakan Ceylan, Ceren Yasa and Metin Sitti; Max Planck Institute for Intelligent Systems, Stuttgart, Germany.

Untethered micron-scale mobile robots can leverage minimally invasive technologies by navigating and performing in hard-to-reach, confined and delicate inner body sites. Such a complex task requires integrated design and engineering strategies, where materials, powering, control, medical functionality and degradability need to be considered altogether. The present study reports a magnetically mobilized, locally responsive and biodegradable microrobotic swimmer for medical cargo delivery and release tasks. We design double-helical, hydrogel-based microswimmers, of 20 \(\mu m\) length, 3D-printed with complex geometrical and compositional features. At normal physiological concentrations, matrix metalloproteinase-2 enzyme can entirely degrade the microswimmer body in 118 h to solubilized non-toxic products. The amount of enzyme around the microswimmers tailors the release kinetics of the drug payload, and the drug bioaccessibility is eventually attained in full from the collapsed network of the microswimmers. Antibody-tagged iron oxide nanoparticles released from the degraded microswimmers serve for targeted labeling of SKBR3 breast cancer cells to realize the potential of medical payload, and the drug bioaccessibility is eventually attained in full from the collapsed network of the microswimmers. Antibody-tagged iron oxide nanoparticles released from the degraded microswimmers serve for targeted labeling of SKBR3 breast cancer cells to realize the potential of medical imaging of local tissue sites following the therapeutic intervention. These results represent a leap forward toward clinical medical microrobots that are capable of sensing, responding to the local pathological information, and performing specific therapeutic and diagnostic tasks as orderly executed operations using their smart composite material architectures.

GI02.08.01
Graphene-Based Fiber for Artificial Muscle Hyunsoo Kim, Ji Hwan Moon and Seon Jeong Kim; Hanyang Univ, Seoul, Korea (the Republic of).

Artificial muscles are actively researched using various materials such as a polymer, carbon nanotube, and graphene for application to soft robotics or replacing motors. Especially, graphene-based actuators are attracted because of low cost and mass producibility. However, previous graphene oxide (GO)-based actuators demonstrated torsional and bending actuations. Her, we developed a torsional and tensile actuating GO-based fiber for expansion of the application to various fields such as an artificial muscle, soft robotics, and indicators. The GO-based fiber was produced by wet-spinning technique with Nylon coagulation bath. This GO-based tensile actuator actuates reversible contraction and elongation without hysteresis by control the twisting direction of mandrel coils of GO-based fiber. Moreover, the GO-based actuator demonstrates lift load over 100 times heavier than itself, stable actuation and able to withstand high temperature over the melting point of the polymer. This novel kind of GO-based actuator, which has multi-directional actuation, have potential for a wide range of applications such as artificial muscles, robotics, and temperature sensing.

GI02.08.02
Algorithmic Stacking for Hyperform and Pluripotent Transformable Materials Yuki Lee1, Young-chang Joo1, Jyh-ming Lien2 and In-suk Chei1; 1Seoul National University, Seoul, Korea (the Republic of); 2George Mason University, Fairfax, Virginia, United States.

Origami and kirigami, an art of paper folding, cutting, and transforming into a specific sculpture, are one of the innovative strategy for hyperform materials, which means scale-changeable materials from small to extremely large scale. In this study, we propose a novel algorithmic kirigami method that provides super compaction of an arbitrary 3-D shape, called “algorithmic stacking”. This super compacted structure can be manufactured in a workspace that is significantly smaller than the provided 3-D shape, by making the product a compacted state and converting it to the original 3-D shape. For example, even a product larger than 3D printer can be printed and used by the 3D printer. In addition, we have shown that the proposed stackable structures have high pluriplasticity and can transform into multiple 3-D target shapes. Our study includes voxelization for creating meshes, solutions for finding Hamiltonian path, mesh stripification, hinge design between adjacent meshes, and its application. Algorithmic stacking can give the solution for manufacturing products or devices in a limited workspace, make packing and transportation easier for a deployable application, and be a universal platform for pluripotent 3-D transformable structures.

GI02.08.03
Helical Nanomotors as Intracellular Probes Malay Pal1, Neha Somalwar1, Anumeha Singh2, Ramray Bhat1, Sandeep M. Eswarappa2, Deepak K. Sunit3, 4 and Ambarish Ghosh1, 5; 1Centre for Nano Science and Engineering, Indian institute of Science, Bangalore, India; 2Department of Biochemistry, Indian Institute of Science, Bangalore, India; 3Department of Molecular Reproduction, Development and Genetics, Indian Institute of Science, Bangalore, India; 4Centre for BioSystems Science and Engineering, Indian Institute of Science, Bangalore, India; 5Department of Electrical Communication Engineering, Indian Institute of Science, Bangalore, India; 6Department of Physics, Indian Institute of Science, Bangalore, India.

Cellular interior is a highly heterogeneous and anisotropic environment, whose physical, especially mechanical properties are difficult to measure. Currently, there are many efforts to develop techniques for such measurements, including atomic force microscopy, microplate, shear twisting cytoometry, optical tweezers, optical stretchers, magnetic tweezers, particle tracking microrheology etcetera. Many of these techniques probe the cells from outside, and
therefore not suitable for direct intracellular investigation as would be possible for probes maneuvered within the cellular interior. The purpose of this study is to develop a nanoprobe that can be manipulated inside the cell in a minimally invasive manner, with an extremely high degree of spatial accuracy at high speeds. As we show here, we have developed a helical shaped magnetic nanomotor, primarily made up of silica, polystyrene and iron, that can be internalized by the cells when incubated for around 24 hours. Subsequently, these internalized nanomotors can be actuated remotely inside the living cell by application of a rotating magnetic field created by a tri-axial Helmholz coil. We will report various interesting observations regarding the motion of the motor, which proves how these tiny motors can promptly detect mechanical changes, that too with a micron scale resolution within a living cell. We believe this can lead to novel studies of the properties of the cellular interior at a single cell level and in future lead to various intracellular sensing and delivery applications.

**GI02.08.04**

**Chemical/Light Powered Hybrid Micromotors with 'On-the-Fly' Optical Brakes**

Songsong Tang; Nanoengineering, University of California, San Diego, San Diego, California, United States.

Hybrid micromotors capable of both chemically-powered propulsion and fuel-free light-driven actuation and offering built-in optical brakes for chemical propulsion are described. The new hybrid micromotors are designed by combining photocatalytic TiO2 and catalytic Pt surfaces into a Janus microparticle. The chemical reactions on the different surfaces of the Janus particle hybrid micromotor can be tailored by using chemical or light stimuli that generate countering propulsion forces on the catalytic Pt and photocatalytic TiO2 sides, respectively. Such modulation of the surface chemistry on a single micromotor leads to switchable propulsion modes and reversal of the motion directionality that reflect the tuning of the local ion concentration and hence the dominant propulsion force. An intermediate Au layer (under the Pt surface) plays an important role in determining the propulsion mechanism and operation of the hybrid motor. The built-in optical braking system allows ‘on-the-fly’ control of the chemical propulsion through photocatalytic reaction on the TiO2 side to counterbalance the chemical propulsion force generated on the Pt side. The adaptive dual operation of these chemical/light hybrid micromotors, associated with such control of the surface chemistry, holds considerable promise for designing smart nanomachines that autonomously reconfigure their propulsion mode for various on-demand operations.

**GI02.08.05**

**Urease-Powered Nanomotors for Enhanced Anticancer Drug Delivery**

Ana Hortelão, Tania Patiño, Rafael Carrascosa and Samuel Sanchez; 1 Institute for Bioengineering of Catalonia (IBEC) The Barcelona Institute of Science and Technology, Barcelona, Spain; 2 Institució Catalana de Recerca i Estudis Avancats (ICREA), Barcelona, Spain.

Urease-Powered Nanomotors for Enhanced Anticancer Drug Delivery

Micro- and nanomotors are structures capable of self-propulsion in fluids, which have been considered interesting for biomedical applications, such as the active transport and delivery of specific drugs to the site of interest. Here, we present the loading of urease-powered nanomotors with the anticancer drug Doxorubicin, as well as the substrate-dependent (urea) drug release and efficient delivery to cells. These nanomotors are based on mesoporous silica core-shell nanoparticles functionalized with urease enzyme. The motion dynamics of these self-propelled silica nanomotors was analyzed using optical tracking and dynamic light scattering. A four-fold increase in Doxorubicin release is achieved by nanomotors after 6 hours exposure to urea, compared to nanomotors in passive conditions (absence of urea). Moreover, active Doxorubicin-loaded nanomotors present an enhanced anticancer efficiency toward HeLa cells, that arises from a synergy between increased drug release and production of ammonia during catalysis. We found that in the presence of urea, Doxorubicin-loaded nanomotors exhibit improved effect on HeLa cells compared to passive carriers, where a higher content of Doxorubicin is uptaken after 1, 4, 6, and 24 hours incubations. Naturally high urea concentrations present in bladder can trigger the motion of anticancer drug loaded nanomotors. This effect generates a more effective drug release, which can be of particular interest for intravesical drug delivery. As a step forward, urease-powered nanomotors, coupled with an antibody, are used as developed to target bladder cancer derived from transitional cell papilloma. The improvement in drug delivery efficiency achieved by enzyme-powered nanomotors may hold potential toward their use in future varied applications, such as the substrate-triggered release of drugs in precise locations.

**GI02.08.06**

**Highly Increased Output Voltage with Diverse Textiles in Triboelectric Nanogenerators for a Wide Variety of Soft Robot Application**

Jae-Bum Jeong; Swanit Biswas, Suwoong Lee and Hyek Kim; 1 Gyeongsang National University, Jinju, Korea (the Republic of); 2 Korea Institute of Industrial Technology, Daegu, Korea (the Republic of).

Triboelectric nanogenerator (TENG) with fabrics has been widely studied due to its potential application in smart textiles, so to be used to wearable electronics. The surface property of fabric affects on the output voltage of TENG because the surface charge density depends on the kind of fabrics. We demonstrated the enhanced output voltage of TENG with a variety of textiles. Elastomer was inserted to support between Cu electrodes. In this process, various fabrics, such as cotton, rayon, wool, acetate, silk, nylon, and acrylic, were covered the elastomer to control surface charge. The output voltages were measured by changing surface frictional charge density. The change of output voltage according to frictional electrostatic voltage from 3 V to 25 V is demonstrated. In addition, effect of the moisture regain of various textiles on output voltage is also studied.

**GI02.08.07**

**Metal-Oxide Based Micromotors for the Removal of Organic Pollutants and Heavy Metals**

Diana Villa; Jemish Parmar, Katherine Villa and Samuel Sanchez; 1 Instituto de Bioengineering, Barcelona, Spain; 2 Institut for Research of Catalonia (ICREA), Barcelona, Spain.

Water contamination is one of the most persistent problems in public health. Micromotors can act as an efficient tool for water remediation because of the enhance mass transfer by active motion. Bubble-propelled micromotors move due to the bubble-recoil mechanism, which are associated to micro/mixing capabilities, resulting in a potential platform for water remediation applications. The choice of the functional material on the micromotors surface depends on the target pollutants. However, several challenges must be addressed before micromotor-based water treatment technology can be used in practical applications, such as the high cost associated with the use of Pt for propulsion. Moreover, these micromotors are typically fabricated by expensive techniques such as, rolled up technology[1] or electrodeposition methods[2]. In order to obtain efficient and inexpensive micromotors for water treatment, we described cobalt ferrite (CoFe2O4)[3] and Fe3O4-decorated SiO2/MnO2 micromotors fabricated[4] by facile and scalable synthesis methods, respectively.
The CoFe₂O₄ micromotors were fabricated by agglomeration of dried CoFe₂O₄ nanoparticles (NPs), which were previously synthesized via solvothermal routes using Co³⁺ and Fe³⁺ salts as precursors in ethylene glycol. The micromotors, self-propelled without the need of a surfactant, carried out an efficient removal of tetracycline antibiotic from wastewater and, after the reaction was complete, were collected and separated using their magnetic properties. In addition, we proved that CoFe₂O₄ micromotors enhanced the production of hydroxyl radicals via Fenton-like reaction due to the presence of cobalt.

The γ-Fe₂O₃-decorated SiO₂/MnO₂ micromotors consisted of mesoporous silica-based microjets with MnO₂ immobilized on the outer surface and decorated with γ-Fe₂O₃ NPs on the outer surface. They were synthesized by growing silica tubes on a polycarbonate template by sol-gel method[5] and immobilizing MnO₂ and γ-Fe₂O₃ catalysts. The inner layer of MnO₂ act as functional material for both propulsion and removal of pollutants and γ-Fe₂O₃ NPs as photocatalytic, adsorptive and magnetic material. Thus, these micromotors enabled the efficient degradation of organic pollutants (dyes and antibiotics) under visible light irradiation, as well as the removal of heavy metal ions. Regarding their magnetic properties, they were magnetically steered facilitating their recovery and further reuse.

Therefore, these approaches open up new inexpensive alternative methods to fabricate other types of metal-oxide based micromotors for different applications in the environmental field.

bacteria-powered biohybrid microrobots have recently shown to actively transport and deliver cargoes encapsulated into their synthetic constructs to specific regions locally. However, use of synthetic materials as cargo carriers can result in inferior performance in load-carrying efficiency, biocompatibility, and biodegradability, impeding clinical translation of biohybrid microswimmers. We have developed a bacteria-powered biohybrid microrobot using RBCs as autologous cargo carriers for active and guided cargo delivery. RBCs were loaded with anti-cancer doxorubicin drug molecules (DOX) and superparamagnetic iron oxide nanoparticles (SPIONs) and functionalized with biotinylated anti-TER-119. Multifunctional biohybrid microrobots were fabricated by attachment of RBCs to bioengineered motile bacteria, Escherichia coli MG1655 expressing biotin attachment peptides, via biotin-avidin-biotin binding complex. Release of DOX molecules from RBC cargoes was investigated over 120 hours at different pH conditions (3.1 - 9.2) and enhanced release rates were observed at low pH conditions. Autonomous and on-board propulsion of biohybrid microrobots was provided by bacteria (∼10^-5 μm/s), and their external magnetic guidance was enabled by SPIONs loaded into the RBCs. Moreover, bacteria-powered RBC microrobots displayed preserved deformability and attachment stability even after squeezing in microchannels smaller than their sizes, as in the case of bare RBCs. Inherent compliance of RBCs further allowed active deformation and passage of RBC microswimmers through confined spaces only by means of bacterial propulsion, while preserving their motility. In addition, an on-demand light-activated hyperthermia termination switch was engineered for RBC microswimmers to control bacteria population after targeted operations.

RBCs, as biological and autologous cargo carriers in the biohybrid microrobots, offer notable advantages in stability, deformability, biocompatibility, and biodegradability over synthetic cargo-carrier materials. The biohybrid microswimmer design presented here transforms RBCs from passive agents into autonomous, active, and guidable cargo carriers toward targeted drug and other cargo delivery applications in medicine.

G102.08.12 Controllable Dynamic Self-Assembly of Mobile Microrobotic Swarms with Programmable Interrobotic Interactions Berk Yigit, Yunus Alapan and Metin Sitti; Max-Planck Institute for Intelligent Systems, Stuttgart, Germany.

Microrobotic swarms are indispensable for amplifying throughput in high-impact microrobotic applications for targeted drug delivery, medical diagnostics, parallel micromanipulation, and environmental sensing and remediation. Bottom-up assembly approaches present facile means for fabrication of microrobot swarms, owing to their parallel assembly capabilities and reconfigurability enabled by modular constituents. Previous studies showed that single microrobots of controlled size, shape, and function can be formed by dynamic self-assembly of magnetic microparticles. However, their controlled fabrication and operation at high densities has remained a challenge as they are susceptible to coalescing into poorly-defined aggregates due to unintended magnetic dipolar attractions. Here, we show that controlling magnetic interactions via precessing magnetic fields enable massively parallel formation and operation of mobile microrobotic swarms at high densities, with well-defined microrobot morphologies, locomotion characteristics and spatial order. Starting from a dispersed suspension of superparamagnetic particles over a planar substrate, we use precessing magnetic fields (dynamic rotating and static unidirectional fields) to form a swarm of linear chain assemblies, each consisting of 3 to 5 superparamagnetic particles. These chain microrobots locomote on surfaces by applying a tilt to their precession axis. Control over the angles of precessing magnetic field allows tuning magnetic interactions among microrobotic chains from attractive to repulsive. Utilizing unidirectional repulsive interactions that prevent aggregations in the plane of the substrate, we show that microrobots are able to maintain structural and functional integrity over macroscale distances (∼1 cm), even in highly compacted swarms travelling through narrow passages. Moreover, interrobotic interactions enabled control over collective order for achieving a homogeneous spatial distribution and a narrow distribution of nearest neighbor distances indicating spatial organization. These swarms can further achieve directional transport of large cargoes on surfaces and small cargoes in bulk fluids. Our results demonstrate that interrobotic interactions are crucial for operation of dynamically self-assembled microrobots without forming aggregates at high densities, and enables controlling collective order inside microrobotic swarms. Overall, described design approach, exploiting physical interactions among individual robots, enables facile and rapid formation of self-assembled and reconfigurable microrobotic swarms with programmable collective order.

G102.08.13 Algal Microswimmers for Cargo Delivery Oncay Yasa, Pelin Erkoc, Yunus Alapan and Metin Sitti; Max-Planck Institute for Intelligent Systems, Stuttgart, Germany.

Nature exhibits intriguing microscopic swimmers with innate energy harvesting abilities from their local environments. Use of natural swimmers as delivery agents presents an alternative platform to transport cargoes inside the body. Their small sizes and intrinsic properties could allow deep tissue penetration, and in this way, to reach difficult-to-access inner body locations. Although bacteria are heavily utilized as actuators in biohybrid microswimmer design for cargo delivery applications, their acute pathogenicity along with rapid growth in physiological conditions limit their clinical applications to inner body cavities and solid tumors, and necessitate search for an agile biological swimmer with better biocompatibility, such as microalgae. Microalgae, eukaryotic micromotile microorganisms with a facile culture process, present high propulsion (~100 μm/sec), autofluorescence and phototactic guidance capabilities. Chlamydomonas reinhardtii [C. reinhardtii], as a unicellular biflagellate microalga species, has been barely explored as an actuator to fabricate biobased micromotile microswimmers for biomedical applications, mainly due to its inefficient motility inside typical cell culture media such as minimum essential medium with phenol red.

We developed a biocompatible algal microswimmer, powered by a unicellular freshwater green microalga, by integrating polyelectrolyte [PE] functionalized magnetic spherical polystyrene [PS] (1 μm in diameter, 20% iron oxide content) cargoes onto the surface of C. reinhardtii through non-covalent electrostatic interactions. The integration using electrostatic interactions allowed non-invasive and facile fabrication of the biobased algal microswimmers without the requirement for any harsh chemical reaction. PE functionalized microparticles were alternatingly fabricated with oppositely charged poly(allylamine hydrochloride) (positively charged) and poly(sodium 4-styrenesulfonate) (negatively charged) polyelectrolytes using layer-by-layer deposition technique. The fabrication of the microparticles was finalized at the 5th layer with the positively charged PE to allow electrostatic interaction of the microparticles with the negatively charged microalgae. Initially, interaction of the microalgae with PE functionalized surfaces was characterized using quartz crystal microbalance with dissipation monitoring. Then, three-dimensional swimming motility of the constructed biobased algal microswimmers was characterized in the presence and absence of a uniform magnetic field (in x-direction) using transmission digital holographic microscope. Finally, motility of the microalgae was investigated in different biological media, and a model drug, fluorescent isothiocyanate-dextran (a water-soluble polysaccharide) molecule, was delivered to mammalian cells.

To conclude, we demonstrate a biocompatible algal microswimmer which can be utilized, as an alternative to bacterial microswimmers with superior properties, in various biomedical applications.

G102.08.14 Recent Advances in the Powering and Actuation of Nanorobots Using Sound Waves Fernando Soto and Joseph Wang; Nanoengineering, University of California, San Diego, La Jolla , California, United States.
Micro and nanoscale robots consist of microscopic mobile devices that can convert local chemical fuels or external inputs into autonomous propulsion. These small-scale tools can perform multiple tasks while propelled in solution, as their motion allows them to transport cargo or reactive materials, increase recognition events and induce fluid mixing. Such functionality could lead to the improvement in human health and disease treatment. Despite the attractive performance and autonomy of chemically-powered nanorobots, they still present limitations that warrant pursuing alternatives. Specifically, these catalytic microrobots have short life spans or require toxic fuels to operate, and their swimming behaviour is commonly hard to modulate. On the other hand, recently introduced acoustically-powered motors make use of acoustic fields sound waves that are relatively innocuous and easy to manipulate, offer unique advantages for enabling efficient and controllable motion (in different biological media), and allow for diverse surface functionalization.

Here, we present recent advances in the design, powering, actuation and application of ultrasound-based nanorobots. Including the use of ultrasound-propelled asymmetric nanorobots, which have been translated towards various biomedical concepts including targeted drug delivery, bacteria and toxin capture, and intracellular drug delivery [1,2]. The use of ultrasound fields to modulate the propulsion and collective behaviour of chemically propel microorganisms [3,4]. New tools for nanosurgery which consist on ultrasound triggered microcannons, capable of firing nanobullets and penetrate tissue, [5,6] and ultrasound powered automated assembly lines capable of manipulating and isolating particles and live cells[7].

References
holding/detaching gripper by electrostatic force is experimentally evaluated. The electrostatic force is generated by the bipolar electrodes. The proposed gripper is expected to work effectively on thin film/textile objects with elastically-deformable bipolar micro-probes. Due to the module structure, the micro-probe tips can be aligned precisely on the large surface area where the module has photolithographically-defined silver circular electrodes. The other side of the PVDF layer has photolithographically-defined silver serpentine-structured strain gauges aligned with the back-side electrodes. The aligned features enables localized measurements. Relative movement is sensed by measuring the change in charge between overlapping silver traces. Applied force is sensed by measuring the change in resistance of the strain gauges. Object proximity is measured using the strain gauge traces for capacitive coupling sensing. We prove the adaptability of the hybrid bio-actuator applying different training protocols at different frequencies, resulting in a modulation of the force and the relative expression of related proteins.

In parallel, the 3D bioprinting technique has succeeded in developing functional three-dimensional tissues. Although 3D printing of artificial materials has been used to fabricate scaffolds or molds for hybrid bio-actuators, 3D bioprinting of skeletal muscle tissue, together with soft skeletons, has not been reported in the field of hybrid bio-robotics. Here, we present our recent advances in the fabrication of 3D bioprinted hybrid bio-actuators based on skeletal muscle tissue, taking advantage of the unique versatility, rapid-prototyping and simplicity of the technique. We report a full characterization and optimization of the printing from the material point of view, but also paying special attention to the biocompatibility, as well as differentiation and maturation of cells inside the bioprinted hydrogel. Furthermore, we demonstrate myotube alignment, following the direction of printing, by immunostaining and scanning electron microscopy. This result is a unique consequence of the use of 3D bioprinting that is typically difficult to achieve by other means. Finally, we take advantage of the multi-material printing capabilities of the technique to 3D bioprint a hybrid biological actuator whose contractions can be completely controlled by external electric fields. We prove the adaptability of the hybrid bio-actuator applying different training protocols at different frequencies, resulting in a modulation of the force and the relative expression of related proteins.

Living beings have evolved to use coupled algorithms, from breathing to walking. It is known local, often small, clusters of neurons (CPGs) perform these essential functions, in the absence of input from the brain. This modular method of control of whole organisms may present advantages over centralized, computational robotic control. An experimental platform, composed of diffusively-coupled PDMS microreactors each containing the oscillatory, light sensitive Belousov-Zhabotinsky (BZ) chemical reaction has been developed. This method allows rapid testing of methods of CPG design out of coupled oscillators. Further it will aid the design of already existent micronscale, hydrogel robotics through revealing how control of diffusive fluxes within a patterned hydrogel could result in different spatiotemporal patterns of actuation. Experimental observations of quadruped gaits in 4 reactors, and a categorization of both individual, and pairs of reactors within the system will be the focus of the presentation.
To date, new handling techniques of thin film/textile materials such as polymer films, papers, and fabrics have been required in order to develop advanced wearable devices, and many other applications, although the conventional electrostatic chucks work successfully typically for flat and hard wafer in the semi-conductor fabrication. In recent years, our research group has been developing compliant bipolar electrostatic grippers through the past studies. Still the critical issue remains to be solved that the effective area for electrostatic force should be enlarged while the spatial density of bipolar electrodes should be increased. In addition, the insulation between the bipolar electrodes is seriously important to avoid the damage from the breakdown in case of spatially high density of electrodes. To solve this issue by layer-by-layer fabrication, 3D printing technology can be considered one of the most useful for applications in relatively large scale.

The module having bipolar probes consists of three-sublayer (conductor-insulator-conductor) structure. The 80mm-long bipolar probes are arranged at 45-degrees to interface. The dimensions of a rectangle tip surface of the bipolar probes are 1.2mm in width and 1.6mm in height. Conductive and insulating layers are 0.4mm and 0.8mm in thickness, respectively. The bipolar probes are fabricated by a fused deposition modeling (FDM) 3D printer having a 0.4-mm-diameter nozzle. Carbon-mixed and ABS filaments are used for conductor and insulator, respectively.

The force curve is experimentally determined to evaluate the compliance, the maximum attractive force, and other characteristics. Additionally pick-and-place demonstrations for a PP film, a printing paper and a fabric are conducted to show that the module work as a handling/detaching device for thin film/textile objects under particular conditions. Furthermore, even if the influence of residual charge is not negligible due to the applied voltage, the detachment is always successful with an appropriate tilt angle that causes peeling effect in the contact interface between probe tips and objects. Therefore the proposed concept will highly contribute to the fabrication technology in the next-generation robotics.

GI02.08.22
From Soft Actuator to Soft Robot Powered with the Oscillating Belousov Zhabotinsky Reaction Baptiste Blanc1, Ning Zhou1, Hyunki Kim1, Eric Y. Liu2, Ali Aghvami1, Hyunmin Yi1, Bing Xu1, Ryan Hayward3 and Seth Fraden1; 1Brandeis University, Waltham, Massachusetts, United States; 2Tufts University, Medford, Massachusetts, United States; 3UMass Amherst, Amherst, Massachusetts, United States.

Yoshida developed a gel in the late nineties that experiences cyclic swelling and deswelling changes without external stimuli. This self oscillating gel contains a catalyst involved in the Belousov Zhabotinsky (BZ) reaction, an oxydo-reduction cyclic reaction, leading to a cyclic change of solubility of the gel.

Our goal here, is to highlight the engineering principle controlling the mechanical oscillation of the BZ gel and to pave the way to the synthesis of controllable autonomous shape changing hydrogel, which could lead to an autonomous motile hydrogel.

We first present a new synthesis technique, offering high modularity in the gel composition and in its functionalization with the catalyst of the BZ oscillating reaction. Thanks to this experimental advance, we optimize the mechanical oscillation of a BZ homogeneous spherical hydrogel, pointing out the critical swelling limitation arising from the minimal size for a BZ gel to chemically oscillate.

We then present a way to "structure" the hydrogel to maximize its mechanical oscillation, and we finally introduce how we are engineering such gels to make them move.

SESSION GI02.09: Materials and Structure
Session Chair: Peer Fischer
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 111

8:00 AM GI02.09.01
Engineering Reaction--Diffusion Networks with Properties of Neural Tissue for Control of Soft Robots Seth Fraden, Mike Norton and Thomas Litschel; Brandeis University, Waltham, Massachusetts, United States.

Neural tissue evolved 3.5 billion years after the origin of life, which is a testament to its complexity, and is found in almost all multicellular life, which is a testament to its importance. At the coarsest level of description, neurons are non-linear oscillators that when coupled together in tissue through excitatory and inhibitory connections give rise to complex spatio-temporal patterns. When organized, these patterns are capable of processing and storing sensory information, and actuating musculature. Extrapolating from this general definition of a neuronal network as a spatiotemporal pattern generator, we posit these dynamics can be captured on an abiotic network--diffusion platform. Here, we report advances in soft lithography that allow the engineering of synthetic reaction--diffusion networks capable of producing a wide variety of spatiotemporal patterns. We employ the well-known oscillatory Belousov-Zhabotinsky reaction and develop methods to create diffusively coupled networks over which we design (i) the topology of the network, the (ii) boundary and (iii) initial conditions, (iv) the volume of each reactor, (v) the coupling strength, and (vi) whether the coupling is of an inhibitory or excitatory nature. It is important to note that the engineering principles we identify are general and can be applied to other oscillatory reaction--diffusion systems. An application for the reaction--diffusion based networks developed here is to the field of soft robotics, where the central pattern generator will serve as the controller of an artificial musculature comprised of chemomechanical gels coupled to the BZ layer.

Supplemental files & movies. DOI: 10.1039/c7lc01187c

8:15 AM GI02.09.02
High Power Density, Humidity Driven Actuators for Robotic Applications Omur Cakmak1, Xi Chen and Ozgur Sahin; Columbia University, New York, New York, United States.

Humidity responsive materials are versatile alternatives to common actuators in robotics systems, due to ease of actuation with humidity gradients and pervasiveness of water. We have shown that as a humidity responsive material, Bacillus spores exhibit high work density actuation 1-2. To take advantage of micrometer sized spores in macroscopic systems, it is necessary to assemble spores into larger materials without significantly compromising function. The granular nature of spores makes this a challenging task because spores don’t adhere well to each other due to small contact areas between adjacent spores, thus making it difficult to transfer mechanical energy. We have shown that combining spores with commercially available UV curable optical and electronic adhesives enable centimeter scale actuators with high work density and specific power. This novel composite is water resistant and retains its function after several liquid water contacts. Upon immersion or exposure to humid air from an ultrasonic humidifier, the actuators respond rapidly, in
and generated 36 mW under one-sun illumination (100 mW/cm²) using the module (total active area is 4.4 cm²). This allows the conformal attachment onto three-dimensional surfaces. In our laboratory, we fabricated such ultra-thin solar cells onto 5 by 5 cm² films.


Energy harvesting systems are important topics for robotic field because the electrical power is inevitable for most devices to be driven. Among various energy harvesting systems, solar cells are one of the best solutions because they can generate milliwatts or higher electric power under the sunshine conditions. Recently we developed ultra-thin organic solar cells which possess high power conversion efficiency (PCE), thermal stability, water-proof property and stretchability simultaneously [1-3]. Our solar cells have ultra-thin properties; the total thickness is only 3 μm and the weight is less than 5 g/m², which allows the conformal attachment onto three-dimensional surfaces. In our laboratory, we fabricated such ultra-thin solar cells onto 5 by 5 cm² films and generated 36 mW under one-sun illumination (100 mW/cm²) using the module (total active area is 4.4 cm²).

In this talk, I will show the performance of our ultra-thin organic solar cells and discuss possibilities for the integration of such power sources with actuators and sensors for the soft robot applications.


Piezotronics for Next Generation Robotics
Zhong Lin Wang1, 2; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

Piezoelectricity, a phenomenon known for centuries, is an effect that is about the production of electrical potential in a substance as the pressure on it changes. For wurtzite structures such as ZnO, GaN, InN and ZnS, due to the polarization of ions in a crystal that has non-central symmetry, a piezoelectric potential is created in the crystal by applying a stress. The effect of piezopotential to the transport behavior of charge carriers is significant due to their multiple functionalities of piezoelectricity, semiconductor and photon excitation. By utilizing the advantages offered by these properties, a few new fields have been created. Electronics fabricated by using inner-crystal piezopotential as a “gate” voltage to tune/control the charge transport behavior is named piezotronics, with applications in strain/force/pressure triggered/controlled electronic devices, sensors and logic units. This effect was also extended to 2D materials such as MoS₂. The objective of this talk is to introduce the fundamentals of piezotronics and their application for robotics and human-machine interfacing.


References:

Metallic Nanowires—Fabrication, Microstructure and Properties
Wenting Huang and Gunther Richter; Max Planck Institute Intelligent Systems, Stuttgart, Germany.

Building nanodevices for applications leads to a myriad of challenges on materials and assembly level. Still nanosized objects have the prospect to be building blocks for future complex smart, autonomous or intelligent systems. A challenge for bringing macroscopic building designs and concepts into the nanoworld, that decreasing dimensions lead to changing physical properties and behaviors. Especially systems below 100 nm and above the size of single molecules exhibit peculiar properties. Surfaces, interfaces, grain boundaries, dislocations that influence the behavior of macroscopic devices will dominate the performance of those below 1 μm. Therefore, to stay relevant and open new research areas by breaking through old limits, the interlinkage of microstructure, fabrication and capacity of devices have to be newly addressed in the same length scale.

We present the fabrication of metallic nanowire structures by physical vapor deposition and will briefly discuss the influences of diffusion on the microstructure formation. Examples from 2D-thin film, island, perlocated structures and one-dimensional nanowires will act as illustration.

The changing physical properties, mechanical, electrical and magnetic, are demonstrated by investigations of metallic nanowires. Due to the absence of internal defects, such as dislocations or grain boundaries, tensile strengths close to the predicted theoretical strength are observed. Cu exhibits a tensile strength of ~6 GPa, Au of ~1 GPa. The deformation is created by partial dislocation nucleation and propagation and consequently by twin formation. Since no defects act as scattering center, the conductivity does not increase with decreasing diameter of the nanowires, but remains close to the perfect bulk values. No size effect is observed but a constant conductivity. The magnetic domain structure was studied by electron holography. Only one single domain is present in ferromagnetic metallic nanowires.

In conclusion we show how microstructural tailoring leads to changing physical properties and therefore to improved performances in nanosystems. In the
long term, this might open the path to new research avenues and reintroduce seemingly old materials systems in novel design concept for nanodevices.

9:45 AM GI02.09.06
Dynamically Tunable Dry Adhesion via Sub-Surface Stiffness Modulation Milad Tatarí1, Amir Mohammadi Nasab1, Kevin T. Turner2 and Wanliang Shan1; 1University of Nevada Reno, Reno, Nevada, United States; 2University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Tunable dry adhesion has a range of applications, including transfer printing, climbing robots, and gripping in automated manufacturing processes. Here, a novel concept to achieve dynamically tunable dry adhesion via modulation of the stiffness of sub-surface mechanical elements is introduced and demonstrated. A composite post structure, consisting of an elastomer shell and a core with a stiffness that can be tuned via application of electrical voltage, was fabricated. In the non-activated state, the core is stiff and the effective adhesion strength between the composite post and contact surface is high. Activation of the core via application of electrical voltage reduces the stiffness of the core, resulting in a change in the stress distribution and driving force for delamination at the interface and a reduction in the effective adhesion strength. The adhesion of composite posts with a range of dimensions were characterized and activation of the core was shown to reduce the adhesion by as much as a factor of six. The experimentally observed reduction in adhesion is primarily due to the change in stiffness of the core. However, the activation of the core also results in heating of the interface and this plays a secondary role in the adhesion change.

10:00 AM BREAK

SESSION GI02.10: Small Robots I
Session Chair: Bradley Nelson
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 111

10:30 AM *GI02.10.01
Shape-Programmable Magnetic Soft-Bodied Millirobots Metin Sitti; Max Planck Institute for Intelligent Systems, Stuttgart, Germany.

Soft functional active materials could enable physical intelligence for small-scale (from a few millimeters down to a few micrometers overall size) devices and robots by providing them unique capabilities, such as shape changing and programming, physical adaptation, and multi-functional and drastically diverse dynamics. In this talk, our recent activities on design, manufacturing, and control of new shape-programmable active soft matter and untethered soft robots at the milli/micronscale are reported. First, a computational design and fabrication method is introduced to create 2D shape-programmable magnetic soft elastomers that can generate desired large shapes using a programmed non-homogeneous magnetization profile and uniform magnetic field control input. Such magnetic shape change/actuation can happen very fast and wirelessly, which are significant advantages. Next, using such methodology, a grand challenge in small-scale mobile robotics is addressed: how to navigate mobile robots in complex environments with multiple terrains (e.g., on solid surfaces, inside fluids, at the fluid-air interfaces) using multiple locomotion modalities like animals in nature? Using programmed dynamic deformations of the robot’s soft elastomeric body and body torques, such soft-bodied robot is demonstrated to be able to have seven locomotion modalities (undulatory swimming, jellyfish-like swimming, water meniscus climbing, jumping, ground walking, rolling, and crawling inside constrained environments) to be able to navigate on complex environments, such as inside the human body. Moreover, dynamic shape control is used to actively transport and deliver cargos integrated to the robot’s body. Preliminary ultrasound-guided navigation of such soft robots is presented inside an ex vivo chicken tissue towards their medical applications to deliver drugs and genes locally and heat the local tissues for hyperthermia and cauterization.

11:00 AM GI02.10.02
Multimodal Control of Magnetic Millibot for Programmable Collective Rotation Hajun Lee, Jeeyoon Yi, Hyeonseo Song, Junkyu Choe and Jiyun Kim; Mechanical Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Creating individual and collective motions in material based distributed systems, e.g. active matter and self-assembling particles, pose challenges in the design of both physical components and control algorithms that can operate at desired scales. Among them, meso-scale floating magnetic components rotating at liquid-air or liquid-liquid interface have been widely engineered to create patterns balancing magnetic rotation and corresponding hydrodynamic interactions, attributing their potentials to remote actuation and easy fabrication. Most of those systems, however, are only composed of identical components, lowering the diversity and the complexity in programming their spatiotemporal collective behaviors. Here, we develop millimeter-scale polymer based magnetic structures, named as ‘millibot’, and map their multi-modal rotational behaviors in a chosen magnetic field intensity and frequency range. Millibots have identical rectangular shapes but diverse magnetic properties, making them have different map in their rotational behaviors. Using these actuation maps, we are able to selectively control the collective rotation of heterogeneous millibot groups or subgroups in a programmable manner.

To achieve this, we developed three types of millibots with different magnetic properties; a millibot can have the magnetic anisotropy with self-assembled magnetic chains, randomly dispersed magnetic particles, or the mixture of ferromagnetic and superparamagnetic particles. To embed magnetic properties in the millibots, magnetic particles were dispersed in the photocurable polymer, PEGDA diluted with DI water, and shaped via photopolymerization. 2-axis magnetic field generator, whose magnetic field ranges in intensity from 100 to 800 Oe and in frequency from 0 to 4 Hz, was used to drive the rotations in millibots and consequently, we mapped the multimodal rotations of each type of millibot.

We observed shift, shrinkage or expansion of individual rotation mode ranges according to the type of millibots. This allows us to choose and program the collective rotation of entire millibot group or chosen sub-group. To show this capability, we demonstrated that four different millibots exhibiting different rotational behaviors under the certain condition were switched their behavior to identical collective rotation in another condition. Also, fifteen millibots which is composed of three sub-groups were controlled to show diverse collective rotations of sub-groups.

As a result, embedding diverse material properties in the physical components of distributed systems provide an advanced way of designing and controlling the collective behaviors of heterogeneous distributed system in a programmable manner. We expect that this approach will enhance the behavioral capability of meso-scale particle collectives for diverse applications including programmable matter, robotics, bio-medical systems and so on.

11:15 AM GI02.10.03
X-Ray Driven Microswimmers Zhaoyi Xu and Ji Tae Kim; Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong.

Light-powered manipulation of small objects in fluids significantly affects fields as diverse as drug/cell delivery, microsurgery, environmental remediation,
and self-assembly/nanofabrication. Although many clever techniques based on UV-visible-NIR light have been devised, new methods that can have sufficient penetrating power into biological bodies are still in great demand. Since discovered by Röntgen, X-rays have long been regarded as the most celebrated light-source for non-invasive, whole-body medical imaging because of its outstanding penetration.

Here, we observed that X-rays can drive propulsive motion of a half-metal coated Janus microparticle in aqueous environment. Using a full-field transmission X-ray microscope (TXM) with synchrotron hard X-rays, we simultaneously triggered and visualized the propulsive motion at single-particle level. Our real-time observation at nanoscale revealed that the motion follows bubble growth induced by radiolysis of water at the metal/water interface under X-ray irradiation. This study opens a potential to operate micro/nanorobots under whole-body medical imaging. In this talk, we will present our results and discuss the prospects of our work for potential applications in medicine.

11:30 AM GI02.10.04
Visible-Light-Gated Reconfigurable Rotary Actuation of Electric Nanomotors Zexi Liang1 and Donglei (Emma) Fan2, 3; 1Materials Science and Engineering, The University of Texas at Austin, Austin, Texas, United States; 2Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Highly efficient and widely applicable working mechanisms that allow nanomaterials and devices to respond to external stimuli with controlled mechanical motions could make far-reaching impact to reconfigurable, adaptive, and robotic nanodevices. Here, we report an innovative mechanism that allows multifold reconfiguration of mechanical rotation of semiconductor nanoentities in electric (E) fields by visible light stimulation. When illuminated by light in the visible to infrared range, the rotation speed of semiconductor Si nanowires in electric fields can instantly increase, decrease, and even reverse the orientation depending on the intensity of the applied light and the AC E-field frequency. This multifold rotation configuration is highly efficient, instant, and facile. Switching between different modes can be simply controlled by the light intensity at an AC frequency. Experimentations, theoretical analysis, and simulations are carried out to understand the underlying principle, which can be attributed to the optically tunable polarization of Si nanowires in aqueous suspension and an external electric field. Finally, leveraging this newly discovered effect, we successfully differentiate semiconductor and metallic nanoentities in a non-contact and non-destructive manner. This research could inspire a new class of reconfigurable nanoelectromechanical and nanorobotic devices for optical sensing, communication, molecule release, detection, nanoparticle separation, and microfluidic automation.

11:45 AM GI02.10.05
Materials for Actuation and Testing of Miniaturized Robots Fengjin Chai1, Fabian Adams2, Kai Melde1, Stefano Palagi1, Tian Qiu1 and Peer Fischer1, 3; 1Max Planck Institute for Intelligent Systems, Stuttgart, Germany; 2Department of Urology, University Medical Center Freiburg, Freiburg, Germany; 3Institute for Physical Chemistry, University of Stuttgart, Stuttgart, Germany.

Miniaturization is critical for many robotic devices, especially in the field of medical robotics. Numerous small-scale robots have been developed for potential medical applications, such as targeted drug delivery[1], minimally invasive surgery[2], measurement of biological fluids[3], and endoscopic imaging[4]. An essential component of these robots are the miniaturized actuators, which need to be small in size, powerful in the actuation force, safe for the interaction with biological tissues, and ideally untethered for more dexterity of the robots. Traditional electronics based systems are often stiff and if multiple wires are used, they are too bulky for instance for minimally invasive applications. The development of new materials is essential to enable new compact actuators and to simplify robot design.

Here, we present a surface actuator – essentially a thin film – that needs no electrical or light input and that is based on functional material interfaces. The interface consists a two-dimensional array of micro-bubbles that can be resonantly excited by ultrasound. The microfabricated thin film causes strong acoustic streaming, when it is wirelessly excited by the low-frequency ultrasound[5]. This smart surface permits unique addressability and thus enables many degree of freedom actuation of multiple actuators. Although the surface actuator is only hundreds-of-micron in thickness, it is powerful enough to remotely actuate a centimeter-scale robot in water and a miniaturized endoscope for urinary tract video-imaging.

In order to test miniaturized devices, such as our ultrasound-activated acoustic streaming devices and to evaluate their performances, we also developed compact actuators and to simplify robot design.

Here, we observed that X-rays can drive propulsive motion of a half-metal coated Janus microparticle in aqueous environment. Using a full-field transmission X-ray microscope (TXM) with synchrotron hard X-rays, we simultaneously triggered and visualized the propulsive motion at single-particle level. Our real-time observation at nanoscale revealed that the motion follows bubble growth induced by radiolysis of water at the metal/water interface under X-ray irradiation. This study opens a potential to operate micro/nanorobots under whole-body medical imaging. In this talk, we will present our results and discuss the prospects of our work for potential applications in medicine.

References

1:30 PM *GI02.11.01
Magnetic Colloidal Microswarm for Targeted Delivery Jiangfan Yu1 and Li Zhang1, 2, 3; 1Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong, China; 2Chow Yuk Ho Technology Centre for Innovative Medicine, The Chinese University of Hong Kong, Hong Kong, China; 3CUHK T-Stone Robotics Institute, The Chinese University of Hong Kong, Hong Kong, China.

In nature, various types of swarm behaviors occur, such as a flock of birds and a swarm of ants, which stem from local communications of limited individuals. Through collective pattern formation and reconfiguration, these animals dramatically change their swarming patterns according to the
environment they interact with. To date, some large-scale robotic systems can well mimic the complex swarm behaviors of natural creatures through algorithm design and wireless communication [1]. However, due to the absence of onboard processors, sensors and actuators, to create a robotic system with functional swarm behaviors at the small scales remains challenging. Herein, we report paramagnetic nanoparticles as building blocks to investigate collective behavior of microbotic swarm in fluid.

Recently, we found a novel method to disassemble paramagnetic nanoparticle chains using a programmed dynamic magnetic field [2]. Thousands or even millions of colloidal agents can be disassembled and spread simultaneously due to hydrodynamic drags and magnetic dipole-dipole repulsive interactions, respectively. As the reversed process, we also presented that the spread colloids can be assembled into vortex-like paramagnetic nanoparticle swarms (VPNS) using a rotating magnetic field [3]. The VPNS exhibits a dynamic-equilibrium structure, in which the nanoparticles perform synchronized motions. Moreover, by tuning the applied magnetic fields, the VPNS was capable of performing multimodal pattern reconfiguration, and we also investigated the reversible merging and splitting of the vortex-like swarms/sub-swarm. We demonstrated that the VPNS is able to pass through curved and branched fluidic channels with high swimming velocity, positioning precision and access rates (over 90%) to a target. Localized energy delivery with tunable and enhanced hyperthermia heating effect was demonstrated as well [4]. In addition, we have discovered a new strategy to reconfigure the paramagnetic nanoparticles into ribbon-like microswarms, which are capable of performing reversible elongation with an extremely high aspect ratio of the dynamic pattern. Our work thus sheds light on the fundamental understanding and control of magnetic micromorbotic swarms.

References

2:00 PM *GI02.11.02
Designing Self-Powered Nano and Microbots Ayusman Sen; The Pennsylvania State University, University Park, Pennsylvania, United States.

Self-powered nano and microscale moving systems are currently the subject of intense interest due in part to their potential applications in nanomachinery, nanoscale assembly, robotics, fluids, and chemical/biochemical sensing. One of the more interesting recent discoveries has been the ability to design nano/microparticles, including molecules, which catalytically harness the chemical energy in their environment to move autonomously. These "bots" can be directed by chemical and light gradients. Further, our group has developed systems in which chemical secretions from the translating micro/nanomotors initiate long-range, collective interactions among the particles. This behavior is reminiscent of quorum sensing organisms that swarm in response to a minimum threshold concentration of a signaling chemical. In addition, an object that moves by generating a continuous surface force in a fluid can, in principle, be used to pump the fluid by the same catalytic mechanism. Thus, by immobilizing the nano/micromotors, we have developed nano/microfluidic pumps that transduce energy catalytically. These non-mechanical pumps provide precise control over flow rate without the aid of an external power source and are capable of turning on in response to specific analytes in solution. In addition, the catalytic pumps can be harnessed for directional delivery of microparticles in specific locations in space.

2:30 PM *GI02.11.03
Ingestible Self-Propelled Microrobots—Toward In Vivo Use Wei Gao; Engineering and Applied Science, California Institute of Technology, Pasadena, California, United States.

While synthetic micromotors have been evaluated extensively under in vitro conditions for over a decade, their in vivo function has rarely been explored. Zn and Mg based micromotors, powered by body fluids, have shown unique advantages to operate at different regions of the gastrointestinal tract. In this talk, I will highlight several examples of recent in vivo investigations based on these biocompatible and biodegradable biofluids powered microrobots, including precise micromotor tissue localization and retention, in vivo imaging, and enhanced drug delivery. I will also cover some early in vitro studies that paved the way for the current in vivo applications. These works open the door to a number of in vivo and clinical applications of these synthetic motors.

3:00 PM BREAK

4:00 PM GI02.11.04
Engineering Hybrid Machines—From Nanobots to 3D BioBots Samuel Sanchez; Smart Nano Bio Devices, Institute for Bioengineering of Catalonia/ICREA, Barcelona, Spain.

The combination of biological components and artificial ones emerges into what we called hybrid machines or robots. Hybrid nano-bots have the ability to convert bio-available fuels to generate propulsion force to swim. They may be eventually used in vivo for transporting drugs to target locations in a controlled manner. Additionally, their active propulsion and multifunctionality of the different components of the nanorarchitecture makes them useful in sensing and cleaning water where they swim. However, before that, fundamental understanding on motion mechanism, materials considerations, in vitro assessment of drug delivery, toxicity, and their shape and size dependence on those parameters is needed. Hybrid nano- and micro-robots combine nanomaterials with enzymes and with motile cells efficient delivery, sensing, imaging and biofilm penetration. On a larger scale, we use 3D bioprinting techniques to fabricate cm-scaled hybrid BioRobots based on the combination of hydrogels and cells that contract in synchrony upon external stimuli, and exercise training, alike artificial muscles.

4:15 PM GI02.11.05
Molecular Direct-Driven Untethered Macro Soft Robots in Liquid—Design, Maneuver and Application Demonstration Zhigang Wu, Liangxiong L, Fen Li, Pan Deng and Kang Wu; Huazhong University of Science & Technology, Wuhan, China.

By extracting the kinetic energy in the molecular cooperation of an active material and its ambient liquid environment, this work reports a new strategy to design and maneuver untethered soft robots in liquid. This strategy gets rid of those tethered pipes/wires which are commonly used for energy transport in current soft robots, without robot design re-designing or changing body materials for the introducing new active materials. Using this newly developed strategy, we demonstrate a world first, molecular directly driven, macro soft robot in a liquid, and a soft robot swarm. This approach may provide a new possibility to design, fabricate and control autonomous robotics in liquid.

Untethered soft robotics inspired from nature with new design, fabrication and control strategies have been totally changing our cognition of robotics.
However, the characteristics of power source forms cannot break through the inherently limitation of thermal/mechanical performance of soft materials. Here, we presented a novel approach through contacting kinds of molecules such as amphiphilic ones with liquids. During the process, the introduced molecules interact with the ambient liquid and lead to a non-equilibrium state, resulting in a higher energy state of Gibbs free energy. Consequently, this energy gap results in a collective molecular movement that can be observed in macro scale due to molecular re-organization in micro scale e.g., oil drops spreading on water. When the molecules of such material leave their initial attached surface on the robot during their molecular re-organization process, a well-directed opposite impulse to their initial attached surface is generated according to the principle of momentum conservation. The movement of soft robots depends on the kinetic energy through a molecular interaction with the external environment without any high energized process or tethered pipes. Further, by deploying materials spatially on the attached robots, the trajectory control can be obtained such as straight going and turning in liquid for single robots. To imitate maneuvering such a robot in practical scenarios, a back dyed robot passed through precisely a toy rockery tunnel following the designed path with an optical detector, and triggered the lighting color change of an LED indicator. Without introducing any mechanical movement components, our approach has a near zero-noise level during the running process. Furthermore, by carefully aligning 32 robots towards a burning flame on an open water surface, we demonstrated a robot swarm that can be highly-centered to the same spot simultaneously to assure a hit on the given target as accurately as possible (here to extinguish the flame).

4:30 PM GI02.11.06
Mechanical Acceleration of DNA Capture and Detection by Robotizing Bio-Photonic-Plasmonic Microsensors Jianhe Guo1 and Donglei (Emma) Fan1, 2; 1Materials Science and Engineering, The University of Texas at Austin, Austin, Texas, United States; 2Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Efficient capture of deoxyribonucleic acid (DNA) on solid surfaces has received immense research interest for various biotechniques, including DNA extraction, preconcentration, detection, and separation. This work reports an original mechanism to actively accelerate the DNA capture process and significantly reduce the detection time by mechanically rotating bio-photonic-plasmonic hybrid microsensors. The photon-plasmonic microsensors consist of diatom frustules with surface-coated magnetic thin films and uniformly distributed plasmonic silver (Ag) nanoparticles. The diatom frustules are made of silica with ordered arrays of nanopores offering large surface-to-volume ratio and synergistic-plasmonic resonance for the capture and detection of DNA with surface enhanced Raman spectroscopy (SERS). By manipulating with magnetic tweezers, the photon-plasmonic microsensors transport and self-assemble in microwells and microfluidic channels, and rotate with tunable speeds for the capture and detection of DNA molecules. Experiments show the capturing rate of DNA can be significantly enhanced by at least 4 times by controlling the rotation speed of the microsensor to 1200 rpm. At a concentration as low as 80 nM/ml, Raman signals of DNA is obtained 3-time faster than those without rotation. The fundamental mechanism is investigated and attributed to the fluidic boundary layer effect, where the Nernst diffusion layer on the surface of the robotized microsensors is monotonically reduced with flow speed.

4:45 PM GI02.11.07
Micromotor-Enabled Active Drug Delivery to Treat Gastrointestinal Diseases Jinxing Li, Pavimol Angsantikul, Berta Esteban, Liangfang Zhang, Joseph Wang and Fernando Soto Alvarez; NanoEngineering, University of California, San Diego, La Jolla, California, United States.

Advances in bioinspired design principles and nanomaterials have led to tremendous progress in autonomously moving synthetic nano/micromotors with diverse functionalities in different environments. However, a significant gap remains in moving nano/micromotors from test tubes to living organisms for treating diseases with high efficacy. Here we present the first, to our knowledge, in vivo therapeutic micromotors application for active drug delivery to treat gastric bacterial infection in a mouse model using clarithromycin as a model antibiotic and Helicobacter pylori infection as a model disease. The propulsion of drug-loaded magnesium micromotors in gastric media enables effective antibiotic delivery, leading to significant bacteria burden reduction in the mouse stomach compared with passive drug carriers, with no apparent toxicity. Moreover, while the drug-loaded micromotors reach similar therapeutic efficacy as the positive control of free drug plus proton pump inhibitor, the micromotors can function without proton pump inhibitors because of their built-in proton depletion function associated with their locomotion.

SYMPOSIUM GI03

Synthetic Biology—An Accelerator of Materials Research and Development
November 26 - November 27, 2018

Symposium Organizers
Wendy Crookes-Goodson, Air Force Research Laboratory
Michael Jewett, Northwestern University
Petra Oyston, Porton Down
Melissa Rhoads, Lockheed Martin

Symposium Support
Materials Today Bio | Elsevier

* Invited Paper
8:30 AM WELCOME AND INTRODUCTION BY MELLISA RHoads, LOCKHEED MARTIN SPACE SYSTEMS

9:00 AM *GI03.01.02

Centralized facilities for genetic engineering, or “biofoundries”, offer the potential to design organisms to address emerging needs in medicine, agriculture, industry, and defense. To date, by applying a diversity of new approaches, we have produced the desired molecule or material that has been asked by clients from the pharmaceutical and biotech industries as well as from the DOD. Specifically, we increased the titers of 1-hexadecanol, pyrrolnitrin, pacidamycin D, and clavulanic acid, found novel routes to the enediyne warhead underlying powerful antimicrobials, established a cell-free system for monoterpene production, and produced an intermediate toward vincristine biosynthesis. Furthermore, we have produced small-molecules of linalool and phloroglucinol that, respectively, serve as precursors to JP-10 that fuels missiles and TATB that detonates the warheads. For materials production, we have encoded 7802 individually retrievable pathways to 540 bisindoles in a DNA pool, and created 61 biosynthetic capsaicin variants that could be central to high-performance polymers. In sum, we constructed several megabases of DNA, built hundreds of strains spanning six species (Saccharomyces cerevisiae, Escherichia coli, Streptomyces albidoflavus, Streptomyces coelicolor, Streptomyces clavuligerus and Streptomyces albovinaceus), established two cell-free systems, and performed nearly a thousand assays developed in-house for the molecules.

9:30 AM GI03.01.03
Synthetic Biology for Protein-Based Materials [4]. Fuzhong Zhang; Energy, Environmental & Chemical Engineering, Washington University, Saint Louis, Missouri, United States.

Advances in synthetic biology have enabled the quantitative engineering of dynamic biological processes for the precise control of cellular reaction networks, allowing engineered cells to perform complex tasks and to produce various small molecules, which can be used as biofuel replacements, polymer precursors, nutraceuticals, and pharmaceuticals. Compared to small molecules, the production of macromolecular biomaterials by synthetic biology approaches is strongly lagging. Nature has evolved various types of protein materials with remarkable mechanical properties and functions. To facilitate the practical use of these materials, we aim to engineer bacterial cell factories to overproduce high-performance protein-based materials, such as spider silks. We have developed synthetic biology strategies that allow us to synthesize ultra-high molecular weight spider silks (556 kDa) at gram per liter scales. Fibers spun from our microbiologically produced silk fully replicate the mechanical performance of natural spider silk by all common metrics, i.e. tensile strength (1.03 ± 0.11 GPa), modulus (13.7 ± 3.0 GPa), extensibility (18 ± 6%), and toughness (114 ± 51 MJ/m3). The developed strategy reveals a path to more dependable production of high-performance silks for mechanically-demanding applications while also providing a platform to facilitate production of other high-performance natural materials.

9:45 AM GI03.01.04
Lipid Droplet Microarrays for High Throughput Screening in Synthetic Biology [5]. Aubrey Kusi-Appiah and Steven Lenhert; Biological Science, Florida State University, Tallahassee, Florida, United States.

A current obstacle in the use of synthetic biology for materials synthesis and discovery is the high throughput characterization of novel materials produced by biological organisms. Furthermore, identifying the environmental conditions that allow biological cells to produce the desired materials is challenging due to the large amount of possible cell culture ingredients and conditions. High throughput screening is currently carried out in the pharmaceutical industry for this purpose, but is cost prohibitive for many materials applications. Miniaturization of high throughput screening promises to lower the cost and allow portable screens suitable for academic use. We have developed a novel screening platform compatible with standard cell culture techniques that is scalable to a screen of 50,000 different materials on the area of a single 96-well plate using cell-based assays.[1] The technology is based on lipid droplet microarrays on surfaces where the droplets encapsulate different compounds or nanomaterials. Development of this technology required solving several technical challenges, including scalable fabrication,[2] quantification of the dosage delivered from the droplets,[3] and most recently chemical processing to ensure stability upon immersion into aqueous solution.[4] The technology is now ready to be applied to high throughput screening in synthetic biology.

References:

10:00 AM BREAK

10:30 AM *GI03.01.05
3D Printing of Engineered Bacteria for the Production of Patterned Living Materials [6]. Anne S. Meyer; University of Rochester, Rochester, New York, United States.

In order to create crisp, defined patterns of biologically-created materials, new technologies need to be developed and implemented. The Meyer lab is developing first-of-their-kind bacterial 3D printers that can deposit engineered bacteria in specific three-dimensional patterns using simple devices and chemistries. Our bacterial 3D printers have fully automated, coordinated control of the pumps and printhead, allowing for high spatial resolution (<mm-scale) printing of bacteria onto wet or dry surfaces. Our printers mix an alginate-containing bacterial culture with a calcium chloride solution upon printing, triggering cross-linking of the alginate matrix to form a stable, biocompatible scaffold to support the bacteria. After printing, the scaffold is removable by dissolving the cross-linked alginate matrix with sodium citrate. We are applying our printer to the fabrication of engineered biofilms, groups of bacteria that live within a spatially structured polymer matrix. We use our 3D printer to deposit engineered E. coli that are able to produce CsgA fibrils, the major protein component of biofilm polymer matrices. These engineered bacteria can stick to the printing surface even after the printing scaffold has been dissolved away, creating free-standing, patterned biofilms. These model biofilms will be crucial for future development of anti-biofilm strategies, for which no reproducible model biofilm test system is currently available, as well as for the reliable production of beneficial living materials, which could be applied
for water and soil purification or mineral extraction.

11:00 AM GI30.01.06
**Bacterial Foundry of the Self-Regenerating and Functional Materials** Anna Duraj-Thatte, Avinash M. Basavanna, Arjirios Sourlis and Neel Joshi; Harvard University, Boston, Massachusetts, United States.

Protein-based materials have been successfully used for several applications in nanotechnology, bioengineering and medicine. Their diverse biofunctions and unique structures make them ideal building blocks to create large scale functional materials. However, there are several challenges: scalable production, isolation, expensive synthesis and processing keep recombinant protein-based materials away from other most commercially successful large-scale living materials such as cellulose or mycelium-based materials.

To tackle this problem, we developed a novel method for the rapid biosynthesis of tailored hydrogels in a single step, directly from bacterial culture, using a protocol that requires no protein purification. The hydrogel scaffold is based on the engineered extracellular matrix protein CsgA, which self-assembles into a fibrous mesh-like network that is 4-7% of hydrogel mass. Most importantly, by genetic engineering of CsgA protein we can modulate a range of rheological properties as well as incorporate any specific functional modules for desired applications. This unique method leaded us to create a novel viscoelastic and shear-thinning 3D printing inks that are entirely biofabricated by genetically engineered bacteria. Due to biofabrication process that we developed, this hydrogel can contain living bacteria capable of producing more living ink or living bacteria can be removed during fabrication. This novel bacterial ink can be used for printing complex large scale materials with specific functions.

11:15 AM GI30.01.07
**3D Printing of Bacteria to Create Living Materials** Patrick A. Rühs; Department of Bioengineering, University of California, Berkeley, Berkeley, California, United States.

Despite recent advances to control the spatial composition and dynamic functionalities of bacteria embedded in materials, bacterial localization into complex 3D geometries remains a major challenge. Here we demonstrate a 3D printing approach to create bacteria-derived functional materials by combining the natural diverse metabolism of bacteria with the shape design freedom of additive manufacturing (1).

For 3D printing we use a recently developed multimaterial direct ink writing technique (2) which allows us to incorporate bacteria in biocompatible inks within the same 3D printed material. Our bioinks are designed by combining different hydrogels to form a paste-like ink, which after printing is crosslinked by low intensity UV light. To obtain accurate 3D printed structures, we determine the ideal rheological properties prior, during and after printing, demonstrating the effect of the printing steps on the bioink. With this approach we are able to obtain a hydrogel which supports bacteria growth while still maintaining a high shape fidelity in 3D printing.

We embedded bacteria in the biocompatible and functionalized 3D printing ink and printed two types of ‘living materials’ capable of degrading pollutants and of producing medically relevant bacterial cellulose. Furthermore, we demonstrate that bacteria proliferation is a function of viscosity and oxygen availability. By fine-tuning the single ink components, we adjust the viscosity to match the growth profile of our cells. With this printing platform, we envision the use of additive manufacturing materials combined together with cells to be used for new and biomedical applications.


11:30 AM GI30.01.08

It is well established that metal-respiring bacteria, such as Geobacter and Shewanella, perform extracellular electron transfer (EET) when grown as biofilms on the surface of electrodes. The electron transport (ET) proteins that enable this microbial electrical wiring in Shewanella have been identified and successfully expressed in *E. coli*, conferring an increase in the amount of current produced over the wild type background. The ability to rationally engineer EET processes in electrochemically active biofilms could result in leap-ahead technological advancements in biomaterials applications including microbial electrosynthesis, bioremediation, and microbial bioelectronics, specifically under austere conditions, such as the ocean. However, these applications are currently limited by a lack of understanding of the physiological constraints of the host bacterium (chassis) to properly and predictably express and orient ET proteins (e.g. c-type cytochromes) in the cell membrane, the ability to rapidly screen a large number of constructs for different ET pathways, and a library of operationally relevant chassis strains. In this talk I will describe results demonstrating the use of a suite of highly-optimized small molecule sensors (Marionette) developed for control over *E. coli* cellular processes to control expression of the *Shewanella* MtrCAB pathway, and accessory electron carriers, in *Marinobacter atlanticus*. First, Marionette sensors were transformed into *M. atlanticus* and assessed for expression of yellow fluorescent protein (YFP) after the addition of 7 different small molecules (choline, vanillin, naringenin, DAPG, cumate, tetracycline, and IPTG) during both planktonic growth and in the biofilm state. For most sensors, a broad dynamic range was observed similar to that demonstrated with *E. coli* when fluorescence was measured during log phase growth. Increasing fluorescence was also observed over time in biofilm associated cells as long as growth medium with small molecule inducer was continuously refreshed. When YFP was replaced with ET proteins, expression of MtrCAB led to an increase in current compared to the wild type strain when induced prior to inoculation into a bioelectrochemical system (BES). However, the effect was not robust enough for biosensing. Moving the MtrCAB pathway from a plasmid construct to the chromosome enabled more control over the quantity of protein expressed, however, no improvement in current was observed. When the same construct was tested in *Shewanella oninesenesis* MR1 lacking the native MtrCAB pathway, current was found to be inducible following biofilm formation. Based on these results, we conclude that although the MtrCAB pathway can be successfully expressed in *M. atlanticus*, further optimization of export of these proteins to the outer membrane and/or connection to the inner membrane electron pool may be necessary. Understanding these constraints will advance the development of engineered bio-electrochemically active biofilms for development of self-healing living materials for energy and next generation electronics for the marine environment.

SESSION GI03.02: Synthetic Biology—Aerospace Applications, Metals and Composites

Session Chairs: Anne Meyer and Petra Oyston
The DOD currently faces a broad range of materials challenges. The changing geopolitical environment has created a need for agile supply chains of critical materials and components. The push for miniaturization and light-weighting has created a need for precise and scalable assembly of materials with limited defects. Additionally, the diverse and challenging operational environments faced by the warfighter has created a need for multifunctional materials that can sense and respond to the human and the surrounding environment. Strategic utilization of synthetic biology has the potential to provide new materials capabilities that can address many of these critical challenges. This talk will highlight work being done in synthetic biology at the Air Force Research Laboratory, Materials and Manufacturing Directorate to enable new solutions to these challenges. Specifically, new strategies and pipelines for the discovery and engineering of novel enzymes and proteins that can be used in the production of critical material components will be discussed.

Microorganisms have the potential to manufacture metallic nanoparticles, irrespective of the source of metal cations, and provide us with new particles with novel functions. To exploit this we are identifying and optimising genetic elements with an aim to increase nanoparticle production and control nanoparticle size and homogeneity; in effect standardising nanoparticle samples by using biology. Whilst developing this process we are exploring its application in the treatment of contaminated waste, water and land. For the former application we are working to remove copper from whisky distillery by-products and for the latter application we are part of a larger collaboration aiming to financially incentivise land decontamination. After using phytoremediation to hyperaccumulate metal contaminants from the soil, plants are harvested, processed and used as a source of metals for bacterial nanoparticle synthesis. Both applications illustrate how synthetic biology might contribute to moving us towards a more sustainable circular economy.

Structural materials synthesized by organisms, such as bones, shells, and wood, exhibit remarkable mechanical properties due to their hierarchical assembly of hard and soft components across the nanometer to the micron scales. While engineering analogs to these materials would open new frontiers, there is currently no route to mimic the 2D hierarchical ordering of natural composites. Here we lay the foundations for bottom-up assembly of engineered living-material composites along the cell body using a synthetic biology approach and demonstrate the hierarchical assembly of these composites confers switchable mechanical properties. We engineer the surface-layer (S-layer) of Caulobacter crescentus to display peptides that permit covalent attachment of proteins, nanocrystals, and protein-based polymers to the extracellular surface without additional engineering. This cell surface binding is uniform, specific, and covalent, and its density can be controlled based on the location of the insertion within the S-layer. Using this platform, we construct composite materials composed of living C. crescentus cells crosslinked by nanocrystals. These ‘hybrid bacterial spheroids’ are 30 times more stiff than cell-nanocrystal composites lacking these crosslinks. Additionally, the stiffness of these composites can be changed dynamically by breaking the cell-nanocrystal crosslinking. Taken together, this work provides a platform for creating hierarchically-assembled living materials with switchable mechanical properties.
This talk will describe an approach for using mass spectrometry and arrays of self-assembled monolayers to perform quantitative experiments in high throughput. The arrays are prepared by individually immobilizing small molecules, proteins, peptides and carbohydrates to self-assembled monolayers of alkanethiolates on gold. This approach allows us to treat the same set of alkanethiolates in the same way in order to remove biological variability. This is particularly useful for screening the activity of enzymes and other molecular modulators. These examples illustrate the broad capability of the SAMDI method to accelerate the design-build-test cycle for materials.

Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. We have begun utilizing the incorporated nCA to functionalize suckerin-protein nanoparticles with tuneable diameters between tens to hundreds of nanometers. Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’ Suckerins are a class of structural proteins that form sucker ring teeth assemblies that display robust mechanical properties and thermoplastic behavior. Using this foundation, we have begun studying a promising target for engineering protein-based materials, sourced from the giant squid, called ‘suckerins.’
TUTORIAL: Life Cycle Analysis from an Industrial Perspective
November 25 - November 25, 2018

* Invited Paper

TUTORIAL
Life Cycle Analysis from an Industrial Perspective
Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 200

Environmental issues keep steadily increasing, thus there is a strong urge to discuss how materials scientists could more rapidly respond to the worldwide concerns. This joint tutorial effort would be organized by the three symposia together. To ensure the success of such synergistic efforts it is also urged a close dialogue with society so to establish guidelines for policymakers, thus this tutorial will incorporate both the societal and the engineering aspects of life cycle analysis (LCA) would be covered. The main objective of this tutorial is to explore communications pathways between companies and materials researchers that further elevate the profile and challenges of sustainability that represents a societal necessity and a viable and critical topic for research.

1:30 PM
Societal Aspect of LCA Jean-Pierre Birat; ArcelorMittal

Materials are not simply the product of an engineering discipline, Materials Science, but also "social constructs" that have entertained a close relationship with society all through the historical timeline and remain a core element of our modern world, what is called a Key Enabling Technology. How this can be analyzed by parallel approaches of hard and soft sciences will be explained in the class as well as the trystic of economic, environmental and social values of materials. Examples reported in the 13 past SAM conferences will be used as examples.

2:45 PM BREAK

3:15 PM
Engineering Aspect of LCA Alan Rae; IncubatorWorks

The instructor will provide an overview on all the aspects considered in a life cycle analysis aimed to the engineering design of an industrial process. A part of the tutorial will involve the interaction with the audience in order to apply some of the concepts described in the first part of the tutorials to common objects.

4:15 PM Sustainability Challenge

The symposia organizers will divide the participants into groups and a sustainability challenge will integrate the concepts presented by the instructors so to review and facilitate networking among participants and instructors

4:45 PM
Final Remarks

SYMPOSIUM BI01

Sustainable Development in Materials Science and Related Societal Aspects
November 26 - November 28, 2018
Thus we have to examine the conditions in which an outcome could be built linking these two issues. This implies to combine two ways of reasoning: the "properties" and "validity" ones which are self-referential and cannot immediately match or even fit.

Society representations, namely associations, are supposed to understand what should be understood. But benefits (or risks) of nanos could be differently assessed, according to professional experts or the difficulty) of defining what a benefit is. In a classical benefits/risks approach, benefits are often considered in a very technical way: professional experts generally supposed. In a perspective, notably in France, framed by "the imperative of precaution", researches on nanos are confronted to the necessity (and the difficulty) of defining what a benefit is. In a classical benefits/risks approach, benefits are often considered in a very technical way: professional experts are supposed to understand what should be understood. But benefits (or risks) of nanos could be differently assessed, according to professional experts or citizens points of views.

In particular, the benefits of a nanotechnology cannot be assessed only in accordance to its technical properties because properties are only part of the problem. As we can learn from the thematization process of risks, any innovation must be submitted to a validity test, which supposes taking into account social norms, notably that, progressively shaped by public debates, relating to the environment and health topics. Based on a social sciences research dealing with a medical nanotechnology and supported by the French CNRS and the Occitanie Region, we will show that a reasoned development of nanotechnologies must rely on, and combine two criteria: technical efficacy and some kind of legitimation by civil society representations, namely associations.

This implies to combine two ways of reasoning: the "properties" and "validity" ones which are self-referential and cannot immediately match or even fit.

Thus we have to examine the conditions in which an outcome could be built linking these two issues.
The Implementation and Role of Automation and Materials Acceleration Platforms (MAPs) in Material Science Jamie Thompson1,2, Gregory Whiting1 and Camille Petri1; 1NASA Ames Research Ctr, Mountain View, California, United States; 2Materials, Imperial College London, London, United Kingdom.

In the age of automation and cloud computing, scientific research has a huge opportunity to reassess its evolved methodology and reinforce some of its core values. Through the implementation of simplistic hardware, data acquisition systems, cloud-based data storage and non-traditional data analysis methods, a mostly automated scientific system is well within reach of most research laboratories. Aside from the obvious advantages of not having to manually operate an experimental apparatus, as well as increasing potential human error in the collected data, there are several key advantages to automating many day-to-day lab tasks. Topics around these concepts are discussed, and preliminary prototype systems for large-scale lab automation and collaboration are presented.

Using a materials laboratory as a testbed and assessing the processes by which we interact with our experiments, the modern scientific process is studied and critiqued. The question of where innovations during the experimental process occur is asked in order to more accurately predict what the role of humans in a rapidly accelerated form of science will be in the near and distant future.

9:45 AM BI01.01.04
A Bright Tomorrow—Design: STEM Teaching and Learning Through the Integration of Design, Material Science and Synthetic Biology Raymond Oliver; Northumbria University, Newcastle upon Tyne, United Kingdom.

Fashion and creative design are a window on how we have and how we will live. By 2099, we will understand how to design and fabricate materials at the molecular and biomolecular level. In between, the development of 3 and 4D bio-nano hybrid materials with functionalities similar or superior to Silicon will allow the evolution of ‘soft’ machines and programmable surfaces and interfaces with intelligence through associated informatics, VR, AR and AI providing tangible materials 2 materiality 2 material experiences. Putting these together, you create a powerful Design:STEM Interactive platform that can significantly influence and enhance both the fabrication and function of novel products and devices that can significantly effect everyone's Future Ways of Living.

The work described in this paper examines some of the ways in which creative design can guide and interact with materials science and material fabrication leading towards programmable material systems through integrated informatics that leads to innovation in ‘calm technology’ that is burdenless for the user. We will present evidence based examples drawn from our ongoing work as follows:

a) Ambient assisted living for both individuals and communities
b) Sensors, sensing and sentient behaviour for anticipatory healthcare and real time monitoring
c) The development of responsive surfaces and interfaces that serve as real time polyvalent interactive skins for ‘smart’ interior environments
d) Sustainable consumer product packaging through the replacement of synthetic polymers with polysaccharide based natural materials

In addition, we will provide Design:STEM insights from our work on the current research and teaching landscape within the School of Design at Northumbria. Finally, the three axes of Design, Materials and Biology are shown to be a very powerful way to address and collaborate with industry to solve identified compelling human centric needs that can significantly benefit everyday life through direct, multidisciplinary Studio, Lab and workplace learning.

Within the School of Design at Northumbria University, we are implementing new MRes masters courses that bring creative designers, material scientists and synthatic biologists together in a common research and teaching environment to accelerate teaching and making practice to address Design led, Needs driven, Materials anchored and solutions focussed Design:STEM Integration.

10:00 AM BREAK

10:30 AM *BI01.01.05
Research, Teaching and Outreach as Examples of Helping to Go Towards a More Sustainable Future Ivana Aguiar1, Maria E. Perez Barthaburu2, Mauricio Rodríguez Chialanza3 and Laura Fornaro2; 1Grupo de Desarrollo de Materiales y Estudios Ambientales, Área Radioquímica, Facultad de Química, Universidad de la República, Montevideo, Uruguay; 2Grupo de Desarrollo de Materiales y Estudios Ambientales, Departamento de Desarrollo Tecnológico, Centro Universitario Regional del Este, Universidad de la República, Rocha, Uruguay.

We are a research group devoted to materials science research since 2000, and we work in the three aspects of Uruguayan University teaching profession: research, teaching and outreach. We started working on ionizing radiation detectors, but through the years our work has evolved to adapt ourselves to our country’s reality. In 2011, 44% of Uruguayan electricity came from fossil fuels, with a strong dependence on foreign countries. Today, we are self-sufficient and 95% of our production comes from renewable sources, mainly wind and hydroelectric. Our group aligns with this policy, developing semiconductor nanostructures for hybrid polymeric-inorganic solar cells. Another remarkable aspect of our country is that water is a resource widely available, but in the last years the quality of our water has aggravated mainly due to bad agricultural practices. In this line, we develop semiconductor nanoparticles for tertiary treatment of water.

We put a lot of effort, not only in research to develop a more sustainable country, but also in teaching and outreach that helps to create consciousness in the population about new technologies and also to give them tools to create their own opinion. Regarding to teaching, in the last year we embarked on a challenging project to change the traditional lecturing courses, in our Introduction to Nanotechnology course. We decided to introduce the Problem Based Learning approach together with collaborative work with emphasis in sustainability issues, to anchor the assessment in performances directly related to the discipline. Moreover, the course design included face-to-face and virtual activities. At the end, the students increased their commitment and showed a deeper understanding of the topics.

Regarding to outreach, we have been working to bring materials science activities to schools and high schools for over 10 years. We started this path with small steps, performing isolated activities in the Science and Technology Week frame. Afterwards, we carried out different outreach projects, such as “Materials that surround us” and “Materials in our home”. In all our activities, we always carry out hands-on activities and try to emphasize how materials have had a major role in human kind development.

Although the availability of funding has been irregular and there are difficulties to sort out, we believe that the best way of improving materials science in our country and to contribute to a sustainable development is through the education of young students, therefore, we plan on continuing this kind of activities in 2019 and beyond.
To promote sustainable development, we must thoroughly understand the landscape ourselves. The Energy and Sustainability Engineering program at the University of Illinois (EaSE.illinois.edu) was launched with a considerable focus on the possibilities for, and fundamental limitations on, improved efficiency in energy conversion and materials use from a life cycle perspective. We have found, however, that the major challenge faced by our graduate students is not technical understanding, but how to articulate problems and potential solutions in the “big picture” context of development and deployment. The recent books by M. F. Ashby (Materials and the Environment, Materials and Sustainable Development) are among the resources that provide a clear conceptual framework and specific approaches for analysis.

We therefore challenge our students to define the following aspects of any proposal intended to improve sustainability. (i) What are the different objectives at play and the constraints on each one? (ii) What is the quantitative scale of the proposal in terms of technology to be deployed, spatial region and timescale? What does this imply in terms of the materials supply chain? (iii) Does the proposal depend on cost reductions as the technology matures? If so, what is reasonable to expect? (iv) What are the inevitable tradeoffs between the objectives – as well as the unintended consequences – and how should those tradeoffs be valued? (v) Who are the important stakeholders, and how should they be engaged? (vi) What are the demands for financial investment and the probable return on investment? How are these influenced by the hidden cost of externalities (which tends to favor investment in sustainability) and by economic discounting (which emphasizes short-term gains over lifecycle impact)?

In summary: we find that to advance sustainability, scientifically trained professionals need to construct and articulate a comprehensive and compelling business case around the technical possibilities made possible by engineering. I will provide key examples of the above challenges, the ways we attempt to provide insight, and welcome discussion with the audience.

11:30 AM B101.01.07
Can Materials Science Save Us (From Ourselves)? Mark A. Miodownik; University College London, London, United Kingdom.

Despite the long history of materials development, materials science as a distinct discipline is relatively new. It only came of age in the 20th century, brought into existence by necessity, as a result two developments. Firstly, industry needed it to understand the complex materials, on which it and society, was becoming ever more dependent such as the silicon chip, jet engine alloys, polymer composites, optical fibres, medical implants, etc. Secondly, it became increasing clear that materials could not be understood by the study of engineering, physics, chemistry or biology alone. So, as the 20th century progressed, so did materials science as a discipline.

We now live in the 21st century and the power of materials science is immense. It is making possible a world where buildings harvest their own energy, bridges heal themselves, clothes monitor a person’s health, and biomaterials increase the average life expectancy to 100 years of age. This all sounds thrilling, but many alternative realities await us, each driven by different cultural, economic and political forces. In these alternative realities, we could find ourselves in the grip of mass migrations, with declining life expectancy, dealing with global pollution and energy blackouts, to name but a few potential scenarios. Which future will we choose?

In this talk, I argue that much hinges on a deeper understanding by materials scientists of all parts of society. To achieve this, public engagement is not enough, the core of the discipline needs to move beyond its current limits in the physical sciences, to a more people-focused approach to materials design and manufacturing. From an educational perspective, this will require understanding of, or at least an acknowledgment of, the importance of psychology, economics, politics and materials culture. I use a case study of the development of self-repairing cities to illustrate the necessity of such changes to materials science as a discipline.

11:45 AM B101.01.08
Engineering Major Students’ Perceptions of Nanotechnology Haci H. Yolcu; Kafkas Univ, Kars, Turkey.

Nanotechnology will be among the most needed workforce areas in the near future. It is also a creative and highly dynamic field of innovative research areas that displays numerous open fields for future graduates. The central thesis of this paper is to better understand undergraduate engineering students’ awareness, exposure, and motivation towards nanotechnology, how those constructs correlate with each other, and whether there are differences by gender or year of study. This exploratory study used mixed methods to answer the research question. Results revealed that engineering students have more motivation to pursue further nanotechnology knowledge or study than they have exposure or awareness about nanotechnology. The results showed that male students have more awareness about nanotechnology than female students. Educational implications are that it is necessary to provide students with more opportunities to learn about and study nanotechnology during their undergraduate experience. While students are interested in learning more, their current levels of awareness and exposure may hold them back in pursuing nanotechnology-related careers.
help in the process of material selection for product design projects.

The Sustainable development 5-step methodology [2] developed by Prof. Michael F. Ashby and Dr. Didac Ferrer, which helps students structure their analyses of the sustainability of a technological development will also be presented. Drawing on data in CES EduPack [1] the methodology encourages students to identify the scope of a development and the stakeholders involved, before fact finding on different aspects and pulling together the newly gained knowledge into a considered opinion.

Alongside the materials selection tools that are a standard part of CES EduPack and can illustrate trade-offs in price and performance, these tools and methodologies help students see the bigger picture around their material decisions.

2:00 PM *BI01.02.02
Focusing on Sustainability—Raising Awareness of the Materials–Sustainability Nexus Ashley White1, Ivana Aguiar2, Jonathan Cullen3, Martin L. Green4, Anthony Ku5, Elizabeth Kupf6, Alan Rae2, Julie M. Schoemung7, Richard Souza8 and Margeaux Wallace9, 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Universidad de República, Montevideo, Uruguay; 3University of Cambridge, Cambridge, United Kingdom; 4National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 5National Institute of Clean-and-Low-Carbon Energy, Mountain View, California, United States; 6The Pennsylvania State University, University Park, Pennsylvania, United States; 7IncubatorWorks, Painted Post, New York, United States; 8University of California, Irvine, Irvine, California, United States; 9Materials Research Society, Warrendale, Pennsylvania, United States; 10GE Global Research, Niskayuna, New York, United States.

As technology enablers, materials play a pivotal role in solving the key challenges our society will continue to face, such as carbon dioxide mitigation, access to clean energy and water, and a dependable supply of raw and recycled materials for infrastructure, devices, and consumables. Meeting these challenges will require new approaches to materials science as well as expertise from related fields, including other scientific and engineering disciplines, sociology, economics, and policy. In recognition of the complexity of tackling sustainable development issues and the importance of materials to enabling solutions, the Materials Research Society (MRS) Board of Directors approved the creation of the Focus on Sustainability Subcommittee of the Public Outreach Committee. The subcommittee’s formation was an important step in the evolution of MRS’s sustainability-related programming and other activities.

This talk will cover the history and evolution of sustainability efforts within MRS, concentrating on the recent impacts of the Focus on Sustainability subcommittee. Its activities have included professional development seminars and workshops, symposia and tutorials, a dedicated booth at MRS meetings, industry panel discussions, hands-on activities, poster sessions, and a series of high-profile panel events organized in collaboration with the MRS Energy & Sustainability journal entitled “Materials for Energy Sustainability by 2050.”

Moving forward, the challenge for us as sustainability enthusiasts is to engage and integrate with the broader materials science community and other related disciplines. Towards that goal, this talk will discuss newer efforts to involve the broader MRS membership in our sustainability activities, raise awareness of the materials–sustainability nexus, and bring a higher level of understanding of the role different materials sub-disciplines play in sustainable development—the defining challenge of our time.

2:30 PM OPEN DISCUSSION

2:45 PM BI01.02.04
PodQESST—A Case Study for a New Form of Science Communication Sebastian Husein, Joseph Karas, Michelle Jordan and Marianna I. Bertoni; Arizona State University, Tempe, Arizona, United States.

This talk will showcase a form of communication severely under-utilized in the scientific community—namely, podcasts. Podcasts are an audio file made digitally available on the internet, typically accessible to anyone by computer or mobile. While early forms of this communication medium have been available since the 1980s, modern podcasts have grown rapidly in popularity since 2004 [1]. Reports estimate over 44% of the U.S. population over the age of 12 has listened to a podcast, with 80% of listeners following an average of 7 podcasts per week [1]. Podcasts are therefore rapidly becoming one of the largest information dissemination methods. Scientific communities must begin engaging at the intersection of podcasting and social media networks, which have become essential in circulating information [2].

Currently, scientific research is often locked away in niche websites and academic journals, with much of the research process (i.e., development of experiments, analysis of collected data, and peer review) obscured by technical jargon and complex topics. While some scientific achievements may spread into popular culture and news, most Americans receive science news by “happenstance rather than intentionally” with only ~17% both actively and frequently seeking it out [3]. To maximize positive societal impact, the scientific community must actively pursue new forms of science communication to both inform the general public and open dialogue between researchers and those potentially impacted by the research.

Through podcasts, collection and dissemination of scientific knowledge can follow a story-telling format. Our podcast, PodQESST, hosted by two Ph.D. students, examines the research process by following the human experience. Rather than discussing complex scientific concepts, this podcast interviews graduate students and research professors about how their work evolved, from conception to process, and in some cases, to real-world implementation and influence. By using this story-telling format, research work and scientific advancements can become relatable to audiences with little to no scientific background. Additionally, communities of current graduate student are potentially strengthened through this shared experience and may impact retention rates in STEM, enhancing workforce development. The impact of this podcast on perception of science and interest in STEM careers is currently being tracked among pre-university students and university students from 8 U.S. institutions partnered through the Quantum Engineering and Sustainable Solar Technology (QESST) Engineering Research Center.

References:

3:00 PM BREAK

3:30 PM *BI01.02.05
How Can Sustainability Become Tangible? Serious Games and Digital Tools Help Learners Develop Sustainability Competences Vasiliki Kioupi; Imperial College London, London, United Kingdom.

Sustainable development is a complex concept, but it is also powerful and transformative. In order for students to make sense of its holistic, interdisciplinary and participatory nature they should become engaged in meaningful educational activities that reveal interconnections between social,
economic and environmental aspects, take into account stakeholder viewpoints and at the same time assist them to develop sustainability competences. Serious games and digital tools for sustainability help shape students’ attitudes when making important decisions regarding sustainability and also think systematically and critically about taking courses of action and evaluating them. In contrast to games designed predominantly as free-time activities taken up for leisure or competition, serious games may be played seriously or casually, but are not intended to be played primarily for amusement. This definition of serious games embraces both digital and analog games whose focus is on a “serious” goal, be it education, skill training, self-development or increased work motivation, etc. Game-based and experiential learning are fun and creative, giving the opportunity to participants to experience real-world situations but in a safe and controlled environment where they can test their ideas, express their opinions, develop strategies and check the outcomes. Also, the focus is on engagement, interaction with peers and reflection on the results and processes. Digital tools help students develop their own questions and hypotheses related to sustainability issues, investigate their current state, understand stakeholder involvement, select alternative courses of action, develop criteria for evaluation and weigh different scenarios in terms of their sustainability capacity to produce viable solutions. Through these educational activities, students develop important knowledge and skills that are required in order to achieve the vision of a sustainable society as it is articulated by the Sustainable Development Goals (SDGs). Those include systems thinking, anticipatory, normative, strategic, collaboration, critical thinking, self-awareness and integrated problem-solving competences.

4:00 PM • BI01.02.06
Responsible Research and Innovation—Some Societal and Ethical Issues
Joelle Lischetto-Alnot; Univ of Lorraine, Nancy, France.

Today, the concept of “responsible research and “responsible innovation” (RI) is one of the main preoccupations in the field of science and technology studies. If nanomaterials and nanotechnologies have of course opened hope for a better quality of life in our societies with a lot of progress and applications, they are not without asking some questions regarding their potential effects, toxicity, and by the way, some ethical issues. Recurring debates shake not only the scientific community, but also citizens, leading sometimes to controversial and contradictory positions. The traditional balance cost-benefit, and the classic “precautionary principle”, gave way to an “uncertainty principle”, and the necessity of considering differently nowadays the question of risk and safety. In fact, if we want to avoid a gap between researchers and citizens, science and society should not be regarded as two distinct spheres, and the way for that is rather to establishing a better and more trustful relationship between science and society. In order to achieve this objective, one of the outcomes could then consist in promoting an interdisciplinary dialogue. In the European Union (UE), responsible research and innovation is becoming an increasingly part of policies, particularly throughout the EU’s Horizon 2020 research work program “Science with and for society” (2018-2020): the challenge is, facing to the evolution of science and society and the open science context, to develop innovative ways connecting science to society, through an inclusive

4:30 PM BI01.02.07
Pathway Toward Sustainable Development of Next Generation Photovoltaics—A Detailed Study on Research Trends Through Social Network Analysis
Jun-Seok Yeo and Yeseul Jeong; Korea Institute of S&T Evaluation and Planning (KISTEP), Seoul, Korea (the Republic of).

Organic-inorganic hybrid perovskite solar cells (PeSCs) have attracted great attention as next-generation photovoltaics due to their high efficiency, low manufacturing cost, facile solution-processability, light weight, and mechanical flexibility. Since the advent of the PeSCs, the researchers have devoted a lot of efforts to improve the PeSC-performance, boosting the progress in the power conversion efficiency (PCE) of over 20%. This progress has gradually shifted the focus of the PeSC research to study of reliability and cost-effectiveness of the PeSCs. In this study, we systemically investigate these research trends of the PeSCs for their sustainable development and market entry by using ‘Social Network Analysis (SNA)’. For SNA data, SCI(E) papers on PeSCs published from 2009 to 2017 are collected, and classified into two categories (research fields and commercialization factors). Next, we conduct respective networks visualization, networks topological analysis, and node centrality analysis. With the aid of SNA, the technology and knowledge networks (flows) for PeSC research fields are investigated in terms of countries, research institutions, research fields, and commercialization factors.

4:45 PM SYMPOSIUM WRAP-UP DISCUSSION

SESSION BI01.03: Sustainability in Industry and Agriculture
Session Chairs: Jean-Pierre Birat and Khosrow Ghavami
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Hampton

8:00 AM BI01.03.01
Self-Healing Polymers Using Reversible Supramolecular Metal-Ligand Interactions
Ulrich S. Schubert, Stefan Zechel, Marcel Enke, Stefan Götz and Martin D. Hager; Friedrich-Schiller-University Jena, Jena, Germany.

Metallo-supramolecular polymers are an interesting class of polymeric materials since they combine the typical character of metals and polymers leading to novel and outstanding features. Furthermore, metal-ligand interaction can feature a reversibility of the binding enabling the design of novel self-healing materials.[1]

For this purpose, terpyridine moieties were incorporated into the side chain of different copolymers using the RAFT polymerization technique.[2,3]

Subsequently, metallo-supramolecular polymer networks were prepared by the addition of different metal salts.[4] The healing of the metallopolymers strongly depends on the chosen metal salt. In particular, the metal as well as the counter ion has a strong impact on the healing behavior.[3] Interestingly, the crosslinking with manganese(II) chloride resulted in the best scratch healing ability (Figure 4). Furthermore, the metallopolymers were studied by temperature-dependent rheological measurements and the supramolecular bond life-time (τb) was determined by the crossover of G’ and G”[A correlation between the presence of the crossover as well as the ability to close cracks could be revealed. Thus, the mechanical properties could be correlated with the self-healing performance of supramolecular networks.[3]

8:15 AM BI01.03.02
The Biomaterial Age Javier Gomez Fernandez; SUTD, Singapore, Singapore.

The history of humanity can be summarized in different periods dominated by the use of a new material bringing a new paradigm and a revolution in engineering, becoming in a short time the engine of development of that historical period. The ages of stone, bronze and iron are clear examples of how certain materials have transformed society and its economy. Nowadays the equivalent to these materials is plastic. Driven initially by a continuous demand from the WWII, the production of plastic began a vertiginous development, finally surpassing in production to all the rest of materials used outside the field of construction in the decade of the 60s.

The first voices of alarm about the impact of plastic on the environment occurred also in the 60s, with the first observations of the accumulation of plastic waste in nests of seabirds. While these early studies were anecdotal and remote for most, today virtually no one is unaware of a problem in continuous growth. We are in a difficult situation; as a society we have developed a greater awareness of the impact of our actions on the environment in general, and the impact of plastic in particular. Moreover, unlike other environmental problems, the problem of plastic is indisputably anthropogenic and easily observable. However, the production of plastic it is accelerating. If in the 50s, we were producing half a million tons of plastic a year, now we are close to the five hundred million tons. At the current rate in 2050 we will double that amount, requiring one fifth of the world's oil production to produce plastic. The apparent failure to produce feasible solutions, both by scientists and legislators, is mainly because the solutions being considered implicitly assume that humanity has reached a kind of technology summit with the invention of plastic and its methods of manufacturing. As legislators we fail because, in the absence of alternatives, we can only limit very specific uses of plastic. As scientists we are failing because we are trying to find materials that replace plastic to make objects that have not been designed to be made with plastic. Moreover, not only the objects, in our search for solutions we also impose the mode of manufacture of the plastic and that is the basis of our industrial system. We mistakenly assume that necessity is the motor of development, but the question we should be asking ourselves is not how can we change an economy and society molded around plastic to get rid of our addiction to it. The question should be: What comes after the plastic and what kind of society will it bring? In this talk we will explore the role that biomaterials will play in the future of manufacturing and the emergence of new economic models, giving rise to what we have called "the biomaterial age". The role of bio-inspired engineering, 3D printing, or new models of organic waste processing will be covered as key pieces in this transition.

8:30 AM BI01.03.03
IMERYS—Sustainable Development for Innovative Mineral Based Solutions Claire M. Theron; External Innovation, IMERYS, Suwanee, Georgia, United States.

Imerys is the world leader in mineral-based specialties for consumer goods, industrial equipment and construction. Its Corporate Social Responsibility is central to the Group's long-term strategy, supporting growth and underpinning long-term relationships with all stakeholders.

While Imerys operates on a global level, the group is committed to play a role in society, to meet its obligations to the countries and communities within which it does business by empowering our people, caring for our planet and building for the future together with our stakeholders. Through these commitments the Group contributes to sustainable development and foster positive changes including regional projects covering education, sanitation, health and diversity, renewable energy, and biodiversity such eradication of invasive species, preservation of protected species.

Following main international standards, in-house Sustainable Development (SD) Challenges have yielded 847 projects during the last 13 years. Those projects are aligned with Imerys high priority areas, such as diversity and inclusion, education, environment management, climate change and relation with communities. The group’s commitments in Imerys Code of Ethics and Business Conduct and CSR Charter are available to all detailed in policies, procedures and protocols gathered on Imerys intranet.

An example of Imerys contribution includes lightweighting of vehicles by delivering functional additives (High Aspect Ratio talcs) to polymers industry. The 3G HAR® product enables weight reduction of the automotive plastic injection-molded parts while its production uses 63% less electricity than previously. Imerys is also active in cosmetics, offering its ImerCare® range is P-Scrub, product using 100% natural minerals designed as an eco-friendly alternative to plastic microbeads.

In agriculture, Imerys Mechanical Insecticides offer three natural mineral solutions, based on diatomaceous earth or kaolin (DiaFil® 610, Celite® 610 and IMERGARD™) which provide effective environmentally friendly solutions.

Building on existing systems and initiatives and going beyond compliance, a program fully aligned with the United Nations' Global Compact and Sustainable Development Goals is being implemented. The ambition is clear: anchoring sustainable development at the heart of the Group's overall strategy and mobilizing employees at every level to achieve Corporate Social Responsibility targets.

9:00 AM BI01.03.04
Sustainable Construction Materials for XXI Century Khosrow Ghavami; Pontificia Universidade Catolica de Rio de Janeiro, Rio de Janeiro, Brazil.

New constructions are being erected scraping the skies with nearly 1000m high. And still in spite of all the advances a large percentage of people of the world live in misery without the minimum of nourishment, clean drinking water and decent housing. Industries are demanding more and more raw materials, existing now mainly in developing countries and creating havoc on earth searching for and exploiting the lands holding these needed raw materials. Nature is responding with climate changes, freak storms and other disasters. The big centralized industries are not able or rather not willing to stop polluting our environment by reducing carbon emissions. Their ambition is to be the owners of the Earth, and do what they think is good for their bottom line, and not the working people of the planet. Now, sustainability goes together with moderation, meeting basic needs and a general well-being of the population. Sustainability of our environment makes possible that a greater part of the population can follow up a life’s dream or at least ability to have a decent meaningful life through preserving remaining natural resources available for the future generations. In schools and universities, yet, only the industrial non-renewable materials such as cement, concrete, steel and recently composites made of polymers research and application. The study of Non-Conventional Materials and Technologies, NOCMAT, has been started in the years of the seventies of the last century. A new line of research has been initiated to investigate local renewable materials such as bamboo, vegetable fibers, soil composite, which is called Kah-gel in Persian language. These materials have been used as construction materials for thousands years, recycled materials, such as rice husk and sugar cane ash among others. This paper will present the recent results of research on NOCMAT and their application in practice. To improve the durability of the studied materials, nano-particles applied in kah-gel and also impregnated into bamboo culm. To achieve the final objective to tune a fine nanocoating of vascular bundles’ of bamboo, internal wall has been done through the interfacial compatibility, based on self-assembling interactions, between the NFs-surface and the lignin-cellulose walls of bamboo vessels.
The lithium-ion battery (LIB) recycling market is becoming increasingly important because of the widespread use of LIBs in every aspect of our lives. Mobile devices and electric cars represent the largest application areas for LIBs. Vigorous innovation in these sectors is spurring continuous deployment of LIB powered devices, and consequently more and more LIBs will become waste as they approach end of life. Considering the significant economic and environmental impacts, recycling is not only necessary, but also urgent. The WPI group has successfully developed a closed-loop recycling process, and has previously demonstrated it on a relatively small scale 1kg spent batteries per experiment. Here, we show that the closed-loop recycling process can be successfully scaled up to 30kg of spent LIBs from electric vehicle recycling streams, and the recovered cathode powder shows similar (or better) performance to equivalent commercial powder when evaluated in both coin cells and single layer pouch cells. All of these results demonstrate the closed-loop recycling process has great adaptability and can be further developed into industrial scale.

9:45 AM BI01.03.06
Reclaiming Sb Metal from Lead Alloy with Electrochemical Method Qiang Wang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Antimony is a widely used element in human’s daily life. For example, Sb2O3 plays role as flame retardant in plastics, coatings, and electronics; functioning as a hardener, 2wt % to 7wt % of antimony metal is added into lead metal to fabricate electrode for lead-acid battery; and antimony can work as catalyst for synthesizing chemicals. In 2016, antimony mine production in the word was 130,000 t, and China, the leading producer, accounted for about 76.9 % of the production. The strong dependence of antimony industry on the import of Chinese antimony drives USA and Europe to seek solution of reclaiming and recovering antimony from secondary resource. Herein, an innovative method composed of electrochemical and chemical reactions is proposed to purify antimony from lead alloy, which is treated as anode in an “H” shape electrolytic cell. Stainless steel sheet works as cathode, and potassium hydroxide solution is applied as electrolyte. O2 is purged into the cathode at the beginning, and the electrolytic cell works in the principle of metal-O2 battery, when voltage is applied on the two electrodes. Lead, antimony, and other metals dissolve into the electrolyte as ions at the first stage. When the ions inside the electrolyte accumulated to a certain amount, O2 is switched off without interference of the electrolysis. At this second stage, lead alloy of the anode dissolve into electrolyte successively, but lead metal deposits on cathode side simultaneously. Lead ions concentration stops increasing, and antimony ions concentration keeps on rising. When antimony concentration is high enough, the electrolysis is stopped, and Na2S is added into the electrolyte to precipitate lead ions in the stage 3. Almost all the lead can be removed from electrolyte, leaving antimony inside, by taking advantage of the low value of Ksp (PbS). At the last step, antimony can be extracted from the electrolyte at low potential of -1.25 V (vs Hg/HgO), leaving other impurity, such as As, Sn, Al inside with low concentration under 50 ppm. The electrolyte can be re-used for the next circle. This flow sheet can purity lead and antimony metals from lead alloy, with lead purity of 99.2 wt% and antimony purity of 92 wt%, and antimony recovery efficiency is ~ 82%. Because the electrolyte can be used repeatedly, no waste is generated in the whole process.

Stage 1. Cathode: O2 + 4e- + 2H2O → 4OH- (1)
Anode: Pb + 4OH- - 2e- → PbO2 + 2H2O + SbO2 + 2H2O (the main oxidation reaction) (2)
Sb + 4OH- - 3e- → SbO2 + 2H2O + SbO2 (3)

Stage 2. Cathode: PbO2 + 2H2O + 2e- → Pb + 4OH- (4)
Anode: Pb + 4OH- - 2e- → PbO2 + 2H2O (the main oxidation reaction) (5)
Sb + 4OH- - 3e- → SbO2 + 2H2O (6)

Stage 3. PbS + S2 → PbS4 (7)
Stage 4. Cathode: 4OH- - 4e-→ O2 + 2H2O (8)
Anode: Sb2O3 + 2H2O + 3e- → Sb + 4OH- (9)

10:00 AM BREAK

10:30 AM BI01.03.07
Cellulose Nanomaterials in 3D Printing and Aerogels—High-Performance Nanocomposites Rigoberto C. Advincula; Case Western Reserve University, Cleveland, Ohio, United States.

Sustainable and renewable materials start with the use of biobased feedstocks or derived raw materials for direct utilization (little conversion or synthetic procedures). The preparation of nanocellulose materials from a variety of sources include agricultural, non-agricultural, and can vary in properties depending on the method of preparation and high fiber source. Cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) have various uses for the fabrication of polymer nanocomposites, making them useful as an additive for improving thermo-mechanical properties and perhaps improving processability. In this talk, we will focus on the use of CNC derived from various sources, Abuaca, coconut fibers, miscanthus grass, mango seeds, etc. The mode of raw materials can be from processed pulp or directly from the agriculture or plant source. These nanofiller materials have been utilized in two types of applications: nanofiller materials for 3D printed parts via SLA, FDM, or VSP and the preparation of smart aerogels with nanoclay. The former enabled strengthening of the thermo-mechanical properties of the 3D printed object and the latter results in a highly porous lightweight media useful also for oil-water separation and clean-up. The talk will discuss the methods of synthesis, fabrication, and characterization for their intended application and a pathway of high value adding from sustainable materials and its societal and technopreneurship impact.

10:45 AM BI01.03.08

There were approx. 1.2 billion motor vehicles in the world in 2015 and industrial forecasts predict the number of cars may reach 2 billion cars globally by 2035. Even with an increasing development of Li-ion technology, lead-acid batteries (LABs) remain the most popular power supply for automotive industry and there are no signs of decline in this market as LABs are also present in state-of-art hybrid and fully electric vehicles. A major challenge facing the lead-acid technology is, however, its toxicity and the environmental impact of lead. To address these issues, we need to develop novel processes to recover high value of lead from spent lead acid batteries. It is critically important to develop sustainable methods with a minimal pollution and low energy consumption in comparison with the traditional smelting and hydrometallurgical routes. We propose a process where Pb-containing battery waste is dissolved into deep eutectic solvents (DES), followed by an electrochemical recovery of metallic lead to provide a low-energy, low-temperature and an environmentally friendly alternative to recycling of spent batteries. In our work, cyclic voltammetry and chronoamperometry were used to determine the mechanism and electrodeposition behaviour of lead, while ICP-OES and EXAFS provided insight into speciation of lead in DESs, and SEM and XPS were used to characterise the lead electrodeposits.

Closed Loop Recycling of Electric Vehicle Batteries to Enable Ultra-High Quality Cathode Powder Mengyuan Chen, Xiaotu Ma and Yan Wang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

The lithium-ion battery (LIB) recycling market is becoming increasingly important because of the widespread use of LIBs in every aspect of our lives. Mobile devices and electric cars represent the largest application areas for LIBs. Vigorous innovation in these sectors is spurring continuous deployment of LIB powered devices, and consequently more and more LIBs will become waste as they approach end of life. Considering the significant economic and environmental impacts, recycling is not only necessary, but also urgent. The WPI group has successfully developed a closed-loop recycling process, and has previously demonstrated it on a relatively small scale 1kg spent batteries per experiment. Here, we show that the closed-loop recycling process can be successfully scaled up to 30kg of spent LIBs from electric vehicle recycling streams, and the recovered cathode powder shows similar (or better) performance to equivalent commercial powder when evaluated in both coin cells and single layer pouch cells. All of these results demonstrate the closed-loop recycling process has great adaptability and can be further developed into industrial scale.
The reform of CO2 through photocatalytic processes to obtain products with high energy value and compatible with the current energy infrastructure, is a compelling strategy to minimize the emission of CO2 at atmosphere, one of the main greenhouse gases. However, practical application of such a photocatalytic system requires significant efforts for improved CO2 photoreduction performance and product selectivity. Thus, in the present work, CuO nanoparticles were combined with Nb2O5 in order to improve the photocatalytic properties of these semiconductors in the CO2 photoreduction process. The Nb2O5/CuO heterojunctions were prepared via solvothermal treatment method, while that experimental tools, such as FESEM, HRTEM, and DRS were employed to evaluate the microstructural and electronic properties. The physicochemical properties of the Nb2O5/CuO heterostructures were characterized and evaluated in the ability of the CO2 photoreduction with different electrolytes (pure water, sodium oxalate, and KBrO3) under ultraviolet radiation (UVC). The use of these electrolytes besides conducting the formation of a certain product enables the elucidation of the mechanisms of the CO2 photoreduction process. Further, the Nb2O5/CuO heterostructures was active also to CO reduction in CH4, HCOOH and CH3COOH, besides this result demonstrated that CO is intermediate in the CO2 reduction to all products. The synthesized heterostructures showed photocatalytic activities superior to the pure Nb2O5 and the TiO2 (P25). This improvement could be attributed to the formation of junctions between CuO and Nb2O5, which facilitated charge transfer, and suppressed the recombination of electron/hole pairs. The FESEM and HRTEM analyzes show that CuO nanoparticles were uniformly distributed on the surface of Nb2O5, showing the formation of a junction between the oxides.

Acknowledgments
The authors are grateful to FAPESP (grants n° 2014/09014-7 and2013/11821-5), CAPES and FINEP for the financial support.

11:15 AM *B101.03.10
Why Non-Conventional Materials are Answers for Sustainable Agriculture Caue Ribeiro de Oliveira; Brazilian Agricultural Res Corp, Sao Carlos, Brazil.

Fertilizers undoubtedly are key factors for agricultural productivity, but their widespread use is continuously impacting the farmers’ economic balance and, indirectly, being associated to many environmental impacts – such as volatilization or lixiviation. These impacts might be significantly reduced if the nutrients could be supplied in constant, controllable rates – as controlled release systems – however any technological alternative should be capable to offer affordable prices and large production scales, since these are often applied in hundreds of kgs per hectare. Therefore we have proposed a strategy to produce composite fertilizers where the matrix is composed by nutrients, i.e., all the constituents play a nutritional role for plants. This strategy allows, for instance, the controlled delivery of phosphate from hydroxyapatite nanoparticles dispersed in a nitrogen-rich matrix (even urea or partially polymerized urea). Recently, we noticed that similar strategies are applicable to sulfur (S), often neglected about its importance as nutrient. The production of S-rich polymeric matrices, using elemental S and biopolymers, provide means for multiple nutrient administrations, by integrating these nutrient matrices to mineral phosphates as dispersed nanoparticles as composites. This structure was shown as very adequate for microorganism colonization (e.g. A. niger), which accelerates the S oxidation to sulfates (which are properly absorbed by plants) while imposes a local acidification solubilizing the mineral phosphates to absorbable species. This complex system can be extend to other structures, keeping very high total nutrient contents (higher that 30% wt) and easy processing steps, since these features allows the fertilizer production by high-output techniques such as extrusion.

Acknowledgements: FAPESP; CAPES; CNPq; FINEP; National System of Nanotechnology Laboratories – SISNANO/MCTI; Rede Agronano/Embrapa

11:45 AM B101.03.11
Sustainable Crop Protection Management in Sub-Saharan Africa Through Biodegradable Seed Wraps Tahira Pirzada and Saad A. Khan; Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Plant parasitic nematodes are one of the major constraints on yield and production of food crops throughout the world. While abamectin has broad nematicidal activity, its poor mobility in soils compromises its efficiency against nematode infestation. Using abamectin as a model pesticide, we present an innovative and cost effective approach for crop protection from plant parasitic nematodes, using a lignocellulosic matrix ‘wrap and plant’ methodology. In our ‘wrap and plant’ approach, we have used abamectin loaded matrices as wraps for seeds to be planted in the soil. To better understand the effect of various processing parameters and nature of the pulp on final properties of the matrix, we have produced lignocellulose matrices using pulp refined at various time intervals. Resulting hand sheets are characterized by the controlled release of abamectin which is incorporated into the matrices through sorption. Pulp refining time as well as various physical and chemical properties of the matrix are found to affect its tendency to let the germinating roots penetrate it and also the release rate of abamectin. We perceive that by varying refining time of the pulp, we can obtain matrices that facilitate in slow and sustained release of abamectin which results in long term nematicide protection to the growing plant roots. We have used these results to develop pilot scale paper rolls which are currently used in field trials in various regions of Africa and initial field trials demonstrate promising results regarding better crop protection in nematode infested soils in Benin and Kenya.
The INEMI project on Value Recovery from Used Hard Disk Drives (HDDs) is an industry-academia-government lab-NGO partnership whose vision is creating a global, circular economy for HDDs. Hard disk drives have a special role in electronics: they are ubiquitous, having been designed to be replaceable and interchangeable in products as diverse as computers, servers, and sensor/monitoring equipment. In Phase 1 of the project, an INEMI multi-stakeholder team developed the groundwork and created a momentum for a Phase 2 collaborative project to build an integrated, sustainable, adaptive CE system for end-of-use HDDs. The project framework has been modeled after sustainable management of common pool resources on which many people rely for their livelihoods. Dr. Elinor Ostrom (2009 Nobel Laureate in Economics) laid out a framework for how people and organizations develop voluntary, community-based solutions involving adaptive, self-governing systems that effectively manage common pool resources without the need for government regulations or privatization. We have applied this framework explicitly to HDDs, as a first demonstration. Phase 1 was built on stakeholders identifying decision pathways for HDD refurbishment, component reuse, and material recovery, incorporating economic and resource recovery analyses, and identifying how they interplay. The Phase 1 findings showed the existence but not the value recovery based on these decisions and established the basis for a more effective, implementable system. The Phase 2 team included a broad cross-section of electronics stakeholders necessary for a working CE supply chain: HDD designers and manufacturers, different types of users/owners (and discarding) of HDDs, IT asset managers, technology developers, reuse and recycling companies that do both pre-processing and final processing, standards development organizations, and R&D organizations that can fill critical technology and materials gaps to increase value recovery and make the circular economy a reality. The US Department of Energy’s Critical Materials Institute is playing an important role by creating new technologies for rare earth metal resource recovery, as well as by using this analysis to propose specific recommendations to strengthen the US manufacturing base. The INEMI team designed and completed Demonstration Projects that showed new, technologically and economically viable pathways for value recovery that enable creation of a Circular Economy.

2:00 PM BI01.04.02
Recovery of Electronics Waste to be Converting into Functional Devices Roberto Basea; Inst Politecnico National, Distrito Federal, Mexico.

Today, processing technologies have generated negative environmental impact as emission of toxic gases and degradation of the earth when certain products are placement in landfills leading to environmental pollution and several biological risks, which damage societies to sustain the planet for future generations. As electronics waste, grain-oriented iron foils, graphite films, and Mo-Zr ferrites has been identified as interesting candidates. Therefore, uncommon physical properties from such materials are available when it is converting technologically. A strategy such as Life-Cycle Assessment (LCA) is employed here to take into account all stages of the life cycle of electronics waste, including processing technology, manufacturing processes, use phase, and end-of-life routes to quantify the recycling performance as a function of the physical parameters that will characterize these to operability into a functional device. Hence, structure and conduction properties in waste materials are exploring by using X-ray diffraction, Raman spectroscopy and electrical characterization techniques with emphasis on knowledge of their physical behavior. Researching waste materials will provide theoretical basis for open-loop recycling, where trends related to green engineering should be attained with material recycling for adaptive structures as functional devices using different performance principles compared to those used with silicon devices.

2:15 PM BI01.04.03
Eumelanin's Biodegradability—Not to be Taken for Granted Eduardo Di Mauro1, Denis Rho2 and Clara Santato2; 1Polytechnique Montréal, Montreal, Quebec, Canada; 2Aquatic and Crop Resource Development, Canadian National Research Council, Montreal, Québec, Canada.


2:30 PM BI01.04.04
Photonic Devices with Reduced In, Ga and Sb Content Thierry Baron1, Marie-Leonor Tourorton2, 1, Tiphaine Cerba1, 1, Mickael Martin1, Jérémie Moeyeart1, Sylvain Droy1, Virginie Loup1, Franck Bassani2, Bassem Salemi2, Karine Samuel2, Blandine Ageron1, Thomas Ernst2, Didier Dutartre1 and Christophe Jany1; 1Univ. Grenoble Alpes, CNRS, CEA/Leti Minatoc, LTM, F-38054 Grenoble, France; 2STMicroelectronics, Crolles, France; 3International Electronics Manufacturing Initiative INEMI, Austin, Texas, United States.

The INEMI project on Value Recovery from Used Hard Disk Drives (HDDs) is an industry-academia-government lab-NGO partnership whose vision is creating a global, circular economy for HDDs. Hard disk drives have a special role in electronics: they are ubiquitous, having been designed to be replaceable and interchangeable in products as diverse as computers, servers, and sensor/monitoring equipment. In Phase 1 of the project, an INEMI multi-stakeholder team developed the groundwork and created a momentum for a Phase 2 collaborative project to build an integrated, sustainable, adaptive CE system for end-of-use HDDs. The project framework has been modeled after sustainable management of common pool resources on which many people rely for their livelihoods. Dr. Elinor Ostrom (2009 Nobel Laureate in Economics) laid out a framework for how people and organizations develop voluntary, community-based solutions involving adaptive, self-governing systems that effectively manage common pool resources without the need for government regulations or privatization. We have applied this framework explicitly to HDDs, as a first demonstration. Phase 1 was built on stakeholders identifying decision pathways for HDD refurbishment, component reuse, and material recovery, incorporating economic and resource recovery analyses, and identifying how they interplay. The Phase 1 findings showed the existence but not the value recovery based on these decisions and established the basis for a more effective, implementable system. The Phase 2 team included a broad cross-section of electronics stakeholders necessary for a working CE supply chain: HDD designers and manufacturers, different types of users/owners (and discarding) of HDDs, IT asset managers, technology developers, reuse and recycling companies that do both pre-processing and final processing, standards development organizations, and R&D organizations that can fill critical technology and materials gaps to increase value recovery and make the circular economy a reality. The US Department of Energy’s Critical Materials Institute is playing an important role by creating new technologies for rare earth metal resource recovery, as well as by using this analysis to propose specific recommendations to strengthen the US manufacturing base. The INEMI team designed and completed Demonstration Projects that showed new, technologically and economically viable pathways for value recovery that enable creation of a Circular Economy.

The access to raw materials is an economic and major geopolitical stake for the 21st century. Some key elements considered today in the emerging devices for the Internet of Things (IoT) must be substituted or saved (by orders of decades) in a drastic way in the near future. Since tens Billions electronics objects are being disseminated all over the world in homes, buildings, cars, roads, etc., it is obviously a major concern to revisit the economic, technological, and societal models to develop a sustainable electronic industry that will care about its impact right from the conception of these objects. III-V semiconductors present interesting properties and are already used in electronics, lightening and photonic devices. More particularly alloys containing Ga, In and Sb are increasingly used by the semiconductors industry for high frequency operation, WIFI technology, high power devices, lasers for communications, sensors… This sector accounts for about 90% of world consumption of gallium for example. With the huge increase of IoT devices there is a real challenge to be able to maximize the consumption of these elements or substitute them but more abundant one to fulfill the same function. In this contribution, we will show strategies to develop processes either to save or substitute In, Ga and Sb to realize specific functions such as light emission

University, West Lafayette, Indiana, United States; 2Seagate, Technology, Bloomington, Minnesota, United States; 3International Electronics Manufacturing Initiative INEMI, Austin, Texas, United States.
and detection, and sensors with technologies compatible with large-scale integration. An important aspect of the work will be devoted to synthesis on large area nano-powders with the concern for compatibility with CMOS processes. We will show that bulk material (InP, GaAs and GaSb substrates) could be substituted by thin layers elaborated on a standard Si(100) microelectronic substrates. Selective deposition will also be considered to put the materials only at the place where it is needed. The physical properties of In, Ga, Sb containing semiconductors elaborated on a silicon platform will be shown and compared with those elaborated on III-V substrates. Demonstration of LEDs emitting in the visible and infra-red region will be shown. As an ultimate solution, 2D materials elaborated on large scale 300 mm Si substrates will be presented and their physical properties will be exposed.

Acknowledgments
This work was supported by the French government managed by ANR under the Investissements d’avenir economic stimulus package, with reference IRT Nanoelec ANR-10-IRT-05, ANR-15-IDEX-02 and LabEx Minos ANR-10-LABX-55-01.

2:45 PM BI01.04.05
Synthesizing Pr4+ / Dy3+ Doped Nd2O3 Nanoparticles from Nd-Fe-B Magnets Sourced from E-Waste
Samane Maroufi, Rasoul Khayyam Nekouei and Veena Sahajwalla; UNSW, Sydney, New South Wales, Australia.

The global supply of rare earth elements (REEs), is under considerable strain. As many countries have no suitable ore deposits within their territories, and deposits elsewhere are both limited and finite, the recovery of REEs through recycling is essential. Currently, less than one percent of REEs are recovered via recycling. Nd-Fe-B permanent magnets are now one of the most widely used type of rare-earth magnets which are implemented in a variety of applications such as electric power generation (computer and laptop hard drive) and transportation (hybrid and electrical vehicles). Given the growing demands for lightweight products with high magnetic strength to support the miniaturization of equipment in many existing and emerging applications, demand for Nd-Fe-B magnets is, likewise, expected to continue to rise, particular for the clean energy/transport sectors.

In this study oxidation-reduction process was used for the recovery of rare earth elements (REEs) (i.e. Nd, Pr, and Dy) from Nd-Fe-B permanent magnets. Nd-Fe-B permanent magnets collected from e-waste were subjected to an oxidation process at 1000°C for 60 minutes followed by carothermal reduction at 1450°C for 60 minutes using waste tyre rubber-derived carbon (WTR-DC) as a reducing agent. Fe-based metal and rare earth oxides (REO) phases were successfully separated from the original magnets. The distribution of elements (i.e., Nd, Dy, Pr, Fe, B, Al, and C) between the Fe-based metal and oxide phases were investigated via Inductively Coupled Plasma (ICP), Energy-Dispersive X-ray Spectroscopy (EDS)/Electron Probe Microanalysis (EPMA) elemental mapping. REEs were confirmed as the main components of the oxide phase and it was shown that the REEs did not remain in the Fe-based metal phase. The oxide phase mainly contained REEs (i.e., Nd, Dy and Pr) and a minor amount of B and Al.

Using REEs (i.e., Nd, Pr and Dy) derived from Nd-Fe-B magnets we applied a low temperature urea-based homogeneous precipitation method and synthesized crystallized RE (i.e., Nd, Pr and Dy) OHCO3 nanoparticles with diameters of 40-50 nm and high specific surface area of 60 m² g⁻¹. The synthesized REOHCO3 was used as a precursor for the synthesis of REO nanoparticles through a thermal degradation process at 700°C. FE-SEM images revealed that the synthesized REO nanoparticles inherited their parent’s morphology. X-ray diffraction spectrum of the synthesized REO nanoparticles showed cubic phase of Nd2O3 with no additional peak corresponding to the secondary phases of Pr and Dy. High resolution TEM (HRTEM) micrographs and electron diffraction of the selected area (SAED) of the as-synthesized REO nanoparticles exhibited the deformation in crystalline structure, shrinkage of the crystalline size and decrease in interplanar distance value indicating that Nd3⁺ in Nd2O3 host lattice were replaced with dopants of Pr3⁺ and Dy3⁺.

3:00 PM BREAK

3:30 PM BI01.04.06
Nanoparticles from the Gas-Phase—A Technical, Ecological and Economical Answer for Sustainble Future Energy Applications?
Sophie M. Schnurre and Tim Huelser; Institute of Energy and Environmental Technology e.V., Duisberg, Germany.

Sustainability should be the objective of every future technology. Especially nanotechnology has shown that worries and concerns of consumers may hamper the development of nanomaterials. Therefore, it is indispensable for a sustainable fabrication of products containing engineered nanoparticles (ENP) to have no adverse effects on the environment. In the face of the conflict between immediate marketing of innovative products containing engineered nanoparticles and precautionary assessments with regard to potential environmental and human risks, a multi-disciplinary approach to work out functional, social and economic effects was established. Within this approach, first, the design and synthesis of sustainable nanomaterials on the pilot plant scale and, second, different aspects along the value chain are considered. Here, political regulations, social and economic effects, technological and social risk potential as well as barriers to economic growth are crucial from the synthesis to the implementation into applications.

For ceria nanoparticles (pure as well as doped), an enormous marketing potential is expected due to their presumed low toxicity and multiple application possibilities. We present methods (e.g. doping particles with Europium) to tune particle morphology, which allows to identify particles in biological systems and enhance low temperature catalytic properties. Results of end of life cycle assessment using new models of nanoparticle distribution scenarios are displayed.

As another application oriented material, we chose silicon nanoparticles, since this material is a candidate for anode material in lithium batteries because of its high storage capacity, good availability of raw material, cost-efficient production method and its sufficient long-term stability.

We demonstrate the formation of silicon nanomaterial by homogeneous gas-phase reactions as a direct and highly economic way to produce the required high-purity raw material for battery applications. We developed a value chain for lithium ion battery materials with respect to market, patent and literature analyses as well as the innovation potential. Here, the synthesis process, the manufacturing, the utilization phase and the end of life phase are taken into account.

The tools will form the basis of a “value chain” regulatory process, which allows NM to be assessed for different applications on the basis of available data and the specific exposure and life cycle concerns for that application. To determine the technology readiness level (TRL) of a technology a scheme has been worked out, which shows a timeline that is divided into laboratory-, pilot plant- and industrial-scale from today to 2030. Technology related topics such as material, processing, component development, assembly and the final product are integrated into scheme. Technology options like social and economic chances as well as limitations like risk potential, social risks and barriers to economic growth are considered.

4:00 PM BI01.04.07
Massive Production of Energy Materials from Fe-P Waste Slag with Novel Technics for Sustainable Development
Guixin Wang, Yun Wei, Yujia Peng, Fei Xu, Yao Cai, Shunxing Wang and Yangping Yan; College of Chemical Engineering, Sichuan University, Chengdu, China.

Recycling solid waste slag as functional materials at low energy consumption and low environmental impact still faces challenges for sustainable development. A novel and green route has been proposed for the synthesis of energy materials like LiFePO4, FePO4, (FePO4)α(OH)2 using Fe-P waste slag with a melting point of 1400 °C via a hydrothermal reaction at no more than 200°C, and the by-product is only water. A 2L autoclave was utilized to synthesize these materials by stirring to further decrease reaction temperature and shorten reaction time. FePO4 or Fe(PO4)α(OH)2 can be obtained by changing the mass ratio between Fe₃P₄ slag, H₃PO₄ and H₂O₂, while LiFePO4 can be obtained by using the raw materials of Fe₃P₄ slag, LiOH, H₃PO₄ and H₂O₂. As the autoclave was cooled to room temperature, a solution with solid particles appears. After being washed, filtered and dried in air, fine product powders were obtained. The reaction process was investigated with thermodynamic calculation and thermogravimetric analysis. The as-
obtained solution and powders were characterized with various techniques, and key factors affecting the synthesis were discussed. The as-obtained FePO₄ or Fe₃(PO₄)₂(OH)₂ can be further used to synthesize LiFePO₄. The electrochemical performance of the as-synthesized LiFePO₄ samples was evaluated with galvanostatic charge/discharge tests, cyclic voltammetry and electrochemical impedance spectroscopy. The LiFePO₄ samples obtained with one step or two steps all have specific electrochemical activity, and the specific capacity can reach 110 mAh/g at 1.0C current rate. In order to improve the electrochemical performance of the samples, glucose was adopted to supply carbons to improve conductivity via calcining at 300 °C and 700 °C in a quartz tube furnace full of Ar. The emissions from the tube furnace were inert an ammonia water to form a NH₄HCO₃ solution. The effects of H₃PO₄ and H₂O₂ on the composition and electrochemical performance of the samples were investigated in detail. After carbon modification, the discharge capacity of the LiFePO₄ samples can reach 150 mAh/g at 1.0C current rate, and the capacity fade after 100 cycles is only 1%, which is comparable to the commercial LiFePO₄ synthesized with expensive raw materials. The successful conversion of alloy with a high melting point into energy materials at low temperature can be used for other alloys, which decreases energy consumption and waste emissions, shortens the traditional reaction process, as well as improves resource utilization efficiency.

4:15 PM BI01.04.08
A Novel Closed-Loop Process for Recycling LiFePO₄ and Graphite Xiaotu Ma, Mengyuan Chen and Yan Wang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

With the rapid consumption of fossil fuel, lithium-ion batteries (LIBs) are widely used in an ever-growing list of consumer electronics, electric cars, energy storage, and other applications. Although LIBs have reduced environmental problems caused by fossil fuel, the spent LIBs waste has become another big problem. Moreover, the shortage of the supply of materials will be a potential risk for LIBs. Therefore, in order to protect the environment and ensure industry sustainability, it is necessary to develop technologies to recover and recycle spent LIBs efficiently and economically. A novel closed-loop hydrometallurgical process for recycling spent LIBs has been developed in our group. The advantages of this technology include no sorting, high-quality recovered battery materials, high efficiency, and applicability to any size and shape of spent LIBs. Here we show the method for recovering cathode, olivine structured lithium iron phosphate, LiFePO₄ (LFP), and anode, graphite. LFP, with high power capability, low cost, non-toxicity, excellent thermal safety, and high reversibility, has been commercialized as cathode materials. After leaching various spent LIBs and filtration, the mixture of FePO₄, graphite and other impurities can be extracted from the remainder. Then the remainder is leached in a HCl solution and FePO₄ is dissolved as FeCl₃ and H₃PO₄ solution. The mixture solution is used to precipitate FePO₄ by adjusting the pH as the precursor to recover LFP. Similarly, graphite and other impurities remain after filtration. The mixture is washed and dried. Then, the mixture is heated at different temperatures in air to remove impurities and crystallize the graphite. The results show good electrochemical performances of recycled cathode and anode materials. Also, this will reduce the production cost, mitigate the shortage of resources and solve environmental problems.

4:30 PM BI01.04.09
Development of Integrated Technologies for Conversion of Industrial Waste CO₂ to MeOH and Other Value-Added Chemicals via Thermochemical Route Sebastian Chirambatte Peter and Soumyabrata Roy; Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru, India.

Two most imminent scientific and technological problems that the mankind is facing now, is that of energy and climate. The energy production and utilization in modern society is mostly based on the combustion of carbonaceous fuels like coal, petroleum and natural gas the combustion of which produces CO₂, which alters earth’s carbon cycle. 30 billion of tons of CO₂ per year get emitted globally as waste from the carbonaceous fuel burning and industrial sector, which if converted to valuable chemicals have the potential to change the economy of the world. We, in our lab are trying to address both issues and are keen upon translating our innovative technologies from the lab to the industrial and commercial scale. The CO₂ conversion technology is in the developmental stage for commercialization. We are capturing CO₂ from industrial flue stream (of any composition) and thermo-catalytically converting it to value added chemicals/fuels methanol, carbon-monoxide, methane, dimethyl ether, C₂-C₅ & C₅-C₁₁ gasoline hydrocarbons. The end to end conversion product in the thermo-catalytic pathway which could not be commercially realized yet due to problems of low catalytic conversion, limited conversion, energy efficiency of the technology and most importantly high cost of hydrogen. We at JNCASR, are working towards solving these bottlenecks of the overall technology through synthesis of efficient catalysts and designing more energy efficient reactor systems. Catalyst design is at the heart of all these technologies and we are developing customized catalysts and reactor systems for targeted product conversions as per the need of different industries. The catalysts have been synthesized through extensive structure property relation study corroborating with 1st Principle DFT calculations. Advanced CFD calculations are used to design energy efficient reactor systems. Nano structuring in the group 13 element doped C₂Z systems showed highly enhanced conversion and methanol selectivity. At present we are scaling up the end-to-end process, the success of which might lead to opening of new directions in CO₂ conversion technology. We are in the process of taking our technology to the pilot plant scale during the course of which we are running for the 20 million-dollar NRG Carbon Cosia XPRIZE, which is a global competition for promoting commercially viable novel technologies for solving CO₂ and climate change issues.
efficacy is fundamental to meet future food demands in a sustainable way. In the present work, we propose a novel S-fertilizer based on the chemical modification of S8 cyclic structure into a linear amorphous form, more available to oxidizing microorganisms, as an approach to improve the oxidation rate. In order to design this type of material, we applied the recently developed inverse vulcanization technique, a simple copolymerization method that guarantees better processing control for sulfur and allows the formation of functional sulfur-rich polymers. In addition, this technique involves some green chemistry principles, such as the lack of solvent use and excellent atom economy. Soybean oil was selected as comonomer for the reaction as a cheap, non-toxic and renewable feedstock. The S-oxidation achieved by the polysulfide products revealed to be more than 50% superior than S8, and the soybean oil fraction of those materials displayed a role as carbon source for microorganism activity. Therefore, the results could support the sustainable development of a non-conventional S-fertilizer with enhanced efficiency and multifunctional properties.

B101.06.02
Amino-Moiety Designed Novel Ionic Liquids for Highly Efficient and Selective Extraction of Platinum Group Metal from Hydrochloric Acid Solution
Chisato Hanazawa, Atsushi Muramatsu and Kiyoshi Kanie; IMRAM, Tohoku University, Sendai, Japan.

Platinum group metals (PGMs) are of significant importance for modern technologies and advanced materials. However, the continuous high demand and scarcity of PGMs are critical issues. Correspondingly, we need to challenge recycling technologies to fill the gap between demand and supply. Conventional organic solvent extraction is widely applied to the practical recovery method of PGM ions. Recently, ionic liquids (ILs) are considered as an alternative green solvent for PGM extraction. In our previous study, we have reported a metal-selective deprotection-mediated Pd(II) extraction by use of ILs with tetrahydropyran-2H-yl-protected thiol moieties. 1) Also, the functionalization of ILs, regarded as task-specific ILs (TSILs), is a promising technique to introduce PGM extraction ability into ILs. In the present work, we have designed and synthesized novel ILs with amino moieties in order to develop the selective recovery method of Pt, Pd, and Rh ions for industrial use. All TSILs (Cn (n means alkyl chain length of dialkylamines) forming a pale-yellow IL state at room temperature were immiscible in water. We next investigated the PGM extraction ability of Cn for Pd(II), Pt(IV), and Rh(III) ions. The initial PGM ion concentrations in the aqueous solutions were adjusted to 100 ppm. Influence of HCl concentration on the extractability was examined in the range from 0.30 M to 4.0 M. The extraction experiments of the PGM ions into the Cn-based IL phases (400 mg) from the aqueous phase (2.0 mL) was carried out by mixture of the solution in a vial, followed by vigorous shaking. The extractability was evaluated through the difference of PGM concentrations in the aqueous phase before and after extraction with IC-PEF measurements. Both dihexylamino-substituted C6 and dioctylamino-substituted C8 exhibited excellent extractability (> 80%) towards Pt(IV) and Pd(II) ions in HCl concentration range from 0.30 to 4.0 M. However, the extractability of dibutylamino-substituted C4 was significantly decreased with an increase in HCl concentration, possibly because of the instability of C4 at higher HCl concentrations. The extractability to Rh ions reached at 73% at maximum for C8 in 3.0 M HCl solution, which exceeded that for C6, 51%. We considered that the high extractability of C8 was attributed to the high hydrophobicity. The extraction/back-extraction abilities of Cn were also investigated.

References

B101.06.03
Efficient Photothermal Water Evaporation from Inked Filtration Paper
Zhiqiang Wang1, 2 and Ming Su1; 1Northeastern University, Boston, Massachusetts, United States; 2Tianjin Normal University, Tianjin, China.

Water evaporation with natural solar energy attracts much attention due to its wide applications as well as energy saving. However, this heating process is very slow under 1 sun shining. So current technology, which needs a large surface, collects the solar irradiation as much as possible, and concentrates the heat to accelerate this process. For future technology, evaporation upon local heating at air-water interface can be facilitated with energy saving, because such locally temperature gradient in the air-water system, compared to the heating scheme of bulk water, can effectively increase the heat utilization. Apparently, the implementation of such emerged photo thermal desalination technique is highly dependent on exploration of excellent photo thermal materials to absorb and evaporate water efficiently. In this work, we reported a low cost high efficient evaporating material. Such an evaporating system achieved an extremely high water production rate of 1.34 kg h−1 m−2 and 89.9 % energy efficiency under 1 sun radiation. The excellent performance is attributed to the combination of multiple properties simultaneously exhibited by this as-prepared material, including its intrinsic blackbody-like high absorption, extremely low thermal loss to environment (low evaporating temperature and 1D water transporting), and automatic water transportation to the evaporating surface by capillary force through the huge microchannels. We also found the general relationships, not limited in our materials but all solar evaporating materials, between evaporating rate, energy efficiency and evaporating surface temperature. Following this relationship, people may control the steam temperature and the evaporating rate for some purpose, respectively.

B101.06.04
Improving the Efficiency of N Fertilizers Using Thermoplastic Starch-Modified with Molecules High N Levels
Amanda S. Giroto1, Caue Ribeiro de Oliveira1 and Gelton G. Guimaraes2; 1LNNA, EMBRAPA Instrumentation, São Carlos, Brazil; 2Epagri, Itajaí, Brazil.

Nitrogen (N) deficiency has been considered as the most important limiting factor for crop yield, explaining the high N fertilizer application worldwide. Among all the N-containing molecules urea is the most used due to its high N content, however, its efficiency is limited by losses such as leaching and volatilization. For this reason, we propose the production of a fertilizer based in urea-melamine-thermoplastic starch using a one-step method aiming to control the nitrogen release as a nutrient. The extrusion process used has been showed to be a simple, continuous, high throughput method, capable to promote melamine incorporation, which was responsible to increase the interaction among urea and starch. The results reveal that melamine plays an important role as structure modifier, increasing the effective use of available N for plants in pot experiments. The characterization shows that this material is a polymeric blend, possible to be processed by continuous method (extrusion) leading a plastic granule, with high homogeneity and high nutrient contents. Pot trials (using maize) shown that this material increases the N efficiency (based in the actual available N) leading to a significant nutrient residual in soil useful for future cultures, confirming that this product might replace with advantages the conventional N fertilizers.

B101.06.05
Investigating the Effects of Different Spun-Cast and Molded Polyactic Acid (PLA) and Polystyrene (PS) Composites on the Proliferation, Differentiation and Biomineralization of Dental Pulp Stem Cells
Kuan-Chieh Feng1, Ethan Ho2, Bhuvna Murthy3, Rushil Patel4, Antony Deluca5, Wenqi Zhao6, Benjamin Chang7, Nicholas Zumba8, Chung-Chua Chiang9, Marcia Simon6 and Miriam Radulovich1; 1Stony Brook University, Stony Brook, New York, United States; 2Northfield Mount Hermon School, Gill, Massachusetts, United States; 3Huron High School, Ann Arbor, Michigan, United

York, United States; 2Northfield Mount Hermon School, Gill, Massachusetts, United States; 3Huron High School, Ann Arbor, Michigan, United

States; 4Youngstown State University, Youngstown, Ohio, United States; 5 unfold, 6Stony Brook University, Stony Brook, New York, United States; 7Northfield Mount Hermon School, Gill, Massachusetts, United States; 8Huron High School, Ann Arbor, Michigan, United

York, United States; 2Northfield Mount Hermon School, Gill, Massachusetts, United States; 3Huron High School, Ann Arbor, Michigan, United

States; 4Youngstown State University, Youngstown, Ohio, United States; 5 unfold, 6Stony Brook University, Stony Brook, New York, United States; 7Northfield Mount Hermon School, Gill, Massachusetts, United States; 8Huron High School, Ann Arbor, Michigan, United

York, United States; 2Northfield Mount Heron School, Gill, Massachusetts, United States; 3Huron High School, Ann Arbor, Michigan, United
Polymers are known to be more combustible than other structural materials, and hence flame retardant formulations are frequently added. Recently it has been shown that many of these formulations, especially those containing halogenated compounds, are toxic and leach into surrounding water and soil. This concern is even more pressing when biodegradable polymers are used, where the degradation process facilitates the environmental release of the toxicant. Here we report on a study of the toxicity of resorcinol diphosphate, RDP, a phosphorous based flame retardant additive. RDP is easily compounded into homopolymers or polymer blends when adsorbed onto clay, where it also facilitates compatibilization. In this study, we show that when included into PLA, RDP appears to have no deleterious effects on cell adhesion, proliferation, and differentiation. When RDP-Clay is added to polystyrene, it has an advantageous influence. Cells do not adhere to PS, but when RDP Clay is added, cell plating efficiency and cell proliferation is drastically improved and the doubling time is comparable to that of the cells plated on PS. In contrast to the cells on PS, those on the PS-RDP-Clay and PLA-RDP-Clay scaffolds underwent differentiation, where large amounts of hydroxyapatite deposits were found. With the appearance of what is believed to be hydroxyapatite deposits (biomineralization), RAMAN spectroscopy will be used to determine any possible developments of an extracellular matrix on the PS-RDP-Clay and PLA-RDP-Clay scaffolds. Additionally, RT-PCR will be conducted on days 28 and 42 in order to evaluate the presence of all genes that may be associated with osteogenic or odontogenic differentiation. Even though further in-vivo testing is required, these results indicate that the probable toxicity of RDP is low, since RDP-Clay preserves both cellular proliferation and function.

B101.06.06
Improved Dispersion of Asphaltenes in Heavy Oil by the Addition of Base and Either Acidic Copolymers or Aliphatic Compounds Terminated with Functional Groups
Myong-Guen Jo, Kwang-Hwan Ko and Joon-Seop Kim; Chosun University, Gwangju, Korea (the Republic of).

Recently, we have been attempting to develop the dispersants for the improved dispersion of the asphaltenes that presented in heavy crude oil and became gel or precipitated upon the agglomeration. It has been known that effective dispersants for asphaltenes in heavy crude oil should have the following factors: a proper amounts of aromatic and functional groups that can interact with those of the asphaltenes, low molecular weight (MW < 10,000) because of the better solubility to heavy crude oil, amphiphilicity for the improved dispersion because the asphaltenes have both polar and non-polar units, and alkyl chains of proper lengths for the better miscibility with heavy crude oil. Thus, in the course of the present work, we prepared two types of dispersants, analyzed their chemical structures, and determined the effects of the dispersants on the dispersion of the asphaltenes. The two types of the dispersants were low MW styrene copolymers and various aliphatic alcohol, carboxylic acid, or amine compounds. In the first part of the work, we compared the effects of the types of the functional groups of the oligomeric styrene copolymers on the asphaltenes dispersion. It was found that the sulfonic acid groups were better than the carboxylic acid groups on the dispersion. In addition, it was also observed that the more carboxylic acid groups in the acidic unit enhanced the dispersion. Furthermore, as expected, with decreasing MW of oligomers, the dispersion behavior of the asphaltenes became more improved. In the second part of the work, we investigated the effects of the addition of the aliphatic acids on the asphaltenes dispersion. It was found that when the types of functional groups and alkyl chain lengths of aliphatic compounds did not affect the asphaltenes dispersion in the heavy oil significantly. However, it was observed that the addition of NaOH to the heavy oil containing aliphatic alcohol or carboxylic acid compounds enhanced the dispersion of asphaltenes strongly. Interestingly enough, even the addition of NaOH to the heavy oil also improved the asphaltenes dispersion, at least to some extent. Furthermore, it was seen that the effect of the NaOH addition to the heavy oil containing aliphatic acids became more pronounced than that to the heavy oil containing aliphatic carboxylic acids. Especially, the NaOH addition improved the asphaltenes dispersion more significantly in the heavy oil containing 2-ethylhexyl alcohol than normal alcohols, having shorter or longer alkyl chains. Thus, we have been trying to find the reason why the base, i.e. NaOH, influences the asphaltenes dispersion; we will present our interpretation on the results.

B101.06.07
Processing of Sulfur–Phosphate Composites—Use of Synergy to Improve the Fertilization Roles
Gelson G. Guimarães1, Amanda S. Giroti2, Rodrigo Klaic2 and Caue Ribeiro de Oliveira3; 1EPAGRI-EEI, Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina, Itajaí, Brazil; 2Embrapa Instrumentação, Empresa Brasileira de Pesquisa Agropecuária, São Carlos, Brazil.

An environmentally-friendly alternative to phosphate fertilization is the supplementation of P from rock phosphates, however, these sources do not have P readily available to plants. In this sense, the reduction of particle size from grinding techniques have been studying to increase the solubility of the phosphate minerals. However, a difficult presented during this process is the tendency of agglomeration of the particles, preventing them from maintaining nanometric dimension. Elemental sulfur (S) comes up as a dispersant potential that through the acidity generated by the S oxidation to sulfate (SO4^2-) can aid in the solubilization of mineral phosphates. The fungus Aspergillus niger has the ability to oxidize sulfur, besides to have a high production capacity of organic acids such as citric acid, oxalic acid, and gluconic acid that increased the solubilization of phosphorus. Thus, A. niger presents two mechanisms that may favour the solubilization of phosphates: first by natural acidification provide by oxidation of S and the second by organic acids production. In this work, a composite was designed based on a matrix of S^0 prepared by low-temperature processing, reinforced by rock phosphate (P) particles acting as P fertilizer, and with encapsulation of Aspergillus niger as an oxidizing microorganism. The effects of dispersion of the phosphate particles on the elemental sulfur matrix and starch were evaluated, as well as the natural acidification provided by the oxidation of S^0 and the production of organic acids in the solubilization of P from the natural phosphate. In addition, after the release of P and SO4^2-, from the composite-fertilizer incubated in the soil, the dynamics and interaction of P with the colloidal fraction of the soil were analyzed using P K-edge X-ray absorption near-edge structure (XANES). The inclusion of A. niger provided a means for improved S^0 oxidation and concomitant faster P release. The proposition of a granule fertilizer with a simultaneous dispersion of particles of phosphate rock, elemental sulfur, and A. niger spores can allow the reduction of pre-processing (e.g., for soluble fertilizer production) and reduces the indirect costs related to the conventional acid solubilization process and waste treatment. Soil inoculation studies, probed by XANES, indicated that the composite structure played a role in nutrient fixation and immobilization, showing that nutrient dynamics was governed by the local pH. This fully integrated material (a smart fertilizer) is an innovative strategy for eco-friendly agronomic practices, providing high nutrient delivery with minimal source pre-processing.

B101.06.08
Nanocomposites Fertilizers Biologically Activated for an Efficient Supply of Sulfur and Micronutrients to Plants
Rodrigo Klaic1, 2, Amanda S. Giroti1, Gelson G. Guimarães1, Caue Ribeiro de Oliveira1, Teresa C. Zangirolami1 and Cristiane S. Farinas1; 1Embrapa Instrumentação, Empresa Brasileira de Pesquisa Agropecuária e Extensão Rural de Santa Catarina, Itajaí, Brazil; 2EMBRAPA-EEI, Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina, Itajaí, Brazil; 3Department of Chemical Engineering, Federal University of São Carlos, São Carlos, Brazil.

Many commercial fertilizers are based on the application of elemental sulfur (S^0) and oxides metallic to supply sulfate and micronutrients to plants. However, the soil ability to solubilize oxides and promote the S-oxidation is low, since it is dependent of the presence of microorganisms capable of carrying out such biological reactions. To overcome this limitation, different strategies have been explored to improve the availability of sources of nutrients such as S^0 or oxides of P. An interesting alternative is the application of microorganisms to promote the oxides solubilization and...
the S-oxidation in the field. The filamentous fungi Aspergillus niger has been applied to promote the phosphorus solubilization from phosphate minerals as well as bioremediation and bioleaching of metals from mining sites. Besides, previous studies also revealed that A. niger can promote the biological oxidation of S° as well as the oxides solubilization. However, the major challenge is to develop a material that would favor the integration of both oxides particles and microorganisms in a single granule to promote oxides solubilization that could be processed and stored, thus when applied in the field the granule would be activated to allow microorganism to solubilize the oxide, this is an innovative concept of "biofertilizer in granule". Herein, we proposed to produce a composite (granule) based on the dispersion of nanoparticles of S° and oxides in a polysaccharide matrix (polymeric gelatinized starch) with simultaneous encapsulation of A. niger spores. Three oxides model (ZnO, MnO and CuO) besides S° were used to produce different configurations of composites. The oxides were physical-chemical characterized as well as the composites produced. Experiments were performed to evaluate the effect of bio-activation of the composite by A. niger and consequent oxides solubilization and S-oxidation in a liquid medium and in soil. The results showed that all the different composites produced (St/Zn, St/Mn, St/Cu, St/Mix and St/Mix+S+) increased solubility of the dispersed material. The effects of dispersion of the oxides and S° particles in starch matrix was analyzed using field emission gun scanning electron microscopy and X-ray microtomography, a high dispersion of the particulate materials was observed with low agglomerates formation. Nevertheless, the St/Mix+S+ show the best results for oxides solubilization, besides being a source of multi-nutrient (S, Zn, Mn and Cu). The St/Mix+S+ also showed considerable shelf time and when evaluated under greenhouse conditions, it showed an efficiency comparable to the experiment carried out with soluble commercial fertilizer for the cultivation of Italian ryegrass (Lolium multiflorum Lam.). This strategy opens a new route for development of smart fertilizer capable of making feasible the use of source of micronutrients of low solubility for plant nutrition.

B101.06.09
Removal of Fluoride from Groundwater Using Alfu Metal Organic Framework (MOF) Impregnated Polyacrylonitrile Beads
Sankha Karmakar, Debasish Roy and Sirshendu De; Indian Institute of Technology (IIT) Kharagpur, West Midnapore, India.

Novel mixed matrix hollow beads were prepared by phase inversion technique using polyacrylonitrile (PAN) as base polymer and aluminum fumurate (Alfu) metal organic framework (MOF) as additive. The beads were characterized in terms of surface morphology, surface charge, surface area and contact angle. With the incorporation of the hydrophilic Alfu MOF, contact angle of the corresponding beads decreases from 80° to 51° indicating an increase in hydrophilicity. The 10 wt% incorporated beads sustained upto 150 hours of operation with fluoride concentration of 10 mg/l at flow rate of 1 l/day. Regeneration study and leaching of aluminum were also investigated.

B101.06.10
Exploring the Stability and Electronic Properties of Za Doped Hematite Surfaces for Photoelectrochemical Water Splitting
Joseph Simfukwe1,2, Refiwi E. Mapasha1, Artur Braun1 and Mmantsae Diale1; 1University of Pretoria, Gauteng, South Africa; 2Physics, Copperbelt University, Kitwe, Zambia; 3Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Switzerland.

First principles studies of Zn doped (0001) and (012) surfaces of hematite for enhanced photoelectrochemical water splitting have been carried out. Doping was confined to planes in close proximity to the termination region, precisely from the top most layer to the third inner layer (plane P1, P2 and P3) of Fe atoms. The two surfaces and the three doped layers were found to be thermodynamically stable and would prefer oxothionene formation under oxygen rich conditions. The analysis of electronic properties reveals that even with mono doping of Zn on the top most layer (P1) of the (0001) α-Fe2O3 surface, the band gap can be decreased without impurity states in the band gap which normally acts as recombination centres. The doping of Zn atom on P2 and P3 (second and third layer respectively) of the (012) surface narrowed the band gap from ~1.43 eV to ~1.0 eV for both systems, without any impurity states in the band gap. Furthermore, the conduction band minimum (CBM) of P2 and P3 of the (012) surface also became wavier and delocalized suggesting improved electron mobility of hematite, while the CBM of the (0001) surface shifted upward between ~0.05eV and ~0.3 eV. The observed upward shift in the CBM is likely to enhance photoelectrochemical splitting of water with a smaller application of external bias. Analysis of the charge density difference plots showed concentration of charge mainly at the top of the surface, which is the termination region. This suggests facile transfer of charges to adsorbed molecules due to the closeness of the charges to the adsorbate. The concentration of the charges at the surface, the decreased band gap and the absence of recombination centres within the band gap suggest improved photocatalytic activity of the Zn doped α-Fe2O3 surface.

B101.06.11
Novel Fluorescent Polymer Sensor for Nitroaromatics Explosives Detection in Solution and Vapor Phase
Vishal Kumar and Soumitra Satapathi; Indian Institute of Technology Roorkee, Roorkee, India.

The highly sensitive and reliable detection of explosives such as nitro substituted compounds (DNT, TNT and TNP) is of paramount importance for civilian and military security. NACs are also recognized as poisonous or carcinogenic explosive chemicals to the environment. Currently, explosive detection either relies on canines or highly sophisticated measurement techniques, such as mass spectrometry, gas chromatography, Raman spectroscopy, etc. High cost and/or complexity of these techniques limit their wide availability, especially in the field. Compared to those fluorescent polymers are particularly interesting for fluorescence based rapid detection as they exhibit large signal amplification due to the delocalization and rapid diffusion of excited states throughout the individual polymer chains. Moreover, the fluorescence polymers having high PL quantum efficiency, favorable redox potential and easy synthesis scheme need to be explored which can act as excellent electron donor for rapid electron transfer to NACs having electron-withdrawing nitro groups on the aromatic ring in order to make them as efficient optical sensor with ultra-high sensitivity.

Here, we report the synthesis and multimodal sensing applications of a highly emissive and electron-rich alanine based dansyl tagged copolymer P(MMA-co-Dansyl-Ala-HEMA) (DCP) which exhibited high sensitivity and selectivity towards DNT, TNT and TNP in solution at lower range of μM level and also with saturated vapour of NACs. The high quantum yield of the co-polymer (77.3%) makes it an ideal candidate for sensing in solution as well as in vapor phase. In solution, the fluorescence signal from DCP co-polymer gets significantly quenched upon addition of aliquots of DNT, TNT, and TNP caused by photo-induced electron-transfer i.e. quantified by plotting Stern–Volmer plot (KSV = 1.1×105 M⁻¹, 1.3×105 M⁻¹ and 1.6×10⁴ M⁻¹ for DNT, TNT and TNP). The quenching mechanism was further established by time-resolved fluorescence and steady state absorption spectroscopy which was found to be predominantly dynamic in nature as lifetime of polymer (14.9 ns) is reduced to 13.9, 13.9 and 13.8 ns for DNT, TNT and TNP. The energetics of sensing process was calculated by Density Functional Theory (DFT) studies this is also in good agreement with the obtained result. To explore the possibility of using the fluorescent co-polymer as sensor array, a prototype thin film polymer sensor was fabricated using drop-casted thin film of DCP which was able to detect saturated nitroaromatic vapor in real time with high selectivity. The initial fluorescence intensity of the 20 nm thin film of DCP was quenched to 19% for DNT, 13% for TNT and 4% for TNP in just 2 min.

In summary, this work opens up a novel approach for designing light weight and compact prototype sensor for field use as well as for environmental monitoring.

References
Nanoscale metamaterials exhibit extraordinary optical properties and have been proposed for various technological applications such as biosensing, superlenses, subwavelength optics, etc. In this talk, our recent efforts in developing a new class of novel nanoscale 2-phase hybrid metamaterials in vertically aligned nanocomposite (VAN) form has been reviewed. Such hybrid systems consist of transition metal nitrides and metals. Taking advantages of the long term stability and thermal stability of transition metal nitrides, we have demonstrated highly stable and mechanically strong metamaterials systems with tunable optical properties, including highly anisotropic reflectance, obvious non-linear optical properties indicating inversion symmetry breaking of the hybrid material, large permittivity tuning and negative permittivity response over a broad wave length range, and superior mechanical strength and ductility. The study demonstrates the novelty of the new hybrid plasmonic scheme with great potential in versatile material selection, and, tunable nanopillar spacing and dimension, all important steps towards future designable hybrid plasmonic materials.


8:30 AM *BI01.07.02*

**Introducing Novel Hybrid Ion Exchange Membrane and ANAMMox Bacteria to Improve Nitrogen Removal Efficacy of Microbial Fuel Cell**

Gourav D. Bhowmick, Koushik Adhikary, Makarand M Ghangrekar and Arunabha Mitra; IIT Kharagpur, Kharagpur, India.

Emission of greenhouse gases due to the burning of fossil fuels led to climate changes drastically over the last few decades, which drives the researchers from all around the globe to seek for alternative renewable sources. On the other hand, high energy consuming wastewater treatment systems need to be replaced with less energy demanding or even energy harvesting treatment systems as wastewater is considered to be the reservoir of high energy content. Microbial fuel cell (MFC), a bio-electrochemical system (BES), can be a reliable alternative over the conventional wastewater treatment systems by simultaneously producing bio-energy through oxidising organic matter present in wastewater anerobically using electrogenic bacteria as biocatalyst. In MFC, removal of nutrients from wastes have largely focused on exploiting organic matter cycle reactions, whereby reactive forms of nutrients are converted to unreactive simpler forms e.g. ammonia to inert nitrogen gas. To remove excess nitrogen present in wastewater, it is required to incorporate processes that primarily involves the elimination of NH₃ followed by reduction of NOₓ. Hence establishment of suitable conditions to facilitate both nitrification and denitrification is necessary. A hybrid membrane structure is developed to permit the exchange of both anions and cations in either way from anode to cathode of the MFC. The cation exchange part of the hybrid membrane was made of ceramic separator blended with 20% Montmorillonite as excellent cation exchanger and anion exchange part with poly(2,6-dimethyl-1,6-phenylene oxide) (PPO) via bromination and subsequent quaternization. Fish processing wastewater was used as target wastewater with chemical oxygen demand (COD) to nitrogen (N) ratio (C/N) of less than one g COD/g N for concurrent denitrification and ANAMMox were assessed in two different MFCs with a working volume of two litre each. MFCs were fabricated one with only cation exchange membrane (CEM) and another one with as fabricated hybrid ion-exchange membrane (HEM) named as R-1 and R-2, respectively. The polarization study revealed the maximum power density of 252 and 163 mW/m² with the respective coulombic efficiency of 18.7 ± 1.2 % and 14.8 ± 1.4 % for R-1 and R-2. The marginally lesser power production of R-2 was because of the competition for electron donor (organic matter) inside the anodic chamber for concurrent denitrification and ANAMMox process. The COD removal efficiency was observed to be 81 ± 3 % and 86 ± 4 %, respectively for R-1 and R-2. The ammonium (NH₄⁺) and total kjeldahl nitrogen (TKN) removal efficiency were found to be around 88 % and 92 % for R-2, which were almost two times higher than R-1 (46 % and 50 %, respectively) conforming hypothesis of introducing HEM with ANAMMox bacteria for treating nitrogen rich fish processing wastewater with superlative efficacy compared to the existing treatment systems for real-life futuristic applications.

8:45 AM *BI01.07.03*

**A Direct Z-Scheme Enhanced Photocatalytic CO₂ Reduction Over g-C₃N₄ Under Visible Light by Coupling of FeWO₄**

Reshma Bhosale¹, Sharsti Jain¹, Santosh Kumar² and Satischandra Ogale¹; ¹Indian Institute of Science Education and Research Pune, Pune, India; ²University of Bath, Bath, United Kingdom.

With increase in the energy demand and thereby the increased consumption of fossil fuels huge amount of anthropogenic CO₂ is released into the atmosphere leading to green-house effect and global warming. One approach which is being actively pursued to address this problem is CO₂ reduction to value added fuels using solar energy which is abundantly available. Many semiconductor materials are investigated for photocatalytic CO₂ conversion. Among them, a new and novel organic photocatalyst, namely graphitic carbon nitride (g-C₃N₄) has emerged as a sustainable, cost effective and environmental friendly semiconductor. It is a promising candidate which absorbs in the visible region (band gap of 2.7 -2.8eV) and has favorable band alignment. Nevertheless, the photocatalytic efficiency is still moderate due to rapid recombination of photogenerated carriers before they could participate in surface reactions. Therefore, coupling of C₃N₄ with other semiconductor has proved to be an effective pathway to promote the activity through the spatial separation of excited electrons and holes across the interface.

In the present work, we introduce a new visible light photocatalyst material FeWO₄ (band gap 1.8-2.5eV) which belongs to the fascinating family of wolframite type system with monoclinic structure. To the best of our knowledge, FeWO₄ has not yet been investigated in the field of photocatalysis. In our work FeWO₄ was synthetically coupled with g-C₃N₄ by wet chemical method. The obtained composite exhibited direct Z scheme mechanism due to appropriate band matching of FeWO₄ with respect to g-C₃N₄ band edges as confirmed by Mott-Schottky plots and Diffuse Reflectance Spectroscopy. Such a Z-scheme without any mediator is a highly beneficial system in the photocatalysis context, as the electrons with high reduction ability in photosystem PS-I and holes with high oxidizing ability in PS-II are preserved and subsequently utilized for respective surface reactions. Therefore, the composite of FeWO₄ with g-C₃N₄ showed an impressive yield of 30µmol/g of CO₂ representing a six-fold increment in photocatalytic CO₂ reduction as compared to pristine C₃N₄. Also, the composite was observed to be stable for CO evolution till 18 hours over which it was tested.
Evaporation from micro/nano structures is a ubiquitous phenomenon which plays an important role in nature and industrial applications, such as transpiration in plants, mammalian perspiration, electronic cooling and water desalination. Thin film evaporation from nanoporous membranes is a promising thermal desalination approach because it utilizes the passive capillary pumping of liquid to the evaporating interface and allows for high heat transfer rates due to the large evaporating area in addition to the capillary pumping driving force. In this study, solar energy was used as a heat source to evaporate seawater through in-house fabricated polyvinylidene fluoride (PVDF) nano/micro-porous membranes. Compromising between the available area for evaporation via changing pore size and the available material for conductive transfer of heat to the liquid thin film is complicated. Since more porous membrane increases the evaporation surface area and at the same time this leads to having less conductive material for heat transfer which at the end will reduce the evaporation rate. The main objectives of this study are, firstly to investigate the pore size effect on the vapor flux by fabricating flat-sheet membranes via a phase inversion process with 12 wt% of PVDF and 500 µm thickness, and varying preparation parameters such as relative humidity and exposure time to achieve different pore sizes. Secondly to examine the thermal conductivity effect by blending different concentrations of fumed silica (1, 2, 3, 4, or 5 wt%) with the polymeric solution. The fabricated membranes were characterized by scanning electron microscopy (SEM), contact angle analyzer (CA), Fourier transform infrared spectroscopy (FTIR), capillary flow porometry (CFP), porosity and AFM, to further understand the observed thin film evaporation effects. The preliminary results showed, the mean flow pore diameter of the fabricated membranes are 117.2 nm, 123.3 nm and 206.6 nm and there porosity 28.4 %, 46% and 33% respectively. Also, the contact angle analyzer proved the hydrophobicity of these fabricated membranes since the contact angle was found to be above 95°.

Furthermore, this study is aiming to show that the polymeric membrane can be implemented as an alternative effective material in thin film evaporation applications with lower cost compared to commercial ceramic alumina anodiscs (AAO).

9:15 AM

Development of Solar Absorbing Nanoporous Membranes for Direct Solar Seawater Desalination

Arwa A. Alishareif1, Mona B. Bahnman1, Faisal Almarzooqi1 and Evelyn N. Wang2; Khalifa University, Abu Dhabi, United Arab Emirates; 2Massachusetts Institute of Technology, Boston, Massachusetts, United States.

In nature solar energy is the primary driving force for the formation of fresh water. Solar based desalination is an attractive technology to meet the ever-increasing water demand.

In this study we develop efficient and optimized nanoporous membranes for direct solar desalination of seawater. We developed black-body like membranes that maximize solar absorption via the structural design and coating. The structural design involves hierarchical shapes that increase roughness and hence forth increase surface area available for solar energy absorption. This is done via simple and low-cost phase inversion membrane fabrication, developed within our labs. The blackbody-like membranes we develop should poses high thermal conductivity, which is the other objective we focus on in this investigation.

To fabricate our envisioned solar absorbing membranes, we developed two distinct approaches, 1) flat-sheet membranes via phase inversion and 2) chemical vapor deposition. In the first, we use polyvinylidene fluoride as the active membrane material. We modified it to incorporate micro/nano particles which are known to have high surface area and good optical and thermal properties. These are graphene nanoplatelets and activated carbon. In the second, we use Anodised Aluminium Oxide (AAO) membranes as the base material and grown high absorbance blackbody like multilayered 3-dimensional graphene coating.

The absorbance of each membrane was measured using a UV(vis) spectrometer. The structures of the prepared membranes were characterized and observed by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM). The Meanflow Pore Size (MPS), Bubble Point Pore Size (BP) and Pore Size Distribution (PSD) were measured using a capillary flow porometer. Also, the porosity was calculated experimentally using a gravimetric method. Contact angle measurements were also performed to find out the hydrophobic/hydrophilic nature of the membranes.

All membranes are tested in a device fabricated specifically for the purpose of this study. The membranes are tested for their ability to evaporate seawater using direct sun light. Measurements of mass fluxes and temperatures are taken, and the overall efficiency of the device is calculated. This study aims at demonstrating these solar absorbing membranes as the core enablers for future direct solar desalination technologies.

The absorbance of the graphene coated AAO was measured using a UV(vis) spectrometer and was found to be 97%. The fabricated membrane with activated carbon (3.5,7g) where characterized and measured the porosity and were obtained to be 35.9%, 65.3%, and 56.8%. The MPS was measured at around 5.61, 6.95, and 2.88 µm for 3, 5 and 7g of activated carbon and also The BP was measured 14.72, 20.83 and 14.61 µm respectively. The complete set of results will be included in the full submission.

9:30 AM

Application of Ion Exchange Membranes in Enhancing Algal Production Alongside Desalination of Saline Water in Microbial Fuel Cell

Neethu B. Pankaj Sarkar and Makarand M Ghangrekar; Indian Institute of Technology Kharagpur, Kharagpur, India.

In the present world scenario where water scarcity around the world coincides with fresh water consumption, there is an increasing demand for a technology that can provide clean water. Microbial fuel cells (MFCs) can be used to treat wastewater along with generation of bioenergy in the form of electricity using microorganisms and natural biological processes. The demand for fresh water and clean energy is driving the need for converting an MFC into an algae-based Microbial desalination cell (MDC) that can support algal growth in addition to desalination of saline water. Ion exchange membranes (IEMs) are most commonly used for desalination of saline water and is a promising tool which, when oriented properly, can be applied in the MDC for algal production. In this study, a five-chambered MDC was designed by placing an alternating series of cation exchange membranes and anion exchange membranes between an anodic compartment (Synthetic wastewater) and cathodic compartment (Chlorella Pyrenoidosa). The middle compartment, either side of which constituted concentrated chamber, was fed with saline water with two different TDS concentrations, namely 2.5 g/L and 5.0 g/L. Algal-based MDC was analyzed for wastewater treatment efficiency, desalinating capacity, power generating efficiency and algal production and overall performance was compared with MDC without algae in catholyte. A maximum operating voltage of 125 mV was produced during the operation of algal-based MDC with TDS of 5 g/L in the middle chamber against 96 mV for TDS of 2.5 g/L due to change in internal resistance. Similarly, a better performance in terms of electricity generation and TDS removal was observed in MDC assisted with the algal cathode as compared to the one without algae in catholyte. The algal-based MDC with 5 g/L TDS in middle chamber exhibited the best results among all other combinations giving a maximum power density of 45.52 mW/m² and TDS removal rate of 71 ± 2 %. The five-chambered MDC also demonstrated effective algal growth in the cathodic chamber and simultaneous TDS removal in desalination chamber along with energy recovery using photosynthetic oxygen, produced by microalgae, as the cathodic electron acceptor. Based on this experimental performance evaluation, it can be inferred that algal-based MDC can provide a promising and sustainable approach for wastewater treatment with the capability of simultaneous desalination, algal production, and electrical energy recovery.

9:45 AM
Red Mud-Fly Ash-Based Geopolymer as an Alternative Construction Material

Zhaotong Yang and Jianyu Liang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Today, the concrete industry is one of the largest producers of greenhouse gases, emitting 5% of the man-made CO2 every year. To reduce this carbon footprint, geopolymers have attracted extensive interest as potential alternatives to Portland cement (OPC) the material traditionally used in structural concrete. Depending on the synthesis recipe of the geopolymer, the manufacturing process may be much less energy intensive and have a very small carbon footprint when compared with the OPC production process. Many different raw materials have been used to synthesize geopolymers, such as various natural minerals and industrial byproducts that are high in both amorphous silica (SiO2) and alumina (Al2O3). A new synthesis method for geopolymer, sourced from two hazardous industrial wastes, red mud (RM) slurry and fly ash (FA) powder, has been developed in this study. Thermal properties including mechanical behavior, thermal shrinkage, weight loss, microstructure change, and crystallization of the RMFA geopolymers were investigated. After curing for fourteen days, RMFA geopolymers exhibited compressive strengths greater than 17MPa. Reaching this strength is significant, since the ACI (American Concrete Institute) building standards require a minimum of 17MPa for use in structural cement. It should also be noted that in geopolymer materials, as with OPC, the strength continues to increase over time. Thermal tests found the materials to be thermally stable up to 600°C, with the retention of mechanical strength. The synthesis process developed in this study provides significant advantages: the removal of the energy-intensive drying process and the repurposing of two overabundant industrial wastes.

A Novel Fire Retardant Solution to Mitigate the Onset of Wildfires

Yuan Xie1, Xianghao Zuo1, Joshua Vilkas2, Pik Hoi Lam1, Nicole Jacobsen3 and Miriam Rafailovich1; Stony Brook University, Stony Brook, New York, United States; 2Hebrew Academy of Nassau County High School, Uniondale, New York, United States; 3Wilson Area High School, Easton, Pennsylvania, United States.

The dangers of wildfires are brought to attention as they frequently ravage wooded areas like California and Greece. The current resolution is reactive rather than preventive, and involves dropping chemicals after the start and expansion of the fire. Additional concerns include the application of non-eco-friendly ingredients to quench the fires. The goal of this research is to engineer aqueous solutions that are sprayed onto leaves prior to the onset of fires to inhibit fires from spreading uncontrollably. Here we describe the results of a formulation that was used on the leaf species, Cornus kousa, a subspecies of the Cornus, or Dogwood family.

The experiments were conducted on three categories: fresh picked leaves, oven-dried leaves, and naturally fallen leaves. FTIR analysis of the leaves indicated that fresh leaves consisted of water (2/3 of the mass) while the dried leaves were predominantly of cellulose. Fresh leaves were coated with a thick waxy layer, while the drying process removed some of the surface wax. Different solutions were first formulated where contact angle goniometry was used to optimize the wetting properties for both dry and fresh leaves and viscometer was used to determine the optimal viscosity for spray applications. The solutions were then applied by spraying onto fresh leaves and piles of dried leaves. Burning tests were performed both on leaf piles, and individual leaves, using a propane torch. The flame was applied continuously for five seconds and then removed, and the time to self-extinguish was recorded together with the extent of the spread of the fire.

Results indicated that for fresh leaves, in the absence of the spray, the fire persisted till at least ½ of the mass was consumed and for the dried leaves the entire mass was consumed before the fire was removed. With the addition of the spray, the fire self-extinguished immediately after the flame was removed, and the fire during the application of the flame consumed less than 25% of the mass. Similar results were obtained for both wet and dry leaves. FTIR and RAMAN spectroscopy was performed at each stage in the testing in order to determine the underlying mechanism leading to the flame retardant properties.

The toxicology of the solution and the individual components is being tested on grass and vegetable plants. Preliminary data, thus far, had not found any significant differences in root size or germination rate between the control plants culture and those watered with the undiluted solutions. The results of ongoing experiments regarding sequestration of the chemicals in the leaves and fruits will be presented.

3D Printing for a Sustainable Approach to Constructions

Marcio Stefancich1, Berry Hendriks2, Alessandro Zampieri1 and Waduh Alzahmi1; 1Dubai Electricity and Water Authority, Dubai, United Arab Emirates; 2Cybe Constructions, Oss, Netherlands.

While 3D printing is having a large impact on many industrial sectors, its contribution in the constructions sector is still in its infancy. Construction is one of the bigger contributors to greenhouse gases and thus, an increase in the efficiency of this process can have a significant societal and environmental impact.

However, dimensional scale factors, optimal printer and nozzle configurations, and, most importantly, the properties of the printable materials (e.g. cement) are still open questions ripe for developments and active research.

Moreover, societal acceptance of a completely novel concept for constructions, where delivery times and construction methodology are substantially different from a model that was substantially unchanged in the last several hundreds of years, is still uncertain.

From a technological point of view, the cement commonly used in construction has long setting times and rheological characteristics that make the direct 3D printing process complex. The use of specialty additives allows tweaking the relevant parameters, but the extrusion process of materials with paste-like rheology and the achievement of structural performances compatible with large scale buildings had been elusive for several years.

Harsh climatic conditions and the preference to print directly on site make things even more complicated due to the variability of environmental conditions affecting the material properties. The lack of established standards, due to the novelty of the approach, adds to the uncertainty level. However, the combination of novel materials combined with specific printing technology, opens the way to fascinating scenarios in a traditionally conservative sector.

From the social acceptance point of view, the revolutionary short building times, the strict adherence of the final product to the initial design and the substantial reduction of the construction crew are all aspects that need to be tested on the final clients. We report here on the first example of a 100+ m² building for civil use, with complete regulatory authorities’ certifications, successfully 3D printed in situ.
Carbon Quantum Dots Deposited Chemically Modified β Cyclodextrin Based Biocompatible Thermoresponsive Composite Hydrogel for Transdermal Drug Delivery Arpita Roy1,2, Sagar Pal1 and Santantu Dhara1; 1Applied Chemistry, IIT (ISM), Dhanbad, Dhanbad, India; 2School of Medical Science and Technology, IIT Kharagpur, Jharkhand, India.

In this study, we have developed a novel thermoresponsive composite hydrogel material (cl β-CD/pVCL/CQDs) by free radical mechanism and ex-situ deposition of carbon quantum dots (CQDs) on chemically crosslinked β cyclodextrin polymeric network [poly(-vinyl caprolactam) (pVCL) crosslinked with β cyclodextrin (β-CD-pVCL)] in presence of crosslinker diethylene glycol dimethacrylate (DEGDMA)]. Here in also, we have explored the effect of carbon dots deposited polymeric matrix on transdermal drug delivery. The potentials for use of different, non-cement based, materials for buildings with enhanced performances and reduced environmental impact (e.g. adobe) and the associated materials, technology ans societal related challenges will, finally, be explored.
With the development of marine fishery, the amount of waste shrimp shells has been grown tremendously leading to serious environment pollution and resource waste. Converting the waste shrimp shells to the value-added products is a meaningful way to solve the problems. Among the products, the chitin-based material has been attracted wide attention due to its biodegradability, non-toxicity, and physiological inertness [1]. However, the traditional method of preparing chitin-based material form shrimp shells needs acid and alkali repeated treatment and additional modification step [2]. It is meaningful to develop a green and simple strategy of chitin-based material synthesis from shrimp shells.

Herein, we report a green and simple method to prepare chitin/Zn composite using deep eutectic solvent (DES) aqueous solution. The used DES aqueous solution involved three functions, namely decalcification, deproteinization and Zn-loading. Under the optimal conditions, the chitin/Zn composite material with 34.6 wt% zinc, 0.2 wt% calcium carbonate and 2.5 wt% protein was obtained, which presented antibacterial effect against Gram-negative bacteria *Escherichia Coli* and Gram-positive bacteria *Bacillus subtilis* at certain bacterial concentration. The reason for calcium removal and zinc loading may be ion exchange and investigated by experiments with metal salt aqueous solution. Protein removal was ascribed to aggregation proved by particle size analysis and morphology observation.

Acknowledgments

This work was supported financially by National Natural Scientific Fund of China (No.21476234, No.21506231).

Reference


2:30 PM BREAK

3:30 PM BI01.09.04

Sustainable Synthesis of Monodisperse Starch-Based Magnetic Polymer Beads Through Molecular Rearrangement of Glucans from Natural Starch

Ke Luo, Ki-Baek Jeong, Sang Mook You and Young-Rok Kim; Kyung Hee University, Yongin, Korea (the Republic of).

Magnetic polymer beads (MPBs) have attracted extensive attention due to their excellent properties of instant action and contactless control driven by the external magnetic field. With combination of inherent features of magnetic particles and polymer, MPBs are used for various biological applications, such as immunomagnetic separation, which is a powerful and widely used technique in bioassay through the selective concentration and isolation of the biological and chemical target molecules from some complex and heterogeneous matrices. However, the conventional methods for synthesis of MPBs are still facing substantial challenges, such as potential toxicity, complicated process, and high energy consumption, which limit their applications and large-scale production. Short-chain glucan (SCG), a linear homopolymer of glucose linked with α-(1,4) glycosidic bonds, could be a promising polymer for synthesis of MPBs due not only to its abundance, renewable nature, low cost, and biodegradability, but also to its intrinsic properties of crystallization and self-association in aqueous solutions without need of energy consumption. Herein, we report a fairly simple and environmental friendly approach for the fabrication of starch-based magnetic polymer beads (SMPBs) with uniform shape and size through rearrangement of SCG produced by enzymatic debranching of waxy maize starch. The paramagnetic materials, dextran-coated iron oxide nanoparticles (Dex@IONPs), were readily incorporated into the starch microstructure and rendered a superparamagnetic property to the SMPBs. The morphology and size of resulting SMPBs turned out to be modulated by Dex@IONPs in concentration dependent manner, of which Dex@IONPs was assumed to be acting as a seed inducing the epitaxial crystallization of SCG and further transforming it into homogeneous microparticles. The surface of SMPBs was readily functionalized with antibody through one step reaction using a linker protein. The immuno-SMPBs showed great capture efficiency and specificity (>90%) to target bacteria. Furthermore, the captured bacteria along with antibody and linker protein were effectively eluted from the surface of SMPBs by free maltose, indicating the excellent recyclability of SMPBs, making this new material suitable for various chromatographic applications. The biocompatible nature of this materials would also be advantageous for its potential applications in diagnostics and delivery of drugs or physiologically active compounds to a target sites.

3:45 PM BI01.09.05

Green Synthesis of Amino-Functionalized Starch Magnetic Beads and Its Application as Recyclable and Rapid Efficient Removal of Bacterial Pathogens in Drinking Water

Sang Mook You, Young-Rok Kim and Ke Luo; Kyunghee University, Yongin, Korea (the Republic of).

Microbial contamination of drinking water is still a cause of major outbreaks of diarrheal diseases and deaths, particularly in developing countries. Polymeric magnetic particles (PMPs) are promising materials for removal of bacterial pathogens from drinking water because of their intrinsic permanent magnetic properties. Nevertheless, current methods for their synthesis generally requires complicated procedures and large energy consumption, which unfavorably hinder their practical implementation of bacterial removal from drinking water. In addition, functionalization of PMPs using recognition elements, such as antibodies, aptamers, and phages, is not suitable for this purpose, since most of contaminated drinking water environments are polymicrobial. In this study, we report a fairly simple and low-cost approach for the fabrication of starch magnetic microparticles (SMMPs) through spontaneous rearrangement of short-chain glucan (SCG) produced by enzymatic debranching of waxy maize starch. The surface of SMMPs was readily functionalized with poly-L-lysine through hydrogen-bonding interaction. The poly-L-lysine-coated SMMPs (PLL@SMMPs) showed great capture efficiency (>90%) for bacteria in water regardless of gram-positive and gram-negative under slightly acidic conditions (pH 5-6). Furthermore, we found that the surface charge of Gram-negative bacteria varied depending upon the length of lipopolysaccharide (LPS) O-side chains since the phosphate groups are mostly located in the inner core of LPS. Upon the presence of LPS, PLL@SMMPs showed greater capture efficiency for Gram-positive bacteria compared to that of Gram-negative bacteria at the same pH-level. More importantly, the captured bacteria were effectively eluted from the surface of PLL@SMMPs by aqueous ammonia solution along with recycling use, making them promising candidates for practical implementation not only for rapid capturing and removal of bacterial pathogens from drinking water but also for the sample preparation giving aid to bacterial detection and identification.

4:00 PM BI01.09.06

Spectroanalytical and Microstructural Investigation for Arsenic Removal from Water Media by Modified Ceramic Filter Membranes (Mo-CFM) for Household Water Treatment Application

Amrita Kaurwar, Manoj K. Tiwari, Ajay Khooha, Ajit Kumar Singh, Abhineet Nighojkar and Anand Seksaria; 1Indian Institute of Technology Jodhpur, Jodhpur, India; 2Raja Ramanna Centre for Advance Technology, Indore, India; 3Shri Govindram Seksaria Institute of Technology and Science, Indore, India.

This study aims to evaluate the effect of modified ceramic filter composition in removing As (V) ions from water media. The filter composition was modified through the addition of low-cost iron-rich waste powder into the local clay-saw dust mixed ceramic matrix. The modified ceramic filters (Mo-CFM) membranes were manufactured with dimensions of 10 cm by 10 cm and 1.5 cm thickness. The membrane fabrication involved mixing of local clay with an equal volume fraction of sawdust and 5% volume fraction of iron-rich waste. The raw materials and modified ceramic membranes were characterized using Energy dispersive X-ray fluorescence (EDXRF) and scanning electron microscopy. The arsenic solution was prepared in the laboratory and filtered through the modified ceramic units. The effect of prominent parameters like – pH, initial pressure head and arsenic concentration on their arsenic removal efficiency by Mo-CFM was examined. The concentration of arsenic before and after filtration process was assessed using Atomic absorption spectroscopy. The spectroanalytical results displayed high removal efficiency up to 99% for the As (V) ions. The ED-XRF and SEM images of
cерамические мембранные после процесса фильтрации показали присутствие арсениевой адсорбции на пористой поверхности модифицированной силикатной мембраны (Mo-CFM).

**4:15 PM BI01.09.07**

**Detection of Cd Ions Using an Ion-Selective Field Effect Transistor with a Chalcogen-Doped Gate Oxide for Water Quality Monitoring**

Priya Vinayak¹, Sushma Yadav², Ajeet Singh¹, Soumen Sahai¹, Henam Sylvia Devi¹, Sameer Sapra¹, Madhusudan Singh² and Bhaskar Mitra¹; ¹Indian Institute of Technology Delhi, New Delhi, India; ²Institut für Physikalische Chemie und Elektrochemie, Leibniz University, Hannover, Germany.

The American Cancer Society lists cadmium and its compounds as group 1 carcinogens in humans as exposure to these species through food, water, and the air is known to increase the lifetime risk of cancer. In this work, we report a field-effect transistor (FET) based electrolyte insulator semiconductor (EIS) sensor with a CdSe doped silica gel used as the sensing membrane. The EIS structure has a metallic layer as the back contact and the sensing membrane as the top layer with a pseudo-reference platinum electrode as top contact. The electrolyte consists of spiked cadmium acetate solutions and 0.1M KNO₃. The back contact (150 nm Al) was first deposited, with a Cr/Au (10nm/50nm) capping layer using thermal evaporation at 4.2 x 10⁻⁶ Torr, followed by a rapid thermal annealing step at 450°C. Silica gel synthesis was carried out using hydrolysis and condensation of tetraethylorthosilicate in ethanol, distilled water, and HCl. Thin film X-ray diffraction (XRD) measurements on spin-coated silica gel revealed amorphous silica sol-gel formation. CdSe nanoparticles (~3.4nm) with photoluminescence (PL) and absorbance peaks at 570nm and 562nm, respectively, were mixed with the silica sol to form a stable ink. This ink was spin-coated over a silicon wafer with 100 nm of thermal oxide. Capacitance-voltage (CV) measurements were carried out using an AC voltage of 50mV superposed on a DC voltage ramp in the range -1.5V to +1.5V at the 100 kHz. The CV curve was detected in current mode with the Stanford Research SR830 lock-in amplifier (gain = 1M Ohm). Threshold voltage shifts (ΔVT) were extracted from the CV curve was monitored as a function of varying Cd concentration (1M to 10⁻⁷M) in solution. The relationship between the shift and the concentration is linear down to the detection limit of 1 ppm in this initial study, which establishes this baseline FET-based platform for real-time detection of Cd ions in the environment in a low-cost and sustainable manner.

**4:30 PM FINAL SYMPOSIUM CONCLUSIONS AND PERSPECTIVES**

**SYMPOSIUM BI02**

The Future of Materials Science Academia—Preparing for a Career in Higher Education  
November 26 - November 28, 2018

**Symposium Organizers**

Allen Kimel, The Pennsylvania State University  
Victoria Miller, North Carolina State University  
Lisa Rueschhoff, Air Force Research Laboratory  
Davey Theresa, Tohoku University

**Symposium Support**

GE Global Research

* Invited Paper

SESSION BI02.01: Preparing a Successful Faculty Application  
Session Chairs: Allen Kimel and Victoria Miller  
Monday Afternoon, November 26, 2018  
Sheraton, 3rd Floor, Dalton

**1:30 PM **BI02.01.01  
**NFL Pros vs MSE Profs—Sizing Up the Competition for MSE Faculty Positions**  
Mark D. Losego, School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Professional athletes are often described as “elite” — reaching a level of athletic excellence that most of us agree we can never achieve. At each level, from Pop Warner to High School to College, football players are cut from teams based on performance until an “elite squad” of 1,696 Pros play each Sunday in the U.S.’s National Football League (NFL). Interestingly, materials science and engineering (MSE) departments across the U.S. employ roughly the same number of professors (~1700), and unlike an NFL player whose average career is only 3 years, MSE professors often retain their position for 30 years. Considering these numbers, it is fair to ask: Who is more elite NFL Players or MSE Profs?

This talk will provide a light but insightful look comparing the competition and process for reaching both the NFL field and an MSE professorship. While elite performance and “total commitment to one’s craft” are obvious similarities, many parallels in “intangibles” come into play when making that final hiring decision, including: specialization / flexibility (e.g., every football team only needs 1 place kicker), character (e.g., Johnny Manziel), your pedigree (DI vs. DIII) and your network (e.g., Christian Hackenberg’s recent move to the Raiders). Perhaps most importantly, though, we must remind ourselves that the faculty hiring committee (like NFL coaches) are human and use a mix of logic and emotion (unless you are Bill Belichick) to reach a final hiring decision — so bringing the proper mix of substance and excitement along with a little luck is usually what’s necessary to land that perfect job. But if you decide that a position outside of academia suits your lifestyle better, that’s ok — then you can relax on Sundays while both the NFL Pros and the MSE Profs
practice their craft (only one of which provides millions of fans amusement).

2:00 PM *BI02.01.02
Finding and Landing an Academic Position  
Michael L. Chabinyc; University of California, Santa Barbara, Santa Barbara, California, United States.

After many years of academic training, one’s main priority turns to finding a job. Of the many career options available for materials researchers, finding an academic position is one of the most challenging. The application process for an academic position requires significant preparation, but it does not need to be a Sisyphean task. This talk will discuss the expectations for faculty candidates, provide tips for preparing the components of an applications, and outline what to expect from the interview process. One of the key messages is that time management is critical.

2:30 PM *BI02.01.03
From Application to Appointment—First Steps Towards a Faculty Position in Materials Engineering  
David F. Bahr; Purdue University, West Lafayette, Indiana, United States.

The initial stages of embarking on a career in academia can be daunting to the candidate (like any career path choice), and at times may seem opaque. This presentation will address some of the common stages that occur in becoming a faculty member in a materials engineering program, and compare and contrast positions within an MSE program, and when a materials researcher is joining a unit which does not offer an MSE (or related) degree. Common points in application materials for faculty positions for a range of departments, schools, and universities will be noted; in particular the presentation will highlight the need to demonstrate independent thought and ownership of research activities, maturity and dedication to education at the appropriate level of the institution, and articulating a vision of career success at both short and long term time scales. Discussion will be prompted on topics which often arise during phone and in-person interviews, ranging from student advising vision, balancing teamwork versus independence within a unit, to identifying audiences in the hiring process. Finally, some details of perceived pitfalls in the process will be presented.

3:00 PM BREAK

3:30 PM *BI02.01.04
Embracing Internationality—Becoming a Faculty Member Abroad  
Daniel R. King; Hokkaido University, Sapporo, Japan; Global Station for Soft Matter Research, Sapporo, Japan.

Working in academia in a foreign country provides for unique opportunities and experiences that would be difficult to achieve through a traditional domestic position. While teaching and training young students anywhere can be fulfilling, introducing students to the benefits of “internationality” is something that is best experienced away from one’s home country. Japan, while possessing the third largest economy on Earth, is still ethnically homogenous, with foreigners making up less than 2% of the total population. Combined with a declining birth rate, the need for foreigner workers will continue to increase, resulting in more opportunities for foreigners to access positions in academia. In this presentation, I will outline the path I followed from being a PhD candidate in the United States (University of Massachusetts Amherst) to the position I have today, as an Assistant Professor at a National University in Japan (Hokkaido University). Specifically, I will address the following topics: finding positions in foreign countries; overcoming and dealing with language barriers; forming a research group and “fitting in” in a foreign environment; understanding and applying for funding; and the future of international faculty working abroad. I hope to express the successes as well as the struggles I have encountered through my journey. Through this presentation I aim to demonstrate the type of people who could be successful in this type of career, and hope to introduce a new path as faculty members at international universities.

4:00 PM *BI02.01.05
A Perspective on Pursuing the Academic Path  
Rebecca Kramer-Bottiglio; Yale University, New Haven, Connecticut, United States.

In this talk, I will discuss my path to academia, experiences with proposal writing, and insights on pursuing an academic career. I will also discuss young investigator and career award opportunities. I intend to keep the talk brief to allow for an engaging interactive session based on topics of interest to the audience.

4:30 PM PANEL DISCUSSION: MARK LOSEGO, MICHAEL CHABINYC, DANIEL KING, DAVID BAHR, REBECCA KRAMER-BOTTIGLIO

SESSION BI02.02: Reaching Tenure through Research, Teaching and Service I
Session Chairs: Allen Kimel and Lisa Rueschhoff
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Dalton

8:30 AM *BI02.02.01
Navigating Your Career with Confidence  
Susan B. Sinnott; The Pennsylvania State University, University Park, Pennsylvania, United States.

As you prepare for a career in higher education, it is not always clear how best to navigate the choices available. This presentation will summarize the ways in which materials science and engineering in academia has changed over the last decade, the implications for the field more broadly, and projections for the future. In addition, thoughts on best practices for navigating the career landscape will be discussed that should be helpful for your current job search or to prepare you for future opportunities.

9:00 AM BI02.02.02
Women in Physics in Ireland—Role Models are Out There  
Yvonne Kavanaugh1, Sheila Gilheany2, Eilish McLoughlin3, Miryam Byrne4, Miryam Arredondo5 and Katja Poppenhaeger5; 1Institute of Technology Carlow, Carlow, Ireland; 2Institute of Physics, Dublin, Ireland; 3Institute of Physics, Dublin, Ireland; 4Dublin City University, Dublin, Ireland; 5National University of Ireland Galway, Galway, Ireland; 6Physics, Queens University, Belfast, United Kingdom.

Physics is one of the core disciplines in Materials Science and Engineering. Therefore, it is important for the next generation of researchers, especially
Research carried out in Ireland has shown that females are successful when they engage with physics. In particular female researchers are very successful in obtaining research funding when compared to other disciplines. Ireland has seen strong females in academia challenge the status quo and this has resulted in positive initiatives to encourage the promotion of females in academia. A study carried out in 2016 by the Higher Education Authority in Ireland captured the typical scissors view, where women are in the majority in the lower paid jobs in academia and greatly underrepresented when looking at the professor and the senior executive management level. This has resulted in the Higher Education Authority making gender equality in higher education a national priority as part of its funding compact with higher education institutions. It has also resulted in the linking of national funding to the attainment of Athena Swan Bronze Awards. This has focused attention on women in STEM, in particular. The Minister for Higher Education has highlighted the lack of movement towards gender equality in STEM and is responsible for the creation of a National Taskforce on Gender Equality. The Taskforce have reported and have produced a list of recommendations to target inequality in the higher education sector.

This presentation tells the story of where women in Physics in Ireland are currently. It demonstrates how this is enabled by government policy. It reinforces the role the International Conference for Women in Physics has in tracking the journey and how Project Juno is enabling the physics community to improve gender equality.

9:45 AM *BI02.02.03

One of the most important lessons learned during grad school is that the vast majority of literature is either incorrect, incomplete, and/or so limited in its applicability to be of little use. The same can be said of career advice, no matter how well-intended or hard-earned. As with literature, the trick—often only recognized in hindsight—is separating signal from noise and synthesizing new insights from multiple inputs plus the researcher’s own datasets, experience, perspective, and interests. As in research, outliers can be incredibly useful, pointing to a need to recast the question and/or reinterpret the data using a different model. They can also be distracting and frequently over-weighted during analysis. Unfortunately, a career is an experiment with too many variables and too few data points to be effectively optimized; fortunately, there are many paths to (and definitions of) a successful academic career.

With the above caveats in mind and far too much reliance on the life-as-an-experiment analogy, a case study involving a transition from a national lab to academia will be presented as a vehicle for discussing and interpreting advice and guidance that too often went unheeded. Your mileage may vary, and free advice is worth what you paid for it, but close inspection will hopefully enable the identification of useful needles of guidance from a haystack of clichés.

9:45 AM BI02.02.04
Training the Next Generation of Materials Scientists to Embrace Broader Impacts and Share Their Work with the General Public Julie Nucci, Cornell Univ, Ithaca, New York, United States.

The Pew Research Center surveyed AAAS scientists in 2014 to inquire about the public’s limited knowledge of science. 86% of respondents stated this is a major societal problem. A second question drilled down into the reasons for this lack of science literacy in the general population. AAAS scientists were asked to rate “not enough K-12 STEM”, “lack of public interest in science news”, “lack of media interest in science”, and “too few scientists who communicate findings” as major or minor reasons. Not surprisingly, the AAAS scientists list their lack of communication as the least important reason for this public shortcoming. I disagree. If the majority of scientists and engineers deemed public communication as important as their research or professional practice, then the public understanding of STEM topics would surely be much better than it is now. This is particularly true for materials scientists, given the dearth of public knowledge of MSE. In an effort to change this at Cornell University, I partnered with WSKG, my local NPR/PBS affiliate to create a new course, ENGRG 3360: Developing Communicative Practice Through Transmedia and Community Engagement. I co-developed and co-taught the course with WSKG’s Director of Science Content, Services, and Programming and we launched it in S2018. Students created publically accessible presentations/videos, leveraged social media platforms to share their science and engineering endeavors, and mentored local high school students. We used the PechaKucha as an innovative presentation format to develop students’ abilities to identify and communicate their key idea in a clear message tailored to a target audience. The video phase of the course was a team effort, with teams composed of high school students, undergraduates, and graduate student. Our high school population, a group of twelve local students spending their entire senior year on the Cornell campus exploring engineering, participated in video production and played the very valuable role of assessing the suitability of the content created for teenagers and the general public. Students were also required create technical social media posts throughout the semester. While they are comfortable with social media in their social lives, it is paradigm shift for them to use these platforms for professional endeavors. We trained the students to do so and gave them ample opportunity to hone these skills.

#CornellEngComm was created to track the content created and Twitter emerged as the social media platform of choice. Video and presentation content created by the students is being aligned to NYS and national education standards and lesson plans are being created for PBS Learning Media, a web-based resource used by students and teachers nationwide. In this talk, I will discuss course development and the partnership with public media. Samples of student work will be shown and opportunities for leveraging the content created will be discussed.

10:00 AM BREAK

10:30 AM *BI02.02.05
Navigating a Career in Academia—From Application to Pre-Tenure and Early-Tenure—Lessons Learned Along the Way Nazanin Bassiri-Gharb1, 2; 1George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Getting ready for a career in academia can seem at times a daunting task, but after years of preparation through doctoral studies and subsequent post-doctoral work, multiple applications to open positions and interviews, finally a match is made. In many cases, however, the process leading to this point is not only the beginning of a lifetime of learning, but also (and maybe even more so) the beginning of an even bigger challenge. The challenge is that of establishing oneself as a new and independent researcher, educator and mentor... and of course, along the path, make it through the tenure process. While tenure is still seemingly the biggest hurdle to pass in the academic career, the process need not to be necessarily an obstacle. The pre-tenure and early tenure years can be instead some of the most satisfying and fulfilling time in the academic life of an early-stage scientist.

This talk will address some of the approaches to tenure – from the start of the tenure-track, through the critical review, tenure, and finally early-tenure stages – that will allow you to enjoy the process and not lose the spirit of wonder: because losing the sense of wonder is much worse than not making tenure. The author will draw on her personal experience through the pipeline, as well as some of those of her close friends and colleagues. She promises to not embellish the truth (yes, chances are things will get tough at some point!), but also not to depress the attendees with endless counts of “a series of
unfortunate events”. And while there is no such a thing as “happily ever after”, she will share some of the ways of keeping the happy before and after tenure.

11:00 AM #BI02.02.06
Future Faculty Expectations Bryan D. Huey; Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States.

An academic's day has changed very little in the last several centuries—you think, share ideas with others, critique, and occasionally sleep. Of course the scope, structure, and finances of universities have shifted more dramatically, but still the expectations of faculty members remain remarkably similar:
create knowledge; serve your institution and more broadly your profession; teach and mentor the next generation. The practical reality, though, is that we are all essentially small business owners, keeping our 'product' viable through publications, talks, student dissertations, funded grants, outreach, and even tangible results. The merit systems (financial, tenure, and respect of your peers) reward and indeed demand excellence in these important areas—all of them. But will universities, and faculties, function the same in the future? Increasing trends towards online learning may be particularly disruptive to the traditional model. How can prospective and new faculty, and their institutions, harness this trend instead of fighting it?

11:30 AM PANEL DISCUSSION: GEOFF BRENNECKA, SUSAN SINTT, NAZANIN BASSIRI-GHARB, BRYAN HUEY, YVONNE KAVANAGH

SESSION BI02.03: Reaching Tenure through Research, Teaching and Service II
Session Chairs: Allen Kimel and Victoria Miller
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Dalton

1:30 PM #BI02.03.01
From “Being Taught” to “Teaching”—A Personal Perspective of a Young Faculty Member Eva Hemmer; University of Ottawa, Ottawa, Ontario, Canada.

This presentation will provide a snapshot on the journey of a materials scientist from Germany moving via Japan to Canada. It will not only tell about the geographical, but also about the scientific and academic journey, and how studying materials science and engineering can lead to an academic position in a chemistry department, conducting research on multifunctional lanthanides in molecules and nanomaterials. In this context, some experience from the time being a PhD student, from the period discovering new countries and research areas as a postdoctoral fellow, and the recent ongoing adventure of starting an independent research group as assistant professor will be shared with the audience. Also, first teaching experiences will be illuminated: another potential (and unexpected) source of culture shock. While the search for the ultimate recipe for the straight forward achievement of a scientific and academic career is still going on, some of the basics that may be required for a scientific trip by any young researcher or scientist will be suggested for discussion. These basics clearly include curiosity, self-motivation and an open mind, not to forget about endurance as well frustration tolerance, while great mentors are found to play a very important role at each stage of career.

2:00 PM #BI02.03.02
From a Personal Experience as a Teacher of an Advanced Course on Materials Micromechanics—How the Background Gap Between Basic Materials Education and Advanced Topics Can be Filled with the Aim of Not Disappointing Enthusiasm of Students Not Suitably Informed on the Preliminary and Basic Notions Needed to Know Roberto Contore; Chemistry, Materials and Chemical Engineering, Politecnico Milano, Milano, Italy.

The aim of this paper is showing that the student expectations can be not disappointed if they are personally involved in a learning itinerary where firstly their passion, ambition and intelligence are appreciated and stimulated. As consequence they will consolidate their self confidence and will accept to measure their real capability to learn notions indispensable to acquire a sufficient and rewarding preparation, not as a tool to overcome the profit examination but mainly to acquire consciousness of being able to win a challenge, sometimes sounded very difficult because of lacks in a previous basic background. In this way this experience might be useful to approach other challenges that unavoidably will meet in their study a professional career. The word of order of a teacher should be identifying best talents and mainly discovering talents which often are hidden in a mass of students who, for several reasons like their familiar and cultural environment or also for a certain personal shyness, tend to do not recognize even to themselves.

The main step of such a learning itinerary, applied to a master course of materials micromechanics will be described with reference to the adopted textbook: FUNDAMENTALS OF MICROMECHANICS OF SOLIDS, Jianmin Qu and Mohammed Cherkaoui, Wiley, 2006. Meaningful home-works will show as examples of final course results and a related brilliant career promoted as well.

2:15 PM #BI02.03.03

Educational institutions that foster inquiry and innovation prepare students for future careers in science and engineering. Inviting students, as young as high school age, to engage in materials science research is mutually beneficial to aspiring scientists, as well as the university faculty who engage them. A case study for such work details research performed by high school students contributing to the Soft Robotics Toolkit. The open source nature of the soft robotics field presents opportunities for students outside of a university research lab to participate and advance the field. Exposing secondary school students to this rapidly growing field allows for evolution of the soft robotics industry in new and imaginative ways. Students at The Haverford School in Pennsylvania are developing materials-based approaches to soft robotics problems. From this, they gain fundamental knowledge in materials, develop technical communication skills, and are empowered to innovate in the future. As a co-curricular program, secondary school students, ranging in age from 13 to 18 years, collaborated to successfully design and build solutions to fundamental materials issues and prototype a soft robotic device to achieve a goal meaningful to them. In year one of the program, students developed gelatin-based actuators which are biodegradable and edible. In year two, the team developed a simple, one-step fabrication process for building actuators and applied them in a glove. The students collaborated with an art teacher to program the glove to transfer motion from accomplished to novice artists. This group now has a new skill set and confidence in the field to allow them to approach larger problems. This presentation will discuss the technical merits of their work as well as the broader benefits to the field of materials science. In a controlled study, we found that when students were presented with an opportunity to innovate: synthesizing a novel solution to authentic problems without the constraints of a prepared kit, common at the high school level, they were more creative and less constrained in future projects or design.
Challenges. Outreach programs like this generate interest in the field of materials science and present opportunities for faculty to perform outreach that will generate the creative and prepared students they want in their laboratories. Soft robotics is just one application of accessible materials science outreach. This presentation will detail methods of developing this type of unique outreach initiative across the materials science field. Making students aware of what is possible will inspire the next generation of materials scientists, while stimulating the current practitioners with creative new ideas.

2:30 PM BREAK

3:00 PM BI02.03.04

Understanding the Impact of Design in High School Outreach Camps Kaitlin Tyler, Nicole Johnson-Glauch, Leon Dean and Jessica A. Kroostad; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Outreach camps are an effective route to increasing interest in STEM disciplines, especially for underrepresented groups. They are also common components in the broader impact plans for many early career researchers. However, there is very little basis for understanding which aspects of outreach camps lead to positive outcomes. This is due in large part to the difficulty in comparing existing camps both within specific STEM disciplines and across them. As a result, there is little science-based guidance for the development of effective outreach camp structure or content. Because of this, we specifically target the process of design in outreach camps due to its importance in engineering degree programs. By comparing different methodologies for incorporating design thinking through a qualitative multi-case study across four engineering disciplines, we have begun to assess whether design can be used to positively affect outcomes of STEM outreach camps and provide guidance for outreach development.

3:30 PM BI02.03.05

Nanovation—An Interdisciplinary Outreach Program to Train the Next Generation of Scientists and Entrepreneurs Rita Blaik¹ and Sarah Tolbert²; California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California, United States; ³Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States; ⁴Materials Science & Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Entrepreneurship plays a crucial role in economic development by promoting technological innovation and job creation. A lack of experience and training in technology entrepreneurship is a problem that often persists up to and including doctoral training, and many universities are at a loss as to how to prepare students interested in an entrepreneurial career path. In order to address this pain point, the California NanoSystems Institute at UCLA created the Nanovation Competition outreach program in the 2016-2017 academic year. In this after-school competition, teams of middle and high school students in Southern California compete with the help of UCLA STEM graduate student mentors to generate nanotechnology-based product ideas and develop business plans which they then pitch in a “Shark Tank”-style event. The nanotechnology topics are primarily based on CNSI’s Nanoscience Institute led by Professor Sarah Tolbert, which is a teacher training program now its 14th year aimed at bringing cutting-edge nanoscience concepts to classrooms in the greater LA area. The larger goal of the Nanovation program is to introduce the growing culture of technology and entrepreneurship to students at an earlier age, which can foster economic growth in Southern California.

In addition to explaining the nature and goal of our Nanovation competition, this presentation will discuss the outcomes of this program over the last two years and cover strategies for fostering positive volunteer and mentoring experiences, creating robust professional development for graduate students and K-12 teachers in STEM and entrepreneurship, and winning financial support to sustain these programs over the long-term.

3:45 PM BI02.03.06

Collaboratively Creating Research-Inspired Materials Science and Engineering Outreach Activities Anne Lynn Gillian-Daniel, Matthew Stilwell, Wendy Crone and Nicholas Abbott; MRSEC, University of Wisconsin–Madison, Madison, Wisconsin, United States.

The emphasis that NSF places on meaningful, effective Broader Impacts can be challenging for researchers developing research proposals. An effective strategy for dealing with the challenge is to collaborate with groups who focus on science, technology, engineering, and math (STEM) outreach to the public. By integrating research and education, the University of Wisconsin Materials Research Science and Engineering Center’s (UW MRSEC) works with researchers to create research-inspired materials science and engineering (MSE) educational resources and programs. These resources, including classroom laboratory experiments, hands-on outreach activities, and research programs for teachers, are designed to inform and excite K-12 students, teachers, and public audiences about MSE research and its applications to the world. The UW MRSEC works with researchers to develop broader impacts plans that align with their goals and interests. For example, some faculty members have collaborated with us to develop outreach activities by modeling the cutting-edge instrumentation funded through an equipment proposal. Other faculty members have supported and hosted a teacher in the Research Experience for Teachers (RET) program. Through the RET, Wisconsin teachers perform research in the laboratory of the faculty members and develop new classroom curriculum based upon their summer research experiences. The new curriculum modules are implemented and evaluated in the RET fellow’s classroom the following school year. The modules can then be adapted for other audiences and outreach venues. Following development and adaptation, UW MRSEC members work with faculty to field test new resources, evaluate them for engagement and efficacy, and iteratively improve them. The faculty members and their students then present the completed activities at outreach events both on and off the UW campus. These activities can also be disseminated online on the MRSEC education website, in-person during workshops, and in professional education journals. Examples of research-inspired educational resources developed by faculty for NSF proposals and the UW MRSEC, along with avenues for dissemination, will be shown as part of the presentation.

4:00 PM BI02.03.07

Funsizephysics—A New Tool for Presenting Your Research to the Public Leigh M. Smith¹, Jocelyn Bosley² and Shireen Adenwalla²; ¹Department of Physics, University of Cincinnati, Cincinnati, Ohio, United States; ²Department of Physics and Astronomy, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

During our scientific training we spend much time preparing ourselves for writing scientific papers, proposals and teaching students. In contrast we spend very little time (almost none) on preparing ourselves to communicate our ideas to the public, and these are extremely different tasks. This is truly unfortunate since our communications to the public are becoming a more important and essential part of our outreach efforts. In this presentation I will describe a new NSF-funded effort to develop a new website (funsizephysics.com) which makes it particularly straightforward to develop graphically pleasing web-based presentations to the public. While it is certainly not easy to design a good and informative page which gets across the excitement and importance of your research in an accessible way, working within your research group can make the process easier and at the same time help to train your students. Funsizephysics now makes it easy to have multiple authors for a page. Have a graduate student draft their work and then have other members critique the good points and bad points of the web page. Then iterate with an eye to improving the presentation. In this presentation we will provide some
simple guidelines and hints which we think can help your outreach efforts.

We acknowledge the support of the National Science Foundation through grants DMR-1725823 and DMR-1726026.

4:15 PM PANEL DISCUSSION: EVA HEMMER, JESSICA KROGSTAD, RITA BLAIK, HOLLY GOLECKI, MATTHEW STILWELL, LEIGH SMITH

SESSION BI02.04: Navigating the Funding Pipeline
Session Chairs: Victoria Miller and Lisa Rueschhoff
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Dalton

9:00 AM *BI02.04.01
Funding Opportunities in Materials Engineering at the US National Science Foundation Alexis C. Lewis; Civil, Mechanical and Manufacturing Innovation, National Science Foundation, Alexandria, Virginia, United States.

This presentation will describe funding opportunities related to Materials Science and Engineering at the National Science Foundation, including current programs, new opportunities, and planned focus areas. Additionally, the NSF Merit Review process will be discussed, including components of a successful proposal, finding the right home for your research, and proposal writing tips for early career faculty.

9:30 AM *BI02.04.02

Maneuvering the diverse and complex funding pipelines has become a significant challenge for even the most promising researcher, and poses a threat to the future of materials science in academia. David Stepp brings nearly twenty years of experience at the U.S. Army Research Office to provide insight and perspective on the "why," the "what" and the "how" underpinning one of the preeminent materials science funding agencies worldwide. This talk will focus on suggested approaches that apply to all funding agencies, both in the U.S. and abroad. It will also include a discussion of some of the most common misunderstandings held by materials science researchers when soliciting funding.

10:00 AM BREAK

10:30 AM *BI02.04.03

Transformative breakthroughs most of the time do not originate from the investigations of materials in the equilibrium state but in contrary at the margins of stability, in a regime at the limit or outside of the textbook knowledge within the discipline. In this context, this presentation will embrace materials and processing science approaches that are far from the thermodynamic equilibrium domain, i.e., directionally solidified eutectic structures, highly doped piezoelectric and thermoelectric materials, and other oxide materials with cage structures for electron emission. The intent is to elucidate the complex interplay between phase transitions for electronic/magnetic phase separation and untangle the interdependence between structural and electronic effects. I will also discuss what I consider to be promising research concentration areas within ceramics research for the aerospace materials for extreme environments portfolio of Air Force Office of Scientific (AFOSR), including the focused development of a ceramics processing science laboratory for ceramic matrix composites, the development of materials for use in the hypersonic regime.

11:00 AM PANEL DISCUSSION: ALEXIS LEWIS, DAVID STEPP, ALI SAYIR

**SYMPOSIUM BM01**

TUTORIAL: 3D Printing of Passive and Active Medical Devices
November 25 - November 25, 2018

* Invited Paper

**TUTORIAL**

3D Printing Methods for Medical Applications
3D printing methods enable distributed manufacturing, mass customization, and rapid prototyping of medical devices. The tutorial "3D Printing Methods for Medical Applications" seeks to impart information to the audience on the use of 3D printing methods to process polymer, metal, ceramic, and biological materials. This course includes coverage of 3D printing principles, advantages of 3D printing over traditional subtractive manufacturing processes, materials for 3D printing, 3D printing methods, and applications of 3D printing.

8:30 AM
**3D Printing Technologies for Healthcare** Roger Narayan; University of North Carolina at Chapel Hill and North Carolina State University

Laser-based processes may be used for additive manufacturing and bioprinting of structures with unique microscale and nanoscale structures. We have demonstrated use of matrix assisted pulsed laser evaporation- direct write for layer-by-layer processing of cells and scaffold materials. Three-dimensional patterning of cells and cell-scaffold composites have been demonstrated using this approach. We have also recently examined additive manufacturing of three-dimensional structures using two photon polymerization. In two photon polymerization, ultrashort laser pulses are used to selectively polymerize photosensitive resins and form complex microscale and/or nanoscale structures. The nonlinear nature of two photon absorption enables polymerization of structures with features below the diffraction limit. Recent medical applications of two photon polymerization have involved fabrication of microneedle arrays and scaffolds for tissue engineering. Our results indicate that matrix assisted pulsed laser evaporation- direct write and two photon polymerization are attractive techniques for additive manufacturing and bioprinting, respectively.

9:30 AM BREAK

10:00 AM
**Printing Cells: Process Challenges and Application** Wei Sun; Drexel University and Tsinghua University

3D Bio-Printing uses cells and biomaterials as building blocks to fabricate personalized 3D structures or functional in vitro biological models. The technology has been widely applied to regenerative medicine, disease study and drug discovery. This presentation will report our recent research on printing cells for construction of micro-organ chips and for building in vitro 3D tumor models. An overview of advances of 3D Bio-Printing will be given. Enabling methods for cell printing will be described. Examples for 3D Printing of tissue engineering model, drug metabolism model and disease model will be reported, along with results of printing parameters on cell viability and 3D tumor structural formation, characterization of cell morphologies, proliferations, protein expressions and chemoresistances. Comparison of biological data derived from 3D printed models with 2D planar petri-dishes models will be conducted. Discussions on challenges and opportunities of 3D Bio-Printing will also be presented.

11:00 AM
**3D Printing of Hard Biomaterials** Amit Bandyopadhyay; Washington State University

3D Printing (3DP) or Additive manufacturing (AM) is an approach to process parts directly from its computer aided design (CAD) file. AM is changing the landscapes of current industrial practices. On-demand manufacturing using 3DP technologies is a new trend that will significantly influence many industries and product design protocols. Since there is no need for any part specific tooling, different parts can be built using the same machine. Most of these parts are near net-shape and require only small finishing operation. Unlike even 10 years back, when most of these 3DP produced parts were used for touch and feel, and design optimization, functional parts via additive manufacturing is becoming common in most industrial sectors.

We have worked on additive manufacturing of hard materials, primarily metals and ceramics, over the last two decades. We have used fused deposition modeling, laser engineered net shaping and powder bed based 3D printing processes. Using these 3DP approaches, we have manufactured parts with compositional, functional and structural gradation mostly for space and biomedical applications. I will focus on some of the key success stories from our research, as well as current challenges in the field.

**SYMPOSIUM BM01**

3D Printing of Passive and Active Medical Devices
November 26 - November 27, 2018

Symposium Organizers
Susmita Bose, Washington State University
Richard Hague, University of Nottingham
Roger Narayan, North Carolina State University
Wei Sun, Drexel University and Tsinghua University

* Invited Paper
Emerging Organ Models and Organ Printing for Regenerative Medicine

Ali Khademhosseini; Department of Bioengineering, Chemical Engineering, Radiology, University of California, Los Angeles, Los Angeles, California, United States.

Engineered materials that integrate advances in polymer chemistry, nanotechnology, and biological sciences have the potential to create powerful medical therapies. Our group aims to engineer tissue regenerative therapeutics using water-containing polymer networks called hydrogels that can regulate cell behavior. Specifically, we have developed photo-crosslinkable hybrid hydrogels that combine natural biomolecules with nanoparticles to regulate the chemical, biological, mechanical and electrical properties of gels. These functional scaffolds induce the differentiation of stem cells to desired cell types and direct the formation of vascularized heart or bone tissues. Since tissue function is highly dependent on architecture, we have also used microfabrication methods, such as microfluidics, photolithography, bioprinting, and molding, to regulate the architecture of these materials. We have employed these strategies to create miniaturized tissues. To create tissue complexity, we have also developed directed assembly techniques to compile small tissue modules into larger constructs. It is anticipated that such approaches will lead to the development of next-generation regenerative therapeutics and biomedical devices.

8:30 AM *BM01.01.02

Laser Based Direct Write Techniques for Studying Cellular Interactions

Douglas B. Chrisey and Jayant Saksena; Tulane University, New Orleans, Louisiana, United States.

Due to their ability to carry out both additive and subtractive processing of a wide range of materials in a non-contact manner with superior precision and speed, lasers are a promising tool to create reproducible constructs for cell-based assays. Laser direct write technologies—as such as our custom-designed matrix-assisted pulsed laser evaporation (MAPLE) bioprinting system—combine the power of laser processing with computer-aided design to allow us to print as well as ablate cells, cell aggregates and biomaterials with high resolution. Here, we present some interesting applications of the excimer laser driven MAPLE platform for cell printing and ablation, tissue dissection, biomaterial micromachining and 3D microbead fabrication for studying interactions between cells and their microenvironmental cues in vitro. We have printed breast and colon cancer cells, fibroblasts and macrophages in spatially defined patterns on hydrogel substrates and live rat mesenteric tissue to develop physiologically relevant models for cancer cell migration and invasion. We have micromachined spoke and channel patterns into PDMS substrates to analyze competitive cell migration in context of cancer and atherosclerosis. We have also developed a reproducible and customizable wound healing assay using laser ablation of adherent cells. We have fabricated and patterned 3D microbeads encapsulating heterogeneous cell types to elucidate cancer-adipose interactions. Finally, we have dissected user-specified regions of excised mouse colonic tissue to create testable sections. Our work demonstrates the immense versatility of laser based direct write technologies in biology and medicine.

9:00 AM *BM01.01.03

3D Printing of Passive and Active Medical Devices—A Clinician-Scientist's Perspective

Shervanthi Homer-Vanniasinkam1, 2, 3; 1Division of Surgery & Department of Mechanical Engineering, University College London, London, United Kingdom; 2Vascular Surgery, Leeds Teaching Hospitals NHS Trust, Leeds, United Kingdom; 3Division of Surgery, University Hospitals Coventry & Warwickshire/University of Warwick, Coventry/Warwick, United Kingdom.

The burgeoning field of 3D printing is rapidly invading the medical sphere with an ever-expanding portfolio of applications in healthcare. Since Charles Hull invented stereolithography in the early 1980s, this printing technology has evolved greatly, and to an exponential degree, in the last decade. The applications of 3D printing in medicine are many, and growing. In this talk, some important uses of the technology will be presented, and, as time permits, discussed from a clinician-scientist’s perspective.

In surgery, 3D printing is being increasingly utilised in patient-specific surgical planning to aid intraoperative navigation in complex operative procedures, using precise personalized anatomical information; in producing implants and prostheses; and in educating and training young surgeons. Other applications include 3D bio- and molecular printing of functional living constructs and organs, in drug delivery, and for custom-made medical equipment and products e.g surgical tools and instruments.

Several groups of researchers, including clinician-scientists, are working on exciting developments in areas embracing all aspects of patient care from surgical procedure planning to printing scaffolds and tissues for clinical implantation. Whilst currently there is widespread interest in harnessing this technology in all fields of medicine, in order to realize the full potential of 3D printing, it is perhaps important to prioritize areas in which to focus our research and development endeavours. Clinician involvement in this process is vital, so that minds can be focused on unmet clinical needs. Currently, despite the huge strides made by 3D printing in recent years, there remain challenges for the routine implementation of this technology in the clinical sphere; these include the time taken to prepare the object or device ie long processing times (and hence, limited applicability in the urgent and emergency settings), the accuracy of the devices or models produced, the expense of doing so (despite the decreasing costs of the printers) and importantly, the associated regulatory aspects.

The clinical community is both excited by the promise of what 3D printing can deliver in terms of patient care, and wary of some of the potential dangers of wholly embracing this new field. Thus, it is important for clinicians, scientists and industry to develop a scientifically and socially conscious platform from which to foster the further development of this technology within clearly defined and ethically responsible boundaries. We should jointly strive to achieve this goal so that the promise that 3D printing holds for improved healthcare, is realized.

9:30 AM BM01.01.04

Towards the Development of Perforant Silicone Elastomeric Compositions for 3D Printing of Customizable Parts

Remi Thiria1, Karsten Schlichter2, Jean-Marc Frances3 and Damien Djam1; 1R&D, Elkem Silicons NA, York, South Carolina, United States; 2Elkem Silicons France, Lyon, France.

Due to their outstanding properties like biocompatibility, hypoallergenicity, chemical inertness, thermo-stability resistance and flexibility at low temperatures, soft silicone elastomers are the material of choice in many healthcare applications such as prosthesis, drug delivery, implantable devices, comfort care, audiology and implantable devices.

Traditional manufacturing processes such as casting and injection molding, are currently used for the preparation of biocompatible materials or medical devices however there is a strong need for customized silicone parts.
Additive manufacturing (AM) and especially 3D printing is a tool that offers increased design freedom and enable users to redesign existing parts but also create entirely new parts that can not be manufactured with any of the current traditional manufacturing processes. This technical lecture will introduce the new challenges and benefits of AM to make personalized silicone elastomers against the traditional ways of conception/processing. Due to its low elastic modulus and poor shape retaining ability during the layer-by-layer process, silicone elastomer AM could be technically challenging. A good understanding of the relationship between input and output parameters during the AM is key. Mastering such parameters along with the 3D printer machine and the silicone chemistry have allowed us to predict both the aspect and performances of the 3D printed part.

9:45 AM BM01.01.05
Patient-Specific Printing of Bioreorbable and Biocompatible Ceramics by Lithography-Based Ceramic Manufacturing Shawn M. Allan1, Martin Schwenzenwein2, Daniel Bomze3 and Johannes Homa4; 1Lithoz America, LLC, Troy, New York, United States; 2Lithoz GmbH, Vienna, Austria.

Lithography-based Ceramic Manufacturing (LCM) has emerged as a state-of-the-art technology for the production of dense high-performance ceramics in field of additive manufacturing (AM). LCM polymerizes ceramic slurries, which consist of ceramic particles dispersed in a photocurable binder matrix, in a layer-by-layer manner using light. The green-body is durable enough for handling and mechanical post-processing. After the AM process, the green-body is thermally processed to remove the polymer binder and densify the ceramic. Tremendously diverse and complex parts can be fabricated directly from CAD files. Parts formed by LCM exhibit the same mechanical properties as parts formed by conventional manufacturing processes. LCM allows fabrication of bio-inert zirconia, an exceptionally tough ceramic, for permanent bone replacements and dental implants, crowns, bridges and orthodontic products. LCM also enables the structuring of bioreorbable ceramics like tricalcium phosphate (TCP) or hydroxyapatite (HA). These bioceramics are used in the biomedical field for patient-tailored implants, derived from CT scans. This provides the best compatibility for the patient and easy-to-use handling for the surgeon. The freedom of design facilitates cell scaffolds with defined macroporosity (e.g. cancellous bone shape) for the ingrowth of cells and vascularisation, allowing the delivery of nutrients and the removal of metabolic waste. This contribution gives an overview about the capabilities of the LCM process, potential applications as well as current challenges. Resolution, reproducibility, surface roughness of the different materials and economic feasibility will also be topic of this presentation.

10:00 AM BREAK

10:30 AM BM01.01.06
Framed Biopapers—Degradeable Substrates for Printing, Handling, Stacking and Device Integration of 3D Printed Tissue Constructs Russell K. Pirlo1,2; 1Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Radiological Sciences, Uniformed Services University of Health Sciences, Bethesda, Maryland, United States.

Despite the expanding use of 3D bioprinting and a growing number of commercially available 3D bioprinters, there has been limited effort to develop a universal cell and tissue culture platform that enables the plethora of new approaches made possible with 3D printing. Traditional cell culture formats like the well-plate and transwell insert are routinely employed as the receiving container for bioprinted tissues but they present challenges when it comes to perfusion, harvesting, transfer of the printed tissues and accessibly to other tools and instruments. The ability to fabricate tissues in “freeform” is one of the advantages of 3D bioprinting, yet tissues remain confined to the receiving substrate, or lack a method of registration with other devices. The U.S. Naval Research Laboratory has developed “framed biopapers” as a novel and potentially universal format for 3D printing, handling, stacking and transferring tissues with registration between layers and devices. In its most basic application, a single framed biopaper may be used as the base substrate for freeform 3D bioprinting. In this way, the framed biopaper provides a method to handle the 3D printed construct and easily releases the tissue construct through dematerialization of the biodegradable biopaper. Additionally, the frames of the biopaper provide for a registration mechanism for transfer from one bioprinting or biofabrication tool to another, as well as to bioreactors and analytical instruments, such as a microscope or plate reader. Furthermore, framed biopapers enable an asynchronous layer-by-layer fabrication approach whereby sheet-like layers are printed to individual biopapers and allowed to mature independently before stacking. This allows for a specific application of growth factors or stimuli and the construction of complex heterotypic tissues, especially those with a laminar architecture. Finally, we envision that the frame of the biopaper may even be used as a surgical guide for implantation of tissue constructs, precision engineered to fit into a defect/void with alignment of implant and native vasculature and other tissue architecture for more rapid suture, anastomosis and integration into the body.

11:00 AM BM01.01.07

Various manufacturing innovations have been developed to facilitate tissue bioprinting processes for better biomedical applications. Among them, maskless (including extrusion-, laser- and inkjet-based) three-dimensional (3D) bioprinting is a revolutionary advance for printing arbitrary cellular patterns as well as creating heterogeneous living constructs. Thus far, effective printing of cell-laden viscoelastic fluids and printing-induced injury to living cells still pose a significant challenge to ensuring the scale-up of robust bioprinting. Using laser bioprinting (laser-induced forward transfer) and inkjet bioprinting as two jet-based model printing systems, we have been studying the bioprint jettability and printability as well as printing-induced cell injury problems, aiming to achieve robotic bioprinting. The jettability and printability of cell-laden viscoelastic bioprinted tissues are defined and characterized using material properties and printing conditions-related non-dimensional numbers. The printing-induced cell injury and post-transfer cell viability are estimated based on the process-induced cell thermomechanical loading during the cell droplet formation and landing processes. In this talk, the perspective of ongoing bioprinting research and various bioprinting technologies are first introduced. Then the jettability and printability of cell-laden viscoelastic bioprinted tissues are discussed using the dimensionless Ohnesorge and capillary numbers to capture the influence of material properties along with the Weber number to capture the influence of printing conditions. Furthermore, the modeling of laser-induced cellular droplet formation and landing processes is presented, and the relationship between the mechanical loading information and post-transfer cell injury/viability is established using an apoptosis signaling pathway-based modeling approach. Finally, this talk shares some thoughts regarding basic scientific challenges related to bioprinting.

11:30 AM BM01.01.08
Photocurable Thiol/Yne Resins for the Manufacturing of Functional Biocompatible Structures Thomas Grieser; Institute of Chemistry of Polymeric Materials & Christian Doppler Laboratory for Functional and Polymer Based Ink-Jet Inks, University of Leoben, Leoben, Austria.

The last years have seen an increasing interest in the development of photo-polymerizable monomers providing low cytotoxicity and high thermo-mechanical properties in their cured state. This fact can mainly be explained by the rapid progress in UV based additive manufacturing technologies such as stereolithography, digital light processing or 3D ink-jet printing, which enables the fast, accurate and individual fabrication of biocompatible structures.
In this context also the tissue compatibility of photopolymers has to be considered in particular for medical devices that are in direct contact with blood or bone.

In this contribution, the versatility of the thiol-yne photo-click reaction\(^2\) for the fabrication of biocompatible photopolymers is shown at the example of tailor-made alkylene and thiol monomers. For that purpose, commercially available acrylate monomers were modified using the carbon and oxa michael addition reaction to obtain multifunctional alkylene building blocks.

It turned out that these synthesized monomers offer curing rates similar to the acrylates, while providing much higher conversion and lower monomer cytotoxicity. This reaction leads to highly uniform polymeric networks exhibiting a sharp and defined thermal glass transition together with outstanding impact resistance, which makes these polymers interesting for challenging applications such as medical implants.\(^3\) Not only non-degradable, but also degradable monomers were designed, enabling the selective adjustment of the resorption behavior of the resulting polymers.\(^4\)

The herein described monomer systems pave the way towards the individual fabrication of tissue compatible photopolymers with tunable thermo-mechanical properties and resorption behavior.


**11:45 AM BM01.01.09**

Manufacturing Microstructured Medical Devices Using Multi-Step 3D Printing Technologies

Roger Narayan; North Carolina State University, Raleigh, North Carolina, United States.

In this presentation, the use of multi-step 3D printing technologies, which incorporate digital micromirror device-based stereolithography, two photon polymerization, pulsed laser deposition, matrix assisted pulsed laser evaporation, piezoelectric inkjet printing, and/or micromolding, to create small-scale medical devices for transdermal drug delivery will be considered. Microneedles are small-scale lancet-shaped devices that may be used for delivery of pharmacologic agents into the skin. We have use 3D printing techniques to microneedles such as digital micromirror device-based stereolithography and two photon polymerization to create microneedles with well-defined tips and complex shapes directly from computer models. Printing techniques including pulsed laser deposition, matrix assisted pulsed laser evaporation, and piezoelectric inkjet printing have been used to decorate the 3D printing microneedles with medically active agents. For example, visible light dynamic mask microstereolithography and micromolding have been used to prepare microneedles out of poly(methyl vinyl ether – co – maleic anhydride) (PMVE/MA); coatings containing agents such as amphotericin B and miconazole have deposited on the microneedles using piezoelectric inkjet printing. Disk-diffusion studies demonstrated the antifungal activity of the inkjet-printing-modified microneedle arrays. Examples involving the use of multi-step 3D printed microneedles for various medical applications will be considered.

---

**SESSION BM01.02: 3D Printing of Passive and Active Medical Devices II**

**Session Chairs:** Rigoberto Advincula and Reginald Hamilton

Sheraton, 2nd Floor, Liberty B

---

**1:30 PM BM01.02.01**

Laser Direct Energy Deposition Additive Manufacturing of NiTi Shape Memory Alloys

Reginald F. Hamilton, Beth Last, Emily Jenkins and Todd Palmer; Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania, United States.

Additive Manufacturing (AM) has gained significant attention in processing shape memory alloys because they have circumvented many of the challenges associated with the conventional methods. Shape memory alloys are a class of multifunctional materials that undergo large shape changes, and upon heating or removing external stimuli “remember” their original shape and form. Underlying reversible solid-state atomic and microstructure length scale phase transitions beget the bulk scale memory. Consequently the shape memory alloy behavior can be tailored using manufacturing techniques that provide freedom to design the microstructure. The AM techniques for NiTi are either powder-bed based technologies such as Selective Laser Melting, or flow-based methods such as Laser Directed Energy Deposition (LDED). LDED deposits powder through nozzles directly into the laser focus melt pool. LDED AM is a potential tool for in-situ, i.e. during fabrication, microstructure design. The laser-based layer-by-layer AM techniques can result in microstructural anisotropy, which is characterized in terms of the grain and microconstituent morphologies. During the additive manufacturing (AM) process, individual passes and layers are deposited. The deposition of passes and layers creates overlapping regions between adjacent passes and interfacial zones between successive layers. Within the overlapping and interfacial regions, previously deposited material is remelted is also reheated as heat is conducted away from the solidifying material. The remelting and reheating in these local regions will bring about microstructure anisotropy. Multi-scale deformation measurements correlate microstructure to underlying physical mechanisms in order to establish the interrelationships between novel fabrication technologies and shape memory functionality. The purpose of this work is to correlate the layerwise built-up microstructures to the shape memory behavior of LDED AM NiTi shape memory alloys.

---

**2:00 PM BM01.02.02**

Hydrogel Bioinks for 3D Printing Applications

Jason Burdick; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Hydrogels represent a class of biomaterials that have great promise for the repair of tissues, particularly due to our ability to engineer their biophysical and biochemical properties. 3D printing approaches are now being developed to process hydrogels into structures with the appropriate shapes and patterns for tissue repair; however, printing processes are often not compatible with hydrogels optimized for a desired cell response. Thus, we have developed techniques to both screen hydrogels for a desired cell response and to process these materials into printable bioinks.

Towards MSC chondrogenesis, we have developed a screening platform using the patterning of photocrosslinkable norborneo-modified hyaluronic acid hydrogels with biochemical signals. These include peptides that mediate cell-matrix adhesion (i.e., RGD) or cell-cell adhesion (i.e., HAVD). When cells are encapsulated within the hydrogels incorporating orthogonal gradients, optimal formulations can be identified through imaging of MSC differentiation markers (e.g., Sox9, aggrecan). As these are non-viscous precursor solutions, they are difficult to 3D print using traditional printing approaches, such as extrusion-based printing. With extrusion-based printing, a bioink must flow during extrusion, but then be rapidly stabilized post-extrusion to maintain the desired printed structure. To address this, we have developed two approaches to 3D print non-viscous bioinks: (i) curing the material with light through a
encapsulate cells with high cell viability. Ultimately, the design of new bioinks and printing processes will lead to successful applications of 3D printing in the repair of tissues.

2:30 PM BREAK

3:00 PM **BM01.02.03**

**3D Printed Ceramic-Metal Composites to Minimize Metal Ion Release from Articulating Surfaces of Load-Bearing Implants**

Anmit Bandyopadhyay, Anish Shivaram, Murat Isik, Jose Avila and Susmita Bose; School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, United States.

Cobalt-chromium-molybdenum (CoCrMo) alloys are widely used in load-bearing implants, specifically in hip, knee, and spinal applications, due to their excellent wear resistance and their being economic compared to titanium-based alloys. However, due to wear induced metal ion release from the implants and poor biocompatibility at implant-tissue interface, there is a significant interest to find an alternative to CoCrMo alloy. We hypothesize that adding calcium phosphate (CaP) based ceramic in the form of hydroxypatite can minimize metal ion release concerns in CoCrMo alloy. CoCrMo-CaP composite coatings were processed using a commercial laser-engineered net shaping (LENS™) system. After LENS™ processing, CoCrMo alloy was subjected to laser surface melting (LSM). Samples were investigated for microstructure, phase stability, and wear induced damage. It was found that wear resistance of CoCrMo was enhanced by ~ 5 times due to the formation of an in situ tribofilm of CaP's, and achievement of a fine dendritic microstructure in the case of LSM treated CoCrMo. In vitro cell material interactions study using human osteoblasts cell line was performed. For in vivo, rat and rabbit distal femur models were used for a period of 5 and 12 weeks. In vitro and in vivo study showed improved biological response for surface modified CoCrMo compared to untreated CoCrMo approximately a 5-fold increase in osteoid formation. Our results show that careful surface modification treatments can simultaneously improve wear resistance and in vivo biocompatibility. The presentation will focus on processing as well as physical, mechanical and biological characterization of 3D printed CaP-CoCrMo composites with a focus on minimizing metal ion release.

3:30 PM **BM01.02.04**

**3D Printing of Multifunctional Tissue Engineering Scaffolds**

Min Wang; Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong, Hong Kong.

Tissue engineering has advanced significantly over the past three decades and many human body tissues may be regenerated successfully, providing desired functions in the human body. A few approaches are used for human tissue regeneration, which include cell- factor- or scaffold-based tissue engineering. Using scaffolds to assist tissue regeneration has been the dominant approach. In scaffold-based tissue engineering, it is important to develop suitable scaffold materials and employ appropriate scaffold manufacturing technologies to make desirable scaffolds, which will lead to successful tissue regeneration. Many materials have been investigated for different scaffolds and scaffold fabrication techniques have been studied by numerous researchers. Materials for tissue engineering are generally biodegradable polymers and scaffolds are produced by either non-designed manufacturing techniques (e.g., solvent casting/porogen leaching) or designed manufacturing techniques. Using designed manufacturing, which includes a host of additive manufacturing technologies (the so-called “3D printing”), for scaffold fabrication has distinctive advantages and has therefore attracted great attention in the tissue engineering field. However, some 3D printing technologies impose stringent requirements for stock materials and studies have been conducted on preparing stock materials and on evaluating the physical and mechanical properties of scaffolds made of these stock materials. Furthermore, existing, general 3D printing technologies may not be suitable for constructing multifunctional tissue engineering scaffolds in which biological molecules or even live cells need to be incorporated. Hence, new 3D printing technologies specifically for handling delicate biomolecules and/or cells are urgently needed. Our group has investigated selective laser sintering (SLS), a well-established 3D printing technology, for making osteoconductive and osteoinductive scaffolds for bone tissue engineering. In this process, we developed nanocomposite materials as scaffold materials which provided osteoconductivity. For the novel scaffolds, we also incorporated a growth factor which provided osteoinductivity. Our studies showed that bone tissue regeneration was greatly promoted with the SLS-formed multifunctional scaffolds. We have also developed a low-temperature, extrusion-based 3D printing technique for constructing relatively strong scaffolds with the incorporation of biomolecules or cells. Very promising results were obtained using this new 3D printing technology. This talk will give an overview of 3D printing and its application in tissue engineering. It will introduce our work in this area and discuss issues in scaffold design and 3D printing.

4:00 PM **BM01.02.05**

**Inkjet Printing of Melanin as a Biocompatible Functional Electronic Material**

Ashkan Shafiei1, Elham Ghadiri2, Warren Warren2 and Anthony Atala1;1 Institute for Regenerative Medicine, Wake Forest School of Medicine, Winston-Salem, North Carolina, United States; 2Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States.

Biocompatible electronic has become a focus of attention owing to the need in biomedical applications. Smart electronic devices capable of communicating with biological structures such as human tissues and organs are the requirement for many sophisticated purposes in medicine. Melanin is one of the most stable biopolymer, found in almost every live organism, versatile for application in the emerging field of bioelectronic devices. Melanin pigments are found in human skin, hair, eyes and the brain in different forms. For many years, it was viewed simply as a coloring agent with some photoprotective properties, but that view always ignored some obvious features. The functionality of melanin as a natural pigment is defined (although not fully understood) by its physical and chemical properties, such as its featureless broad UV-NIR optical absorption, antioxidant properties, and temperature/water dependent photocconductivity. Melanin also shows in vivo and in-vitro biocompatibility. All these properties identify melanin as a unique alternative for using as the functional material in the bioelectronic devices.

This paper report the inkjet printing of synthetic melanin nanoparticles with different size for electronic applications. Inkjet printing deposition with computer-assisted abilities can pattern different types of materials on various flexible or rigid substrates. Inkjet printing deposits pattern with Pico-liter size droplets of the functional materials with micrometer resolution. This economic consumption makes this technique much more affordable compared to other deposition techniques such as spin coating and dip coating.

Through solution-based chemical synthesis, we have prepared melanin nanoparticles with controlled size and chemical structures of melanin-like nanoparticles, pheomelanin and eumelanin. The active layer of the electronic device consists of melanin nanoparticles based film prepared with inkjet printing technique. Nanoparticles solutions with different sizes of 70 nm, 100 nm, and 250 nm were printed on transparent conductive electrode using Jetlab II Microlab, piezoelectric printer. The optoelectronic and photophysical processes in the films are studied using steady-state UV-NIR diffuse reflectance spectroscopy and ultrafast time-resolved broadband pump-probe spectroscopy technique. Using ultrafast broadband spectroscopy
measurements, we identified the spectral signature of excited state formation and compared excited state relaxation in melanin nanoparticles with different sizes. This research can open up the new avenue of research toward biocompatible electronic manufacturing.

4:15 PM BM01.02.06
Rheology and Direct Ink Writing of Strong Cellulose Reinforced Composites
Michael Hausmann1,2, Gilberto Siqueira1, Rafael Libanori2, Patrick Rihs1, Dimitri Kokkinis2, Tanja Zimmermann1 and André Studart1; 1Empa, Swiss Federal Laboratories for Materials Science and Technology, Dubendorf, Switzerland; 2ETH Zürich, Dubendorf, Switzerland.

Cellulose nanocrystal (CNC) is a bio-based and renewable material extracted from wood and algae or produced by bacteria. The alignment of CNCs is crucial for direction specific enhanced mechanical properties in composite applications. We utilize direct-ink writing (DWI) to assemble complex cellulose-based geometries with controlled orientation and spatial distribution of nanocrystals within the printed structure. Using polarized imaging we correlate the dynamic flow behavior of CNC-based inks with the quality of nanocrystal alignment occurring during 3D printing. In order to control the quality of alignment during the 3D printing process, the printing pressure and the viscoelastic properties of the material have to be well characterized. After printing, the resulting part and its mechanical properties are determined in order to create composites with well-defined properties. By understanding the effect of the concentration of reinforcing nanocrystals on the rheological properties of the ink during the printing process, 3D objects with improved printability and mechanical properties were obtained. Our findings pave the way towards the fabrication of high-performance materials with renewable resources using a cost-effective additive manufacturing technique.

4:30 PM BM01.02.07
Structure-Function Relationships of Varying Microarchitecture and Surface Topography of 3D Printed Ti-6Al-4V Fabricated by Selective Laser Melting
Cambre N. Kelly1, Nathan T. Evans2, Cameron W. Irvin2, Savita Chapman2, Ken Gall2 and David L. Satsal2; 1Duke University, Durham, North Carolina, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States; 3Medshape, Atlanta, Georgia, United States.

As the manufacturing of medical devices via additive manufacturing (3D Printing) continues to increase, better understanding of structure-function relationships of microarchitecture and surface topography are needed. Selective laser melting (SLM) of Ti-6Al-4V of implants with interconnected porosity have become widespread in orthopedic and other load bearing applications where porous structures encourage bony ingrowth and the stiffness of the implant can be tuned to reduce stress shielding. SLM allows high resolution control over design, including the ability to introduce porous surfaces or regions with spatial variations in pore size, shape, and connectivity. Investigation of the effect of construct microarchitectural design and surface topography on mechanical behavior of 3D printed Ti-6Al-4V showed a dominating effect of porosity on monotonic and fatigue behavior as compared to solid samples. Irrespective of surface treatment and resulting surface roughness, the fatigue strength of 3D printed samples containing bulk or surface porosity was approximately 20% to 25% of the ultimate tensile strength of identical printed porous material. For the vast range of microarchitectures which can be fabricated to tune construct porosity and resulting stiffness, creation of predictive models of fatigue behavior based on monotonic properties would allow for rapid iteration of design for devices with microarchitecture specified not only to patient anatomy, but also bone quality and loading profiles for tailored reduction of stress shielding.

4:45 PM BM01.02.08
3D Printed Functional and Biological Materials on Moving Freeform Surfaces
Zhijie Zhu, Shuang-Zhuang Guo, Tessa Hirdler, Cindy Eide, Xiaoxiao Fan, Jakub Tolar and Michael McAlpine; University of Minnesota, Minneapolis, Minnesota, United States.

Conventional 3D printing technologies typically rely on open-loop, calibrate-then-print operation procedures. An alternative approach is adaptive 3D printing, which is a closed-loop method that combines real-time feedback control and direct ink writing of functional materials in order to fabricate devices on moving freeform surfaces. Here we demonstrate that the changes of states in the 3D printing workspace in terms of the geometries and motions of target surfaces can be perceived by an integrated robotic system aided by computer vision. A hybrid fabrication procedure combining 3D printing of electrical connects with automatic pick-and-placing of surface-mounted electronic components yielded functional electronic devices on a free-moving human hand. Using this same approach, cell-laden hydrogels were also printed on live mice, creating a model for future studies of wound-healing diseases. This adaptive 3D printing method may lead to new forms of smart manufacturing technologies for directly printed wearable devices on the body and for advanced medical treatments.

SESSION BM01.03: Poster Session: 3D Printing of Passive and Active Medical Devices
Session Chairs: Richard Hague and Roger Narayan
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

BM01.03.01
Vascularized Heterogeneous Cardiac Tissue Network by a Direct Patterning with a 3D Bioprinter
Joonan Kim and Jin Seok Lee; Sookmyung Women's University, Ithaca, New York, United States.

3D bioprinting is a widely used technology to dispense cell-laden biomaterials for rapid fabrication of complex 3D tissue constructs or artificial organs. To date, many studies have been investigated the deposition and patterning of cell-laden bioinks with a 3D bioprinter. However, the precise positioning, reasonable mechanical properties, and controlled cell distributions of constructs in 3D bioprinting system still remains technical challenges. In this study, we developed heterogeneous cell-laden microchannel network using human umbilical ven endothelial cell-cardiomyocytes by a direct patterning with a 3D bioprinter. We fabricated 3D tissue constructs consisting of the core (human umbilical ven endothelial cell -laden collagen) and the sheath (cardiomyocytes-laden gelatin methacrylate). We could achieve a stable 3D multilayered core-sheath structure with the reasonable elastic modulus. This system also facilitated cell alignment and migration within each constructs and promoted vascular network with high cell viability. Calcium imaging was used to optically probe intracellular calcium ion signals during excitation-contraction coupling in cardiomyocytes within 3D vascular network.

This paper presents the new approach for fabricating vascularized heterogeneous 3D scaffolds and highly controlled deposition technique of bioinks. The cell-laden 3D constructs could be extended to serve as in vitro models for clinical cardiovascular disease researches and cardiovascular tissue regenerations.
Three-Dimensional Printing of Magnetic Data Storage Structures

BM01.03.05

Periodontal ligament (PDL) with structural connectivity between cementum and alveolar bone tissues has key functions to optimize positional stabilities of teeth, transmit and absorb various stresses under masticatory/occlusal loading conditions, or promote tissue remodeling by mechanical stimulations. The oriented PDL formations with micron-scaled dimensions and calcified interfacial tissue formation with fibrous tissue anchorages are challenging in bone-ligament complex neogeneses. We investigated the 3-D microarchitectures, which can spatiotemporally organize PDL for fibrous connetive tissue formations.

The periodontal regeneration scaffolds had three compartmentalized microarchitectures; cementogenesis platform (~200um), PDL-guiding architectures, and bone scaffolds. After computer designs, 3-D printing system manufactured micron-scaled wax molds and biodegradable material (poly-e-caprolactone; PCL) was casted into wax molds. The architectures were characterized with micro-CT, SEM, and confocal microscope for topographies. In in-vitro human PDL cell cultures and in-vivo subcutaneous model system, cell orientations or angulations were analyzed with nuclear morphologies and deformations.

In in-vitro experiments, microgrooves on scaffold architectures can angularly organize and geometrically control cell orientations for 7-day and 21-day cultivations. In particular, micro-patterns on microarchitectures can predictably and accurately control PDL cell orientations with high proliferations. Moreover, microgroove-patterned scaffolds promisingly provided more predictable cell alignments and cell orientations were significantly angular-controllable with statistical difference in in-vivo.

The additive manufacturing system can fundamentally manufacture various microarchitectures with micro-scaled patterns, which are designed in CAD. Based on topographical cues, PDL stem cells can be spatiotemporally regulated for fibrous connetive tissue and mineralized tissue formations as well as scaffolds can control specific orientations of ligament cells and tissues. Therefore, the investigation demonstrates the compartmentalized microarchitectures facilitate to regenerate periodontal complexes which have structural similarities to natural periodontia.

BM01.03.03

3D Printing of Antimicrobial PLA/GO Nanocomposite Implants

Viavvedhan Jayanthihakiriksharn1, Digiqiyv Shind1, Prabir Patra1, Tae Won B. Kim2, Sarosh Patel2 and Tarek Sobb3; 1Biomedical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States; 2Mechanical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States; 3Orthopaedic Oncology, Cooper University Health Care, Camden, New Jersey, United States; 4Computer Science and Engineering, University of Bridgeport, Bridgeport, Connecticut, United States.

Graphene based medical implants have sparked widespread interests in the field of 3 D bioprinting due to its anti-microbial nature, very large aspect ratio associated with its 2D structures, and its ability to form functionally graded printable structures with polymers. Here we explore the 3 D printing of Poly L-lactic acid/Graphene oxide (PLA/GO) nano-composite for its anti-microbial property as bone implant and scaffold for bone cell proliferation. The nanocomposites were prepared through FDM (Fused deposition modelling) and our laboratory built LDM (Liquid deposition modelling) 3D printing. GO was dispersed in 1,4 dioxane using ultrasonication followed by dissolving PLA in the GO dispersions. LDM utilized the viscosity driven controlled stretching of the PLA/GO solution to print the solid structural form onto a heated bed that vaporizes the solvent and leaves behind the required structure. For the FDM process, the nano-composite was fed in the form of a filament. We utilized the dried and powdered form of the nano-composites to form the essential PLA/GO filamentous structures using the filament extruder. We plan to integrate electrostatic jetting of PLA/GO nanocomposites through the micro nozzle using FDM system for attaining controlled porosity and microstructure, thereby closely mimicking the bone microenvironment. Anti-microbial activity of GO was measured with staphylococcus aureus, 60% reduction of bacterial growth was achieved.

BM01.03.04

A Multi-Structured 4D Stent with Large Deformation and Faster Temperature Response

Je Hoon Oh1, Wonjin Jo2, Jongbeom Ghim3, Myoung-Woon Moon4 and Kuy Hwan Oh1; 1Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); 23D Printing Group, Computational Science Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

4D printing is a technology that makes the 3D printed structure deformed by responding the environmental stimuli such as water, temperature or UV. Especially, 4D printing has been actively studied for applications in medical devices such as a stent or a scaffold, which can be deformed under body fluid conditions to the intended shape. Even though the 4D structures transform properly under temperature or water, one may wait for longer duration to achieve its final configuration, which is not desired in medical level application.

In this presentation, we introduce a multi-structured 4D stent with large deformation and faster response to the small temperature change. A multi-structure 3D printing scheme is presented by printing a raster line in curved or coiled configuration by using a fused deposition modeling (FDM) type 3D printer with a shape memory polymer (SMP). The printed configurations in several curved shapes such as wavy or coiling shape were achieved by setting two main parameters of the interval between the printer bed and the nozzle as well as the filament flow rate. As increased the interval from 0.2~0.3 mm to 1~2 mm, the flow speed of 3 times faster than the normal printing conditions, the extruded raster line patterns were changed from straight to wavy or coiled.

Since the thermoplastic SMP has a viscoelastic property, the configuration of the printed patterns was formed by a liquid rope-coiling effect that is a phenomenon based on buckling instability of viscoelastic material. It was also found that by tuning the deformation temperature below or above the glassy temperature, Tg, of the SMP, the curved line was deformed 1.5 times more than the straight line with much faster recovery rate. By alternating stacking layers printed with the curved line pattern over the straight line pattern, we fabricated a 4D stent structure with larger and faster response to warm temperature of our body fluid. It is expected that this 4D stent can alleviate the problem of blood vessel scarring during the insertion of the stent.

BM01.03.05

Three-Dimensional Printing of Magnetic Data Storage Structures

Corey Breznak and Paris von Lockett; The Pennsylvania State University, University Park, Pennsylvania, United States.

Traditionally, barcodes encode data in a binary format by using groups of parallel lines with varying distance between them. Although a barcode is simple to print, the complexity of the data that can be stored is limited. This research aims to design a method to encode more complex forms of data with higher information densities using 3-d printed magnetic structures. The work presented investigates the basic principles for 3-d magnetic patterning as a means of information storage, tagging, and/or part identification.

In this work, a structure is fabricated using proscribed patterns of magnetic and nonmagnetic regions. These structures are similar to present day barcodes, where the magnetic regions generate an external magnetic field, the stray field, that can be interrogated with a Hall effect or similar magnetic probe. The regions of magnetic and nonmagnetic field can be spaced apart at varying distance, or the thickness of each region can be varied, both of which affect the resolution of the magnetic signature of the stray field generated by the pattern. The patterns yield a magnetic equivalent to the binary optical nature of barcodes.
codes. Unlike with the fabrication of barcodes, other processing variables influencing the stray field of the structure can be altered to add complexity to the data encoding. For example, by using hard magnetic powders such as barium hexaferrite, which consists of magnetically anisotropic plate-like particles, the magnetic regions can be oriented in arbitrary directions yielding more intricate stray fields, and consequently more complex magnetic signatures and higher information density.

This work first provides a proof of concept using neodymium magnets inserted into a 3-d printed patterned structure to produce the stray field, which is characterized using a gaussmeter. The creation of this structure is the simplest proof of concept of a magnetic bar code. A second proof of concept 3-d prints both the nonmagnetic and magnetic parts of the structure using Protopasta magnetic filament (consisting of PLA with 45 wt.% iron particles) and standard ABS filament in a dual material FDM printer. Printing alternating regions of magnetic and nonmagnetic material form the now passive magnetic structure. A force gauge with a magnetic tip is used to determine the signature of the stray field resulting from the magnetic pattern. Finally, a computational model is developed to simulate stray field and resulting signature of the printed magnetic structures for comparison with experiments.

Future work includes using magnetic filament consisting of hard magnetic particles such as barium hexaferrite, whose magnetic anisotropy facilitates complex magnetic alignments within the magnetic regions of the printed structure. Complex alignments allow increasingly sophisticated magnetic signatures, permitting an increase in the complexity of stored data, as well as an increase in information density.

**BM01.03.06**

3D Printing of Multifunctional Hydrogel Actuators for Biomedical Application

Youzhou Yang, Jianfeng Zang, Hanchuan Tang and Yueying Yang; School of Optical and Electronic Information and Wuhan National Laboratory for Optoelectronics, Huazhong University of Science & Technology, Wuhan, China.

Hydrogels are wet and biocompatible and are used as scaffolds for tissue engineering, vehicles for drug delivery, actuators for optics and fluids, and model extracellular matrices for biological studies. Three-dimensional (3D) printing methods, especially direct ink writing, have been widely used, allowing the rapid and complex design and fabrication of hydrogels. Taking advantages of 3D printing, hydrogels with different properties can be easily manufactured. Lots of existing works have reported 3D printing of tough hydrogels for biomedical application. We employed responsive particles embedded in hydrogel precursor as the ink for the direct ink writing process. Subjected to the in situ external fields, the as-prepared precursor was printed in well-designed paths with on-demand properties. In this way, we prepared hydrogel actuators not only with notable mechanical property, but also with large deformation and programmable deformation mode. Moreover, using our strategy we demonstrate a soft active bandage that can rub the ointment on affected areas with a controllable manner, and an untethered gripper for medicine.

**BM01.03.07**

3D Printed Tissue Engineering Constructs Embedded with Electrospun Nanofiber Mats Using Various Biomaterials

Suk-Hee Park, Young Won Kim, Han Bit Lee, Ye Ji Yoon and Yong Son; Korea Institute of Industrial Technology, Ansan-si, Korea (the Republic of).

Recently, the most important issues in the tissue engineering field are to mimic the natural extracellular matrix (ECM) and to manufacture the customized structures with patient-specific morphology. These are the critical factors for regulating functions of cultured cells and being used as the clinical-level applications. In these respects, nanoscale fabrication and 3D printing technologies have attracted much attention from the scientists and engineers in the relevant fields. In this presentation, we are going to introduce new hybrid bio-printed constructs, which consist of 3D printed parts and electrospun nanofiber mats. When it comes to electrospinning process, it could formulate not only randomly-network fibrous mat of it natural processed form but also highly-oriented fiber arrays. Depending on the fiber orientation, the cultured cells on the scaffolds could be modulated in terms of their biological functions and behaviors. The biomaterials for 3D printing could be classified to two groups; i) thermoplastic rigid polymers and ii) hydrogel-based bio-ink. When the thermoplastic biomaterials, for which polycaprolactone (PCL) was used in our studies, were combined with the electrospun mats, they were effectively supportive to sustain the morphologies of nanofiber mats. Since the supportive constructs were fabricated in the way of CAD/CAM-fashioned process, they were expected to overcome various obstacles in practical uses of the fragile nanofiber scaffold and meet the needs for clinical applications in specific surgeries. As for the hydrogel-based materials, which physically involved living cells, they were 3D-printed in the layer-by-layer manner. When the layering of bio-inks were processed with insertion of nanofiber mats between the hydrogel layers, the integrated constructs had enhanced properties in terms of structural resolution as well as mechanical toughness and stiffness. The improved performances of fiber-reinforced hydrogel constructs were expected to achieve the morphological and biophysical mimicry of native soft tissues. Taken together, the combinatorial fabrication techniques involving 3D printing and electrospinning would allow for a wide range of feasible applications in the scaffold-based tissue engineering.

**BM01.03.08**

3D Printing and Post-Processing of PEEK Structures and Their Potential Applications to Bone Tissue Engineering

Suk-Hee Park, Seong Je Park, Ji Eun Lee, Han Bit Lee, Jae Won Choi and Yong Son; Korea Institute of Industrial Technology, Ansan-si, Korea (the Republic of).

3D printing, CAD/CAM-based processing approach, has been considered as an effective tool to satisfy the many requirements in the trends of manufacturing industry changing rapidly from mass production to mass customization. Fused deposition modeling (FDM), or material extrusion (ME) in ASTM terminology, has been one of the most commonly and widely used processes owing to its various advantages, such as low-cost material and hardware, simple processing mechanism, and wide material usage. Recently in the industry of 3D printing manufacturing fields, high-strength polymers with reliable performances have attracted much attention from the relevant researchers and engineers. In this presentation, we introduce the FDM-based 3D printing and the post-processing of polyetheretherketone (PEEK), which is one of the representative super engineering polymers. PEEK is the material as difficult to be processed as its high mechanical performance. We first developed custom-made 3D printing system, which was able to deal with the engineering plastic materials. Specifically, the 3D printer included several thermostatic control systems to modulate the environmental conditions of printing, such as the temperature of the surrounding air in the printing chamber. The use of temperature-controlled conditions in not only the nozzle but also in the chamber instead of room temperature was necessary in order to stably print the engineering polymers without defects or delamination in the final product. We studied the optimized parameters for the stable printing process, such as nozzle/chamber temperature, nozzle speed, printing tool-path, and extruding rate. With these process parameters, the maximum tensile strength of the resulting PEEK parts was achieved at approximately 80% of the bulk material property. In addition, we studied the effects of heat treatment on the mechanical property and crystallinity. The heat-based post-processing could improve the tensile strength up to 90% of the bulk material property, which was comparable to mechanical properties of bone. Based on the optimized conditions from process design to post-process, we tested the feasibility of manufacturing of orthopedic products and bone implants.

**BM01.03.09**

Thiol-Yne Photo-Click Chemistry—Towards Biocompatible and Tough Photopolymers for 3D Printing

Delara Hartmann, Andreas Oesterreicher and Thomas Grieser; Institute of Chemistry of Polymeric Materials & Christian Doppler Laboratory for Functional and Polymer Based Ink-Jet Inks, Montanuniversität Leoben, Leoben, Austria.

Recent years have seen an increasing interest in the development of photo-polymerizable monomers providing low cytotoxicity and high impact resistance in their cured state. This fact can mainly be explained by the rapid progress in UV based additive manufacturing technologies such as stereolithography,
digital light processing or 3D ink-jet printing which enables the fast, accurate and individual fabrication of biocompatible structures for hard tissue engineering. In this contribution, the versatility of the thiol-ynel photo-click reaction for the fabrication of biocompatible photopolymers is shown at the example of tailor-made bi- and multifunctional alkynyl and thiol monomers. This reaction leads to highly uniform polymeric networks exhibiting a sharp and defined thermal glass transition together with outstanding impact resistance [1] making these polymers interesting for challenging applications such as medical implants. A particular focus was set on the development of low odour thiols as promising alternatives to commercially available mercapto propionic acid derivates. Thiol-ynel resins based on these monomers provide both, high reactivities comparable to those of acrylates and mechanical properties appropriate for the fabrication of medical devices in their cured state. The herein described monomers pave the way towards the fabrication of tailor-made photopolymers suitable for hard tissue engineering.


**BM01.03.11**

*In Vitro Perforation of the Round Window Membrane via Direct 3D Printed Microneedles* Aykut Aksel1, Wenbin Wang1, Daniel N. Arteaga2, Miguel Arriaga1, Yan Wang1, Hirobumi Watanabe1, Karen Kasza1, Anil K. Lalwani1, 2 and Jeffrey W. Kysar1, 2; 1Mechanical Engineering, Columbia University, New York, New York, United States; 2Otolaryngology, Columbia University, New York, New York, United States.

We report the use of Two-Photon-Polymerization (2PP) lithography to manufacture precision microneedles for the purpose of intracochlear drug delivery. The cochlea, or inner ear, is a space fully enclosed within the temporal bone of the skull, except for two membrane-covered portals connecting it to the middle ear space. One of these portals is the round window, which is covered by the Round Window Membrane (RWM). A longstanding clinical goal is to deliver therapeutics into the cochlea to treat a plethora of auditory and vestibular disorders. Standard of care for several difficult to treat diseases calls for injection of a therapeutic substance through the tympanic membrane into the middle ear space, after which a portion of the substance diffuses across the RWM into the cochlea. The efficacy of this technique is limited by an inconsistent rate of molecular transport across the RWM.

A solution to this problem involves the introduction of one or more microscopic perforations through the RWM to enhance the rate and reliability of diffusive transport. Hence, ultra-sharp polymer microneedles specifically designed to perforate the RWM are made using direct 3D printing via 2PP lithography.

The needles are 3D printed, developed and mounted on sterile 23 Gauge blunt syringe tips for practical use. The needles are then used to perforate freshly excised guinea pig membranes. The perforation force is collected, and the resulting holes are analyzed via confocal microscopy, which has the benefit of visualizing the fibers that give the RWM its mechanical properties.

The microneedle has tip radius of curvature of 500 nm and shank radius of 50 µm. It perforates the RWM with a mean force of 1.19 mN. The resulting perforations performed in-vitro are lens-shaped with major axis equal to the microneedle shank diameter and minor axis about 25% of the major axis, with mean area 1670 µm². The major axis is aligned with the direction of the connective fibers within the RWM. The fibers were separated along their axes without ripping or tearing of the RWM suggesting the main failure mechanism to be fiber-to-fiber decohesion.

The needles are imaged using a Scanning Electron Microscope (SEM) after use, and it is seen that the tips of these microneedles are bent to some extent, limiting their reusability. Therefore, radii of curvature of the tips are systematically changed in order to find an optimal shape for the needles with the purpose of enhancing the mechanical strength and preventing blunting.

These results establish a foundation for the use of 2PP as a means to fabricate microneedles to perforate the RWM and other similar membranes requiring precision manufacturing of complex geometries. The small perforation area along with fiber-to-fiber decohesion are promising indicators that the perforations would heal readily following in-vivo experiments. An optimal needle geometry is currently being researched for the purpose of RWM perforation.

**BM01.03.12**

*Study of Fusion in 3D Printing of PLA/Graphene Composites* Yuval Shmueli1, Xiaoxin Wang2, Steven Wu3, Derek Zheng4, Lan Jiang5, Caroline Zeng6, Dilip Gersappe7, Miriam Rafailovich1; Matthew York7 and Zhuolin Xia1; 1Stony Brook University, Stony Brook, New York, United States; 2Padua Franciscan High School, Parma, Ohio, United States; 3Clear Lake High School, Houston, Texas, United States; 4Monta Vista High School, Cupertino, California, United States; 5University High School, Irvine, California, United States; 6Wayzata High School, Plymouth, Minnesota, United States; 7Case Western Reserve University, Cleveland, Ohio, United States.

Fused deposition modeling (FDM) printing is an emerging 3D printing technology in which thermoplastic filaments are extruded and deposited in certain manner according to computer input design. Polylactic acid (PLA) is a common biodegradable polymer being used in FDM printing and has great potential to be the main component in future biomedical devices. However, since it has poor thermal conductivity properties it is often leads to failing interfilaments fusion and hence reduces the overall product mechanical and functional properties.

In this work we incorporate graphene nano platelets (GNPs) to examine their effect on the thermal profiles during printing and the resulted mechanical properties. We studied the conditions of different nozzle temperatures and varied the distance between adjacent filaments and between deposited layers by adjusting the Gcode input to the printer. We used high resolution infra-red thermal camera to monitor the temperatures at the printing process. Then we correlated these profiles with (scanning electron microscopy) SEM analysis and dynamic mechanical analysis (DMA) properties of the printed structure. We also used microbeam small angle X-ray scattering (SAXS) measurements to study the macrostructure of the printed filaments as function of the radial position from the interfilaments interface to the filaments core. In addition, we modeled the temperature profiles and the flow mechanics of GNPs flow in the polymer matrix using Lattice Boltzmann Modeling (LBM).

We show the great effect of GNPs inclusion on the fusion process while printing and how it affects the resulted properties and can be used in future potential applications. The experimental results combined with the modeling results enable us to present the optimal conditions and composition to improve the fusion and hence the strength of the printed structures.

We Acknowledge support from the National Science Foundation (Inspire Award No. 1344267) and The Morin Foundation Trust.

**BM01.03.13**

*Self-Folding of 3D Printed Shape Memory Polymers with High Degree of Shrinkage* Akhiro Nojiri1, 3, Eiji Iwase2, and Michiako Hashimoto1, 2; 1Digital Manufacturing and Design Centre, Singapore University of Technology and Design, Singapore, Singapore; 2Pillar of Engineering Product Development, Singapore University of Technology and Design, Singapore, Singapore; 3Department of Applied Mechanics, Waseda University, Tokyo, Japan.
Self-folding is a strategy to fabricate 3D shapes from planar sheets. 3D printed planar structures have been demonstrated to form 3D shapes via self-folding due to shrinkage of 3D-printed polymers. The degree of polymer shrinkage due to heat is typically low, and achievable 3D shapes have been limited in size and complexity. In this work, we demonstrated self-folding of a polyurethane-based shape memory polymer (SMP) printed by a fused deposition modeling (FDM) 3D printer. SMP transfers from rubber states to glass states by the change of temperature, and this phase transition is typically used to memorize specific shapes. We used this characteristic not for shape memory but for self-folding. When SMP is printed in rubber states by FDM, internal stress is introduced to the printed SMP structures on the build plate. Above its glass transition temperature \( (T_g) \), the SMP structure releases internal stress and shrinks. This shrinking is due to the phase transition and the release of internal stress. We demonstrated that the 2D structures consisting of 3D printed SMP were readily transformed to the 3D structures through this mechanism. We achieved to control the degree of shrinking by varying (1) printing temperature, (2) FDM nozzle speed and (3) multilayer design of the planar sheet. These parameters allowed defining bending angles and directions of resulting 3D structures (such as valley folds, mountain folds and their combinations) due to the difference in the internal stress between adjacent layers of SMP printed under different conditions. The folding angle of 3D printed SMP sheets was precisely controlled between -180° to 180° by changing the printing parameters. The developed principles allowed fabricating complex 3D shapes ranging from a dice to a crane.

We highlight that the polyurethane-based SMP patterned by 3D FDM printer exhibits high degree of shrinking. In our demonstration, the radius of curvature of the resulting structures was as small as 1.8 mm, which was one order smaller than the corresponding structures consisting of 3D printed polyactic acid (PLA). As the result, fabrication of complex 3D structures on the order of millimeters was readily achieved. The use of SMP added an advantage; the 3D structures after shrinking were memorized. The obtained structures were recovered above glass transition temperature \( (T_g) \) multiple times after manually deformed. Overall, we demonstrated fabrication of the 3D structures with shape memory via programmed shrinkage of 2D structures printed by FDM. Unlike previous demonstrations, our design principle relied on the phase transition of SMP that offered high degree of shrinkage, which permitted fabrication of complex structures with the combination of anisotropic folds and convex/concave features.

BM01.03.14

The Effect of Surface Roughness of 3D-Printed PLA Scaffolds on the Cell Attachment, Proliferation and Differentiation of Dental Pulp Stem Cells Kuan-Che Feng1, Wenqi Zhao2, Benjamin Chung1, Bhuvana Murthy1, Ethan Ho1, Rushi Patel1, Antony Deluxe2, Marcia Simon1 and Miriam Rafailovich1; 1Stony Brook University, Stony Brook, New York, United States; 2Milton Academy, Milton, Massachusetts, United States; 3Herricks High School, New Hyde Park, New York, United States; 4Woodbridge High School, Irvine, California, United States; 5Northfield Mount Hermon School, Gill, Massachusetts, United States; 6Wheatley High School, Old Westbury, New York, United States; 7Haroon High School, Ann Arbor, Michigan, United States.

Three-dimensional (3D) printed scaffolds provide a promising approach in the field of tissue-engineering for its ability to precisely control scaffold architecture at the micron-scale. Previous studies have shown that topographical features on the surface of scaffolds can determine the efficiency of cell attachment and proliferation; yet, little is known about their effect on cellular differentiation. Here, we aimed at investigating the influence of the surface roughness of 3D-printed polyactic acid (PLA) scaffolds on cellular response. We conducted experiments with three different thicknesses of sharkskin and samples of pure PLA, all produced by the FDM 3D printer. The sharkskin employer is known to affect the cell behavior. We investigated the effect of the printing process on the cell attachment and differentiation of dental pulp stem cells on these substrates. We also analyzed the effect of surface roughness on the cell attachment, proliferation and differentiation of dental pulp stem cells. The results showed that the sharkskin employer significantly increased the cell attachment and proliferation, while the pure PLA scaffolds did not show any significant differences. These results indicate the potential of using 3D printing technology to control the surface morphology of dental pulp stem cells.
nanoparticles as a coating on PLA. This coating can promote a rapid and prolonged release of silver ions able to inhibit biofilm formation. PLA scaffolds were printed using two 3D printers, a Makerbot Replicator 2X and Ultimaker 2 Extended+, with corresponding filaments, and characterized with a laser microscope and FTIR. The Brunst method was used with two concentrations of AgNO3 (0.1M and 0.01M) and 0.001M NaBH4 for the in situ deposition of silver nanoparticles. We tested the ability of the PLA-AgNO3 scaffolds to inhibit biofilm formation and growth against two strains of bacteria, Staphylococcus aureus (gram-positive) and Escherichia coli (gram-negative). The PLA-AgNO3 scaffolds were also evaluated for the interaction of the modified surfaces with Dental Pulp Stem cells (DPSCs).

We found significant differences in surface chemistry and roughness of scaffolds produced by different printers. PLA scaffolds coated with 0.1 M nanoparticle showed significantly smaller size of the biofilms for both microorganisms than the one with 0.01 M nanoparticles. Bacterial adhesion and biofilm formation was higher on Ultimaker 2 Extended+ printed scaffolds for both strains. The DPSCs had a similar correlation and attached better to the Ultimaker samples in comparison to the Makerbot samples.

8:00 AM *BM01.04.01

3D Printing of Synthetic Materials for Structural Implants Ken Gall1, Duke University, Durham, North Carolina, United States.

In this talk I will overview the 3D printing of biomedical implants from synthetic materials, including soft polymers (PCU), hard polymers (PEEK), and metals (Titanium). We will focus on basic materials science regarding the mechanical properties of the printed structures and relationships between structural porosity and resulting mechanical properties. Examples of how the basic science research has supported translation into various implants will be provided. Discussion will also center on regulatory paths for various printed implants, and the opportunities new materials and new printign methods could play in the future of medicine.

8:30 AM BM01.04.02

Multifunctional 3D Printed Implant/Biomaterial Surfaces Richard Jackson1, Stephen Patrick1 and Joe Bear2,3; 1University College London, London, United Kingdom; 2Kingston University, London, United Kingdom.

Stem cell proliferation, adhesion and differentiation on implants and biomaterial substrates are affected by the three dimensional morphology, topology, and interconnectivity of their immediate environment. This in turn means that the chemistry of, and the biochemistry at the material surface is of paramount importance. For example, the hydrophobicity of polymer objects means initial cell adhesion is insufficient in many cases which is of critical importance in bone implants. In this paper we show that by 3D printing polymers using Selective Laser Sintering (SLS) it possible to control porosity and use that porosity to chemically modify the materials properties of the implant.

We present results on the synthesis of nylon-12 scaffolds by 3D printing and demonstrate their versatility as matrices for cell growth, differentiation, and biomineral formation. We demonstrate that the porous nature of the printed parts makes them ideal for the direct incorporation of preformed nanomaterials or material precursors, leading to nanocomposites with very different properties, such as tunable hydrophobicity, enabling conducive or non-conducive environments for cell growth.

Additives such as those derived from sources such as tetraethyl orthosilicate applied at a low temperature promote successful cell growth, due partly to the high surface area of the porous matrix. The incorporation of pre-synthesized nanomaterials such as iron oxide nanoparticles led to a material that showed rapid heating in response to an applied ac magnetic field, showing promise for the control of gene expression and chemical-free sterilization. These methods also avoid using altered polymer feedstocks and contaminating or even damaging commonly used selective laser sintering printers, as well as being compatible with each other and interchangeable with each other in the modification process.

We believe this technique for chemically treating 3D printed matrices has great potential for use in addressing current issues surrounding bone grafting, implants, and skeletal repair, and a wide variety of possible incorporated material combinations could impact many other areas.

8:45 AM BM01.04.03

3D Printing of Silk Fibroin/Calcium Phosphate for Bone Regeneration Vincent Fitzpatrick1, Jin Guo1, Chunmei Li1, Sagvan Balata2, Alekya Karpuragu1, Michael Strunk2 and David Kaplan1; 1Tufts University, Medford, Massachusetts, United States; 2Zimmer ETEX, Cambridge, Massachusetts, United States.

Non-union bone fractures are a major issue in orthopedic surgery, from diagnosis to healthcare costs, and more importantly regarding treatment-related complications (Nandra et al. 2016). While autografts are the gold standard for non-union fracture repair, they can be associated to pathological symptoms at the donor site, including pain, risk of infection, blood loss, and increased operative time (Silber et al., 2003; Sass0 et al., 2005). These fractures are also limited by the amount of donor material available, which is usually harvested on the iliac crest. Allografts, on the other hand, alleviate donor site issues and are available in larger quantities, but do not provide the same quality of patient outcomes as autografts, especially in terms of osteoconductivity (Lohmann et al., 2000; Bostrom et al., 2005). Therefore, there is a need to find alternative solutions to both techniques, using new biomaterials and a tissue engineering approach. This includes the use of synthetic bone fillers such as calcium phosphate (CP)-based materials and biological factors like growth factors or miRNAs to improve bone regeneration. However, these bone fillers do not allow refined control of the geometry of the graft, and seldom offer adequate porosity for rapid colonization of the implant by cells, efficient exchange of nutrients and timing of implant degradation with replacement by newly synthesized bone. Additive manufacturing techniques like 3D printing provide tight control of geometry and porosity, and are therefore of interest for non-union bone fracture repair. These techniques include pre-fabricated and fully set CP scaffolds, which reduce operative time and prevent the risk of setting failures.

In this study we developed a slow setting reactive CP-based bionik, using silk fibroin as a binder, and used this bionik to generate porous 3D constructs for bone regeneration. These structures were bioincompatible and presented adequate mechanical properties in physiological conditions, and their shape was well-controlled even for complex geometries. Finally, their porosity could be precisely tuned to be within a range compatible with efficient osteogenesis (Karageorgiou & Kaplan, 2005). From a biological perspective, our 3D constructs induced osteoblastic differentiation in vitro, and we observed a rapid cell response and efficient neo-
osteogenesis when combined with biological factors, namely bone morphogenetic protein 2 (BMP-2) and miRNA-214 inhibitor. Furthermore, the materials could be loaded with antibiotics, providing an encouraging solution to prevent infections in patients of non-union fractures, which has been associated with a myriad of symptoms in patients, including deformities and limb-length inequalities (Jain & Sinha, 2005).

Overall, our 3D-printed CP/silk fibroin constructs offer an exciting research avenue in patient-specific treatment of non-union bone fractures, while reducing the risk of negative side effects and eliminating the need for donor site surgery.

9:00 AM BM01.04.04
3D Printing of Spatially Patterned Magnetically Responsive Hydrogels Patricia Monks1,2, Robert Murphy1, Shane Clerkin1, John Crean1, Dermot F. Brougham2 and Andreas Heise1; 1Department of Chemistry, Royal College of Surgeons in Ireland, Dublin, Ireland; 2School of Chemistry, University College Dublin, Dublin, Ireland.

Hydrogels, having similarities to the extracellular matrix and having excellent water retention capabilities, have emerged as a biocompatible material for applications in tissue engineering and as drug delivery devices. Next generation gel applications include as “bio-inks” for 3D printed bio-materials for cell scaffolding and ultimately organ printing. To realise this potential, it is critical to finely control the deposition of the hydrogel in the printing process to produce high fidelity structures.

Due to their small size, superparamagnetic iron oxide nanoparticles offer distinguishable advantages from bulk, arising from rapid reorientation of their moments. This results in rapid heating in AC magnetic fields and in attractive forces in permanent magnetic fields irrespective of initial moment orientation. The integration of magnetic nanoparticles into hydrogels has the potential to alter the properties of the original material and create a hydrogel matrix that can be manipulated in situ using magnetic fields.

We are working towards the incorporation of magnetic nanoparticles in the fabrication of novel 3D printable architectures which allows for unique applications as stimulus responsive materials. Specifically, high resolution printing (~100 μm) of these structures, will facilitate control over magnetic response with cellular resolution. The potential for high throughput with printed gel bed arrays also opens up new screening possibilities.

An open-source 3D printer was successfully built and modified to allow extrusion of hydrogels with parameters of moderate temperature and pressure that will support cell viability. Magnetic nanoparticles were synthesised, stabilised and incorporated homogenously into a printable hydrogel network with concentrations of up to 120 mM Fe which yields a temperature rise of 15°C in bulk.

A star copolypeptide based ink, which spontaneously forms hydrogels through hydrophobic interactions, allows for rapid prototyping enabling the fabrication of defined intricate microstructures. The chemical design allows the bulk phase of the hydrogel to remain intact after application of shear (during extrusion) due to its self-recovery behaviour. Here we demonstrate: (i) reproducible and robust extrusion of a polypeptide hydrogel network; (ii) spatial patterning of thermally active components and drug loading, and; (iii) in situ manipulation using applied magnetic fields with high resolution thermal mapping. The technical development of the responsive nanocomposite gels and preliminary results showing cell specification will also be described.

References
4. R. Murphy et al, Biomacromolecules, 2018, Article ASAP.

9:15 AM BM01.04.05
A 3D Microdevice for the Isolation of Cancer-Associated Circulating Cells Within the Bloodstream Elise Bou1, Kayum Jiménez Zenteno1, Aurore Estève1, David Bourrier1, Christophe Vieu1, Bernard Malavaud2 and Aline Cerf1; 1LAAS-CNRS, Toulouse, France; 2Department of Urology, Toulouse Cancer Institute, Toulouse, France.

This work introduces an engineered 3D microdevice for the capture of circulating tumor cells (CTCs) directly from the bloodstream. Our innovation relies on an intravascular label-free device enabling the trapping of CTCs based solely on their physical characteristics.

CTCs are tumor cells detaching from a primary tumor to reach the bloodstream. They represent a reliable tool for diagnostic and prognostic purposes as an alternative to solid biopsies. Therefore, many technologies have been developed to isolate CTCs from blood. In vitro systems are limited by the volume of blood that can be analyzed, manipulation factors including blood sampling and preprocessing, as well as cellular exposure to high pressure levels. In vivo approaches could offer the advantages of probing higher volumes of blood, increasing the interrogation frequency, and preserving the viability of collected cells. Thus, our approach combines both the advantages of a label-free and an in vivo isolation of CTCs.

Our capture devices are designed to be inserted into the human forearm vein through a conventional medical catheter. They are composed of a microfilter and a guiding strip. Both parts are fabricated in Nickel through a two-step process using photolithography and electrodeposition. The first step consists in the fabrication of the filtering membrane containing uniformly distributed micrometric pores. In a second step, the walls of the microfilter and the guiding strip are produced. After fabrication, microfilter are mounted onto the guiding strips in order to obtain 3D-like devices perpendicular to the incoming flow.

The prototype has been validated in vitro using a fluidic platform mimicking in vivo conditions of blood pressure and flow velocity. We succeeded in capturing human prostate cancer cells (PC3) spiked into whole blood in a few minutes, with no blood preprocessing required and with extremely low contamination levels. We also succeeded in capturing cells injected into the bloodstream of a rat model confirming its robustness to withstand in vivo conditions as a further step towards its application in clinical routine. Captured cells can be easily characterized and collected for further functional and downstream analysis. This minimally invasive technology could offer high-quality information to physicians and serve as a tool for personalized therapeutic follow-up in clinical routine.

References
10:00 AM BM01.04.06
3D Printing Scaffolds Based on Calcium Phosphate and Glass Slurries Optimized Using Statistical Experimental Design Carlos Paez1, Natalia Jaramillo1, Claudia P. García1, Alejandro Pelaez2, Sebastian Restrepo1, Niza Otero1 and Ana Moreno1; 1National University of Colombia, Medellín, Colombia; 2Universidad Cooperativa, Medellín, Colombia.

Wound healing in oral tissues (i.e. gingiva and bone) exhibit a complex equilibrium between eukaryotic and prokaryotic cells. Ceramic 3D printing allows rapid prototyping of scaffold with controlled features as shapes, porosity, size, connectivity and differential density layers to mimic bone structure. However, bulk are strong related with chemical composition and thermal processing to obtain degradability and bioactivity. The slurry plasticity affects the size layer and mechanical properties during “green” state. Experimental design approach implies the use of statistical tools that allow the multivariate analysis with the minimum number of experiments to mixtures.

The aim was to optimize a ceramic paste based on calcium phosphate and bioglass to produce 3D printing scaffolds for dentistry. A full factorial statistical design was conducted to optimize the plasticity of calcium phosphate and bioglass slurry. Plasticity ad-hoc model included variables defined as particle size and ratio calcium phosphate/bioglass. Sintering was conducted at 950°C/3h. Scaffold characterization was conducted using XRD, FTIR and SEM. Biological characterization includes bacterial adhesion of S. mutans as oral bacterial model.

Optimized Surface response of plasticity was found using 70 wt% calcium phosphates, 30wt% bioglass. Successful scaffolds were produced by 3D printing- They shown a Schwarz Diamond shape, interconnected pores, wide size pore distribution and minimum thickness layer (~200 µm). XRD diffractogram shows presence of β-TCP and amorphous glass. S. mutans shown a reduced adherence to 3D printing scaffold compared to control. Synergy between 3D printing, material processing and Statistical Experimental Design can be considered as robust methodology to develop new scaffolds with potential use in dental applications.

10:15 AM BM01.04.07
Preparation and Application of Functional Polymeric Nanoparticles Based on Poly(methacrylate)s Stephanie Schubert, Turgay Yildirim and Paul Klemm; Friedrich-Schiller-University Jena, Jena, Germany.

The development of functional polymeric nanoparticles is essential for breakthroughs in nanomedicine. By tuning the polymer characteristics and subsequently applying optimized formulations for the procedure of nanoparticles, tailored nanoparticles with varying release properties, degradation behavior, targeting groups and size distributions can be developed. For the preparation of polymeric nanoparticles, nanoprecipitation is a good choice since it is a facile, mild, and low energy input process. In combination with high-throughput devices such as microfluidics, pipetting robots, inkjet printers, and automated analytical instrumentation, the abilities of nanoprecipitation can broaden tremendously with significant effects on new applications. Selected examples in the field of gene- and drug delivery vehicles will be presented, e.g. dual pH-value and redox responsive nanoparticles and polymersomes based on a methacrylate copolymer library [1,2,3]. The functionalization of the polymers with Raman active targeting structures enables the label-free visualization of cell uptake processes [4].

References

10:30 AM BM01.04.08

In this research, we will demonstrate for the first time the use of 3D printing to realize customizable high-throughput ultra-high density arrays of 3D microelectrode probes for biological applications. The electrode density in the probe is several thousand per square centimeter; an order of magnitude improvement over the current state of the art. The proposed probes are critical in achieving a better understanding of biological systems such as the dense neural networks in a brain or enabling the next-generation neural interface for neural prosthetics. The electrodes of the probes are fabricated in a layer by layer fashion from a dense aerosol stream of silver nanoparticle ink from an aerosol-jet 3D printer. Probes with extremely high aspect ratios (up to 30:1 height to diameter ratio or more) are achieved with heights exceeding 2 mm. Flexibility and versatility of this technique are demonstrated by the realization of a variety of microelectrodes and tip geometries. Further, we have studied and optimized the electrode metallurgy; mechanical properties; electrical isolation and response; adhesion to soft and hard substrates; and biocompatibility. As a result of this investigations, a complete process parameter control was developed to adjust the mechanical properties of the electrode arrays over a wide range of strong-brittle and ductile-tough behavior. Further, we also report the buckling behavior of high aspect ratio electrodes under compression and their correlation with materials grain size have been reported.

10:45 AM BM01.04.09
Robust Hydrogel-Solid Hybrids in Biomedical Applications Hyunwoo Yuk and Xuanhe Zhao; Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Taking advantage of superior biocompatibility and tissue-like physical and mechanical properties, hydrogels have found a widespread usage in various sectors of biomedicine. Despite their unique advantages, integration of hydrogels in biomedical applications typically suffers from several technical challenges. Particularly, weak and unstable assembly between hydrogels and other solids (e.g., inorganic materials, polymers, and tissues) significantly limits the realization of functional hydrogel-based biomedical applications. Recently, we have developed a range of technologies to achieve robust interfacial bonding between hydrogels and other solids, enabling the new class of robust hydrogel-solid hybrids. In this talk, taking advantage of this new developments, we will discuss various examples of experimental translation of robust hydrogel-solid hybrids in biomedicine. We will first cover general mechanisms for robust wet adhesion of hydrogels followed by specific example applications, including hydrogel hybrid neural probes for long-term neural sensing and modulation, hydrogel skins for diverse polymers with arbitrary shapes, and tissue adhesives for flexible devices.

11:00 AM BM01.04.10
Designing shape morphing materials featuring dynamic molecular motions in response to external stimuli will enable the development of next generation smart materials. Traditional shape morphing design relies on (1) engineering the (de)hydration process and (2) programming the heat-induced shape changing polymers. Incorporating smart molecular systems and controlling their dynamic features across the nano-to-macroscopic scale, in combination with the state-of-the-art 3D printing technology could enable the development of fast-responsive 3D printing materials. In this presentation, we report the synthesis of a polypseudorotaxane-based 3D printing inks that consists of α-cyclodextrins and dimethacrylamide polyethylene glycols. After 3D printing and photo-crosslinking, the mechanically interlocked rings in the polypseudorotaxane network can be switched between stationary and randomly shuttling states through the (de)protonation their hydroxyl groups. This nanoscale ring motion is aligned in a synchronized manner, resulting in fast shape morphing macroscopically. Copolymerizing acrylate monomers with the polypseudorotaxanes affords a copolymer network, which respond to pH and ionic strength. We also performed dual-material 3D printing using two hydrogel inks mentioned above, and fabricated a hybrid monolith with multiple shapes macroscopically. Our work demonstrates that, by switching the ring motions in a molecular interlocked architecture in combination with pH/ionic-sensitive moieties, a fine spatiotemporal control of the hybrid 3D printed object’s shape morphing process has been achieved.


11:15 AM BM01.04.11
Development of a Ceramic—Polymer Biofilament to Obtain Scaffolds Using Additive Manufacture Claudia P. Garcia1, Paula A. Nevado1, Alex Lopera1,2, Marlon Rincon Fulla1,2, Juan Luis Palacio1, Maria A. Zaghete3, Glenda Biasotto3, Juan Rivera2, Hugo Estupinán4 and Carlos Paucar5; 1Física, Universidad Nacional de Colombia sede Medellín, Medellín, Colombia; 2Ciencias, Instituto Universitario Pascual Bravo, Medellin, Colombia; 3Universidade Estadual Paulista Júlio de Mesquita Filho – Unesp, Araquara, Brazil; 4Materiales, Universidad Nacional de Colombia, Medellín, Colombia; 5Quimica, Universidad Nacional de Colombia, Medellin, Colombia.

One of the most common materials to be used in scaffolds for osseous regeneration applications are calcium phosphates (CaPs) and more specifically bicalcic phosphates (BCPs) because to their properties of osteoconductivity, biocurarability, biocompatibility and composition similar to the mineral phase of the bones. In the manufacture of scaffolds it is important to consider not only the biocompatibility but also the porosity, topography, morphology and mechanical behavior that are adequate to promote osteogenesis and angiogenesis. The additive manufacturing (AM) offers many possibilities to control these characteristics entering in the field of personalized medicine satisfying the particular needs of each patient. Currently research in the manufacture of scaffolds for bone regeneration from CaP are focused on obtaining formulations of ceramic pastes with the appropriate rheological and mechanical characteristics to be used in 3D printing on bioploters with ceramic paste printing kits. Many of these formulations are expensive due to the conditions of obtaining, storing, handling and the difficulty to guarantee repeatability of the appropriate conditions of each print in time as well as the high cost of the bioploter or appropriate printing kit for each paste. In this work a biofilament to be used in any low cost commercial 3D printer was developed. The biofilament is a ceramic / polymer composite based on calcium phosphates (CPs) and polyacrylic acid (PLA). The chemical route used to obtain the particles of CPs was the combustion method in solution. This method allowed to obtain in a simple way nanoparticles with a good price / quantity ratio. X-ray diffraction showed that the particles without thermal treatment consisted of the mixture of hydroxyapatite (HAP) and tricalcium phosphate (both alpha and beta phases), while the heat treatment of the CPs at 800°C for 2 hours enhanced the crystallization of HAP and B-TCP. Field Emission Electron Microscopy showed that the powders obtained with and without thermal treatment consisted of porous aggregates of micrometric size conformed by 100 nm nanoparticles. These powders were used to obtain biofilaments by hot extrusion in a Wellzoomextrude equipment with a Ceramic-Polymer ratio of 15%-75% weight respectively. The biofilaments obtained were characterized by scanning electron microscopy, EDS, FTIR, biodegradability and cytotoxicity. The filaments were tested in a low cost cast filament printer (Micromake 3D-Delta printer) obtaining different pieces with appropriate geometries to be used as scaffold.

11:30 AM BM01.04.12
Cell Proliferation Assessment of PLA and Alumina Scaffolds Fabricated by Additive Manufacturing Jhon A. Ramirez, Valentina Ospina, Angie Alejandro Rozo, Maria Isabel Viana, Sebastian Ocampo, Sebastian Restrepo, Neil Aldrin Vasquez, Carlos Paucar and Claudia P. Garcia; Universidad Nacional de Colombia sede Medellín, Medellín, Colombia.

Every day around the world people are being diagnosed with some kind of disease where the only solution is to replace the damage tissue or organ. Tissue Engineering is an alternative and promising approach that pretends to replace the damaged tissues or organs by using structures known as scaffolds which mimic the extra cellular characteristics of the specific tissue what is desired to replace where later healthy cells obtained from the patient will be harvested in an appropriated media to guarantee in vitro proliferation, compatibility and normal tissue growing at the moment of the implantation. The scaffolds could be biodegradable and be completely replaced with new tissue which is the case of the poly-lactic acid (PLA) that degrades to form lactic acid, nevertheless, there are also biocompatible scaffolds that do not degrade and are also bioinert which is the case of the scaffolds made with alumina which, despite not interacting with the surrounding tissue, are being studied thanks to their excellent mechanical properties. The triply periodic minimal surfaces (TPMS) are mathematically defined so that they occupy a minimum area given a boundary in R³ presenting crystallographic groups symmetry that repeat three-dimensionally guaranteeing an interconnected porosity. The porosity percentage and pore size can be controlled from the design, being this a great advantage for scaffolds design for the use in regenerative medicine. In this work scaffolds based on two different geometries were fabricated by additive manufacturing (AM): one based on a TPMS, the Schwarz D surface, and another one based on a rectangular geometry with orthogonal through-holes. For the scaffolds fabrication two different materials were used: PLA in filament form, and alumina in printable paste form. The obtained scaffolds structure was characterized by X-ray diffraction and scanning electron microscopy and the cell proliferation was assessed for each geometry and material using fluorescence microscopy and DNA quantification by nanodrop. The additive manufacturing allowed to obtain scaffolds with the assessed materials guaranteeing the pores interconnection in each one of them. Curve surfaces fabricated with PLA were more favorable for cell attachment and proliferation of the CHO K1 cell line.
Fused deposition modeling (FDM) printing is an emerging 3D printing technology in which thermoplastic filaments are extruded and deposited in certain manner according to computer input design. FDM is a rapidly developing new area where new methodology is required to explore phenomena far from equilibrium. In this study, we use in-situ synchrotron X-ray scattering and high resolution infra-red imaging to study in-situ the relationship between the extrusion parameters, the filaments deposition directionality and the internal structure of the nanocomposite. In two steps study we place first “home-made” extrusion setup and then open-walls 3D printer in the beamline. 

The results are then compared with Lattice Boltzmann Modeling which simulates the welding between filaments as a function of nozzle parameters, printing protocols, and the system thermodynamical response function. In filled systems, using in-situ X-rays scattering, we observed the effect of extrusion shear forces on the orientation of the nanoparticles and the influence of the particle/polymer interactions on the polymer crystallization. This phenomenon (“Transcrystallization”) leads to templating of the polymer crystalline structures by the fillers which, we show, can enhance the thermal, mechanical and electrical properties of the printed nanocomposite structures, under directional control by the printing algorithm. The results of in-situ printing measurements show how the parameters of sample temperature, printing orientation and materials composition affect the internal structure and crystalline structure formation.

We Acknowledge support from the National Science Foundation (Inspire Award No. 1344267) and The Morin Foundation Trust.

**1:30 PM BM01.05.01**

*In Situ X-Ray and Thermal Characterization of FDM 3D Printing* 

Yuval Shmueli, Jialong Jiang, Thomas Howell, Ellen Wachtel, Gad Marom, Dilip Gersappe and Miriam Rafaely, Weizmann Institute of Science, Rehovot, Israel; The Hebrew University of Jerusalem, Jerusalem, Israel; Stony Brook University, The State University of New York, Stony Brook, New York, United States.

1:45 PM BM01.05.02

**3D Printed Functionalized Organic Electrochemical Transistors for Glucose Sensing**

Jiaxin Fan, Darren Majak and Manisha Gupta; Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

The invention of organic semiconductors unravels new possibilities for fabricating electronic devices specially with 3D printing techniques. The development of flexible and wearable biosensing devices, based on organic electronics, has received a great amount of attention due to demands for affordable, non-invasive, and continuous monitoring of physiological parameters for healthcare and biomedical diagnostics. PEDOT:PSS based organic electrochemical transistors (OECTs) are ideal candidates for flexible and customizable biosensors which, due to the simple device structure and material stability, can be fabricated with 3D printing techniques.

In this study, we have 3D printed functional OECTs, using an Optomec Aerosol Jet 5X 3D printer with commercially available materials. These devices were assembled as follows: first, a Parylene C substrate was thermally deposited, then a gate electrode as well as the source and drain electrodes were printed with commercially available platinum and silver nanoparticle ink respectively, the channel was then printed using PEDOT:PSS ink, and finally the passivation layer was printed with commercially available UV-curable polymer that was cured in-situ. The printed OECTs with similar channel dimensions \((W=95\, \text{mm}, \, W/L = 4, \, d=374\, \text{nm})\) have shown high peak transconductance \((g_{m}=998.3\, \text{mS})\), low threshold voltage \((0.51\, \text{V})\) and high current ON/OFF ratio \((I_{\text{ON}}/I_{\text{OFF}}=3.3\times10^5)\).

Functionalization improves the capability of detecting a particular analyte. OECTs have been demonstrated as glucose sensors, which show electrical response to changes in glucose concentration levels. Expanding on this work, we have also conducted studies of surface immobilization of glucose oxidase (GOX), which is commonly used for glucose detection. We have conducted the functionalization by the standard technique of dip-coating and also implemented 3D printing of the GOXs. Results from glucose measurement with no functionalization and with the dip-coated and 3D functionalized will be presented here.

**2:00 PM BM01.05.03**

**3D Printing of Hexagonal Boron Nitride Nanocomposites for Biomedical and Electronic Applications**

Linda M. Guiney, Nikitha D. Mansukhani, Adam E. Jakus, Shag Y. Wallace, Ramille N. Shah and Mark C. Hersam; Northwestern University, Evanston, Illinois, United States.

Two-dimensional (2D) materials possess a broad range of interesting properties enabling applications in energy, electronics, and biomedicine. Additionally, the field of three-dimensional (3D) printing has become increasingly attractive for both biomedical applications as well as printed electronics. By incorporating 2D materials into 3D printable inks, their properties can be harnessed for functional and customizable biological constructs, specifically in bioelectronics. For example, as implantable electronics are developed, thermal management will be a major challenge, where even small changes in temperature can result in deleterious perturbations to the surrounding tissue. Thus, there is a need for thermally conductive but electrically insulating flexible materials that can be incorporated into novel electronic implants. Hexagonal boron nitride (hBN) nanocomposites offer one potential solution due to their thermally conductive yet electrically insulating nature in addition to the high biocompatibility of hBN. Here, a high-content hBN-polymer nanocomposite ink is reported, which can be 3D printed to form mechanically robust, self-supporting constructs. To achieve these 3D printable nanocomposites, hBN is dispersed in poly(lactic-co-glycolic acid) and extruded at room temperature to form complex architectures that maintain their shape upon extrusion and can span large gaps without sagging or deformation. These constructs possess high mechanical flexibility and stretchability following 3D printing at compositions of up to 60% vol. hBN (solids content). The enhanced thermal conductivity, up to 2.1 W K\(^{-1}\) m\(^{-1}\), due to the presence of hBN within the matrix suggests utility in thermal management applications. Furthermore, the constructs show high levels of cytocompatibility with human mesenchymal stem cells for up to one month, suggesting their utility for printed bioelectronics.

**2:15 PM BM01.05.04**

**3D and 4D Printing of Biomedical Grade Thermoplastic Polyurethanes (TPUs) and Nanocomposites**

Rigoberto C. Advincula; Case Western Reserve University, Cleveland, Ohio, United States.

The use of 3D printing to create prototypes and devices from biocompatible polymeric materials has appended the design functionality of polymeric materials for biomedical devices enabling rapid development for new applications. Biomedical grade polymers can be further classified into thermoplastics, thermosets, and elastomers based on their thermo-mechanical properties. However, it is not as simple as the classification into these groups when it comes to their intended in-vivo or in-vitro applications. The transition to a final phase or cross-linked structure results in new properties. This is more evident with the choices of 3D printing methodologies (FDM, SLA, SLS, VSP) which can make use of blended or formulated compositions. We have demonstrated the 3D printing of biomedical grade thermoplastic polyurethanes (TPU) with compatibility to mammalian NIH 3T3 cells. However, 4D printing allows the design of new materials and applications based on integrating the chemistry of conversion with the printing mode. In this talk, we demonstrate the fabrication of concept objects and elastomeric actuators based on the use of biomedical grade TPU melts and extruded viscous solutions. The result is an extrudable precursor nanocomposite elastomer which can be printed via viscous extrusion printing (VEP) or VSP and then converted to an elastomeric actuating material with very high cyclic compressibility. Other work based on the use of SLA, SLS, FDM, towards high strength nanocomposite and biomaterials will be discussed.
The ability to three-dimensionally interweave biological and functional materials could enable the creation of devices possessing unique and compelling geometries, properties, and functionalities. Indeed, interfacing active devices with biology in 3D could impact a variety of fields, including regenerative bioelectronics, smart prosthetics, biomedical devices, and human-machine interfaces. Biology, from the molecular scale of DNA and proteins, to the macroscopic scale of tissues and organs, is three-dimensional, often soft and stretchable, and temperature sensitive. This renders most biological platforms incompatible with the fabrication and materials processing methods that have been developed and optimized for functional electronics, which are typically planar, rigid and brittle. A number of strategies have been developed to overcome these dichotomies. Our approach is to use extrusion-based multi-material 3D printing, which is an additive manufacturing technology that offers freeform, autonomous fabrication. This approach addresses the dichotomies presented above by (1) using 3D printing and imaging for personalized, multifunctional device architectures; (2) employing ‘nano-inks’ as an enabling route for introducing diverse material functionality; and (3) 3D printing a range of functional inks to enable the interleaving of a diverse palette of materials, from biological to electronic. 3D printing is a multiscale platform, allowing for the incorporation of functional nanoscale inks, the printing of microscale features, and ultimately the creation of macroscale devices. This blending of 3D printing, functional materials, and ‘living’ platforms may enable next-generation 3D printed devices, from a one-pot printer.

Collagen hydrogels show promise for use as bioinks in extrusion-based 3D bioprinting. However, compared to some other natural and most synthetic hydrogels, collagen displays slow gelation times and poor mechanical stability, resulting in inferior printing characteristics. Recent efforts to improve the printability of collagen have shown that the rheological properties of collagen bioinks are a good indication of their printing accuracy. However, little is known about the effect of surface tension of bioinks and its effect on printability. In this study, we examine how hydrophobic surface coatings affect the contact angle of collagen bioinks and how this relates to printing accuracy. Type I collagen hydrogels were either fabricated to form a final collagen concentration of 4, 8, or 12 mg/mL, and riboflavin crosslinked gels were fabricated by adding 0.5 mM riboflavin and photocrosslinking with blue light for 10 seconds at the beginning of bioink dispensing for both contact angle and printability testing. Contact angle measurements were taken on glass coverslips either cleaned with 70% ethanol or coated with a polysiloxane solution (Rain-X™) and printability was assessed by printing lines (50 x 0.8 mm) on cleaned or coated glass coverslips using a Fab@Home 3D printer. Collagen drops printed on coated glass had dramatically higher contact angles than those printed on uncoated glass. On uncoated glass, collagen concentration had a more modest effect on contact angle than that of the coating. The addition of riboflavin did not have a significant impact on contact angle. The accuracy of printed lines increased with both collagen concentration of the bioink and the use of coated glass. Similar to the contact angle measurements, the effect of the coating decreased as collagen concentration increased. For printability testing, this is likely related to the fact that 12 mg/mL bioinks on uncoated glass were already approaching the 0.8 mm intended line width imposed by the diameter of the printing nozzle. These results will be used to change printing accuracy without changing bioink formulation and allow for a wider range of printabilities with finer resolution in the future.

References

Characterization and Validation of 3D Printed Polycarbonate Urethane for Biomedical Applications Andrew T. Miller, Natalia von Windheim, and Ken Gall
Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; 3restor3d, Durham, North Carolina, United States.

Polycarbonate urethanes (PCUs) are gaining in popularity in many biomedical applications due to their low stiffness, biocompatibility, and high strength. As a thermoplastic, PCUs can be 3D printed through a process known as fused deposition modeling (FDM). FDM offers many benefits such as: cheaper, faster, and easier prototyping, custom or complex geometries and architectures, and potentially even final component or device manufacturing. However, such processing will have implications on the material microstructure and ultimately the mechanical properties, particularly fatigue performance. The purpose of this study was to assess the effects and viability of FDM with PCU in an effort to realize new opportunities in the biomedical field for this promising soft material.

PCUs of three different hardnesses (75A, 85A, and 95A) were obtained in pellet form. Test samples were formed through either injection molding (IM) of pellets or extrusion into filament and then processing via FDM. Material structures were characterized through DSC, DMA, 1H NMR, and FTIR. Mechanical tests included monotonic tension, compression, shear, and tensile fatigue. In addition, monotonic tension and tensile fatigue tests were performed on printed crosshatch scaffolds, which are fundamental to the biomedical field, to probe the effects of architecture.

FDM parameters were identified that resulted in samples consistently >99% solid. Monotonic tests indicated FDM samples matched IM in terms of tensile failure stress, while exhibiting significantly larger failure strain. Shear tests demonstrated no significant difference in shear strength between FDM and IM samples, which indicates strong layer bonding for FDM samples. Fatigue tests show an apparent improvement in strain-based fatigue for FDM samples. When plotted against stress amplitude, fatigue data indicates that solid FDM samples successfully matched IM samples in tensile fatigue despite the small percentage of voids. The crosshatch architecture resulted in a minor detriment to fatigue performance, even after adjusting for porosity. However, the effects were small relative to stiffer materials such as PEEK and titanium. Overall, the results show great promise for printed specimens of PCU, both solid and with architecture.

This study demonstrated the effectiveness of FDM as a processing method for PCU based on the performance of FDM samples. The results are both unexpected and significant, as they indicate potential for printing soft devices while maintaining a high level of performance, including in fatigue. This is
promising for biomedical applications where custom geometries or complex architectures utilizing a soft, biocompatible material are desired. Potential applications are numerous, ranging from transvaginal meshes to custom, composite osteochondral devices.

4:00 PM BM01.05.08
Hierarchical Co-Assembly Enhanced Direct Ink Writing Longyu Li, Qianming Lin and Chenfeng Ke; Chemistry, Dartmouth College, Hanover, New Hampshire, United States.

The development of smart materials and devices has attracted increasing attention owing to their capability of altering the macroscale properties in a controlled manner. Integrating these synthetic functional materials with 3D printing technology, i.e. the extrusion-based direct ink writing (DIW) enables the amplification of their nanoscale properties into the macroscale by taking advantage of the controlled hierarchical assembly and pre-designed macroscale 3D geometry. Currently, small-molecule-based 3D printing materials are very rare owing to the difficulties of facilitating 3D printability as well as preserving their molecular functions macroscopically. In this presentation, we report a general approach of integrating functional small molecules into 3D printing materials and transferring their molecular features to the macroscale through supramolecular templation, post-printing hierarchical co-assembly, and covalent crosslinking. A variety of inorganic and organic inks were 3D-printed, and their superstructures were refined by post-printing hierarchical co-assembly. Our method not only enhances the printing resolution up to one order of magnitude, but also enables precise spatial control over nanoscale features as well as macroscopic shape change over a large scale. Fluorescence tracking experiments provided a molecular understanding of the dynamic co-assembly process at the macroscale and enabled the development of simultaneous color- and shape-changing 4D printable materials in response to the external stimuli. Furthermore, we showcased a benzene-1,3,5-tricarboxamide-based monolith capable of expanding and contracting through the insertion and removal of the correspondent supramolecular pillars. We believe that this new approach will initiate the development of small-molecule-based 3D printing materials and greatly accelerate the development of smart materials and devices that are capable of accomplishing complex tasks in response to environmental stimuli.

References:

4:15 PM BM01.05.09
3D Printing of Shape-Memory Thermoplastic Polyurethane for Biomedical Applications David Safirman1, Natalia von Windheim2 and Ken Gall1; 1MedShape, Inc., Atlanta, Georgia, United States; 2Duke University, Durham, North Carolina, United States.

Thermoplastic polyurethanes are used in a variety of biomedical devices, such as catheters, implantable defibrillators, wound care dressings, and orthopaedic implants. Due to their easy melt processing, these polymers areideal for 3D-printing via fused deposition modeling. Prior studies of the shape-memory behavior of thermoplastic polyurethanes has been limited to either cast, pressed, or injection molded parts. The overall goal of this work is to determine the effect of build orientation on thermo-mechanical properties, mechanical behavior, and shape-memory performance of a 3D-printed shape-memory thermoplastic polyurethane. A biomedical grade shape-memory thermoplastic polyurethane was extruded into 3.0 mm filament for 3D-printing via a LulzBot TAZS. ASTM D638 Type V dogbones and rectangular samples were printed in each of three build orientations (flat, on-side, and vertical). The print speed was set to 500 mm/min and the nozzle temperature was 215°C. Dynamic mechanical analysis (TA Q800) was used to determine the glass transition temperature and rubbery modulus. Tensile behavior was determined using an MTS Inspert 2 with a laser extensometer according to ASTM D638. Toughness was calculated as the area under the stress-strain curve. Unconstrained recovery for each build orientation was assessed with a 180° bend recovery test. The glass transition temperature as determined from the peak of the tan delta curve was nearly equivalent for all three build orientations at 78°C. However, the storage modulus was increased for the flat orientation at 1515 MPa, compared to 1042 MPa and 1122 MPa for the on-side and vertical orientations, respectively. Rubber modulus above the glass transition temperature was nearly equivalent amongst the build orientations at 29 MPa. All tensile samples displayed linear elastic behavior, followed by yielding and plastic deformation. The on-side and flat orientations displayed strain-hardening; however, the vertical build orientation did not experience hardening at higher strains. The failure strain was 70, 152, and 212% for the vertical, on-side, and flat orientations, respectively. The ultimate stress was 19.8, 30.8, and 44.4 MPa for the vertical, on-side, and flat orientations, respectively. The toughness was 13.1, 37.3, and 63.5 MJ/m² for the vertical, on-side, and flat orientations, respectively. Shape-recovery was near 97% for each build orientation for the bend recovery test. Unconstrained shape-recovery was not dependent upon build orientation; however, tensile properties improved when the flat build orientation was used. However, a 70% failure strain in the vertical build orientation is still 10x greater than other common FDM thermoplastics, such as ABS or nylon. These superior mechanical properties will allow for the design and manufacture of complex biomedical devices.

4:30 PM BM01.05.10
3D Patterned Hydrogels for Controlled Growth Factor Release Pengrui Wang; University of California, San Diego, La Jolla, California, United States.

3D printed hydrogels can provide dimensional control over the release of molecules enveloped in them. Owing to their controllable degradability, capability to protect envelope molecules from degradation, hydrogels provided physiochemical interactions with agents such as growth factors to regulate their release kinetics. Amongst the commonly used hydrogels, heparin have shown prolonged release due to its high negative charge density. Researches have shown heparin gels can trap positively charged molecules such as growth factors by electrostatic forces to delay their delivery. Another negatively charged hydrogel, hyaluronic acid, has been widely engineered for applications such as wound healing and cosmetic surgeries due to its role in granulation and cell migration. Recent development in 3D printing of modified hyaluronic acid has inspired its application in controlled drug release. Engineered release of growth factors are potent strategies for regulating cell regeneration in tissue engineering, but spatially patterning them in a facile manner to achieve releasing of multiple factors in a controlled manner is still challenging. Additionally, mathematical modeling of the drug release from engineered structure is also lacking. In this work, we presented a heparin and hyaluronic acid-based hydrogel system that was 3D printed to allocated multiple growth factors at different locations within the same construct to achieve sequential release over weeks. Mathematical models of release kinetics were developed and verified. Furthermore, we have observed the stimulus effect on angiogenesis in vitro and tissue regeneration in vivo from engineered sequential release. We hope that our findings could provide a more comprehensive understanding of release kinetic of hydrogels for the community.

4:45 PM BM01.05.11
3D/4D Printed MicroRobotic Machines for Biomedical Applications Hen-Wei Huang; ETH Zurich, Zurich, Switzerland.

BM01.05.10

BM01.05.09
In the past decade, the development of microelectromechanical system (MEMS) and smart nanocomposite materials has enabled roboticists to construct miniature three-dimensional (3D) mobile machines with programmable morphology and motility from two-dimensional (2D) materials through self-folding (1, 2). These self-folded micromachines wirelessly driven by electromagnetic fields exhibit great potentials in revolutionizing current procedures in minimally invasive medicines by means of targeted drug delivery, micro-tissue transplantation, and robotic cell scaffolds (3, 4). However, self-folded functional micromachines are mostly limited to their monotonous cylindrical structures, such as tubular, helical, and spiral shapes, which in turn constrains the possibility of integrating multiple functionalities into a single machine.

Owing to the progress in 3D printing techniques with the resolution at micro/nano scales, robotic micromachines with sophisticated 3D shapes and spatially controlled mechanical properties can be engineered via direct-laser-writing (DLW) on polymers capable of spatiotemporally modulating the cross-linking degree (5). Extra functionalities can be extended on the printed structures simply by incorporating other functional materials. In this work, 3D printed compound microstructures, which is impossible to be implemented through folding 2D materials, are devised to be a robotic microtransporter composed of a helical propeller for wireless-controlled propulsion and an Archimedes screw for delivering therapeutic micro-agents. We demonstrate such compound machines can implement on-demand loading, encapsulation, and transport of multiple, various therapeutic micro-agents, ex. different sizes of cells and various kinds of drugs. Furthermore, using environmentally stimuli-responsive hydrogels as the printing materials endow the micromachines with sensing and shape morphing capabilities, also known as 4D printing. By coordinating the sensory input with shape morphing output, the control loop can be closed without external imaging feedback and intricate integrations of sensors and actuators, paving the way of autonomous targeted delivery inside the human body.

Reference:

SYMPOSIUM BM02

Electronic and Coupled Transport in Biology
November 26 - November 28, 2018

Symposium Organizers
Caroline Ajo-Franklin, Lawrence Berkeley National Laboratory
Renata Bilewicz, University of Warsaw
David Cahen, Weizmann Institute of Science
Pau Gorostiza, Catalan Institution for Research and Advanced Studies

8:15 AM *BM02.01.01
Microstructuring and Characterization of Redox-Active Polydopamine Films Jing Lin, Dominik Blaimer, Sven Daboss and Christine Krantz; Ulm University, Ulm, Germany.

Polydopamine (PDA) a synthetic eumelanin polymer is highly interesting as thin film surface modification for a multitude of applications ranging from adhesive coatings for cell immobilization\(^1\) to biomimetic electron gates for artificial photosynthesis\(^2\). The polymerization of dopamine can be obtained via a chemical process at basic pH values higher than 7.4\(^3\). Improved control of surface morphology can be achieved via electrochemical deposition e.g. by cyclic voltammetry, leading to thin films offering various functional groups such as amines, imines and phenolic groups at conductive surfaces.

In this contribution, we report the microstructured deposition of PDA using pulsed electrochemical deposition techniques, in order to improve film uniformity and thickness. To form microspots of PDA, scanning electrochemical microscopy in direct mode\(^4\) was used with the substrate as working electrode and the microelectrode as the counter electrode. The electron transfer properties of the microspots were investigated in dependence on the pulse number, the distance between substrate and microelectrode, the RG value (ratio of the radius of the insulating sheath and the electrode radius) of the microelectrode and the used redox mediator. As PDA has redox-active phenolic/quinone groups, surface properties of the polymer can be electrically switched. Our group recently introduced a new type of AFM-SECM probe bearing a conductive colloid\(^5\). Such conductive colloidal probes will be modified with polydopamine films and first results on force spectroscopy under potential control will also be presented.

Electron transport in proteins and peptides is crucial for energy conversion in biological processes including photosynthesis, respiration and enzymatic reactions. Therefore, the important goal of the fundamental research is to provide insight into the mechanisms determining peptide-mediated electron transport. Peptides are known to adopt variability of structural motifs and when suitably designed, they can also serve as components of biosensing devices or nanoscale bioelectronic circuits. In this area of research, significant progress has been made due to the development of experimental methods, which enable fabrication of nanoscale junctions with peptide monolayers bridging two conductive electrodes. Among them, scanning probe microscopy (SPM) offers unique capability to investigate electric properties of individual molecules or molecular films. Such approach involves entrapment of the assemblies of molecules between two metallic contacts established by metal support and conductive probe of SPM. When the bias voltage is applied between the contacts, the resulting current flow depends on the properties and structural features of peptide molecules forming the assembly including their length, secondary structure, dipole moment, the nature of the constituent amino acids or charge. Importantly, SPM-based method enables control of the mechanical strain or stress of the molecular film incorporated into the junction.

Among variety of structural motifs, α-helical peptides were proved to be efficient mediators of electron transport. However, their use is limited to compounds containing at least 8 amino acid residues. To overcome this problem, we have designed molecular junctions utilizing β-hellicomimetic foldamers based on oligourea backbone. These particular compounds possess important features: (a) it is possible to synthesize oligoureas containing side chains of all natural amino acids; (b) the folding process of oligomers is not affected by the nature of side chains. Such characteristics make them highly robust, tunable and hence useful in the studies of electron transport processes. Additionally, only four acyclic residues are sufficient to drive complete helical turn formation. We have demonstrated that oligoureas may act as efficient electron transport mediators and the oligourea helix is more stable than the helix formed by peptides. Interestingly, electron transmission through longer analogs shows strong directional dependence, which is characteristic for diode-like behavior.

References:

9:15 AM BM02.01.03
Controlling the Mechanism of Charge Transport via Au-Azuin Junctions by Chemically Modulating Protein-Electrode Interactions Jerry A. Freerik, Gilad Porat, Mudi Sheves, Israel Pecht and David Cahen; Weizmann Institute of Science, Rehovot, Israel.

A tremendous effort has been made by researchers to explore the possibility of using biomolecules, including proteins, in molecular electronics. The idea is to exploit their built-in functionalities, introduced by millions of years of evolution, for the task of electron transport. However, despite great progress that was made, fundamental questions regarding the effects of relative energies, of the contacts and protein-contact coupling, as well as the nature of the internal electrostatic potential profiles remain unclear.

We will report on the results, obtained from a systematic study of conductance, current-voltage plots and IETS measurements at low temperatures to investigate the mechanism of charge transport via different Az-Au-Az junction configurations. In all the configurations that were studied Az was covalently bound to a Au substrate on one side and chemical modifications were carried out with linker molecules to the contact that was made on the opposite side of the protein. The conductance and IETS profiles obtained from different configuration strongly suggest that by chemically fine-tuning the coupling strength to the electrodes, we can switch the tunneling mechanism ‘IN’ and ‘OUT’ of resonance. The shape of the conductance plots, intensity of the IETS spectrum and the barrier height ( ) values, obtained from fitting the I-V curves, provide the position of the frontier energy levels with respect to the electrode Fermi level, indicating that the energy levels are pushed apart upon increased coupling (fits simple MO/tight binding models). This shows that the energy-level alignment in Az-based junctions can be regulated by chemical modifications of the electrical contact to the protein. The results presented here provide a strategy suitable for altering the transport mechanism through solid state protein monolayers, by chemically modifying the interaction between the protein and the linker in protein based two-terminal device, i.e., without a gate electrode.

9:30 AM BM02.01.04
Electron Transport Through Linear Peptide Cunlan Guo; College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China.

Biomolecules display great potential for future functional molecular electronic devices, due to biomolecules’ unexpected conductance, multiple structure, unique bio-recognition and self-assembly. Peptides are suitable as one of the building blocks to bridge conductive electrodes in solid state electronic devices. To design and apply peptide junctions for solid state devices, the relations of peptide electron transport to their amino acid composition and structure need to be understood as well as the peptide electronic structures on the electrode surface. Such information may also help understanding the electron transfer processes that occur in/with proteins in biological energy conversion, sensing and signaling systems. Here, we take linear peptides as the model and construct series peptide junctions on the solid state. Combining theory and calculations, we studied the controlled ways to modulate the electrical properties of peptide junctions which display a versatile, readily available tool for future (bio)electronic applications.

Acknowledgments: The author thanks all the kind helps from the collaborators.

References:

9:45 AM BM02.01.05
Discovering the Structural Factors Governing Proton Transport in Self-Assembled Peptide Fibers Obad Silberbush1, Subhashish Roy1 and Nurit
The ability to de-novo design peptides (short proteins segments) to self-assemble into functional structures has attracted an extensive attention in recent years, especially towards their implementation in biomedical and biotechnological applications. Many of the self-assembling peptide sequences include charged amino acids, making the resulting nanostructures amenable to proton conduction. Motivated by the opportunity to employ this phenomena in novel bioelectronic applications, the aim of the work I will present was to discover the structural factors that govern proton transport processes in these biomimetic structures. I will demonstrate that proton transport is enhanced significantly by the introduction of even a single charged amino acid into the sequence of a hepta-peptide that self-assembled into fibrils. Moreover, I will show that acidic residues are more effective than basic ones in promoting proton-conduction of the peptide fibrils due to two orders of magnitude larger doping effect, and a threefold higher charge carrier mobility value. I will further demonstrate that both structural motif of the monomeric peptides and the secondary assembling structure have a critical impact on proton conductance of their assemblies. I will show that assemblies originating from helical structures exhibit higher conductivity than assemblies of β-sheet forming peptides with a similar sequence. Nanotube forming D, L γ cyclic peptides with β-sheet structure, however, demonstrated superior conductivity to both linear assemblies. The amount of charge carriers’ density was found to be structural independent and that peptide molecule configuration and self-assembled structure influence proton mobility. Finally, I will demonstrate that acidic molecules can be used for external doping of the peptides assemblies.


10:00 AM BREAK

10:30 AM BM02.01.06
Mechanisms of Charge Transport and Large Tunnel Magnetoresistance Across Ferritin-Based Molecular Junctions Christian A. Nijhuis; National Univ of Singapore, Singapore, Singapore.

Electron transport (ET) is important in countless biological processes including enzymatic catalysis or photosynthesis. The efficiencies of ET over long distances in biological systems can be remarkably high. Unraveling the underlying mechanisms governing long range ET across such systems is not only interesting from a fundamental point of view, but could also lead to interesting technological applications in biomolecule-based sensors or biomolecular electronics. We study ET across biomolecular junctions of ferritin which is a cage-like iron storing protein consisting of 24 subunits with an outer diameter of 12 nm and inner diameter of 8 nm. We found that the ET mechanism is independent of the temperature when the ferritin is loaded with iron, but temperature independent when no iron is present. Junctions formed with Ni bottom-electrodes and ferritin monolayers show a tunneling magnetoresistance of 30% at room temperature. Finally, I will also discuss ET in the inverted Marcus region observed across molecular diodes; this ET mechanism may be also relevant to biological systems.

11:00 AM BM02.01.07
Large-Scale Conformational Changes Induce Tunable Electronic and Mechanical Functionality in Proteins Sibel Ebru Yalcin1, J. Patrick O’Brien1, Atanu Acharya2, Yangqi Gu3, Winston Huynh4, Sophia M. Yi1, Subhayotti Chaudhuri2, Victor Batista2 and Nikhil S. Malvankar1; 1Molecular Biophysics and Biochemistry, Yale University, New Haven, Connecticut, United States; 2Chemistry, Yale University, New Haven, Connecticut, United States; 3Molecular, Cellular and Developmental Biology, Yale University, New Haven, Connecticut, United States; 4Biomedical Engineering, Yale University, New Haven, Connecticut, United States.

The ability to understand and modulate charge transport in molecules is of central importance in many basic chemical and biological processes and for the development of electronic devices. This charge transport sensitively depends on molecular conformations. Large-scale conformational changes are particularly attractive because they can serve as information carriers for switches in memory and logic devices. However, conformations affecting conductivity were previously found to remain local and < 2 Å, thus yielding at most a 10-fold change. Here we report the ability to control molecular conductivity via conformational switching at an unprecedented scale.

Although biomolecules are considered electronic insulators, Geobacter sulfurreducens pili protein filaments show metal-like conductivity [Malvankar et al. Nature Nano 6, 573 (2011)]. However, very little is known about how to manipulate the conformation of pili in order to controllably switch conductivity. Lack of solved structures for pili, previous assumptions of homology-based models of pili filaments, and the common perception that proteins are electronic non-conductors have led to great scepticism about conductivity in these biomaterials.

To overcome these hurdles, here we directly visualize the structure of individual pili using infrared nanospectroscopy. This imaging platform has empowered us to engineer conformational changes that facilitate π-stacking of aromatic rings, enhancing both pili conductivity and stiffness. This controlled conformational change constitutes a unique combination of tunable electronic and mechanical properties in pili.

Atomic force microscopy showed that individual Geobacter sulfurreducens pili protein filaments undergo > 20 Å conformational change that propagates over micrometer-lengths of pili upon changing the environment or amino acid composition of pili. Infrared nanospectroscopy revealed that this conformational change is driven by an internal structural transition in pili. A suite of complementary experimental and computational methods such as X-ray diffraction, raman, fluorescence emission spectroscopy and circular dichroism further demonstrated this structural transition in pili. Molecular dynamics simulations confirmed that conformational change in pili leads to improved stacking of aromatic residues to enhance their conductivity and stiffness. Our studies thus establish nanoscopic approaches to visualize and quantify large-scale conformational changes in biomolecules and present novel strategies for tuning their structure and conductivity. The demonstrated conformation-induced conductance switching in proteins will guide the creation of a new class of programmable biomaterials with precisely controlled electronic and mechanical properties. Such tunable biomaterials will aid in the development of seamless, bidirectional interfaces between biology and electronics to transduce mechanical and chemical stimuli into electrical signals.

11:15 AM BM02.01.08
Proton Conductivity in a Thin Film of Self-Assembled Peptides Takuma Narimatsu and Yuhei Hayamizu; Tokyo Institute of Technology, Otsuka, Japan.

Developments of bio-inspired materials have shown a remarkable progress due to their biocompatibility and environmentally-friendly functions. Proton conductivity is a one of the keys in biological function. Learning from natural proteins which have high proton conductivity, researchers have recently demonstrated high proton conductive bio-materials, such as natural protein and polysaccharide. Peptides are another candidate to promote the development of biomaterials with high proton conductivity. Due to its short amino acid sequence, we can design and synthesize arbitrary peptide sequence. The self-assembly of peptides has been intensively investigated and there are variety of peptides known to spontaneously form fibrils in solutions.
In this work, we design a series of peptides which contains simple amino acid sequence to investigate the proton conductivity of their thin films on a silicon wafer. Using a drop-casting method, we formed thin film of peptides on Si-wafers, and characterized the conductivity by electrochemical impedance spectroscopy. We found that these peptide thin film shows an over 5 mS cm⁻¹ of conductivity at room temperature, and this value is higher than those of pure water. Moreover, the conductivity depend on amino-acid residues as well as its crystallinity. This result indicates that proton conductivity could be designed by the peptide sequence.

11:30 AM BM02.01.09
Energy Transport in RNA—Fundamental Design Principles and Applications for Sensors Juan M. Artes Vivas, Y Li, P Feldstein, MP Anantram, J Hihath.

Energy transport is a critical process in biology, being crucial in respiration and photosynthesis. Different biomolecules have evolved to be exquisitely tuned to transfer and transport energy (including excitons and charges) with astonishing efficiency. Recent literature shows multiple examples of this natural design in different biomolecules, including proteins and nucleic acids. As a recent example, I will present recent results we obtained studying charge transport in nucleic acids, including DNA:RNA hybrid sequences from E. Coli.

The continued discovery of new RNA modalities (non-coding, micro, enhancer, etc.) has resulted in an increased desire for detecting, sequencing, and identifying RNA segments for a variety of applications in food safety, water and environmental protection, plant and animal pathology, clinical diagnosis and research, and bio-security.

We have recently demonstrated that molecular conformation profoundly influences the conductance of nucleic acids and that RNA can support long-range charge transport in specific sequences. We show that single-molecule conductance techniques can be used to extract biologically relevant sequence and opens new possibilities for developing electrically-based sensor and diagnostic platforms.

REFERENCES

11:45 AM BM02.01.10
Peptide Folding Influence on Electronic Properties of Bioinspired Peptide Based Materials Nurit Ashkenasy; Ben Gurion University of the Negev, Beer Sheva, Israel.

The three dimensional structure of proteins has a critical role in determining their functional behaviour in nature. As a result, proteins' misfolding is directly associated with different illnesses. The capture of these structure function relationships in self-assembled peptide nanostructures can provide a flexible handle to control their function. In this presentation, I will demonstrate the manipulation of the properties of bioelectronic materials and hybrids by the modulation of the folding of their peptide monomeric units.

I will first demonstrate the influence of subtle changes to the peptide backbone on the electronic properties of semiconductor nanostructures can provide a flexible handle to control their function. In this presentation, I will demonstrate the manipulation of the properties of bioelectronic materials and hybrids by the modulation of the folding of their peptide monomeric units.

In this study, the electronic properties of GaAs functionalized with dipeptides with the same sequence (Val-Tyr) but different backbone registry were characterized. Changes both to the electron affinity and the surface potential will be demonstrated, with the magnitude of which depends on the backbone registry. In the second example I will present, specifically designed self-assembling peptides bearing natural, as well as non-natural side chains, that promote electron conduction have been used. I will demonstrate that the self-assembly medium can be used to control the specific interactions deriving the self-assembly. These interactions, as a result, influence the resulting peptide nanostructure morphology and conductivity. All together these examples demonstrate an exceptional flexibility in controlling the properties of peptide based bioelectronic materials.

References
Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of energy conversion processes. This talk will focus on recent advances in the theory of PCET and applications to artificial photosynthesis and photoreduced nanoparticles. The quantum mechanical effects of the active electrons and transferring proton(s), as well as the motions of the proton donor-acceptor mode and solvent or protein environment, are included in a general theoretical formulation. This formulation enables the calculation of rate constants and kinetic isotope effects (KIEs) for comparison to experiment. A combined experimental and theoretical study of a series of substituted benzimidazole-phenol model systems inspired by the Tyr-His redox proton relay found in photosystem II provides insight into the physical principles underlying proton relays. Theory predicted a concerted two-proton transfer process associated with the electrochemical oxidation of the phenol, accompanied by a decrease in the redox potential of the phenol and a small KIE, when the benzimidazole substituents are strong proton acceptors such as primary or tertiary amines. Subsequent electrochemical, spectrophotometric, and KIE experiments were consistent with these predictions. More recent efforts to design a concerted three-proton transfer process associated with oxidation have also been successful. These bioinspired molecular systems demonstrate the potential use of multi-proton relays to enable the transport of protons over longer distances along specified pathways, as well as the tuning of redox potentials through this movement of positive charge. In a different direction, experiments have shown that photoreduced ZnO nanocrystals react by PCET with organic hydrogen atom acceptors such as the nitroxyl radical TEMPO. The application of PCET theory to these systems indicates that the electron transfers from the conduction band of the ZnO nanocrystal to TEMPO concerted with proton transfer from a surface oxygen of the ZnO nanocrystal to the oxygen of TEMPO. Moreover, proton diffusion from inside the nanocrystal to reactive sites on the surface was found to explain the experimentally observed nonexponential kinetics. These applications illustrate the significant role of theory in the design of both molecular and heterogeneous catalysts to control the movement and coupling of electrons and protons.

Bioelectronic Control of pH and Applications Marco Rolandi; Department of Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California, United States.

The concentration of H+ measured by pH plays an important role in many biological processes including energy conversion in mitochondria and archaea, enzymatic activity, and neuronal excitability. Using pH/PdHx as a transducer between electronic and H+ currents we have created bioelectronic devices that are able to control H+ concentration in solution and modulate pH at different biologically relevant levels. Here, I will present recent results on how we can use this pH modulation to control enzymatic activity in bioluminescence, targeted drug delivery, and cellular function during proliferation and growth.

Conjugated Polymer Nanoparticles as Versatile Bioimaging Probes Anitha Ethirajan1, 2; 1Hasselt University, Institute for Materials Research, Hasselt, Belgium; 2imec Associated lab IMOMEC, Diepenbeek, Belgium.

Conjugated polymers have been extensively studied for their opto-electronic properties in the field of organic electronics. In the recent years, they have emerged as promising class of materials for bioimaging owing to their excellent optical properties. Moreover, new synthesis procedures have enabled custom-built functional conjugated polymers that facilitate the one-pot synthesis of semiconducting polymer nanoparticles (NPs) with tunable properties and interesting functionalities for use in biomedical applications.1-10 The possibility to formulate hydrophobic conjugated polymers as water-based nanoparticle dispersions allows for the employment of these versatile materials in biological systems. In this contribution, the potential of interesting class of conjugated polymer nanoparticles (CNPs) for bioimaging will be addressed. Additionally, poly(p-phenylene vinylene) (PPV)-derivative based CNPs will be focussed due to their interesting optical properties, design flexibility for surface functionalization, and benign biological characteristics.

PEGylation strategy has been widely used for surface functionalization of nanoparticles for imparting stealth effects. In this study more profound insight into the various ways in which PEG, with different chain lengths, can affect this particular type of bioimaging probe will be highlighted.11 Subsequently, the consequences of PEGylation on the colloidal, optical and biological characteristics using cell populations within the central nervous system of the bioimaging probe will be shown.

Alongside surface functionality, NP size is one of the most critical concerns for biomedical applications as it has been identified to play a key role in biological processes like cellular uptake, biodistribution and cytotoxicity. Effective internalization by cells is essential to achieve the successful application of NPs for bioimaging objectives. In addition, adjusting the size can have an influence on the optical properties of conjugated polymer NPs. In here, the potential consequences of lowering the size of functional PPV-based NPs on the optical and biological characteristics of a conjugated system specifically designed for bioimaging purposes will be shown.12

The obtained results valorize the potential of conjugated polymers in biomedical applications and open bright prospectives as well as unexplored pathways for these materials.

References:

Magneto-Mechanical Forces Coupled Nanostraw Electroporation System for Enhanced Intracellular Delivery During Cancer Immunotherapy Andy Kah Ping Tay and Nicholas A. Melosh; Stanford, Menlo Park, California, United States.

According to the American Cancer Society, 1.8 million new cases of cancer are expected in 2018. Despite better treatments, mortality rates of cancer like melanoma remain high. Chimeric Antigen Receptor (CAR)-T cell, with on-going clinical trials, offers a promising strategy to engineer immune T cells that recognize and kill cancer cells. Unfortunately, it is difficult to deliver genes and integrate them into the genome of T cells (∼10% efficiency) for effective cancer immunotherapy.

Here, we describe a technique where we integrated magneto-mechanical modulation of cell deformability and intracellular cargo trafficking with magnetic nanoparticles (MNPs) during nanostraw electroporation (NE) to boost the transfection efficiency of Jurkat cells, a model cell line of T cells, from 12.8% to 48%. This method created minimal cellular stresses, as measured with intracellular calcium levels and RNAseq data, compared to other transfection techniques, leading to 2-3 folds shorter waiting time to generate high cell numbers (10⁹) for therapies.

We first compared the efficiencies to deliver a fluorescent protein plasmid with viruses (lentiviruses with Ubiquitin or EF1-α promoters), biochemical
polymers (Fugene, Lipofectamine), bulk electroporation (Biorad Gene Pulser, Lonza Nucleofector) and NE System (NES), and found similar efficiencies, about 10-20%, for Jurkat cells. It was shown that biomechanical forces enhanced transfection in adherent cells. To test if this holds true for non-adherent Jurkat cells, we utilized FDA-approved starch-coated magnetic nanoparticles (MNPs) with cyto-protective effects to generate magneto-mechanical forces. Starch-coated MNPs were biocompatible, and were membrane-bound and internalized after 24 hrs of incubation. We applied static magneto-mechanical forces to the Jurkat cells during NE and found that this boosted the transfection efficiency from 12% to 30% due to a decrease in physical distance between NES and Jurkat cells which minimized the loss of plasmid cargo. After NE, we applied low frequency (to avoid generating heat) alternating magneto-mechanical forces through internalized MNPs to perturb the cytoskeletal network connected to the nuclear envelope. This increased intracellular cargo trafficking and opening probability of the nuclear pore complexes to enhance cargo entry into the nuclei. This modulation step further increased the transfection efficiency from 30% to 48%. Next, by monitoring calcium stress signals and RNaseq, we found that across all the different transfection methods, NES with magneto-mechanical modulation resulted in minimal cellular stresses and treatment did not significantly lengthen cell doubling time unlike other techniques. Actin perturbation also promoted membrane resealing after electroporation. As FDA has approved T cell isolation using magnetic beads like we did, we plan to next apply the concept of magneto-mechanical modulation to enhance T cell transfection efficiency for cancer immunotherapy.
Plants comprise our primary source of food, but are also a source of oxygen, renewable energy, materials, medicines and regulators of the ecosystem. Stomata, the microscopic pores in the leaves of plants are fundamental to the plant function as they control the photosynthesis and transpiration rate. When the stomata are open the plant can exchange gases with the environment and allow the water evaporation enabling photosynthesis and transpiration. Abscisic acid, ABA, also known as the stress hormone, plays an essential role in the signaling mechanism that triggers the stomata closure. Here we report for the first time the use of a bioelectronics device for electronic control of stomata in intact plants. The organic electronic ion pump is an electrophoretic device that allows precise delivery of ions and charged biomolecules with high spatiotemporal resolution. This device has been mainly applied in mammalian systems for therapy. For the delivery of the phyto-hormone ABA we used a new generation of the ion pump that is based on glass capillary and has an overall diameter of 60um. The small diameter of the pump allows easy insertion in leaves of intact plants through the epidermis into the internal area of the leaf. We demonstrated that the stomata close after delivery of ABA with the ion pump and that the stomata close to the pump closer faster than the ones further away implying dose dependence. In addition we didn't observe any significant wound effect from the insertion of the pump signifying the potential of our method as non invasive. With our technology we can offer a new tool for fundamental understating of plant physiology but also adaptation of plants to environmental changes.

**SESSION BM02.03.03: Charge Transfer in Bacterial Systems**
Session Chairs: Renata Bilewicz and Xiaodong Chen
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Independence East

**8:45 AM *BM02.03.01**
**Electron Transfer andTransport in Multi-Heme Proteins**
Jochen Blumberger; University College London, London, United Kingdom.

Certain bacteria have evolved an astonishing survival mechanisms in response to low oxygen concentrations. When cytoplasmatic O2 becomes scarce they start to grow μm-long electrically conducting cellular appendages to export electrons from the cytoplasm to extracellular space for reduction of extracellular substrates (e.g. rocks!) in place of O2. Recently it was shown that arrays of Fe-containing multi-heme cytochromes (MHC) confer electric conductivity to those appendages, which garnered much interest for their use in ionanotechnological applications, e.g. bio-compatible field effect transistors. Here I will present recent experimental measurements probing electron transfer (ET) and electron transport (ETp) through multi-heme cytochromes (MHCs) as well as their interpretation by theory, electronic structure calculations and molecular dynamics simulation. I will discuss recent pump-probe spectroscopy results on Ru-labeled MHCs aimed at the determination of heme-heme ET rates and intrinsic electron flow in aqueous MHCs and the measurement of the I-V characteristics of dry MHCs in bioelectronic junctions (scanning tunneling microscope and protein monolayer junctions). While the ET mechanism appears to be well established for MHCs in aqueous solution, the ETp mechanism in single protein bioelectronic junction remains elusive partly due to the complexities of the electrode-protein interface and the resulting challenges for molecular modelling.

**8:45 AM *BM02.03.02**
**Proton-Coupled Extracellular Electron Transport via Microbial Outer Membrane Flavocytochromes**
Yoshidehi Tokunou; Kazuhiro Hashimoto; and Akihiro Okamoto; 1National Institute for Materials Science, Tsukuba, Japan; 2The University of Tokyo, Tokyo, Japan.

Bacterial electron transport to a solid substrate or electrode located extracellularly is accomplished by unidirectional electron flow via an array of more than twenty heme redox centers arranged in the outer membrane c-type cytochrome complex (OM c-Cyts). This interfacial electron transport between OM c-Cyts and solid substrates is termed extracellular electron transport (EET). The rate of EET is largely enhanced by self-secreted flavin molecules associated with the formation of semiquinone (Sq) state as a binding redox cofactor in the OM c-Cyts. However, the more negative redox potential of bound flavin Sq than the hemes in OM c-Cyts is energetically unfavorable for the kinetics of EET. Given the primary focus of related work in the recent past has been the electron carriers and the redox potential landscape of reaction centers, the importance of associated proton transport has not been widely investigated in EET. We, herein, show that proton transfer in the OM flavocytochromes limits the rate of EET in Shewanella oneidensis MR-1. Using an in vivoelectrochemical assay, we observed a large kinetic isotope effect (KIE) following D2O addition (< 4%), specifically when EET was the rate-determining step for the current production of lactate oxidation. Replacing flavin cofactors with twelve analogous molecules, the rate of EET correlated well with their pKa at the nitrogen atom at position-5 (N(5)) in the isoalloxazine ring calculated by a quantum chemical approach. Because higher pKae, represents stronger proton acceptability at N(5) in flavin associates and limits the rate of EET. We will further discuss about the rate-determining step of proton transport coupled with the redox reaction of the bound flavin cofactor in OM c-Cyts, with dataset for solvent KIE with partial deletion of OM c-Cyts complex.

**9:15 AM BM02.03.03**
**How Do Electrons Pass Through Multi-Heme C-Type Cytochromes?**
Kavita Garg; Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

Multi-heme cytochrome c (CytC) proteins are key for transporting electrons out of cells, to allow intracellular oxidation to proceed, also in the absence of O2. While the mechanism of the process is not well understood at the molecular level, these hemes may well function as "molecular wires", which makes such multi-heme cytochromes of prime interest for, e.g., potential bioelectronics and bio-sensing and integrating such proteins into electronic circuits is an exciting prospect. Figuring out how electrons pass through these proteins is a scientific challenge. We tackle this by measuring solid state electron transport (ETp) along dry multi-heme protein monolayers, a process that has similarities with, but also clear differences from ET in aqueous solution.

Earlier we studied ETp for a variety of proteins, using "dry" monolayer junctions, with structurally bound H2O retained. In such junctions the donor and acceptor, used in ET in solution, are replaced by nm - mm sized metallic contacts. Electron transport is measured as current, I, in function of applied voltage, V (I-V characteristics) and temperature, T (I-V-T). Here we ETp across two multi-heme CytC-type proteins: the membrane-bound MtrF (deca-heme CytC), the globular STC (tetra-heme CytC) and bilayers of these proteins. Transport is measured between Au electrodes. These proteins show length-normalized conductance that is 1,000x higher than what we measured across single heme (Cytochrome C), or heme-free protein monolayers, but similar to monolayers of conjugated organics. dI/dV of the junctions were also measured using lock-in-amplification at low temperatures, to calculate the protein and protein-contact energy level landscapes, involved in electron conduction. Conductance is found to be temperature-independent (320-80K), suggesting tunneling as limiting transport mechanism. Modelling of the I-V curves was done using Simmons's model and Landauer model, results of which are consistent with that electron transport can be described as tunneling and that protein-electrode coupling, rather than transport in the proteins is rate-
known as bacterial nanowires. To explore the role of biological electron conduits in long-distance (micrometer scale) electron transport along cellular conduits naturally evolved for biotic-abiotic coupling, a fundamental understanding has special implications for a new generation of bioelectrochemical systems. The activation energy of this process matches those obtained from electron hopping calculations through the Mtr-Omc cytochrome pathway. Since EET of EAB networks shared similar characteristics to electron hopping in conductive polymer matrices, including a DC-like mechanism in the low frequency region, and AC induced additional electron hopping when the applied frequency is above the critical frequency (10^4 Hz). The current work represents a strategically new approach for non-invasively probing EET with rationally defined micro-environment and cellular interactions across a wide range of length scales, which is expected to open up new opportunities for tackling the fundamentals and implications of EET.

9:30 AM BM02.03.04
Core/Shell Bacterial Cables—A One-Dimensional Platform for Probing Microbial Electron Transfer

Huan-Hsuan H. Hsu and Xiaocheng Jiang; Tufts University, Medford, Massachusetts, United States.

Comprehensive interpretation and interrogation of extracellular electron transfer (EET) mechanisms of electrochemically active bacteria can provide valuable information to enhance microbial fuel cells performance, which, however, are still restricted by the intrinsic complexity of natural biofilm. Here, we design core/shell bacteria-encapsulating cables as a one-dimensional model system to facilitate EET studies, where demonstrate the precise modulation of fiber diameters (from 6.9±1.1 mm to 25.1±2.4 mm) and bacteria interactions. As-formed bacterial cables exhibit that their conductivities are highly dependent on the bacteria density as well as the nature and number of intercellular interconnections. The closely contacted bacteria promote the development of high density self-assembling nanomaterials at cellular interfaces which can be directly translated to the increase of EET efficiency (16.2 mS cm⁻¹) as compared with isolated, remotely-connected bacteria samples (6.4 mS cm⁻¹). Introducing exceeding concentrations of soluble electron acceptors during cell culture, however, substantially suppresses the formation of cellular interconnections and leads to significantly reduced conductivity (2.5 mS cm⁻¹). Frequency-dependent measurements further revealed EET of EAB networks shared similar characteristics to electron hopping in conductive polymer matrix, including a DC-like mechanism in the low frequency region, and AC induced additional electron hopping when the applied frequency is above the critical frequency (10^4 Hz). The current work represents a strategically new approach for non-invasively probing EET with rationally defined micro-environment and cellular interactions across a wide range of length scales, which is expected to open up new opportunities for tackling the fundamentals and implications of EET.

9:45 AM BM02.03.05
Design, Synthesis and Characterization of a Bioanode for Microbial Fuel Cells

Jérémie-Luc Sanchez and Christel Laberty-Robert; Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université-Faculté de Sciences et d’Ingénierie, Paris, France.

Today the need for clean energy technologies appears urgent. Therefore, the idea of harvesting the metabolic activity of microorganisms becomes feasible. Amidst those devices microbial fuel cells focus on converting chemical energy from organic matter into electricity by gathering electrons produced by bacteria degrading these molecules. Such fuel cells may be used as renewable energy sources, but a lot of challenges need to be addressed before we can see them as an efficient, stable and profitable technology. Many approaches to tackle these problems exist. For instance, the electronic transfer between the bacterium and the electrode can be improved by working on the organism or the consortium used to degrade the organic matter. Here we rather seek to improve the material and the architecture of the electrochemical system and especially those of the bacteria-colonized anode. We start from the observations of the limitations of current carbon felt electrodes for microbial fuel cells to design a better system. This work focuses on the conception of the bioanode of a microbial fuel cell by electrospinning. This process allows the shaping of nano to micro-scaled polymer fibers through electrically-assisted extrusion. We obtain a nonwoven mat of polymer fibers which is made conductive by the addition of anisotropic carbon-based materials. The colonization of these hybrid carbon polymer electrodes by the electroactive bacteria Shewanella oneidensis is conducted through diverse approaches: core-shell encapsulation or natural biofilm development. Once prepared, the anode is then integrated into a functional lab-scale fuel cell in order to evaluate its electrochemical characteristics. The impact of the colonization of these conductive electrodes on the electrochemical performances of a full bio fuel cell will be discussed.

10:00 AM BREAK

10:30 AM *BM02.03.06
Hotwired Life—What Can Bacterial Electron Conduits Teach Us About Biological Energy Conversion and Bioelectronics?

Moh El-Naggar; University of Southern California, Los Angeles, California, United States.

Microorganisms have evolved exquisite electron conduits, including multiheme cytochromes, to extend their metabolic reach to external abiotic surfaces. This process, known as extracellular electron transfer (EET), is being heavily pursued for wiring microbes to electrodes in renewable energy technologies. Here we focus on biophysical measurements, electron transfer simulations, and electron cryo-tomographic studies of the multiheme cytochrome conduits that perform EET in the dissimilatory iron-reducing bacterium Shewanella oneidensis MR-1. We show how the electron transport rates gleaned from single molecule conductance measurements and stochastic simulations can be linked to electrochemical measurements of single cells and whole biofilms. We also describe our current understanding of the distribution and functionality of extended multiheme cytochrome networks along filamentous membrane tubes known as bacterial nanowires. To explore the role of biological electron conduits in long-distance (micrometer scale) electron transport across cellular membranes and across cells, we report in vivo electrochemical measurements of redox conduction through cells linking electrodes, and show that the activation energy of this process matches these obtained from electron hopping calculations through the Mtr-Omc cytochrome pathway. Since EET conduits naturally evolved for biotic-abiotic coupling, a fundamental understanding has special implications for a new generation of bioelectrochemical technologies and living electronics that that harness the advantages of microbes in detecting external signals (e.g. biosensors) or hosting synthetic genetic circuits (e.g. biocomputing).

11:00 AM *BM02.03.07
Mimicking Biological Energy Systems—From Multilayer Membrane Stacks to Molecular Electron Conduits

Lars Jeuken; George R. Heath; Ee Taek Hwang; Valentin Radu; Menggu Li; Anna Sitkan; Khizar Sheikh; Katherine Orchard; Chong Yong Lee; Manuela A. Gross; Tai Kwon Park; Emma Ainsworth; Colin Lockwood; Stefan Frielingdorf; Tadafumi Adschiri; Oliver Lenz; Erwin Reisner; and Julea N. Butt; 1School of Biomedical Sciences and Astbury Centre, University of Leeds, Leeds, United Kingdom; 2Department of Chemistry, University of Cambridge, Cambridge, United Kingdom; 3Advanced Institute for Material Research, Tohoku University, Miyagi, Japan; 4Centre for Molecular and Structural Biochemistry, School of Chemistry, and School of Biological Sciences, University of East Anglia, Norwich, United Kingdom; 5Institut für Chemie, Technische Universität Berlin, Berlin, Germany.

In nature, energy systems rely on efficient electron transfer across redox chains for charge transport across lipid membranes. Multilayered or stacked lipid
membranes spatially organize and compartmentalize these energy processes, while greatly increasing the lipid membrane surface area. Here, I will present two approaches aimed to mimic these fundamental features of bioenergetics.

Long-distance charge separation in photosynthesis was mimicked by coupling dye-sensitized TiO₂ nanocrystals and CdS quantum dots to two decaheme protein, MtrC and OmcA from *Shewanella oneidensis* MR-1, where the decahemes form a ~7 nm long molecular wire between the light harvesting nanoparticle (NP) and the underlying anode. The system is assembled by forming a densely-packed decaheme film on an ultra-flat gold electrode, followed by the adsorption of monolayer of NP. The step-by-step construction of the decaheme/NP system is monitored with (photo)electrochemistry, quartz-crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM). When using TiO₂ nanocrystals, dye-sensitized with a phosphonated bipyridine Ru(II) dye, photocurrents are observed that are dependent on the redox state of the decaheme, confirming that electrons are transferred from the TiO₂ nanocrystals to the surface via the decaheme conduit. In other words, TiO₂/decaheme wires function as hybrid photodiodes in which the decaheme traps the conduction-band electrons from TiO₂ before transferring them to the electrode. To the best of our knowledge, the TiO₂ nanocrystal/decaheme system is the first demonstration of a photobioelectrochemical system that uses a redox protein to mimic charge separation found in biological photosystems.

Stacked lipid membrane system were mimicked by using poly-L-lysine to electrostatically assemble multilayers of negatively charged lipid membranes on gold electrodes. When membrane enzymes are incorporated, either an ubiquinol oxidase (cytochrome b₅₃ from *Escherichia coli*) or an oxygen tolerant hydrogenase (the membrane-bound hydrogenase from *Ralstonia eutropha*), cyclic voltammetry (CV) reveals a linear increase in biocatalytic activity with each additional membrane layer (oxygen reduction or hydrogen oxidation, respectively). Electron transfer between the enzymes and the electrode is mediated by the quinone pool that is present in the lipid phase. We deduce by atomic force microscopy, CV and fluorescence microscopy that quinones are able to diffuse between the stacked lipid membrane layers via defects sites where the membranes are interconnected. This assembly is akin to that of interconnected thylakoid membranes or the folded cristae of mitochondria and have significant potential for mimicry in biotechnology applications such as energy production or biosensing.

11:30 AM BM02.03.08
Biological Electron Transfer Over Centimeter Distances in Cable Bacteria
Rob Cornelissen¹, RaghavendraTT. Eachambadi¹, Robin Bonné², Silvia Hidalgo Martinez²,³, Ji-Ling Hou¹, Jeanne S. Geelhoed¹, Jan D’Haen¹, Henricus T. Boschker²,³, Roland Valcke⁵, Bart Cleuren⁶, Jean V. Manca¹ and Filip J. Meyesman¹,³, 1X-LAB, Hasselt University, Hasselt, Belgium; 2Department of Biology, University of Antwerp, Antwerp, Belgium; 3Department of Biotechnology, Delft University of Technology, Delft, Belgium; 4Institute for Materials Research, Hasselt University, Diepenbeek, Belgium; 5Molecular and Physical Plant Physiology, Hasselt University, Hasselt, Belgium; 6Theoretical Physics, Hasselt University, Hasselt, Belgium.

Biological electron transfer is generally thought to occur over nanometer to micrometer-scale distances, as is the case in cellular respiration or extracellular electron transport via conductive nanowires in metal-reducing bacteria. Yet, various lines of evidence suggest that the recently discovered multicellular cable bacteria¹ can induce biological electron transfer over centimeter-scale distances²,³ – three orders of magnitude longer than previously observed. However, up until now, no direct quantification of an electrical current flow through a cable bacterium filament has been reported.

In this contribution we present some recent insights and advances on the characterization of the electron transport and the conductive structures in cable bacteria. Using SEM, TEM and AFM, we examined in detail the cell envelope of cable bacteria filaments. A fiber network residing in the periplasmic space was discovered, which we propose to be universally present in different species of cable bacteria. The fibers are running in parallel to the longitudinal axis of the filaments. Using amperometric measurements on custom-built electrodes, we successfully measured the conductivity of single intact cable bacteria filaments as well as isolated periplasmic sheaths that contain the fibers. These results demonstrate that the periplasmic fibers are indeed responsible for long-distance electron transport in cable bacteria.

Understanding the conductive structures of the cable bacteria and the associated mechanism of long-distance electron transfer will not only help to understand the role of cable bacteria in their natural environment, but could also enable the development of new applications in bioelectronics.


11:45 AM BM02.03.09
Electrochemical Investigation of Extracellular Electron Transport Through *Pseudomonas aeruginosa* Biofilms
Leonard Tender¹, Matthew Yates¹, Scott Saunders² and Dianne Newman³; ¹Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; ²Biology and Biological Engineering, Caltech, Pasadena, California, United States.

Electroactive microorganisms (EM) can utilize a non-corroding electrode as an inexhaustible electron acceptor or donor for respiration and/or metabolism. During the past 6 years we have applied electrochemical gating measurements (EGM) using interdigitated microelectrode arrays (IDA) to study multi-cell-length-long extracellular electron transport (LE-DET) through electrode-grown EM biofilms. For all biofilms we have examined thus far, EGM reveals that the biofilms act as redox conductors, whereby LD-DET occurs via electron transfer reactions among immobilized extracellular redox cofactors. Here, we apply EGM to study LD-DET occurring in the pure-culture *Pseudomonas aeruginosa* biofilm (PAB). *P. aeruginosasecretes* phenazines, small redox molecules, which among other things, export electrons resulting from respiration by oxygen-limited cells residing deep in PAB. It is conventionally thought that this occurs by physical diffusion of phenazines out of PAB. Our results indicate however that an appreciable amount becomes immobilized within PAB, imparting redox conductivity to the biofilm. Moreover, PAB appears to have different affinities for the different phenazines – with pyocyanin (PYO) contributing most to LD-DET. A model is presented in which PYO exhibits bounded diffusion analogous to certain redox polymers. *P. aeruginosa* is an opportunistic pathogen which forms biofilms in the lungs. The results presented have implications for improved treatment strategies.

SESSION BM02.04: Light and Oxygen Mediated Charge Transport
Session Chairs: Pau Gorostiza and Eleni Stavrinidou
Tuesday afternoon, November 27, 2018
Sheraton, 2nd Floor, Independence East

1:30 PM *BM02.04.01
Self-Assembly and Electron Transport of Photosystem I in Tunneling Junctions and Soft Photovoltaic Devices Yan Chiechi1,2, Andreas Herrmann2, Xinai Qui3, Olga Casianeda Ocampo1,2, Mark Loznek, Henry de Vries1,2 and Pavlo Gordielchuk4, Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands; 2Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Photosystem I (PSI) is a trimeric protein complex capable of converting light into spatially separated electron/hole pairs. In Nature, this process is used to convert light-energy into chemical-energy to drive photosynthesis. Ex vivo, the electron/hole pairs can be injected directly into electrodes and/or redox couples, turning PSI complexes into nanoscale photovoltaic devices with an internal quantum efficiency of unity. Because PSI is a membrane protein, the complexes are flat and the edges are non-polar, facilitating self-assembly on (electrode) surfaces. However, they assemble with an equal probability of the two possible orientations of the electron transport chain, meaning they will inject holes and electrons with equal probability, resulting in zero photocurrent. We successfully biased this orientation through functionalizing the surfaces of electrodes with either hydrogen-bond donors or ionic groups to exploit the slight differences in the nature of the polarity of the two faces of PSI to demonstrate thin-film, solid-state bio-photovoltaic devices.

The focus of this talk will be examining the mechanism of charge-transfer through self-assembled monolayers of complexes of PSI with and without orientational bias. We find that, in all cases, non-resonant tunneling is remarkably efficient even though tunneling electrons do not interact strongly with the electron transport chain. Rather, the effect of built-in electric field generated by the alpha helices in the periphery of the complexes dominates transport. Using the insights gained from these studies, we used phage display to find linker units capable of biasing the self-assembly of complexes of PSI completely in one direction. We then inserted nano-structured electrodes into microfluidic chips made by soft lithography. When the electrodes are properly functionalized, PSI self-assembles on them resulting in soft, stretchable photovoltaic devices in a single fabrication step. We followed the performance of the devices over time, showing that they are capable of self-regeneration via the circulation of active PSI through the devices in operando.

2:00 PM *BM02.04.02
Oxidative Stress is Tightly Regulated by Cytochrome c Phosphorylation and Respirasome Factors in Mitochondria Alexander Guerra-Castellano, Antonio Diaz-Moreno, Gonzalo Perez-Mejias, Carlos A. Elena-Real, Katsukia Gonzalez-Arzola, Sofia M. Garcia-Mauriño, Miguel A. De la Rosa and Irene Diaz-Moreno; Institute for Chemical Research - cisCartuja, Seville, Spain.

Respiratory cytochrome c has been found to be phosphorylated at tyrosine 48 or 97 in the post-ischemic brain upon neuroprotective insulin treatment, but how such post-translational modification affects mitochondrial metabolism is unclear. Here, we report the structural features and functional behavior of phosphomimetic cytochrome c mutants, which were generated by site-specific incorporation at position 48 or 97 of p-carboxymethyl-L-phenylalanine (PCMF) using the evolved tRNA synthetase method. We found that the point mutations do not alter the overall folding and heme environment of cytochrome c, but significantly affect the whole oxidative phosphorylation process. In fact, the electron donation rate of the Y97/CMF mutant heme protein to cytochrome c oxidase, or complex IV, within respiratory supercomplexes was higher than that of the wild-type species, in agreement with the observed decrease in reactive oxygen species (ROS) production. Direct contact of cytochrome c with the respiratory supercomplex factor HGH1A (hypoxia inducible domain family member 1A) is herein first reported, with the Y97/CMF mutant heme protein exhibiting a lower affinity than the wild-type species. Interestingly, phosphomimetic cytochrome c also exhibited a lower caspase-3 activation activity. Altogether, these findings yield a better understanding of the molecular basis for mitochondrial metabolism in acute diseases, such as brain ischemia, and could thus allow the use of phosphomimetic cytochrome c as a neuroprotector with therapeutic applications.

2:30 PM *BM02.04.03
A Novel Biological p-n Junction for Modulating the Proton Transport in Bacteriorhodopsin Yan Xiang1,2; 1Southen New Hampshire University, Manchester, New Hampshire, United States; 2Beihang University, Beijing, China.

Hampered by the absence of evidence and theoretical model of biological semiconductor, the unidirectional electron transport via the p-n junction structure between functional proteins and abiotic materials remains a challenge for bioelectronics. Bacteriorhodopsin (bR), a representative transmembrane protein, has demonstrated exceptional optoelectronic effects in bR/semiconductor hybrid materials and offers a possible pathway for addressing this challenge. In the present work, bR is found to be an n-type semiconductor with an indirect electron transition. Thereby, we successfully explain the mutual cohesion and unidirectional interfacial electron transport between bR and p-type semiconductor, specifically, the enhanced yet stable photocurrent, in regard to optoelectronics and the acceleration of the bR photocycle, via a distinctive bio-p-n junction mechanism. We believe the concept of protein based p-n junction will underscore research on bioelectronic applications for bR and its homologues.

2:45 PM BREAK

3:15 PM BM02.04.04
New Insights on the Electrical Resistive Switching Behavior of Eumelanin—Toward Memory Application Devices Manuel Real1 and Abdelaziz M. Gouda; Engineering Physics, Polytechnique Montréal, Montréal, Quebec, Canada.

Eumelanin is a black biopigment present in flora and fauna [1]. It features fascinating properties such as radical scavenging, metal chelation, photoprotection, broadband optical absorption and hydration-dependent electrical conductivity [2]. Remarkable research efforts have been devoted to unravel its optical and electrical properties to integrate eumelanin in optoelectronic and energy storage devices [3]. A debate whether eumelanin is an amorphous semiconductor (ASC) or a mixed ionic-electronic conductor (MIEC) is open among the scientific community. The discovery of a resistive switching behavior in eumelanin pellets [4] along with theoretical simulations that predict the existence of mid-gap states in eumelanin have been considered primary evidence for the ASC model [5]. Recently, it has been proposed that adsorbed water would activate a comproportionation equilibrium between redux active eumelanin moieties, favouring a Grothuss-like charge transport [6]. Even though the MIEC conduction model excludes the ASC model, the causes of the resistive switching are not well understood.

In this work, we fabricated wet and dry Sepia eumelanin pellets (hydrated at different percentages of relative humidity (%RH) or processed in Ar glove box), sandwiched in coin cell configuration, using Cu and stainless-steel electrodes. Hydrated samples show a reproducible resistive switching over many cycles with an on/off ratio of ca. 10^−4. Dry samples switch only during the first cycles, with an exponential I-V behavior. SEM images of Cu electrodes taken after the electrical characterization of wet samples reveal CuO dendritic structures. These dendrimers could bridge the two electrodes. The I-V electrical response of dry samples could be interpreted as evidence of an electronic transport in bulk eumelanin thus supporting the ASC model.

Understanding the mechanisms of the resistive switching behavior and shedding light on the electrical properties of eumelanin under different hydration conditions is critical to demonstrate eumelanin-based memory devices.

References
into charge separated states with efficiency close to 100% [1]. Upon its isolation from the living bacterium, the RC retains stability and enzymatic activity [3].

3:30 PM BM02.04.05
Photonic Nanoparticles as Molecular Sensors Holly Clinpan, Vladimiro Mujica and Antonio Garcia; Arizona State University, Tempe, Arizona, United States.

The Reaction Center (RC) is the photoenzyme used by photosynthetic bacteria, such as the purple Rhodobacter Sphaeroides R26, to convert solar energy into surfactant aqueous media and is envisaged as a promising biological system to generate new photoactive materials for bioelectronics [2].

4:15 PM BM02.04.08
Biohybrids from Organic Semiconductors and Photosynthetic Bacteria Gianluca M. Farniola¹, Francesco Milano¹, Roberta Ragni¹, Marco Lo Presti¹, Simona la Gatta¹, Angela Agostano¹² and Massimo Trotta¹²; ¹University degli Studi-Bari Aldo Moro, Bari, Italy; ²Dipartimento di Chimica Università degli Studi di Bari “Aldo Moro”, Bari, Italy, CNR IPCF UOS BARI, Bari, Italy.

The Reaction Center (RC) is the photoenzyme used by photosynthetic bacteria, such as the purple Rhodobacter Sphaeroides R26, to convert solar energy into charge separated states with efficiency close to 100% [1]. Upon its isolation from the living bacterium, the RC retains stability and enzymatic activity in surfactant aqueous media and is envisaged as a promising biological system to generate new photoactive materials for bioelectronics [2]. However, the applicability of RC in bioelectronic devices is strictly related to (a) finding suitable deposition methods enabling controlled orientation of the protein on conducting or semiconducting substrates and (b) employing chemical strategies to enhance the protein light absorption in the visible region. A
successful approach to extend the RC visible absorption is covalently binding tailored organic molecules that harvest white light and efficiently transfer it to the protein [3, 4]. A variety of molecular fluorophores acting as efficient antennae will be presented, highlighting their role in the enhancement of biohybrids’ photoconversion efficiencies. The lecture will also discuss strategies to efficiently affix the RC on organic semiconductors layers in photoconversion devices and to embed the RC in polymeric thin films at the electrodes [5].

Design and construction of smart supramolecular architectures by the multiple combination of different enzymes assembled with tailored linkers will be also presented as a proof of the concept that supramolecular bioinspired machineries based on the functioning of the bacterial RC photoenzyme can be developed for solar energy conversion.

References


4:30 PM BM02.04.09
Coupling Electron and Proton Transfer—The Lesson From the Photosynthetic Reaction Center Massimo Trotta1, Francesco Milano1, Roberto Ragni2 and Gianluca M. Farinola2; 1Istituto per i Processi Chimico Fisici, Consiglio Nazionale delle Ricerche, Bari, Italy; 2Department of Chemistry, Università degli Studi di Bari Aldo Moro, Bari, Italy.

Photosynthetic reaction centers from photosynthetic bacteria are integral membrane proteins able to transform the electromagnetic radiation associated to solar light in a biological hole-electron couple amenable for being used in a number of possible applications. The hole-electron couple formed upon light absorption is characterised by a long-living property: the charge-separated state can survive from 100 milliseconds to 3 seconds, depending on the environmental conditions.

One of the key issues for this extent lifetime of the dipole within the scaffolding of the protein is that the formation of the charge-separated state draws proton, from the aqueous solution within the inner part of the protein, eventually modulating the redox chemistry of the final electron acceptor. The role of the proton uptake from the photoenzymes during its functioning will be addressed along with some possible consequences on the applicable use of the Reaction Center as organic-biological biohybrid.


4:45 PM BM02.04.10
Intracellular Au Nanocluster Photosensitized Bacteria for Solar Fuel Production Hao Zhang1 and Peidong Yang1,2; 1Department of Chemistry, University of California, Berkeley, Berkeley, California, United States; 2Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The demand for renewable and sustainable fuel has prompted the rapid development of advanced nanotechnologies to effectively harness the copious flux of solar power. Although the solar-to-energy efficiencies of inorganic semiconductor devices can easily surpass 20%, the transduction of solar energy into photoconversion devices and to embed the RC in polymeric thin films at the electrodes aims to link preassembled biosynthetic pathways with inorganic light absorbers. This strategy inherits both the high light-harvesting efficiency and the superior catalytic performance of solid-state semiconductors and whole-cell microorganisms, respectively. Recently, we have demonstrated a version of membrane-bound CdS nanoparticle on nonphotosynthetic bacterium, Moorella thermoacetica for artificial photosynthesis. To eliminate potential mass and energy losses during transporting electrons across cell membranes, the spatial conjugation between inorganic material and microorganism could be designed in cytoplasm. Here, we introduce an intracellular, biocompatible light absorber, namely gold nanoclusters (Au NCs), to circumvent the sluggish kinetics of electron transfer for existing PBSs. Translocation of these Au NCs into nonphotosynthetic bacteria enabled photosynthesis of acetic acid from CO2. Besides, Au NCs also serve as reactive oxygen species (ROS) inhibitors to maintain high bacterium viability. Taking the dual advantages of light absorption and biocompatibility, this new generation of PBS can efficiently harvest sunlight and transfer photo-generated electrons to cellular metabolism, realizing CO2 fixation continuously over several days. Moreover, intracellular PBS represents a promising platform to investigate the charge transfer, and leads to a deeper understanding of the burgeoning complex nexus of inorganic materials and biological systems.
The charge transport investigation through peptides and proteins offers an unique opportunity to study the supramolecular interaction, information transmission, and even bio-catalytic process in biological systems, however the single-molecule experimental measurement of charge transport through peptides and proteins remained as experimental challenges due to the difficulties in the binding of peptides/proteins on electrodes and also the extraction of low current signals through the single peptide/proteins junction. On the other hand, the calculations predicted that the conductance of peptides junctions exhibited low conductance, while the experimental measurement provides relatively high conductance, then what is the dominated conduction channel through the single peptide/protein?

Here we studied the charge transport properties through a series of peptide-supramolecular interactions, including hydrogen bonds and π-π stacking, and we measured the supramolecular charge transport between two peptides anchored on two separated gold electrodes using scanning tunneling microscopy break junction (STM-BJ) technique. The combined molecular dynamic simulations further revealed the conformation evolution of supramolecular peptides junctions. It is found that the supramolecular interaction between the peptides offer the conduction channel, and the charge transport through the supramolecular process could be further tuned by the environments.

As perspective, we further applied the technique to investigate the charge transport through an enzyme, oxidoreductase, and our preliminary results suggested that the charge transport process are correlated to the bio-catalytic process, which offer an unique testbed to look into the bio-catalysis from the single-molecule level.

Transducing between ion and electron currents is a key challenge underpinning the emerging field of bioelectronics [1]. In general, ions (including protons) are the dominant signal carrying entities in biology, and modern electronics relies on semiconductors where the carriers are electrons and holes. Solid state ionic conductors (SSICS), whilst not rare, are somewhat few and far between – so-called ionic glasses such as silver iodide or sodium alumina being classic and early examples. Of more relevance to bioelectronic applications are polymeric-SSICs and there are several well-known examples such as DuPont’s Naion (a proton transport membrane). Polymeric matrices such as polyethylene oxide can also conduct ions when suitably ‘doped’ (or solvated depending upon your nomenclature) with for example, water or lithium perchlorate [2]. Finally, several biopolymeric matrices such as melanin and proteins [1, 2, 3] show respectable proton conductivities when hydrated.

In my talk I will present several examples of polymeric and biopolymeric SSC materials and exemplify the ‘conduction physics’ at play. I will also describe recent progress in utilising these materials as transducing elements in hybrid and all-organic transistors which represent prototype bioelectronic logic elements [4, 5].


Electron transfer is central to all life processes. Every living cell must get rid of a large number of electrons left behind in metabolism when nutrients convert into energy. Electron transfer in proteins occurs through either tunneling or hopping a few nanometers via inorganic cofactors. However, the common soil bacteria Geobacter sulfurreducens transfer electrons over hundreds of micrometers, to insoluble electron acceptors or syntrophic partner species. These bacteria use surface appendages called pili for extracellular electron transport, allowing them to survive in environments that lack membrane-permeable electron acceptors such as oxygen. Near room temperature, the conductivity of wild-type pili exhibits temperature dependence similar to that of metallic polymers, which recently was confirmed independently. However, the composition and structure of pili as well as the mechanism of pili conductivity has remained unclear.

I will present our recent structural, molecular and biophysical studies to identify the mechanism of metallic-like conductivity in pili. We elucidate the physical mechanism of electron transport by measuring the electrical and optical conductivity of pili from multiple mutant strains as a function of molecular length, temperature, frequency, pH and stacking. We demonstrate that intrinsic conductivity of individual pili can be accurately described by...
nearest-neighbor, tight-binding model as predicted theoretically for quasi-one-dimensional materials. To determine the molecular architecture responsible for conduction, we are using a suite of complementary experimental and computational methods such as molecular dynamics, x-ray diffraction and near-atomic resolution cryo-electron microscopy. Our studies suggest a pi stacking-like interaction in pili, that can cause intermolecular electron delocalization, conferring metallic conductivity to pili. Furthermore, increasing p-stacking in pili improves their crystallinity, yielding a longer mean free path for electrons, and stronger electronic coupling in pili which is 1000 times higher than other proteins or DNA. Pili thus represent a new class of electronically functional proteins that can transport electrons at rates and distances unprecedented in biology. These findings will help development of genetically programmable biomolecular materials with tunable functionality through precise control of their electronic and protein structure.

9:30 AM BM02.05.04

Biological charge transfer processes are mostly based on the controlled diffusion of charges (electrons, protons, ions) across specific pathways within proteins over distances of ~100 nm. Rather recently, long electron transfer has been found in bacterial wires for distances of few μm’s, which is probably also mediated by proteins. With this biological inspiration, we report here on the formation of free-standing films that were formed from the serum albumin protein, which were bioinspired functionalized to exhibit efficient electron transport on the centimeter length scales. Furthermore, we show that the protein-based films can be functionalized in a different way for the formation of efficient ionomers with measured ionic conduction of >5 mS/cm at room temperature. Our formed films have attractive mechanical properties, with a high elastic modulus of ~160 MPa, but at the same time they are highly stretchable, capable of stretching more than 4 times their length. They have high resistance to harsh organic solvents and acids, they are very easy to form, and have a very low price tag with materials cost of around a $1/cm². We believe that our newly formed films can be used as a universal scientific test bed for exploring protein-based long range conduction, and even can find themselves in various applications, from biomedical ones all the way to membranes for fuel cells.

9:45 AM BREAK

10:15 AM BM02.05.05

We present a combined theoretical study of density functional theory and molecular dynamics simulations of a copper-binding protein azurin from Pseudomonas aeruginosa and some selected mutants. Contrary to previous studies where only the copper complex and its surroundings were considered, we here analyzed, for the first time, the whole structure of the protein. We found that the peripheral part actually also plays an important role in the electronic structure at energies close to the Fermi level [1]. Furthermore, our results are in good agreement with recent experiments [2]. We also explored the role of thermal fluctuations and how they affect both the geometrical conformation and the electronic structure.


10:30 AM BM02.05.06

A great effort has been made in recent years to incorporate proteins as functional components in electronic junctions [1]. A number of studies report the surprising efficiency of electron transport (ETp) in proteins, as well as temperature-independent conductance over distances of up to ~10 nm, calling into question the applicability of known ETp mechanisms to these systems. From molecular and organic electronics we know that the positions of the molecule’s frontier energy levels, relative to the electrodes’ Fermi level (EF), play a key role in charge transport. In protein electronics, very little is known about these energy levels; to make things worse, the leading “normal” method to determine these levels, photoemission spectroscopy has not yet been applied successfully to protein monolayers.

Gating measurements provide an ideal platform to study energy levels by means of modulating the positions of the frontier orbitals, relative to those of the electrodes. However, geometric considerations make implementing a gate in protein-based junctions challenging, primarily due to the difficulty in binding proteins inside nano-gaps.

Here we report a new method that does allow for gating of proteins, and in a highly reproducible manner, to provide an energy level description of ETp in Azurin (a blue copper, bacterial electron-transfer protein). Drain and gate gold (Au) electrodes are separated by ~80 nm, on a SiO2 substrate (fabricated by electron-beam lithography), with an AFM tip acting as the source. Source-drain current-voltage measurements at different gate bias, and gate-bias sweeps at low source-drain bias, show reversible gate-induced conductance in Azurin. Current onset was observed only at positive VG, indicating that transport in Azurin is dominated via the tail of the LUMO. The importance of Cu(I) in Azurin for ETp was tested by comparing measurements with Apo-Azurin, i.e., Cu-depleted Azurin. The results emphasize the contribution of the Cu(II) ions towards energy alignment for efficient ETp.

Comparing gating measurements performed with an Au and a Pt AFM tip as source, shows that a lower VG is required to induce a current onset in Azurin with Au than with Pt tips. Furthermore, the difference in measured work function of Au and Pt electrodes, served as reference to calibrate VG with the energetic distance from the Fermi level to the LUMO tail. Calibrating the energy in this way quantitatively allows for gating of proteins, and in a highly reproducible manner, to provide an energy level description of ETp in proteins inside nano-gaps.

Eumelanin, as a subset of melanins, is a type of biological pigments and is widely present in living organisms. Eumelanins are synthesized in the melanocytes by templated antioxidative polymerization using 5,6-dihydroxyindole carboxylic acid (DHCA) and 5,6-dihydroxyindole (DHI). Molecular subunits are formed into oligomeric macromolecules that π-stacked into microstructures. Despite the chemical similarity of subunits, it is challenging to reproduce eumelanins in a synthetic way due to the absence of templates. Research herein focuses on synthesizing biologically-derived melamins with various topographies and examine structure-property relationship. Microscopic structures of melamins are controlled by the templates made of tripeptides sequences. Three types of peptides including aspartic acid (D), phenylalanine (F), and tyrosine (Y) are self-assembled with various sequences to form distinct templates, which can formulate melamins into fibrous or sheet-like microstructures. These class of melanin electrodes with tunable microstructures would serve as the next generation biodegradable charge storage materials that can power various types of biomedical electronics devices. Microstructures are characterized using scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area measurement. Electrochemical performance of electrodes are examined by cyclic voltammetry and chronopotentiometry within aqueous electrolytes containing either Na⁺ or Mg²⁺. Structural changes along with chemical signatures are analyzed by Fourier transform infrared and raman spectroscopy after coordinating with cations.

11:00 AM DISCUSSION SESSION

SESSION BM02.06: Materials and Systems for Bio-Inspired and Bio-Compatible Electronics
Session Chairs: Irene Diaz-Moreno and Wenjing Hong
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Independence East

1:30 PM *BM02.06.01 Peptides as Bio-Inspired Electronic Materials and Sensing Motifs Andrew Abell1,2, John Horsley1,2 and Jingxian Yu1,2; 1University of Adelaide, Adelaide, New South Wales, Australia; 2Centre for Nanoscale BioPhotonics, Adelaide, South Australia, Australia.

Bio-inspired molecular electronics is a particularly intriguing paradigm, as charge transfer in proteins/peptides, for example, plays a crucial role in energy storage and conversion processes in all living organisms. However, the structure and conformation of even the simplest protein is complex, and as such, model synthetic peptides containing well-defined geometry and pre-determined functionality, present as ideal platforms to mimic nature for the elucidation of fundamental biological processes, while also advancing the design and development of single-peptide electronic components and other devices. We present studies on intramolecular electron transfer in synthetic peptides of well-defined helical conformation and also ill-defined geometry, using electrochemical techniques and constrained density functional theory simulations. Two definitive electron transfer pathways are apparent, the nature of which is dependent on secondary structure. Electrochemical results indicate that peptides constrained by either Huisgen cycloaddition, ring-closing metathesis or lactam-bridge exhibit remarkable positive formal potential shifts (> 460 mV) and significant electron transfer rate constant drops (up to 15-fold), which represent two distinct electronic ‘on/off’ states. The additional backbone rigidity imparted by the side-bridge constraints leads to an increased reorganization energy barrier to restrict the torsional motions necessary for facile intramolecular electron transfer along the backbone. A clear mechanistic transition from hopping to superexchange, stemming from side-bridge gating, is apparent. The electronic properties of peptides can be fine-tuned through both structural and chemical manipulation, to reveal an interplay between backbone rigidity and electron rich side-chains on electron transfer. The side-bridge constraints provide an additional electron transport pathway, to provide two distinct forms of quantum interferometers. The effects of destructive quantum interference occur essentially through the backbone and the additional tunnelling pathway provided by the side-bridge in the constrained β-strand peptide, as evidenced by a correlation between electrochemical measurements and molecular junction conductance simulations for both linear and constrained β-strand peptides. In contrast, an interplay between quantum interference effects and vibrational fluctuations is revealed in the linear and constrained helical peptides. Collectively, these findings not only augment our fundamental knowledge of charge transfer dynamics and kinetics in peptides, but also open up new avenues to design and develop functional bio-inspired electronic devices, such as on/off switches and quantum interferometers, for practical applications in molecular electronics. These studies also provide an opportunity to develop peptide-based sensors for detecting biological Zn²⁺ and also protein-protein interactions, aspects of which will also be discussed.

2:00 PM *BM02.06.02 Mechano-Adaptable Electrodes for In Vivo Electrophysiological Interfacing Xiaodong Chen; Nanyang Technological University, Singapore, Singapore.

Polymeric microelectrode arrays are emerging as a new generation of biointegrated microelectrodes to transduce original electrochemical signals in living tissues to external electrical circuits, and vice versa. So far, the challenge of stretchable polymer microelectrode arrays lies in the competition between high stretchability and good electrode–substrate adhesion. The larger the stretchability, the easier the delamination of electrodes from the substrate due to the mismatch in their Young's modulus. Here, I will present our recent work on designing mechano-adaptable electrodes and their application for conformally recording the electrocorticograph signals from rats.

2:30 PM BREAK

3:00 PM *BM02.06.03 Dynamic Materials Inspired by Cephalopods Alon Gorodetsky; University of California, Irvine, Irvine, California, United States.

Cephalopods, e.g. squid, octopuses, and cuttlefish, have captivated the imagination of both the general public and scientists for more than a century due to their visually stunning camouflage displays, sophisticated nervous systems, and complex behavioral patterns. Given their unique capabilities and characteristics, it is not surprising that these marine invertebrates have emerged as exciting models for novel materials and systems. Within this context, our laboratory has developed various cephalopod-derived and cephalopod-inspired materials with unique functionalities.5 Our findings hold implications for next-generation adaptive camouflage devices, sensitive bioelectronic platforms, and advanced renewable energy technologies.

References
hydrogen-bonding network enabling cooperative interactions. The selective and label-free single-molecule IgG detection is strikingly demonstrated in diluted saliva while 15 IgGs are assayed in whole serum. The suggested sensing mechanism triggered by the affinity binding event, involves a work-change that is assumed to propagate in the gating-field through the electrostatic hydrogen-bonding network. The proposed immunoassay platform is general and can revolutionize the current approach to protein detection.

Single Molecule Detection of Markers with a Label-Free Bio-Electronic Sensor

Cinzia Di Franco, Matteo Ghittorelli, Domenico Alberga, Giuseppe F. Mangia, Gerardo Palazzo and Gaetano Scamarcio; 1Chemistry, Università degli Studi di Bari Aldo Moro, Bari, Italy; 2Università degli Studi di Bari Aldo Moro, Bari, Italy; 3Università degli Studi di Brescia, Brescia, Italy.

Label-free single-molecule detection has been achieved so far by funnelling a large number of ligands into a sequence of single-binding events with few recognition elements host on nanometric transducers. Such approaches are inherently unable to sense a cue in a bulk milieu. Conceptualizing cells’ ability to sense at the physical limit by means of highly-packed recognition elements, a millimetric sized field-effect-transistor is used to detect a single molecule. To this end, the gate is bio-functionalized with a self-assembled-monolayer of trillions of capturing anti-Immunoglobulin-G and is endowed with a hydrogen-bonding network enabling cooperative-interactions. The selective and label-free single-molecule IgG detection is strikingly demonstrated in diluted saliva while 15 IgGs are assayed in whole serum. The suggested sensing mechanism triggered by the affinity binding event, involves a work-change that is assumed to propagate in the gating-field through the electrostatic hydrogen-bonding network. The proposed immunoassay platform is general and can revolutionize the current approach to protein detection.

Fast Dissolving Transient Electronics Incorporating Peptide Insulator

Soek Daniel Namgung, Min-Kyu Song, Taehoon Sung, Jaehun Lee, Misong Ju, Ki Tae Nam and Jang-Yeon Kwon; 1School of Integrated Technology, Yonsei University, Incheon, Korea (the Republic of); 2Department of Material Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Transient electronics has been suggested as one of the formats of human implantable devices, since the device disappearing within human body at programmed time may reduce risk of immune response or inflammation caused by remaining rigid electronic components. There have been many demonstrated applications including biosensors, circuits, memories, RF antennas and etc, in which silicon dioxide (SiO2) has been frequently used as an insulator. However, SiO2 still has limit on slow dissolution rate and it may cause inflammation at the targeted organ. Toxicity issue, also, can arise because insulator is the largest part of device, and the absolute amount of insulator might exceed appropriate range, as a device is expanded to circuit application. From this context, we suggest specific tyrosine-based peptide sequence, Tyr-Tyr-Ala-Ala-Cys-Ala-Tyr-Tyr (YYACAYY), as an insulator component, since it has high biodegradability, intrinsic biocompatibility, and previously shown high dielectric constant. In this report, we fabricated biocompatible and biodegradable thin film transistors (TFTs) consisting of tungsten (W) conductor, zinc oxide (ZnO) semiconductor and peptide insulator. The device structure is bottom gate top contact, in which 100 nm-thick W and 30 nm-thick ZnO are patterned using shadow mask, and 400 nm-thick YYACAYY peptide that is dissolved in trifluoroacetic acid(TFA) is spin-coated. The device shows field effect mobility of ~21.80 cm2V-1s-1 and ON/OFF current ratio of ~105, which are comparable to SiO2 based TFT. The device further dissolves at 37 °C in bio-fluids such as deionized water, phosphate-buffered saline (PBS, pH~7.4) and bovine serum, and it is optically observed that all the device components dissolve within 12 hours, which is faster than that of SiO2 based TFT. The fast dissolution is attributed to peptide film, and dissolution rate of the film at 37 °C in deionized water is ~1300 Å/m, which is ~20,000 times faster than that of e-beam deposited SiO2, that is previously reported. Mechanism on dissolution of peptide film is inspected through X-ray Photoelectron Spectroscopy (XPS) analysis and destruction of overall device interfaces incorporating peptide film is investigated through cross-sectional Transmission Electron Microscopy (TEM) analysis. In conclusion, peptide insulator is newly suggested toward transient electronics as an alternative of SiO2 insulator, in which the peptide shows advantages on high degradability, biocompatibility and high dielectric constant. Biocompatible and biodegradable TFT incorporating peptide film is further demonstrated and shows moderate device performance and fast dissolving property. This strategy to select fast dissolving material at human implantable device may significantly reduce the risk of inflammation within human body.

Exploring Fast Proton Transfer Events Associated with Lateral Proton Diffusion on the Surface of Membranes

Nadav Amdursky; Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel.

Proton diffusion across biological membranes is a fundamental process in many biological systems, and much experimental and theoretical effort have been employed for deciphering it. Here we report on a new spectroscopic probe, which can be tightly tethered to the membrane, for following fast (ns) proton transfer events on the surface of membranes. Our probe is composed of a photoacid that serve as our light-induced proton source for the initiation of the proton diffusion process. We use our probe to follow this diffusion, and its pH-dependence, on the surface of lipid vesicles composed of either a zwitterionic headgroup, a negative headgroup, a headgroup that is composed only from the negative phosphate group or a positive headgroup without the phosphate group. We reveal that the kinetic parameters of proton diffusion are highly sensitive to the nature of the lipid headgroup, from a fast lateral diffusion at some membranes to the escape of protons from surface to bulk (and vice-versa) at others. By referring to existing theoretical models for the diffusion process of protons on the surface of membranes we found that while some of our results confirm the quasi-equilibrium model, other results are in line with the non-equilibrium model.ases for fuel cells.
Wood is a biological material with outstanding mechanical properties resulting from its hierarchical structure across different scales. While the cellular structure and the winding angle between the stiff cellulose fibrils and the wood cell axis have been reported to be key factors for its high stiffness and strength at light weight, the role of the molecular organization of its chemical components: cellulose, hemicellulose and lignin, is still to be fully understood. At the molecular scale, most of the hemicellulose molecules attack on the surface of the stiff crystalline cellulose fibrils, while lignin molecules fill the rest space. By applying a recently developed full atomistic model of the wood cell wall material, we studied how wood benefits from this intriguing molecular organization by intentionally varying the material distribution so that hemicellulose and lignin are randomly mixed or lignin molecules attach on the cellulose surface. It is found that better adhesion between the cellulose fibrils are achieved with the material distribution found in natural wood. Further detailed studies on individual molecules reveal that the hemicellulose show higher adhesion than lignin with cellulose and the three-dimensional structure of lignin originates its higher rigidity. Moreover, the covalent crosslinks between hemicellulose and lignin molecules enhance the load transferring between them. Therefore, the material distribution found in natural wood forms a pathway for load transferring that materials with stronger interactions are paired together. Our study reveals the molecular principles that wood adapts to achieve the outstanding mechanical properties at the macro-scale, which could shed light on the design of composite materials.

Bacterial Microcompartments (BMC) are roughly icosahedral shells found in bacteria that sequester enzymes involved in certain metabolic processes. Experiments suggest that some BMCs assemble by a pathway in which the enzymatic cargo first undergoes phase separation, after which the shell assemblies around the dense cargo droplet. Other types of BMCs assemble in a single step, with simultaneous cargo coalescence and shell assembly. Computational studies suggest that the strength of interactions between cargo particles are a key determinant of the assembly pathway. However, the physical origins of these interactions remain unclear; in particular, whether they result from direct attractions between enzymes or are mediated by scaffolding proteins.

In this presentation we describe coarse-grained computational and theoretical modeling to study the effect of cargo interactions and cargo topology on microcompartment assembly. We present results of dynamical simulations that compare shell assembly when cargo coalescence is driven by direct cargo-cargo attractions or scaffold-mediated attractions. We find that cargo properties can dramatically influence assembly pathways. Depending on conditions, the presence of cargo may increase or decrease shell size in comparison to the intrinsic protein curvature. This result may explain recent experiments on different BMC systems in which empty BMC shells were respectively smaller or larger than full shells. In comparison to direct cargo-cargo attractions, our simulations identify a richer set of assembly behaviors for scaffold-mediated cargo attractions, and suggest that there are experimentally distinguishable differences between the two classes of systems. Understanding factors that control encapsulation of cargo by self-assembling shells is the first step for reengineering BMCs to construct drug delivery vehicles or customizable nanoreactors that encapsulate a programmable set of enzymes.
Polyethylene (PE) is one of the widely used commercial polymers. Cross linking improve many properties of PE such as high dielectric strength, mechanical strength, low water permeability. Cross-linked PE (XLPE) has emerged as the insulator of choice for high-voltage direct current (HVDC) power transmission cables due to its favorable dielectric properties, low water permeability, structural integrity at high temperature and chemical resistance. Dicumyl Peroxide (DCP) has been used as an accelerating agent in cross linking PE. We investigated cross linking mechanisms and mechanical and electrical properties of XLPE systems using large scale molecular dynamics simulations. We first started with a non-reactive force field to understand diffusion of DCP molecules into the PE matrix with and without the influence of external electric field. Second, we employed eReaxFF to investigate cross linking mechanisms. ReaxFF reactive force fields first developed for hydrocarbons and later ported to different systems such as ceramics, metals and their oxides and provided precise results for those systems. eReaxFF is an extension to ReaxFF in which electrons are treated explicitly in a pseudo classical manner. We adopted a previous ReaxFF reactive force field and developed eReaxFF reactive force field to capture DCP-PE interactions, and investigated reaction mechanisms of crosslinking of PE via DCP under the external electric field using large scale molecular dynamics simulations. We investigated the effects of different parameters such as temperature, density, pressure and the ratio of peroxides to polyethylene on the formation of byproducts, distribution of functional groups and cross-linking. Furthermore we investigated mechanical ( tensile strength, bulk modulus) and electrical properties ( dielectric strength ) of the cross linked PE.

9:00 AM BM03.01.05
Modeling the Influence of Emergent Interactions Between Nascent Oligomers on the Sequences of Step-Grown Copolymers Kateri H. DuBay and Zhongmin Zhang; University of Virginia, Charlottesville, Virginia, United States.

The sequences of synthetic copolymers are notoriously difficult to control, and numerous complex protocols have been developed to help us do so. However, we lack a comprehensive understanding of what governs the sequential incorporation of different monomers into a chain for even the simplest of copolymerizations. To learn more, we performed coarse-grained modeling of a linear, step-growth copolymerization between two monomers. Our results demonstrate that transient associations and emergent self-organization among the reacting monomers and nascent oligomers can exert considerable influence over the sequential arrangement of monomers in the resulting chains, even when reaction barriers between the different monomer pairs are held constant. The magnitude of the effect we observe for differing co-monomer attractions can be explained by an emergent phase separation among the nascent oligomers – a phase separation that is both initiated and limited by the copolymerization.

9:15 AM BM03.01.06
Computational and Experimental Studies of Peptide: Silica Interactions Victor V. Volkov and Carole C. Perry; Nottingham Trent Univ, Nottingham, United Kingdom.

Structural properties of bioinorganic composites are of contemporary research interest in fields such as drug delivery, bone repair and biomimetics. While being a key material in bio-engineering applications, silica may be either hazardous or biocompatible depending on parameters such as particle size, shape or surface properties. Effective simulation at the quantum level of large silica-based bio-composites is necessary to gain a deeper insight into the properties of such materials. How to bridge between structural extraction from large scale classical simulation to predictions by quantum chemistry for silica based structures is the focus of our contribution. In this presentation we present MD and DFT simulation data, complemented by experimentally derived vibrational and optical spectroscopic data for the study of (a) 2nm silica nanoparticles, (b) the possible effects of local fields next to such nanoparticles and (c) the interaction of silica with 7-mer peptides.

9:30 AM BM03.01.07
Predicting Viscoelasticity, Strength and Fracture for Ideal Reversible Polymer Networks German A. Parada and Xuanhe Zhao; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Ideal Reversible Polymer Networks have well-controlled network structures similar to ideal covalent networks but exhibit transient properties due to the presence of reversible crosslinks. We have developed a theory to describe the mechanical properties of these ideal reversible polymer networks under small shear deformation, and have predicted that the networks behave as a single Maxwell element of a spring and a dashpot in series, with the instantaneous shear modulus and relaxation time determined by the concentration of elastically-active chains and the dynamics of reversible crosslinks, respectively. Due to the use of short polymer chains, we expected no contributions from polymer chain entanglements or chain relaxation, as the Rouse relaxation time is much shorter than the reversible crosslinks’ characteristic time. The theory also provided general methods to (i) independently control the instantaneous shear modulus and relaxation time of the networks, and to (ii) quantitatively measure kinetic parameters of the reversible crosslinks, including reaction rates and activation energies, from macroscopic viscoelastic measurements. The theory and methods were validated experimentally using a 4-Arm polyethylene glycol hydrogel system. We have also employed the theoretical and experimental system developed to characterize the fracture modalities and mechanical properties under large uniaxial deformation at varying loading rates.

9:45 AM BM03.01.08
Revisiting the Strong Stretching Theory for pH-Responsive Polyelectrolyte Brushes Harnoor S. Sachar and Siddhartha Das; Mechanical Engineering, University of Maryland, College Park, College Park, Maryland, United States.

Polyelectrolyte brushes grafted to a substrate attain a brush like configuration above a critical grafting density. Polyelectrolyte brushes (PE) have gained significant attention in the last few decades due to a myriad of applications like flow control, biosensing, current rectification, ion manipulation etc. We present a self-consistent model of backbone charged pH-responsive PE brushes using the Strong Stretching Theory (SST). State of the art theoretical model (we refer to it as model 1) for the pH-responsive PE brushes assume a Boltzmann distribution for hydrogen ions both inside and outside the PE layer. In other words, the effect of the coupling between the brush ionization and local hydrogen ion concentration is not considered. This is a major limitation of the existing theory that has been hitherto overlooked. We propose a new theory that self-consistently calculates the correct hydrogen ion distribution by accounting for the appropriate coupling between the brush ionization and local hydrogen ion concentration. We obtain a pair of coupled ordinary differential equations in electrostatic potential and hydrogen ion concentration that are solved numerically to obtain (a) the monomer profile, (b) the distribution of chain ends, (c) the electrostatic potential, and (d) the hydrogen ion distribution. Our results indicate a larger deviation from the results of model 1 at lower bulk salt concentrations and higher pH values. The self-consistent theory always predicts a smaller brush height in comparison to that predicted by model 1. In addition, we observe an enhanced biasness of the monomer concentration profile towards the base than the brush tip.

10:00 AM BREAK

10:30 AM BM03.01.09
Multiscale Modeling of Polymer at Solid and Soft Interfaces

Paola Carbone; The University of Manchester, Manchester, United Kingdom.

The prediction of the adsorption and dynamics properties of polymers at solid and soft interfaces is an important technological and biological problem. Solid interfaces are indeed present in all polymer composites (where particles are dispersed into a polymeric matrix with the aim of improving its mechanical and rheological properties) but also relevant for many applications such as for coating. Polymers absorb also at liquid interfaces in many industrial processes, such as liquid/liquid extractions, solvent displacement methods, or emulsifications, and also when used for biological applications, such as drug nanocarriers, biocompatibilizers, or protective coatings.

In this talk we will present a set of multiscale approaches developed over the years to predict the adsorption properties of polymers at solid surfaces (specifically carbon black) and soft interfaces (liquid/liquid and lipid membrane).

The aim of the multiscale technique is to balance the need to retain important chemical details allowing long simulations and ultimately to identify design rules to predict the polymer-interface adhesion properties as a function of surface roughness and polymer composition.

M. Zaki, P. Carbone, Langmuir 2017,33, 13284

11:00 AM BM03.01.10
Effect of Structural and Material Heterogeneity on Failure in Fibrous Materials

Sai S. Deogekar, Mohammad R. Islam and Catalin Piciu; Rensselaer Polytechnic Institute, Troy, New York, United States.

Fiber networks occur abundantly at all length scales in the biological and non-living worlds. Various applications of such fibrous materials require them to maintain their structural integrity. Hence, an accurate understanding of the factors affecting failure at system subscale is important. Since these materials are structurally stochastic, heterogeneity plays a major role in determining the dominant failure mechanism and affects strength and toughness of the material. In addition, most of these networks naturally occur as composites (e.g. in various types of tissue). Previously, we studied the effect of heterogeneity in the strength of the inter-fiber bonds on the overall network strength. In this work we study the effect of structural heterogeneity and network architecture, on the macroscopic strength and strain-at-failure. We observe that increasing the structural heterogeneity increases the strain-at-failure while the strength remains unaffected. Thus, we propose to use structural disorder of these materials to control their toughness. Further, we investigate the behavior of network-based composites formed by embedding spherical inclusions, rigid or deformable, in a fibrous network. A small fraction of inclusions strongly affects the network deformation and alters drastically the microscopic deformation and failure mechanisms. This is due primarily to the confinement effect of inclusions on the deformation of the network.

11:15 AM BM03.01.11
Simulating Polymers with Reactive MD—Cross-Linking, Stress/Strain, Degradation, Solvation

Adri van Duin\(^1\), Nick Austin\(^1\) and Fedor Goumans\(^1\); Software for Chemistry & Materials (SCM), Amsterdam, Netherlands; \(^1\)Department of Mechanical & Nuclear Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Reactive molecular dynamics techniques such as ReaxFF afford insight at the atomic level for complex chemical processes as well as for material properties which involve chemical bond breaking and formation. We will discuss recent developments in the ADF-ReaxFF software in the context of polymers.

A new bond boost method enables the atomistic simulation of cross-linking processes such as epoxy resin hardening at reasonable time scales. The cross-linking densities from these simulations are in good agreement with experiments.

Stress/strain properties and yield points can be obtained with ReaxFF while straining the system, including the underlying atomistic processes. Similarly, degradation rates and mechanisms under extreme conditions can be simulated with ReaxFF.

Finally we will discuss how the information from reactive MD runs, in particular the dynamic charges, may be used to refine our COSMO-RS thermodynamic predictions for solubilities and related properties.

11:30 AM *BM03.01.12
Diffusioosmotic and Thermoosmotic Transport in Nanochannels Grafted with End-Charged Polyelectrolyte Brushes—Continuum Calculations and Molecular Dynamics Simulations

Siddhartha Das, Raja Mahheedhara, Parth Rakesh Desai, Haoyuan Jing and Harnoor S. Sachar; University of Maryland, College Park, Maryland, United States.

Liquid flows in nanochannels grafted with polyelectrolyte brushes have been invariably retarded owing to the significant drag force imparted by the PE brushes. In a recent study, we proposed a paradigm shift in this understanding – we showed that for nanochannels grafted with end-charged brushes (having a charge density of $\sigma$), the electroosmotic (EOS) transport got massively augmented as compared to the brush free nanochannels having a wall charge density of $\sigma$. We argued that the presence of the end-charged brushes localized the charge density of the induced electric double layer (EDL) and hence localized the EOS body force away from the nanochannel wall, thereby ensuring a massive manifestation of the EOS body force eventually enforcing a larger EOS transport. Here we report our first Molecular Dynamics (MD) simulations based verification of this phenomenon. Furthermore, we carry out continuum calculations for the diffusioosmotic (DOS) and thermoosmotic (TOS) transport in such end-charged PE-brush-grafted nanochannels in presence of an axial concentration and an axial temperature gradient respectively to establish that these transports too get enhanced due to the corresponding enhancement in the induced EOS transport. Furthermore, MD simulations are carried out to validate the continuum findings.

*SESSION BM03.02: Multiscale Modeling of Soft Materials and Interfaces II

Session Chairs: Siddhartha Das and Sanket A. Deshmukh
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Back Bay B

1:30 PM BM03.02.01
Effect of Solvent on the Molecular Structure and Electrical Conductivity of DNA

Busra Demir\(^1\), Sumeyye Gokce\(^1\), Hashem M. Mohammad\(^2\), Sunil R. Patil\(^1\), Yuanhui Li\(^1\), Josh Hihath\(^1\), M. P. Anantram\(^2\) and Ersin Emre Oren\(^1\); \(^1\)Department of Biomedical Engineering, TOBB University of Economics and
DNA is a promising molecule for molecular electronics due to its unique electronic and self-assembly properties. Understanding the nature of electrical conductance of DNA is essential for rational design and engineering of these soft materials for use in molecular electronics. The structure of double-stranded DNA (dsDNA) is known to be sensitive to solvent conditions and thus its electrical conductivity. Here, we first used Molecular Dynamics (MD) simulations to determine both the transformation path and the stable molecular conformations of DNA (CCCGGGCCC and TTATATTTT) in various solvent (water-ethanol mixtures) conditions. The MD trajectories revealed that there is a specific ethanol concentration, below which the B form DNA is stable. Above this threshold value, which also depends on the sequence, we observed that A form DNA is the stable form. These observations also validated by the circular dichroism experiments for the same DNA sequences. The MD simulations also revealed that for extremely high ethanol concentrations the DNA helix is destabilized and collapsed. We then selected representative structures along the transformation path using structural clustering algorithms, and calculate the wave functions near the HOMO-LUMO gap using Density Functional Theory (DFT). Finally, we used Green’s functions based transport modelling to analyze conductivity of DNA. Our calculations reveal that the solvent conditions is an important factor that determines the device characteristics because it can significantly change the conformation and conductance of the DNA.

1:45 PM BM03.02.02
Determining the Binding Mechanisms of All 20 Natural Amino Acids to (hkl) Facets of Hydroxyapatite as a Function of pH
Sam Hoff, Juan Liu and Hendrik Heinz; University of Colorado Boulder, Boulder, Colorado, United States.

Mineralization of hydroxyapatite is a complex and highly controlled process involving interactions of biological and mineral components. Understanding the basic interactions between individual amino acids and hydroxyapatite at the (001) and (020) surfaces at pH 7 and 5 is a crucial step in understanding the mineralization process and potentially aiding in designing peptides to direct and control bone growth and biomimetic materials. In our study, a combination of steered and unrestrained molecular dynamics simulations using the CHARMM36 and Interface force field parameters are used to study the dynamic nature of hydroxyapatite as well as the binding conformations of N and C capped amino acids. The results indicate that charged amino acids have a distinctly higher affinity to the mineral surface than non-charged amino acids. Binding site preferences, conformations, and the effects of pH and surface facet on the affinities are reported, and significant differences for Arginine, Glutamic Acid, Aspartic Acid, and Lysine quantified. The trends provide valuable insight into the affinity and binding mechanism of the building blocks of larger biological structures such peptides and proteins onto hydroxyapatite surfaces. The results will be useful in designing peptides to target specific bone facets for growth or suppression as well as potentially offering the ability to target specific bone sites where infections exist.

2:00 PM BM03.02.03
Elucidation of the Induced Chirality of Dansylglycine by Its Interaction with Human Serum Albumin
Aquinaldo R. Souza 1, Izabelle Amorin Ferreira Boza 1, Valdecir F. Ximenes 1, Mauricio L. Yoguiun 1, Nelson Morgon 2 and Ignace Caracelli 1; 1Chemistry, Sao Paulo State University - UNESP, Bauru, Brazil; 2Chemistry, Campinas State University, Campinas, Brazil; 3Physics, Federal University at Sao Carlos, Sao Carlos, Brazil.

Human serum albumin (HSA) plays an important role in the transport of substances with pharmacological properties due to their high plasma concentration and specificity, placing it as the fundamental protein responsible for the pharmacokinetic implication of the drugs. The dansylglycine amino acid derivative (DG) is a fluorescent marker specific for the II site on the HSA. In addition, when binding to the protein, DG acquires chirality, a feature that can also be used to characterize the binding site of new compounds in albumin. This work aimed to elucidate the induction of chirality in the DG by its binding to the HSA. Experimental Electronic Circular Dichroism (ECD) spectra of DG (100 μM) in the absence or presence of HSA (30 μM) in 50 mM sodium phosphate buffer pH 7.0 were obtained in a Jasco J-815 spectropolarimeter at 25 °C. The spectra were obtained with a resolution of 1 nm and a scanning speed of 50 nm/min. The theoretical ECDs were simulated using the Density Functional Theory (DFT) approach with the hybrid functional B3LYP and CAM-B3LYP in the base set 6-311 + + G (2d, p) and the implicit Solvation Model based on Density (SMD) for the solvents ethanol, methanol, acetonitrile, water and tetrahydrofuran; the calculations were performed with the Gaussian09 program. The DG-HSA complex formation in buffer resulted in the appearance of a positive ECD spectrum centered at 346 nm. Considering that the ECD signal should arise from a chiral conformation of the DG acquired by binding in the protein, calculations were initially performed to obtain the stable conformations focusing on the inversion of configuration centered on the nitrogen atom: alpha-amino group. However, both configurations: R and S showed similar and positive ECD signals. Calculations of the potential energy surface (PES) of the DG were performed, focusing on the dihedral angles formed by the bonding of the -N(CH3)2 group of the naphthalene ring. The analysis of the various conformations obtained and their respective theoretical ECDs revealed that the 150° dihedral (ECD positive centered at 320 nm) presented excellent similarity with the experimental spectrum. On the other hand, the 80° dihedral showed a signal of the ECD spectrum opposite to that observed experimentally. In addition, we observed that the nitrogen atom of the -N(CH3)2 group presented the greatest contribution to the HOMO-LUMO transition that gives rise to the n-p* electronic transition involved in the generation of the ECD signal. The molecular docking analysis, using the GOLD 5.5 program, of the complexation between DG and HSA revealed a conformation with a dihedral similar (150°) to that obtained theoretically (DFT) and whose ECD is in agreement with the experimental result. In conclusion, through the study of the possible conformations for dansylglycine and the calculation of its theoretical ECD, it was possible to identify the origin of the ECD signal obtained by the complexation between DG and HSA.

2:15 PM BM03.02.04
Understanding Malaria Pathogenesis Through Coarse-Grained Computational Modeling
Sulin Zhang, Yao Zhang, Leann Tilley, Ju Li and Subra Suresh; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Northwestern University, Evanston, Illinois, United States; 4The University of Melbourne, Melbourne, Victoria, Australia; 5Nanyang Technological University, Singapore, Singapore.

A normal human red blood cell (RBC) is characterized by two distinct features: high deformability and discocyte shape, which underlie its biological functions, demonstrated by the repeated transit of RBCs (diameter ~8 mm) through narrow capillaries and in 1-2 mm interendothelial slits in the spleen. These two distinct features of RBCs can be comprised genetically or in a variety of pathological conditions, leading to severe RBC diseases. Here we present a coarse-grained RBC membrane model integrating an one-agent-thick lipid bilayer model and a string-of-bead spectrin network model to simulate the change of deformability of the infected RBCs by the malaria parasites (plasmodium falciparum). In particular, we show how malaria parasites harness several RBC membrane principles simultaneously to render the RBC losing its deformability during asexual stage (disease-causing stage) and how the parasites alter the entropy of the spelin network to enable the RBC regain the deformability during the sexual stage (disease-transmission stage). Our simulation results suggest potential targets for the development of new antimalarial therapies.

2:45 PM BREAK

3:15 PM BM03.02.06

Technology, Ankara, Turkey; 2Department of Electrical Engineering, University of Washington, Seattle, Washington, United States; 3Electrical and Computer Engineering Department, University of California Davis, Davis, California, United States; 4Department of Physics, College of Engineering Pune (COEP), Pune, India.
Behavior of Polyethylene Glycol in Bulk and in Water as Studied by Multi-Scale Simulations

Gokhan Kacar; Genetics and Bioengineering, Trakya University, Edirne, Turkey.

Polyethylene glycol (PEG) is an important polymer that has an enormous area of application especially in biomedical field such as drug carrier agent, hydrogel, and tissue engineering material. A thorough understanding of the molecular structure of PEG at different environments is important to devise better routes to develop materials with desired purposes. Although, PEG has been a widely studied material its molecular structure in bulk and in aqueous environment has been poorly investigated. In this work, we strive to perform multi-scale molecular simulations in order to study the physical behavior and molecular structure of PEG in dry environment and interacting with water. We initially perform Dissipative Particle Dynamics (DPD) simulations to create the structure of PEG. Later, we perform reverse-mapping of the atomistic coordinates to perform atomistic molecular dynamics simulations in order to observe the chain configurations and material properties of PEG.

DPD simulations result in successful prediction of the negative volume excess of PEG upon mixing with water. Here, we use a recent extension of the DPD method, where the non-bonded potential of DPD is modified by a Morse potential term to mimic the intermolecular attraction. The parameterization of the Morse potential is done by a mapping of the mixing energies of different hydrogen bonding bead pairs and from radial distribution functions (RDF) for the energy and equilibrium hydrogen bond length terms, respectively. DPD simulations yield preferential attraction of some chemical groups to water as quantified by radial distribution functions. Moreover, PEG chain structure is observed to deviate significantly from a random coil structure as a result of the end-to-end distances and radius of gyration values. Moreover, DPD simulations reveal that water plays a significant role in increasing the flexibility of PEG chains. The helical structures of PEG chains are quantified and a significant helicity of PEG chains is noted with a higher fraction in wet environment.

The reverse-mapped coordinates of DPD simulations of bulk PEG structure are used in atomistic simulations to compute the material properties such as coefficient of thermal expansion, elastic modulus and Poisson’s ratio. The computed values mainly reveal that PEG becomes more elastic and less compressible upon addition of water. In addition, the experimental coefficient of thermal expansion is in line with the experimental values of water. Moreover, PEG chain structure is observed to deviate significantly from a random coil structure as a result of the end-to-end distances and radius of gyration values. Moreover, DPD simulations reveal that water plays a significant role in increasing the flexibility of PEG chains. The helical structures of PEG chains are quantified and a significant helicity of PEG chains is noted with a higher fraction in wet environment.

Machine Learning Methods to Design Next-Generation Gas Separation Membranes

Sanat K. Kumar; Columbia University, New York, New York, United States.

Machine Learning (ML) has been used for quite some time in analyzing large sets of data in a variety of disciplines in order to make predictions on new data. Although gas permeability data has been collected for polymer membranes for decades, only hundreds of data points are available in the literature out of the thousands of possibilities. In order to address the intractability of running thousands of different gas permeability studies, we use ML to build a model on existing data and predict which untested polymers are most likely to achieve superior gas separation performance.

Using Gel Actuated Smart Capsules for Particle Capture

Svetoslav Nikolov1, Alberto Fernandez-Nieves2 and Alexander Alexeev1; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Physics, Georgia Institute of Technology, Atlanta, Georgia, United States.

Advancements in nanotechnology over the last two decades have allowed researchers to tackle a number of critical biomedical problems on the microscale, like site-specific drug delivery and micro-sensing. Microgels which can selectively capture nanoparticles at a given rate are particularly interesting as they are critical for the development of enzymatic bioreactors which are used in many in vivo micro-sensing applications. These devices could also be used for origin of life studies, where the ability to bring in particles at predefined rates can be used to carry out complex chemical reactions. In our work, using dissipative particle dynamics, we leverage the large volume changes of microgels to design a novel microdevice which can be used for nanoparticle capture. Our device is made up of a perforated rigid spherical shell that is embedded with a spherical microgel. Upon application of an external stimulus the gel swells, expanding through the perforated holes and making contact with the external nanoparticle rich solution. After removal of the external stimulus the microgel collapses into the shell interior, bringing along with it nanoparticles from the external solution. The area around each of the perforations is functionalized with a polymer brush which is used to achieve chemical gating, when the gel is in the collapsed state. We study how the capture rate depends on the swelling period and gel-nanoparticle interactions and we quantify the optimal swelling period which maximizes capture rates.

Project supported by the National Science Foundation of U.S.A. (DMR-1255288, TG-DMR180038, and DGE-1650044)
BM03.03.01

Confinement Effect of Nanoscale Biological Systems
Arvand M. Navabi and Nima Rahbar; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

The nanoscale molecular dynamics of the confined organic matrix in the biological material, nacre and its contribution to the exceptional toughness of this biomaterial has been studied. While under stress, the dynamics of the nanoscale structure of nacre have significant influence on the energy dissipation of the system and ultimately on the fracture toughness of the material. For better understanding these mechanisms, a solution of the c-domain consensus of the protein, Lustrin A, was confined between two ceramic layers of aragonite by employing molecular dynamics computations. Then the aragonite walls were subjected to shear, and the polymeric system responded by unfolding. This study reports increase in the energy dissipated through unfolding mechanisms of the protein system as the confinement size decreases. The dominant energy dissipation method in larger systems transition from unfolding to polymeric interactions and entanglements.

BM03.03.02

2D Powerless Capillary Microchannel Device for Efficient Capture of Circulating Tumor Cells
Yiting Zheng; Northeastern University, Boston, Massachusetts, United States.

Introduction: Liquid biopsy of circulating tumor cells (CTCs) can help find cancer at an early stage and determine whether treatment is effective or not. Secondary microscale features such as micropillars, microstripes and silicon nanowires, microfluidic channels can be functionally modified with cell selective species such as anti-epithelial cell adhesion molecules (Anti-EpCAM) and aptamers to enhance efficacy of CTC capture. However, the surface bound cell adhesion molecules have less flexibility to interact with receptors over-expressed on the surfaces of flowing cancer cells, leading to low capture efficiency. Meanwhile, the microfluidic devices require sophisticated processes to make and accessory such as pumps and tubing to work, which makes microfluidic device not an ideal tool for point-of-care diagnosis and prognosis.

This work describes a method for efficient capture of CTCs from human whole blood using a two dimensional (2D) capillary microfluidic device modified with long chain polymers that have cell-adhesive terminals. The height of microchannel is designed to approximate the diameter of single cells. Given its low cost, easy operation, repeated usage, and zero-power consumption, this device would find its use at points-of-care.

Results: CEM cells solution with PBS was studied in channels with different heights and capture efficiency is inversely proportional to channel height to the second power which agrees well with the modeling of cell sedimentation in channels. Cells are injected in channels by flow and the flow filling time in our device is not long enough to let all the cell settling. The 30 μm channel can achieve 95% capture efficiency. This optimal parameter was applied in cell capture in human blood. Figure 2 shows fluorescence images of CEM cells captured on folic acid modified channel. The capture efficiency of the channel has calculated to be 88.3 ± 14.6% for CEM cells in spiked blood with concentration of 5×10^6 cell/ml and 90±4% with concentration of 5,000 cell/mL. CEM cells are found firmly attached on the substrate. The capture efficiency agrees well with the assumed theory of cell rolling and cell sedimentation.

Conclusions: Circulating tumor cells (CTCs) spiked in human blood can be captured efficiently with 2D capillary microchannel device which was modified with polymer brush. Blood or cell suspension can be sucked in the channel by capillary force. The kinetics of channel filling for buffer solution containing cells agreed with theoretical models. The capture efficiency decreases with increased height of channel due to cell rolling and tethering in microchannels. In high channel, less cells are captured by cell rolling and tethering while more cells have ligand receptor reaction by cell settling. The polymer brush modified glass can be easily disassembled for further analysis of captured cells. This non-sealing and pump-less device does not have blocking or leaking problems as normal fluidic device.

BM03.03.03

The Effect of Microenvironment Stiffness on Oligodendrocyte Differentiation
Alexander Evenchik; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Understanding how a cell senses its environment is key to understanding how it acts and responds to different stressors, such as changes of pH, temperature, or concentration of small molecules. Oligodendrocytes are a type of glial cell found in the central nervous system; they are responsible for wrapping axons in myelin, a sheath that allows neurons to effectively transmit electrical impulses in the brain. Oligodendrocyte dysfunction leads to debilitating diseases such as multiple sclerosis. Polystyrene petri dishes, which are currently used to culture and study these cells, are poor models of the brain (e.g. the Young’s Modulus of polystyrene is approximately 10^8 times larger than that of the brain). It is hypothesized that this lack of biomimicry may contribute to inaccurate or incomplete understandings of oligodendrocyte and myelin biology, as well as hinder the pace of therapeutic development. The goal of our research is to help bridge that gap of understanding by studying the effect of various mechanical cues on the differentiation and myelination of human oligodendrocyte cells. Here we fabricate and characterize various substrates that recapitulate key physical properties of the oligodendrocyte microenvironment. Human oligodendrocytes are derived from induced pluripotent stem cells and cultured in these engineered microenvironments. The extent of differentiation and myelination is assessed via immunocytochemistry and fluorescence microscopy. These results may help lead to more effective methods to culture human oligodendrocytes, and shed light on how these cells may respond to pathological mechanical changes in the in vivo environment.

BM03.03.04

Continuous Elasto-Capillary Clustering of Tilted Nano-Pillars
Sang Moon Kim, Junsoo Kim, Seongmin Kang, Daeshik Kang, Segeun Jang, Seung Eon Moon, Hong Nam Kim and Hyunsik Yoon; 1Harvard University, Massachusetts, Massachusetts, United States; 2Chungnam Univ., Daejeon, Korea (the Republic of); 3Ajou Univ., Seoul, Korea (the Republic of); 4Seoul National University of Science and Technology, Seoul, Korea (the Republic of); 5Incheon National University, Incheon, Korea (the Republic of); 6Analytics and Telecommunications Research Institute, Daedeo, Korea (the Republic of); 7Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Complex structures of clustered micro/nano pillars from the elastocapillarity have been extensively studied for the application of mechanical electrical micro system devices and sensors systems. Herein, we investigate the unidirectional clustering property of initially slanted nanopillars. The deionized water droplet was dispensed onto the slanted nanopillars fabricated by using of Faraday cages and was dried off to generate cluster formation of the patterns. We observed non-continuous clustering of the low-tilted (initial tilting angle of −0° and −15°) nanohairs and unidirectional clustering of the nanopillar arrays with tilting angles of −30° and −45°. We proposed theoretical model to analyze the unidirectional cluster formation and set a criterion for a unidirectionality. Furthermore, we predicted the shape of clustered pillars for the case of the non-continuous clustered pillars based on our proposed model.

BM03.03.05

Investigation of Self-Assembly of Polypeptoids in Aqueous Solution—From Atomistic to Coarse-Grained Simulations
Pu Du and Revati Kumar; Louisiana State University, Baton Rouge, Louisiana, United States.

Polypeptoids or poly N-substituted glycines are a type of peptide mimetic polymers that are highly tunable, and hence an ideal model system to study self-assembly as a function of chemical groups in aqueous soft matter systems. In this study, atomistic simulations were performed on sequence-defined ionic peptoid block copolymers consisting of a hydrophobic and a hydrophilic segment (with one singly charged and the remaining uncharged polar groups) in
aquous solution. These studies revealed that the placement of the charged moiety on the polymer chain affected the micellar structure and shape. However, the computational expense limits simulation times and system sizes to a hundred nanoseconds and tens of nanometers, respectively, necessitating the development of coarse-grained models to study more complex polypeptoids with multiple types of hydrophilic side groups. A coarse-grained (CG) model for N, N-dimethylacetamide (DMA), which represents the polypeptoid backbone, is developed as a step towards developing a CG model of the complex polypeptoid systems. The DMA CG model is parameterized to reproduce the structural properties of DMA liquid as well as a dilute aqueous solution of DMA using a reference all atom model, namely the OPLS-AA force-field. The intermolecular forces are represented by the Stillinger-Weber potential, which consists of both two- and three-body terms that are very short-ranged. The model is validated on thermodynamic properties of liquid and aqueous DMA, as well as the vapor-liquid interface of liquid DMA and the structure of a concentrated aqueous solution of DMA in water. Without long-ranged interactions and the absence of interaction sites on hydrogen atoms, the CG DMA model is an order of magnitude faster than the higher resolution all-atom (AA) model.

BM03.03.06
Artificial Exosomes—Tailored Conjugation of Fusogen to Lipid/Polymer Hybrid Vesicles for Enhanced Drug Delivery
Jeong Yi Kang1 and Jin Woong Kim1,2; 1Bionano Technology, Hanyang University, Ansan, Korea (the Republic of); 2Chemical and Molecular Engineering, Hanyang University, Ansan, Korea (the Republic of).

The development of a wide spectrum of nanoscale technologies is beginning to change the scientific landscape in terms of disease treatment. The small size, customized surface, improved solubility, and multi-functionality of nanoparticles will continue to open many doors and create new biomedical applications. Indeed, the novel properties of nanoparticles, including carbon nanotubes, nanofibers, self-assembling polymeric constructs, liposome, and nano-sized silicon chips, offer the ability to interact with complex cellular functions in new ways. Among them, recent technology pays attention to exosomes, nano-sized vesicles that are released from various types of cells into the extracellular space, since they are able to provide a practical means of intercellular communication and transmission of macromolecules between cells. Moreover, they are able to act as useful vectors for drugs because they are composed of cell membranes, rather than synthetic polymers, and as such are better tolerated by the host. In this study, we propose an exosome-analogous drug delivery system which is established by using lipid/polymer hybrid vesicles with fusogenic peptide conjugates. The lipid/polymer hybrid vesicles are fabricated by co-assembly of phosphatidylcholine and poly(ethylene oxide)-b-poly(caprolactone)-b-poly(ethylene oxide). Thanks to large size and slow dynamics of amphiphilic triblock copolymers at the bilayer membrane, the hybrid vesicles show long-circulating time and high drug loading efficiency. Fusogenic peptide, penetratin, induces vesicular interaction with cell membrane, thus enhancing cellular uptake. To evaluate the cell affinity of fusogenic exosomes, the interaction force between an exosome and a cell is characterized via microscale thermophoresis. Finally, in vitro cell-penetration study demonstrates the practical applicability of our artificial exosome as a remarkable cell delivery nanocarrier.

BM03.03.07
Systematic Control of Flory-Huggins Interaction Parameter of Block Copolymer Forming Sub-10 nm Perpendicular Lamellar Pattern
Seung Won Song, Voon Hyung Hur and Yoon Sik Jun; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Directed self-assembly of block copolymer is one of the most promising candidates for sub-10 nm scale lithography due to its cost effectiveness and nanometer scale pattern resolution. However, further improvements of line edge fluctuation and pattern resolution to sub-10 nm region of Poly(styrene-b-methyl methacrylate) (PS-b-PMMA) block copolymer remain as critical challenges. To improve pattern resolution, higher Flory-Huggins parameter ($\chi$) is required. However, too high of $\chi$ value induces horizontal lamellar pattern which cannot be used in devices. Therefore, deliberate design of block copolymer with medium $\chi$ value is required so that $\chi$ value is high enough to achieve sub-10 nm pattern formation and small enough to prevent horizontal lamellar pattern. Here, we suggest a newly designed block copolymer that can form sub-10 nm sub-10 nm lamellar pattern which is aligned by graphoepitaxy template. The block copolymer was synthesized by reversible addition-fragmentation chain-transfer polymerization copolymerized with a fluorine containing monomer, which is hydrophobic. The modified block copolymer showed controlled $\chi$ value as the fraction of hydrophobic monomer changed. Block copolymer pattern with sub-10 nm feature size could be achieved due to a three times higher $\chi$ value than the conventional PS-b-PMMA. Even though the newly synthesized block copolymer has a high $\chi$ value, the polymer could form perpendicular lamellar morphology by short thermal annealing.

BM03.03.08
Theranostic Pluronic Nanoparticles for Glioblastoma Treatment—Synergic Application of Chemotherapy and Photodynamic Therapy
Diego S. Pellosi1, Leonardo B. de Paula2, Maryanne T. de Melo2, Danielle R. Mota2, Giovanni A. Lima2 and Antonio C. Tedesco2; 1Chemistry, Federal University of São Paulo, Diadema, Brazil; 2Chemistry, University of São Paulo, Ribeirão Preto, Brazil.

Despite advances in the fight against cancer, glioblastoma multiform treatment continues inefficient due inhibitory activity of brain-blood barrier (BBB) that causes low efficacy and selectivity for temozolomide (TMZ) chemotherapy. In order to improve therapeutic outcomes aiming side effects reductions the present work followed two strategies: (i) the use of theranostic pluronic nanoparticles and (ii) application of photodynamic therapy (PDT) as adjuvant treatment. Pluronic P85/F127 nanoparticles were engineered as multifunctional theranostic/targeted nanoparticles (m-NP) through the chemical functionalization of its surface with biotin (target moiety) and rhodamine-B (fluorescent probe). The chemical-modified pluronic copolymers self-assemble into m-NP that present the advantage of overcoming BBB and encapsulate multiple cargo for the application of multiple tumor treatment modalities with an optimized drug ratio. In addition, PDT characteristics such as its high selectivity upon light-driven activation and the non-development of cross-resistance mechanisms make it a valuable option as adjuvant for TMZ chemotherapy. m-NPs formulations were firstly optimized to obtain best drug loading conditions (for both TMZ and PDT agent) and formulation long-term stability. In these studies we demonstrated that lyophilization of formulation was the best methodology to obtain a longer shelf life for the proposed system. Due theranostic characteristics of m-NP and PDT agent, in vitro confocal microscopy studies on U87-MG, T98-G, U343 glioblastoma cells and NIH-3T3 fibroblast as control were evaluate in order to understand m-NPs role in uptake and intracellular drugs distribution. Uptake experiments demonstrated that the proposed nanoparticle possess higher affinity toward cancer cell lines in detriment of the non-tumor cell line NIH-3T3. In addition, confocal images revealed a broad intracellular distribution for both m-NP and encapsulated drugs at cells cytoplasm, but not in the nucleus. Blank formulations were not cytotoxic while formulations containing TMZ or PDT agent separately presented a reduced effect in cell viability. Nevertheless, PDT/TMZ concomitant treatment presented high efficiency due their synergic action even at low and safe drug concentrations. As demonstrated by flow cytometry experiments, this synergism is due to the different mechanisms of action of each proposed drug in the cell cycle arrest and their selective/controlled delivery at the intracellular level. In conclusion, these results point m-NP are a promising nanostructure to carry different drugs and selectively release encapsulated cargo in cancer cells.

BM03.03.09
Computational Design of Dendron-Grafted Soft Materials-Based Nanoparticles
Akash Banerjee and Meeakashi Dutt; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.
Many drug delivery strategies demand the need for the adsorption and transport of charged, therapeutic biomolecules. These requirements can be met by nanoparticles (NPs) encompassing multiple molecular species that endow electrostatically-induced interfacial binding of specific biomolecules. We are interested in understanding the role of the architecture and composition of the molecular species on the morphological characteristics of the NPs. We study multicomponent NPs encompassing phospholipids and lipids bearing hyper-branched polyelectrolytes (namely, polyamidoamine (PAMAM) dendrons) via the Molecular Dynamics simulation technique. The bonded and non-bonded interactions between the particles is captured by the Martini force field. We examine the impact of interfacial area, dendron generation and relative concentration on the NP morphology. Our studies can potentially guide the design of multicomponent amphiphile-based nanoparticles for applications in medicine and environmental sustainability.

BM03.03.10
A Multiscale Approach to Study Molecular and Interfacial Characteristics of Colloids Xiang Yu and Meenakshi Dutt; Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

The functions of colloidal particles are dictated by interfacial properties which are determined by an interplay of physical interactions and processes spanning multiple spatiotemporal scales. The multiscale characteristics of colloidal particles can be resolved by the hybrid Molecular Dynamics- Lattice Boltzmann technique. This technique enables the resolution of the particle dynamics along with long range electrostatic and hydrodynamic interactions. We have examined the feasibility of an implementation of the hybrid technique to capture the molecular and interfacial characteristics of colloidal particles, such as vesicles. For simplicity, we have examined two types of vesicles whose molecular components have different sustained interactions with the solvent. One of the vesicles encompassed phospholipids and the other vesicle was composed of phospholipids and polyethylene glycol (PEG)-grafted lipids. The molecular and interfacial characteristics of the phospholipid vesicle and PEGylated, or hairy, vesicles are found to be in good agreement with earlier experimental, computational and theoretical findings. These results demonstrate that the multiscale hybrid technique is suitable for capturing the molecular and interfacial characteristics of colloidal particles. The results of our investigations demonstrate the potential of the hybrid technique in capturing multiscale interfacial characteristics of intra- and inter-colloid interactions in suspensions under different flow conditions, and their relation to molecular properties.

BM03.03.11

The Rhesus D (RhD) as well as A and B antigens are important immunogenic epitopes on red blood cells (RBCs) which need type matching during blood transfusion, and mismatching will lead to fatal reactions. Producing antigen negative RBCs, which are universal for transfusion, are necessary especially in emergency situation. While the conversion of A and B antigens into immunity negative cells have been achieved, however, the transition of D-positive cells to D-negative is still problematic. To solve the problems in transfusion, we developed a rational approach to shield the antigens on the Rh D-positive RBCs for D-negative blood production by using the surface-anchored and cross-linked nanogel framework. A thin and uniform nanogel layer, which is consisted of algicin acid and tyramine, was constructed on individual RBCs catalyzed by surface-anchored enzyme. The physical and biological properties of modified RBCs were similar with native RBCs. More importantly, the D antigens on surface of engineered RBCs were shielded completely by the framework layer, preventing the recognition of immune system both in vitro and in vivo. The distribution of “the D-negative blood” in tissues including heart, liver, spleen and kidney was similar with native ones in blood circulation. The resulting stealthy effects achieve complete sheltering of blood group D antigens on RBCs membrane, providing a potential methodology of cell surface engineering for universal blood transfusion regardless of blood types.

BM03.03.12
Lipid Morphology in Solid Lipid Nanoparticles Demi L. Pink1, Jayne Lawrence2  and Christian D. Lorenz3; 1King’s College London, London, United Kingdom; 2University of Manchester, Manchester, United Kingdom.

Solid lipid nanoparticles (SLN) first came to attention in 1991 as they were considered promising particles to investigate with regards to potential applications in drug delivery. These nano-colloidal particles are typically spherical and are comprised of a solid lipid core. This solid lipid core is not perfectly crystalline and so it contains defects which can be used to trap and solubilise lipophilic and hydrophobic drug molecules. Surfactant molecules are then utilised to further stabilise the lipid core. The exact properties of SLN depend on their composition and preparation, with lipid and surfactant selection being key in the development of non-toxic, stable nanoparticles. Since SLN properties can be modified by using different lipids and surfactants, SLN can be optimised for encapsulation and delivery of specific molecules. Whilst the potential for their use in healthcare has been the dominant area of research, there are also options for the application of SLN in a range of other industries, including cosmetics and agriculture.

A significant challenge concerning the use of SLN in drug formulations is the tendency of the solid lipids to converge towards a perfectly crystalline lattice when stored over time. This is due to the increased thermodynamic stability this confers. However, the transition towards a perfect crystalline lattice removes the defects in which the drug molecules are stored. This can result in the expulsion of the drug molecules during storage or rapid expulsion of the drug upon administration, potentially rendering them ineffective. The triglycerides used in SLN can exist in 4 distinct conformations and by examining the conformations of triglyceride in the SLN we aim to better understand the mechanisms behind drug encapsulation and drug expulsion.

This work uses molecular dynamic simulations to investigate the overall morphology of the SLN as well as looking closely at the conformation of lipids in solid lipid nanoparticles. Through this we have gained a detailed understanding of the role of lipids within SLN. By modifying the temperature of our simulations we were able to compare the conformations of lipids in both liquid and solid lipid aggregate as well as in the SLN. This simulation worked is paired with experimental work in order to develop a multi-scale and experimentally relevant understanding of solid lipid nanoparticles.

BM03.03.13
Design Guidelines of Optoelectronics Devices Based Triboelectrification Abdelsalam Ahmed1, Islam M. Hassan1, Ali Radhi1 and Jean Zu2; 1University of Toronto, Toronto, Ontario, Canada; 2Stevens Institute of Technology, Hoboken, New Jersey, United States.

Triboelectric nanogenerators (TENGs) are a new power generation technology with high affinity to ambient energy harvesting from the surrounding media. This has driven many researchers towards coupling such technologies into numerous electronic devices, introducing the field of tribophototronics. An analytical framework has been established for practical evaluation of the multiphysics aspects of tribophototronics devices. The work shows the numerous operating modes of TENGs and their impact on the electrical performance from structural, material and ecological perspectives. Scalability, electrical regulatory systems, supply channel control features are presented. The attributed properties of lightweight, low-cost, high material selections will be shown to have a significant impact on tribophototronics devices.

BM03.03.14
Corrosion Modelling of Ti-20Zr in Body Environment Conditions Julia Mirza Rosca1, Hosam Sak1, Alexandru Pasecu2 and Elena Xiang Yu and Meenakshi Dutt; Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.
positive torsional stress. To model a mismatched base-pair we eliminate hydrogen bonding between the two nucleotides. Using this modification of the molecule magnetic tweezers-based DNA supercoiling measurements found that plectonemes nucleate, and are localized, at a mismatch. Localizing the pathway. MutS recognizes mismatches through a process that involves introducing a sharp bend and flipping out a DNA base at the mismatch site. Single-moth-eye TiO2/PDMS pad by using conventional lithography, imprinting, and thin sacrificial layer. It is noted that the embedded TiO2 nanoparticles acted The capability of fabricating multifunctional polymeric structures has great advantages to satisfy the increasing demand for flexible and wearable energy conversion devices, electronics and displays. In this work, we have demonstrated a novel fabrication method for structuring bioinspired multifunctional moth-eye TiO2/PDMS pad by using conventional lithography, imprinting, and thin sacrificial layer. It is noted that the embedded TiO2 nanoparticles acted

BM03.03.15
MD Simulation and Cellular Potts Model for Neuronal Differentiation on Polymeric Nanoscaffolds

Over the past decades, a great progress has been made in the field of tissue engineering and regenerative medicine especially in the differentiation and proliferation of stem cells into desired lineages in vitro on 2D scaffolds. The purpose of this study is to simulate and design of nanofibrous Polycaprolactone-Graphene (PCL-G) scaffolds, for neuronal differentiation and investigate subcellular and cellular level interactions of cells with the scaffold using MD simulation and Cellular Potts Model (CPM). We explore the interactions between PCL, graphene, and F-actin towards better understanding of neuron cell mobility on PCL-G scaffold. F-actin protein is associated with controlling the mobility and influences the dendritic spines for neuronal cell. Here we use VMD (Visual Molecular Dynamics) for modeling and visualization, NAMD for Molecular Dynamics (MD) computations and Cellular Potts Model (CPM) for cell-cell, cell-scaffold interaction study. After 10ns of MD simulation data and trajectory visualized in VMD, we observed that PCL chains shows affinity towards graphene sheet and try to fit into the graphene sheet. Further, we plan to repeat MD simulations using different sizes of graphene sheet allowing further to investigate the interactions between F-actin and PCL-G. For the CPM simulation, the interactions such as cell-cell, cell-scaffold adhesion and cellular motility contribute to the system’s energy given by a function known as Hamiltonian which manages the lattice rearrangement using the stochastic Monte Carlo’s probabilistic model by minimizing the system’s total energy. In our simulation we set 1 pixel to correspond to 4µm and the time, which is given by Monte Carlo Steps (MCS), to corresponds to 2s of the real experimental time. One simulation is set for as long as 12h to also consider that cells can undergo duplication or apoptotic events. We found out that the cells are moving and changing their shapes, their mobility and growth. More investigations are underway on altering cell-cell and cell-scaffold adhesion energy that can be the key on achieving an alignment of cells on the scaffold and migration afterwards.

BM03.03.16
Superoiled DNA with Mismatched Base Pair—Probing the Role of Structural Defect on Plectoneme Pinning by Molecular Dynamics Simulation

Mismatched base pairs in DNA can result in mutations. Mismatched base pairs are recognized by the MutS enzyme, which initiates the mismatch repair pathway. MutS recognizes mismatches through a process that involves introducing a sharp bend and flipping out a DNA base at the mismatch site. Single-molecule magnetic tweezers-based DNA supercoiling measurements found that plectonemes nucleate, and are localized, at a mismatch. Localizing the mismatch at the end of the plectoneme loop may facilitate mismatch detection by MutS due to the stabilization of the bent and base-flipped out conformation. The plectoneme end loop containing a mismatch can kink more easily, which reduces the energy of the end loop. However, these experiments were limited to positively supercoiled DNA at salt concentrations of 0.5 M NaCl and higher. Theoretical studies predict that for positively supercoiled DNA under physiologically relevant conditions, i.e., at salt concentrations of 0.2 M NaCl, plectoneme nucleation at the mismatch becomes probabilistic rather than deterministic. Here, we use molecular dynamics simulations to study the effect of a mismatched base pair on DNA supercoiling. We employ the oxDNA model to simulate DNA under torsional stress. The oxDNA model is a coarse-grained model in which each nucleotide is treated as a rigid ellipsoid with three interaction sites. The oxDNA model has been shown to accurately reproduce the response of an intact DNA to both negative and positive torsional stress. To model a mismatched base-pair we eliminate hydrogen bonding between the two nucleotides. Using this modification of the oxDNA model, we first determine the effect of a mismatched base-pair on the bending free energy of a short 15 base-pair DNA and compare the results to atomistic simulations. We find that the bending free energy of a short DNA containing a G-T mismatch is close to the bending free energy predicted by atomistic simulations. We then perform simulations of a 600 base-pair DNA with 0, 2, 4 and 6 consecutive mismatched base pairs. We find that for positively supercoiled DNA at high salt, i.e., 1 M NaCl, the plectoneme always localizes at the mismatch, in good agreement with experiments. Extending this framework to study the case of both positively and negatively supercoiled DNA at 0.2 M NaCl, we find that plectoneme localization at the mismatch indeed becomes probabilistic. We will present the relation between the probability of plectoneme localization and the number of mismatches in addition to an analysis of the shape of the loop of the plectoneme for different mismatches.

BM03.03.17
Bioinspired Multifunctional Surfaces for Versatile Optical Applications

The capability of fabricating multifunctional polymeric structures has great advantages to satisfy the increasing demand for flexible and wearable energy conversion devices, electronics and displays. In this work, we have demonstrated a novel fabrication method for structuring bioinspired multifunctional moth-eye TiO2/PDMS pad by using conventional lithography, imprinting, and thin sacrificial layer. It is noted that the embedded TiO2 nanoparticles acted
as an effective UV-protector. As a result, the high energy UVB-light is perfectly blocked by the embedded TiO₂ nanoparticles and the UVA-light is partially penetrated though the surface. Also, the moth-eye inspired nanostructures on the surface show high transparency in a visible wavelength range as well as self-cleaning effect due to nano-roughness on the surface. Further, we successfully fabricated hierarchical structured surface, where we want, by controlling partially-cured region using the multifunctional polymeric pad with partial blocking property of UVA ray.

BM03.03.18
Temperature-Independent Zero-Birefringence Polymer and its Compensation Mechanism for Temperature Dependence of Birefringence Kenji Wada¹, Akihiro Tagaya¹ and Yasuhiro Koike¹,²; ¹Graduate School of Science and Technology, Keio University, Yokohama, Japan; ²Keio Photonics Research Institute, Kawasaki, Japan.

Optical polymers are used as key materials for liquid-crystal displays (LCDs) due to their ease of processing, high transparency, and low-cost. Most of polymers exhibit orientational birefringence because polymer chains tend to become oriented by processing. In LCDs, the birefringence in polarizer protecting films cause light leakage. This light leakage decreases the contrast ratio and increases color shift depending on the viewing angle. Therefore, orientational birefringence of the polymers is ideal to be zero for LCDs. Orientational birefringence is always zero no matter how much a polymer is orientated by processing if intrinsic birefringence Δn₀ which is a specific value of each polymer is zero. Our group proposed and synthesized zero-birefringence polymers (ZBPs) which exhibited almost no Δn₀ [1]. Recently, we found temperature dependence of Δn₀ of the polymers [2]. It becomes a problem for in-car LCDs which generally require no birefringence in the large temperature range from around −40 to 85°C, compared with the range for interior LCDs. However, the mechanism of temperature dependence of Δn₀ has not been clarified. For synthesis of temperature-independent zero-birefringence polymers (TIZBPs) which exhibited almost no Δn₀ in the wide temperature range, the detail clarification of the behaviors of polymer molecules is necessary. The purpose of this article is clarification of the mechanism of temperature dependence of Δn₀ for design and synthesis of TIZBP by the method of birefringence compensation.

Poly(methyl methacrylate (MMA)/benzyl methacrylate (BzMA)) and poly(MMA/phenyl methacrylate (PhMA)) in various composition ratios were synthesized. Then, uniaxial heat-drawn films of these copolymers were made. Absorbance spectrums in IR region of the copolymer films were measured from 25 to 65°C by FT-IR. The spectrums were analyzed to clarify the behavior of main chains and side chains of the polymer in the heating process. Also, Δn₀ of the films from 15 to 65°C were evaluated by automatic birefringence measurement system to calculate temperature dependence of Δn₀ of them. From the above, it suggested that increasing or decreasing of Δn₀ in heating process is related to the orientation behavior of a polymer molecule. Based on the results, the composition of monomers in a system of MMA, BzMA, and PhMA was calculated to compensate birefringence and its temperature dependence for designing a TIZBP. Moreover, poly(MMA/BzMA/PhMA) (39:38:23 wt.%) was synthesized and exhibited almost no intrinsic birefringence Δn₀ from 15 to 65°C.


BM03.03.19
All Atom and Coarse-Grained Molecular Dynamics Simulations of an Interdigitated Multilamellar Phase of a Mixed Surfactant System Arpita Srivastava and Ananya Deb Nath; Indian Institute of Technology, Jodhpur, Jodhpur, India.

A coarse-grained (CG) molecular dynamics simulation of a cationic surfactant behenyl trimethyl ammonium chloride (BTMAC), co-surfactant (SA) in presence of water is performed at a ratio of 2:1 at 283 K from an all atom (AA) simulation [1]. The CG bonded potentials are derived by the Boltzmann inversion of their respective AA distributions [2]. A good match in the CG and AA bonded distributions validate the bonded potentials derived for the model. The MARTINI non-bonded potentials [3] are used to obtain the interdigitated (L₃) multi-lamellar phase as in the AA simulation. The single chain conformational entropies of both BTMAC and SA reveal that around 4% of the molecules have relatively higher entropy than the rest of the molecules, indicating coexistence of both ordered and disordered phases in the bilayer. The molecules with higher entropy and low order parameter are confined to the upper monolayer of a bilayer without flipping to the other layer as evident from their cosine angles with respect to the bilayer normal. The coexistence between ordered and disordered phases is attributed to the oscillation between the bent and stretched conformers of disordered BTMAC molecules with an energy barrier of 5 kJ/mol whereas all ordered molecules stay stretched throughout the simulations. Our calculations show the suitability of MARTINI force field in predicting the phase behavior of interdigitated bilayer and reveal that the coexistence of two phases arise due to the strong interdigitation between two layers dictated by the chain length of shorter SA which do not allow longer BTMAC to flip-flop and traverse. Thus our analysis will be helpful in understanding the multi-component membrane dynamics with various applications in the field of biological membranes, pharmaceuticals or industry.

References:

BM03.03.20
Mechanical Basis for the Morphology of Fibrillar Aggregates Thomas C. Michaels and I. Mahadevan; Harvard University, Cambridge, Massachusetts, United States.

The self-assembly of fibrillar aggregates is of importance in biology, biomedicine and materials science, yet understanding the range of possible shapes for these structures remains an open question. We propose a coarse-grained approach that averages over specific molecular details to suggest that the spatial complexity of self-assembling fibrillar structures is due to the competing effects of (the bending and twisting) elasticity of individual filaments and the adhesive interactions between them. We show that a theoretical framework accounting for this allows us to capture a number of diverse fibril morphologies observed in natural and synthetic systems, ranging from Filopodia to multi-walled carbon nanotubes, and leads to a phase diagram of possible fibril shapes. We also show how the extreme sensitivity of these morphologies can lead to spatially chaotic structures. Together, these results suggest a common mechanical basis for the microscale fibril morphology as a function of the nanoscale mechanical properties.
BM03.03.21

Crack Formation in Wet Colloidal Pillars

Justin Beroz, Alvin Tan, Ken Kamrin and A. John Hart; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

A basic and well-established assumption about solid materials is that they do not crack when subject to uniform compression. Intuitively, it is paradoxical to imagine how a solid material could conspire to split apart while being uniformly compressed together. In this talk, we present an example of such a case, wherein cracks appear during the drying of vertically freestanding water-saturated colloidal pillars we constructed using a direct-write technique. Paradoxically, the cracks form at the free end, far from the substrate, where the particle network is unconstrained in contracting its volume as it bears compression by a uniform capillary pressure acting at its outer surface. We first detail our experiment results and then provide a theoretical explanation for the cracks based on a dominant balance of wetting energy terms, from which follows a simple relationship between the colloidal particle size and pillar dimensions that captures the presence or absence of cracks. Our theoretical result agrees with experiment, and demonstrates that having an evaporating liquid exert the pressure is fundamentally different compared to the typical balance of surface energy and bulk stress considered for dry materials.

BM03.03.22

sasPDF—Pair Distribution Function (PDF) Analysis of Nanoparticle Assemblies

Chia-Hao Liu1, Ellie Buenning1, Eric M. Janke2, Igor Coropceanu2, Dmitri V. Talapin2, Sanat K. Kumar1 and Simon J. Billinge1,4; 1Chemical Engineering, Columbia University, New York, New York, United States; 2Chemistry, The University of Chicago, Chicago, Illinois, United States; 3Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States; 4Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York, United States.

Nanoparticle superlattice assemblies (NPSA) are being developed for their special properties in applications such as flat-panel displays. The properties of the resulting assemblies can be further engineered by controlling interparticle spacings and arrangements. It is therefore crucial to be able to determine the structure of these NPSAs as quantitatively and accurately as possible. In general, they may have only short-range (on the nanoparticle length-scale) structural correlations (though some assemblies are highly crystalline), making the quantitative determination of NPSA structure difficult. TEM is popular for visualizing mesoscopic structures. Small angle scattering (SAS) may also be applied. However, conventional analysis of SAS data as so far resulted only in semi-quantitative analyses and TEM images can be subjected to sample bias and are not suitable for sample-average measurements. Atomic pair distribution function (PDF) analysis of x-ray and neutron powder diffraction data is a powerful approach for studying non-periodic structural signals, for example from nanoparticles themselves. It yields local structural information from nanomaterials with high precision and quantitative accuracy. Here we describe how we have extended the PDF analysis to the SAS regime, where we can apply similar quantitative modelling methods that are proving powerful at the atomic scale, but to the extraction of structural information about superlattice assemblies. In this presentation, we will present PDF analysis in SAS regime (sasPDF) and we will also present applications of sasPDF techniques to systems with different levels of ordering, from highly crystalline assemblies to isotropic, amorphous polymer coated silica nanoparticles that have promise in gas separation membranes.

BM03.03.23

Synthesis of Metal and Polymer Nanoparticles for Hybrid Nanoassembling and Functional Properties

Nikunjkumar Visaveliya; The City College of New York, New York, New York, United States.

Nanoscale metal and polymer particles have captured broad attention and allowed enormous technological progress in various fields from biomedical and photonics to catalysis and sensing. In this work, surface-active polymer nanoparticles as well as polymer-polymer and polymer-metal nanoassembly particles are synthesized, and different parameters such as their size, morphologies and assembling strength have been studied. Nanoassembly particles are attractive because of the coupled properties with a large surface to volume ratio. A key challenge is to produce the core shell polymer nanoparticles via single-step processes. To address this concern, here, microfluidics approach and precise interfacial reaction strategies is highly promising, and hence different types of surface layered polymer nanoparticle systems were obtained in one-step processes. An inner core material is hydrophobic whereas a hydrophilic surface layer (in-situ formed during the polymerization process) swells in the aqueous environment. On other side, polymer-metal nanoassembly particles as well as metal catalyzed metal deposited four layered nanoassembly particles of tuned size and compositions were produced. It is shown that these particles can be used as nano-sensor particles for surface-enhanced Raman spectroscopy.

BM03.03.24

Toward Self-Healable Multifunctional Coatings Containing Catechol in Hybrid Polysilsesquioxane

Sohyeon Park, Sungwon Jung and Jinkee Hong; Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea (the Republic of).

The polysilsesquioxane (PSQ) is an organic/inorganic hybrid material and has excellent biocompatibility and mechanical properties. Thus, PSQ is regarded as a promising candidate for coating materials for various medical devices. From a medical device point, the ideal coating should have the ability to exert excellent biocompatibility, durability, antimicrobial effect and drug delivery capabilities. However, most of the developed coatings for medical devices were limited in exhibiting this simultaneous ability. Here, we fabricated catechol-functionalized PSQ hybrid coatings with various functions. First, well-defined PSQ matrices were synthesized by sol-gel reaction using hydrophilic precursors, and catechol groups were functionalized in carboxymethyl cellulose (CMC). Subsequently, the catechol-functionalized PSQ hybrid coatings were prepared by excellent compatibility of organic primers in PSQ to catechol-functionalized CMC. Synthesized PSQs were highly durable and exhibit superhydrophilic properties that contribute to the antimicrobial effect, through their morphological changes. On the other hand, the catechol residues of the coating were initiated and promoted by rapid and strong hydrogen bonding between them when cracks were formed in the coating, and their strong wet adhesive properties also contribute to the regeneration of the coating by generating other noncovalent interactions. We have attempted to introduce a drug delivery function into this self-healable antimicrobial coating. We have also applied this coating to a variety of medical devices and verified its versatility.

BM03.03.25

Diffusion Modeling for the Prediction of Bacterial Patterning on Vascularized Polymers

Kayla Marquis, Benjamin Chasse and Caitlin Howell; University of Maine, Orono, Maine, United States.

The creation of rationally designed and spatio-temporally controlled surfaces for cell culture is of great interest in the pursuit of the next generation of advanced biointerfaces. Here, we explore the use of COMSOL Multiphysics modeling to calculate the mass transport of antibiotic compounds through a bio-inspired vascularized polymer system, and use this model to predict the growth pattern of a bacterial biofilm on the surface of the polymer. The vascular system geometry, antibiotic concentration, and diffusion coefficients define the model, and are used in conjunction with known bacterial growth parameters such as minimum inhibitory concentration and critical time to determine the final arrangement of the biofilm on the surface. The theoretical models are then compared to an experimental validation. This approach may prove useful in applications such as compact methods for separation of bacterial multi-cultures based on antibiotic resistance or the creation of multiple spatially isolated colonies from a single culture sample for high-throughput diffusion studies.
BM03.03.26
Prediction of Surface Wettability of Fresh and Aged Graphite Surfaces from First-Principles Density Functional Theory Simulations Chun Yu Lu, Chia Yun Lai, Mariam S. Mansouri, Tuza Olukan, Harry Apostolierois, Ibrahim Almansouri and Matteo Chiesa; Khalifa University, Abu Dhabi, United Arab Emirates.

Elucidating the surface wettability of graphite has increased attracting much attention owing to its applications in several engineering fields, including the CMOS industry, energy storage technology and steel casting. However, despite the abundant information in literature, the underlying mechanism for the temporal surface property variations is still not fully elucidated yet, particularly the role played by water vapor. Prediction of the intrinsic surface wettability of graphite from first-principles density functional theory simulations offers an opportunity to clarify the overall evolution. In this study, by combining density functional theory (DFT)-predicted water contact angles and DFT-predicted AFM force-distance curves with experimental temporal observations, we provide conclusive evidence to demonstrate that water adsorption itself causes the graphite surface to be more hydrophobic. This finding helps to explain the variations of surface properties between fresh and aged graphite surfaces in ambient air. Moreover, in this study, we propose a methodology to predict the surface wettability at the nanoscale by linking the adhesive energy at the solid/liquid interface and cohesive energy at the liquid/liquid interface with the DFT AFM-predicted force of adhesion through the Young–Dupre equation.

BM03.03.27
Investigation on Micromechanical Behavior of Living Cell with FEM Simulation Guanlin Tang1, Massimiliano Galluzzi2, Yu-Lin Shen3 and Florian J. Stadler1; 1Shenzhen University, Shenzhen, China; 2The University of New Mexico, Albuquerque, New Mexico, United States.

Atomic force microscopy (AFM) indentation is a powerful technique to characterize micromechanical properties of soft materials including living cells, such as detecting alterations of single cell rigidity correlated to pathophysiological conditions. However, the mechanical data obtained from deep indentation measurements can be problematic to interpret due to heterogeneity of a cell, nonlinearity of indentation contact, and constitutive relations of hyperelastic soft material. In this work, living MDA-MB-231 cells were indented by spherical probes, and the morphological and mechanical data obtained were adopted to build an accurate finite element model (FEM) for a parametric study. Living cells can be considered as complex multi-layered systems comprising membrane, cytoskeleton layers (actin, tubulin, intermediate filaments), nucleus, and internal organelles. Initially, a 2D-axisymmetric numerical model was constructed with the main purpose of understanding the effect of geometrical and mechanical properties of constitutive parts such as cell body, nucleus, and lamellipodium. Then, a 3D finite element model was constructed to simulate indentation events with an asymmetric misalignment geometry. Deformation field from FEM simulations were directly compared with atomic force spectroscopy to resolve the mechanical convolution of heterogeneous parts and quantify Young’s modulus and geometry of nuclei. The results showed that nuclei of adherent MDA-MB-231 in standard conditions are 3-4 times stiffer than the surrounding cell body. 3D simulations demonstrated the nucleus shifting laterally during asymmetric indentation, underlining how a stiffer nucleus can prevent deformability (and therefore damage) caused by external force stimuli.

BM03.03.28
Preliminary Multiscale Studies of the Montmorillonite, Amylose, Fatty Acids and Water for Polymer-Clay Nanocomposite Modeling Felipe A. Azevedo Rios Silva1, 2, Elaine R. Maia1, Maria José A. Sales1, Latifa Chebil2 and Mohamed Ghoul2; 1Instituto de Química, Universidade de Brasília, Brasília, Brazil; 2Ecole Nationale Supérieure d’Agronomie et des Industries Alimentaires, Université de Lorraine, Vandœuvre lès Nancy, France; 3Escola de Exatas, Arquitetura e Meio Ambiente, Universidade Católica de Brasília, Brasília, Brazil.

More than ever, biodegradable polymers attract much attention in polymer science. Although, some biopolymers, such as starch, presents disadvantages such as poor processability. In order to circumvent those disadvantages, researchers mix those polymers with compounds such as clays. This work presents the final part of a theoretical study of a Polymer-Clay Nanocomposite (PCN) composed by: starch, Pequi vegetable oil and montmorillonite (MMT), a phyllosilicate. In the present study, amilose oligomers, oleic, palmitic and stearic acids in the proportion found in the vegetable oil, montmorillonite and water, acting as solvent involved in the experimental medium, were studied, as an simplified model, in order to simulate in multiscale their structural and behavioral correlations. The calculations were carried out by Molecular Mechanics, Dynamics (MM/MD) and Dissipative Particle Dynamics (DPD) methods at 363 K and variable dynamic times, using Materials Studio™ software. In the dynamic trajectories, the organic molecules organized near the MMT, strongly interacting with it. The MD simulations were used as a basis to calculate the interaction parameters for the DPD model, which showed similar characteristics. The organic material concentrated near the MMT surfaces, what correlated with the MD results, implying in the validity of the model. The new knowledge acquired about those molecular systems, works as a starting point to build more complex models and, if the theoretical work converge with the experimental findings, will encourage further studies in the design of PCNs with biopolymers.

Acknowledgements: This work was supported by CNPq, CAPES, UnB and Université de Lorraine.

References:
3 Schlemmer, D.; Angelica, R. S.; Sales, M. J. A.; Compos. Struct. 92, 2010.

BM03.03.29
Enhanced Icephobic Surface Using Porous Silica Particles Mi-jin Kim1, Beom Jin Yoon1, Jin Hwan Kim1, Byungsu Lee2, Daechul Kim2 and Younseok Kim1; 1Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of); 2Kangnam Jevisco Co., LTD., Gunpo, Korea (the Republic of).

Icephobicity is usually defined as the ability to delay and prevent ice nucleation and formation on surfaces induced either by pouring a supercooled water. Formation, adhesion, and accumulation of ice, snow, frost, glaze, rime, or their mixtures can cause severe problems for solar panels, wind turbines, aircrafts, heat pumps, power lines, telecommunication equipment, and submarines. Recently, extremely low ice adhesion was introduced by tailoring the cross-link density of different elastomeric coatings and by enabling interfacial slippage of surface. But, the icephobicity for such surfaces can be short-lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal. Here, we introduced oil-impregnated silica particles into modified hydrophobic polyurethane. The swelling capacity of oil was greatly increased by the lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal.

BM03.03.30
Solvent Induced Coil-to-Globule Conformation Change of a Single Poly(acrylic acid) Chain Yaxin An, Karteeek K. Bejagam and Sanket A. Deshmukh; Virginia Tech, Blacksburg, Virginia, United States.

Icephobicity is usually defined as the ability to delay and prevent ice nucleation and formation on surfaces induced either by pouring a supercooled water. Formation, adhesion, and accumulation of ice, snow, frost, glaze, rime, or their mixtures can cause severe problems for solar panels, wind turbines, aircrafts, heat pumps, power lines, telecommunication equipment, and submarines. Recently, extremely low ice adhesion was introduced by tailoring the cross-link density of different elastomeric coatings and by enabling interfacial slippage of surface. But, the icephobicity for such surfaces can be short-lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal. Here, we introduced oil-impregnated silica particles into modified hydrophobic polyurethane. The swelling capacity of oil was greatly increased by the lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal.
Poly(acrylic acid) (PAA) is a polymer with carboxylic acid as pendant side-chains. The conformation of the PAA chains is sensitive to changes in the pH, salt concentration, and solvents, which makes it a good candidate as stimuli-responsive polymers. To investigate the effects of solvents on the structure of the PAA polymers at atomistic level, the all-atom (AA) PAA model was solvated in pure water, pure dimethylformamide (DMF), and mixtures of these two solvents of varying concentrations. Molecular dynamics (MD) simulations were performed to analyze the conformation of the PAA and the local solvent structure around the PAA chain. The radius of gyration (Rg) of the PAA chain in pure water and pure DMF were \( -10.0 \pm 1.0 \) Å and \( -14.0 \pm 1.0 \) Å at 300 K, representing its globule-like and coil-like state, respectively. The local structure of the solvents at the polymer-solvent interface was characterized by the radial distribution functions (RDFs) between polymer and solvents. The intra-molecular and inter-molecular hydrogen bonds of PAA, and the hydration free energy of the monomer of PAA in different solvents were calculated to probe the polymer-polymer interaction and the polymer-solvent interaction. This study of the AA model of PAA paves the way for developing coarse-grained PAA models.

Amino acids are important structural units of biomolecules and biomaterials such as peptides, proteins, and peptide amphiphiles (PAs). The focus of this study is on developing accurate transferable coarse-grained (CG) models of twenty standard amino acids. In CG models a group of a few or several atoms is represented by a bead, which can allow the modeling of processes like self-assembly of biomolecules and biomaterials. A 2:1 to 4:1 mapping scheme, where a CG bead is comprised of two to four heavy atoms and associated hydrogens, is employed to represent functional groups in amino acids. The amino acid backbone is comprised of two beads, while the side chains are comprised of one to five beads. The bonded parameters for the CG model are obtained from atomistic distributions of all-atom models of dipeptides. Nonbonded parameters are optimized using the particle swarm optimization (PSO) method to reproduce experimental properties (e.g. solvation free energy, surface tension, and density) of analogues of the side chains and backbone of the amino acids. In the near future, we plan to utilize these new CG models to construct PAs and simulate their self-assembly in the presence of explicit water models to elucidate the mechanism of their self-assembly. The knowledge gained from our study could then be used to aid the successful development of new PAs with potential applications in the field of drug delivery, regenerative medicine, tissue engineering, and stabilized photosynthetic complexes.

We report a new implicit-solvent simulation model for studying the self-assembly of surfactants, which the hydrophobic interactions were captured by calculating the relative changes of the solvent accessible surface area (SASA) of the hydrophobic domains. Using histogram-reweighting grand canonical Monte Carlo simulations, we demonstrated that this approach allowed us to match both the experimental critical micelle concentrations (cmc) and micellar aggregation numbers simultaneously with a single phenomenological surface tension \( \gamma_{\text{SASA}} \) for the poly(oxyethylene) monoalkyl ether (C\( _m \)E\( _n \)) surfactants in aqueous solutions. Very good transferability was observed that the same model can accurately predict the experimental cmc and aggregation numbers for the C\( _m \)E\( _n \) surfactants with alkyl lengths \( m \) between 6 and 12, and poly(oxyethylene) lengths \( n \) between 1 and 9. The implicit-solvent model with SASA calculations put forward in this study is general and may be applied to study the more complex amphiphilic systems such as the surfactants with branched alkyl chains, or the surfactant and hydrocarbon mixtures.

Proteins are one of the basic biopolymers that can be generally found in many different forms in the body of living organisms. A protein molecule is usually composed of one or several polypeptide chains that combine to form a certain folded three-dimensional protein structure. The protein structures are easily excited by external force causing vibration or structural transition. One efficient way to extract the natural frequency of a protein is normal mode analysis (NMA), which provides the frequency and normal modes of the most general motion of a protein structure. However, NMA can be difficult for large protein structures since it will be both compute and memory intensive to solve the eigenvector and eigenvalue of the Hessian matrix, which is a square matrix composed of second-order partial derivatives of the potential energy function of all the constituting atoms of the protein structure. Here, we developed a machine-learning algorithm that allows us to efficiently compute the vibrational spectra of a protein without solving the hessian matrix nor using any chemical force field. To build the algorithm, we wrote our own code to compute and build a database of the first 70 normal modes of over 100,000 protein structures available in the Protein Data Bank by using NMA in a consistent manner. We train our algorithm by randomly pick 80,000 proteins out of the database (80%) and explore the correlation between their natural frequency and the other structural features of the protein (size and secondary structure content) that are easier to be measured with a convolutional neural network. We test the performance of the machine-learning model by predicting the natural frequency of the rest 20,000 protein structures (20% of the database) by giving their structural features. We find the predictions given by our algorithm can largely explain the natural frequency of these protein structures, especially for their low-frequency region (<20 cm\(^{-1}\)). The correlation coefficient between the predicted frequency and the frequency given by NMA is over 0.9, demonstrating the reliability of this machine learning algorithm.

This method will be useful to obtain the natural frequencies of protein structures without knowing their detailed atomic geometry, which may be helpful for the analysis of a frequency spectrum and the quick recognition of the unknown chemical molecules. Besides frequency prediction, we conclude the presentation with the demonstration of a new musical instrument, the EigenProt, that creates complex sounds based on the vibrations of more than 100,000 protein structures.
Molecular dynamics (MD) simulations provide key insights into the microscopic behavior of materials and, as a predictive tool, allow theory-driven design of functional materials. However, because of the large temporal and spatial scales involved in thermodynamic and kinetic phenomena in materials, atomistic simulations are often computationally infeasible. Coarse graining methods are widely used to tackle the challenge of expensive atomistic simulations. Current coarse graining methods require intensive manual tuning to determine both the coarse graining rules and the force field parametrization [1]. Inspired by recent works that achieve deep learning based accelerated calculation in Density Functional Theory [2], molecular kinetics [3] and free energy landscape calculations [4], we propose an alternative data-driven framework utilizing auto-encoders to map the atomistic trajectory into a latent space of coarse grained “super-atoms”. By training on data from atomistic molecular dynamics trajectories or electronic structure calculations, this approach adopts stochastic gradient optimization of the coarse-graining rules, the force field parametrization and the up-resolution rules. Thus, it can provide parameters for large scale coarse-grained calculations and also map the coarse-grained trajectory back to dynamic information with atomistic details. Through this approach, systematic coarse graining pipelines can be built for fast molecular dynamics simulations and high-throughput predictions of the thermodynamics and kinetics of materials.


9:00 AM BM03.04.05
A Hierarchal Approach to Understand Kevlar Using Quantum and Classical Molecular Dynamics Subodh C. Tiwari, Sungwook Hong, Paulo S. Branicio, Rajiv Kalia, Aichiro Nakano and Priya Vashishtha; Univ of Southern California, Los Angeles, California, United States. The outstanding strength-to-weight ratio of para-aramid fibers, such as Kevlar and Twaron, can be largely attributed to their high content of p-phenylene terephthalamides (PPTA) crystals. Here, we perform non-adiabatic shock loading on large PPTA crystal models along different low-index crystallographic directions using quantum molecular-dynamics simulations. Results reveal an anisotropic shock response displaying elastic, plastic, and phase transformation from crystalline to para-crystalline configuration. A reactive forcefield is developed and verified based on the shock data obtained using quantum molecular dynamics. Further, we performed reactive forcefield simulation to include the effect of chain end in PPTA. The simulation results provide an atomistic view on the shock absorbing mechanism during shock in para-aramid synthetic fibers.

9:15 AM BM03.04.06
Using Particle Swarm Optimization to Develop Lennard-Jones Parameters Between Hexagonal Boron Nitride and Water Preeya F. Achari, Kartee K. Bejagam and Sanket A. Deshmukh; Chemical Engineering, Virginia Tech, Blacksburg, Virginia, United States.

Hexagonal boron nitride (BN) has shown great potential in lubrication, electronic devices, sensors, and as an additive for cosmetic products due to its light weight, thermodynamic and chemical stability, great strength-to-weight ratio, and increased resistance to oxidation. Its used in microfluidic and nano-fluidic applications at the molecular level demands accurate force-field parameters to describe the interactions between BN and water molecules. In this study, particle swarm optimization (PSO) and machine learning (ML) were coupled with molecular dynamics (MD) simulations to accelerate the development of Lennard-Jones (LJ) parameters, which are used to describe the non-bonded interactions between a water droplet and a sheet of hexagonal BN. Three commonly used water models, namely, SPC, SPC/Fw, and SPC/E were employed to describe water, while the BN sheet was modelled using REBO potential. The LJ parameters were optimized to reproduce the nanoscopic contact angle of water on the BN sheet.

9:30 AM BM03.04.07
Coupling Lattice Boltzmann and Molecular Dynamics—A Versatile Tool for the Study of Soft-Matter Hydrodynamics Burkhard Duenweg1, 2; 1Max Planck Institute for Polymer Research, Mainz, Germany; 2Department of Chemical Engineering, Monash University, Melbourne, Victoria, Australia. The talk outlines the methodology of Lattice Boltzmann (LB) simulations for hydrodynamics, and its stochastic version to include thermal fluctuations. To study colloidal dispersions, polymer solutions, and similar systems, a particle system is run by Molecular Dynamics, and coupled to the LB background by a Stokes friction force and a Langevin force. The method can be shown to represent both statistical mechanics and hydrodynamics fully consistently. A particularly successful application was the solution of the problem of hydrodynamic screening in semifluid polymer solutions. If time permits, the talk will also outline new (and so far not yet fully successful) attempts to base stochastic LB rigorously and approximation-free on the underlying Boltzmann entropy that governs the statistical mechanics of the system.

10:00 AM BREAK

10:30 AM BM03.04.08
State of Trapped Matter Inside Graphene Nanobubble Petr Zhilyaev, Evgeny Iakovlev and Iskander Akhatov; Skolkovo Institute of Science and Technology, Moscow, Russian Federation. Graphene nanobubbles are formed when material is trapped between graphene and atomically flat substrate. Van der Waals interaction between graphene and the substrate results in the high pressures up to 1 GPa inside the graphene nanobubble. Such extreme pressures and confinement could lead to phase transition in trapped material. Here we present multiscale model that describes both the state of matter inside the graphene nanobubble and its mechanical properties. Adhesion energies and their dependence on the thermodynamics parameters is calculated on atomistic level, energy is evaluated in continuum. We apply developed model to the graphene nanobubble on the graphite substrate with argon inside. Super critical state of argon is predicted at room temperature for graphene nanobubbles with radius in range from 100 to 500 nm. Gas phase of argon is emerged inside graphene nanobubbles with radius greater than 500 nm.
Interfacial Effects on Free Volume, Mobility and Glassiness

Jane Lipson, Ronald White and Jeffrey DeFelice; Dartmouth College, Hanover, New Hampshire, United States.

Finite homogeneous materials are contained by interfaces, whose influence on bulk properties is typically unremarkable. However, as the interfacial presence begins to dominate, for example in an ultrathin film or a sample loaded with nanoparticles, significant perturbations in behaviour may result. While it is evidently the material in very close proximity to an interface - e.g. within several nanometers - that is directly affected, the consequences can extend tens of nanometers into the sample. As a result, sample averaged properties might be significantly different from those of the bulk.

This talk will focus on links between changes in local mobility and free volume as interfaces are introduced, and how those changes translate into altering dynamic relaxation and the glass transition. We have recently shown that the Cooperative Free Volume (CFV) theory can resolve bulk dynamic relaxation data over a broad temperature and pressure range, including the span from Arrhenius to non-Arrhenius behaviour. Most recently, we have turned to studying thin films, and found intriguing connections between interfacial confinement and pressure. Application of CFV analysis to experimental dielectric relaxation data will be described, as well as prediction of trends.

The work discussed will also include simulation results using our simple Limited Mobility (LM) model. Here the focus will be on predicting interfacial effects caused by introducing additives into a bulk sample. The LM data reveal connections between the unfavourability of short-range polymer-additive interactions and sample-wide changes in glassiness and local mobility. The LM predictions show good agreement when tested both against experimental data and relative to results from more detailed simulation treatments.

From Small to Large—Multi-Scale Modeling of Biomolecular Structures in Implicit Solvent

Alexey Onufriev; Virginia Tech, Blacksburg, Virginia, United States.

Water is as important to biomolecular simulations as it is to biology. However, accurate treatment of solvation effects explicitly, by representing solvent as discrete particles, can be computationally expensive. A popular alternative that can speed-up practical simulations is based on representing solvent as a continuum: solvent effects on the biomolecule in question are accounted for implicitly, at various levels of approximation. Molecular simulations within this so-called implicit solvent can speed up conformational search dramatically. Here I will discuss the foundations of the methodology and some of its new multi-scale variants. I will also discuss applications across many length scales: from atomistic simulations of the folding of small proteins to studies aimed at understanding chromatin compaction and dynamics at the level of the entire cell nucleus.

Understanding the Thermomechanical Response of Polymer Nanocomposites via Predictive Coarse-Grained Modeling

Wenjie Xie; North Dakota State University, Fargo, North Dakota, United States.

Understanding and predicting the thermomechanical responses of polymer materials are challenging as their responses are greatly influenced by many factors, such as interfacial energy and filler volume fraction, giving rise to the presence of nanoscale interfaces. To overcome the spatiotemporal limitations of atomistic modeling, we have recently established an atomistically informed coarse-graining technique, called energy-renormalization approach, to achieve temperature transferability for coarse-grained (CG) modeling. Here, we employ our CG models to investigate how the nanoscale interface and free surface influence the mechanical and glass transition properties of polymer films and nanocomposites. Taking cellulose nanocrystal and poly(methyl methacrylate) (PMMA) nanocomposites as a relevant model system, we present a multi-scale framework built upon our CG approach and machine learning algorithms to allow the prediction of thermomechanical properties of nanocomposite as a function of interfacial energy and filler volume fractions. Our established multi-scale framework is validated by recent experiments and breaks new ground in predicting key structure-property relationships for polymer nanomaterials.

Nanostructure and Interfacial Characterisation Using Image Classification and Machine Learning

Baichuan Sun and Amanda S. Barnard; CSIRO, Parkville, Victoria, Australia.

Restricting materials informatics to the numerical parameters output from conventional materials modelling software restricts us to a subset of machine learning methods capable of uncovering structure/property relationships and driving materials discovery and design. Presented here is a simple way of converting materials structures in to unique image-based fingerprints suitable for image processing methods that does not require subjective pre-assessment of the data and selection of descriptors by the user. This combination of methods is shown to classify the morphologies of in a meaningful way, and predict the correlation with the functional properties in agreement with other machine learning methods that required user intervention. This image-based, rather than feature list-based, description of nanoparticle surfaces can be extended to more complex interfaces including macromolecules.

A Multiscale Model for Solute Diffusion in Hydrogels

Eneco Aspe1, Giovanni Offeddu3, Yin Chang4, Doreen Chan2, David Merida4 and Eric A. Appel1; 1Materials Science and Engineering, Stanford University, Stanford, California, United States; 2Chemistry, Stanford University, Stanford, California, United States; 3Biological Engineering, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 4Engineering, University of Cambridge, Cambridge, United Kingdom; 5Electricity and Electronics, University of the Basque Country, UPV/EHU, Bilbao, Spain.

Currently, solute diffusion in hydrogels is modeled by at least one of three main theories (hydrodynamics, free volume and obstruction theory), proceeding from distinct diffusion mechanisms. However, a comprehensive predictive model is lacking, so that time and capital intensive trial-and-error procedures are used to test the viability of hydrogel applications. In this presentation, a model for the diffusivity of solutes in hydrogels that combines the three main theories will be introduced. The model is verified by a combination of (i) positron annihilation lifetime spectroscopy (PALS) to measure the sub-nanoscopic free volume, (ii) instrumental indentation to quantify mesh size, and (iii) fluorescence recovery after photobleaching (FRAP) to quantify the diffusivity of dextran solutes of different sizes in poly(ethylene glycol) hydrogels with various mesh sizes. The model presented here outperforms
2:15 PM BM03.05.03
Multiscale Modeling Framework with Application to the Facet Capsule Ligament and Podocytes Jacob Merson, Sai S. Doogekar, William R. Tobin, Catalin Picu and Mark S. Shephard; Rensselaer Polytechnic Institute, Troy, New York, United States.

A multiscale strategy is presented which is used to model various types of biological structures such as the cervical facet capsular ligament (FCL), and the podocyte; a cell responsible for filtration in the kidney. This strategy allows the micromechanical representation of the biological tissues as collagen networks, and the direct use of the detailed geometry obtained through various microscopy techniques.

In the FCL we start from the observation that the volume of the ligament is divided in a patchwork of sub-domains, each having a different direction of preferential fiber orientation. Such preferential orientation produces hydrostatic stress amplification and increased fluctuations. We construct a model based on the FCL geometry and perform a parametric study to determine the effect of the preferential orientation on the overall mechanical properties, and microscale fiber reorientation. This study is pertinent because the microscale fiber reorientation has been linked to FCL damage and pain. The multiscale method is also applied to study the deformation of podocytes due to capillary distention. This study is relevant for podocyte degeneration which is associated with degradation of renal function. We determine the threshold strain beyond which such degradation is expected.

2:30 PM *BM03.05.04
Rheology and Relaxation of Entangled Polymers in Strongly Nonlinear Extensional Flows Thomas C. O'Connor1, Austin Hopkins1, Nicolas Alvarez2 and Mark O. Robbins1; 1Johns Hopkins Univ, Baltimore, Maryland, United States; 2Drexel University, Dept Chemical Engineering, Philadelphia, Pennsylvania, United States.

Nonlinear extensional flows are common in polymer processing but remain challenging theoretically because dramatic stretching of chains deforms the entanglement network far from equilibrium. Tube and slip-link models that describe flow of melts near equilibrium must be enriched to describe these states, but it is not clear what physics is missing. Here, we address this problem by performing coarse-grained simulations of extensional flows in entangled polymer melts for Rouse-Weissenberg numbers Wi=0.06-52 and Hencky strains ->6. Simulations reproduce experimental trends in extensional viscosity with time, rate and molecular weight. Studies of molecular structure reveal an elongation and thinning of the confining tube with increasing Wi. The rising stress is quantitatively consistent with the decreasing entropy of chains at the equilibrium entanglement length. Molecular weight dependent trends in viscosity are related to a crossover from the Newtonian limit to a high rate limit that scales differently with chain length. Stress relaxations from steady state reveal chains rapidly retract and recover their equilibrium tube diameter even when chain primitive paths are fully aligned and do not intersect. Contrary to some geometric models of entanglement, our results suggest the degree of chain confinement is independent of the orientation of the entanglement network. The results are used to test and constrain generalizations of tube and slip-link models to strongly nonlinear flows.

3:00 PM BREAK

3:30 PM BM03.05.05
Integral Equation Coarse-Graining Simulation Approaches for the Mixtures of Polymer Melts—Composition-Dependent Effective Potentials Mohammad Hasan Dinpaech and Marina Guenza; University of Oregon, Eugene, Oregon, United States.

Mixtures of polymers with different compositions are of great importance for many technological and industrial applications because as the composition of polymers change, the mixture structure and dynamics can change significantly. Molecular simulations may be used to study polymer mixtures but their properties develop on such an extended range of time and length-scale that they cannot be investigated by atomistic simulations. In this regard, the integral equation coarse-graining (IECG) approach has been developed in which the polymers are either represented as soft spheres or multi coarse-graining (CG) sites, where each CG site consists of a large enough number of monomers to use Gaussian statistics to obtain the intramolecular correlations. The IECG method is based on the liquid state theory and solves the Ornstein-Zernike equation to obtain the intermolecular correlations, and consequently the effective CG potentials. Representing melts with a given degree of polymerization at various resolutions, we use the IECG theory and/or perform the IECG simulations to investigate the properties of the same polymer melt represented by mixtures of CG models at various resolutions. We show that the structural and thermodynamical properties, such as pressure and pair correlation functions, for such mixtures are consistent with pure CG liquids as well as the underlying atomistic simulations. We also address the compositional dependence of the effective IECG potential, along with its range for various types of mixtures.

3:45 PM BM03.05.06
Replica Exchange Enhanced Self Assembly of Ultrashort Peptides Srinivasan Mushnoori2, Vivek Balasubramanian1, Doaa Altarawy4, Benjamin Pritchard2, Shanthu Jha1 and Meenakshi Dutt5; 1Electrical and Computer Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 3Electrical and Computer Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 4Molecular Sciences Software Institute, Virginia Tech, Blacksburg, Virginia, United States.

Replica-Exchange (RE) is a class of simulation techniques used to enhance sampling and comprehensively explore phase space of simulations. Originally proposed using Monte Carlo methods, RE techniques have since found their way into Molecular Dynamics (MD) methods, particularly for addressing problems of large, complex biomolecular systems. RE simulations are generally used for exploring single proteins or peptides, but seldom to explore assembly. Assembly of biomolecules constitutes a class of physical processes which are especially susceptible to kinetic traps. RE provides enhanced sampling that aids the systems in overcoming these kinetic traps. In this study, we apply the REMD technique to the assembly of ultrashort peptides and explore the morphological diversity of the supramolecular structures.

4:00 PM BM03.05.07
Bridging Time Scales with Variationally Enhanced Sampling Omar Valsson; Max Planck Institute for Polymer Research, Mainz, Germany.

The usefulness of atomistic simulations is generally hampered by the presence of several metastable states separated by high barriers leading to kinetic bottlenecks. Transitions between metastable states thus occur on much longer time scales than one can simulate. Numerous enhanced sampling methods have been introduced to alleviate this time scale problem, including methods based on identifying a few crucial order parameters corresponding to the relevant slow degrees of freedom and enhancing their sampling through the introduction of an external biasing potential [1].

Here we will discuss Variationally Enhanced Sampling [2], a generally applicable enhanced sampling method where an external bias potential is constructed by minimizing a convex functional. We present numerous examples from physics, chemistry, and materials science which show the flexibility
Two SWNT(5,5)- and SWNT(10,10)-containing nanocomposite systems, as well as a control PAN, were constructed. Higher stresses were observed in both polyacrylonitrile–single-wall carbon nanotube (PAN-SWNT) nanocomposites, to a draw ratio of two, which mimics fiber-spinning and drawing processes. The most studied polymeric system because it strongly interacts with CNTs and is the most common source of high-performance carbon fibers. In order to exploit the anisotropies and structures of CNTs. Among various types of polymer-CNT nanocomposite fiber, polyacrylonitrile (PAN) has been among the most studied polymeric systems because it strongly interacts with CNTs and is the most common source of high-performance carbon fibers.

Bone displays structural hierarchy spanning from the molecular scale to the macroscale, beginning with well-organized arrays of collagen molecules and nanoscale hydroxyapatite which in turn form the fibrils followed by concentric lamella and the osteon and finally the macroscopic bone. The role of molecular interactions between the nanosized hydroxyapatite and collagen on the mechanics of collagen is evaluated using molecular dynamics simulations. In addition, detailed steered molecular dynamics studies on the mechanics of full length collagen of 300nm size, are conducted and the impact of inter-chain molecular interactions on the structure of collagen and mechanics on the collagen are mechanistically evaluated. The mechanical response obtained from molecular scale studies are incorporated into a 3D finite element model of fibril using a hierarchical multiscale modeling approach. Simulations using the finite element models of collagen fibril are conducted to study the elastic and inelastic response of the fibril. These simulations provide an insight into key mechanisms that influence the mechanics of fibril and indicate that the molecular scale interactions at collagen-mineral interfaces have a significant impact on the mechanics of the fibril. Further, we report the role of crosslink densities in collagen fibrils on the mechanics of the fibril. These studies are vital towards understanding ageing and diseases in bone.

**Literature:**


**4:15 PM BM03.05.08**

**Hiking on the Energy Landscape—All-Atom Computational Understanding of the Universality of Long Timescale Phenomena and Rare Events in Non-Equilibrium Matter—Metal, Water and Protein Yong Zhang**

In the last few years, we have developed an all-atom metadynamics method, which allows intelligently sampling statistically rare events in complex materials, and a Relaxation-Excitation Mode Analysis (REMA) theoretical framework, which links the computationally sampled statistics of the energy landscape to experimentally measurable two-point correlation functions. This synergistically integrated experimental and computational approach opened the way for qualitatively examining a range of non-equilibrium matter and the associated complex processes that occur over a very long timescale, such as the viscous flow of supercooled liquids and glasses, nucleation and crystal growth, the folding of polypeptide chains into structured proteins, the self-assembly of micro-units into functional objects, and aging and degradation of materials. In this talk, first I will show the intriguing energy landscape characteristics of three apparently-different systems: glass-forming metallic liquids, water, and protein; then, I will describe our quantitative investigations of how confinement blocks the transition pathways on the energy landscape of proteins and thus prevents their thermal unfolding/denaturation.

**4:30 PM BM03.05.09**

**Multiscale Modeling of Fibrils in Bone—Bridging Collagen-Mineral Interaction to Macroscale Properties**

Dinesh R. Katti and Kalpana Katti; North Dakota State University, Fargo, North Dakota, United States.

Bone is an essential biological nanocomposite found in the human body that plays a vital role in providing structural integrity and mobility to the human body. Bone displays structural hierarchy spanning from the molecular scale to the macroscale, beginning with well-organized arrays of collagen molecules and nanoscale hydroxyapatite which in turn form the fibrils followed by concentric lamella and the osteon and finally the macroscopic bone. The role of molecular interactions between the nanosized hydroxyapatite and collagen on the mechanics of collagen is evaluated using molecular dynamics simulations. In addition, detailed steered molecular dynamics studies on the mechanics of full length collagen of 300nm size, are conducted and the impact of inter-chain molecular interactions on the structure of collagen and mechanics on the collagen are mechanistically evaluated. The mechanical response obtained from molecular scale studies are incorporated into a 3D finite element model of fibril using a hierarchical multiscale modeling approach. Simulations using the finite element models of collagen fibril are conducted to study the elastic and inelastic response of the fibril. These simulations provide an insight into key mechanisms that influence the mechanics of fibril and indicate that the molecular scale interactions at collagen-mineral interfaces have a significant impact on the mechanics of the fibril. Further, we report the role of crosslink densities in collagen fibrils on the mechanics of the fibril. These studies are vital towards understanding ageing and diseases in bone.

**4:45 PM BM03.05.10**

**Structural Evolution in Polymer Nanocomposite Fibers—A Molecular Dynamics Simulation Approach**

Sojeong Hoo1, Jeong-Eun Lee1, Seunggeol Lee2 and Han Gi Chae1; 1UNIST, Ulsan, Korea (the Republic of), 2Pusan National University, Busan, Korea (the Republic of).

Carbon nanotube (CNT)-based polymer nanocomposites have often been processed into fibers because fibrous shapes are one of the best methods of fully exploiting the anisotropies and structures of CNTs. Among various types of polymer-CNT nanocomposite fiber, polyacrylonitrile (PAN) has been among the most studied polymeric system because it strongly interacts with CNTs and is the most common source of high-performance carbon fibers. In order to understand the structural evolution and related mechanical properties under extensional flow, molecular dynamics (MD) simulations were performed on polycrylonitrile–single-wall carbon nanotube (PAN-SWNT) nanocomposites, to a draw ratio of two, which mimics fiber-spinning and drawing processes. Two SWNT(5,5) and SWNT(10,10)-containing nanocomposite systems, as well as a control PAN, were constructed. Higher stresses were observed in both nanocomposite systems. In addition, higher Young’s (4.76 GPa) and bulk (4.09 GPa) moduli were observed when the smaller-diameter SWNT(5,5) was used, compared to those of PAN-SWNT(10,10) (4.41 GPa and 3.96 GPa, respectively), suggesting that SWNT(5,5) resists stress better. Furthermore, we also observed the formation of void structures at both ends of the SWNTs, especially for the large-diameter SWNT(10,10); these voids became larger in the drawing direction with increasing draw ratio and may adversely affect the mechanical properties of the nanocomposite fibers.
Uptake in Microspheres from Crystalline Nanocellulose—Modelling Diffusion and Kinetics Junqi Wu and Mark P. Andrews; Department of Chemistry, McGill University, Montreal, Quebec, Canada.

Crystalline nanocellulose (CNC) is a crystalline rod-like particle, derived from sustainable forests and biomass. CNC has emerged as a leading "platform" material with potential for broad spectrum applications in technology, including microarrays for intelligent drug delivery and microreactors. In the present work, CNC nanorods are kinetically assembled into microspheres by spray drying. The transport properties of these micro-object are investigated by measuring methylene blue dye uptake. Methylene blue dye adsorption kinetics are predicted using both pseudo-first, pseudo-second kinetics and film-pore diffusion models. The film-pore diffusion model equations were solved numerically by the method of lines, and the initial estimates of external-film transport coefficients were obtained using single resistance models. Dye uptake Isotherms were investigated for large range of initial concentrations (from 5mg/L to 100mg/L) and isotherm type (Langmuir, Freundlich, and Temkin). The thermodynamics of dye adsorption were evaluated based on the kinetic data at different temperatures. The Gibbs free energy was estimated using both chemisorption kinetic models and diffusion kinetic models. Knowledge of CNC dye adsorption mechanisms and uptake is important to extract microstructural information of CNC microspheres. This can be used to further understand how small molecules can be delivered in and out of the micro-particles, and therefore to provide insight into how to control small molecule delivery using CNC micro-vehicles.

8:15 AM BM03.06.02
Bridging Scales of Diverse and Complex Crystal Structures from Atoms to Colloids Julia Dshemuchadse1, Michael Engel1,4, Pablo F. Damasceno2,5, Carolyn L. Phillips1, Matthew Spellings1 and Sharon C. Glotzer1,2,3; 1Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Applied Physics Department, University of Michigan, Ann Arbor, Michigan, United States; 3Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; 4Department of Chemical and Biological Engineering, Friedrich-Alexander-University Erlangen-Nuremberg, Erlangen, Germany; 5Department of Cellular and Molecular Pharmacology, University of California, San Francisco, California, United States; 6Argonne National Laboratory, Argonne, Illinois, United States.

Soft condensed matter research has led to the discovery of increasingly intricate crystal structures over the last 15 years: systems of dendrimer or block copolymer micelles, colloids, and polymer- or DNA-grafted nanoparticles are found to crystallize in structure types that are known from atomic compounds (e.g., [1–5]). Examples for these crystal structure types are Laves phases (e.g., Fe24-MgCu2, hP12-MgZn3), Frank-Kasper phases and quasicrystal approximants (e.g., cP8-CrSi, cP30- CrFe), or clathrates (e.g., cP54-KrSi4). Some of these building blocks can be tuned smoothly and span entire phase diagrams of structural behavior that can be likened to that of a multicomponent atomic system [6].

In this study, we simulate the self-assembly of one- and two-component systems of attractive particles that interact via short-ranged, isotropic pair potentials. Previous exploratory work had found these simple systems to be capable of forming highly complex structures, such as an icosahedral quasicrystal [7]. Here, we inspect large areas in such parameter spaces and find a variety of crystal structures with varying degrees of complexity, including structures with super-large unit cells. We systematically screen two phase spaces of one-component systems, and we explore the higher-dimensional design spaces of the two-component systems by incorporating machine-learning methods into our simulation scheme.

Although our model is short-ranged and fairly simple, we observe many geometric equivalents to atomic-scale structures. The continuous variation of the simulated interaction potentials results in a breadth of structures that spans the entire range of chemical interactions, from low-coordinated, covalent-like environments to highly-coordinated, metallic-like dense sphere packings. Our agnostic phase space exploration grants us a design flexibility beyond that of the periodic table and allows us to engineer new crystal structures to be synthesized in the future under exotic growth conditions or on the mesoscale.


8:30 AM BM03.06.03
Interface-Mediated Assembly of Nanoparticles into Anisotropic Structures Tsung-Yeh Tang1 and Gaurav Arya2; 1Materials Science and Engineering, University of California, San Diego, La Jolla, California, United States; 2Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States.

A significant challenge in the bottom-up fabrication of nanomaterials is assembling spherical or near-spherical nanoparticles into anisotropic architectures. One promising strategy is to use the interfacial tension between two immiscible solvents to trap particles at the interface; however, this approach is typically limited to producing two-dimensional assemblies. Here we demonstrate through molecular dynamics simulations that the interfacial tension across two immiscible polymers combined with the grafting of nanoparticles with polymer chains can be used to assemble spherical nanoparticles into unique anisotropic clusters, such as dimers with a tunable tilt angle at the interface, and more complex three-dimensional architectures, such as chiral ribbons with tunable curvature. We show that this approach can also be used to tune the orientation, and subsequent assembly, of shaped nanoparticles at the interface. Our results suggest that such interfacial assembly of nanoparticles could be a promising approach for fabricating next-generation polymer nanocomposites, where precise spatial and orientational organization of nanoparticles is required for proper function.

8:45 AM BM03.06.04
Multiscale Modeling of Polymer-Colloid Interactions in Waterbased Coatings Alyssa Travitz1, Wenlin Zhang2 and Ronald G. Larson2; 1Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Formulations containing rheology-modifying polymers and nanometer-sized colloids have widespread use in pharmaceuticals, personal care products, and water-based coatings. A typical rheology-modifying polymer consists of a hydrophobic backbone that associates with the hydrophobic surface of the colloids. These hydrophobic interactions drive the polymer to form either a loop on a single colloid or a bridge between adjacent colloids. The continual breakage and formation of loops and bridges results in a transient network with relaxation times that span several orders of magnitude. Because it is computationally infeasible to capture the full range of relaxation times while maintaining atomistic resolution, our group has developed a highly efficient hybrid population balance-Brownian dynamics model (Pop-BD). The Pop-BD model reduces the system to pairwise colloidal interactions with attractive contributions from bridging and repulsive contributions from the layer of loops on the colloid’s surface. Currently, the Pop-BD model approximates the interactions between polymer-coated colloids as a steep, short-range repulsion. However, experimental data suggest that the layer
of polymer loops is often a brush with much longer-range interactions. In this work, we use molecular dynamics simulations to study pairwise interactions of polymer-coated colloids with experimentally relevant coverage fractions. We compare the polymer density profiles from these simulations with small angle neutron scattering data and analytical calculations. Our results are in good agreement with self-consistent field theory and show repulsive potentials with ranges several times longer than previously assumed. In future studies, these repulsive pair potentials will allow us to study equilibrium phase behavior as well as to inform current models that capture the dynamics of these transient networks to ultimately predict and design the rheology of such systems.

9:00 AM BM03.06.05
Inverse Design of Pressure-Induced Solid—Solid Transitions in Colloids Using the Alchemical Ensemble

Chris Yixiu Du1, 2, Greg v. Anders1, Julia Dshemuchadse1, Paul Dodd1 and Sharon C. Glotzer1; 1University of Michigan, Ann Arbor, Michigan, United States; 2School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Recent developments in anisotropic particle synthesis have shown promise for using these particles as building blocks for functional materials. However, due to the large design spaces that are available to us, it can be challenging to find appropriate building blocks for target behaviors. Here, instead of mapping out the phase behavior for a range of particle shapes, we present a new, alternative computational statistical mechanical approach that couples together multiple systems within the “alchemical ensemble”—a generalized, statistical mechanical framework in which model attributes are allowed to fluctuate along with thermodynamic variables. The alchemical ensemble has application to a wide variety of design problems within statistical mechanics and this modeling and simulation approach bridges multiple scales by linking bulk properties to molecular simulations through design. Here, we demonstrate its use in the design of particle shapes for target materials properties, and present examples of candidate colloidal-and nano-particles designed within the alchemical ensemble specifically for structurally reconfigurable colloidal crystals.

9:15 AM BM03.06.06
Twisted Domains Get Edgy—Microrafts in Colloidal Membranes of Length-Asymmetric Rod Mixtures

Douglas M. Hall1, Joia Miller3, Johanna Robaszkiewski3, Prema Sharma1, Michael Hagan1, Zvonimir Dogic1, 2 and Gregory M. Grason1; 1Polymer Science and Engineering, Univ of Massachusetts-Amherst, Amherst, Massachusetts, United States; 2Physics, University of California, Santa Barbara, Santa Barbara, California, United States; 3Physics, Brandeis University, Waltham, Massachusetts, United States; 4Physics, Indian Institute of Science, Bangalore, India.

Osmotically-condensed colloidal membranes of rod-like, chiral filaments offer an experimental platform for directly probing intra-membrane microstructure formation processes that would be far more difficult, if not impossible, to observe at the nanometer scales of phospholipid membranes. In particular, membranes formed by two component mixtures of rods (either wild-type or mutant fd-virus particles) exhibit a remarkably rich set of intra-domain phase-separated morphologies, most notably the formation of raft domens whose lateral dimensions are self-limiting in equilibrium yet much larger than the range of rod-rod interactions. The prevailing theoretical model to explain this phenomenon focuses on the asymmetry in the chirality—a distinct preference for right- vs. left-handed intra-membrane twist for different species—as the stabilizing factor in raft formation. Notwithstanding its successes to capture the raft formation at a qualitative level, several recent experimental observations are not captured by this chirality-driven phase separation (CDPS) model. In particular, the degree of raft twist is shown to be a non-monotonic function of its radius, and there is a pronounced asymmetric behavior of rafts of tall vs. small rods, independent of their chirality. Small rods in background membrane of tall rods form finite size, twisted rafts. In contrast, tall rod domains in a background membrane of short rounds refuse to twist at their outer edge, and instead, become unstable to invaginated or annular morphologies that enclose stable, twisted small-rod rafts.

To understand these observations with develop a model to predict the microstructure and thermodynamic effects of the intra-rod domain edge. We show that geometrical constraints imposed by the twisting of (rigid) rods require splay of the mid-plane of the raft that has important consequences for the shape of the inter-domain edge. Our model predicts the existence of a thermodynamic coupling between domain edge curvature and rod-tilt through the dependence of membrane excluded volume to the 3D geometry of rod packing. We show that the thermodynamics of this the curvature/tilt coupling not only captures the asymmetric dependence of raft behavior on their height (i.e. tilted domain edges generically favor bending towards the shorter rod domain) their effects are quite distinct from the CDPS model (i.e. they lead to free energy terms that are achiral and proportion to domain edge curvature). We argue further, based on symmetry principles, that this curvature/tilt coupling is generic, and as such should exist in any model of phase-separating membranes as a coupling between in-plane tilt and second-derivatives of (scalar) composition.

9:30 AM BM03.06.07
Clustering and Collective Dynamics of Microwimmers—Effects of Shape and Hydrodynamics

Roland G. Winkler and Gerhard Gompper; Institute for Advanced Simulation, Forschungszentrum Jülich GmbH, Jülich, Germany.

Structure formation of active colloidal particles is governed by their shape and hydrodynamic interactions [1], but the effective dimensionality of the system, i.e., three-dimensional bulk fluid versus thin film, plays also a major role. In order to address these various aspects, we have studied structure formation of active dry and wet colloidal systems. Dry matter is modeled by active Brownian particles (ABPs), whereas in the presence of fluid, the active agent is described by a recently developed spheroidal squirmer [2]. The fluid is explicitly modeled by the multiparticle collision dynamics (MPC) approach, a mesoscale hydrodynamic simulation technique [3].

We have studied the swimming behavior, cooperative motion, and motility-induced phase separation (MIPS) of spheroidal squirmers in a narrow slit. For two squirmers, we find a strong influence of confinement on their cooperative motion caused by surface hydrodynamic interactions [2]. Considering the phase behavior of many squirmers, we find that hydrodynamic interactions suppress MIPS for spherical squirmers, but motility-induced clustering (MIC) is present. This is in agreement with results in strictly two-dimensional systems [4], but disagrees with other simulation results for slits [5]. In contrast, hydrodynamic interactions enhance MIPS for elongated squirmers. Moreover, the swimmer type, characterized by the hydrodynamic multipole expansion of its flow field, i.e., puller, pusher, and neutral squirmer, strongly affects the phase behavior. A negative active-stress parameter (puller) is advantageous for MIPS, while a positive value (pusher) is disadvantageous.

The observed clustering of spheroidal squirmers is in contrast to the behavior of motile bacteria, e.g., *E. coli*, in suspensions, which display active turbulence [6]. At the moment, there is no detailed understanding of the different behavior and the underlying mechanisms. Possible hydrodynamic mechanisms will be discussed in the presentation.

References:
Materials adopting the diamond structure possess useful properties in atomic and colloidal systems and are a popular target for synthesis in colloids where a photonic band gap is possible. The desirable photonic properties of the diamond structure pose an interesting opportunity for reconfigurable matter: can we create a crystalline material to switch reversibly to and from the diamond structure with a photonic band gap in the visible light range? Drawing inspiration from high-pressure transitions of diamond-forming atomic systems, we design a system of polyhedrally-shaped colloidal particles that transitions from diamond to a tetragonal diamond derivative upon a small pressure change. The transition can alternatively be triggered by changing the shape of the colloidal particles in-situ. Additionally, our modeling and simulation approach bridges multiple length-scales by linking bulk property calculations to molecular simulations. We propose that the transition provides a reversible reconfiguration process for a potential new colloidal material and draw parallels between this transition and phase behavior of the atomic transitions from which we take inspiration.

10:45 AM BM03.06.09
Structure-Property Relationships of the Crystal-Amorphous Interface During Deformation of High-Density Polyethylene by Molecular Dynamics Simulations
Andrew L. Bowman1,2, Sungkwang Mun2, Steven Gwaltney3, Mei Chandler4, Michael Baskes5 and M F. Horstemeyer1,2; 1Mechanical Engineering, Mississippi State University, Mississippi State, Mississippi, United States; 2Center for Advanced Vehicular Systems (CAVS), Mississippi State University, Mississippi State, Mississippi, United States; 3Chemistry, Mississippi State University, Mississippi State, Mississippi, United States; 4U.S. Army Engineer Research and Development Center, Vicksburg, Mississippi, United States; 5Aerospace Engineering, Mississippi State University, Mississippi State, Mississippi, United States.

Molecular Dynamic (MD) simulations using a Modified Embedded Atom Method (MEAM) for saturated hydrocarbons is used to investigate the complex crystal-amorphous interface of High-Density Polyethylene (HDPE) at various applied strain rates (1e7 – 1e9) and stress states (tension and shear). A random walk algorithm is developed to model the crystalline-amorphous interface through the insertion of four types of amorphous chains within a crystalline domain: 1) tie chains connecting separate crystalline surface, 2) loop chains connecting separate points on the same crystalline surface, 3) chains originating from a crystalline domain and terminating within the amorphous region, 4) chains both originating and terminating within the amorphous region. To better understand the complex structure-property relations of the various polymer chains emanating and terminating within the crystalline and amorphous domains, a Design of Experiments (DOE) methodology is implemented to independently investigate the influence of eight parameters (number and length of each of the four chain types) concerning the crystalline-amorphous interface in uniaxial tension and simple shear boundary conditions. The relative volume fractions of amorphous to crystalline regions are studied in order to bridge the stress-strain behavior of a completely amorphous polymer and a completely crystalline polymer system. The addition of a small number of amorphous segments is shown to drastically lower the ultimate stress of the further investigation of the crystalline-amorphous interface under more mechanically and chemically complex boundary conditions.

11:00 AM BM03.06.10
A Theoretical Framework for Raft Interactions in Ternary Colloidal Membranes
Chaitanya Joshi1, Joia Miller1, Douglas M. Hall2, Arvind Baskaran2, Gregory M. Grason3, Zvonimir Dogic3, Michael Hagan1 and Aparna Baskaran1; 1Brandeis University, Waltham, Massachusetts, United States; 2University of Massachusetts, Amherst, Massachusetts, United States; 3University of California, Santa Barbara, California, United States.

Colloidal membranes are a recently developed experimental system of rod-like chiral particles that self-assemble into one rod-length-thick mono-layers under the influence of a tunable depletion interaction. Despite being monolayers that are 1 micron thick, colloidal membranes are described by the same continuum theory as lipid bilayers, and their colloidal scale enables study of behaviors that cannot be visualized in lipid bilayers. Forming membranes from a mixture of short right-handed rods and long left-handed rods results in a rich phase behavior, including microphase separation, wherein one species forms finite-sized domains, or rafts, floating in the background of the other species. This talk will discuss the theoretical analysis of colloidal membranes comprised of three rod species: one with a shorter length and right-handed chirality, the other two with longer lengths and respectively right- and left-handed chirality. Controlling the composition of a mixture of rod lengths allows tuning the chirality of the background. Experiments have shown that making the long rod mixture effectively achiral leads to complex, non-pairwise interactions between the short rod rafts. We employ a Ginzburg-Landau description of the system to understand how this behavior arises from a combination of chirality, rod length mismatches, and the depletion interactions. In particular, we find that raft interactions and their non-pairwise-additivity can be explained from the deformations of the background membrane. We also theoretically examine the experimental observation that there is an asymmetry between rafts of short rods in a background of long rods, or rafts of long rods in a short rod background --- the two systems lead to very different ensembles of raft morphologies.

11:15 AM BM03.06.11
Computational Design of Multi-Component Superstructures with Multi-Element Colloidal Building Blocks Using a Genetic Algorithm-Based Framework
Mehdi Zanjani1 and Dhananjai Rao2; 1Mechanical and Manufacturing Engineering, Miami University, Oxford, Ohio, United States; 2Computer Science and Software Engineering, Miami University, Oxford, Ohio, United States.

Engineering micro/nanoscale structures and interfaces through self-assembly of colloidal particles is a powerful approach in material design and processing. Colloidal building blocks, with a variety of shapes, sizes, and compositions, can self-assemble into different structures with desirable electronic, photonic, and phononic properties. Recent advances in synthesis and characterization of complex colloidal units, such as colloidal clusters and patchy particles, has provided a library of multi-element building blocks that can significantly expand the current scope of metamaterial self-assembly. However, the complexity of these building blocks makes it significantly harder to predict the resulting structures and their transport properties. Therefore, developing predictive tools based on computational and machine learning approaches becomes a necessity for successful implementation of new material design procedures with multi-element colloidal units.

In this study, we establish a computational framework to help identify feasible multi-component supercrystals of multi-element colloidal building blocks. Specifically, we investigate various designs for multi-component crystalline structures of four or more elements and map out feasible supercrystal phases. We also develop a computational framework to predict transport properties of the target multi-component supercrystals. Band structure calculations are performed to capture the influence of key parameters such as structural features and building block size/shape on the photonic and phononic properties of various proposed metamaterial designs. Finally, we present a Genetic Algorithm (GA) that is established based on the computational analysis of structural...
The Multi-Facetted Nature of Nanocrystal Growth Revealed by Multi-Scale Simulations

We develop a computational model to describe the behavior of active, flexible sheets in solution that can undergo spontaneous self-sustained motion. The active sheets are uniformly coated with a catalyst that decomposes the reagent in the surrounding fluid. The resulting variations in the fluid density give rise to a convective flow around the catalyst-coated sheets. The chemically-generated fluid flow, in turn, dynamically “sculpts” the shape of the sheet and thereby enables it to perform a range of functions. For example, with a periodic influx of reagent, an initially flat, rectangular sheet undergoes repeated shape transformations and thereby exhibits directed crawling along the wall. We also consider a petal-shaped sheet that is anchored to the surface of the solution-filled microchamber. When all four petals are coated with the same catalyst, the generated flow propels the petals to bend and unbend, allowing the sheet to wrap and unwrap a particle localized on its surface. Finally, we examine how four-petal sheets that are coated with different catalysts, and thereby respond to different reagents, can be used to construct logic gates. The findings provide guidelines for creating autonomously moving active fabrics that can be made to crawl, envelop particles in solution or perform simple logic operations in a microfluidic device.

Design of Nanomaterials for Gene Delivery Using Molecular Modeling

The design of ligand functionalized inorganic nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. However, comprehensive understanding of ligand design principles lies in the cost associated with synthesizing and characterizing diverse ligand chemistries and ability to carefully assess the structural integrity of biomolecules upon interactions with NPs. It is known that the interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsDNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlling wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

Predictive Engineering of High-Density Lipoprotein-Mimetic Nanomaterials—Structural and Functional Analysis on Paraoxonase-1

Incorporation, Jiae Young Kim, Yoshitaka J. Sei, Michael Toth, Sang Eun Jee, Seung Soon Jang and Yong Tae Kim; Georgia Institute of Technology,

and transport features of the multi-component supercrystals. This GA uses Machine Learning techniques to define material design rules with respect to structure and transport properties of the desired multi-component supercrystals.
Recent studies have introduced that compositional alteration of HDLs in patient with CVD or chronic kidney disease (CKD) lead to HDL functional heterogeneity. The resulting dysfunction of HDL may lead to the failure to demonstrate that raising plasma high-density lipoprotein (HDL) levels are associated with reducing cardiovascular disease (CVD). This challenge highlights the importance of better understanding of HDL functional heterogeneity. Paraoxonase-1 (PON1) is a major anti-inflammatory and anti-atherosclerotic component of HDL. However, our understanding of the mechanism with which PON1 interacts with HDL relies on the results from bare measurement of plasma HDL levels. Here, we present a new combined approach that leverages both molecular dynamics simulation and microfluidic synthesis of engineered HDL-mimetic nanoparticles (eHNPs) to predict and validate PON1 interactions with or incorporations into eHNPs (apolipoprotein A1 based eHNPs). We found that PON1 binds to both discoidal and spherical eHNPs, both of which have the double-belt apoA1 structure while spherical eHNPs have cholesterol in the core, but not to apoA1-free micelle structure nor to trefoil model structure for spherical eHNPs, which are composed of three apoA1’s. Energy analysis of MD simulation confirmed that PON1 binds to the apoA1 helix 7 of a discoidal eHNPs, while adhering to the apoA1 helix 17 and helix 18 of a spherical eHNPs. More interestingly, we found that the hydrophilic N-terminal domain of PON1 (PON1-H1) serves as a binding area of PON1 to a spherical eHNPs, whereas it has nothing to do with a discoidal eHNPs. Furthermore, we explored possible incorporation of multiple PON1’s into a single eHNPs, resulting in distinct helix interaction from the single PON1 cases. Our integrated approach will bring a new ground-breaking approach to the analysis and development of engineered nanomaterials as well as analysis of natural nanocomposites, addressing the current challenge of costly and vague experimental approaches to the measurement and quantification of complex nanomaterials.

3:45 PM BM03.07.04
Determining of the Structure of Rosette Nanotubes Using Multi-Scale Molecular Modeling—Ring Stack vs Helical Tube

Arthur A. Gonzales2,1, Hector Grande1, Takeshi Yamazaki3 and Hicham Fenniri1; 1Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; 2Chemical Engineering, University of the Philippines, Quezon City, Philippines; 3Vancouver Prostate Centre, Vancouver, British Columbia, Canada.

Rosette Nanotubes (RNTs) are tubular soft materials self-assembled from guanine-cytosine (GAC) hybrid molecules, which can be covalently functionalized for use in various applications. They have been shown to be effective assemblies in regenerative medicine, drug display and delivery, and catalysis.

Previous spectroscopic studies suggest they have a structure which is formed by hexamer rings, maintained by self-complementary hydrogen bonds, that are further stacked and supported by π-π interactions, which form the ring-stacked RNTs. While this mode of association maximizes the hydrogen bonding interactions and results in efficient π-π stacking, it is also possible to envision that the GAC modules assume a helical organization defining a tubular core. We investigated this possibility by using the lysine-functionalized RNT (K1-RNT) and applying multi-scale molecular modeling methods, which include Monte-Carlo conformational search, molecular dynamics, and the statistical mechanical theory of molecular liquids, 3D-RISM theory. We considered three structures of the K1-RNT: stacked arrangement (ST), left-handed helical coil (LHT), and right-handed helical coil (RHT). Our results suggest that the formation of ST, LHT, and RHT K1-RNTs in water are favorable and are enthalpically driven. Moreover, 3D-RISM analysis suggests that the RHT conformation is more probable than the ST and LHT RNTs and this is due to a more favorable solute-solvent interaction energy. Using the 3D distribution of solvent sites around the RNTs (from 3D-RISM calculations), we were also able to determine the solvation structure and estimate the free energy of binding of each water molecule in the RNT channel. The results also corroborate the higher probability of occurring for the RHT nanotubes. Further experimental studies are underway to verify these findings.

4:00 PM BM03.07.05
Specific Adhesion and Non-Specific Adhesion of Nanoparticles Influenced by the Surface Charge of Plasma Membranes

Shayandev Sinha, Haoyuan Jing, Harmoo S. Sachar and Siddhartha Das; University of Maryland, College Park, Maryland, United States.

Nanoparticle (NP) driven drug delivery is preferred for its target specificity and effectiveness. But it is a well-known problem that this technique cannot eliminate the non-specific adhesion (NSA) to healthy cell, which in turn leads to cytotoxicity. Specific adhesion can only occur when the NP can adhere to the surface of the plasma membrane through the receptor-ligand (R-L) bond formation. The surface charge of plasma membrane and the presence of the Electric Double Layer (EDL) around the cells can change this scenario in such a way that the electrostatic repulsion of the negatively charged plasma membrane and the negative charge induced on the NP might not be enough to overcome the van der Waals attraction and the thermal fluctuations. In those cases, the surface effects will play a role in engulfing the NP and cause the NSA. Here we propose an electrostatically motivated design of NPs and also propose to cover the NPs with a lipid bilayer thus making them biomimetic. We show that doing so we will have a condition where we can resist NSA and increase the chances of specific adhesion. On the other hand, a bare NP in specific cases can be of use to deliver drugs to cells that have stiffer membranes—a very common case in cholesterol rich systems. We show that tuning the ionic environment can lead to adhesion of NPs on cells with stiffer membranes. We would discuss about the membrane surface charge and salt concentration phase-space where such situations are possible.

4:15 PM BM03.07.06
Nanoparticles Organization Controls Their Potency as Universal Glues for Polymer Interfaces

Nicola Molinarį2,1 and Stefano Angioletti-Uberti1,2; 1Imperial College London, London, United Kingdom; 2SEAS, Harvard University, Cambridge, Massachusetts, United States; 3Vancouver Prostate Centre, Vancouver, British Columbia, Canada.

In recent years, nanoparticles (NP) have been shown to have the potential to answer the centuries-old question of how to mechanically strengthen an interface between soft materials. The wide range of tunable parameters and properties make glues composed of nano-sized particles appealing to a variety of fields and applications. Despite the simplicity of the idea, the design of novel and universal adhesives based on NPs would benefit from a deeper understanding of the parameters that concur to determine the final adhesion strength.

Using a molecular-simulations-based approach we investigate the trends in, and the fundamental drivers of, the mechanical reinforcement of NP-reinforced interfaces between polymer melts. A coarse-grained model is adopted to describe both the polymer melt and the nanoparticles, and the systems are uni-axially strained and stress-strain curve constructed. We shine light on the interplay of three key properties: size of the NPs, strength of the NP-polymer interaction, and NP density. Our main result shows a non-monotonous strengthening of the mechanical response depending on the layering of the nanoparticles at the polymer interface, which we are able to identify and quantify thanks to the molecular resolution of the computer experiments. Our results confirm recent experimental speculations made to justify the existence of a maximum reinforcement at different NPs’ density. Furthermore, our findings are in good qualitative agreement with a simple analytical model of the melt adhesive energy that we adapted from the literature. The results from this investigation help disentangling the contributions to the strengthening of the interface and can be used as a guide to experimental design of nanoparticles-based adhesives.
Using kinetic Monte Carlo simulations of a simple coarse-grained model, we demonstrate that the self-assembly of oppositely charged nanoparticles is a promising approach to design efficient bulk heterojunction (BHJ) solar cells. Simulations are performed starting from a random configuration of oppositely charged nanoparticles in solution for a range of concentrations. Interconnected percolated morphologies form at high nanoparticle concentrations, when the aggregate growth ceases after certain time. If only Coulombic interactions are present, the observed morphologies have very high interfacial area but too small domain size, whereas optimum values of both the interfacial area and domain size are desired for BHJ. We therefore propose and establish that an additional hydrophobic attraction between nanoparticles of same type is desired to obtain the ideal BHJ morphology. We also discuss the effects of solvent dielectric constant and the size- and charge-asymmetry of nanoparticles, which may provide additional means to control the BHJ morphology.

References

SESSION BM03.08: Multiscale Modeling of Soft Materials and Interfaces VII
Session Chairs: Siddhartha Das and Meenakshi Dutt
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Back Bay B

8:15 AM BM03.08.01
The Molecular Sciences Software Institute Jessica Nash: The Molecular Sciences Software Institute, Virginia Tech, Blacksburg, Virginia, United States.

The Molecular Sciences Software Institute (MolSSI) is a nexus for research, education, and cooperation serving the worldwide community of computational molecular scientists - a broad field including of biomolecular simulation, quantum chemistry, and materials science. The Institute focuses on the software infrastructure, education, standards, and best-practices that are needed to enable the molecular science community to open new windows on the next generation of scientific Grand Challenges, ranging from the simulation of intrinsically disordered proteins associated with a range of diseases to the design of new catalysts vital to the global chemical industry and climate change. The MolSSI is working to enable the computational molecular sciences community to work together to leverage its diverse capabilities that will reduce or eliminate the gulf that currently delays by years the practical realization of theoretical innovations. Ultimately, the Institute will enable computational scientists to tackle problems that are orders of magnitude larger and more complex than those currently within our grasp. This lecture will provide an overview of the Institute’s activities, goals, and vision.

8:30 AM BM03.08.02
Hybrid Simulations of Gas Permeability of Carbon Nanotube Network Materials Alexey N. Volkov, Omid A. Ranjbar and Md Abu Horaira Banna; University of Alabama, Tuscaloosa, Alabama, United States.

Carbon nanotube (CNT) network material, including buckypaper, films, vertically aligned arrays, and aerogels, are microporous materials that can be used for gas separation, purification, and storage. Scaffolds of CNTs can be also used as reinforcement in nanocomposite materials, fabricated by chemical vapor deposition, chemical vapor infiltration, or atomic layer deposition of inorganic materials on networks of carbon nanotubes. Utilization of the potential of CNT materials in these applications requires understanding of relationship between structural properties of random CNT networks and their gas permeability. The goal of this work is to develop a hybrid computational approach for simulations of gas flows through networks of CNTs, as well as deposition from the gas phase on CNT surface. Our computational model includes (1) a mesoscopic model of CNT materials, (2) an atomistic-mesoscopic model of molecular motion through a random network of nanotubes, and (3) a gas kinetic model of gaseous flow through CNT materials. In the mesoscopic model, every nanotube is represented by a chain of cylindrical segments. This model is used to generate samples of CNT films and aerogels with well-defined structural properties, including bundle and porous size distributions, in dynamic simulations of self-assembly of dispersed nanotubes into networks of bundles. In the atomistic-mesoscopic model, gas flows through generated CNT networks are simulated using molecular dynamics-type approach based on
direct solution of equations of motion of individual gas molecules. In this model, gas molecules interact with a fixed CNT network through a specially designed mesoscopic force field that accounts for the absorption of molecules at the CNT surfaces. The gas kinetic model is used to study the diffusion process at larger length scales that are not accessible in mesoscopic simulations. In this case, the material sample is modelled by a regular two- or three-dimensional arrays of straight CNT bundles with structural parameters that resemble the average structural parameters of in silico generated material samples. The gas kinetic model is implemented in the form of the Direct Simulation Monte-Carlo method, where interaction of gas molecules with CNTs is described by the model of diffuse scattering. This hybrid approach allows us to study gas permeability of CNT materials and material deposition in a broad range of length scales, from nanometers to millimeters. The simulations of gas permeability are performed in a range of pressure from 1000 Pa to 1 MPa and for density of CNT films and aerogels varying from 0.01 g/cm³ to 0.4 g/cm³. The simulations reveal the strong effect of porous structure and density of the CNT materials on self-diffusivity of gases, effective permeability, and homogeneity of deposition of materials inside CNT networks. This work is supported by the NSF CAREER award CMMI-1554859 and NASA Early Stage Innovations program (project NNX16AD99G).

8:45 AM BM03.08.03
Bio-Inspired Structural Coloration Obtained from Micro-Kirigami Photonic Structures—A Computational Study
Amina Matt,1,2 Fabien Sorin1 and Craig Carter;1 Institute of Materials, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural coloration is a macroscopic phenomenon resulting from the interaction of light with microscopic, i.e. sub-wavelength, structure features. It is naturally observed in diverse applications, notably the vivid blue color of certain butterfly wings, due to a combination of elementary optical processes such as thin-film interference and diffraction gratings. Recently, the dynamical effects of such artificial structures under stresses and deformations have received a great deal of attention, hinting towards tunable bio-inspired materials. Simple photonic structures have succeeded in replicating bright and vivid structural colors observed in nature, while more complicated structures address the issue of angle-dependent reflectivity, achieving a stable color across wide viewing angles with the introduction of irregularity but at the cost of manufacturing complexity.

Here, we suggest and illustrate an alternative approach using micro-kirigami photonic crystals, which achieves bright and vivid colors across wide viewing angles and allows tunability of the obtained color. Micro-kirigami are three dimensional buckled structures, obtained from the deformation of two dimensional materials with patterned microscopic cuts. Recent advances in the field have extended such techniques to the obtention of mesoscale structures from micro/nanomembranes with complex shapes resulting upon buckling from the wide variety of cut patterns [1]. The demonstration of micro-kirigami structures could lead the way further in the miniaturization of such assemblies. Numerical calculations on periodic arrays of simple polymeric ribbons with parallel cuts and more complex micro-kirigami structures, exhibit the required design objectives. The introduction of irregularity, facilitated by the notch patterning, helps stabilize the obtained color across a range of viewing angles while tunability is inherent in the buckling process. The large parameter space is efficiently optimized using a combination of Finite Element and Finite Difference Time-Domain modelling to produce various structures with bright and stable colors.

References:

9:00 AM BM03.08.04
Using Simulations of Rare Earth Elements in Aqueous Solution, in Organic Acid Complexes and at Interfaces to Suggest Improved Processing Routes
Aaron Finney,1 Sebastien Lecet,2 Linghan Kong,1 Colin L. Freeman1, Stephen Stackhouse2 and John H. Harding;1 1Materials Science and Engineering, The University of Sheffield, Sheffield, United Kingdom; 2School of Earth and Environment, University of Leeds, Leeds, United Kingdom.

Researchers are searching for more efficient and environmentally-friendly extraction and processing methods. This is particularly true in the case of rare earth elements (REEs), the security of supply of which has been identified as ‘critical’. [1] New and sustainable extraction, processing and recycling methods for REEs are urgently needed. Since REEs can be mobilised and concentrated in hydrothermal fluids [2] and from easily leachable clays [3], fractionating REEs from solution offers a cheap way to increase their yield from deposits. Biologically active molecules, such as organic acids can accumulate specific groups of REEs from solution, [4] and so understanding their action should help to design better additives for materials processing. In the present study, density functional theory and classical force field molecular dynamics have been applied to investigate Nd³⁺, Gd³⁺ and Er³⁺ REEs in solution. The solvation structure, energetics and mobility of REEs compared well with experimental measurements. Ligand binding simulations were performed with common anions, e.g. chloride, and organic acids using advanced sampling methods—including Umbrella Sampling and metadynamics—and complex stability constants were calculated. Ligand exchange mechanisms and preferential organic acid binding to REEs were characterised by analysis of free energy surfaces. Our results show that ion size is crucial for the type of ligand exchange mechanism.

Simulations were performed to understand the sorption of REEs onto kaolinite clays where they are often found in nature. By studying reversible exchange reactions for REE binding at the kaolinite–solution interface we can quantify the strength of interaction and identify barriers to REE release for processing. Furthermore, the simulations, by spanning light to heavy REEs (Nd to Er), allow us to investigate why REE clay deposits are a good source for heavy REEs. Combined, these simulations at the nanoscopic level provide new information to aid in the design of REE processing methods from unconventional deposits in the search for economical, environmentally friendly ways to secure REE supply.


9:15 AM BM03.08.05
Active Micromechanics of Blood Clot Contraction
Alexander Alexeev; Georgia Institute of Technology, Atlanta, Georgia, United States.

Blood clotting is the final step in hemostasis resulting in the sealing of an injured blood vessel and the bleeding arrest. Clotting is a highly complex multi-stage and multi-scale process involving platelet activation, polymerization of fibrin networks, and development of a platelet-fibrin hemostatic plug in the damaged vessel that retracts to restore normal blood flow. Blood clotting disorders may result in a variety of life threatening conditions, including excessive bleeding, stroke, and heart attack. Understanding of the physics underlying the clotting process is critical for effective treatment of these and other blood disorders.

We develop an experimentally-informed mesoscopic model to obtain fundamental insights into the active process of blood clot contraction. We employ the model to examine how the clot size and microstructure evolve in time due to the fibrin-platelet interactions and to explore the role of the platelet activation pattern in the clot contraction kinetics. Our results pinpoint the critical role platelet heterogeneity plays in the effective clot contraction.

9:45 AM BREAK
A liquid drop on a soft elastic surface equilibrates by selecting a contact angle demonstrated by Neumann’s law. A hydrophobic drop itself deforms and causes a deformation in the substrate. Studying this phenomenon necessitates a combination of macroscopic and microscopic description of the contact angles. We develop new scaling theory to quantify the interplay of the two effects of drop wetting, i.e. the drop compressing the polymer brush and the polymer brush repelling the drop. Our scaling theory predicts that for a case of low stiffness the polymer compression is independent of stiffness and for high stiffness there is a monotonous decrease of polymer compression due to its interaction with the droplet. To verify this scaling theory, we perform molecular dynamics simulation of a 2-D LJ droplet wetting a flat polymer brush grafted plate. We simulate a case where the polymer brush is solvophobic. We find that the drop causes a deformation in the polymer brush that agrees quantitatively with the scaling theory we develop. We also find that the stiffness of the polymer brush influences the motion of the drop on the surface of the polymer grafted plate. Our theory, which is verified by MD simulations, predicts that the stiffness of polymer brush will cause the transition of the equilibrium contact angle from Young’s law (rigid limit) to Neumann’s law (soft limit). Our scaling theory will be useful in development of self-cleaning surfaces, and in the development of new nanofluidic devices.

The stress wave dissipation in sinusoidal patterned interfaces that were inspired by biological sutures was investigated using Finite Element (FE) analysis. Although man-made shock absorbers such as car bumpers or guardrails are designed to absorb impact energy through plastic deformation, biological materials do not use this strategy as severe plastic deformation may cause fatal damage. Biological materials use elastic and viscoelastic responses effectively to dampen impacts and absorb energy in an effort to maintain structural integrity. In nature, suture joints are found where two stiff components interlock each other and where dynamic impacts are needed to be dissipated. For example, in mammalian skulls, turtle shells, woodpecker beaks, and ammonoid shells, a wavy sinusoidal interface was observed. An idealized bar with a sutured interface (i.e., sutured bar) and an idealized bar with a flat interface (i.e., unsutured bar) were created and analyzed from two-dimensional FE analysis in Abaqus/Explicit under dynamic conditions. FE results from this study show that a sutured interface decreased the pressure 37% more than an unsutured interface did, which arose from wave scattering and energy dissipation via interaction between the viscoelastic material in the gap and sinusoidal boundaries. Wave scattering is an interaction of waves with a boundary resulting in wave reflection, transmission, or refraction. Since the compressive incidence impinged the sinusoidal interfaces, stress wave scattering resulted in converting compressive waves (S11) into flexural waves (S22) and shear waves (S12). This decreased both the peak pressure (attenuation) and wave speed (dispersion). Also, higher strain energy occurring at sutured interfaces brought energy loss within the viscoelastic gap. Several variables related to the suture interfaces for their influence on stress wave mitigation were also parameterized. The following seven parameters were examined in this study: 1. waviness of suture (ratio of suture height to suture period), 2. ratio of the suture height over the entire structure thickness, 3. gap thickness, 4. elastic modulus, 5. type of the boundary, 6. impact amplitude and 7. impact duration. The results of the parametric study revealed that wave attenuation increased by the following three factors: a higher ratio of the suture over the entire structure thickness, shorter impact duration, and a lower elastic modulus. Wave dispersion was caused by the following two factors: a higher ratio of the suture over the entire bar thickness and a lower elastic modulus. If the material properties and impact duration cannot be controlled in the engineering design of a structural component or system, then making the suture height greater becomes the only controllable design variable that matters. These findings can be applied to design structures that resist impact yet maintain structural integrity by optimizing sutures designs for impact scenarios.

Anti-agglomerant (AA) molecules are chemical inhibitors that help prevent the blockage of oil and gas transmission pipelines due to the aggregation of gas hydrate crystals. However, the effectiveness of these inhibitors is reduced at high water content, which makes it critical to design molecules tailored for water-dominated environments. Furthermore, salinity has been shown to improve the performance of most industrially-deployed anti-agglomerant molecules, including simple quaternary ammonium salts. Understanding the energetics and mechanisms of AA-hydrate interactions in aqueous water-dominated environments of varying salinity can help production chemists and flow assurance engineers design better AA molecules with reduced experimental trial- and-error. We used molecular dynamics simulations to examine the surface adsorption of a model anti-agglomerant (AA) molecule binding to a sII methane-propane hydrate in environments of different salinity. From our simulation data, we identified the preferred binding sites on the hydrate surface and characterized the equilibrium binding configurations. In addition, for a subset of these binding configurations, we calculated the standard binding free energy in different concentrations of brine using potential of mean force free energy calculations. We demonstrated that in higher salinity environments, the surface adsorption of the AAs is enhanced through two distinct mechanisms. First, the salt decreases the solubility of the AA in the solution, which increases the thermodynamic driving force for surface adsorption. Second, the salt ions create a negatively charged interfacial layer close to the hydrate surface that effectively solvates the cationic head of the AA molecule. Quantitatively, we found that the presence of 3.5 wt% and 10 wt% NaCl decreases the standard binding free energy of the long hydrocarbon tail binding configuration by 0.8 and 1.4 kcal/mol, decreases the standard binding free energy of the catonic head binding by 1.5 and 3.3 kcal/mol, and decreases the standard binding free energy of simultaneous head and tail binding by 1.9 and 4.3 kcal/mol, respectively.

In this talk, a “good”, a “bad” and an “ugly” stories will be telling around the behaviour of water at nanoscale solid-liquid interfaces. The understanding of water transport in nanoconfined configurations has revealed a prominent significance to predict the performance of biomedical phenomena and to guide the rational design of other engineering devices. First, molecular dynamics simulations are used to compute the self-diffusion coefficient of water within nanopores, around nanoparticles, carbon nanotubes and proteins. For almost 60 different cases, the diffusion coefficient is found to scale linearly with a dimensionless parameter which represents the confinement degree of the water molecules [1]. Such relationship, coupled with the “good” understanding of water transport behaviour, has shown to accurately predict the response of contrast agent for magnetic resonance imaging [1]. Later on, this relationship has been experimentally and
individually validated by the Oak Ridge National Laboratory, beyond biomedical applications [2].

Second, experiments and atomistic simulations are used to elucidate the non-trivial interplay between nanopore hydrophilicity and the overall water transport through zeolite crystals. A poor correspondence between the experiments and simulations has suggested the presence of a “bad” surface diffusion resistance at the interface between the zeolite porous matrix and water [3]. This suggests future experimental works to address these surface imperfections, as an essential prerequisite for improving water permeability of such membranes.

Finally, the complexity of water-solid interfaces will be fully revealed by “ugly” surfactants wrapping nanoparticle (NP) in aqueous solutions. Despite the large use of nanoparticle suspensions, tuning NP interactions and identifying desired NP assembly processes, in presence of surfactants, still represent a challenge for the design of nano-suspensions. We present a multiscale model for investigating nanoscale interfacial phenomena, stability, and aggregation of nanoparticles in aqueous solutions, including the dynamics of realistic surfactants [4]. In addition, the developed multiscale model is able to predict thermal properties of NP suspensions in reasonable agreement with the relevant experimental data from the literature, overcoming limitations of traditional theories obtained by coupling the DLVO (Debye-Hückel-Overbeek) theory with the kinetic theory of aggregation. Our results will enable the formulation of design rules for engineering NP aqueous suspensions suitable for a wide range of applications.


11:30 AM BM03.08.10
How Graphene Inclusions Increase Mechanical Toughness of Epoxy Resins Maxime Vassaux, Robert Sinclair, Robin Richardson, James Suter and Peter Coveney, University College London, London, United Kingdom.

Adding graphene to an epoxy matrix is experimentally known to improve its mechanical properties [1], most specifically enhancing toughness. The mechanisms responsible for this increase of dissipated energy at failure are far from clear [2]. By means of molecular dynamics simulations, we have explored the interactions between pure small graphene sheets (~10 Nm) and a crosslinked epoxy network, but the 2D nanoparticles do not appear to enhance the properties of the original polymer. Conversely, in the case of previously studied clay and linear polymer nanocomposites [3], the strength of the resulting nanocomposite is reduced and the interaction energy between the sheet and the network remains relatively low. The difference in behaviour is due to the high degree of crosslinking found in epoxy resins.

It appears that the benefits of adding graphene arise at larger scales, in particular at the continuum level. At the atomic scale the toughening is not observed because the single defect doesn’t induce diffuse cracking but merely the fatal crack. In order to investigate mechanisms emerging in the transition from atomistic to continuum descriptions, we have implemented a concurrent multiscale model based on the heterogeneous multiscale method [4]. Using this method we can in turn explore how an isotropic distribution of nanoparticles influence the fracture processes.

Furthermore, due to processing limitations, pure graphene is rarely employed in nanocomposites and is often replaced by oxidized graphene. Hence our proposed methodology is also applied to provide insights on the influences of bonded and non-bonded interactions between the polymer and the sheets on emerging mechanical properties.

We present a model to investigate the formation of two-length scale surface patterns in biological and synthetic anisotropic soft matter materials through the high order interaction of anisotropic interfacial tension and capillarity at their free surfaces. The unique pattern-formation mechanism emerging from the presented model is based on the interaction between lower and higher order anchoring modes. Analytical and numerical solutions are used to shed light on why and how simple anisotropic anchoring generates two-lengthscale wrinkles whose amplitudes are given in terms of anchoring coefficients. The novel finding is that the surface energy landscape with its maxima and minima can be imprinted onto the surface geometric landscape. Symmetry relations and scaling laws are used to provide the explicit relations between the anchoring constants and surface profile of the two length scale wrinkles. These new findings establish a new paradigm for characterizing surface wrinkling in biological liquid crystals, and inspire the design of novel functional surface structures.

Fuel cells have attracted enormous interest due to their high efficiency to convert chemical energy into electrical energy with very low emission. It can be used in stationary, portable, and transport power generation. It also reduces the CO₂ emission when compared with the conventional hydrocarbon fuels, therefore considered as environmentally clean energy source. Fuel cells are classified based on the electrolyte/electrode material and operating temperature range. Solid oxide electrolyte based fuel cells operate at high temperature and are the most efficient fuel cells. They can handle variety of fuels such as H₂, CO and various hydrocarbons CH₄. [1-2]

Perovskite is a family of compound having ABX₃ type crystal structure, where A and B are cations whereas X is an anion. They exhibit variety of properties due to ferroelectric, dielectric, pyroelectric, and piezoelectric behaviours. There is paramount interest to replace conventional Ni-YSZ cermet electrode with doped perovskite in solid oxide fuel cell [3]. SrTiO₃, a member of perovskite family, is a well-known band insulator. Doping of La significantly enhance the electronic conductivity of SrTiO₃. Experimentally, perovskite (LaTiO₃), pyrochlore oxide (La₂Ti₂O₇) and lanthanide (La₂TiO₅) phase can coexist at higher temperatures (∼1500 °C) [5]. Thus, it is essential to investigate the effect of doping in these phases of La and Sr. To satisfy the valency, O vacancy is created in pyrochlore oxide and lanthanide phase after Sr doping.

In the present study, we have used GGA-DFT to investigate the various La doped structures of SrTiO₃, Sr doped structures of La₂Ti₂O₇ and La₂TiO₅ and O vacancy in Sr doped structures of La₂Ti₂O₇ and La₂TiO₅. The concentration of dopant is varied between 0-100 ‰ considering all possible configurational structures. We have varied the concentration of dopant to establish its dependence on electronic energy, band gap, fermi level and formation enthalpy. We have also estimated the elastic properties of these phases. We observed a band insulator to a metallic behaviour by doping La in SrTiO₃. It became band insulator again after 100% La replacement in SrTiO₃. Such behaviour is not observed in the pyrochlore oxide phase. At the end, we shall report the preferential doping among these phases in a mixture where they all can coexist.

References

It is widely anticipated that many future materials will be engineered at the nano-scale, be comprised of dissimilar materials, and possess multi-functional properties and behaviour. In coming decades, in silico prediction and testing – that is, R&D performed on a computer – will be commonplace for these materials, in both academia and industry, given the increasing capabilities and diminishing costs of high performance computing.

We are working towards a multiscale computing environment to seamlessly simulate the properties of functional multicomponent 2-d materials. This is designed to encompass electronic, classical and coarse-grained molecular dynamics and continuum methods with correctly designed and implemented coupling between the levels. We aim to produce high fidelity and actionable predictions, subjected to full verification, validation and uncertainty quantification. Ultimately, the aim is to construct between the key properties of 2-d and other nanocomposites that are linked to the underlying chemical building blocks. [1,2,3]

References

Membraneless organelles are aggregates of disordered proteins that form spontaneously to promote specific cellular functions in vivo. The possibility of
synthesizing membraneless organelles out of cells will therefore enable fabrication of protein-based materials with functions inherent to biological matter. Scattered copolymers contain various reactants of both amphiphilic and solvophilic groups, they are expected to function in non-biological media similarly to a set of disordered proteins in membraneless organelles. Interestingly, the internal environment of these organelles has been noted to behave more like an organic solvent than like water. Therefore, an adsorbed layer of random copolymers that mimics the function of disordered proteins could in principle protect and enhance the proteins’ enzymatic activity even in organic solvents, which are ideal when the products and/or the reactants have limited solubility in aqueous media. Here we demonstrate via multiscale simulations that random copolymers efficiently incorporate proteins into different solvents with the potential to optimize their enzymatic activity. We investigate the key factors that govern the ability of random copolymers to encapsulate proteins including the adsorption energy, copolymer average composition and solvent selectivity. The adsorbed polymer chains have remarkably similar sequences, indicating that the proteins are able to select certain sequences that best reduce their exposure to the solvent. We also find that the protein surface coverage decreases when the fluctuation in the average distance between the protein adsorption sites increases. The results herein set the stage for computational design of random copolymers for stabilizing and delivering proteins across multiple media.

3:45 PM BM03.09.06
Miscibility and Nanoparticle Diffusion in Ionic Nanocomposites Argyrios Karatrantos1, Yao Koutsawa2, Philippe Dubois3, Nigel Clarke4 and Martin Kröger5; 1Physics, Univ of Sheffield, Sheffield, United Kingdom; 2Materials, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg; 3University of Mons, Mons, Belgium; 4Materials, ETH Zürich, Zürich, Switzerland.

We investigate the effect of various spherical nanoparticles on dispersion, chain dimensions and entanglements in ionic nanocomposites for dilute and high nanoparticle loading, by means of molecular dynamics simulations. The nanoparticle dispersion can be achieved, due to the presence of ionic bonding, in oligomer matrices, in contrast to conventional nanocomposites where the electrostatic interaction is absent. We show that the overall configuration, as characterized by the radius of gyration, of ionic oligomer chains is unperturbed by the presence of charged nanoparticles. In addition, nanoparticle diffusion is reduced due to the electrostatic interaction and deviates from the predictions of the Stokes Einstein relation.

4:00 PM BM03.09.07
High-Speed Contact Mechanics Between Amorphous Carbon Nanoparticles Weifu Sun and Pengwan Chen; Beijing Institute of Technology, Beijing, China.

The contact mechanics plays an important role in describing behaviours of granular matter, such as packing, flow of particles. With the development of precision processing, the high-speed motions (including translation, rolling, sliding) between nanosized building blocks are often experienced in nanodevices, such as nano-electro-mechanical system (NEMS). However, the contact behaviours between amorphous nanoparticles have seldom been explored, in particular, whether the contact models still hold or not at the nanoscale remains unknown. In this work, the dynamic behaviours between amorphous carbon nanoparticles will be studied using molecular dynamics simulations during the head-on impact and the validity of conventional continuum contact models will be tested.

4:15 PM BM03.09.08
A Coarse-Grained Molecular Dynamics Model of Single-Stranded DNA-Functionalized, Shaped Nanoparticles Benjamin E. Swedlow1, Fang Lu2, Matthew Spellings3, Julia Dhemuchade4, Oleg Gang5,6, and Sharon C. Glotzer3,4; 1Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Center for Functional Nanomaterials, Energy & Photon Sciences Directorate, Brookhaven National Laboratory, Upton, New York, United States; 3Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 4Biointerfaces Institute, University of Michigan, Ann Arbor, Michigan, United States; 5Chemical Engineering, Columbia University, New York, New York, United States; 6Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States.

Typical materials science follows a top-down approach: processing conditions influence the formed structure, dictating the key material properties. Conventional processing often limits fine control over structure-property relationships. However, advances in nanotechnology, such as DNA nanoparticle (NP) functionalization, enable a bottom-up approach for materials design. By coating NP surfaces with DNA strands that terminate in unpaired bases, specifically engineered DNA sequencing can programmatically enforce NP binding. Yet this enthalpic basis alone is insufficient to explain all aspects of NP self-assembly: entropic parameters such as particle size and shape, as well as DNA flexibility and length, all contribute to the observed equilibrium structures. Computer simulations of these systems allow us to screen candidate building blocks and probe the effects of interactions between nanoparticles more easily and efficiently via computational rather than experimental exploration. Previously, a coarse-grained molecular dynamics model using the Discrete Element Method implemented in HOOMD-blue was used to simulate structures assembled in one-component double-stranded DNA (dsDNA) NP systems. Here we expand this implementation to replicate experimental results for assembly of two-component flexible single-stranded DNA (ssDNA) NPs and to predict the assembly behavior of new systems of binary shapes, where we find unique phase behavior. Our experimental studies on binary mixtures of DNA coated shaped NP are in agreement with computational results. We find that core NP shape and ssDNA flexibility are critical to self-assembly in these systems.

4:30 PM BM03.09.09
Stable Frank-Kasper Phases of Self-Assembled, Soft Matter Spheres Abhiram Reddy1, Michael Buckley2, Akash Arora1, Frank Bates1, Kevin Dorfman1 and Gregory Grason; 1University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; 2University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Self-assembly of soft-molecules into spherical domains adopting Frank Kasper lattices have been observed in a variety of systems, including liquid-crystalline dendrimers, charged surfactants and block copolymers (BCPs). The formation of these complex phases has been previously attributed to optimal self-assembly of soft-molecules into spherical domains adopting Frank-Kasper lattices have been observed in a variety of systems, including liquid-crystalline dendrimers, charged surfactants and block copolymers (BCPs). The formation of these complex phases has been previously attributed to optimal assembly and/or volume asymmetry (polydispersity or Voronoi partition of cells) leading to the question: What selects volume asymmetry in these assemblies and how does this impact surface area of the partitions? We will address these in the context of BCPs by drawing comparisons between Diblock Foam Model (DFM) that captures the Polyhedral Interface Limit (PIL) and SCFT for diblock melts. DFM describes thermodynamics of sphere phases in terms of competing geometric quantities: surface area and dimensionless stretching (or radius of gyration) of cellular volumes enclosing domains. DFM correctly predicts not only which of these lattices is favored in equilibrium (the sigma phase) but also their relative ranking in terms of entropy and enthalpy, and their equilibrium volume distribution among spheres. Comparison to SCFT results show that increasing conformational asymmetry between blocks drives a transition to radial-chain stretching and towards the PIL described by DFM calculations. We further show that the degree of polyhedral “warping” of the spherical domains is directly correlated with the dimensionless stretching-moment of distinct cells.

4:30 PM BM03.09.10
A Computational Study on Thermo-Mechanical Characterization of Carbon Nanotube Reinforced Natural Rubber Manish Dhawan and Raj
A computational study based on molecular dynamics simulation technique has been used to predict the mechanical and thermal behavior of carbon nanotube (CNT) reinforced natural rubber (NR) composites. A single-walled 5,5 armchair type CNT has been used for this purpose. In this study, a comparison has been made between pristine and functionalized CNTs. The functionalization groups used in this study were carboxylic (COOH), ester (COOCH3) and hydroxyl (OH). The studies show the improvement in elastic properties of developed composites in the presence of functionalization group. In addition, the effect of volume fraction and 1-25% addition of functionalization group has been studied. The obtained simulation results show the better load-transfer capacity in developed polymer system and improved elastic modulus. Thermal properties of developed composite systems were studied by non-equilibrium molecular dynamics method (NEMD). The addition of functionalized CNTs shows enhanced mechanical and thermal properties.

**SYMPOSIUM BM04**

Biomaterials for Regenerative Engineering  
November 27 - November 29, 2018

**Symposium Organizers**  
Josephine Allen, University of Florida  
Guillermo Ameer, Northwestern University  
Gulden Camci-Unal, University of Massachusetts Lowell  
Junji Fukuda, Yokohama National University

**Symposium Support**  
Acta Biomaterialia (Acta Materialia Inc.) | Elsevier  
Acuitive Technologies, Inc.  
The Center for Advanced Regenerative Engineering (CARE), Northwestern University

* Invited Paper

**SESSION BM04.01: Biomaterials for Regeneration of Tissues I**  
Session Chairs: Guillermo Ameer and Gulden Camci-Unal  
Tuesday Morning, November 27, 2018  
Sheraton, 2nd Floor, Independence West

8:00 AM *BM04.01.01  
**Bioresorbable Electronic Materials for Wireless Neuroregenerative Therapy** John A. Rogers; Northwestern University, Evanston, Illinois, United States.

Peripheral nerve injuries commonly result in lifelong disability. Even the most advanced surgical procedures and pharmaceutical treatments have limited ability to improve clinical outcomes. Intraoperative electrical stimulation performed at the site of nerve repair is a well-established treatment that can accelerate and improve overall rates of functional recovery. Clinical utilization of electrical stimulation has, however, been limited to the intraoperative period, wherein injured tissue is physically accessible. This talk describes bioresorbable electronic materials and devices that allow for non-pharmacologic neuroregenerative therapy via prolonged post-operative electrical stimulation throughout the healing process, enabling substantially improved outcomes in nerve regeneration and functional recovery compared to the existing intraoperative mode. An essential characteristic of these implantable systems is that they undergo complete dissolution and elimination from the body via natural biochemical processes over timescales matched to operational requirements and without adverse biological effects. The result thereby eliminates the need for secondary surgical extraction and associated risks to the patient and to site of the nerve repair. This type of bioresorbable technology represents a new vehicle for the delivery of non-pharmacologic bioelectric and neuroregenerative therapies in a variety of clinical settings, and a significant paradigm shift in the treatment of critical nerve injuries with limited potential for sensorimotor recovery.

8:30 AM *BM04.01.02  
**Elastomeric Polymers for Microfabrication of Organs-on-a-Chip** Milica Radisic; Univ of Toronto, Toronto, Ontario, Canada.

Recent advances in human pluripotent stem cell (hPSC) biology enable derivation of essentially any cell type in the human body. However, limitations related to cell maturation, vascularization, cellular fidelity and inter-organ communication still remain. Here, biological wire (Biowire) technology will be described, developed to specifically enhance maturation levels of hPSC based cardiac tissues, by controlling tissue geometry and electrical field simulation regime (Nunes et al Nature Methods 2013). We will describe new applications of the Biowire technology in engineering a specifically atrial and specifically ventricular cardiac tissues, safety testing of small molecule kinase inhibitors, potential new cancer drugs, and modelling of left ventricular hypertrophy using patient derived cells.

For probing of more complex physiological questions, dependent on the flow of culture media or blood, incorporation of vasculature is required, most commonly performed in organ-on-a-chip devices. Current organ-on-a-chip devices are limited by the presence of non-physiological materials such as glass and drug-absorbing PDMS as well as the necessity for specialized equipment such as vacuum lines and fluid pumps that inherently limit their throughput.
An overview of two new technologies, AngioChip (Zhang et al Nature Materials 2016) and inVADE (Lai et al Advanced Functional Materials 2017) will be presented, that overcome the noted limitations and enable engineering of vascularized liver, vascularized heart tissues and studies of cancer metastasis. These platforms enable facile operation and imaging in a set-up resembling a 96-well plate. Using polymer engineering, we were able to marry two seemingly opposing criteria in these platforms, permeability and mechanical stability, to engineer vasculature suitable for biological discovery and direct surgical anastomosis to the host vasculature. Finally, to enable minimally invasive delivery of engineered tissues into the body, a new shape-memory scaffold was developed that enables delivery of fully functional tissues on the heart, liver and aorta through a keyhole surgery (Montgomery et al Nature Materials 2017).

9:00 AM BM04.01.03

Acellular PCL Scaffolds Laden with Fibroblast/Endothelial Cell-Derived Extracellular Matrix for Bone Regeneration Radoslaw Junka and Xiaojun Yu; Stevens Institute of Technology, Hoboken, New Jersey, United States.

Biological scaffolds derived from decellularized tissues function as tissue remodeling templates during bone regeneration. This isolated extracellular matrix (ECM) provides a structural framework that regulates adherence, migration, proliferation, and differentiation of bone residing cells and those in surrounding tissues. Nonetheless, decellularization protocols, like the ones used in isolation of demineralized bone matrix (DBM), require use of acids and other harsh chemicals that render osteoinductive proteins in DBM denatured. Also, lack of vascular cues in DBM presents another impediment to bone healing, and results in non-unions from poor vascularization of the regenerating tissue. To address these limitations, we used tissue engineering approach and tested the regenerative capacity of decellularized ECMs derived from sequential cultures of fibroblasts and endothelial cells grown on polycaprolactone (PCL) fibers. We hypothesized that this vascular ECM would enhance osteoblast proliferation, differentiation, and matrix deposition in vitro. The bottom-up strategy eliminated competition between cell types with varying proliferation rates and allowed for ECM remodeling. ECMs from decellularized cultures were evaluated via methylene and Coomassie blue stains, and their protein and DNA content was quantified. Staining also revealed that endothelial cells grown on fibroblast ECM (Fibro/Endo) form networks resembling capillaries. These structures stained positively for endothelial markers CD31 and vWF. Analysis of SEM images indicated changes in morphology and preferential attachment of endothelial cells to PCL fibers laden with fibroblast ECM. Osteoblasts grown on this Fibro/Endo ECM yielded higher proliferation rates at each time point during 28 day culture. Significantly higher ALP activity in these cultures suggest better capacity of osteoblasts to form bone tissue and higher degree of differentiation. The color area and intensity of Alizarin Red staining of Fibro/Endo cultures revealed uniform and greater calcium deposits than in cultures with only single type of ECM. Relative expression of osteoclacin and osteopontin between culture conditions was compared via immunostaining. Successive culture/decellularization cycles enriched the ECM product, which in turn significantly enhanced proliferation and differentiation of osteoblasts in vitro. Thus, addition of vascular ECM cues to biological scaffolds might lead to improved bone healing rate in vivo. The use of this hybrid ECM can expanded to other combinations with additional cell types, which might further improve regeneration of tissues.

Acknowledgements:

The work was partly supported by the Assistant Secretary of Defense for Health Affairs, through the Peer Reviewed Medical Research Program under Award No. W81XWH-16-1-0132, and the National Institute of Biomedical Imaging and Bioengineering of the National Institutes of Health (award number R01EB020640).

9:15 AM BM04.01.04

Influence of Cerium Oxide Nanoparticles on the Properties of Gelatin-Alginate Scaffold for Bone Tissue Engineering Shiv D. Purohit1, Rakesh Bhaskar2, Hemant Singh1, Indu Yadav1, Mukesh K. Gupta2 and Narayan C. Mishra1; 1Polymer and Process Engineering, Indian Institute of Technology Roorkee, Roorkee, India; 2Biotechnology and Medical Engineering, National Institute of Technology Rourkela, Rourkela, India.

It has been observed that polymeric scaffolds loaded with cerium oxide nanoparticles (CeONP) hold great potential for tissue engineering applications. In this study, nanocomposite scaffolds (NCS) have been fabricated by freeze drying of aqueous mixture of the CeONP, gelatin and alginate, with a goal of obtaining CeONP incorporated porous biocompatible scaffolds for bone tissue engineering applications. Further, influence of varying concentration of CeONP, on the scaffold properties, was evaluated in terms of mechanical, biodegradation, cell attachment and cell proliferation properties of the scaffold. Field emission scanning electron microscopy images of the NCS revealed presence of interconnected pores. The NCS was highly porous with porosity ranging from 82-89%. The CeONP covered the surface of the composite matrix and made the surface of the NCS rougher. Compressive strength of the NCS was found to be significantly higher than the gelatin/alginate scaffolds which are not having any CeONP. This may be due to the CeONP present in the NCS. High % swelling (~640%) of the NCS indicates its hydrophilicity. Slow biodegradation (~26% in 30 days) indicates its suitability for bone regeneration. In vitro cell culture studies, by seeding MG-63 osteoblast-like cells on NCS and performing cell attachment studies, MTT assay, Environmental Scanning Electron Microscopy of cell-scaffold construct and Giensta staining, showed an enhancement in cell attachment, proliferation and adhesion as compared to the gelatin/alginate scaffold which are not having any CeONP: this indicates the influence of the CeONP of such enhancement in the scaffold properties which, in turn, can enhance bone regeneration process ultimately. Thus, it could be stated that the incorporation of CeONP to gelatin-algininate, or in other words, the CeONP incorporated composite scaffold has vital importance for applications in bone tissue-engineering in future regenerative therapies.

9:30 AM OPEN DISCUSSION

9:45 AM BM04.01.06

In Vivo Bioreosorbability and Tissue Reaction of Hydroxyapatite/Collagen–(3-Glycidoxypropyl)Trimethoxysilane Injectable Bone Paste Taira Sato1, Yuki Shroska2, Sho Oshimai3, Yoshishia Koyama2, Mamoru Aizawa2 and Masanori Kikuchi4; 1Department of Applied Chemistry, Meiji University, Kawasaki, Japan; 2Department of Materials Science, Kyushu Institute of Technology, Kitakyushu, Japan; 3National Institute for Materials Science, Tsukuba, Japan; 4Major in Industrial Science, Ibaraki University, Hitachi, Japan.

Injectable self-setting bone pastes are a user-friendly bone void filler in comparison to dense, porous and granular ones, because pastes are applied for minimal invasive surgeries and are shaped easily to fit bone defects. However, surgeons desire biodegradable bone paste strongly because present bone pastes are very slow biodegradable and brittle and a risk to be a cause of secondary bone fracture. Presently available biodegradable bone void fillers in Japan are β-tricalcium phosphates, carbonated apatite and hydroxyapatite/collagen bone-like nanocomposite (HAp/Col). The HAp/Col demonstrates good viscoelasticity and excellent bioreosorbability with bone formation ability by incorporating into bone remodeling process. We focused on the HAp/Col as a base material for novel injectable bone cement. In the previous report, the HAp/Col biodegradable self-setting pastes were prepared by a mixing of the HAp/Col powder and aqueous solution of (3-glycidoxypropyl)trimethoxysilane (GPTMS), which is a setting agent by cross-linking of collagen and forming siloxane network by self-condensation. The HAp/Col-GPTMS bone pastes implanted into porcine tibia were resorbed and replaced by newly formed bone within 12 weeks. In this study, the pastes were implanted in the rat tibia and the biological tissue reaction and the absorption behavior of the pastes up to 4 weeks after transplantation were investigated in detail.
The HAp/Col (80/20 in mass ratio) powder at 100 μm or less in particle size was prepared by ball-milling of the HAp/Col compact prepared by a uniaxial pressing after synthesis by the melt-casting/crystallization method. The de novo bone formation when seeded with adipose-derived stromal/stem cells and stromal vascular fraction (SVF) and implanted in murine critical-sized cranial defects. Murine models of critical-sized bone defects due to disease, degeneration, trauma, and aging, bone loss occurs in the body. Although there have been remarkable improvements in development of functional bone scaffolds, it remains difficult to fabricate porous and biocompatible constructs in physiologically relevant sizes (cm-scale). Herein we developed biomineralized origami-inspired paper scaffolds in three-dimensions (3D). To our knowledge, this work is the first demonstration that paper can be used as a 3D construct to induce template-guided mineralization by osteoblasts. In this work, we used the principles of origami to fabricate free-standing paper scaffolds in cm-scale. Because paper is an extremely flexible material that can easily be cut, creased, and folded to form 3D structures, the scaffolds were easily fabricated in a variety of different geometries. This feature can potentially be useful in generation of constructs for patient-specific applications especially for patients who have defects of irregular sizes and shapes. After sterilizing the constructs, they were seeded with osteoblasts in a collagen matrix. The samples were cultured up to 21 days and mineralization was monitored using alizarin red S staining and X-ray micro-computed tomography. We have demonstrated the osteoinductive properties of PCL-DCB scaffolds by assessing the de novo bone formation when seeded with adipose-derived stromal/stem cells and stromal vascular fraction (SVF) and implanted in murine critical-sized cranial defects. Murine models of critical-sized bone defects due to disease, degeneration, trauma, and aging, bone loss occurs in the body. Although there have been remarkable improvements in development of functional bone scaffolds, it remains difficult to fabricate porous and biocompatible constructs in physiologically relevant sizes (cm-scale). Herein we developed biomineralized origami-inspired paper scaffolds in three-dimensions (3D). To our knowledge, this work is the first demonstration that paper can be used as a 3D construct to induce template-guided mineralization by osteoblasts. In this work, we used the principles of origami to fabricate free-standing paper scaffolds in cm-scale. Because paper is an extremely flexible material that can easily be cut, creased, and folded to form 3D structures, the scaffolds were easily fabricated in a variety of different geometries. This feature can potentially be useful in generation of constructs for patient-specific applications especially for patients who have defects of irregular sizes and shapes. After sterilizing the constructs, they were seeded with osteoblasts in a collagen matrix. The samples were cultured up to 21 days and mineralization was observed for the paste with 10-2% GPTMS, it is expected to be substituted completely with newly formed bone deduced from the results of pig test. In addition, the results of histological observations will be presented on a podium.
Cryogenically Electrosprun Fibrous Sponge Scaffolds as Stromal Extracellular Matrix for Salivary Gland Regeneration

A Multicellular Tissue Model for Vascularized Osteogenesis

A close correlation between vascularization and bone formation in endochondral ossification as maximum extent of bone formation follows maximum levels of VEGF expression. This suggests that osteogenesis and vascularization are coupled by spatiotemporal regulation of paracrine signaling in which the invading vascular endothelial cells secrete osteogenic morphogens to stimulate cell differentiation and bone formation. The objective of this work was to develop a tissue model to investigate the effect of spatial patterning of mesenchymal stem cells and endothelial progenitor cells and spatiotemporal delivery of osteogenic and vasogenic morphogens on vascularized osteogenesis in a 3D culture system. To achieve the objective, a 3D co-culture system was developed consisting of a cell-adhesive, degradable polyethylene glycol matrix with gelatin methacrylate-filled microchannels for patterning of human mesenchymal stem cells (MSC) and endothelial progenitor cells (EPC). MSC were encapsulated in the matrix and a combination of MSC+EPC were encapsulated in the microchannels. Self-assembled polyethylene glycol nanogels (PEG NG) were synthesized for timed delivery of BMP-2 and VEGF morphogens. The osteogenic BMP-2 was conjugated to 1-day release NG and added to the MSC-laden matrix. The vascularogenic VEGF was conjugated to 5-day release NG and added to the MSC+EPC-laden microchannels. The 3D tissue model was cultured in osteogenic-vasogenic medium. At each time point, the tissue model was evaluated for osteogenesis and vasogenesis by biochemical, mRNA, and protein analysis.

Groups included MSC/EPC patterned tissue model without BMP-2/VEGF (None), with dissolved BMP-2/VEGF, and with BMP2-NG/VEGF-NG. Osteogenic control group was MSC encapsulated in degradable PEG gel with BMP-2 or BMP2-NG. Vasogenic control group was MSC+EPC encapsulated in gelatin methacrylate with VEGF or VEGF-NG. Based on the results, the extent of vascularized osteogenesis was higher in patterned constructs compared to un-patterned controls. Further, time-release of VEGF and BMP-2 in the patterned cellular constructs significantly enhanced the extent of vascularized osteogenesis compared to the direct addition of VEGF and BMP-2. We further discovered that the spatial patterning of MSC and EPC and the spatiotemporal of BMP-2 and VEGF sharply increased the expression of vasogenic factors bFGF and PDGF and osteogenic factor TGF-β in the tissue constructs. The results suggest that osteogenesis and vasogenesis are coupled by localized secretion of paracrine signaling factors during bone formation.
Dentinogenic Peptide Hydrogels for Pulpal Regeneration

Endodontic root canal therapy is one of the most common clinical procedures to treat infected dental pulp. This non-regenerative treatment removes the dental pulp as well as the vascular and nerve tissues and replaces them with elastomeric composites, such as gutta-percha. The resulting tooth is devitalized and fragile, which may require additional intervention within 3 years. Our self-assembling peptide hydrogels (SAPHs) aim to establish a regenerative solution to this problem by replacing the inert material used in endodontic therapy with materials that promote dental pulp regeneration. In this work, we have used solid-phase peptide synthesis to create dentinogenic self-assembling peptides that form hydrogels under physiological pH and ionic strength.

Physical characterization of these hydrogels, using circular dichroism, atomic force microscopy, and scanning electron microscopy, revealed that our peptides formed β sheet nanofibers, which in turn are non-covalently crosslinked to create robust hydrogels. We demonstrated the thixotropic nature of these hydrogels through oscillatory rheometry, and further verified their injectability and in situ reassembly into strong hydrogels through in vivo subcutaneous injection studies. In both in vitro and in vivo studies, we were able to show the efficacy of our SAPHs to support and promote the proliferation of dental pulp stem cells. Additionally, in our in vivo studies we observed the infiltration of blood vessels into our hydrogels, suggesting their ability to provide a suitable environment for dental pulp regeneration. The goal of these SAPHs is to provide an improved regenerative alternative to conventional endodontic therapy.

2:15 PM BM04.02.03
3D Self-Foldable Silk-Based Nanoladder Scaffold for Directional Axonal Outgrowth and Functional Regeneration After Spinal Cord Injuries

Neurons are naturally encompassed by a network in a highly aligned manner. After spinal cord injury (SCI) in the central nerve system (CNS), the organized extracellular matrix (ECM) within the spinal cord is profoundly disrupted, which causes axonal regeneration over injury sites challenging due to the lack of orientational guidance. Because of the nature of the spinal cord, bioengineered scaffold in a three-dimensional (3D) format is of great importance for the functional recoveries after injuries. Herein, we report a self-foldable 3D silk-based nanoladder scaffold to mimic the hierarchic structure of the spinal cord with no spatial constraints, comparable mechanical properties, controllable biodegradation rate and sustainable growth factor release. In this study, we fabricated a silk-based nanoladder film with the integration of two scales, micron-meter fibers, and nanoprotrusions. We have proved that micron-meter fibers can provide directional guidance to the regenerated axons, while nanoscale protrusions can serve as mechanical cues to stimulate neurite outgrowth and synapse formation. We further developed the 3D self-foldable nanoladder by coupling the hydrophobic silk nanoladder film with a hydrophilic thermal expanding hydrogel layer. By controlling the biodegradation rate of the 3D nanoladder, a sustainable release of growth factors embedded in the silk film was achieved to trigger the axonal regeneration after injuries. We further applied organotypic spinal cord tissue slices as the ex vivo injured model to demonstrate an enhanced axonal regeneration and functional connection between two slices placed in a distance of 2-3 mm. In all, we suggest that 3D silk-based nanoladder can serve as a grafting bridge to guide axonal regenerations to desired targets for functional reconnections after SCI.

2:30 PM BREAK

3:00 PM *BM04.02.04
Citrate Chemistry and Biology for Orthopedic Engineering

Citric acid, historically known as an intermediate in the Krebs cycle, is a multifunctional, nontoxic, readily available, and inexpensive cornerstone monomer used in the design of citrate-based biomaterials. In addition to the convenient citrate chemistry for the synthesis of a number of versatile polymers that may be elastomeric, mechanically strong and tough, injectable, photocrosslinkable, tissue adhesive, bioimaging/biosensing-enabled, and/or electrically conductive, citric acid also presents inherent anti-bacterial, anti-clotting, angiogenic characteristics and modulates cellular energy levels leading to facilitated stem cell differentiation, which make citrate biomaterials ideal for a number of medical applications. We have attained a comprehensive new understanding of the citrate roles on osteo-phenotype progression and identified a new mechanism pertaining to the metabolic regulation of citrate to elevate cell energy status for bone formation, referred to as citrate metabolic regulation. This previously unexplored citrate metabolic regulation has allowed us to design new biomaterials to meet the dynamic biological, biochemical, and biophysical needs in bone regeneration. In this presentation, we methodology for the design of biomimetic citrate biomaterials and their applications in regenerative engineering, drug delivery, bioimaging and biosensing will be discussed with a focus on orthopedic engineering.

3:30 PM *BM04.02.05
Multifunctional Biomaterials Containing Amino Acid Based Segments for Tissue Regeneration and Efficient Transfection of Primary Human Cells

Modern medicine requires biomaterials combining multiple functions such as degradability, stimuli-responsivity, cell instructivity or carrier capabilities for bioactive molecules. Complex polymer network architectures are a versatile molecular design for integrating different functions in one material system. Such networks often contain physical netpoints for adjusting mechanical properties or implementing stimuli-sensitivities. For this purpose macromolecules are potentially equipped with chain segments being able to exhibit strong physical interactions. Here amino acid based oligomeric segments are built either from L-lysine disocyanate or from morpholinoacids. Pure oligodepsipeptides, alternating copolymers of an α-amino acid and an α-hydroxy acid, have been selected as a hydrophobic block in segmented polymers in order to achieve strong physical interactions for stabilizing nanoparticles during their formation [1] or for providing high formstability to thermoplastic elastomers. Degradable triblock copolymers having a central oligodepsipeptide block have shown great potential as transfection agent combining high transfection capability with low toxicity [1]. Depsipeptide based multiblock copolymers are suitable for creating soft actuators with excellent performance in shape stability and reversible strain [2]. L-lysine-based oligoacids are incorporated as dangling side chains or crosslinking segments in gelatine based polymer networks. In architectural gelatin-based hydrogels (ArcGel) the local elastic modulus was adjustable independently from the macroscopic compression modulus by the molar ratio of L-lysine disocyanate to freely available amino groups in gelatin. The dynamic alteration of cellular microenvironments accommodating mesenchymal stem cells is studied during degradation. Along with the degradation-related pore growth cell migration and differentiation were followed. The potential of ArcGels for a purely material-induced regeneration was demonstrated in a critical femur defect [3] and a cranial defect [4] in rat models.
properties of the resulting 3D PLA/apatite composite scaffolds are then determined. Second, GelMA photopolymer is synthesized from porcine gelatin and potassium phosphate dibasic to form a precipitate that is mineralized into apatite at physiological pH. The architectural, microstructural, and mechanical

**References**


**4:00 PM BM04.02.06**

**Nanofibrous Scaffolds with Both MSC-Laden Cell Fibers and Growth Factor-Loaded Fibers for Tissue Regeneration**

Huihua Li, Haoran Sun and Min Wang; Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong.

Tissue engineering scaffolds with biomimetic nanofibrous topography can facilitate the regeneration of tendon and ligament which are fibrous connective tissues composed of specific fibroblasts and aligned nanofibrous extracellular matrix (ECM). As a versatile and effective method to produce nanofibers, electrospinning has been extensively investigated to make nanofibrous scaffolds. Apart from physical cues, biological signaling molecules such as growth factors, are also often used in tissue engineering. Meanwhile, using mesenchymal stem cells (MSCs) for tissue regeneration has many advantages. Among various types of growth factors, basic fibroblast growth factor (bFGF) is a typical biomolecule that upregulate gene expression of tendon and ligament-specific ECM proteins and hence promote the proliferation and differentiation of MSCs toward fibroblasts. Therefore, the combination of incorporating MSCs in a scaffold and having controlled delivery of bFGF in the scaffold should provide a good strategy for tendon/ligament regeneration. MSCs can be encapsulated in fibers via cell electrospinning developed in our group and the fibers can be aligned parallelly in scaffolds to simulate the cell distribution in native tendon/ligament tissue. In this study, multilayered scaffolds consisting of cell fibers and bFGF-containing nanofibrous membranes were fabricated. Bone marrow-derived MSCs were encapsulated in cell fibers while bFGF was incorporated in nanofibrous membranes for its controlled delivery to promote MSC differentiation. Medical grade poly(lactic-co-glycolic acid) (PLGA) was employed for fabricating bFGF-containing fibers in scaffolds. Cell fibers were made from Na-alginate solutions and contained MSCs. The Na-alginate was crosslinked into Ca-alginate using a CaCl2 solution. In in vitro experiments, the constructs with bFGF-containing PLGA nanofibers and MSC-laden cell fibers were cultured for up to 21 days. In day 1, a sodium citrate solution was dripped onto scaffolds to disrupt the crosslinked Ca-alginate cell fibers to release to MSCs. The viability and proliferation of MSCs were studied using LIVE/DEAD assay and MTT assay. On Day 1 and Day 3, the cell viability was all above 90%. MSCs proliferated well during the culture period up to 21 days. The MSCs in scaffolds with encapsulated bFGF proliferated faster than the control group and elongated notably, indicating that MSCs cultured under bFGF release had fibroblasts-like differentiation. The morphology and structure of scaffolds before and after different culture periods were investigated using SEM. Mechanical properties of the constructs were also examined.

**4:15 PM BM04.02.07**

**Growth Factor-Laden Microparticles Incorporated into Polyactic Acid/Apatite Composite Scaffolds for Tooth Regeneration**


Growth factors such as bone morphogenetic protein 2 (BMP2) have been found to stimulate the odontogenic differentiation of mesenchymal stem cells (MSCs) of the dental pulp. This is particularly important for the regeneration of the dentin tissue of the tooth. However, the short half-life and poor distribution of growth factors like BMP2 may present problems with high cost and inconvenience due to the need for repeated dose injections to sustain tissue regeneration and healing. Consequently, strategies that combine slow, sustained release of BMP2 with three dimensional (3D) bioactive scaffolds are important for the differentiation of the MSCs into the odontoblast lineage to accelerate dentinogenesis. Herein, we present the results of in vitro studies of the controlled release of BMP2 from gelatin methacrylate (GelMA) microparticles to human dental pulp stem cells (hDPSCs) growing on 3D polyactic acid (PLA)/apatite composite scaffolds. First, 3D printing is utilized to fabricate PLA scaffolds, which are then surface-coated with biomineralized apatite particles synthesized via a bioinspired mineralization process. This involves alternate immersion of the PLA scaffolds in solutions of calcium nitrate and potassium phosphate dibasic to form a precipitate that is mineralized into apatite at physiological pH. The architectural, microstructural, and mechanical properties of the resulting 3D PLA/apatite composite scaffolds are then determined. Second, GelMA photopolymer is synthesized from porcine gelatin and methacrylyc anhydride. After that, BMP2-laden GelMA microparticles are fabricated using an oil-in-water emulsion technique and ultraviolet photor crosslinking. Subsequently, a scaffold/microparticle hybrid construct is produced by the attachment of the BMP2-laden microparticles to the 3D PLA/apatite composite scaffolds. The microstructure of the GelMA microparticles and the release profiles of BMP2 from the microparticles are characterized prior to and following attachment to the PLA/apatite scaffolds and the differences are highlighted. Finally, the effect of the controlled release of BMP2 on hDPSC cells growing on the PLA/apatite scaffolds is investigated. This is done by assessing hDPSC cell proliferation, odontogenic differentiation, and extracellular matrix production and mineralization. The implications of the results for tooth regeneration are then discussed.
Oxygenating Bioinks for Organ-Like Cell Density Constructs

In tissue engineering and bioplotting, the major limitation to building large constructs with physiological cell densities is the poor diffusion of oxygen and nutrients. Organs and many tissues have cell densities in the range 1-5x10^8 cells/ml, yet bioinks can only sustain up to 25x10^6 cells/ml. Oxygen concentration in culture medium is one of the major limiting factors for cell survival and its concentration is about 30 times lower than glucose. This limits the tissue models that can be printed. Furthermore, upon implantation cell survival is dependent on revascularization rate and limit the potential applications in vivo.

Using oxygen releasing microparticles we designed a bioink system capable of prolonging cell survival at high cell density (2x10^7 cells/ml), mimicking physiological organ cell densities.

Oxygen releasing microparticles (OµP) were produced by phase separation method using poly caprolactone (Mw 80000, Aldrich, USA) and calcium peroxide (Aldrich, USA). Particle size measurement was confirmed using field emission scanning electron microscope (FE-SEM, FEI Inspect F-50, USA). The bioink was prepared by mixing 10% (w/v) of OµP in a 1% alginate solution. Oxygen release was measured in 250µL of bioink coinkersed with 0.1M calcium chloride solution and immersed in 1ml PBS at 37°C using an AL300 oxygen sensor (OceanOptics via Gamble Technologies, Canada). Organ-like high density cell culture was performed by seeding a high density (4x10^7 cells/ml) by combining 125µL CHO cells and 125µL of 2% alginate solution alone or containing 20% OµP. The mixture was then extruded through a 20G needle in a 0.1M calcium chloride solution to form 20µL beads. Cells were then cultured for 48h. Cell viability was assessed using MTT.

Scanning electron microscopy revealed that the size of the microparticles ranged from 200µm to 5µm. Oxygen measurements indicated that the dissolved oxygen content of the bioink was kept at 41 ± 5% for 72h. Bioinks with organ-like cell densities without OµP had a cell viability of 27 ± 19% and 13 ± 4.8% at 24 and 48h respectively, whereas with OµP viability was significantly higher at both times; 87 ± 18% and 63 ± 20% at 24 and 48h respectively (N=9, p<0.001).

Lack of oxygen can be detrimental to cell function and survival. In tissues the diffusion of oxygen around a capillary is reported to be around 200µm. By incorporating OµP to a bioink it was possible to create organ-like density construct (2mm thick) with a high viability. This new approach to bioinks may enable printing of more complex and physiologically relevant tissue models.
The extra-cellular matrix (ECM) conveys different biochemical, mechanical and structural cues to cells. These signals are highly orchestrated in space and time. Precise instructions from the ECM dictate cell fate processes, such as proliferation, differentiation and migration. The ECM exerts mechanical forces on cells, which are sensed by cells through different mechanisms, and are translated into biological outcomes. However, these mechanisms are not well understood. One of the main limitations in deciphering this language of forces on cells has been the lack of in vitro systems, which can generate forces on cells that mimic natural stresses.

The present-day methods, which attempt to apply such forces on cells, include single cell manipulation techniques that are highly invasive and although very cell-selective, do not mimic natural stresses. Other techniques rely on the use of flexible elastomers, which better replicate natural stretches, but do not provide user-defined cell selectivity. Therefore, it remains a challenge to develop a system for manipulating cells with mechanical forces, which are precisely controlled in space and time domains.

Here we demonstrate a novel hydrogel system, which can reversibly apply precise, user-defined mechanical forces on selected cells in a cell population. Our approach comprises a smart ECM-mimic hydrogel system, which responds to a light trigger. This causes reversible local deformations of the cell growth substrate and leads to the generation of mechanical forces on cells. These forces are transient and can be controlled at a sub cellular and sub-population scale, in a wide range of time scales (up to ms), with pre-defined directionality.

Such a system for opto-mechanical stimulation of cells is an effective tool for investigating how repeated actuation of a soft hydrogel affects cells. This is experimentally demonstrated in a case study using fibroblast cells to show the proof-of-principle of the concept.

The dynamic hydrogel swelling/shrinking closely replicates the stretches experienced by soft tissues in the body during activities, such as movement, growth etc. We believe that this system bridges the gap between single cell manipulation techniques and cell sheet deformation techniques. This system shows great potential in fields of 'mechano-diseases' and in understanding cell-ECM interactions.

**BM04.03.06**

**Improved Antibacterial Properties of Titanium Implants After Acid Etching and Atomic Layer Deposition**  
Paria Ghannadian, James W. Moxley and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Despite the progress tissue engineering has made in the development of improved biomaterials, inhibiting bacterial infection has not been a central focus to date. Infection is a leading cause of implant failures with many agencies (such as the Centers for Disease Control) predicting more deaths from bacteria than all cancers combined by 2050. Gram-negative bacteria are naturally resistant to numerous treatments and are difficult to kill due to their robust and hydrophobic outer lipopolysaccharide membrane which helps to prevent the flow of antibiotics or drugs into the cell. Moreover, due to extensive antibiotic use, gram-positive Staphylococcus aureus has evolved to a methicillin-resistant strain, which can overcome other classes of antibiotic treatments. The development of an implant capable of reducing bacterial growth (without resorting to the use of antibiotics which causes antibiotic resistant bacteria) would be an effective way to improve implant success. Recently, scientists have been investigating novel materials and techniques to meet growing orthopedic tissue engineering needs. The first step in implant infection is bacterial adhesion, which can potentially result in the formation of antibiotic resistant biofilms for some species. Bacterial adhesion, growth, and subsequent biofilm formation on surfaces are particularly resistant towards the body’s defense mechanisms and antibiotic treatments, which can cause implant rejection. Multiple substrate properties, including chemical composition, hydrophobicity, and surface roughness, are believed to be of significance in the bacterial attachment process. In this study, multiple titanium samples were etched with different concentrations of nitric acid (10N or 12N) for varying durations (60 or 90 minutes), followed by a consistent and extended heat treatment (400 for one hour) for all samples. As a comparison to these samples, which were modified through conventional acidic etching treatment, another group of titanium samples were prepared by coating with 25 nm of titanium dioxide at 200 for approximately 4 hours through an atomic layer deposition (ALD) technique. To assess the potential effect of both approaches on inhibiting bacterial adhesion, and thus conferring antibacterial properties, samples were cultured with Staphylococcus aureus and colony forming unit (CFU) assays were conducted. ALD treatment, in comparison to conventional acidic etching treatment, demonstrated reduced bacterial density. As such, ALD treatment may pose a promising way to inhibit the growth of infectious bacterial populations, on a vast variety of surfaces and materials, without the need for antibiotics.

**BM04.03.07**

**Bio-Plotting Facial Cartilage Replacements**  
Raymond Oliver¹, Michelle Griffin², Peter Butler² and Chawisa Deesomboon¹; ¹School of Design, Northumbria University, Newcastle upon Tyne, United Kingdom; ²Division of Surgery and Interventional Science, Centre for Nanoscience and Technology, London, United Kingdom.

Several diseases include cancer, skin diseases, inflammatory conditions, trauma and congenital deformalities cause ear and nose defects that require reconstruction. Due to the wide patient population that this affects, nose reconstruction creates a huge social and economic burden. Each year, 1/6000 children are born with a small or missing ear, a condition called microtia. This devastating facial disfigurement causes high physical, social and mental burden for both the child and parent. Current surgical reconstruction involves harvesting tissue from elsewhere in the body, to recreate the cartilage framework of the ear and the nose. As such, this is not only painful and time consuming, it is also limited by tissue availability. As such, bio-printing could be an effective way to improve implant success. Recently, scientists have been investigating novel materials and techniques to meet growing orthopedic tissue engineering needs. The first step in implant infection is bacterial adhesion, which can potentially result in the formation of antibiotic resistant biofilms for some species. Bacterial adhesion, growth, and subsequent biofilm formation on surfaces are particularly resistant towards the body’s defense mechanisms and antibiotic treatments, which can cause implant rejection. Several synthetic and biological hydrogels and synthetic polysaccharide composite materials to act as the replacement for the cartilage framework of the ear and the nose. We describe the concepts being developed from 3D to 4D biofabrication using a high precision Bioplotter robot (Envisiontec) to ensure we are creating accurate patient focused auricular and nasal relacements. The bioplotter has proven capable of printing several materials sequentially in very precise locations with and without cells incorporated in the material. Now, in the second stage of our current programme, we are exploring suitable combinations of synthetic and biological material for nose and ear reconstruction, printing of the patient's own cells within the biological component of the material will be optimised. The ability of the cells to survive, grow and support tissue formation is driven by novel laminar(low shear) flow mixing to ensure maximum stem cell survival.

**BM04.03.08**

**Peptide-Based Polyelectrolyte for Neural Tissue Engineering**  
Wei-Fang W; Su, Chia-Yu Lin, Jia-Shing Yu and Shy-Chyang Luo; National Taiwan Univ, Taipei, Taiwan.

Neural tissue engineering has emerged as a potential technology to cure neural damages. Although various synthetic polymers with good biocompatibility
and biodegradability are adopted as candidate materials for scaffolds, most of them require incorporation of biomolecules or conductive materials to promote the growth of long axon. Here we propose a peptide-based polyelectrolyte which is conductive and contains neurotransmitter of glutamic acid. The designed copolymer of poly(γ-benzyl-L-glutamate) and poly(L-glutamic acid) sodium salt (PGBA/Na+) is electrosprun into 3D scaffold with aligned fibers. Neuron-like rat pheochromocytoma (PC12) cells are cultured on the scaffolds to evaluate cell proliferation and differentiation. The results show with both electrical and biochemical chemicals, the polyelectrolyte PGBA/Na+ gives longer axon outgrowth and higher differentiation ratio compared with the neutral copolymer of poly(γ-benzyl-L-glutamate) and poly(L-glutamic acid) (PGBA).

**BM04.03.09**

**Graphene Oxide as a Drug Carrier for Delivery of Zoledronate in Metabolic Bone Disease and Secondary Bone Cancer Treatment**

Sepideh Takavoli and Duygu Ege, Bogaziçi University, Istanbul, Turkey.

In this study, Zoledronic acid (ZOL), a type of nitrogen containing bisphosphonate, was loaded on graphene oxide (GO) particles to increase the particle size of the drug-nano-carrier complex which reduces drug filtration by the kidney and consequently, increases drug circulation time and its tumor uptake. The conjugation between ZOL and GO occurs via π-π stacking and hydrogen bonding interactions, and therefore, the drug may be gradually released from GO in physiological conditions which eliminates the need to apply high doses of the drug. Loading and release profile of ZOL on GO particles was investigated by using UV-Vis spectroscopy. Samples with different concentrations of 0.025-1.25 mg/ml of ZOL were loaded on 0.2 mg/ml GO. UV analysis showed that the maximum loading happens at ZOL to GO ratio of 1.0:2. This loading was obtained when 1 mg/ml of ZOL was initially loaded on 0.2 mg/ml of GO nanoparticles. The drug and drug carrier complexes were characterized using FTIR, AFM, and UV-Vis spectroscopy. Cell culture studies were carried out with MCF-7 breast cancer cells for three dosages of ZOL, ZOL-GO and GO. Cell migration was assessed using Bio-Coat cell migration chambers and cell proliferation was investigated by alamarBlue assay. Cell viability was evaluated by staining dead cells with propidium iodide (PI) and live cells with acridine orange (AO). Overall, the characterization results confirm loading of ZOL on GO nanoparticles and cell studies results show that GO conjugated ZOL complexes are promising to reduce MCF-7 breast cancer cells migration, proliferation and viability.

**BM04.03.10**

**Bioinspired Mineral-Organic Bioreorbable Bone Adhesive**

Alina Kirillova, Cambre N. Kelly, Natalia von Windheim and Ken Gall; Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States.

Bioreorbable bone adhesives have potential to revolutionize the clinical treatment of the human skeletal system, ranging from the fixation and osseointegration of permanent implants to the direct healing and fusion of bones without permanent fixation hardware[1]. With sufficient strength bioreorbable bone adhesives could ultimately become an ideal means for fixing bone fractures instead of conventional plates, nails, pins and screws used today. [2] Despite the evident clinical need, there are currently no bioreorbable bone adhesives in clinical use that can form a bond to bone in a wet environment strong enough to bear clinical loads and sustainable enough to allow fracture healing.[1] Inspired by the sandcastle worm that creates a protective tubular shell around its body by gluing together sand grains and shell fragments underwater using a proteinaceous adhesive, we introduce a novel mineral-organic bone adhesive (aka Tetranite®) that cures in minutes in an aqueous environment and provides high bone-to-bone adhesive strength. The new bioreorbable material is measured to be more adhesive than both bioreorbable calcium phosphate and poly(methyl methacrylate) bone cements, which are standards of care in the clinic today. Osteointegration and bioreosorbability of the bone adhesive are demonstrated over a 25-week period in a critically sized distal femur defect in rabbits. Based on its unique capabilities, Tetranite is the first in a new class of biomaterials, which may spark innovative clinical treatments and revolutionize procedures in which bone regeneration or fixation is critical for treatment.


**BM04.03.11**

**Silicon-Based Nanoneedles to Guide and Regulate Stem Cell Behaviour**

Hyejeong Seong1, Stuart G. Higgins1,2,3, Spencer W. Crowder1, Julia Sero2, Jelle Penders1, Charlotte Lee-Reeves1, James Armstrong1 and Molly Stevens1,2,3; 1Department of Materials, Imperial College London, London, United Kingdom; 2Department of Bioengineering, Imperial College London, London, United Kingdom; 3Institute of Biomedical Engineering, Imperial College London, London, United Kingdom.

In recent years, surfaces with nano/micronscale topography have been widely used to control stem cell behaviour. These patterned substrates possess fascinating qualities that render them more valuable than conventional flat surfaces in many bio-applications, such as neuronal differentiation, biosensing, tissue engineering and DNA analysis. Among these, nanopillar and nanoneedle structures have been extensively investigated because they are beneficial in terms of increasing enhancing cell adhesion and growth, and ability to penetrate cells for facilitating drug/biomolecules delivery. We have co-developed high-aspect ratio, porous silicon nanoneedles made by electrochemical wet etching for in vitro and in vivo manipulation of cell behaviour1,2. These structures are highly biocompatible and can be used to directly interact with the cell membrane, cytoskeleton, and nucleus of primary human cells, generating distinct responses at each of these cellular compartments.

Moreover, we have recently developed a new generation of non-porous nanoneedles using a deep reactive ion etching process. Our new system provides high chemical stability in cell culture media, making it suitable for the long-term investigation of stem cell fates and differentiation at a nanoneedle interface. Furthermore, by systematically tuning the sharpness of the nanoneedles, we could precisely probe their effect on cellular mechanotransduction. The structural effect on cell morphology, alignment, and gene-level expression was observed with scanning electron microscopy, immunofluorescence, and real-time polymerase chain reaction. Our findings provide an ideal framework for manipulating and exploiting stem cell behaviour for longer periods, as a means for understanding cell-material interfaces and differentiation capacity of stem cells. Moreover, we used focused ion beam scanning electron microscopy to determine the critical sharpness required to achieve close interaction between the surface and the cell membrane. We expect elucidating the interfaces between nanoneedles and cells to enable new applications in bioengineering, especially in the sensing and monitoring of live cell cultures via 3D-structured electronic devices.

1. C. Chiappini et al., ACS Nano 2015, 9, 5500-5509
2. C. Chiappini et al., Nat. Mater. 2015, 14, 532-539
Early detection of cancer plays an important role in successful treatment. Therefore, there is an urgent need for more effective and less toxic biomarkers to detect cancer. Cancer cells use exosomes to survive and metastasize to other tissues. Exosomes are small vesicles released to blood by cells, and they can deliver proteomic and genetic information unique to each cell. Therefore, isolating the exosomes secreted by cancer cells can provide us valuable information about the state of a tumor. Since every cell in the body releases exosomes, separating those coming from cancer cells can be a cumbersome task. Current techniques to isolate exosomes are time consuming and costly. Hence, our aim in this study is to use magnetic nanowires (MNWs) to magnetically isolate cancer cells’ exosomes in an efficient way through a simple blood biopsy and a magnetic stand.

In this work, we have used Fe/Au segmented MNWs to separate exosomes released by osteosarcoma cancer cells. These MNWs have been functionalized with PEG, and their concentration has been optimized in order to improve their capture and internalization by the cancer cells. We have observed by TEM that most of the MNWs end up inside the lysosomes in cancer cells. Once inside the cells, these MNWs tend to be broken into smaller pieces that can be released inside the exosomes. This way, by using a magnetic stand, we can easily and efficiently separate only the cancer cells’ exosomes, since they contain segments of magnetic nanowires.

In addition, our Fe/Au segmented MNWs can also be used as customized radio frequency identification (cRFID) labels. MNWs have magnetic (Fe) and nonmagnetic (Au) segments which resemble barcodes, and their structure can be engineered (e.g., by changing the length of each segment) to produce different cRFID signatures. Hence, distinct nanowires can be attached to different types of cancer cells in order to distinguish between the exosomes derived from each type, thereby further improving the efficacy of our blood biopsies.

Electrospun fibrous scaffolds have shown great promise in promoting axon regeneration to improve repair of peripheral nerve defect. Especially, when the fibers are collected as uniaxially aligned arrays, the growth of neurites can be guided and accelerated. Despite the progress, it remains a challenge to place temporally and spatially controlled delivery of biological effectors such as growth factors from the electrospun fibrous scaffold. Such a requirement can be met by integrating electrospun fibers with a controlled release system based upon a stimuli-responsive material. We have developed a temperature-regulated system for the on-demand release of nerve growth factor to promote neurite outgrowth. The system was based upon microparticles fabricated using co-axial electrospray, with the outer solution comprised of a phase-change material (PCM) and the inner solution containing the payloads. When the temperature was kept below the melting point of the PCM, there was no release due to the extremely slow diffusion through a solid matrix. Upon increasing the temperature to slightly pass the melting point, the encapsulated payloads could be readily released from the melted PCM. By leveraging the reversibility of phase transition, the payloads were released in a pulsatile mode through on/off heating cycles. When the PCM microparticles (co-loaded with nerve growth factor and a near-infrared dye) were sandwiched between two layers of electrospun fibers, the nerve growth factor could be released on-demand upon photothermal heating with a near-infrared laser. The nerve growth factor was released with well-preserved bioactivity and stimulated the extension of neurites from spheroids of PC12 cells. By choosing different combinations of PCM, biofactor, and scaffolding material, this controlled release system can be applied to a wide variety of biomedical applications.

Reprogramming cellular functions through the design, fabrication and use of engineered platforms that mimic the physiological cellular environment is a major goal of cell engineering. Indeed, it has been widely demonstrated that the use of 3D systems, compared to 2D, is crucial for a more physiological relevant study of cellular systems, since the third dimension could differently and strongly affect diverse cell functions. However, the precise engineering of 3D systems often results challenging, consequently limiting the control over cellular fate. Here, we report the fabrication of 3D instructive platforms that modulate cellular behaviour in terms of cellular polarization, membrane curvature and uptake capability. By means of two-photon polymerization (2PP) technology, we processed a commercial biocompatible photosensitive to fabricating a cage-like 3D structure capable to entrap cells. We then investigated the cell-material interaction and the effect of different micro-topographies (grooves) on cellular response. To evaluate the effect of such topographies on cellular membrane curvature, we took advantage of the SEM/FIB technology and ultra-thin plasticization (UTP) of cells, which gives the opportunity to directly observe cell-material sections with nanometric resolution. We thus gathered
important information on the relations between membrane curvature and caveola formation, known to be fundamental in endocytosis processes. Moreover, by functionalizing our structures with fluorescent nanoparticles (NPs) we were able to observe how different topographies modulate the cellular uptake by evaluating NPs internalization with confocal microscopy. Our results clearly show that by modulating cellular membrane curvature through specific topographical micro-features, it is possible to tune cellular membrane curvature and, thus, the cellular uptake capabilities. Such results could then give new guidelines for the design of innovative and more efficient delivery systems based on 3D scaffold-like devices.


BM04.03.16 Tunable Visible Light Polymerization of Poly(Ethylene Glycol) Hydrogels for Post-Polymerization Modulation of Material Properties Katherine Wiley, Elisa Ovadia and April Kloxin; University of Delaware, Newark, Delaware, United States.

Synthetic hydrogels, such as those formed with multifunctional poly(ethylene glycol) (PEG) or poly(vinyl alcohol) (PVA) macromers, are of great interest for a variety of biological applications. The high degree of property control that these materials afford, including mimicking the elasticity or ‘stiffness’ of tissues in the human body, makes them particularly useful as biomimetic, multidimensional culture environments for hypothesis testing in studies of disease and regeneration. Traditionally, control of synthetic hydrogel mechanical properties has been achieved with polymer concentration, molecular weight, or reactive group stoichiometry. Recently, the rate of hydrogel formation also was demonstrated as an effective handle for controlling mechanical properties. For example, the rate of hydrogel formation by oxime chemistry was controlled using pH, where the resulting differences in mechanical properties were determined to arise from differences in network heterogeneity (e.g., defects) that depended on the rate of gelation (Zander et al, Advanced Materials, 2015). Inspired by this, in this work we investigated if a rate-based approach for controlling mechanical properties could be used with photoinitiated (lithium acrylphosphate, LAP) synthetic thiol-ene hydrogels (PEG-8-norbornene, PEG-2-thiol) and the resulting defects exploited for temporal property modulation. Specifically, we established a system for hydrogel formation using different doses of visible light (455nm LED, 70-90 mW/cm², 1-10 min) to tune the mechanical properties. We confirmed dependence of hydrogel mechanical properties on factors beyond polymer concentration, including light intensity and exposure time. Elasticity, measured by dynamic mechanical analysis (DMA), indicated that, for precursor solution of the same composition, elasticity increased with both increasing light intensity and exposure time. To better understand the source of defects contributing to differences in hydrogel mechanical properties, end group conversion during hydrogel formation was monitored with magic angle spinning (MAS-NMR) and correlated with mechanical properties over the polymerization time. Through these comparisons, both reduced end group conversion and looping were determined to contribute to differences in mechanical properties observed at different rates of hydrogel formation. Control of end group conversion subsequently was exploited to stiffen hydrogels post-polymerization by covalent incorporation of a secondary thiol-ene network using photopolymerization (365nm, 10 mW/cm²). In sum, we have demonstrated the high level of property control afforded by this visible light polymerization system and the potential utility of this approach for post-polymerization modulation of material properties. This method of modulating properties is promising for studying cell response to dynamic stiffness in three-dimensional culture, with applications in the study of cancer progression and wound healing.

BM04.03.17 Microcapsule Sensors for In Situ Monitoring of pH in Microenvironment Sangmin Lee, Chan Ho Park and Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

In-situ monitoring of pH is of great importance in biomedical fields as pH affects activities of enzyme and drug and is a symptom of certain diseases. It is known that the microenvironment of cancer cells is weakly acidic due to the secretion of lactic acid through anaerobic respiration. Therefore, pH can be an effective indicator for cancers. However, it is very difficult to use conventional litmus papers or pH-meters for measurement of local pH in cellular environments. To provide an injectable, implantable, suspendable platform of pH sensors, we suggest a microcapsule-type sensor that is composed of the pH-responsive optical sensor in the core and semipermeable polymer in the shell. As a template to produce microcapsules, monodisperse water-in-oil-in-water (W/O/W) double-emulsion droplets are prepared using a capillary microfluidic device. The innermost water phase water contains molybdenum disulfide (MoS₂) nanosheets whose surfaces are grafted by pH-responsive polymers with a fluorescent group at the distal end. As the middle oil phase, a photocurable resin of polysiloxanes modified with methacrylate is used. The double-emulsion drops are irradiated by ultraviolet, which leads to the polymerization of the resin, forming a semipermeable solid shell. The pH-responsive polymer that links the MoS₂ nanosheets and fluorescent groups are designed to show a drastic conformation change in the range of pH 6.0-7.4. At physiological condition of pH 7.4, the pH-responsive polymer is collapsed so that the fluorescent groups are brought to the optical quencher of MoS₂, yielding a weak fluorescence due to the Förster resonance energy transfer (FRET). By contrast, at cancer microenvironment with pH 6.3, the pH-responsive polymer is highly extended, increasing fluorescent intensity. As the pH sensors are encapsulated by a semipermeable shell, they are free from dilution with physiological fluids and adhesion of proteins and lipids, thereby maintaining the sensing performance in a physiological environment. The microcapsule sensors can be injected, implanted, and suspended in any target volumes, which enables the in-situ monitoring of pH in the microenvironment where the microcapsules are located.

BM04.03.18 Piezoelectric Performance and Biocompatibility of (Ba,Ca)(Zr,Ti)O₃ Ceramics for Biomedical Applications Kara K. Poon¹, Matthias Wurm², Mari-Ann Einsarsh¹, Rainer Lutz² and Julia Glaum¹; ¹Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway; ²Department of Oral and Maxillofacial Surgery, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany.

The replacement of bone tissue in surgical interventions with artificial materials is a standard procedure in current clinical practice, however, it is a substantial surgery with high patient morbidity and high healthcare costs. It is therefore desirable to develop artificial bone materials which induce controlled, guided and rapid healing to improve patient recuperation and which allow for a stable fixation between bone and implant for immediate loading.

Interest in piezoelectric ceramics for biomedical applications has risen in recent years, due to the need for biocompatible materials with active functionalities. Several studies have proposed that osteogenic regeneration may be improved with the application of electrical stimuli. Barium titanate doped with calcium and zirconium, (Ba,Ca)(Zr,Ti)O₃, are a class of lead-free piezoelectric ceramics which generate electric surface potentials under a mechanical load due to its non-centrosymmetric crystal structure. This class of piezoelectric ceramics may serve as bioactive bone replacement materials.

However, the biocompatibility of BCZT is not well established.

In the present study, we investigate the suitability of BCZT as an artificial bone replacement material. Several compositions of bulk BCZT ceramics were synthesised via solid-state synthesis, including a morphotrophic phase boundary composition (MPB) and several other tetragonal compositions. The MPB composition was chosen for its expected high piezoelectric performance, and the tetragonal compositions for the different stabilities in piezoelectric...
BM04.03.19
Adhesion Effect of Elastin-Like Polypeptide-Supplemented Composite Cement on the Tooth Sun-Young Kim1 and Hyun-Jung Kim2; 1Seoul National University, Seoul, Korea (the Republic of); 2Kyung Hee University, Seoul, Korea (the Republic of).

I. Objectives

Elastin-like polypeptide (ELP) has a variety of application in biomedical field. ELPs are composed of repeats of the pentapeptide Val-Pro-Gly-Xaa-Gly; the guest residue Xaa can be any amino acid except Pro. We have tried to improve the mechanical property of dental cement by ELP supplementation in previous studies. Specially, we found the supplementation of ELP increased the adhesion ability of composite cement to tooth. Here, the objective of this study was to investigate the adhesion effect of ELP supplementation on the tooth between the ELP-supplemented dental cement and tooth surface.

II. Materials & Methods

ELP genes either with or without octaglutamic acid termination were genetically engineered: V125 and V125-E8. Pure ELPs were gathered through a series of protein synthesis process using E.coli through gene transformation, expression, protein purification. 10 wt% ELP solutions were then prepared. The crown of human third molar without caries and restorations was horizontally sectioned to have 2mm thickness by high-speed sawing machine (Buehler). Two holes in tooth specimen were made 4.1 mm in height and 1.4 mm in diameter. 0.3 ratio in liquid/powder were prepared: cement + 60mL of either DW, V125, or V125-E8. Mixed cements as given ratio, were loaded at tooth cavities (20 cavities x 3 subgroup) and set in 37°C incubator for 7 days under 100% humidity. Push-out strength of samples were measured in universal testing machine (SHIMADZU, Japan) at a cross-head speed of 1mm/min with compressive mode. Data were analyzed using Two-way ANOVA and Bonferroni’s post-hoc test at 95% significance level.

III. Results

V125-E8 group showed the highest push out strength significantly (p<0.001). V125 group showed lower strength than V125-E8 group, but higher push-out strength than DW group (p<0.001). V125-E8 groups showed significantly less viscosity and high flow compared to other groups. V125-E8 group showed a narrower gap between composite cement and dentin and composite tag in dentinal tubule while other group showed wider gap and no tag inserted in dentinal tubule.

IV. Conclusion

ELP-supplemented dental cement has higher push-out strength than DW-mixed MTA. V125-E8 showed the highest adhesion ability to tooth. The increased adhesion ability might be due to rheologic property through low viscosity and high flowability.

BM04.03.20

Type I collagen forms fibrous viscoelastic networks that comprise a dominant fraction of the extracellular matrix (ECM). Through interactions with single cells and tissues, networks of type I collagen can be remodeled to form anisotropic networks, which are observed in biological processes as diverse as branching morphogenesis and metastatic invasion. However, replicating the structure of anisotropic collagen networks ex vivo is challenging because current collagen fiber alignment techniques are often limited to unidirectional alignment over small mm-scale areas or in thin films. Here, we adapt three-dimensional (3D) microextrusion printing as a technique to fabricate anisotropic networks of type I collagen with tunable fiber alignment and geometry.

Changing the concentration of Matrigel in the collagen-Matrigel ink allowed the geometry of collagen fibers to be tuned. By modifying the aforementioned parameters, we 3D-printed complex patterns of collagen fiber alignment and geometry that were separated by sharp interfaces. 3D-printed networks of type I collagen have great potential for studies that assess the role of collagen fiber alignment in developmental biology and tissue engineering.

BM04.03.21
Rational Design of Antimicrobial Peptide Nanofibers Bijlal Sarkar1, Steven Park2, Peter Nguyen1, Zain Siddiqui1, Michael McGowan1, David Perlin2 and Vivek Kumar1; 1New Jersey Institute of Technology, Newark, New Jersey, United States; 2Public Health Research Institute, Rutgers, The State University of New Jersey, Newark, New Jersey, United States.

Natural antimicrobial peptides are crucial components of the innate immune system against invading pathogens. Inspired by these natural peptides, we designed a set of cationic amphipathic peptides that can self-assemble into injectable hydrogels. Our self-assembled system employs non-covalent forces to yield hierarchical assembly of these materials capable of disrupting cell membranes of pathogens, such as bacteria (e.g. Pseudomonas aeruginosa) and fungi (e.g. Fusarium solani). The self-assembly of the nanofibrous hydrogel was characterized with spectroscopic techniques as well as high-resolution microscopy techniques such as atomic force microscopy and scanning electron microscopy. We tested the self-assembling peptide hydrogels were tested for compatibility with stromal cells with in vitro cell culture. Moreover, we subcutaneously implanted the hydrogels and observed no systemic toxicity. We screened the antimicrobial platforms against a spectrum of pathogens that were associated with nosocomial infections. In addition, we determined the mechanism through which the nanofibers disrupt the pathogen colonies. The hydrogel can be either be applied as a topical antibiotic or can be integrated into medical devices, such as catheters and grafts. In addition, due to their shear-thinning viscoelastic properties, these hydrogels can be syringe aspirated and injected directly onto or into a target site. The rational design of the nanofiber should provide researchers and clinicians a viable platform to build therapies against multi-drug resistant pathogens that threaten to complicate even the most routine surgical procedures.

BM04.03.22
Biodegradable pH-Activated Polymeric Nanoparticle Modulate Lysosomal Acidification and Autophagy in Parkinson's Disease Jialiu Zeng1,
We have developed a novel polymeric pH-activable, acidifying nanoparticle (acNP) that restores the pH of compromised lysosomes to rescue autophagic flux and cellular function in neurons (PC-12 cells) under exposure to either 1-methyl-4-phenylpyridinium (MPP+) or 6-hydroxydopamine (6-OHDA). Parkinson’s disease (PD) occurs in 13 per 100,000 people in the population, and about 60,000 new cases are identified each year. It is characterized by the accumulation of alpha synuclein (a-syn) within Lewy bodies and neurites of the nervous system in the form of amyloid fibrils. Recent studies have indicated that perturbations in the autophagy-lysosome pathway, especially impaired lysosomal acidification that mediate the degradation of a-syn may play a role in its pathogenesis. Therefore, targeting lysosomal acidity represent a new target for therapeutic development. Although some studies have demonstrated that genetic restoration of autophagy can inhibit the development of PD, to date no effective therapeutic approach has been developed. In this study, we designed an acidic nanoparticle (acNP) that contains caged acid which can be released upon moderate pH changes to enable controlled acidification of the impaired lysosomes under lipotoxicity. The non-cytotoxic acNPs are taken up into the lysosomes of PC-12 cells, rescue cell death caused by MPP+ and 6-OHDA neuro-toxins, restore lysosomal acidity, and decrease the accumulation of autophagic proteins LC3II and p62 expression levels, indicating an overall rescue of autophagic flux. The acNPs also decreased a-syn accumulation in the PC-12 cells, effectively improving the function of PC-12 cell lines. These results established a primary causative role of impaired lysosomal acidification on the de-regulation of autophagic flux and cellular materials that are biocompatible. Towards this aim, we have screened several hundred acrylamide copolymer hydrogels by studying their non-fouling properties to identify top-performing materials that resist protein absorption and blood platelet adhesion. Further, we have examined the biocompatibility of poly(meth)acrylates; however, these coatings suffer from instability and short lifetimes. In contrast, polyacrylamides exhibit remarkable stability and thus are a broad class of polymers, but have been poorly studied as non-fouling coatings, driving the need for the development of novel ultra-low fouling surfaces transferred YAP into the nucleus. These results indicate that the YAP activity can be regulated by the molecular mobility independently of the initial adhesiveness. It had reported that the YAP nuclear localization led to dedifferentiate hepatocytes and impaired hepatic functions [3]. Highly mobile growth factor-tethered PRX surfaces. Previously, we have succeeded in tethering growth factor tethered surfaces. In recent years, we clarified the relationship between the cell differentiation of mesenchymal stem cells (MSCs) and the molecular mobility on PRX coated surfaces (PRX surfaces). The highly mobile surfaces were preferable to adiogenic differentiation, whereas the less mobile surfaces induced their osteogenic differentiation [1]. For the further advancement of the control of cellular behaviors, we designed growth factor tethered surfaces. Previously, we have succeeded in tethering positively charged heparin-binding growth factors onto sulfonated PRX surfaces via electrostatic interaction. The surfaces enhanced osteoblast differentiation by the mobility of PRX and tethering of growth factors [2]. Based on the surface design, we attempted to improve hepatic functions in vitro of hepatic-derived cells (HepG2) in the present study. In particular, a sulfonated PRX triblock copolymer, which consists of a sulfated PRX as a middle block segment and poly(benzyl methacrylate) as both terminal segments, was coated to a polystyrene substrate by a simple casting method. Subsequently, alpha heparin-binding epidermal growth factor-like growth factor (HB-EGF) as a survival factor for hepatic function was bonded to a sulfonated PRX surface. As a control surface, HB-EGF was adhered on a non-sulfonated PRX surface by hydrophobic interactions. For assessing mechanical signalings by the molecular mobility, initial adhesion and subcellular localization of Yes associated protein (YAP) which is an essential transducer of mechanical signals was analyzed by microscopic observation. After 24 h in culture, the number of adhered cells on sulfonated surfaces was almost the same as that on non-sulfonated PRX surfaces, regardless of the molecular mobility. Although highly mobile surfaces suppressed nuclear localization of YAP, less mobile surfaces transferred YAP into the nucleus. These results indicate that the YAP activity can be regulated by the molecular mobility independently of the initial adhesiveness. It had reported that the YAP nuclear localization led to dedifferentiate hepatocytes and impaired hepatic functions [3]. Highly mobile growth factor-tethered PRX surfaces. Previously, we have succeeded in tethering growth factor tethered surfaces. In recent years, we clarified the relationship between the cell differentiation of mesenchymal stem cells (MSCs) and the molecular mobility on PRX coated surfaces (PRX surfaces). The highly mobile surfaces were preferable to adiogenic differentiation, whereas the less mobile surfaces induced their osteogenic differentiation [1]. For the further advancement of the control of cellular behaviors, we designed growth factor tethered surfaces. Previously, we have succeeded in tethering positively charged heparin-binding growth factors onto sulfonated PRX surfaces via electrostatic interaction. The surfaces enhanced osteoblast differentiation by the mobility of PRX and tethering of growth factors [2]. Based on the surface design, we attempted to improve hepatic functions in vitro of hepatic-derived cells (HepG2) in the present study. In particular, a sulfonated PRX triblock copolymer, which consists of a sulfated PRX as a middle block segment and poly(benzyl methacrylate) as both-terminal segments, was coated to a polystyrene substrate by a simple casting method. Subsequently, alpha heparin-binding epidermal growth factor-like growth factor (HB-EGF) as a survival factor for hepatic function was bonded to a sulfonated PRX surface. As a control surface, HB-EGF was adhered on a non-sulfonated PRX surface by hydrophobic interactions. For assessing mechanical signalings by the molecular mobility, initial adhesion and subcellular localization of Yes associated protein (YAP) which is an essential transducer of mechanical signals was analyzed by microscopic observation. After 24 h in culture, the number of adhered cells on sulfonated surfaces was almost the same as that on non-sulfonated PRX surfaces, regardless of the molecular mobility. Although highly mobile surfaces suppressed nuclear localization of YAP, less mobile surfaces transferred YAP into the nucleus. These results indicate that the YAP activity can be regulated by the molecular mobility independently of the initial adhesiveness. It had reported that the YAP nuclear localization led to dedifferentiate hepatocytes and impaired hepatic functions [3]. Highly mobile growth factor-tethered PRX surfaces. Previously, we have succeeded in tethering growth factor tethered surfaces. In recent years, we clarified the relationship between the cell differentiation of mesenchymal stem cells (MSCs) and the molecular mobility on PRX coated surfaces (PRX surfaces). The highly mobile surfaces were preferable to adiogenic differentiation, whereas the less mobile surfaces induced their osteogenic differentiation [1]. For the further advancement of the control of cellular behaviors, we designed growth factor tethered surfaces. Previously, we have succeeded in tethering positively charged heparin-binding growth factors onto sulfonated PRX surfaces via electrostatic interaction. The surfaces enhanced osteoblast differentiation by the mobility of PRX and tethering of growth factors [2]. Based on the surface design, we attempted to improve hepatic functions in vitro of hepatic-derived cells (HepG2) in the present study. In particular, a sulfonated PRX triblock copolymer, which consists of a sulfated PRX as a middle block segment and poly(benzyl methacrylate) as both-terminal segments, was coated to a polystyrene substrate by a simple casting method. Subsequently, alpha heparin-binding epidermal growth factor-like growth factor (HB-EGF) as a survival factor for hepatic function was bonded to a sulfonated PRX surface. As a control surface, HB-EGF was adhered on a non-sulfonated PRX surface by hydrophobic interactions. For assessing mechanical signalings by the molecular mobility, initial adhesion and subcellular localization of Yes associated protein (YAP) which is an essential transducer of mechanical signals was analyzed by microscopic observation. After 24 h in culture, the number of adhered cells on sulfonated surfaces was almost the same as that on non-sulfonated PRX surfaces, regardless of the molecular mobility. Although highly mobile surfaces suppressed nuclear localization of YAP, less mobile surfaces transferred YAP into the nucleus. These results indicate that the YAP activity can be regulated by the molecular mobility independently of the initial adhesiveness. It had reported that the YAP nuclear localization led to dedifferentiate hepatocytes and impaired hepatic functions [3]. Highly mobile growth factor-tethered PRX surfaces. Previously, we have succeeded in tethering growth factor tethered surfaces. In recent years, we clarified the relationship between the cell differentiation of mesenchymal stem cells (MSCs) and the molecular mobility on PRX coated surfaces (PRX surfaces). The highly mobile surfaces were preferable to adiogenic differentiation, whereas the less mobile surfaces induced their osteogenic differentiation [1]. For the further advancement of the control of cellular behaviors, we designed growth factor tethered surfaces. Previous
surfaces would be suitable to maintain or enhance the functions. In order to evaluate the functions, albumin secretion from HepG2 on surfaces was quantified. Highly mobile sulfonated PRX surfaces with tethered HB-EGF induced the highest secretion of albumin among all culture conditions. These results strongly suggest the synergistic effect of the mobility of PRX and tethering of HB-EGF via electrostatic interactions.


BM04.03.26
Synthesis of Selenium-Incorporated Alpha-Tricalcium Phosphate and Evaluation of Its Cement-Type Reactivity
Bersu Bastagiul1, 2 and Caner Durukan1, 2
1Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; 2BIOMATEN Center of Excellence in Biomaterials and Tissue Engineering, Middle East Technical University, Ankara, Turkey.

Alpha-tricalcium phosphate (α-TCP) is a promising hard tissue analog due to its cement-type hydraulic conversion to the mineral component (calcium deficient hydroxyapatite, CDHAp) of natural bone tissue. A variety of different inorganic and organic agents can be incorporated to α-TCP in order to enhance its regenerative and regenerative properties. In this study, an ionic incorporation - selenium (Se) - was accomplished to impart anti-carcinogenic property to α-TCP. Se-incorporated α-TCP (α-TCP:Se) was obtained by a solid-state reaction of custom synthesized Se-incorporated mononette (CaHPO₄:Se) and calcium carbonate (CaCO₃) precursors at 1200 °C for 2 h. The effect of Se-incorporation on crystal structure of α-TCP and on its cement type hydraulic reactivity at 37 °C was investigated in detail by crystallographic analysis (Rietveld refinement) and by isothermal calorimetry, respectively. At low amount of Se-incorporation (< 5 wt%), α-TCP remains phase pure, however relatively higher amount of Se addition (10 wt%) leads to formation of β-polymorph of TCP lacking the cement-type setting behavior. The SEM examinations showed that the morphological properties of α-TCP remain unaffected after doping with Se. However, Se-incorporation occurs at a limited extent, lower than the theoretically expected values as revealed by spectroscopical analyses. Se-incorporation does not change the reticulated needle/plate like morphology of the CDHAp, which is characteristic to cement-type hydration and hardening. Se-incorporated TCPs fully convert to CDHAp, but Se-incorporation changes the reaction kinetics and mechanic path for α-TCP to CDHAp cement conversion and higher amount of Se addition slows down the reaction kinetics. The results imply that an optimal Se amount is critical to preserve intrinsic cement nature/behavior of α-TCP.

BM04.03.27
NanoComposite for Wound Dressing Applications Obtained by 3D Printing

Infection in exposed wounds is one of the most important factors affecting wound healing. Thus, antimicrobial engineered biomaterials have been addressed in clinical applications for regenerative medicine [1]. Wound dressings used in the treatment of diabetic foot ulcers, affliction causing 85 % of non traumatic lower limb amputations, may prevent infections and possible amputations providing an environment to improve wound healing [2]. Herein, a 3D printed novel nanocomposite with tissue regeneration and antimicrobial properties constituted by a bacterial cellulose (BC) membrane and a biocompatible polymer matrix was produced. BC presents attractive applications, especially in the medical area due to its high degree of crystallinity, purity, reticulated conformation, biodegradability and biocompatibility [3]. For this research, BC was obtained from mango pulp, an industrial waste used in the formulation of alternative culture media. In addition, BC membrane was supported by biocompatible polymers (polycaprolactone and poly(vinyl alcohol)) at varying ratios and functionalized with grapefruit seed extract to enhance antimicrobial properties and durability. Physico chemical properties of the nanocomposite were analyzed by SEM, TGA, FTIR, tensile testing and water holding capacity techniques. In vitro assays consisted of evaluating biocompatibility, viability, antimicrobial and antifungal activity. In vivo studies comprised the analysis of intracutaneous reactivity, cytotoxicity, and mutagenic activity. As BC membranes exhibit biocompatibility properties, high mechanical resistance in wet conditions, high capacity for hydration and permeability of liquids and gases; in addition to the null or low irritation that causes to the skin, these membranes are a useful material in the care and regeneration of cutaneous wounds [4]; complementing the BC membrane with biopolymers and an antimicrobial agent to create a nanocomposite suggests the biocompatibility and bioactivity behavior may increase. Hence, the developed nanocomposite may be used in diverse regenerative engineering applications such as wound dressings.


BM04.03.28
Integrated Design Scheme Based on Mechno-Biology and Level Set Based Topology Optimization for Bone Scaffolds
Mehmet S. Aydin1, 2, Busra Kaloglu1, Caipa Sipahi1, Berkay Cayir1 and Guliu Kiziltas1, 2; 1Sabanci University, Istanbul, Turkey; 2Sabanci University Nanotechnology Research and Application Center, Istanbul, Turkey.

One of the key requirements of scaffolds is the balance between mechanical function and mass transport to aid biological delivery and tissue regeneration. Computational topology design and Solid Free-Form Optimization methods can overcome this challenge. In this work, we developed a computational design tool based on the integration of the level set method and mechano-regulatory models for optimizing scaffolds based on desired multi-functionality including elasticity, diffusivity, and permeability as well as tissue differentiation. First, for the level set method, computational models are implemented using COMSOL Multiphysics which provides the opportunity to build an FEA (Finite Element Analysis) model where various boundary value problems are coupled and studied at the same time to reach an optimally performing tissue. Response of the scaffold is analyzed using solid mechanics, general form PDE and fluid flow modules. These modules are integrated to resolve respective governing equations simultaneously. Level-set method is performed by utilizing Hamilton-Jacobi equation in the general form PDE module. A initial level-set surface is updated according to the sensitivity of the desired metrics with respect to material parameters. The change in the level-set surface is automatically reflected on the scaffold structure and an optimum structure with desired stiffness, porosity and diffusivity is obtained by finding an optimum level-set surface. As a second capability, the level set based topology scheme is integrated to a self-healing simulation capability, via a mechano-regulatory model developed to mimic tissue regeneration. For the topology optimization design method the level-set method is employed, where the design process starts with an initial geometry that satisfies physical constraints. At each time step, this geometry is improved based on sensitivity analysis results until convergence is reached. Results of both the mechneregulatory and the topology optimization methods validate well-known benchmark design problems in literature. One design that resulted from the integrated framework on both is successfully fabricated using non-solvent-induced phase separation and 3D printing. Characterization studies using micro-CT and mechanical testing are underway. Finite element method integrated to the level-set based topology optimization is proven to be among the most computationally efficient and generic design tool for solving non-intuitive tissue engineering problems. Hence, the proposed design framework,
Brain pathologies often arise from the dysfunction of specific neural circuit nodes. Interrogation of these nodes is a primary goal of neuroscience research. Reliable targeting of these microstructures can be difficult, however. Nodes are often small (sub-mm) and irregularly shaped. Current approaches employ stereotactic mapping and rely on large (>300μm) guide cannulas to ensure minimal deflection of probes during insertion. Such techniques can result in extensive glial scarring. This can substantially modify the local microenvironment to be investigated and limit chronic viability of implants. This is especially the case for fluidic targeting and drug delivery. Acutely inserted needles used for drug microinfusions (100nl-2μl) are large (23-25G), causing insertion trauma and backflow of infusate.

We present a toolkit for manufacturing multimodal neural probes (termed Miniaturized Neural drug Delivery systems (MiNDs)) for use in both small and large animal models. Probes can be customized according to desired functionalities. Here we show in vivo functionality of MiNDs containing fluidic and electrical functionalities and an MRI-compatible MiNDs with 2 fluidic channels in a 200μm footprint. We also report the ability to independently insert and steer individual 60μm fibers of various materials, allowing access to multiple brain sites from a single burr hole. We characterize the mechanical insertion properties of different probe sizes and materials, elucidating the various advantages of each. The microinvasive footprint of the probes limits gliosis and enhances neural regeneration, allowing for chronic viability and functionality up to 1 year post-implantation.

High sensitivity MicroPET was used to characterize distinct infusion dynamics of nanoliter fluid infusions through chronic implants, emphasizing the ability to finely tune volume to target brain microstructures. We supported this by inducing volume-dependent behavior modulation in rodents with unilateral stimulation of GABA circuitry in the substantia nigra. These techniques are readily transferable to other laboratories seeking to develop custom neural probes for multimodal chronic neural interfacing. MiNDs is a powerful tool for the dissection of deep brain microstructures in small and large preclinical models.

Cancer is an uncontrolled disease affecting millions of patients a year. To overcome the critical drawback of conventional therapies, targeted-therapy has gained attention as next generation strategy to cure cancer patients with less toxicity. Among many designs, biological material based nucleic acid as drug agent was demonstrated by numerous groups from early 2000s. Small interfering RNA, or siRNA, is non-coding short RNA molecules capable of regulating protein expression using RNA interference machinery. Utilizing siRNA as biological drug to repair cancerous metabolism caused by mutated protein has resulted in positive outcome with anti-cancer effects in pre-clinical experiments and clinical trials. In fact, siRNA therapeutics by Alnylam Pharmaceuticals is FDA-approved for clinical use for respiratory syncytial virus infections. However, the delivery of siRNA has been major hurdle in translating the efficacy in various cancer patients. Here, we incorporated nanoparticle to enhance the delivery of siRNA to target tumor sites under systemic administration. Bio-compatible and bio-degradable glycol chitosan was self-assembled with polymerized siRNA to form stable delivery complex to tumor sites to downregulate oncogenic expression. Phosphoinositide 3-kinase (Pi3K) and Ras are the most commonly activated oncogenic pathways in solid malignancies and have interdependent relationship via feedback loop system. Many previous reports have shown that dual-inhibition of Pi3K and Ras pathway has therapeutic effects in various cancer models. Though use of multi-drug achieves simultaneous inhibition of specific pathways, undesired side-effects and resistance occasionally occur from collision of pharmacokinetics of small molecule inhibitors. In addition, currently none of Ras inhibitor is potent enough for pathway inhibition, instead secondary inhibitor on downstream protein, MEK, is more commonly used. Here, we used siRNA therapeutics in collaboration with pan-Pi3k inhibitor to demonstrate anti-tumor effects in ovarian cancer. Ovarian cancer cell line with PTEN deficiency and Kras(G12D) mutation were obtained from spontaneous tumor model to examine synergistic effect of Pi3k and Ras inhibition. In cellular level, GDC and siKRAS impeded the activity of Pi3k activity and expression of Ras, respectively. When both pathways were simultaneously inhibited, cell proliferation and migration significantly delayed. In allograft ovarian cancer model, tumor sizes were critically reduced when both Pi3k and Ras were inhibited together. The immunoblot and immunohistochemistry results verified that that dual-inhibition impeded tumor growth and induced apoptosis. Here, we demonstrate that combination inhibition of Pi3k and Ras using different treatment strategies is an exceeding alternative over conventional single-agent treatments.
Conclusions: Nanoparticles or 3D-printed constructs releasing drugs could constitute a therapeutic promise to combat metastatic spine tumors. Nanoparticles can be integrated into commercial bone cements to develop a bioactive bone graft following bone tumor resection to deliver localized drug facilitating bone stability and healing while preventing tumor recurrence. Likewise, 3D printed scaffolds can be made to perfectly fit patients’ defect sites while at the same time be loaded with chemotherapeutics to block cancer recurrence and promote bone repair.

BM04.03.32
Development of Biodegradable Polyurethane Elastomers with Chain Regulators for Bone Tissue Engineering Retul S. Yasar1 and Eda Ayse Aksoy1, 2; 1Faculty of Pharmacy, Department of Basic Pharmaceutical Sciences, Hacettepe University, Ankara, Turkey, 2 Institute of Science, Department of Polymer Science and Technology, Hacettepe University, Ankara, Turkey.

Bone injuries necessitate the use of scaffold-based tissue engineering approaches and development of hard tissue supports and innovative biomaterials are important. In this study it is aimed to develop novel biodegradable polyurethane elastomers as based bone regenerative films. For this purpose, firstly synthesis of polyurethane prepolymer were studied and condensation polymerization between polycapro lactone diol and hexamethylene diisocyanate monomers were carried out. Monomer ratios, catalyst amount, synthesis time and temperature were changed and obtained prepolymer were characterized according to their chemical properties, average molecular weights and solubility in solvent systems. During the second step of polymerization with chain regulators were integrated in to diisocyanate-terminated polyurethane prepolymer via their difunctional groups. As chain regulator agent organic and inorganic compounds and an amino acid molecule were used. The chemical, thermal, viscoelastic and surface free energy of chain regulated polyurethane films were investigated by FTIR, DSC, TGA, DMA and goniometer, respectively. The bioactive chain regulator containing polyurethanes had shown of urethane, urea hydrogen bonds and provided all the transitions of viscoelastic behavior. Biodegradation behaviors were examined in enzymatic and oxidative media in 75 days period. The bioactive chain regulator containing polyurethanes have showed surface erosion type of biodegradation and over 20 % and 60 % weight loss were recorded gravimetrically in oxidative and enzymatic medias respectively. Significant and positive findings were obtained for the developed biodegradable polyurethane elastomers as bone regenerative film.

Acknowledgement: This study is financially supported by Hacettepe University BAP Carrier Transition Project TKG-2017-15635.

SESSION BM04.04: Hydrogel-Based Biomaterials
Session Chairs: Josephine Allen and Gulden Camci-Unal
Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Independence West

8:00 AM *BM04.04.01
Nano- and Microfabricated Hydrogels for Regenerative Engineering Ali Khademhosseini; Department of Bioengineering, Chemical Engineering, Radiology, University of California, Los Angeles, Los Angeles, California, United States.

Engineered materials that integrate advances in polymer chemistry, nanotechnology, and biological sciences have the potential to create powerful medical therapies. Our group aims to engineer tissue regenerative therapies using water-containing polymer networks, called hydrogels, that can regulate cell behavior. Specifically, we have developed photocrosslinkable hybrid hydrogels that combine natural biomolecules with nanoparticles to regulate the chemical, biological, mechanical and electrical properties of gels. These functional scaffolds induce the differentiation of stem cells to desired cell types and direct the formation of vascularized heart or bone tissues. Since tissue function is highly dependent on architecture, we have also used microfabrication methods, such as microfluidics, photolithography, bioprinting, and molding, to regulate the architecture of these materials. We have employed these strategies to generate miniaturized tissues. To create tissue complexity, we have also developed directed assembly techniques to compile small tissue modules into larger constructs. It is anticipated that such approaches will lead to the development of next-generation regenerative therapeutics and biomedical devices.

8:30 AM *BM04.04.02
Decellularized Extracellular Matrix Based Hydrogels for Regenerative Engineering Karen L. Christman; University of California, San Diego, La Jolla, California, United States.

The extracellular matrix (ECM) is nature’s scaffold, and in recent years, researchers have isolated these scaffolds for tissue engineering applications by removing all of the cellular components, a process called decellularization. These scaffolds are known to promote cell influx, regeneration, and healing in a variety of tissues, and their degradation products have angiogenic, chemoattractant, and antimicrobial properties, as well as promote cell proliferation. By removal of the cellular antigens, these scaffolds are considered biocompatible, and xenogeneic sources can be used. While these scaffolds retain the native ECM structure, they are not amenable to minimally invasive, injectable procedures. We have developed a variety of injectable ECM derived hydrogels that self-assemble to form porous, nanofibrous scaffolds once injected in vivo or brought to physiological conditions in vitro. These ECM based scaffolds have been shown to increase tissue specific differentiation and maturation of a variety of progenitor and stem cells in vitro, and are showing promise in vivo in several tissues including the myocardium and skeletal muscle. This talk will cover the recent progress with these materials.

9:00 AM BM04.04.03
Self-Assembling Peptide Hydrogel for Enhanced Cholesterol Uptake Biplob Sarkar, Peter Nguyen, Zain Siddiqui and Vivek Kumar; New Jersey Institute of Technology, Newark, New Jersey, United States.

Blocking proprotein convertase subtilisin/kexin type 9 (PCSK9) is an important therapeutic target for lowering circulation of low density lipoprotein (LDL) particles, which can improve cardiovascular health. We have developed a self-assembling peptide hydrogel that can bind PCSK9, leading to increased uptake of LDL particles in the liver cells. The cholesterol-lowering therapeutic hydrogel may be locally applied/implanted for sustained release. The
The cultivation is expected to be useful for studying in vitro model of nerve injury and regeneration. Local damage was observed at the illuminated spot. The developed method that can manipulate neurite outgrowth by photothermal stimulation even during damage by applying photothermal stimulation to neurites directly. NIR beam was focused on the neurites that grew along the melted agarose channel and hydrogel was successfully melted by localized heat of GNRs under NIR illumination. Through the micro-sized channel produced by the melted agarose, the neurites grew in contact with the gold-coated substrate following by photodeposition of Ppy using a current density of 0.3-0.9 mA/cm² for 60-240 sec. The resultant gradients are characterized by fluorescence microscopy and Energy Dispersive X-ray Spectroscopy (EDS) analysis and are compared to theoretical model of diffusion. The fluorescence imaging of both the hydrogel stamp and the corresponding deposited CP film demonstrate that the profile of molecular gradient within the hydrogel is time-dependent. These results are further confirmed using EDS analysis. The present approach can be effectively applied to generate CP films of various geometries with controlled molecular gradients for guiding cellular behavior for tissue engineering purposes.

Photoclickable thiol:norbornene poly(ethylene glycol) (PEG) hydrogels are promising for in situ delivery of chondrocytes to promote tissue regeneration in focal cartilage defects. This platform offers a high degree of tunability through the introduction of thiolated matrix components and growth factors, achieving a range of mechanical properties and degradation behaviors with spatiotemporal control offered by photo-polymerization. In particular, degradation is critical for allowing the transition from hydrogel to neo-tissue as cells secrete new extracellular matrix (ECM) molecules. Using a combined experimental and computational approach to design degradable hydrogels, we have identified two mechanisms that facilitate the transition from gel to neo-tissue: 1) interactions between the cell and polymer precursors, which reduce crosslinking near the cell and 2) cell clusters, which enable early localized tissue growth and eventual connection to form neo-tissue. This work aimed to identify the interplay of cell clusters and heterogeneous crosslink density and its influence on neo-cartilage growth in PEG hydrogels.

We defined three parameters: \( R_x \), the distance over which the crosslink density varies from the cell membrane to the bulk gel; \( F \), the volume fraction of clusters relative to the total construct volume; and \( c_z \), the ratio of cluster cell density to the background cell density. Computationally, we identified that gels with high \( F \) and \( c_z \) led to interconnected ECM prior to reaching reverse gelation due to an overlapping \( R_x \). Experimentally, we developed methods to induce cell clusters via agitation pre-encapsulation. The ratio of clusters to single cells was controlled pre-encapsulation in hydrolytically degradable gels enabling the cluster size to be varied while holding \( F \) and \( c_z \) constant. When cultured for 4 weeks, there was no difference in ECM deposition measured by sulfated glycosaminoglycans (sGAGs) and collagen as a function of cluster size. Moreover, the modulus decreased from ~20 kPa to ~5 kPa indicating an overall loss in gel without sufficient matrix production. However, the gel was expected to reach reverse gelation prior to 4 weeks indicating that the little ECM produced had formed enough of a connected network to maintain the construct, which was supported by histology imaging for collagen and sGAGs. The clinical viability of the constructs was tested over longer times in in vivo experiments by placing cellular gels subcutaneously in nu/nu mice. TGFβ3 was immobilized in gels to help support and maintain the chondrogenic phenotype. With a 9 week culture there was a ~2x increase in the modulus of the gels compared to a 25% decrease in in vitro gels.

To conclude, we combined experimental and computational methods to identify that heterogeneous distribution of cells and crosslinks contribute to the transition from hydrogel to neo-tissue. We are able to induce clusters and design gels that promote tissue formation.

To control the position of neurons and connection of their neurites on culture substrates, various cell-attractive or cell-repellent materials have been used for micropatterning techniques. However, when neurons are cultured on an engineered substrate fabricated by conventional patterning methods, it is difficult to change their patterned distribution again during the cultivation. In this study, we utilized gold nanorods (GNRs) that has the property of photothermal effect in the near-infrared (NIR) region to fabricate thermoplasmonic interface on a culture substrates. By integrating this interface with a micropatterning method using thermosensitive agarose hydrogel, we demonstrate the manipulation of neurite outgrowth even after the neuronal cultures formed confined networks. GNRs, which was synthesized by seed-mediated method, were immobilized on glass culture substrates through the electrostatic binding. Following by poly-D-lysine coating on the thermoplasmonic interface for neuron attachment, agarose hydrogel was patterned using micro-molding in capillary method to fabricate micro-sized square wells. On the patterned substrate, E18 hippocampal neurons were seeded and they connected each other only within individual agarose wells because of the repellency of the hydrogel for cell adhesion. At one or two weeks after cell seeding, agarose hydrogel was successfully melted by localized heat of GNRs under NIR illumination. Through the micro-sized channel produced by the melted agarose, the neurites extended from neuronal networks in agarose wells. We also show that the heat generated from GNRs can be used for inducing localized neurite damage by applying photothermal stimulation to neurites directly. NIR beam was focused on the neurites that grew along the melted agarose channel and local damage was observed at the illuminated spot. The developed method that can manipulate neurite outgrowth by photothermal stimulation even during the cultivation is expected to be useful for studying in vitro model of nerve injury and regeneration.
Hydrogels are attractive matrices for delivering mesenchymal stem cells (hMSCs) for cartilage repair given its injectability and tunable properties. However, conventional hydrogels often result in slow cartilage formation due to the time needed to degrade and remodel the original hydrogel network. Our group has recently reported sliding hydrogels with molecular mobility as a novel 3D cell niche, which is characterized by mobile crosslinks and biochemical ligands, and enable cells to reorganize biochemical ligands and protrude in 3D hydrogels. The goal of this study is to develop sliding hydrogels with tunable mobility and biochemical ligands to evaluate the effect of introducing molecular mobility and varying biochemical ligand types on modulating cartilage formation by MSCs in 3D. Previous studies show that HyA hydrogels support vascular network formation via optimized ligand density, heparin-mediated growth factor tunable mechanical and biological properties. Accordingly, we have developed HyA hydrogels to assess the effects of adhesion ligand presentation, matrix microdroplets of the pre-gel solution. The ejected microdroplets were solidified into hydrogel microparticles by crosslinking using ionic reaction, culture and tissue encapsulation for in vivo implantation. Here I introduce recent progress on simple centrifuge-based techniques for synthesizing 3D. While previous study has suggested that HAVDI incorporation into hyaluronic acid-based hydrogels enhanced chondrogenic differentiation and cartilage matrix production and deposition by MSC in 3D, MSCs were encapsulated in sliding hydrogels crosslinked by MβCDNecleopatide (COPGQIGWGC) to allow cell-mediated degradation. To assess the effect of varying ligand types in sliding hydrogels on MSC chondrogenesis, two types of biochemical ligands (1 mM) were incorporated into sliding hydrogels including CRGDS and N-cadherin mimicking peptide HAVDGGGC. Molecular mobility in non-degradable sliding hydrogels substantially accelerated and enhanced cartilage matrix deposition by MSCs in 3D. Incorporation of cell-mediated degradation synergized with molecular mobility, and further enhanced neo-cartilage formation throughout the hydrogels. Compared to no ligand control, CRGDS significantly inhibited the chondrogenesis of hMSCs, as shown by downregulations of cartilage markers as well as decreased SaGAG deposition in 3D. Our results validate sliding hydrogels as promising matrices for enhancing stem cell-mediated cartilage regeneration, and provide a materials tool to uncover the novel role of molecular mobility in modulating stem cell differentiation and tissue formation in 3D. Our group has recently reported sliding hydrogels with molecular mobility as a novel 3D cell niche, which is characterized by mobile crosslinks and biochemical ligands, and enable cells to reorganize biochemical ligands and protrude in 3D hydrogels. The goal of this study is to develop sliding hydrogels with tunable mobility and biochemical ligands to evaluate the effect of introducing molecular mobility and varying biochemical ligand types on modulating cartilage formation by MSCs in 3D. Future studies will further examine the effects of varying the types and density of mobile ligands on modulating chondrogenesis in 3D. Our results validate sliding hydrogels as promising matrices for enhancing stem cell-mediated cartilage regeneration, and provide a materials tool to uncover the novel role of molecular mobility in modulating stem cell differentiation and tissue formation in 3D. Acknowledgements: This work was supported by the National Research Foundation of Korea grant (NRF-2015R1A2A1A0003605, NRF-2018R1A2A1A05022604, NRF-2016H1A2A1907681) funded by Korea government (MSIP).
formation in more complex 3D angiogenesis models.


11:45 AM BM04.04.10
Long-Term Maintenance of an Mesenchymal Stem Cell Niche Through Self-Assembly of Injected Monodisperse Hydrogel Particles into a Microporous Scaffold

Jaekyung Koh1, Donald Griffin2, An-Chieh Feng3, Thomas Horn1, Michael Margolis1, Hamed Haddadi1, Tatiana Segura5, Philip Scumpia1 and Dino Di Carlo1, 2; 1Department of Bioengineering, University of California, Los Angeles, Los Angeles, California, United States; 2Department of Biomedical Engineering, University of Virginia, Charlottesville, Virginia, United States; 3David Geffen School of Medicine, University of California, Los Angeles, Los Angeles, California, United States; 4Jonsson Comprehensive Cancer Center, University of California, Los Angeles, Los Angeles, California, United States; 5Biomedical Engineering, Duke University, Durham, North Carolina, United States. Rate of migration and proliferation of BMSCs into microporous scaffolds could be modulated by adjusting mechanical properties. The scaffold made from these monodisperse (CV < 5%) particles yielded increased expansion and retention of embedded MSCs. Therefore, this new class of injectable microporous biomaterial should accelerate the development of stem cell therapies by creating an injectable microenvironment for self-renewal and expansion.

Mesenchymal stem cell (MSC) therapies hold promise for numerous intractable diseases arising from their immunosuppressive and tissue repair properties. However, systemic administration, the most common delivery method in clinical settings, suffers from poor survival and engraftment of transplanted stem cells. Moreover, loss of stem cell properties of the engrafted cells due to the unique environment in regenerating tissue can decrease therapeutic effects. Local delivery of MSCs using biomaterial has shown promising results. Ideal materials should deliver cells in a minimally invasive manner, enhance viability during and after transplantation as well as creating a microenvironment that stimulates self-renewal and expansion. Naturally-derived extracellular matrix (ECM) components, including Matrigel, have been applied but their high variability potentially impacts the reproducibility of the therapy. Artificial hydrogels with a high degree of tunability enable reliable and precise control of biophysical properties. However, the nanoscale porosity confines cells, thus interfering with migration, proliferation and cell-cell communication. Introduction of microscale porosity (e.g. through introduction of porogens) often compromises the ability to modulate mechanical properties and injectability of the hydrogel scaffold independently.

Here, we describe the development of an injectable microporous stem cell niche using microfluidically-generated monodisperse modular hydrogel particles. Delivered with MSCs, these particles are enzymatically assembled in situ, generating a highly-controlled interconnected microscale pore space, where cells can easily migrate and proliferate, leading to enhanced survival of transplanted cells. Moreover, the properties of the particles, including stiffness, degradability and cell binding motif concentration, can be modulated independently. By modulating these properties, the microporous scaffold can mimic the natural ECM for high maintenance of stem cell properties.

The scaffold made from these monodisperse (CV < 5%) particles yielded increased expansion and retention of embedded MSCs in vitro and in vivo. The diffusivity through the scaffolds for small molecules (0.3kDa) and large proteins (70kDa) was 70% and 40% respectively of that through pure buffer. Bone-marrow-derived C57BL/6 mouse MSCs incorporated in the scaffold expanded at a rate 7-fold faster than cells in the nanoporous scaffolds over the course of two weeks. The retention of subcutaneously injected MSCS in vivo was 4-8 times higher than with the nanoporous scaffold or PBS over a two-week period. We also demonstrated that scaffolds with 2.5kPa modulus and 2.5mM RGD concentration particles showed the highest retention of stemness of MSCS. Therefore, this new class of injectable microporous biomaterial should accelerate the development of stem cell therapies by creating an injectable microporous niche that enhances function.

SESSION BM04.05: Polymeric Biomaterials for Regenerative Engineering I
Session Chairs: Guillermo Ameer and Junji Fukuda
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Independence West

1:45 PM *BM04.05.01
Nanoengineered Biomaterials for Regenerative Medicine

Akhilesh K. Gaharwar; Texas A&M University, College Station, Texas, United States.

Two-dimensional (2D) nanomaterials have gained unprecedented attention due to their unique atomically thin, layered, and well-defined structure. As the dimensions of 2D nanomaterials are only a few nanometers thick, they interact with biological moieties in a unique way and have raised exciting questions about their interactions with cellular components. We have used next-generation sequencing technology (RNA-seq) to understand the effect of a synthetic 2D nanomaterials (nanosilicates) on human stem cells at the whole transcriptome level. Our results identify more than 4,000 genes that are significantly affected, and several biophysical and biochemical pathways that are triggered by nanosilicates treatment. This approach in understanding nanosilicates-cell interactions, illustrates how change in transcriptomic profile can predict downstream effects following nanomaterial treatment. Based on our transcriptomic data, we will demonstrate the application of nanosilicates towards bone and cartilage tissue engineering. The high surface area and charged characteristics of 2D nanomaterials is leveraged for sustained and prolonged delivery of pro-angiogenic molecules to stimulate angiogenesis. We have also evaluated the application of nanosilicates in the emerging field of 3D bioprinting to print complex organ and tissue.

2:15 PM BM04.05.03
Hybrid Nanogels with Self-Integrated Plasmonic Nanoparticles for Light-Induced Molecular Delivery

Seungki Lee, Jung A Kwon, Yunjeong Lee, Hyo Sil Kim, Chang Min Jin and Inhee Choi; University of Seoul, Seoul, Korea (the Republic of).

Nanoscaled hydrogel (nanogels) have drawn much attention as one of the promising materials in developing drug delivery system. Owing to superior water swelling property, nanogels are profitable to load large amounts of molecules including drugs, growth factors, and genes. Recently, many efforts have been made to develop hybrid nanogels which exhibit multi-functions and stimuli-responsive characteristics as well as encapsulation of the molecules. Herein, we present a novel method for synthesizing light (or heat)-responsive hybrid nanogels composed of biocompatible polymers, plasmonic gold nanoparticles, and thermo-responsive linkers (e.g., N-isopropyl acrylamide or N-vinylcaprolactam). We systemically characterize the physicochemical properties including size, shape, surface functionality, and light and thermo-responsive properties. By using the optimized hybrid nanogels, we demonstrate light-induced releases of the encapsulated molecules via photothermal-conversion effect of the embedded gold nanoparticles. Furthermore, we achieve the successful light-induced molecular delivery into the live cells. We envision that the proposed light-responsive hybrid nanogels would be beneficial materials in developing new drug delivery systems and further applying to regenerative engineering.

2:30 PM BREAK

3:30 PM *BM04.05.04
Optical Cell Manipulation Using Biomaterial-Based Photodegradable Hydrogels

Shinji Sugiuira; Biotechnology Research Institute for Drug Recovery,

States; 2Department of Biomedical Engineering, University of Virginia, Charlottesville, Virginia, United States; 3David Geffen School of Medicine, University of California, Los Angeles, Los Angeles, California, United States; 4Jonsson Comprehensive Cancer Center, University of California, Los Angeles, Los Angeles, California, United States; 5Biomedical Engineering, Duke University, Durham, North Carolina, United States.

Here, we describe the development of an injectable microporous stem cell niche using microfluidically-generated monodisperse modular hydrogel particles. Delivered with MSCs, these particles are enzymatically assembled in situ, generating a highly-controlled interconnected microscale pore space, where cells can easily migrate and proliferate, leading to enhanced survival of transplanted cells. Moreover, the properties of the particles, including stiffness, degradability and cell binding motif concentration, can be modulated independently. By modulating these properties, the microporous scaffold can mimic the natural ECM for high maintenance of stem cell properties.

The scaffold made from these monodisperse (CV < 5%) particles yielded increased expansion and retention of embedded MSCs. Therefore, this new class of injectable microporous biomaterial should accelerate the development of stem cell therapies by creating an injectable microporous niche that enhances function.
We have developed a photocleavable crosslinker for preparing photodegradable hydrogels by means of a one-step mixing reaction between the crosslinker and biocompatible polymers. We could control the chemical property of the photodegradable hydrogel by choosing the base polymer. We could prepare the biomaterial-based photodegradable hydrogels, on which cells adhered, and in which cells were encapsulated. So far, we have demonstrated cell separation from three-dimensional culture environment, cell micropatterning, and perfusion culture in the microfluidic devices. These studies will create new opportunities as novel the cell manipulation technologies in science and industry.

4:00 PM *BM04.05.05
Promoting Endogenous Tissue Repair with Materials Tatiaba Segura, Duke University, Durham, North Carolina, United States.

We believe that all tissues in the body have the capacity to repair through local stem or progenitor cells, but that due to unfavorable environmental conditions during the normal healing process they are not able to do so. We investigate the engineering of materials to “unlock” the regenerative capacity of damaged or diseased tissue to promote repair. Our general strategy is to combine our biomaterials engineering with designing materials that promote the formation of a space filling vascular plexus that could serve as part of a reparative niche directly at the wound site. In addition, our materials are engineered to modulate the immune system to decrease scarring and remove inhibitors to regeneration. The idea is that this vascular plexus would lay the groundwork for the recruitment of endogenous stem cells located in the local tissue surrounding the damaged area and immune modulation would generate an environment that would foster repair rather than scarring.

4:30 PM BM04.05.06
Stress/Strain and Degradation Tests on Nanofibrous Scaffold for Cardiovascular Regeneration Amanda Kennell, Anthony Brayer and Andrei Stanishevsky, University of Alabama in Birmingham, Birmingham, Alabama, United States.

Cardiovascular disease-related mortalities are predicted to rise to 23.3 million per year worldwide by 2030 [1] with the main cause being cardiovascular diseases (CVD) [2]. The current procedures to correct CVD are time consuming, because a surgeon needs a healthy artery to perform bypass surgery which is not readily accessible. However, if hospitals had a healthy blood vessel scaffold in storage the patient’s recovery time would decrease. Such a scaffold must be biodegradable, easily manufactured, and environmentally safe. To make this scaffold, AC electrospinning is used to create nanofibrous sheets (NFs) from a base polymer solution (fish skin gelatin, FSG). Additions of polysaccharides (Chitosan and Cellulose) are added in to strengthen the scaffold. These NFs are then thermally crosslinked and placed in synthetic body fluid (SBF). In increments, over a period of 3 weeks, the NFs sheets are removed to test their degradation and strength. Preliminary data has shown these NFs to last for two weeks in SBF at 37°C. These NFs were able to withstand a range of applied forces from 30 to 70mN at 80%-100% elastic deformation which translates into 0.15-0.85MPa. To increase the NFs strength a larger percentage of polysaccharides is being used. These NFs will further be seeded with endothelial cells. These NFs meet the requirements for the blood vessel scaffold. They are a “green” scaffold (made from an aqueous solution), easily manufactured (AC electrospinning is a “high yield” technique, 15-30g/h productivity), and “biodegradable”. It is expected that these nanofibrous tubular scaffolds will help reduce the mortality rate, patient recovery time, and need for organs at a lower price and higher acceptance rate. Further studies in vitro and in vivo are planned to evaluate the feasibility of the approach.


4:45 PM BM04.05.07
Short-Term Evaluation of Antithrombogenicity of a PMPC-Grafted PEEK Mechanical Heart Valve in a Porcine Aortic Valve Replacement Model Yusuke Kambe1, Atsushi Mahara1, Kyoko Fukazawa2, Yihua Liu3, Kazuhiko Ishiha2 and Tetsuji Yamaoka1; 1Department of Biomedical Engineering, National Cerebral and Cardiovascular Center Research Institute, Suita, Japan; 2Department of Materials Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Japan.

Improved antithrombogenicity of mechanical valves is desired to decrease the risk of thromboembolism and thrombosis and to reduce the dosage of anticoagulation with a vitamin K antagonist (e.g., warfarin). For several mechanical valves, design-derived features are responsible for their improved antithrombogenicity. However, it remains unclear whether material-derived features provide a practical level of antithrombogenicity of mechanical valves. Here we studied the effect of a bileaflet valve made of poly(ether ether ketone) (PEEK) with a poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC)–grafted surface (PEEK-g-PMPC). PEEK has a benzophenone-like structure in its unit, where radicals can be generated by photoirradiations. Thus, PMPC, which is a well-known antithrombogenic polymeric material, was directly graft-polymerized on the PEEK valve surface by a 27-mN/cm² ultraviolet light irradiation at 60°C for 30 min. Surface characterization, such as Fourier-transform infrared analysis, X-ray photoelectron spectroscopy, and transmission electron microscopy, showed the existence of a 250-300-nm thick PMPC layer on the PEEK-g-PMPC valve surface. Porcine aortic valve replacements were conducted using neither an anticoagulant nor an antiplatelet agent and the animals were observed up to 26 h. It was shown that the PEEK-g-PMPC valve opened and closed normally with an allowable transvalvular pressure gradient. Unlike an untreated PEEK valve, no thrombus formed on the PEEK-g-PMPC valve because fibrous fouling was still observed on the leaflet. The authors thank Prof. Hiroshi Tanaka, Prof. Kenji Minatoya, Dr. Sachiro Kakinoki, and Dr. Masayuki Kyomoto for their assistance.

BM04.04.06.01
Enhanced Cell Adhesion on N-Cadherin Modified Graphene Oxide Stimulates Neuronal Growth and Intracellular Transport Ellen Qin1, Mikhail
In the nervous system, cell-cell contacts are predominantly mediated via the homophilic interactions between N-cadherins on adjacent cells. Recombinant N-cadherin molecules are often attached to cell culture substrates via physical adsorption to recapitulate the neural environment. However, those methods typically involve more complicated surface chemistries or result in poor cell adhesion. To address this issue, we hypothesized that the additional noncovalent interactions of graphene derivatives with proteins would enhance the specific activity of immobilized recombinant N-cadherin. Results showed a substantial enhancement of neural cell adhesion on recombinant N-cadherin physisorbed on graphene oxide (GO) and reduced graphene oxide (rGO) relative to N-cadherin on glass, with improvements in the microstructure and physiological activity of neural networks. Biophysical measurements showed the mean adhesive force between AFM tips and N-cadherin coated GO or rGO flakes was ten times higher than that measured with N-cadherin physisorbed to uncoated glass. The latter behavior correlated with increased dendritic arborization and neural network formation on the GO- or rGO substrates, relative to cells on glass. Furthermore, intracellular mass transport was higher along the neurites on N-cadherin coupled to GO- or rGO-coated glass, as visualized using spatial light interference microscopy. The results of this study will be broadly useful for recreating active neural tissues in vitro and for improving our understanding of the development, homeostasis, and physiology of neural networks.

BM04.06.02
Proliferation Acceleration of Mesenchymal Stem Cells on Nanostructured Surfaces Hyeji Park and Jin Seok Lee; Sookmyung Women’s University, Seoul, Korea (the Republic of).

Biophysical properties of the microenvironment, such as nanotopography, modulate proliferation and differentiation of stem cells. Cells directly probe and respond to the physicochemical properties of their extracellular environment through adhesion complexes. Many previous studies have been investigated cell behavior such as cell adhesion, spreading area, cell proliferation, and migration using various topographical cues and the results have indicated topographical confinement by nanostructured architecture affects cellular behavior significantly. Up to date, overall control of cellular response has been carried out by cell isolation in the structure through geometry. However, there is little research about the effect of surface topography on cellular behavior. It is essential to study the surface topography by controlling the size, shape and density of the nanostructure.

In this study, we investigated the effects of the nanostructured silica bead arrays on cellular behavior, particularly proliferation. Human mesenchymal stem cells (hMSCs) were selected to investigate the nanotopological effects on cell proliferation. In the first step, the silica beads were synthesized by Stöber Method by controlling the amount of reagents or injection rates. The silica bead arrays can be achieved by utilizing a rubbing method, which is simple and fast, to obtain a monolayer of silica beads with various diameter sizes from 200 nm to 1900 nm. In the second step, the hMSCs were seeded onto the flat glass and silica bead arrays and then cultured for 24 hours to figure out the nanotopological effect on the cellular behavior. The results have shown that the cell spreading areas and proliferation on the different nanotopological substrates were significantly different. This paper will discuss how the silica bead arrays influence hMSC cellular behavior and optimize cell proliferation within the system. This study could be extended to serve as a model for stem cell therapy in terms of cell proliferation.

BM04.06.03
Skin-Penetrating Peptide-Based Micelle for Transdermal Drug Delivery Do Hyun Bae1, Yong Ho Kim2,3, Jin-Chul Kim2 and Ki Sung Kang4; 1Department of Biomedical Engineering, Sungkyunkwan University, Suwon-si, Korea (the Republic of); 2SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon-si, Korea (the Republic of); 3Natural Products Research Institute, Korea Institute of Science and Technology, Gangneung-si, Korea (the Republic of); 4College of Korean Medicine, Gachon University, Seongnam-si, Korea (the Republic of).

Transdermal drug delivery has been extensively studied to overcome the enzymatic degradation of drugs delivered via oral administration because it not only passes metabolic digestion passage, but also has a possibility to sustain the release of drugs. However, low permeability of stratum corneum inhibits deep penetration of drugs into target area and reduces percutaneous adsorption of drugs. Therefore, a new carrier system that can efficiently transport drugs into the stratum corneum would greatly enhance transdermal drug administration. Here, we demonstrated a formation of skin-penetrating peptide-based micelle for efficient transdermal drug delivery. Skin-penetrating peptides (SPPs) can be used as an excellent transdermal drug transporter due to its biocompatibility and exceptional cell-penetrating ability. We examined various cell-penetrating peptides (CPP) that adapt adsorptive-mediated transcytosis to verify their skin-cell permeability and identified one CPP that showed high cellular uptake inside the dermal papillae cells. The newly discovered SPP was further modified by conjugating an aliphatic chain at the N-terminal of the peptide to induce self-assembly for lipopeptide-based micelle formation. The micelle was found to achieve enhanced thermodynamic stability compared to SPPs only, which suggests that it can maintain its conformation in biological condition. The self-assembled micelle could securely encapsulate the minoxidil, a drug for hair regeneration, and increased cellular uptake of the drug into the dermal papillae cells. We believe that our new transdermal drug delivery system can be applied in the field of cosmetics and pharmaceuticals to increase skin administration efficiency of functional components.

BM04.06.04
RF Coupling of Interdigitated Electrode Array on Aerogels for In Vivo Nerve Guidance Applications Jacob Hadley, Jack Hirschman, Bashir Morshed and Firozeh Sabri; University of Memphis, Memphis, Tennessee, United States.

Aerogels are light-weight porous materials that can tolerate the processing steps required for designing and creating an interdigitated electrode (IDE) array using sputter coating with a shadow mask where the aerogel can be utilized as a substrate. Previous studies have shown the biostability and biocompatibility of polyurea crosslinked silica aerogels both in vivo and in vitro and have demonstrated the potential use of aerogels in biomedical applications. In vitro studies have shown that in the presence of an applied electric field neurites regeneration rate was greater on crosslinked silica aerogels than on tissue culture petri dishes that served as control. Currently, Epineural suturing and nerve grafting are the gold standards for surgical reconstruction of severed nerves. However, because these techniques rely on passive mechanisms for reapproximating the distal and proximal terminals they often lead to partial or limited recovery leaving room for improvement. The present study investigates the feasibility of a wireless aerogel –based electrically-stimulating implant intended for nerve repair applications. Here the authors report on a transcutaneous RF coupling between a primary coil (external) and a secondary coil (internal) connected to an IDE array consisting of eleven interdigitated fingers, created on a silica aerogel substrate. The coupling strength was tested using sputter coating with a shadow mask where the aerogel can be utilized as a substrate. Previous studies have shown the biostability and

BM04.06.05
Nanostructured Biomaterials for Functional Neurons Debika Debnath1, Krishnan Gopal Jain1, Manu Dalela1, Sonali Rawat1, Amtoj Kaur1, Neha Kaushik1, Ankarao Kalluri1, Bhushan Dharmadhikari1, Prabir Patra1 and Sujata Mohanty1; 1Stem Cell Facility, All India Institutes of Medical Sciences, New Delhi, India; 2Biomedical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States; 3Electrical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States.
We fabricated Polycaprolactone-graphene (PCL-G) biomaterials scaffolds by stretching graphene dispersed viscoelastic PCL solution uniaxially under an applied voltage with an aim to provide microenvironment in vitro for differentiation and proliferation of functional neurons from mesenchymal stem cells (MSCs). Varied amount of graphene (0.05 - 0.5 wt percentage of graphene) was dispersed in PCL matrix for scaffold formation. We induced MSCs to differentiate into neurons by taking advantages of topological and electrical effect of scaffold, and biochemical effect of FGF2 and Oxyester. SEM images of PCL-G scaffolds were taken to study the effect of the scaffolds on cell morphology. We performed confocal imaging to confirm differentiation of MSCs into neurons. Confocal images of Vinculin and FAK on MSC grown on scaffolds were observed. We measured Contact angle of water on scaffolds to determine hydrophobicity and hydrophilicity of scaffold. Calcium ions being the most important ions for regulating biological processes we did the Ca2+ ion imaging. Cell culture and in vitro cell adhesion studies showed that PCL-G scaffolds was most effective for promoting stem cells adhesion and spreading. Microscopic images show that the PCL-G fibers are structurally similar to ECM proteins like collagen, laminin and fibrils. This work also demonstrates the key role of graphene in aligning neurons. With its optimum dose as 0.05 wt percentage as filler in composite scaffolds significantly provides permissive surfaces for protein and cell adhesion as well as electrically stimulate axon growth that increases over all biological responses. Thus, we envisaged that such a platform could serve as a powerful tool for developing future therapies for any diseases and injuries of the spinal cord.

BM04.06.06
Pulsed Laser Deposition and Biocompatibility of Titanium Nitride Coatings Meenakshi Singh1 and Svitlana Fialkova2; 1STEM Early College at NC A&T, Greensboro, North Carolina, United States; 2Mechanical Engineering, North Carolina Agricultural and Technical State University, Greensboro, North Carolina, United States.

The purpose of this study is to evaluate the effect of Titanium Nitride (TiN) thin films deposited on magnesium substrates using a pulsed laser deposition method. The application of a TiN coating on magnesium implants has the potential to remove the necessity for a second surgery for patients undergoing the process of healing. The coating developed has been shown to help reduce the degradation rate of the magnesium implant such that the Mg would remain stable for the time required for healing before beginning to degrade. Magnesium was chosen as a substrate due to its biocompatible and biodegradable properties. TiN was chosen due to its stellar properties of high hardness, good diffusion barrier, high hardness and good electrical conductivity, and scattered reports in the literature about its biocompatibility. The crystallographic orientation and surface morphology of the films were studied using X-ray diffraction (XRD) and scanning electron microscope (SEM). The hydrophilic nature of the films was investigated using contact angle measurements. Preliminary results on the biological behavior of the TiN coated Mg substrates suggest that TiN is a biocompatible material and has great promises in biological applications.

BM04.06.07
Magnetic Nanoparticles as a Therapeutic Biomaterial in Magneto-Ultrasonic Hyperthermia Arkadiusz Jozefczak, Katarzyna Kaczmarek and Tomasz Hornowski; Institute of Acoustics, Adam Mickiewicz University, Poznan, Poland.

In medicine, a controlled increase in temperature up to 41–45°C is called hyperthermia. It induces heat in cancer cells which leads to their weakening. Weakened cells are therefore more susceptible to radiotherapy or chemotherapy. The heating can be induced by means of ultrasonic waves or magnetic field. The effectiveness of ultrasound therapy can be significantly improved by using so-called sonosensitizers, for example, magnetic nanoparticles that locally increase the attenuation of the ultrasonic wave [1]. Magnetic particles can also be used for selective induction of heat by an externally applied alternating magnetic field (AC) [2]. Recently, there has been a great interest in the application of multimodal thermal treatments. Magnetic and ultrasonic hyperthermia may work synergistically to produce a more efficient treatment. This sonomagnetic therapy is a promising new technique based on the synergistic interactions of ultrasound and AC magnetic field. The presence of magnetic nanoparticles also improves contrast in both ultrasonic and magnetic resonance imaging, which facilitates control of temperature during hyperthermia therapy. Magnetic nanoparticles can act as theranostic nanoparticles.

In the study, we have focused on evaluating the influence of magneto-ultrasonic heating on phantom temperature in the presence of superparamagnetic iron oxide nanoparticles (SPION). The experiments are performed with the use of agar tissue mimicking phantoms doped with magnetic sonosensitizers. Integrated treatment by means of simultaneous application of a focused ultrasound wave and alternating magnetic field (bimodal sonomagnetic hyperthermia) leads to a higher temperature increase, which enables more precise control over the heating process. Magneto-ultrasonic heating creates very innovative, promising approach which has an application potential to treat cancer at a lower SPION concentration. We demonstrate that bimodal stimulation of nanoparticles provides better heating efficiency.

References:

BM04.06.08
Antibacterial Coating on Contact Lens Using Polyethyleneimine Based Polymers Suresh Kumar Raman Pillai, Yogesh Shankar Vikhe, Zheng Hou, Sheethal Reghu and M. B. Chan-Park; Nanyang Technological University, (NTU) Singapore, Singapore.

Microorganisms such as bacteria that grow on the surface of contact lenses cause irritation to the eyes. These infections that are difficult to treat and can cause to vision loss. Besides the availability of new contact lens materials and better cleaning solutions, the risks of the above conditions remains the same for many years. Silver coating have been commonly studied, but the material can leach out of the lenses and their antimicrobial effect fades over time. In this report, we have synthesized PEI-PEGMA polymer and used for the application of an antimicrobial coating on contact lenses in order to prevent bacterial infection and reduce the risk of extended wear. Different types of failures such as (1) reduction of coating adherence to the substrate of contact lens and (2) disintegration of interface between coating and substrate of contact lens exists. To improve coating formulations to resist failures caused by the applied normal load with fingers of users, monomer (3-Acrylamidopropyl) trimethyl ammonium chloride (AMPTMA) or [2-(Methacryloyloxy) ethyl] dimethyl-(3-sulphopropyl) ammonium hydroxide (SBMA) was added to the antimicrobial polymer PEI-PEGMA.

Two different coating strategies were adopted to form PEI-PEGMA-AMPTMA or PEI-PEGMA-SBMA polymeric film on the surface of the contact lens. In the first method, the silicone contact lenses were treated with ozone to activate the surface and form the peroxide groups. Vanadate solutions of PEI-PEGMA and AMPTMA/SBMA dissolved in DI water and degassed the solution using Argon for 45 min. The contact lenses were immersed into the solution and the radical initiation polymerization reaction was activated by the addition of Ammonium iron(II)sulfate. The polymerization reaction was carried out at 37°C for 24 hrs. The lenses were thoroughly washed with DI water and isopropanol (IPA) before doing the antibacterial testing. Antimicrobial activity of the coated lenses were tested with 1x 10^6 CFU of Methicillin-resistant Staphylococcus aureus (MRSA). The coated contact lenses were found to be effective for antibacterial activity with killing rate > 99.9 % and log reduction of 3.20. Cell viability for the coated lenses were found to be 80 % using MTT assay protocol. In the second method, the radical initiation was activated thermally. The lenses were treated with ozone to form peroxide group on the
Sub-Compartmentalized Microreactors as Cell Implants for Conducting Enzymatic Cascade Reactions


Could regenerate the arterial vascular tissue in three months. and αSMA positive cells existed as same as the results for three month transplantation. Although the cell density in media layer was sparse as compared and Flk-1. For evaluation of the medium layer, the tissue was stained with antibody against α-smooth muscle actin (αSMA)

Graft was extirpated. Luminal surface was evaluated by histological staining using HE, vWE, as well as primary antibody against CD31, CD34, CD105, and CD105, and Flk-1. For evaluation of the medium layer, the tissue was stained with antibody against α-smooth muscle actin (αSMA).

Thus, herein, with the aim to design a highly-sophisticated artificial organelle we present a carrier containing multiple compartments consisting of polymeric capsules entrapping thousands of liposomes and gold nanoclusters. Liposomes are chosen as the subcompartments since, by means of their lipid bilayer which makes them biomimetic, are ideal candidates to encapsulate fragile biomolecules such as enzymes protecting them from misfolding or degradation in the bloodstream and then from the intracellular degrading contents, will greatly diminish current limitations of enzyme replacement therapy. However, the delivery of enzymes has been proven so far very challenging and, thus, so far it has shown very limited success. The reason being that enzymes are very fragile entities prone to degradation in the bloodstream. This fact makes them difficult to reach the target site, which is usually a diseased cell, and remain active for a reasonable amount of time. Thus, the creation of artificial organelles encapsulating enzymes that will protect them first from degradation in the bloodstream and then from the intracellular degrading contents, will greatly diminish current limitations of enzyme replacement therapy. Biological organelles operate by conducting multiple sets of (enzymatic) reactions with high specificity and accuracy without cross-contamination. They can separate multiple functions while protecting internal contents thanks to compartmentalization. This compartmentalization can be clearly seen in the Golgi apparatus or the mitochondria, where several enzymes for the citric acid cycle are situated in the intermembrane space. Thus, herein, with the aim to design a highly-sophisticated artificial organelle we present a carrier containing multiple compartments consisting of polymeric capsules entrapping thousands of liposomes and gold nanoclusters. Liposomes are chosen as the subcompartments since, by means of their lipid bilayer which makes them biomimetic, are ideal candidates to encapsulate fragile biomolecules such as enzymes protecting them from misfolding or denaturation. The polymer carrier shell possesses the structural integrity and it is able to protect the liposomes from degradation and the gold nanoclusters, thanks to their fluorescent properties, allow us to detect and tract the artificial organelles inside the host cell. We demonstrate preservation of functionality of our artificial organelles by encapsulating two different enzymes within different liposomes and conducting an enzymatic cascade reaction inside the cell. In particular, artificial organelles loaded with the enzymes glucose oxidase (GOx) and horseradish peroxidase (HRP) are internalized by macrophages. Next, upon incubation with D-glucose, it gets converted by GOx into D-glucuronolactone and hydrogen peroxide. The latter is utilized by HRP to convert the Amplex Red probe into the fluorescent product resorufin which is detected by fluorescent spectroscopy to confirm that the enzymatic cascade reaction has successfully taken place.

In-Flow Preparation of Collagen Sheets with Tunable Fibril Alignment for the Engineering of Arterial Substitutes That Recapitulate Blood Vessel Microstructure

David Miranda-Nieves1, 2, Shashi Malladi3, Daniel Wong1, Constantine Tarabaris1, Carolyn Hailer3, Axel Gruenther4 and Elliot Chaikoff1, 2; 1Massachusetts Institute of Technology, Boston, Massachusetts, United States; 2University of Toronto, Toronto, Ontario, Canada; 3Harvard University, Boston, Massachusetts, United States.

Lower extremity peripheral arterial disease (PAD) affects up to 15% of the population over 65 years old. The number of endovascular and bypass operations has doubled in the past decade, yet outcomes after surgical and catheter-based interventions remain compromised with low complication rates. Tissue-engineering strategies have been explored as alternatives; however, no clinically available graft exists. The main limitation of most approaches is failure to recapitulate the blood vessel microstructure, and, as a consequence, native physiological properties. Considering that the arterial wall is a circumferentially aligned fibrous matrix, the capacity to create highly structured, oriented structures is critical for the generation of physiologically responsive arterial substitutes. Over the years, various methods have been designed to influence the organization of self-assembling collagen fibrils, including the use of magnetic fields and fiber spinning. However, none of these approaches represent a one-step, scalable technique for the generation of collagen films with precise control over fibril orientation. Here, we present a solution that leverages molecular crowding and hydrodynamic focusing to fabricate ultrathin collagen sheets with tunable fibril alignment and mechanical properties, and our initial attempts to engineer arterial substitutes using these sheets.
Monomeric rat-tail tendon collagen was dissolved in 10 mM HCl, and injected into the middle layer of a multilayered, PDMS-based microfluidic device at varying flow rates. As shear flow, a polyethylene glycol (PEG) solution was used. The presence of PEG caused molecular crowding, which triggered the gelation of the collagen solution. Hydrodynamic focusing was achieved by modifying the flow rates of the two solutions.

Extruded collagen sheets had thicknesses of 3-8μm and widths of 15-30 mm. The degree of alignment and compaction of the collagen fibrils was controlled, with up to 40% of fibers aligned within ± 5° of one another, and up to 95.5% of compaction. As a result, ultimate tensile strengths of 1.25-13MPa, Young’s moduli of 1.3-130MPa, and strains to failure of 15-55% were achieved. Molecular alignment of the collagen sheets induced preferential alignment of vascular smooth muscle cells (VSMC), maintained cellular expression of phenotype markers, and guided active film contraction.

Efforts involving the controlled assembly of the ultra-thin, robust, anisotropic collagen sheets seeded with VSMC have yield arterial constructs with circumferential collagen fibrils and high density of VSMC that closely recapitulate native blood vessel microstructure. Biomechanical characterization has revealed that the constructs can withstand high pressures and tensile strengths. Ultimately, we believe that these biological and mechanical properties will translate to the mimicry of physiologic responses in vivo.

BM04.06.12
DMD Printed Scaffold for Vascularized Tissue Roya Samanipour1-3 and Mina Hoorfar; 1 Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 2 University of British Columbia, Vancouver, British Columbia, Canada.

In this paper, we developed a high resolution stereolithography-based bioprinter (DMD printing) to fabricate micron size of vasculature using CT images. The development of in-vitro highly organized-vascularized three-dimensional (3D) complex constructs is of great importance in tissue engineering. While several microfabrication strategies (ranging in micromolding, photolithography, stereolithography, and bioprinting,) have been used, these technologies lack the spatial control for the formation of complex vascular networks. Current 3D bioprinting techniques cannot provide the required printing resolution, throughput, and complex and biomimetic microarchitectural features. Here, we developed a DMD (Digital Mirror Device) 3D printing technology platform capable of rapidly fabricating tissue constructs with smooth features and high cell viability. DMD 3D printing was developed to fabricate variety of microscale resolution vascularized tissue. Blended prepolymer solutions consisting of varying ratios of GelMA (synthesized by the method described by Cha et al [3]) and polyethylene glycol diacrylate (PEGDA, M₄₇00, Sigma Aldrich) with LAP photoinitiator (Sigma Aldrich) were tested to optimize the polymer composition for printing. To ensure proper material properties needed to withstand subsequent perfusion, mechanical testing of the different prepolymer formulations was performed using a CellScale MicroSquisher system (Waterloo, ON, Canada). The optimized optimized polymer composition of 7.5 wt % GelMA+10 wt % PEGDA 700+25 LAP was used to 3D print 310 um microchannels with fine structural features. Afterwards, Human umbilical vein endothelial cells (HUVECs, Lonza, Portsmouth, NH) were injected into microchannel to create entheselial microchannel construct. To create a uniform monolayer of cells, the whole construct was manually rotated every 1.5 hours after the HUVECs-laden polymer solution was injected into the channel. The seeded cells into the printed structure were cultured for 14 days. The F-actin-Dapi was performed on the cultured samples on days 7 and 14. The CD31/Dapi was performed on the cultured samples on days 7 and 14. The results show that the endothelial cells proliferated and uniformly covered the microchannel. PrestoBlue assay was performed to assess proliferation on days 1, 3, 7, 10 and 14.

References:

BM04.06.13
Block Copolymer Nanoparticles Remove Biofilms of Drug-Resistant Gram-Positive Bacteria by Nanoscale Bacterial Debridement M. B. Chan-Park; Nanyang Technological Univ, Singapore, Singapore.

Bacterial biofilms are the main cause of chronic infections and typically 1000-fold more resistant to conventional antibiotics and/or antimicrobial agents. Hence, many antibiotics, natural antimicrobial substances and synthetic antimicrobial agents fail to eradicate biofilms. Besides, various antibiofilm agents such as metallic or inorganic nanoparticles have shown the ability to remove biofilm, but they are usually suffered from the problem of toxicity and limited life span. In this paper, we developed a novel antibiofilm polymer nanoparticles which showed excellent preformed antibiofilm dispersal ability with non-hemolytic in vitro and low in vivo cytotoxicity. This polysaccharide-based polymer can self-assemble into nanoparticles which can effectively remove biofilms of multi-drug resistant clinically relevant Gram-positive bacteria (i.e. Methicillin-resistant Staphylococcus aureus (MRSA), Vancomycin-resistant Enterococcus (VRE) and Enterococcus faecalis (OG1RF)), with efficacy superior or comparable to that of current standard antibiotics. Interestingly, the antibiofilm property of these nanoparticles is not come from the antibacterial effect, but a new mechanism which we term “nanoscale bacterial debridement”. The nanoparticles can diffuse into biofilms and complex with bacterial surface. Further, its hydrophilic polysaccharide corona enhances the solvation of the bacteria/nanoparticle complex leading to detachment of bacteria from biofilm. Our in vitro data also shows the nanoparticles can remove the MRSA biofilm by 3.7 order of log reduction, compared to 2.1 order achieved by vancomycin antibiotic. Overall, this novel biofilm removal approach provides exciting opportunities for eradication of multi-drug resistant biofilm and which further may have widespread applications.

BM04.06.14
Short Aromatic Peptide Carriers for the Targeted Delivery of Cranberry Extracts Yasaman Hamedani, Elvira Lou Evangelista, Catherine Neto and Milana Vasudev; University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States.

In recent years, drug delivery using nanoparticles has gained attention due to their ease of synthesis, high effectiveness due to ease of uptake in cells, increased half-life in systemic circulation and the ability to target certain organs or group of cells. Such nanoparticles can be fabricated from natural or synthetic biopolymers, and lipids. Peptide-based nanoparticles are potential candidates as nanocarriers for the enclosure of various drugs. Peptides have complex structures and biological recognition abilities. Hydrophobic interactions, hydrogen bonding and p-p stacking all lead to formation of stable structures via self-assembly. Depending on the conditions for synthesis, peptides can self-assemble into various structures such as nanotubes, nanofibers and nanospheres. In this study, we have demonstrated the self-assembly of tripeptides to form nanospheres through a process called electrospraying. By optimizing the electrospraying conditions, we were successfully able to form hollow peptide nanospheres which are suitable candidate for delivery of various drugs. Moreover, cationic amphiphilic peptide sequences were designed to form peptide-based micelles for encapsulating various therapeutic drugs. Scanning electron microscopy (SEM) as well as Transmission Electron Microscopy (TEM) techniques have been utilized to investigate the morphology of the fabricated spheres/micelles. Chemical characterization of the samples were performed using Fourier transform Infrared (FT-IR) and Raman spectroscopy. Cranberry extracted compounds such as flavonoids/polyphenols and triterpenoids are amongst the natural therapeutic compounds which recently have gained considerable attentions due to their effectiveness in prevention of cardiovascular, carcinogenic, neurodegenerative and immune
Bicontinuous interfacially jammed emulsion gels (“bijels”) can be used as templates to fabricate bijels-derived structures, which maintain the bicontinuous internal structure of bijels and hence possess unique properties for various applications. Bijels-derived structures are potential delivery vehicles for the controlled release of growth factors (GFs) in tissue engineering. To apply bijels-derived structures in tissue engineering, the biocompatibility requirement must be met but most existing bijels-derived structures are not biocompatible. Using biocompatible materials such as hydrogels may provide solutions for solving the problems. Bioactive molecules, particularly GFs, have been used in tissue regeneration. Vascular endothelial growth factor (VEGF) and platelet derived growth factor (PDGF) are often used in the regeneration of tissues such as skin and gastrointestinal tract. Controlled delivery of GFs through appropriate vehicles can promote tissue regeneration. This study investigated the fabrication and characteristics of hybrid hydrogels consisting of biocompatible materials made via bijels for VEGF and PDGF delivery. A modified solvent induced phase separation process was used to fabricate bijels-derived hybrid hydrogel membranes. A ternary liquid mixture was made by adding pure ethanol, hexadecylidocylcetate (HDA), 2-hydroxy-2-methylpropioophenone (HMP), deionized water, Ludox TMA (silica nanoparticle suspension) and CTAB in ethanol. A glass plate was immersed in the ternary mixture for forming a mixture film on its surface. It was taken out and then immersed in a water bath to form bijels membranes through phase transition. A high-intensity UV light was applied to cure HDA and harden the bijels structure. Then bijels films were immersed in VEGF- or PDGF-containing Na-alginate solutions, taken out and immersed in CaCl₂ solution for crosslinking, forming GF-containing bijels-derived hybrid hydrogel membranes. The bicontinuous microstructure in membranes could be clearly seen under SEM. UV-cured HDA polymer and crosslinked CA-alginate hydrogel formed two continuous phases in the membrane. The diameter of the bicontinuous structure (channel size) could be adjusted by UV-curing time and other parameters. In vitro experiments of as-fabricated hybrid hydrogel membranes, human dermal fibroblasts (HDF) were cultured on membranes whose biocompatibility was assessed using LIVE/DEAD assay. At Day 3, fibroblasts proliferated on membranes and nearly no cell death was observed. MTT assay was used to evaluate cell proliferation on membranes. Results showed good cell proliferation after 1, 2, 3-day culture. Following the established test protocol, the in vitro release behavior of VEGF and PDGF for bijels-derived membranes was studied. Steady and sustained releases of VEGF and PDGF were both seen within test durations. This study demonstrates the high potential of bijels technology in the tissue engineering field.

BM04.06.15
Delivery of Growth Factors via Bijels-Derived Hybrid Hydrogels
Haoran Sun and Min Wang; Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong.

In the present study, we demonstrate a rapid and low-cost method to prepare biomaterials with anisotropic, gradient micro-ridge/groove arrays having variable local pattern width. It was anticipated this study will demonstrate the ability of gradient micro-topographies to influence preferential neuronal adhesion and maturation, dendritic tree expansion, and synaptic network formation, providing a comprehensive understanding of the neuron-microenvironment interaction for the design of neuroregenerative devices.

The surface topography of biomaterials with specific spatial structure mimic the physical microenvironment of neurons, regulating their orientation and neurite outgrowth. However, most topographical structures used in neuron culture are fabricated with simple geometries. This necessitates bulk fabrication, which is both inefficient and laborious, while also increasing potential contamination. A single gradient micro-topographical device with variable geometries of a single orientation begins to ameliorate these issues, although few studies have examined the influence of linear micro-ridge/groove structures on synaptic network formation and dendritic tree structure.

The physicochemical properties of the prepared gradient micro-ridge/groove array were characterized by analyzing the surface morphology and wettability. The patterning structure and dimensions were confirmed to be intact through scanning electron microscopy and viable for cell contact. Additionally, cell adhesion was increased through surface treatment with poly-L-lysine and laminin. The chemical composition of the surface modification was verified through FTIR-ATR spectroscopy. Uniformity of the surface treatment was verified through fluorescent intensity of FITC-poly-L-lysine. Cell experiments were subsequently carried out using primary rat hippocampal neurons.

Immunofluorescent images of neurons in culture for 14 days revealed smaller pattern widths regulate neuron growth and increase orientation along the microtopography direction. Neurons cultured on these substrates demonstrate a preference to attach in areas of smaller pattern width. Additionally, cell somas located within a 5μm groove demonstrate heightened aspect ratios. Dendrites of these neurons extended less when introduced to a linear topography, decreasing their coverage area with respect to decreasing geometry. Preferential axon maturation was found to grow more within the groove as opposed to on top of each ridge. Finally, the density of synapses formed and relative protein expression significantly decreased in the presence of topography, with large increases when the geometry becomes smaller than the neuron soma. Thus, the effect of gradient micro-topography on neuron behavior was achieved and systematically understood by a one-step screening on a single integrated chip, lending itself to potential advances in the design of neuroregenerative micro-devices.

BM04.06.16
Gradient Micro-Topography for Morphological Control and Synapse Formation
Ryan McNaughton, Yuda Huo, Guicai Li, Hengye Man and Xin Zhang; Boston University, Boston, Massachusetts, United States.

Stem cells are sensitive to both chemical and mechanical changes in the environment, which proliferation and differentiation depend on three main factors: the type of stem cell, the underlying scaffold, and the signaling molecules added. It has been shown that stem cells isolated from the dental pulp (dental pulp stem cells (DPSCs)) can differentiate and express markers of odontoblasts, osteoblasts, adipocytes or neuronal cells when they are grown in specific inducing media. However, the external chemical inducers such as steroids can cause adverse side effects such as hyperglycemia and a weakened immune system in clinical studies. Therefore, we focus on engineering the underlying substrates to induce DPSCs differentiate along the desired pathway without external chemical inducers added. Titanium, a material used as dental implant, has shown to promote its osseointegration with specific surface treatment to manipulate its surface roughness and topography. Herein, we introduce a new method to fabricate titanium substrate by atomic layer deposition (ALD), which deposits a homogeneous 2~3nm thickness of titanium on silicon wafer substrates. Due to surface chemistry changed, DPSCs have shown to proliferate well on ALD titanium substrates compared to bare silicon surface. At week 4, mineralization were characterized by SEM/EDS and Raman microscopy.
spectroscopy. RT-PCR was also used to identify odontogenic and osteogenic differentiation markers. The results showed that biomineralized deposits (Ca/P) along with collagen fibers were observed on ALD titanium substrates, and RT-PCR results showed that osteocalcin (OCN) was upregulated from week 2 to week 4 but Dentin Sialophosphoprotein (DSPP) expression remained low over 4 weeks. It suggests that DPSCs growing on ALD titanium surface might induce them to differentiate along osteogenic pathway. The ALD method provides a fast and easy process to coat a homogeneous thin layer of titanium on the substrate, where only surface chemistry changes but which roughness and topography remain the same. This method could be a potential application to coat a thin layer on titanium on any biomaterial to further promote stem cells differentiation and proliferation.

We would like to thank the NSF-INSPIRE program (Grant #1344267.)

BM04.06.18
Substrate Mechanics in Combination with Nanoparticles Effects on Dental Pulp Stem Cells Proliferation and Differentiation Ya-Chen Chuang1,2, Chung-Chueh Chang2, Marcia Simon3, Miriam Rafaelovich1, Samantha Ying4 and Mindy Li5; 1Materials Science and Engineering, Stony Brook University, Stony Brook, New York, United States; 2ThINC Facility, Advanced Energy Center, Stony Brook, New York, United States; 3Oral Biology & Pathology, Stony Brook University, The State University of New York, Stony Brook, New York, United States; 4South Side High School, Hempstead, New York, United States; 5Princeton High School, Princeton, New Jersey, United States.

Stem cells are sensitive to both chemical and mechanical changes in the environment, which proliferation and differentiation depend on three main factors: the type of stem cell, the underlying scaffold, and the signaling molecules added. It has been shown that stem cells isolated from the dental pulp (dental pulp stem cells (DPSCs)) can differentiate and express markers of odontoblasts, osteoblasts, adipocytes or neuronal cells when they are grown in specific inducing media. In our previous study, we have shown that monodisperse polybutadiene (PB) can be used to produce biocompatible flat thin films with different surface mechanics by simply altering the film thicknesses where surface chemistry remains the same. We have also shown that DPSCs can sense and adjust their cell mechanics accordingly to the underlying substrate mechanics. In addition, without the addition of inducing media, dexamethasone, biomineralized deposits and up-regulation of osteocalcin (OCN) gene marker were observed on hard PB surfaces. In contrast, extremely low level of biomineralized deposits and OCN were observed on the softer PB surfaces. On the other hand, the rise of nanotechnology also promotes the study on the effects of nanoparticles (NPs) on stem cell and shows that nanoparticles can also offer a means of regulating cell function. However, stem cells are extremely sensitive to the extracellular signals where the stimuli from substrate mechanics and NPs should be studied simultaneously. Hence, in this study, we want to investigate how DPSCs proliferate and differentiate when both substrates mechanics and NPs cues were involved. Briefly, TiO2 NPs (0.1 mg/mL) were added post-plating onto soft and hard PB substrates after DPSCs fully attached. Cell proliferation and cell mechanics were measured at week 1 by hemocytometer and shear modulation force microscopy (SMFM). At week 4, biomineralized deposits were characterized by SEM/EDS and Raman spectroscopy. RT-PCR was also used to identify odontogenic and osteogenic differentiation markers. The results showed that with TiO2 NPs added, collagen fibers along with biomineralization were deposited on the substrates, and it showed up-regulation of OCN gene at the later stage of differentiation process no matter the substrate is soft or hard. The results suggest that TiO2 NPs override substrate mechanics effect and dominate DPSCs differentiation in this system, which could be a potential application for nanoparticles using as stem cell differentiation inducer.

We would like to thank the NSF-INSPIRE program (Grant #1344267.)

BM04.06.20
Non-Invasive Transdermal Photomedicine Using Hyaluronic Acid Derivatives Ki Sa Kim; Department of Organic Materials Science and Engineering, Pusan National University, Busan, Korea (the Republic of).

A variety of drug delivery systems have been investigated for high therapeutic efficacy via easy administration. Among them, transdermal delivery is presented as an attractive alternative to needle-based drug delivery because of patient preferences. Although transdermal microneedles are less invasive promising alternatives, needle-free topical delivery without involving physical damage to the natural skin barrier is still sought after as it can further reduce needle-induced anxiety and is simple to administer. However, this long-standing goal has been elusive since the intact skin is impermeable to most macromolecules. Also, the depth of light penetration in skin in photomedicine is a serious constraint on clinical applications. Here, we show an efficient, noninvasive transdermal delivery using Hyaluronic acid (HA) derivatives as carrier. For vaccine delivery, following topical administration in the skin, a model vaccine ovalbumin (OVA) and HA (HA–OVA conjugates) penetrated into the epidermis and dermis in murine and porcine skins, as revealed by intravital microscopy and fluorescence assay. Topical administration of HA–OVA conjugates significantly elevated both humoral and mucosal antibodies, with peak levels at four weeks. An OVA challenge at week eight elicited strong immune-recall responses. With pretreatment of the skin using non-ablative fractional laser beams as adjuvant, strong immunization was achieved with much reduced doses of HA–OVA.

In addition, we also developed implantable light-delivery devices using HA. With this light delivery system, we successfully demonstrated the facilitated photochemical tissue bonding (PTB) using hyaluronic acid (HA)–rose bengal (RB) conjugate and upconversion nanoparticle (UCNP). The UCNP emitting red and green light in the skin tissue by skin-penetrating near infrared (NIR) laser illumination could activate the RB dye and crosslink the collagen, inducing skin repair and deep tissue wound healing. Furthermore, hyaluronate–hollow gold nanosphere–adipocyte–targeting peptide (HA–HAuNS–ATP) conjugates will be presented for the photothermal ablation of adipose tissues.

BM04.06.21
Enhancing Biocompatibility of Tantalum via Anodization for Orthopedic Applications Ece Ush1,2 and Batur Ercan1,2; 1Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; 2BIOMATEN, Middle East Technical University, Center of Excellence in Biomaterials and Tissue Engineering, Ankara, Turkey.

Tantalum and its alloys have been investigated as the next generation of orthopedic implant materials in the last decade. Being a valve metal, tantalum forms a naturally occurring stable oxide layer approximately 3-5 nm on its surface at ambient conditions and this layer both prevents heavy ion release from the metal and provides a natural barrier for implant corrosion. In fact, due to its chemically inert nature, tantalum has the highest corrosion resistance of all metals used in orthopedic applications. Tantalum also exhibits higher fatigue properties compared to the currently-used implant materials. Despite having ideal properties for orthopedic applications, bioinert nature of tantalum surfaces, which limits osseointegration with the juxtaposed tissue, is the leading problem to be addressed before its widespread use in implants. To overcome this problem, surface modification of tantalum within nanoscale could be a potential remedy to enhance its bioactivity.

Anodization is an electrochemical process which produces oxide based nanofeatured surfaces on various metals. It gained popularity in the last decade due to its versatility in controlling biomaterial surface topology. In literature, it was shown that anodized nanostructured surfaces having different morphologies, topographies and feature sizes enhanced bone cell adhesion, proliferation and cellular functions in orthopedic applications. Specifically, anodized titanium and its alloys were well characterized to enhance cellular functions in vitro. However, there is very limited data on the anodization of
tantalum for orthopedic applications. In this study, tantalum samples were anodized using 1M H₂SO₄, 3.3 wt % NH₄F, 1:9 (v/v) concentrated and aqueous HF/H₂SO₄ solutions to obtain oxide based nanofeatures on its surface. Upon anodization, 4 different surface morphologies, namely nanodimple, nanotubular, nanoporous and nanocoral, were successfully obtained on tantalum surfaces. Furthermore, anodization duration (1min-4hr) and voltages (10-80V) were fine-tuned to control feature sizes between 25 to 140 nm for the nanodimple, nanocoral and nanoporous morphologies. Topographical investigations indicated higher nanophase surface roughness on anodized surfaces compared to as-received tantalum. Anodized samples also expressed enhanced surface hydrophilicity independent of the morphology and feature size. To investigate biocompatibility of the samples, osteoblast (ATCC CRL-11372) adhesion and proliferation were examined up to 7 days of culture. Results indicated enhanced cellular functions on nanodimple, nanocoral and nanoporous morphologies compared to non-anodized surfaces. Furthermore, immersing these samples into simulated body fluid up to 1 month showed enhanced bioactivity of these surfaces compared to non-anodized tantalum. In conclusion, surface modification of tantalum via anodization could be a potential way to enhance biocompatibility of tantalum for orthopedic applications.

**BM04.06.22**

Suppression of Platelet Adhesion on Decellularized Vascular Graft by High Density REDV Peptide Immobilization

Kentaro Kojima1, Atsushi Mahara2, Yoshiki Hirota3 and Tetsuji Yamaoka4;1 Department of Biomedical Engineering, Kansai University, Suita, Osaka, Japan; 2 Department of Biomedical Engineering, National Cerebral and Cardiovascular Center Research Institute, Suita, Osaka, Japan.

**[Purpose]** Suppression of thrombus formation is required for graft patency of small caliber blood vessels. In our previous work, we succeeded in proving the good patency of the small diameter long bypass graft by modifying the luminal surface with a bioactive peptide [1]. The peptide consists of REDV and POG repetitive sequence which are the integrin α4β1, ligand and collagen binding sequence, respectively. We found that the REDV modified surface captured endothelial progenitor cells and inhibited the blood coagulation during initial contact with the heparinized blood. However, platelets were adhered on the REDV modified surface when platelet-rich plasma (PRP) was statically incubated with the surface. The REDV density was 8.4×10⁶ molecules/mm² when the REDV was immobilized via POG binding sequence. Therefore, the surface would not be fully covered by the peptide, and we assumed that the platelet adsorption was caused by exposed collagen. In this study, we developed the REDV peptide-conjugated silane coupling agents (PCSi) for high density REDV immobilization to decellularized vascular graft. The platelet adhesion on the PSCI modified surface and EPC binding affinity were evaluated.

**[Method]** REDV peptide was conjugated with the 3-(triethoxysilyl) propyl isocyanate (PCSi). The 0.02 - 10.0% PCSi solution was dropped into decellularized ostrich carotid artery and incubated under evacuation condition. The modification was evaluated by EDS and FT-IR. The density was quantified with ¹²⁵I-labeled PCSi. PRP was isolated from mini-pig arterial blood, and the tissues were incubated with the PRP for 1 hour. Human EPCs were seeded on the surface, and cell binding was evaluated by WST-8 assay.

**[Results]** Si signal and Si-O-Si band around 1020 cm⁻¹ in EDS and FT-IR were observed after PCSi treatment, and the REDV immobilized density was 8.4×10⁶ molecules/mm², which is almost 1000 times higher than that immobilized by the previous method using POG sequence. Platelets scarcely adhered on the PCSi treated tissue, but EPCs were adhered and spread out on the surface. These results suggested that the REDV was immobilized at a high density via PCSi, and the surface suppressed platelet adsorption and promoted the EPCs adhesion.


**BM04.06.23**

Biodegradable Hollow Capsules for the Efficient Delivery of Therapeutic Molecules and Nanoparticles

Isabel Gessner, Eva Krakor, Sven Santernik and Sanjay Mathur; University of Cologne, Cologne, Germany.

For the interconnection between a synthetic material and living matter, hollow mesoporous silica capsules (HMSC) have recently gained intense attention as drug delivery vehicles due to their biocompatibility, high loading capacity and sufficient stability in biological milieu. Compared to most of the published data, which mainly focus on the formation of spherical mesoporous silica particles, in this work, a simple and reproducible synthesis of ellipsoid-shaped HMSC (aspect ratio – 2) via a hematite template assisted route is presented. Hollow structures were formed through, coating of solid templates with a silica sol followed by acidic leaching of the core material. The porosity of prepared capsules was demonstrated by gas sorption studies, revealing mesoscopic pores around 4 nm and a high surface area of 308.8 m²/g. Both, cell uptake studies as well as cell viability assays, revealed the high biocompatibility of HMSC. Moreover, the successful cellular internalization was proven by confocal microscopy using human cervical cancer (HeLa) cells. The morphology of HMSC for drug delivery and nanoparticle applications was tested by loading antibiotic (ciprofloxacin) and anticancer (curcumin) compounds. A pH dependent drug release over several days under physiological conditions at 37°C was demonstrated (UV-vis spectroscopy) in both cases, which showed the versatility of HMSC in transporting hydrophilic as well as hydrophobic drugs. Ciprofloxacin-loaded HMSC were additionally evaluated towards gram negative (E.coli) bacteria to clearly demonstrate a complete bacterial growth inhibition over 18 hours using particle concentrations of 10 µg/ml. Besides the delivery of therapeutic molecules, metallic nanoparticles such as Cu or Ag were incorporated whereby a controlled leaching of metal ions demonstrated their usefulness for antibacterial applications. Additionally, hollow capsules slowly degraded into non-toxic molecules which is of crucial importance considering their application as biocompatible and clearable drug transporter.

**BM04.06.24**

Bacterial Cellulose Growth in Three-Dimensional Micrometric Molds—Production, Characterization and Biomedical Applications

Prospects Adriano J. Ottaka1, Rafael R. Domengeuzzi2, Mollizia Santos1, Sidney Ribeiro1 and Cleber Mendonça1; 1 Photonics Group, São Carlos Institute of Physics, University of São Paulo - USP, São Carlos, Brazil; 2 Laboratory of Photonic Materials, Institute of Chemistry, São Paulo State University - UNESP, Araraquara, Brazil.

Bacterial cellulose (BC) has emerged as an interesting candidate to fabricate advanced biomaterials, aiming applications in the tissue engineering, such as, artificial skin for burns treatment and wound healing. This biopolymer exhibits a nanofibrous porous network highly moldable, with high strength, low density, high biocompatibility, and which can be easily functionalized with drugs or other biological agents for selective applications. In this work, we fabricate several polymeric microenvironments with distinct geometries, to evaluate and study the growth dynamics of bacterial cellulose. The microenvironments were produced by two-photon polymerization using a Ti:Sapphire laser oscillator, centered at 780 nm, operating at a repetition rate of 86 MHz and delivering 100 fs pulses. The polymeric resin used in the microenvironments is composed by two acrylate monomers, tri(2-hydroxyethyl) isocyanurate triacrylate and dipentaerythritol pentaacrylate, which are combined to provide hardness to the structure and a smoothed surface after the polymerization, preventing deformations on the final structure. These monomers are mixed with an acrylpholine oxide photoinitiator, ethyl-2,4,6-trimethylbenzoyl phenylphosphinate, an organic compound responsible to generate free radicals after laser pulse irradiation. The laser beam is focused through a microscope objective (10X, NA=0.25) into the sample and scanned in the x-y direction by a pair of movable mirrors, while the sample's axial (z) positioning is performed by a motorized stage. The photopolymerization experiment can be monitored in real time, by an illumination source and a CCD camera. After complete fabrication of the molds and sterilization, bacteria Gluconacetobacter xylinus (ATCC 23760) are inoculated into the microenvironments, receiving all the necessary conditions for their development. We evaluate the bacterial cellulose growth for one week, monitoring the...
samples in specific times (hourly and daily). The formed biofilms were characterized morphologically and structurally by scanning electron microscopy (SEM), infrared spectroscopy (IRS) and Raman spectroscopy (RS). The structure and composition of growth bacterial cellulose in the microenvironments are similar to those grown in macro systems. The results obtained in this work open new opportunities for tissue regenerative engineering studies, as well as, show other possibilities to evaluate drug delivery mechanisms due to selective permeability of the formed biofilms.

BM04.06.25
Brain HDL-Mimetic Nanomaterials Designed to Mitigate Microglia-Mediated Neuroinflammation in Alzheimer’s Disease Jin-hwan Kim, Song Ih Ahn and Yong-Tae Kim; Department of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Microglia are the innate immune cells of the brain that mediate opposing deleterious pro-inflammatory and protective anti-inflammatory functions in Alzheimer’s Disease (AD). Multiple evidences showed microglia-mediated neuroinflammation has been recognized as a prominent manifestation of the AD brain. As disease-modifying treatments for AD are lacking, specific inhibitors of pro-inflammatory microglial functions with high brain bioavailability are needed. Kv1.3 is a microglial potential and pro-inflammatory functions and is highly expressed by amyloid beta plaque-associated microglia in human AD brains. However, the delivery of the inhibitor into the brain remains ineffective due to the blood brain barrier (BBB) that limits the bioavailability of therapeutic molecules. One possible route to deliver drug molecules across the BBB is to leverage physiologically relevant BBB-on-a-chip device.

We engineered apoE3-based HDL-mimetic nanoparticles (eHNP-E3) in a controllable and reproducible manner using a microfluidic synthesis technology. Lipids derived from 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) were mixed through a series of microvortices in defined ratios with human recombinant apoE3. A ShK223 peptide (ShK3), an effective Kv1.3 blocker, was conjugated with cholesterol to anchor the peptide on the surface of eHNP-E3. Our microfluidic platform creates a series of controlled microvortices that enabled the rapid assembly of precursors (DMPC and apoE3) into discoidal structures of eHNP-E3 at a Reynolds number (Re ~ 50), followed by the incorporation of ShK into the nanoparticle (eHNP-E3-ShK). The size of eHNP-E3-ShK was approximately 18 ~ 20 nm as demonstrated by DLS and TEM. Successful cellular internalization of eHNP-E3-ShK was also monitored in microglia, suggesting the biological potential function as Kv1.3 channel blocker of this nanoparticle at the subcellular level. We are currently examining the biological function of eHNP-E3-ShK both in our microengineered human BBB-on-a-chip model and in the 5XFAD model.

In summary, we demonstrated successful synthesis and physicochemical characterization of eHNP-E3-ShK and are testing the biological functions for the delivery of a therapeutic molecule into the brain. We are evaluating the biological activities of our nanoparticle targeting anti-inflammatory effects on microglia in vitro and in vivo.

BM04.06.26

In the field of neuronal transplantation therapy, there has been a strong demand for a neuron-electrode interface to make it possible to monitor the process by which a graft is integrated into a host neuronal circuit. Since cell migration and glial scar formation lead to a loss of contact between an electrode and a graft, it is technically difficult to monitor the sequential changes in the circuit between the graft and the host tissue. Fabricating a graft by encapsulating neurons with a self-foldable and biocompatible electrode is a potent strategy for the maintenance of electrode-graft contact, because the graft can be enclosed and fixed by the folded electrode. The encapsulation of neurons with self-foldable metal films has been intensively studied, and close contact between encapsulated neurons and film has been achieved. However, conventional metal films are not applicable with this approach because 1) metal film has insufficient biocompatibility and optical transparency, and 2) the enclosed structure only allows partial connections between the encapsulated graft and the host tissue. In this study, we developed a self-foldable graphene film that has high biocompatibility, optical transparency and permeability with high electro-conductivity. Micro-pores patterned on the film allowed axonal passage, thus providing connections between the graft and host tissue.

The self-foldable graphene film with micro-pores was composed of monolayer graphene and parylene thin film laminated on a sacrificial layer of calcium alginate. Following the dissociation of the sacrificial layer, the graphene-parylene bilayer film was spontaneously rolled up to form a tubular structure by the π-π stacking interaction between these layers. To keep neurons (φ > 10 mm) inside the micro-roll and allow only their axons (φ < 2 mm) passage, an array of 8 mm micro-pores was photo-lithographically formed. We seeded primary hippocampal neurons and induced self-folding. The neurons were successfully kept inside the micro-roll. Furthermore, we confirmed that the micro-pores allowed the passage of axons outside the pore-patterned tube, unlike the plane tube. Time-lapse images of the micro-roll showed that encapsulated neurons extend neurites through the pore-patterned tube onto the bottom of the dish, while neurites grow only from the end of a plane tube. In addition, staining results indicate that Tau-1-positive axons grow more extensively from the pore-patterned tube than from the plane tube. MAP2-positive dendrites and cell bodies were localized within both types of tube, indicating that neurons were kept within the tubes. These results show that the self-folding of our graphene film can be applied to neuron encapsulation and that micro-pores pass axons selectively, providing a pathway for connections between the graft and host tissue. This encapsulation technique with self-foldable graphene film is promising as a tool for realizing a reliable neuronal graft-electrode interface.

BM04.06.27
Inert Metal/Degradable Metal Hybrid Stent Enabling Sustainable and Controllable H2O2 Generation for Antirestenotic Functionality Hyunseon Seo, Jinmin Park, Yu-Chan Kim and Myoung-Ryul Ok; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Significant advances in design of biocompatible metals allowed development of bare metallic stents (BMSs) utilizing these metals for the treatment of vascular diseases. However, restenosis, caused by abnormal accumulation of smooth muscle cells (SMCs) near BMSs, has hindered BMSs to have practical clinical use. Therefore, a different strategy to selectively inhibit the endothelial cells (VECs).

In our previous studies, we investigated delamination phenomenon of Mg thin film coated on the NiTi stent by using both experimental and simulational (finite element analysis) stretching test, we optimized coating pattern of Mg that can stably maintain the adhesion with NiTi stent even under highly deformed condition. Our
achieve offers a new insight on development of metallic stents by proposing a simple but novel approach to solve restenosis, which has been a major constraint on clinical application of the stent.

**BM04.06.28**

A New Hydrogel System Encapsulated Single Red Blood Cell for Transfusion

Mingjie Fan, Yueqi Zhao, Ruikang Tang and Ben Wang; Zhejiang University, Hangzhou, China.

The blood groups severely restrict blood transfusion owing to the antigens on red blood cells (RBCs) recognized by the immune system, which result in vast loss of mismatching blood or shortage of matching blood, sometimes occurrence of significant influence following transfusion in emergency. The red blood cell (RBC) membrane is architecturally complex and is characterized by significant biochemical diversity. The glycoprotein on the surface of RBC determined the blood type, while the different blood type lead to huge obstacle during clinical blood transfusion, especially in natural hazard, terrorist attack and warfare acute transfusion. Here we constructed a cell surface engineering system for hydrogel encapsulated single RBC, which based on the hydrogel formation by enzymatic crosslinking. Using biocompatible anchors for membrane, enzyme which could catalyze for the formation of a layer of hydrogel shell was introduced onto cell surface, and encapsulation of a single RBC by hydrogel shell was produced. We made a system of mTG-gelation hydrogel system which can shield cell surface antigen, more importantly, the physical properties, biological functions, tissue distributions and in vivo biocompatibility of the encapsulated RBCs were similar to those of the native RBCs, indicating a promising application for development using an enzyme catalyzed hydrogel system. These results may provide a new feasible solution for related research and applications for emergency blood transfusion.

**BM04.06.29**

A Robust Thin Film with a Selective Antibacterial Property for Infection-Resistant Medical Application

Goro Choi, Eunjung Lee and Sung Gap Im; Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Rapid advances in medical and healthcare system brought about a great attention in antibacterial surface coating since bacterial infection of biomedical device are emerging as an urgent issue. Device-associated infections (DAI) have become a serious issue due to the increased risk of infectious diseases requiring hospitalization. Changing the surface properties of medical devices is a simple and direct approach to prevent DAI and intense research efforts have been focused on this aspect. Several surface modification methods such as non-adhesive, antibiotic releasing, silver-coated, or direct killing have been developed and evaluated to prevent bacterial infection on implant surfaces. However, these methods contain inherent limitations such as complicated, laborious procedures, the lack of controllability, cytotoxicity, and leaching problem. Herein, we propose a new strategy for anti-infective surfaces made of a cross-linked ionic polymer film to achieve dual functionality that kill the bacteria while at the same time favor the survival of mammalian cells. A one-step polymerization process, termed initiated chemical vapor deposition (iCVD) process could generate a cross-linked ionic polymer film from 4-vinylbenzyl chloride (VBC) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) monomers in vapor phase. Especially, the deposition process produced a polymer network with quaternary ammonium crosslinking sites, providing the surface with ionic moieties with excellent contact-killing antibacterial property. This method possesses substrate compatibility, which enable the ionic polymer film coating on various materials of medical implants. Moreover, the ionic polymer-deposited surfaces supported the healthy growth of mammalian cells while selectively inhibited the bacterial growth in co-culture models without any detectable cytotoxicity. Thus, the cross-linked ionic polymer-based antibacterial surface developed in this study can serve as an ideal platform for biomedical application requiring highly sterile environment.

**BM04.06.30**

Labeling and Specifying the Magnetically Aligned Collagen Fibrils for Hyperthermia Cancer Treatment

Mohammad Reza Zamani Kouhpainji, Daniel Shore, Joseph Um, Yali Zhang, Rhonda Franklin and Bethanie J. Studler; University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Collagen is the major component of connective tissues and accounts for one-third of all proteins in the human body. The fibril nature of the collagen, especially collagen type I, provides advantages in biological studies, such as imaging and cancer treatment, such as hyperthermia and drug delivery. In these applications and many others, labeling and identifying the cells in order to distinguish and separate the healthy and unhealthy cells is a crucial task to not damage healthy cells while treating the unhealthy ones.

In this work, different ferromagnetic nanowires were electrodeposited, characterized and incorporated into collagen fibrils. The nanowires were crosslinked with the collagen fibrils to achieve one-step bi-directional alignment of the collagen fibrils as verified using optical microscopy techniques. A new technique for radio-frequency identification (RFID) was demonstrated by placing the aligned collagen matrix onto a coplanar waveguide under a fixed microwave frequency while sweeping the magnetic field. The ferromagnetic resonance (FMR) of the nanowires provided distinct signatures for each collagen matrix. Finally, an alternating magnetic field was applied to control and manipulate the temperature of the matrices and investigate the possibility of hyperthermia cancer treatment.

Specifically, variation in the trends of FMR absorption vs. applied field at 240GHz were successfully measured. Engineered effective fields included shape anisotropy of the nanowires/matrix and the dipole moments that the nanowires apply to each other. Minimum detectable concentration of the nanowires in aligned collagen fibrils was quantified to be within a few percent, resulting in optimization of the magnetic properties of aligned collagen fibrils as well as labeling process. Furthermore, the hyperthermia experiments showed that aligned nanowires can prove specific absorption rates up to 1600W/g of ferromagnetic metal. These values are sufficient for both cryowarming of preserved tissues and cancer treatment using aligned collagen fibrils prior to denaturation of the collagen fibrils.

**BM04.06.31**

Effect of Microporous Structure on the Mechanics and Permeability of Polymer Films

Angelica Rose Galvan, Kendell M. Pawelec and Jeff Sakamoto; Mechanical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

There are approximately 700,000 peripheral nerve injuries per year, yet there are few technologies to repair damage to nerve tracts > 3cm. Porous poly ε-caprolactone (PCL) multi-channeled scaffolds are a technology that demonstrates nerve regeneration following traumatic nerve injury. However, further enhancing nerve regeneration requires tuning the microstructure within the scaffold architecture to improve nerve regeneration.

The size, shape and interconnectedness of pores in the scaffold walls affect the mechanics and permeability, which are important for suturability, patient mobility, nutrient diffusion and cell adhesion. The ideal scaffold is robust enough to maintain structural integrity during implantation, but also compliant enough to prevent microchannels from collapsing. The scaffold’s porous microstructure is determined by the type of porogen (e.g., NaCl), or the soluble particle that acts as a template for pores.

In order to investigate how microstructure affects scaffold mechanics, characterization was conducted on PCL films with 70 vol% porosity fabricated with porogen (NaCl), with particle sizes ranging from (10 – 60 μm), obtained via ball-milling and roller-milling. The tensile elastic modulus of the films were analyzed and compared. It was found that the elastic modulus decreases as the particle size decreases from 2.40 ± 0.34 to 1.06 ± 0.15 MPa for 62.2 and 9.2
μm particles, respectively. This correlation is likely due to better packing with smaller porogen size.

Permeability tests were also performed to characterize how the varying porogen sizes affected pore interconnectivity, which in turn influences cell adhesion and diffusion. The permeability decreases as the particle size decreases, from 9.91 x 10^{-13} m² at 62.2 µm to 2.53 x 10^{-13} m² at 9.2 µm, due to a reduction in the size of the pore interconnections and increased tortuosity in films with smaller porogen.

Characterizing the effect of scaffold microstructure on mechanics and permeability can help us predict how these properties will affect cell proliferation and adhesion, leading to improved scaffolds for nerve repair.

**BM04.06.32**

Enhancing Biocompatibility of Calcium Carbonate Particles for Biomedical Applications

Açıkgöz Mert Oral1, 2, Derya Kapusuz3 and Batur Ercan1 3; 1Middle East Technical University, Ankara, Turkey; 2Metallurgical and Materials Engineering, Gaziantep University, Gaziantep, Turkey; 3BİOMATEN, Middle East Technical University, Center of Excellence in Biomaterials and Tissue Engineering, Ankara, Turkey.

Calcium carbonate (CaCO₃) is a widely occurring biomineral synthesized by marine creatures. In nature, CaCO₃ mainly exists in its anhydrous forms, namely vaterite (unstable), aragonite (metastable) and calcite (stable). Though it is possible to synthesize these anhydrous polymorphs for biomedical applications, it still remains a challenge to fine-tune physical and chemical properties of CaCO₃ particles due to different stabilities of anhydrous polymorphs and their complex crystallization behavior. This situation is especially critical for vaterite particles, which have been proposed for bone cement and drug delivery applications, because of their unstable characteristics.

In our study, pH values and [Ca²⁺]/[CO₃²⁻] ratios of precursor solutions were altered and their effects on the polymorph, morphology and size of CaCO₃ particles were investigated. At low pH values, spherical and ellipsoidal vaterite particles were synthesized, whereas cuboidal and flower-like calcite particles were obtained at high pH values. Importantly, transformations from vaterite to calcite were observed at different pH values depending on [Ca²⁺]/[CO₃²⁻] ratio of the precursor solutions. In addition, average particle size was constantly decreased from micron to submicron sizes with decreasing pH values. Since ethylene glycol concentration was considered as one of the critical factors determining CaCO₃ particle properties, control experiments were performed to distinguish the effects of ethylene glycol concentration and pH values of precursor solutions. pH was observed as the dominating factor controlling CaCO₃ particle properties as opposed to findings in literature, although ethylene glycol concentration was also influential on some of the CaCO₃ particle properties. Since bone cell functions differ depending on physical and chemical properties of particles they interact with, the synthesized CaCO₃ particles were also investigated in vitro using human osteoblasts (bone cells). Results showed that none of the synthesized CaCO₃ particles exhibited any toxic effect upon their interaction with osteoblasts up to 5 days of culture, while polymorph morphology altered bone cell functions.

To conclude, pH and [Ca²⁺]/[CO₃²⁻] ratio of precursor solutions were shown as effective variables on polymorph, morphology and size of CaCO₃ particles without affecting their biocompatible characteristics. In contrast to findings in literature, pH, an ignored variable in most CaCO₃ particles synthesis protocols, was found to be the dominating factor as opposed to ethylene glycol concentration of the precursor solutions. In vitro tests also showed that bone cells performed their cellular functions without any compromise to their viability.

**BM04.06.33**

Exploiting Inherent Instability of 2D Black Phosphorus for Controlled Phosphate Release from PLGA/BP Composite Nanofibres

Negin Kamyar1; Ryan D. Greenhalgh2, Tatiana R. Nascimento2, Eliton S. Medeiros2, Peter D. Matthews3, Liebert P. Nogueira4, David J. Lewis1 and Jonny J. Blaker1; 1School of Materials, University of Manchester, Manchester, United Kingdom; 2Department of Materials Engineering, Federal University of Paraíba, João Pessoa, Brazil; 3School of Chemical & Physical Science, Keele University, Newcastle, United Kingdom; 4Department of Biomaterials, University of Oslo, Oslo, Norway; 5Department of Physics, Cambridge University, Cambridge, United Kingdom.

Black phosphorus (BP) is a two-dimensional (2-D) semiconductor with a tunable direct band gap and highly anisotropic properties. It is inherently unstable and degrades into phosphate ions in aqueous media via oxidation 1. Whilst the current paradigm with 2D materials leans toward stabilization, in this study, we do the opposite and explore the use of 2D BP as a source of phosphate ions by exploiting its inherent instability for controlled phosphate ion release. Liquid exfoliated BP 2 was incorporated into degradable poly (lactide-co-glycolide) (PLGA) fibres via solution blow spinning 3, forming a flexible 3-D nanocomposite with a continuous open-fibre structure. With increasing BP concentration, the average fibre diameter increased by 43%, which we attribute to changes in the precursor solution properties including surface tension and viscosity. Raman spectroscopy along with ICP-AES confirmed the incorporation of BP into the nanocomposite. By increasing the initial loading of BP there was an increase in the BP optical phonon mode intensity in Raman spectra. ICP-AES was used to quantify exact BP loading and demonstrated that modifying the initial loading of BP in the PLGA fibres permitted tuneable release rates of phosphate ions over 8 weeks in vitro. Hence, the release rate of phosphate ions from PLGA-BP nanocomposite fibres can be controlled by compositional tuning of brittle and lactide to glycolide ratio in the PLGA. Such nanocomposites have advantages over conventional bioactive glasses as they do not exhibit brittle behaviour which imparts great potential for non-load-bearing bone tissue applications and flexible therapeutic implants.

References:

**BM04.06.34**

Hybrid Mats for Wound Dressing Applications from “Green” Renewable Resources

Adnan Memiçi; Tuerdemimaiti Abudula; Lassaad Gzara1, Giovanna Simonetti2, Ahmed Al-Shahrani, Numan Salah1, Pierfrancesco Morganti1, Angelo Chiamenti3, Afsoon Fahlahi1, Ali Tamayol3 and Sidi Benchere1; 1King Abdullah1 University, Jeddah, Saudi Arabia; 2Northeastern University, Boston, Massachusetts, United States; 3University of Nebraska-Lincoln, Lincoln, Nebraska, United States; 4University of Rome, Sapienza, Rome, Italy; 5Nanoscience Centre, MAVI Sud, Aprilia, Italy.

In the local treatment of both chronic and acute wounds it is crucial to prevent infections, control the removal of exudates and create a moist environment to allow for skin healing. To address these challenges it is necessary to develop the next generation of wound dressings. Chitin and lignin are bio-waste resulting from byproducts of crustacean crusts and plant biomass that have recently been proposed for bioengineering applications. However, their weak mechanical properties need to be accomplished this we fabricated hybrid mats composed of a chitin–lignin (CL)-based sol–gel mixture and elastomeric poly
Degradable Polyphosphazenes—Development of First, Second and Third Generational Polymers

Kenneth S. Ogueri, Harry R. Albeck and Cato T. Laurencin

The design of advanced biomaterials with a wide range of properties has been fueled by new fields such as regenerative engineering, defined as the convergence of advanced materials science, stem cell science, physics, developmental biology and clinical translation for the regeneration of complex tissues. The complexity and demands of this innovative approach have inspired the synthesis of new polymeric materials that can be tailored to meet application-specific needs. Polyphosphazenes are composed of an inorganic backbone with alternating phosphorus and nitrogen atoms. Each phosphorus atom bears two substituents, with a wide variety of side groups available for property optimization. Polyphosphazenes have been investigated as potential biomaterials for regenerative engineering. The polymers have received a great deal of attention due to their outstanding synthetic flexibility and their ability to exhibit properties.

Polyphosphazenes for use in biomedical tissue regeneration applications have evolved as a class to include different generations of degradable polymers. The 1st generation of polyphosphazenes for tissue regeneration entailed the incorporation of hydrolytically active side groups such as imidazole, lactate, glycolate, glucosyl, or glycerryl groups. These side groups were selected based on their ability to sensitize the polymer backbone to hydrolysis, which allowed them to break down into non-toxic small molecules that could be metabolized or excreted. The 2nd generation of polyphosphazenes developed for regenerative applications consisted of polymers with amino acid ester side groups. When blended with PLAGA, it showed the feasibility of neutralizing the acidic degradation products of PLAGA but formed mostly partially miscible blends. To overcome the miscibility issue, third generation degradable polyphosphazenes have been designed by incorporating dipeptide side groups which impart significant hydrogen bonding capability on the polymer for the formation of completely miscible polyphosphazene-PLAGA blends. The 3rd generation exhibits a unique degradation behavior by which the polymer is allowed to break down into non-toxic small molecules that could be metabolized or excreted.
study, we have shown that monodispersed polybutadiene forms a convenient biocompatible scaffold, to which the cells can adhere without additional coating. Furthermore, we have verified that the film modulus can be continuously tuned while maintaining the same functional form over a wide range of film thicknesses. The films were then coated with a continuous thin film material which was able to be varied by more than an order of magnitude simply by changing the film thickness. DPSC plated on these PB substrates were able to adjust their moduli in response to the film thickness, obeying the same functional form as the PB films. Yet, despite the continual change in cell hardness, an abrupt change occurred for substrates moduli greater than 2.3 MPa when large amounts of biomineralized deposits were observed after 28 days. RT-PCR analysis indicated that the substrate mechanics induced differentiation of the cells without any additional chemical inducers. Florescent immunohistochemically staining indicated that all the cells in the tissue that formed expressed OCN, a protein necessary for biomineralization and an indicator for osteogenic differentiation, on thin, hard PB films, while no OCN was found in cells on the softer, thick PB films. Hence direct contact with the hard substrate was only required for one of the layers, and the effect was propagated further into the scaffolds. Scaffolds with mechanical patterns surface patterns were then produced with length scales ranging from the macro to the nanoscale. The patterns were produced simply by imprinting on the substrate and adjusting the film thickness, without chemical cross linkers introduced into the PB films. Hence the influence of purely mechanical heterogeneity could be probed. In the case of microscale patterns, the results indicate that the influence of the substrate mechanics is communicated within the tissue via cell-cell contact. In this study, where both hard and soft patterns were present, in a manner with enabled cell-cell contacts to form between patterns, no biomineralization was observed. If cell-cell contacts were prevented, differentiation and non-differentiated cells were able to coexist within a single culture, where the phenotype was governed by the substrate mechanics. This study is important when applying printed scaffolds as dentin/tooth regenerative biomaterials, which surface is rough and the mechanics is not homogeneous.

8:45 AM BM04.07.03
Bioactive Aligned Conducting Polymer Nanofibers Using Laminin-Derived Biomolecules for Neuritogenesis Milad Khorrani, Zhihui Guo, Mohammad Reza Abidian and Anthony M. Kisselev; University of Houston, Houston, Texas, United States.

Peripheral nerve transaction occurs commonly in traumatic injury, causing deficit distal to the injury sites. Many studies have been devoted to promote nerve conduits for nerve injury repair including fabrication of hollow tubes or fibers. However they often fail due to short and slow regeneration over long gap. An ideal nerve conduit for regeneration should provide physical and/or biochemical guidance cue to direct the neural axons. To that end, conducting polymer have been widely used for neural applications due to 1) facile functionalization process with biomolecules to tune biological response, 2) soft mechanical properties that mimics the tissue properties and 3) the ability to transduce mixed ionic and electronic conductivity.

In this research, we investigated the fabrication of bioactive aligned conducting polymer nanofibers (CPN) to potentially directly the extension of neural processes. The fabrication process includes (1) electrospinning of poly(l-lactic acid) (PLLA) template nanofibers from homogeneous solutions of 3% (w/w) PLLA and 2% BTEAC (w/w) dissolved in chloroform at 100 kV/m electrical field and rotation rate of 1500 RPM, (2) electrochemical polymerization of laminin-doped poly(3,4-ethylenedioxythiophene) (PEDOT) from 0.02M PEDOT and 6.17µM laminin-derived peptide ((DEDEDYFQRYLI) in water/acetonitrile (1:1) solution with charge density of 600mC/cm². Scanning electron microscopy showed that the size of PLLA fibers was 302.6±101.66 nm diameter (n=100). The X-ray photoelectron spectroscopy results have proved the presence of laminin-derived peptide on the surface of CPN. We characterized the electrical properties (i.e. impedance and capacity of charge transfer) of the bioactive CPN. We will use rat dorsal ganglia to study the effect of laminin-doped aligned CPN on growth of neuronal cells and neurite outgrowth. Future study will also focus on creating a gradient of human lamin on the surface of aligned CPN as guidance for axonal growth.

9:00 AM BM04.07.04
Enhancing Osteointegration on Biodegradable Polymer Scaffolds with ALD Deposition of Titania Kuan-Che Feng1, Adriana Pinkas-Sarafova1, Likun Wang1, Ya-Chen Chuang1, Linxi Zhang1, Chung-Chueh Chang1,2,3, Marcia Simon1 and Miriam Rafailovich1; 1Stony Brook University, Stony Brook, New York, United States; 2Advanced Energy Center, ThINN Facility, Stony Brook, New York, United States.

Fused deposition modeling (FDM) is a rapidly growing method for device fabrication. The technique is inexpensive and the product, such as bone inserts, dental devices, can be printed directly from CT scans or impressions, and hence specifically tailored for the individual. However, from the former study shows that the cell did not attach well on the FDM printed surface due to the roughness of FDM printed surface and hydrophobicity of the polyactic acid (PLA).

In this study we produced FDM printed scaffolds that were then coated with titanium dioxide via the atomic layer deposition (ALD) method. TiO2has been shown in numerous studies to enhance osseointegration. Hence by this technique one can produce scaffolds that are at once biodegradable, and yet support osteogenic or odontogenic differentiation. In order to probe this concept we plated dental pulp stem cells on these scaffolds, incubated for 28 days, in media with glycerol phosphate, but without the commonly used induction factor, dexamethasone. The culture was then harvested for qRT-PCR and the surfaces were imaged with scanning electron microscopy. Cell mobility, proliferation, and differentiation were studied and significant differences in both biomimeralization and differentiation were observed between coated and uncoated surfaces.

9:15 AM BM04.07.05
Mechanical Perfromances of Engineered Polymer Scaffolds Ozlem Yasar1 and Ozgul Yasar-Inceoglu2; 1City University of New York, Brooklyn, New York, United States; 2Mechanical Engineering, California State University, Chico, Chico, California, United States.

There are more than 114,000 people are waiting in the waiting list for an organ transplantation and on average 20 people die each day waiting for a transplant. In recent years, tissue engineering has brought to the attention to do organ/tissue regeneration as an alternative way to the organ transplantation. Success rate of tissue regeneration strongly depend on the accurate scaffold fabrication. In this research, scaffolds were fabricated with Poly(ethylene glycol) diacrylate (PEGDA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA). PEGDA is a biocompatible polymer that can be easily cured in the room temperature. DMPA is used as a photoinitiator, which starts the polymerization reaction when it interacts with the UV light. The mechanical characterization of PEGDA and DMPA mixture have been considered in some range in tissue engineering field. However, it is not fully studied.

In this research, firstly, PEGDA was diluted with water to prepare 20% and 40% PEGDA and 80% PEGDA. With these different PEGDA concentrations, cylindrical samples were prepared with photolithography process. On the other hand, 0.02% (w/v), 0.06% (w/v), and 0.1% (w/v) photoinitiator-solvent mixtures were prepared to alter the DMPA concentration. Then, cylindrical samples with altered DMPA concentrations were also prepared with photolithography process. After that, compression tests for all the cylindrical samples that were prepared with different PEGDA and DMPA concentrations performed with the Instron 3369 universal testing machine. Our results indicate that, as the PEGDA concentrations increased, compressive strength of the hydrogels also increased and PEGDA concentration had significant effects on elastic modulus and ultimate strength. Average ultimate strengths for 20%, 40% and 80% PEGDA concentrations were in the order of 1 MPa, 1.5 MPa, and 4.5 MPa, respectively. Our results related to the effect of photo-initiator on mechanical properties of engineered scaffolds showed that as the DMPA concentration was increased, ultimate strengths were decreased. For 0.02% (w/v),
While silver salts are frequently used as a source of antimicrobial silver ions (Ag\(^+\)), their elution in commercial external wound care products is immediate and therefore their solubility is used to control Ag\(^+\) availability, often leading to exposure to unnecessarily high and cytotoxic levels. In approach (1), silver nitrate (AgNO\(_3\)) is dissolved into the PLGA/PEG blowspinning solution, establishing consistent loading and elution profiles: The PLGA/PEG:Ag fibers release Ag\(^+\) quickly in a controlled manner over 24 hours, and they continue to release Ag\(^+\) over 30 days. AgNO\(_3\) concentration was tuned to 1 mg/mL to produce a dressing that inhibits microbial growth but does not affect cell viability. In a porcine burn graft donor model, PLGA/PEG:Ag can be applied once and requires few, if any, reapplications during the course of healing, and produces no delay in healing compared to a conventional polyurethane dressing. Because it is biodegradable, the polymer is incorporated into the scab and can be removed after the wound bed is reepithelialized and no longer requires a dressing.

Polymers can also be used internally as surgical sealants to prevent fluid leaks and promote hemostasis by occlusion of blood flow. However, uncharged synthetic polymers lack a mechanism to trigger the coagulation cascade. Approach (2) incorporates silica particles into PLGA/PEG to trigger the coagulation cascade via the “glass effect”, which takes advantage of the strongly negative charge present on bare silica. Composite sealants cause citrated blood to clot in scenarios where PLGA/PEG alone does not. The effect is also size-dependent: composites containing 20 nm silica particles cause blood to clot 25% faster with coexisting 600 nm particles. The composite sealant was tested in a liver laceration model, and achieved near-complete hemostasis within 15 minutes, while PLGA/PEG did not. Additionally, silica particles increase adhesion and can be used to modify the stiffness and extensibility of the sealant.

Delivery of therapeutic cargo to hematopoietic stem cells (HSCs) is a challenging problem whose solution could transform the treatment of many diseases, ranging from autoimmune disorders to hematological malignancies [1]. HSCs are multipotent cells that can differentiate into all blood cell types in the body, so delivering agents that promote lineage-specific differentiation of HSCs could transform medical practice. However, delivering therapeutic cargo to HSCs in vivo is extremely difficult given that HSCs reside in bone marrow and are notoriously difficult to transfect. To overcome this challenge, we have developed a biomimetic nanoparticle (NP) platform that enables targeted cargo delivery to HSCs.

We hypothesized that polymeric poly(lactic-co-glycolic acid) (PLGA) NPs coated with membranes derived from megakaryocytes (Mks) could enable specific recognition of HSCs for targeted cargo delivery. This hypothesis was based on prior work that showed megakaryocytic microparticles (extracellular vesicles that bud off Mk cells) could specifically bind and enter HSCs in vitro [2,3]. Here, we provide the results of our in vitro studies, which demonstrate the synthesis of Mk membrane-wrapped PLGA NPs (MkNPs) and validate that these MkNPs can effectively bind and enter HSCs to deliver their cargo.

To create MkNPs, ~100 nm diameter DiD-loaded PLGA NPs were co-extruded with empty membrane vesicles derived from Mk cells, which were labeled with PKH26, using an Avanti Mini Extruder. DLS and TEM measurements showed that MkNPs were monodisperse and spherical, with wrapped NPs having a diameter 10-20 nm larger than bare NPs. Bare NPs had a zeta potential of -48.55 mV, and the charge of MkNPs (-19.18 mV) was similar to that of membrane vesicles (-20.93 mV), indicating successful wrapping. Successful wrapping was further confirmed by stability in PBS, as MkNPs placed in PBS at 4°C did not swell, while bare NPs swelled from 120 nm to 600 nm in <1 h. Flow cytometric analysis of CD41, an outer membrane marker, on MkNPs versus membrane vesicles confirmed through similar expression levels that the membranes were right-side out on the MkNPs. Confocal imaging showed that CD41+ HSCs take up MkNPs within 24 hours of incubation, and super-resolution microscopy confirmed that PKH26 and DiD signals colocalize within HSCs. The MkNPs preferentially interact with the uropod region of HSCs, similar to what has been reported for megakaryocytic microparticles [2,3].

In summary, PLGA NPs can be wrapped with Mk-derived membranes, allowing the resultant MkNPs to bind HSCs to deliver their cargo. These data support continued development of MkNPs for HSC manipulation.


10:00 AM BREAK
Cellulose materials have shown great potential for biomedical applications owing to their intrinsic characteristics, such as biocompatibility, hydrophilicity, porosity, and tunable mechanical properties[1]. Wood-derived nanocellulose, coming from the most abundant biomass on earth, is naturally low cost and suitable for mass production. Compared to widely studied and commercially developed bacterial nanocellulose[2], wood-derived nanocellulose supports easy post-polymerization processing, both mechanically and chemically, making it a favorite candidate for applications such as 3D bioprinting[3].

In this study, we used cellulose nanofibrils (CNF) prepared from bleached birch kraft pulp, chemically oxidized using 2,2,6,6-Tetramethylpiperidinyloxy or 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) and mechanically treated[4]. This CNF consisted of fibers with a dimension of ca. 5 nm in width and hundreds of nanometers in length and had a consistency of 1 w%/v with 1.14 mmol/g negative charge attributed to carboxylic acid groups from TEMPO-oxidization. The prepared CNF demonstrated excellent rheological properties in demand for 3D printing, in terms of high yield stress and shear thinning properties. Herein, we report for the first time 3D printed scaffolds with high resolution features printed using a single CNF component.

A secondary cross-linking approach was also investigated to further enhance and adjust the stability and mechanical properties of the 3D printed CNF scaffolds. CNF scaffolds were first cross-linked through ionic interaction between Ca²⁺ and carboxylic groups on the fiber surface of CNF, which provided a fast and in situ mechanism for 3D printing. The printed CNF scaffolds were then chemically cross-linked by 1,4-butandiol diglycidyl ether (BDDE) to form irreversible covalent bonds.

A series of characterizations were performed on the biofabricated CNF scaffolds, including rheology, swelling ratio, mechanical tests and cell culture, etc. The CNF scaffolds had demonstrated long term stability in PBS and a high ratio for water re-adsorption after freeze-drying. The compressive Young’s modulus and shear modulus were in the suitable range for skin wound healing and the cell studies showed positive results in supporting human dermal fibroblast cells adhesion and proliferation.


10:45 AM BM04.07.09
Aligned Conducting Polymer Nanotubes for Precisely Triggered Release of Proteins
Mohammadjavad Eslamian and Mohammad Reza Abidian;
University of Houston, Houston, Texas, United States.

Conducting polymers actuators are one of the most promising materials for development of controlled drug delivery systems, owing to their outstanding capability to reversibly change their volume during electrochemical process. We previously demonstrated the precise release of drugs such as dexamethasone from conducting polymer nanotubes. The fabrication process involved electrospinning of drug-loaded biodegradable nanofibers on microfabricated electrodes, followed by electrochemical deposition of conducting polymers on microelectrodes and around the electrospun nanofibers. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most versatile conducting polymers employed in the field of polymer electronics, owing to its superior electrical conductivity and chemical stability. Soluble growth molecules such as nerve growth factor (NGF) provide trophic support for neurons and are vital for axonal growth. The goal of this research is to develop a nanoscale device for precise delivery of NGF. To accomplish this task, NGF is encapsulated in aligned poly (lactic-co-glycolic acid) (PLGA) nanofibers via emulsion electrospinning process on gold coated silicon-based electrodes. Then, a thin layer of PEDOT is galvanostatically deposited on the electrodes and around the electrospun nanofibers at the current density of 1 mA/cm² for 1 min to form NGF-loaded aligned PEDOT nanotubes. The outer diameter of PEDOT nanotubes is 440±91 nm. The release behavior of NGF from PEDOT nanotubes is investigated by electrical actuation of PEDOT nanotubes in phosphate-buffered saline (PBS) using enzyme-linked immunosorbent assay (ELISA). The electrical actuation will be performed using cyclic voltammetry (CV) at the potential range of -0.8 V to +0.4 V at different scan rates, including 10, 50, 100, and 200 mV/s, and for different numbers of CV cycles (up to 100 cycles). Finally, the NGF release rate will be assessed as a function of scan rates and CV cycles. The results of this study may have impact for development of NGF delivery platforms for modular growth of axons in both central and peripheral nervous systems.

11:00 AM BM04.07.10
Solvent-Free Preparation of Porous Poly(L-Lactide) Microcarriers for Cell Culture and Bone Tissue Engineering
Mirasbek Kuterbekov1, 2, Paul Machillo2, Pierre Lhuissier3, Catherine Picart4, Alain M. Jonas1 and Karine Glinel1; 1BSMA, IMCN, Université catholique de Louvain, Louvain-la-Neuve, Belgium; 2IMBM, LMGP, Communauté Université Grenoble Alpes, Grenoble INP, CNRS, Grenoble, France; 3SIMAP, Communauté Université Grenoble Alpes, Grenoble INP, CNRS, Saint Martin d'Heres, France.

One of the main challenges in regenerative medicine is the development of appropriate biomaterial constructs that can guide cell behavior. Microcarriers are particularly attractive in this regard due to their small size. This feature allows them to circumvent many of the issues facing more traditional monobloc constructs such as low nutrient-metabolite exchanges and uneven cell infiltration into the bulk while still being suitable for dynamic culturing and engineering of large-scale tissue grafts [Declercq et al. Biomaterials 2013]. Porous microcarriers made of synthetic biodegradable polymers have the added advantage of a larger surface area, improved mass transfer and the tunability of their bioactive properties.

Currently, most methods for the production of porous polymeric microcarriers rely on creating emulsions, which require potentially toxic organic solvents and relatively complex setups [Silva et al. J. Tissue Eng. Regen. Med. 2007]. Alternatives limiting the use of organic solvents have been proposed; however, such methods often fail to replicate the tunable microcarrier morphologies that can be obtained with the emulsion-based methods. This in turn hinders the wider adoption of microcarriers due to concerns over safety to human health and potential limits in large-scale production.

To address this issue, we developed a novel organic-solvent-free approach for the production of porous poly(L-lactide) (PLLA) microcarriers. The method is based on the isothermal spherulitic crystallization of PLLA in its blend with polyethylene glycol (PEG). Resulting PLLA spherulites are easily recovered as microcarriers by simple removal of water-soluble PEG. Independent control and tunability of microcarrier size and porosity were demonstrated, with high crystalization temperatures leading to larger sizes and higher PLLA content resulting in lower levels of porosity. Moreover, microcarriers were shown to support not only the long-term proliferation of murine myoblast and human adipose stromal/stem cells (hASC) but also differentiation of hASCs towards osseous tissues. Furthermore, while no significant differences were observed during cell proliferation on microcarriers of two different porosities, microcarriers of lower porosity induced a stronger hASC osteogenic differentiation, as evidenced by higher alkaline phosphatase enzymatic activity and matrix mineralization. Consequently, the proposed organic-solvent-free method for the fabrication of biocompatible porous PLLA microcarriers represents an innovative methodology for ex vivo cell expansion and its application in stem cell therapy and tissue engineering.

In this study, we show that by combining physical reversible soft bonds with stiff covalent bonds in p(HEMA-co-EGDMA) based hydrogels, different properties were screened successfully. The principal finding is that fucoidan favours islet survival inside hydrogels and is effective in reducing the immune response, suggesting that fucoidan hydrogels can be used for regeneration (GBR). GBR consists of applying a barrier membrane to separate inflamed gingival tissue from bone, restricting invasion and allowing regeneration of osteoblasts. Current barrier membranes, however, do not fulfill all the desired properties of high biocompatibility, cell impermeability, and, in particular, high mechanical strength. As such, the following study synthesized novel Gelatin-Pluronic F127 hybrid hydrogels, thoroughly analyzing their in vitro viability as potential cell barrier membranes for use in GBR. Rheological analysis demonstrated high mechanical strength as hybrid hydrogels’ elastic moduli drastically increased with increasing percentages of the chemical cross-linker microbial transglutaminase (mTG). The surface of the hybrid gels was visualized with laser microscopy to show topographic changes among different crosslinking density. Cytotoxicity tests were first conducted to show the biocompatibility of hybrid gels. To investigate levels of cell adherence, confocal microscopy was performed on hybrid hydrogels plated with human dermal fibroblasts, which demonstrated significantly reduced cell attachment as compared to pure gelatin. Cell impermeability was further investigated by observing cell migration from gelatin gel to hybrid gel compared with from gelatin to gelatin, with a control setup consisting of Gelatin / Gelatin / Gelatin and an experimental setup of Gelatin / Hybrid / Gelatin. Human dermal fibroblasts plated on gelatin gels migrated through the middle gelatin, but, particularly at the highest mTG concentration, were unable to migrate through middle hybrid gels, showing hybrid hydrogels’ impermeability to cells. Our findings, identifying in vitro high mechanical strength, cell impermeability, and biocompatibility, point to novel Gelatin-Pluronic F127 hybrid hydrogels as promising biomaterials for use as GBR cell barrier membranes in treatment of periodontitis.


Type-1 diabetes is an autoimmune disease affecting ~90,000 children each year. Destruction of the insulin-producing islets by the autoactivated immune system leads to type-1 diabetes. Implantation of cells from other sources cannot reverse the condition owing to the immune response as the cells remain in contact with an activated immune system. In previous works, encapsulation of islets inside a hydrogel has shown promise but the cells were not protected from small inflammatory cytokines. Therefore, advanced functionality in a carrier with immunomodulatory capacity is a strategic goal for islet implantation. Marine-sulphated polysaccharides possess unique features that are shared among the extracellular matrix polysaccharides and have immunomodulatory properties. In the present work, fucoidan and three carrageenans (with different numbers of sulphate groups) were functionalised with methacrylate groups for photopolymerisation; the number of functional group in the polysaccharide chain was controlled precisely. The toxicity of the polysaccharides was evaluated by the cell growth inhibition assay on fibroblast L929 cells and all of them were found noncytotoxic. Fucoidan treatment resulted in a significant decrease in the LPS-stimulated expression of CD86, a costimulatory molecule essential to exert a full immune response to implanted islets, on PMA-differentiated THP1 cells; this response was comparable to that of IL-10, an anti-inflammatory cytokine. Fucoidan had a protective effect on THP1 cells from LPS- and IFN-mediated growth inhibition. Fucoidan also decreased the LPS-stimulated production of nitric oxide. For islet encapsulation, methacrylated polyvinyl alcohol (PVA) was synthesised and used as the base polymer and the marine polysaccharides were incorporated in order to support cell survival and impart immunomodulatory properties. Mouse insulinoma cell line, MIN6 cells were encapsulated in hydrogels (20 wt%) by UV photopolymerisation. Cell viability was assessed over a period of 28 days by live/dead assay, revealing a positive correlation between the number of sulphate groups in the disaccharide units and cell survival. Cell viability was found to be maximal in the fucoidan hydrogels that remained stable over this period. The protective effect of the hydrogels from inflammatory cytokines was evaluated by incubating the encapsulated islets in a medium containing inflammatory cytokines (IL-1β, TNF-α, & IFN-γ) for 48 h. Cell viability in the fucoidan hydrogels remained unaffected, which indicates the protective role of fucoidan, whereas decreased cell viability was observed in other hydrogels. The results show that marine polysaccharides with immunomodulatory properties were screened successfully. The principal finding is that fucoidan favours islet survival inside hydrogels and is effective in reducing the immune response, suggesting that fucoidan hydrogels can be used for in vivo islet implantation for the treatment of type-1 diabetes.
SESSION BM04.08: Polymeric Biomaterials for Regenerative Engineering III

1:30 PM BM04.08.01
Photo-Responsive Peptide Hydrogels for Tailorable Epitope Presentation Zain Siddiqui1, Peter Nguyen1, Biplob Sarkar1, David Sabatino2 and Vivek Kumar1; 1New Jersey Institute of Technology, Newark, New Jersey, United States; 2Seton Hall University, South Orange, New Jersey, United States.

Self-assembling peptides can form nanoporous hydrogels that can deliver cells, small-molecule drugs, and growth factors to potentiate phenotypic modulation. Here we show a modification of this platform that may tailor the in vitro and in vivo phenotype of a cellular niche via caged short pro-apoptotic sequences. We demonstrate the dose-dependent cell viability in vitro and show sequence dependent cellular infiltration in vivo. Although cytocompatible cellular carriers are promising delivery vehicles, potential for maladaptive responses, such as teratoma formation, are potential roadblocks for clinical translation. We designed and assembled sacrificial scaffolds that can be tuned on-demand. Peptides with cell adhesive RGD or pro-apoptotic WEWT moieties were introduced to create cell-adhesive and cell-arresting hydrogels. Culture of fibroblasts and stem cells demonstrated signaling efficacy of the hybrid peptides. Photobleaching caging of adhesive and arresting groups show remarkable potential for triggerable adhesion, proliferation, or apoptosis. “Caging/uncaging” of cellular signaling domains can act as an “on/off” switch in cell-loaded 3D hydrogels. Photo-patterning of cell-loaded gels yielded well-resolved niches of specific cells. Subcutaneous implants of the hydrogel showed biocompatibility through cellular infiltration and lack of a fibrous capsule around the implant. Light-activated switching of cellular behavior and phenotype could be broadly useful for construction of new photo-responsive scaffolds with encoded signals for controlling cellular outcome. Multicomponent tissue-engineered scaffolds based on this technology may be crucial next steps for our design paradigm.

1:45 PM BM04.08.02
Self-Expanding and Biodegradable Porous Scaffolds Based on Magnesium-Hydroxide and Hydrocolloids for Bone Tissue Engineering Domenic T. Cipollone1, Cerasela Dinu2 and Konstantinos Sierros1; 1Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States; 2Chemical and Biomedical Engineering, West Virginia University, Morgantown, West Virginia, United States.

The repairing and regeneration of large bone defects is a significant clinical challenge and has garnered considerable research attention over the past few decades. Typical methods for bone regeneration include allografts (from patient to patient), autografts (from one site to another), or metal implants. While useful, these practices limit availability, donor site morbidity, and the risk of disease transfer. Moreover, metal scaffolds may require a secondary surgery for removal of the implant. Therefore, the controlled engineering of biodegradable, biocompatible, porous, and mechanically robust scaffolds is crucial.

This work reports on the fabrication and characterization of self-expanding, biodegradable, porous magnesium-hydroxide-hydrocolloid scaffolds for use in bone tissue regeneration. In particular, the proposed interconnected porous network is engineered through in-situ hydrogen gas generation, thus providing the framework for a biodegradable and osteoconductive scaffold, while offering control over the pore size distribution and the resulting mechanical properties. The engineered foam is shown to be self-expanding in confined spaces, thus able to fill irregular and complex geometries. Furthermore, the use of magnesium-hydroxide, in combination with cross-linked hydrocolloids, aims to provide a solution to the high corrosion rates typical of magnesium scaffolds currently utilized. Surface morphology and porosity of the scaffolds are characterized though micro-computed tomography, scanning electron microscopy, and porosimetry, while uniaxial compression tests are used to study the resulting mechanical properties. In vitro studies are then used to determine cell viability and bioactivity of the scaffolds. It is found that the total porosity and pore size distribution of the scaffolds may be tailored through control of the magnesium-solvent reaction and resultant hydrogen generation. Moreover, this leads to control over the scaffold’s relative density and compressive modulus. It is believed that this work may hold the key for the development of next generation - low-cost, highly porous, biodegradable, and self-expanding - scaffolds for use in bone tissue engineering and regeneration.

2:00 PM BM04.08.03
Biodegradable Nitric Oxide (NO) Storage and Delivery Hyaluronic Acid-Based Nanofibers—Potent Applications for Tissue Engineering and Regenerative Medicine Kihak Gwon and Jae Ho Shin; Department of Chemistry, Kwangwoon University, Seoul, Korea (the Republic of).

Nitric oxide (NO) is one of the smallest pharmaceutical gas molecules, which mediates versatile physiological processes including stem cell regulation, angiogenesis, immune response, vasodilation, blood pressure regulation, antibacterial property, and wound healing. These several physiological functions have motivated researchers to develop various NO delivery systems for therapeutic applications. Recently, electrospun nanofibers as a NO carrier have received a great interest because of their facile functionalization, tunable mechanical properties, and large effective surface areas. In our previous studies, we have developed a series of polymethylmethacrylate (PMMA)-based NO-releasing nanofibers where NO donor N-diazienumidolate-modified aminoalkoxysilane and silyl-modified PMMA are covalently bound via sol-gel chemistry, displaying tunable NO storage amount and release kinetics. However, PMMA-based NO-releasing nanofibers are difficult to be degraded in the physiological milieu, restricting its potential in vivo applications. Our recent work has thus, aimed to develop biodegradable, NO-releasing hyaluronic acid (HA)-based nanofibers. The NO donor N-diazienumidolates are covalently bound to the HA backbone via use of appropriate conjugate chemistry. Various chemical compositions (e.g., HA concentration and NO donor amount) and electrospinning conditions (e.g., applied potential and flow rate) are tuned to control fiber diameter, degradability, and NO release properties (e.g., maximum flux, total NO release amount, and half-life time). In addition, cell proliferation and migration controlled by such NO-releasing nanofibers and its cytotoxicity are evaluated.

2:15 PM BM04.08.04
Fabrication of 3D Scaffolds Based on Nano-Biomimetic Collagen Hybrid Constructs for Skin Tissue Engineering Abolfazl Akbarzadeh1, Soodabeh Dovaran2, Ebrahim Mostafavi1 and Azizeh Rahmani Del Bakhshayesh1; 1Northeastern University, Boston, Massachusetts, United States; 2Tabriz University, Tabriz, Iran (the Islamic Republic of).

Three dimensional (3D) biodegradable and biomimetic porous scaffolds are ideal frameworks for skin tissue engineering. In this study hybrid constructs of 3D scaffolds were successfully fabricated by freeze-drying method from combinations of the type I collagen (Col), and synthetic poly (lactic acid) (PLLA) or polycaprolactone (PCL). Four different groups of 3D porous scaffolds including PCL, PCL-Col, PCL-PLLA, PCL-PLLA-Col were fabricated and systematically characterized by HNMR, FT-IR and SEM. Adipose tissue derived mesenchymal stem cells (AT-MSCs) were seeded in all scaffolds and the
viability, proliferation and adhesion of the cells were investigated using MTT assay and scanning electron microscopy (SEM). The results showed that scaffolds containing Col, particularly PCL-PLLA-Col scaffold, with pore sizes close to 400nm and sufficiently interconnected, have significantly greater potential (p<0.01) for encouraging AT-MSCs adhesion and growth. The PCL-PLLA provided a mechanically stronger mesh support and the type I Col microsponges encouraged excellent cell adhesion and tissue formation. The scaffold with the best properties could be an appropriate functional candidate for preparation of artificial skin constructs.

2:30 PM BREAK

3:00 PM BM04.08.05
Hydrogels with Tunable Degradability for Tissue Engineering Applications—Characterization of Morphological Changes Using Cryo-SEM
Bonhye Koo1, Soyon Kim2, Jiwen Zheng3 and Min Lee3; 1U.S. Food and Drug Administration, Silver Spring, Maryland, United States; 2University of California, Los Angeles, Los Angeles, California, United States.

Photopolymerizable hydrogels are commonly used as tissue engineering scaffolds. Under visible blue light irradiation (VBL), methacrylated glycol chitosan (MeGC) can be photopolymerized with riboflavin (RF, vitamin B2 derivative) and applied to support the encapsulated cell proliferation and deposition of extracellular matrix. MeGC alone, however, is not a perfect candidate for a scaffold due to its relatively slow degradation rate. This is critical for a tissue engineering scaffold since it might hinder cell recruitment and delay tissue regeneration. Thus, there is strong impetus to develop a degradable tissue engineering scaffold to allow subsequent tissue regeneration and/or the release of encapsulated bioactive molecules.

In this report, we designed hydrogels with tunable degradation by incorporating lysozyme (Lys) with various concentrations (0, 0.1, and 1 mg/mL) in MeGC, based on its ability to degrade chitosan by cleaving the polysaccharide backbone. A suitable characterization technique is required to demonstrate the degree of hydrogel degradation. Cryogenic scanning electron microscopy (cryo-SEM) allowed to preserve the native structure of hydrogels in a frozen hydrate state and enabled direct imaging of the mesh structure of hydrogels degraded at atmosphere at 37 °C at a nanometer resolution. Our cryo-SEM micrographs of three hydrogels clearly showed differences in size of the mesh structure and the size change from day 0 to day 10. At day 0, the average pore size of the mesh structure was 38.6, 36.7, and 37.9 nm respectively for MeGC, Lys0.1 and Lys1. Their size changed to 67.6, 86.4, and 408.6 nm respectively for MeGC, Lys0.1 and Lys1 after 10 days. In addition, the maximum pore size increased up to 1,200 nm for Lys1 at day 10. This supported that MeGC hydrogel became degradable with lysozyme and the degree of degradation was controllable by adjusting the amount of lysozyme.

3:15 PM BM04.08.06
Fabrication of Composite Bone Scaffolds with Controlled Multi-Scale Porosity Using Non-Solvent Induced Phase Separation Based 3D Printing
Mehtemt S. Axdin1, Gullu Kiziltas1, 2 and Busra Kologlu1; 1Sabanci University, Istanbul, Turkey; 2Sabanci University Nanotechnology Research and Application Center, Istanbul, Turkey.

Bone fracture is a widespread injury associated with individual disability and loss of social productivity resulting in very high treatment costs. Well-designed scaffold implants are good alternatives in bone tissue engineering known to result in effective healing. An ideal bone scaffold should be biocompatible, porous, interconnected and strong, i.e. multi-functional. Therefore, composite materials stand out as desired material candidates. Advances in the design and production of porous composite scaffolds took place owing to solid free-form fabrication (SFF) techniques with mechanical and biological functions tailorable to specific bone defects. Aim of this study is to develop an effective SFF based technique capable of printing composites with well controlled macro-micro porosities making primarily use of commercial 3D printers. Similar features are displayed by novel designs obtained via topology optimization. Poly(ε-caprolactone) (PCL) was chosen as the scaffold polymer, which is FDA approved. A variety of SFF techniques have been developed to produce controlled porous PCL scaffolds. Also, incorporation of bioactive, stiff inorganic materials into PCL polymer led to significant enhancements in mechanical properties, bioactivity, and bone regeneration ability. However, only a few attempts have been made to create scaffolds with macro-micro porosity, despite their potential to more closely mimic the hierarchical architecture of native bones. Recently, non-solvent-induced phase separation (NIPS) seems capable of producing these scaffolds with multi-scale porosity if integrated into the 3D printing based process. Using this method, here we develop scaffolds with multi-scale porosity (~10 μm and ~100 μm) where, PCL pellets are dissolved in the THF solvent and mixed with various amounts of HA powders. Resulting solution is extruded and deposited in ethanol bath at RT. Microporous PCL/HA composite filaments are created via exchange of the solvent and the non-solvent (EtOH). Printing parameters were optimized in order to match the designed scaffold geometry. Morphological parameters such as porosity and connectivity of scaffolds were analyzed via micro-CT and SEM. FTIR, TGA and mechanical testing for tensile and compressive strength were carried out. Biological in-vitro tests for cytocompatibility and osteo-forming ability are underway to measure cell attachment, proliferation and growth. Initial results show that using NIPS and commercial printing, scaffolds displaying both macro and micro-porosity (%10-20) were successfully fabricated. Further characterization should prove that these scaffolds are bio-compatible, strong and well-designed. The capability to directly manufacture novel designs should open up new possibilities for other applications demanding multi-functional scaffolds, thereby allowing effective patient specific treatment.

3:30 PM BM04.08.07
3D Woven Metallic Lattices as Bio-Scaffolds with Hydroxyapatite Coatings
Ju Xue1, Ashley Farris2, Yunfei Wang3, Cristina Romany1, James Guest3, Warren Grayson3, Shoji Hall1 and Timothy P. Weihs1; 1Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 2Biomedical Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 3Civil Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Fabrication of composite bone scaffolds with controlled multi-scale porosity using non-solvent induced phase separation based 3D printing of mehtemt s. axdin1, gullu kiziltas1, 2 and busra kologlu1; sabanci university, istanbul, turkey; sabanci university nanotechnology research and application center, istanbul, turkey.

Bone fracture is a widespread injury associated with individual disability and loss of social productivity resulting in very high treatment costs. Well-designed scaffold implants are good alternatives in bone tissue engineering known to result in effective healing. An ideal bone scaffold should be biocompatible, porous, interconnected and strong, i.e. multi-functional. Therefore, composite materials stand out as desired material candidates. Advances in the design and production of porous composite scaffolds took place owing to solid free-form fabrication (SFF) techniques with mechanical and biological functions tailorable to specific bone defects. Aim of this study is to develop an effective SFF based technique capable of printing composites with well controlled macro-micro porosities making primarily use of commercial 3D printers. Similar features are displayed by novel designs obtained via topology optimization (Hollister, S. J., Nature Materials, 2003; Aslan, O. S. and Kizilitas, G., Proc. of TERMIS-EU, 2013). Poly(ε-caprolactone) (PCL) was chosen as the scaffold polymer, which is FDA approved. A variety of SFF techniques have been developed to produce controlled porous PCL scaffolds. Also, incorporation of bioactive, stiff inorganic materials into PCL polymer led to significant enhancements in mechanical properties, bioactivity, and bone regeneration ability. However, only a few attempts have been made to create scaffolds with macro-micro porosity, despite their potential to more closely mimic the hierarchical architecture of native bones. Recently, non-solvent-induced phase separation (NIPS) seems capable of producing these scaffolds with multi-scale porosity if integrated into the 3D printing based process. Using this method, here we develop scaffolds with multi-scale porosity (~10 μm and ~100 μm) where, PCL pellets are dissolved in the THF solvent and mixed with various amounts of HA powders. Resulting solution is extruded and deposited in ethanol bath at RT. Microporous PCL/HA composite filaments are created via exchange of the solvent and the non-solvent (EtOH). Printing parameters were optimized in order to match the designed scaffold geometry. Morphological parameters such as porosity and connectivity of scaffolds were analyzed via micro-CT and SEM. FTIR, TGA and mechanical testing for tensile and compressive strength were carried out. Biological in-vitro tests for cytocompatibility and osteo-forming ability are underway to measure cell attachment, proliferation and growth. Initial results show that using NIPS and commercial printing, scaffolds displaying both macro and micro-porosity (%10-20) were successfully fabricated. Further characterization should prove that these scaffolds are bio-compatible, strong and well-designed. The capability to directly manufacture novel designs should open up new possibilities for other applications demanding multi-functional scaffolds, thereby allowing effective patient specific treatment.

3:30 PM BM04.08.07
3D Woven Metallic Lattices as Bio-Scaffolds with Hydroxyapatite Coatings
Ju Xue1, Ashley Farris2, Yunfei Wang3, Cristina Romany1, James Guest3, Warren Grayson3, Shoji Hall1 and Timothy P. Weihs1; 1Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 2Biomedical Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 3Civil Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

There is a strong need for the next generation of bio-scaffolds that combine biologically activated coatings with porous and biodegradable substrates. Here we present results of studies of 3D woven metallic lattices that are designed using topology optimization to enhance fluidic permeability and mechanical stiffness and are coated uniformly with hydroxyapatite (HAp) to improve bioactivity and osteointegration. The ultimate goal is to weave and coat Mg alloy wires. Here we present initial results describing successful coating of HAp on 304 stainless steel wires and a study of in vitro corrosion of Mg alloy wires of various chemistries and diameters.

304 stainless steel wires with ~200 diameters were woven into pieces with dimensions of 3.6mm x 36mm x 500mm using a 3D weaving machine. Weave samples were then electrochemically coated with HA using an aqueous solution containing and . Various coating parameters were explored to obtain a systematic understanding of the deposition process. The HA coatings are distributed relatively uniformly across the multiple layers of the weave, suggesting that ion flux is high during deposition and local depletion zones within the 3D weaves are avoided. The coatings consist of “nano flakes” or crystals, and X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and Raman spectroscopy data confirm that the coating is HAp under the optimized deposition conditions. An in vitro study was then conducted to compare coated and uncoated scaffolds. Live/dead stain and PicoGreen DNA/MTS assays were employed to characterize the overall cell viability as well cell number/metabolism. Post-mortem scanning electron microscopy (SEM) was utilized to investigate to the morphology of the cells on coated and uncoated samples.

Prior to weaving with Mg-based wires, immersion testing was conducted on a range of Mg alloy wires using a modified-simulated body fluid (m-SBF) at
In infiltration and gene delivery relative to nonporous hydrogels. Biomimetic mineralized collagen scaffolds with antimicrobial peptide coating for osteogenic applications

by 1.6x and in MAP gels by 3.3x, relative to nonporous controls. These results show the potential for injectable macroporous gel strategies to facilitate cell transduction compared to roughly 100µm in nonporous gels. Bioluminescence due to transduced cell expression of firefly luciferase similarly increased in PEG-MP gels transduction compared to nonporous gels. Infiltrated distance of cells almost doubled in PEG-MP conditions and penetrated the entirety of MAP gels, hydrogels

We demonstrate that the delivery of firefly luciferase-over expressing virus through PEG-MPs or MAP gels both enhance cell infiltration and viral structure. Tunable

In the second system, encapsulated degradable PEG microparticles (PEG-MPs) act as degradable porogens which can be injected alongside an forming hydrogels have been developed to facilitate regeneration by providing structural support, introducing mechanical cues, and delivering cells, gene vectors, or soluble signals in a controlled manner. However, injectable scaffolds have limited macrostructural control compared to their implantable counterparts, leading to limited cell infiltration or transduction by gene vectors.

Currently, macroporous injectable scaffolds have been produced using microparticles which can either be 1) annealed in situ to provide porous space between particles, or 2) encapsulated within an in situ forming gel and degraded to leave behind pores. We investigated the efficacy of both techniques for improving cell infiltration and in vivo transduction from viral vectors compared to nonporous controls.

In the first system, particles are formed by water-in-oil emulsion from thiolated hyaluronic acid (HA) and maleimide-terminated poly(ethylene glycol) (PEG). These particles are produced with an excess of thiol moieties to allow for disulfide-crosslinking between particles to form gels from microporous annealed particles (MAP). Void space between particles allows for loading of viral vectors and infiltration of cells.

In the second system, encapsulated degradable PEG microparticles (PEG-MPs) act as degradable porogens which can be injected alongside an in situ forming hydrogel composed of cross-linked HA and PEG. Thiolated HA and vinyl sulfone-terminated PEG are mixed before injection, forming hydrogels in situ within an hour. PEG-MPs degrade rapidly in vivo, providing a pore template which facilitates cell infiltration

We demonstrate that the delivery of firefly luciferase-over expressing virus through PEG-MPs or MAP gels both enhance cell infiltration and viral transduction compared to nonporous gels. Infiltrated distance of cells almost doubled in PEG-MP conditions and penetrated the entirety of MAP gels, compared to roughly 100µm in nonporous gels. Bioluminescence due to transduced cell expression of firefly luciferase similarly increased in PEG-MP gels by 1.6x and in MAP gels by 3.3x, relative to nonporous controls. These results show the potential for injectable macroporous gel strategies to facilitate cell infiltration and gene delivery relative to nonporous hydrogels.

3:45 PM BM04.08.08
Multi-Responsive Self-Healing Gels as Cellular Delivery Vehicles Aderito J. Amaral and George Pasparakis; University College London, London, United Kingdom.

The development of materials that mimic aspects of self-healing is of paramount importance as it could solve a number of problems in the biomedical field. Interesting self-repair properties have emerged with suitable chemical strategies in bulk materials, which include the incorporation of healing agents in the form of nanoparticles/capsules, or the introduction of dynamic chemical bonds as structural elements. In this regard, remotely controlled healing strategies that allow for on-demand repairing of the material at the site of interest are of utmost importance. In this work, we propose the construction of remotely healable and transiently malleable soft gels based on the dynamic, albeit covalent, boronate ester bonds formation. We designed a system comprising a synthetic thermoresponsive boronic acid copolymer that is crosslinked with poly(vinyl alcohol) to form hydrogels within seconds under physiological conditions. These constructs can further be impregnated with colloidal stable polyvinylpyrrolidone-coated gold nanoparticles, which render the gels optically active without compromising their mechanical properties significantly. The gel nanocomposites can undergo a rapid and reversible gel-sol transition owing to the disruption of the boronate ester crosslinks by thermal (heating above 37 °C) or optical stimuli (irradiation with green light) that are spatiotemporally confined at the area of interest. The reconstituted gels exhibit shear-thinning behaviour, excellent and fast healing properties, even without the application of any external stimuli. It was also demonstrated that the constructs were able to encapsulate living cells and release them without affecting their viability.

We believe that these materials constitute a versatile biocompatible platform for the construction of remotely healable (soft) gels as cell capture and release systems or soft fillers of biological cavities for tissue engineering.


4:00 PM BM04.08.09
Gene Delivery from Injectable, Hyaluronic Acid-Based Hydrogels with In Situ-Forming Macropores Ardina Ehsanipour, Tommy Nguyen, Tasha Aboufadel, Philip Cox, Chris Walthers, Weikun Xiao and Stephanie Seiditts; University of California, Los Angeles, Los Angeles, California, United States.

Injectable biomaterial scaffolds are ideal for minimally invasive treatments for conditions where the area of injury is difficult to access or ill-defined in structure. Tunable in situ forming hydrogels have been developed to facilitate regeneration by providing structural support, introducing mechanical cues, and delivering cells, gene vectors, or soluble signals in a controlled manner. However, injectable scaffolds have limited macrostructural control compared to their implantable counterparts, leading to limited cell infiltration or transduction by gene vectors.

Currently, macroporous injectable scaffolds have been produced using microparticles which can either be 1) annealed in situ to provide porous space between particles, or 2) encapsulated within an in situ forming gel and degraded to leave behind pores. We investigated the efficacy of both techniques for improving cell infiltration and in vivo transduction from viral vectors compared to nonporous controls.

In the first system, particles are formed by water-in-oil emulsion from thiolated hyaluronic acid (HA) and maleimide-terminated poly(ethylene glycol) (PEG). These particles are produced with an excess of thiol moieties to allow for disulfide-crosslinking between particles to form gels from microporous annealed particles (MAP). Void space between particles allows for loading of viral vectors and infiltration of cells.

In the second system, encapsulated degradable PEG microparticles (PEG-MPs) act as degradable porogens which can be injected alongside an in situ forming hydrogel composed of cross-linked HA and PEG. Thiolated HA and vinyl sulfone-terminated PEG are mixed before injection, forming hydrogels in situ within an hour. PEG-MPs degrade rapidly in vivo, providing a pore template which facilitates cell infiltration

We demonstrate that the delivery of firefly luciferase-over expressing virus through PEG-MPs or MAP gels both enhance cell infiltration and viral transduction compared to nonporous gels. Infiltrated distance of cells almost doubled in PEG-MP conditions and penetrated the entirety of MAP gels, compared to roughly 100µm in nonporous gels. Bioluminescence due to transduced cell expression of firefly luciferase similarly increased in PEG-MP gels by 1.6x and in MAP gels by 3.3x, relative to nonporous controls. These results show the potential for injectable macroporous gel strategies to facilitate cell infiltration and gene delivery relative to nonporous hydrogels.

4:15 PM BM04.08.10
Biomimetic Mineralized Collagen Scaffolds with Antimicrobial Peptide Coating for Osteogenic Applications Zhou Ye, Xiao Zhu, Christine Lui, Yipin Qi and Conrado Aparicio; Minnesota Dental Research Center for Biomechanics and Biomaterials, University of Minnesota, Minneapolis, Minnesota, United States.

Bone and tooth are organic-inorganic composites with hierarchical nanostructures. The major organic component is type I collagen and the major inorganic promise is hydroxyapatite (HAp). Biomimetic mineralized collagen scaffolds with similar compositions and structures have been developed for bone and tooth tissue engineering. A good example is bio mineralization using the polymer-induced liquid-precursor (PILP) process, which shows a great promise in clinical applications. Mineralized collagen scaffolds present strong mechanical properties due to the aligned intrafibrillar HAp crystals and good biocompatibility and osteogenesis. However, the fabricated extracellular matrix also provides an excellent environment for microbial adhesion and biofilm development. Thus, infection could be significant and cause the failure of bone and tooth repair or regeneration.

The use of antimicrobial peptides (AMPs) is a promising approach as they have broad-spectrum antimicrobial activity with low bacterial resistance, as opposed to antibiotics. GL13K is an AMP derived from a salivary protein, which has shown low cytotoxicity and notable antimicrobial activity against gram-positive and gram-negative bacteria and biofilms. In this work, we incorporated GL13K within biomimetic mineralized collagen scaffolds and studied its antimicrobial and osteogenic activity. The collagen gels were mineralized by PILP process for different days and characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The degree of mineralization was quantified by thermogravimetric analysis (TGA) to study the effect of mineral content on the GL13K coating. The distribution of the coated GL13K was investigated by confocal fluorescence microscopy with fluorescent-labeled peptides. Water contact angle analysis revealed that GL13K coating significantly increased the hydrophobicity of the mineralized collagen scaffolds. To study the coating stability, we monitored the released GL13K in solution by mass spectroscopy. To evaluate the
antimicrobial activity, *Streptococcus gordonii* was incubated in the scaffolds for 24 hours and the viable cell number was compared using microbial ATP assays. The attached bacteria was also stained by LIVE/DEAD assays and imaged by confocal fluorescence microscopy. Osteogenic activity was evaluated by the adhesion, proliferation and differentiation of mesenchymal stem cells in the fabricated scaffolds. In this work, we introduced antimicrobial peptides in biomimetic mineralized collagen scaffolds. These scaffolds showed strong antimicrobial activity and osteogenic potential. We also evaluated the specific interactions of collagen and HAp with the antimicrobial peptide so that we will be able to control and further study the effects of each component on the biological properties to optimize their antimicrobial and osteogenic activity.

**SESSION BM04.09: Poster Session III: Biomaterials for Regenerative Engineering**

**Kayla Barton, Tayler Laycox, Ella Bonfield, Sara Hopper and Jason W. Nichol; Endicott College, Beverly, Massachusetts, United States.**

**Phenotype and Gene Expression of Human Mesenchymal Stem Cells in Response to Varied Mechanical Environment in 3D GelMA Hydrogel Models Cultured In Vitro**

Mechanical stiffness has been shown previously to direct stem cell differentiation and phenotype in multiple in vitro studies, however, many of these studies use 2D surfaces rather than more physiological 3D environments, as well as 3D encapsulation in materials where stiffness and concentration cannot be independently altered. As such, knowledge of the expression profiles of stem cell differentiation in response to 3D mechanical environment alone is unclear. Biomimetic materials should mimic the extracellular matrix (ECM) and the complex architecture of native tissues to be successful in vitro models that give valid cues as to how these cells and tissues would perform *in vivo*. The most popular biomimetic scaffold material for these purposes are hydrogels and we have chosen to work with gelatin methacrylate (GelMA) which has been extensively characterized in numerous models and with various cell types. The degree of methacrylation of GelMA can be controlled to vary the crosslinking density of the resultant hydrogel, allowing for variation of the mechanical properties independent of concentration, while further modulation of stiffness can be effected by altering the gel concentration. Furthermore, the authors and others have demonstrated that GelMA is a versatile and suitable hydrogel for culture of many cell types with positive cellular attachment and natural degradation properties, within a mechanical stiffness range typically up to 30-50 kPa. For these studies, multiple formulations of GelMA were used to study human mesenchymal stem cell (hMSCs) elongation, morphology, proliferation and gene expression using the TruSeq RNA stem cell expression panel over 14 days of static culture. It was hypothesized that the varying elastic moduli of the hydrogels in both the composite and gelMA hydrogels would result in morphological and expression differences typical of what is seen in 2D systems. The data showed that hMSCs elongation occurred early (day 1-4) in both the medium and high stiffness hydrogels with continued growth at day 14 but limited elongation of the hMSCs in the low stiffness hydrogels over 14 days. The morphological differences of the hMSCs between the low, medium, and high hydrogels could indicate the beginning of elastic modulus regulated differentiation. More thorough analysis of cell morphology and RNA expression profiles are still ongoing, but appear to validate the use of this model system both to study stem cell differentiation, as well as to provide an open transcriptome reference data set for other studies.

**Behavior and Phenotype of Cancer Cell Lines in Response to Varied Mechanical Environment in 3D GelMA Hydrogel Models Cultured In Vitro**

Kayla Barton, Tayler Laycox, Ella Bonfield, Sara Hopper and Jason W. Nichol; Endicott College, Beverly, Massachusetts, United States.

Normal, healthy cells will react in response to changes in their mechanical environment typically in an attempt to return their surroundings to homeostatic conditions. In cancerous cells this response is varied, which is one reason why the extracellular matrix (ECM) and mechanical stiffness play key roles in cancer cell phenotype and tumor formation/progression. It is known that cancer cells originating from tissues of different stiffnesses will sense and respond to their environment differently, which could yield important information in better understanding cancer cell physiology. Gelatin methacrylate (GelMA) is a UV-crosslinkable hydrogel that has been shown to be effective in the 2D and 3D culturing of cells in a wide variety of applications including cancer models. Cells can easily bind to GelMA 2D surfaces and within 3D structures, and can proliferate, elongate, and remodel the surrounding due to the presence of natural binding and enzymatic degradation sites in the gelatin backbone. GelMA is a highly elastic material with mechanical stiffnesses demonstrated in the 1 to 30 kPa range through variation of gel concentration and degree of methacrylation. Recently, we have been able to reliably produce hydrogels with compressive moduli below 1 kPa to better mimic the native environment of healthy soft tissues such as breast tissue. It has been established that normal breast tissue has a compressive modulus of roughly 200 Pa, whereas precancerous regions have a modulus of roughly 600 Pa and cancerous regions can be as high as 1-2 kPa, while other tissues have different, but analogous, stiffness ranges as well. The major aims in these studies were to create robust GelMA hydrogels in the 3 mechanical ranges (normal, precancerous, tumor) for breast and other tissues, and once validated to investigate the differences in behavior, morphology and gene expression of cancer cells encapsulated in these hydrogels. Gene expression profiles for normal and cancer specific phenotype will be investigated to determine the relative role in cell behavior in response to changes in stiffness. Initial phenotypic results suggest that cancer cells are less likely to spread, elongate and proliferate when at physiological stiffness, as compared to super-physiological stiffness more on the order of tumor tissues.

**Doping of Carbon Nanodots with Silver Nanoclusters for Saving Cells from ROS Induced Nanotoxicity**

Bodhisatwa Das1, 2 and Santanu Dhara3; 1Biomedical Engineering, Rutgers University, Piscataway, New Jersey, United States; 2SMST, Indian Institute of Technology, Kharagpur, Kharagpur, India.

Silver nanoparticles are explored for many advanced biological applications including the development of antimicrobial surfaces on implants, SERS imaging, nanotherapeutics, biosensing etc. However, recent research findings suggest silver nanoparticles provide blockade of differentiation of mesenchymal stem cells (MSCs), especially into osteogenic lineage through the generation of ROS. These studies suggest that application of silver nanoparticles in orthopedic implants should be prohibited. In the current study, carbon nanodots(CND) supported silver clusters (AgC) is explored as a remedy to solve this problem. The nanostructure was synthesized in a microwave irradiation induced rapid method and characterization was conducted via UV-Vis spectroscopy, fluorescence spectroscopy, HRTEM, XRD, FTIR, Raman spectroscopy, DLS, AFM, and XPS. Fluorescence spectrum showed a quantum yield of 0.25 while Raman spectroscopy showed rapid amplification of CND specific peaks implicating significant SERS property. Further *in vitro* biocompatibility (MTT) and bio-imaging capability was assessed culturing Whatman’s jelly-derived MSCs. In this study, its efficacy as *in-situ* cellular oxidative stress scavenger is also studied using NBT and DCFH-DA assay. Via ALP assay, alizarin red staining, cell membrane nanoindentation studies,
PCR analysis and immunocytochemistry for osteoblast-like gene expression it was confirmed that AgCs can control silver nanoparticle-inhibited induction of osteogenic differentiation in vitro. Further, in vivo implantation of AgC-Gelatin-MSC composite in rodent model showed comparable ectopic osteogenic differentiation potential. Thus AgCs are not only considered to be a dual mode bio-imaging nanoprobe but also a remedy to the silver-induced ROS generation and osteogenic differentiation blockade of MSCs.

**BM04.09.04**

**Enhancement of Hydrophobic Drug Loading in Polymeric Nanoparticles Using a Coaxial Turbulent Jet Mixer**

Hyeon-Woo Han and Jong-Min Lim; Soonchunhyang University, Asan-si, Korea (the Republic of).

The development of targeted nanoparticle platforms can indeed open a new age of well-design and tuneable release of drug that would revolutionize the field of pharmaceuticals. A range of formulation parameters and nanoparticle physicochemical properties has been studied for preclinical evaluations during the development of therapeutic agent loaded targeted polymeric nanoparticles. Although conventional bulk nanoprecipitation methods were widely adopted to prepare polymeric nanoparticles in laboratory scale due to its simplicity and versatility, loading of hydrophobic drug that maintain uniform NP size distribution is limited. When initial loading of hydrophobic drug is increased to enhance the final loading in nanoparticles, formation of large hydrophobic drug aggregates is inevitable in conventional bulk nanoprecipitation method. Here, we demonstrated a simple and versatile methods to enhance the loading of hydrophobic drug in polymeric nanoparticles, which were synthesized in coaxial turbulent jet mixer by rapid nanoprecipitation. In this work, we used docetaxel as a model hydrophobic drug and PLGA-PEG as a biodegradable nanoparticle matrix. To enhance the docetaxel loading, we systematically studied the following three steps during the nanoparticle preparation. First, we could remove docetaxel aggregates, which were originated from a high initial loading of docetaxel, by adding one more centrifuge step prior to nanoparticles washing in conventional bulk synthesis method. Second, we could enhance the drug loading as well as explore the possibilities of scaling up the nanoprecipitation process by using a coaxial jet turbulent mixer. Finally, we enhanced the drug loading further with the addition of organic co-solvent that would trap the docetaxel and make it easier to be encapsulated in the hydrophobic PLGA core of the PLGA-PEG nanoparticles. The novel strategy has strong possibility to reduce the gap between nanoparticle formulation prepared in academic laboratories and that in pharmaceutical industry thanks to enhanced hydrophobic drug loading (up to 6.5%) in polymeric nanoparticles and extremely high production rate (up to 3.15 kg/d).

**BM04.09.05**

**Self-Assembled Nanoconstructs Modified with Amplified Aptamers Inhibited Tumor Growth and Retinal Vascular Hyperpermeability via Vascular Endothelial Growth Factor Capturing**

Yeong Mi Lee and Won Jong Kim; POSTECH, Pohang, Korea (the Republic of).

Here, nanoconstructs consisting of a DNA-amplified aptamer with a biocompatible polymer backbone for capturing target biomolecules are presented. First, the polymer–DNA nanon constructs were prepared by hybridization of two complementary single-stranded DNAs that were each conjugated to a dextran polymer backbone. The designed polymer–DNA amplified aptamer nanoconstructs (PA-aNCs) were then prepared by utilizing polymer–DNA nanon constructs conjugated with an aptamer (PA-NCs) using a rolling circle amplification reaction to amplify the aptamer. These PA-aNCs were successfully applied to alleviate tumor growth and vascular endothelial growth factor (VEGF)-induced retinal vascular hyperpermeability in vivo through the highly effective capture of human VEGF as a target molecule. These PA-aNCs could be used as therapeutic agent for anti-VEGF therapy by efficiently capturing human VEGF.

**Keywords:** anti-VEGF therapy; antitumor therapy; DNA nanoconstructs; polymer–DNA conjugates; retinal vascular hyperpermeability

**BM04.09.06**

**Sterilization by Gamma Radiation of Hydroxyapatite with Brazilian Native Propolis**

Antonio M. Scatolini, Silvana M. Pugine, Luci C. Vereck, Andres Vereck, Mariza P. Melo and Eliana C. Rijo; University of Sao Paulo, Pirassununga, Brazil.

The aim of this work was to evaluate the possible bactericidal activity the hydroxyapatite (HA) powder containing extracts of green and red propolis, before and after sterilization by gamma radiation (Co60) with a load of 25 Kgy. Ethanol extracts of green (GP) and red (RP) propolis were obtained in 80% alcohol solution. Green and red extracts (8 mg/mL) were incorporated into the material at 10% (w/v) via spray drying, obtaining HA-GP and HA-RP samples. Powder characterization was done by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The cytotoxicity of the materials was determined by the neutral red uptake method. The antimicrobial activity was evaluated by the minimal inhibitory concentration (MIC) and the minimal bactericidal concentration (MBC) against Staphylococcus aureus (S. aureus). The characterization of the powders before and after the sterilization showed crystalline structure and apparently spherical morphology, indicating a decrease in the degree of agglomeration with the addition of propolis, regardless of whether they were sterilized or not. FTIR indicated the presence of functional groups characteristic for HA and propolis. The cytotoxicity assay before and after sterilization showed similar values for IC 50 (concentration reflecting 50% of cell viability) for the HA-GP and HA-RP samples. Higher bactericidal activity was observed for samples without sterilization by gamma radiation. The obtained results in this work suggest that the sterilization process of HA powders with propolis influenced the antimicrobial capacity, however, without any signal indicating that these materials could not be used in medical devices with antimicrobial agent, regarding the requirements of maximum values for the IC 50 index.

**BM04.09.07**

**Graphene Oxide as an Inhibitor of the Interactions Between Nucleoside Diphosphate Kinase (NDPK) and G Proteins**

Rohit Kanaparthi and Isaac Macwan; Univ of Bridgeport, Bridgeport, Connecticut, United States.

During a heart failure, due to the lack of calcium ion homeostasis in cardiomyocytes, the systolic and diastolic functions are affected leading to a higher amount of nucleoside diphosphate kinase (NDPK) enzyme in the sarcolemmna membrane. This inhibits the synthesis of second messenger cyclic adenosine monophosphate (cAMP) that regulates the calcium ion balance for normal functioning of the heart. In a dependent pathway, NDPK normally phosphorylates the stimulatory guanosine diphosphate, GDP, to a guanosine triphosphate, GTP, on the heterotrimeric (α, β and γ subunits) guanine nucleotide – binding protein (G protein) resulting in the stimulation of the cAMP formation. However, in case of a heart failure, an increased quantity of NDPK also reacts with the inhibitory GDP, which is converted to a GTP, resulting in the inhibition of the cAMP formation. Typically the βγ dimer of the G protein binds with hexameric NDPK – B/C complex and receives the phosphate at the residue His266 (histidine ID 266) from His118 of NDPK – B. Previous studies have stated that any enzymatic activity can be inhibited by graphene oxide (GO), which is an oxidized carbon allotrope. In this work, these interactions between NDPK – B and – C are quantified in the presence and absence of GO with respect to the binding site His118. These results are further utilized to simulate the interactions between the heterotrimeric GDP and NDPK – B/C with and without GO to explore the binding events between His118 (on NDPK) and His266 (on Gβ). The system was modelled using visual molecular dynamics (VMD) and four 100ns – 1ns simulations were carried out using nanoscale molecular dynamics (NAMD). The co-ordinate files for the enzyme and the G proteins were acquired from the pdb database and GO X (10A X 9A) having a chemical structure (C4H4O4(OH)2(COOH)2) was modeled using nanotube builder in VMD and further modified using TCL scripting and VegaZZ software. CHARMM (Chemistry at HARvard Macromolecular Mechanics) force field is used for modeling and simulating the interactions.
environment. The temperature is maintained at 300K using Langevin Thermostat and the pressure of 1atm is set through Nose – Hoover Langevin piston barostat with a period of 100ps and a decay rate of 50ps. It is found that GO is capable of suppressing and the interactions between NDPK and G proteins, where it specifically blocks the His118 binding site on ND PK, thereby preventing it to come in contact with His266 on Gβ. Based on the quantification of the van der Waals, electrostatics and conformational energies, it is seen that the affinity of ND PK to GO is higher compared to its affinity to the G proteins. Root mean square deviation (RMSD) and center of mass analysis agrees well with the energetics and the secondary structure analysis of the ND PK and G protein showed only a minor structural arrangement in the protein secondary structure indicating favorable interactions between NDPK and GO.

**BM04.09.08**

Anti-Tumour Property of Pyrrole Doped Electros spun Pei Fibrous Scaffold—A Novel Breast Cancer Therapy

Ahmet E. Mevdın; Ahsen Seyrek and Mehmet Mutlu; TOBB University of Economics and Technology, Ankara, Turkey.

In this study, antitumor biomaterial fabrication targeting the cancer cells without affecting healthy cells was aimed. In accordance with this purpose, heterocyclic pyrrole ring which has antitumor property was doped at 5%, 10% and 20% (w:w) concentrations to PCL scaffolds via electrospinning. The average fiber diameter of PCL, 5%, 10%, and 20% pyrrole doped scaffolds are measured 1.907 ± 0.286 μm, 1.393 ± 0.177 μm, 0.882 ± 0.218 μm, and 1.100 ± 0.285 μm, respectively, with homogenous, bead free and continuous fiber formation. According to the MTT assay, with 11.045% increase, the highest cell viability was observed in PCL in reference of TCP. Besides, less cell viability was seen in pyrrole doped PCL (PdPCL) scaffolds with increase in pyrrole concentration that resulted in 17.357%, 24.457%, and 36.489% decrease, respectively. According to the DAPI staining results which supported MTT assay data, highest cell viability was observed on PCL to decrease in PdPCL scaffolds accordance with increase in pyrrole concentration. As a consequence of this research, first time in literature, antitumour property of pyrrole doped into electros spun fiber matrix was achieved. With this study, a novel approach to cancer treatment methods is developed by supporting different biomaterials with pyrrole.

**BM04.09.09**

pH-Activable Polymeric Nanoparticles Modulate Lysosomal Acidification and Autophagy in Beta Cells

Julian Zeng1, Kevin Smith1, Orian Shirihai1 and Mark Grinstaff2; 1Boston University, Boston, Massachusetts, United States; 2University of California, Los Angeles, Los Angeles, California, United States.

We have developed a novel polymeric pH-activable, acidifying nanoparticle (acNP) that restores the pH of compromised lysosomes to rescue autophagic flux and cellular function in pancreatic beta cells (INS1 cells) under lipotoxicity. In beta cells, chronic exposure to high levels of fatty acids (lipotoxicity) leads to an inhibition of autophagic flux and subsequent cellular dysfunction, which has been recently associated with impaired lysosomal acidification and elevated lysosomal pH. Therefore, restoration of lysosomal pH is essential in alleviating the block in autophagy and promote proper cellular quality control and function. In this study, we designed an acidic nanoparticle (acNP) that contains caged acid which can be released upon moderate pH changes (pH 6.0) to enable controlled acidification of the impaired lysosomes under lipotoxicity. Rhodamine labelled acNPs demonstrate dose dependent uptake into lysosomes of INS1 cells. pH-activation of acNPs in dysfunctional lysosomes at pH 6.0 environment demonstrate acidification of lysosomes and restored lysosomal pH with minimal cytotoxicity. acNPs also increased lysosomal cathepsin enzyme activity, and decreased both autophagic proteins LC3II and p62 levels, indicating a rescue of lysosomal function and autophagic flux due to restoration of lysosomal acidity. Additionally, acNPs restored glucose-stimulated insulin secretion that is reduced in INS1 cells and mouse islets under lipotoxicity. These results indicate that acidifying lysosomes with acNPs improved lysosomal function and autophagic flux in INS1 cells under lipotoxicity, and are of therapeutic interest for pathologies associated with lysosomal acidity impairment such as type II diabetes and non-alcoholic fatty liver disease (NAFLD).

**BM04.09.10**

Synthesis and Characterization of Non-Cell-Adhesive Gelatin/Pluronic Hybrid Hydrogels

Ju-Yi Li, Clement Marmarot, Miriam Rafaelovich and Marcia Simon; Stony Brook University, Stony Brook, New York, United States.

Non-cell-adhesive hydrogels stand important roles in many in vivo applications. In the case of periodontitis, a biodegradable non-cell-adhesive material could isolate the soft gum tissue from the hard bone and promote selective growth of both tissues on each side of the membrane. Many shortcomings are associated with the use of current materials like polytetrafluoroethylene including degradability, workability, cost or cytotoxicity. In this study, we introduce a novel cost-effective material, a hybrid biodegradable of gelatin and Pluronic F127, strong enough to withhold mechanical degradation during the surgical procedure but yet degradable in vivo, non-cytotoxic, porous to promote the diffusion of nutrients and physiological fluids while remaining anti-adhesive. The hybrid films, would be ideal for this type of application. The hybrid gels were crosslinked via microbial transglutaminase (mTG). Hybrid gels with different ratio of gelatin, F127 and mTG were synthesized. Rheological properties of those gels were determined by rheometer and the surface and side cut section of those gels were observed by laser scanning microscope and scanning electron microscope. UV-vis and FT-IR spectroscopy were used for structure characterization of the hybrid gels. Fibroblast with green fluorescent were seeded on the surface of hybrid gels to determine cell adhesive ability. Our results showed the synthesized hybrid gels preserve the mechanical stability of gelatin-based hydrogels, while also exhibiting excellent workability and non-cell-adhesive properties of Pluronic F127.

**BM04.09.12**

Antibiotic Eluting Contact Lenses for the Treatment of Bacterial Keratitis

Lianguo Kuang1, Lokendrakumar C. Bengani1, Amy Ross1, Daniel S. Kohane2 and Joseph B. Ciolino1; 1Department of Ophthalmology, Massachusetts Eye and Ear Infirmary, Harvard Medical School, Boston, Massachusetts, United States; 2Departments of Anesthesia and Surgery, Boston Children’s Hospital, Harvard Medical School, Boston, Massachusetts, United States.

Bacterial keratitis is one of the leading causes of corneal blindness. The current standard of care involves an intensive regimen of hourly antibiotic drops to eradicate the infection. A major unmet need for the treatment of bacterial keratitis is a sustained approach of drug delivery to improve treatment efficacy and patient adherence. Contact lenses are emerging as a promising platform for controlled ocular drug delivery and potential release of drugs to the back of the eye. We report here an antibiotic-eluting therapeutic contact lens (TCL) that incorporates a thin drug-polymer film within the periphery of a contact lens using standard materials, which enables the sustained release of drugs at therapeutic rates, while allowing unimpeded vision through a central aperture in the lens. Antibiotic–polymer films were encapsulated in methacrylon via ultraviolet light polymerization and then lathed into contact lenses. Various UV polymerization conditions were examined to achieve the suitable physical properties of TCLs. The physical properties and morphology of antibiotic-eluting TCLs were characterized. Fourth-generation fluoroquinolones and polymers in the drug-polymer films were characterized by Fourier-transform infrared spectrometer. In vitro drug release was evaluated under infinite sink conditions. TCLs enabled the sustained release of besifloxacin and moxifloxacin for more than 24 hours in clinically relevant mass. The release of gatifloxacin from TCLs was also achieved in a temporally controlled manner but was faster than that of besifloxacin and moxifloxacin. Additionally, in vitro drug release profiles were tuned by polymer characteristics (hydrophobicity, hydrophilicity, and molecular weight), polymer/drug ratios, polymer/plasticizer ratio, and polymer ratios in the blend film. The antibiotic-eluting TCL may be used as a convenient alternative for extended ocular drug delivery with translational potential for the treatment of bacterial keratitis.
Self-assembled, a process that assembles molecules into ordered structures can form numerous structures in various conditions. Self-assembled structures when made from biomolecules such as DNA and peptides, form functional and biocompatible nanostructures such as nanotubes, fibers, spheres, which could be used in different biomedical applications. We have synthesized aromatic dipeptide-based nanotubes using dityrosine and tryptophan-tyrosine through solution-phase self-assembly (SPSA) and eco-friendly plasma enhanced chemical vapor deposition (PECVD). Insights into the self-assembly process and driving forces involved were obtained using quantum chemical computational methods at different levels of theories like dispersion-corrected density functional and Moller-Plesset perturbation.

The morphological features of SPSA and PECVD nanotubes were studied using confocal and scanning electron microscopes. These nanotubes were characterized using thermally and spectroscopically using differential scanning calorimetry and thermogravimetric analysis, Fourier transform infrared spectroscopy, liquid chromatography-mass spectroscopy, and Raman scattering, and circular dichroism spectroscopy, and powder x-ray diffraction. The cytotoxicity and biological interactions of these nanotubes with rat adrenal pheochromocytoma (PC-12) and human bone marrow neuroblasts (SH-SY5Y) cells were studied using MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide), dopamine-enzyme linked immunosorbent assay and real-time polymerase chain reaction (q-PCR). We observed substantial differences in proliferation and expression between the cells grown on tissue culture treated and nanotubes coated surfaces.

Creating Rechargeable Anti-Thrombotic Surfaces via Enzyme Mediated Ligation Hyun Ok O. Ham1, 2, 3, Madhukar S. Patel1, 2, 3, Carolyn Haller1, 2, 3, Erbin Dai1, 2, 3, David R. Liu1, Jian Liu1 and Elliot Chaikof2, 4, 5; 1Harvard Medical School, Boston, Massachusetts, United States; 2Wyss Institute, Boston, Massachusetts, United States; 3Beth Israel Deaconess Medical Center, Boston, Massachusetts, United States; 4Harvard University, Cambridge, Massachusetts, United States; 5University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Foreign body reactions at the blood-material interface frequently result in implant failure. Current engineered anti-thrombotic coatings are challenged by bioactive surface breakdown resulting in device-associated complications. This study aims to develop a system for generating ‘rechargeable’ surfaces utilizing reversible bond formation between bioactive molecules and modified implant surfaces through enzyme-mediated ligation. In this scheme, reversibility allows for stripping of degraded coatings with subsequent surface recharging.

Variants of laboratory evolved Staphylococcus aureus sortase A (eSrtA) were generated for reversible transpeptidation of two anti-thrombotic molecules (recombinant thrombomodulin [TM] and heparin oligosaccharide [HS]) on implantable medical devices. Two eSrtA variants were designed to specifically recognize different peptide tags available on therapeutically active TM and HS. Using eSrtA, repeated charging/ stripping of TM was conducted in vitro in whole blood, and subsequent generation of activated protein C (aPC) was demonstrated. Similarly, chemo-enzymatically synthesized ultra-low molecular weight heparin oligosaccharide (HS), which binds to antithrombin III that can inhibit factor Xa activities involved in the blood coagulation cascade reaction, was repeatedly immobilized and striped utilizing reversible enzyme ligase. Within an hour of incubation on pentaglycine-modified surfaces, eSrtA variants could selectively charge/stripe of TM and HS in a sequential or simultaneous manner. Alternating charging/stripping of TM/HS on the surface and thereby switching on/off of aPC generation and anti-Fxa inhibition from the surface was also validated. For a translational application, reactions were subsequently performed and confirmed on the luminal side of implantable vascular catheters.

The ability to regenerate bioactive coatings using eSrtA variants is a means by which engineered implant surfaces can be functionally preserved. Furthermore, using this system to perform site-specific co-immobilization of different anti-thrombotic moieties on vascular catheters and selectively regenerate bioactivity has potential to decrease long-term implant related morbidity through targeted action on distinct parts of the coagulation cascade.

Self-Assembled Peptide Nanotubes for Neural Cell Proliferation Prathyushakrishna Macha, Vikas Soni, Maricris Mayes and Milana Vasudev; University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States.

In the field of tissue engineering, design and fabrication of precisely patterned, highly porous scaffolds/matrices are required to guide overall shape of tissue growth and replacement. Although Rapid Prototyping fabrication techniques have been used to fabricate the scaffolds with desired design characteristics, controlling the interior architecture of the scaffolds has been a challenge due to CAD constraints. Moreover, large thick tissue scaffolds have reported limited success primarily due to the inability of cells to survive deep within the scaffold. Without access to adequate nutrients, cells placed deep within the tissue construct die out, leading to non-uniform tissue regeneration. This study aims to overcome these design and fabrication limitations. In this work, research has been expanded to design of scaffolds which have inbuilt micro scale fluidic networks. In this procedure, inbuilt channels serve as material delivery paths to provide oxygen and nutrients for the cells. First of all, negative of a cylindrical shape with a single channel was designed with AutoDesk Inventor and printed with a 3D printer to be used as a mold. Then, 3D printed mold was filled out with Poly(ethylene glycol) diacrylate (PEGDA) which is a photo-curable solution to fabricate the cylindrical hydrogel. Once PEGDA was exposed to UV light with the wavelength of 365nm, polymerized completely in about 3 minutes. After that, the same procedure was repeated for cylinders with two and three channels respectively. Then, their mechanical characterization tests were done to compare the compressive strengths of the scaffolds that has different internal architectures. Our preliminary results indicate that, 3D printing and polymerization techniques can be used together to control the interior architectures as well as the compressive strengths of scaffolds.

BM04.09.16
Antibacterial Properties of 2D Black Phosphorus Nanosheets for Regenerative Engineering Emre Firlar1, 2, Laura Alzate1, Ramin Rojaee2, Reza Shahbazian-Yassar1 and Tolou Shokhparvar1; 1Bioengineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois, United States; 3Biomedical Engineering, EIA University, Envigado, Colombia.

2D black phosphorous is an emerging new material with implications for regenerative engineering. Bacterial infection during implant surgeries has been a major concern for the long-term stability of the installed implant due to the health and cost burdens on the patients. Osseointegration between the implant and tissues will deteriorate due to the presence of bacteria in addition to the spread of bacteria through-out the body. Therefore, novel biocompatible nanomaterials should be developed to fight against the bacteria. Black phosphorus (BP), which is biocompatible, has been proven to be effective in this regard, but mainly with irradiation with near infrared light. Extensive irradiation of photons to emit singlet oxygen will worsen the effectiveness of BP and cause hypoxia to the cells. Thus, independent irradiation strategies should be developed to kill the bacteria using BP. In this work, E. coli and M. magneticum were cultured and the effectiveness of BP was tested for their antibacterial properties through fluorescence imaging, cell counting and
Materials and Methods:

Patient-derived GBM and brain endothelial cells (ECs) – both critical components in the perivascular invasive niche. In general, cells do not interact directly with substrates. Rather, extracellular matrix substrates will depend on the conformation of the adsorbed ECM. Therefore, in order to comprehend the mechanism through which graphene affects stem cell differentiation, it is important to understand the influence of graphene on ECM protein structures. We have previously shown that the differentiation of dental pulp stem cells is greatly affected by the substrate morphology of poly(4-vinylpyridine) (P4VP). It provides a perfect platform to study the additional effect of graphene on the cells. We found that graphene can be easily distributed into this system by electrospinning and spin coating process.

The Effects of Graphene in Different Morphologies of Polymer on Dental Pulp Stem Cells

Linxi Zhang, Kuan-Che Feng, Chung-Chueh Chang, Marcia Simon and Miriam Rafailovich; Materials Science and Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; Oral Biology and Pathology, Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Graphene and graphene-based materials have been developed and widely used in tissue regeneration engineering, due to their excellent physical properties. Many studies have shown that graphene can control and accelerate multi-lineage differentiation of stem cells in vitro. Graphene are commonly used, in most studies, as the substrates which have direct contact with the cells. In general cells do not interact directly with substrates. Rather, extracellular matrix proteins secreted by the cells adsorb first, coating the substrates, enabling cell adhesion. Hence as was previously shown, the response of the cells on these substrates will depend on the conformation of the adsorbed ECM. Therefore, in order to comprehend the mechanism through which graphene affects stem cell differentiation, it is important to understand the influence of graphene on ECM protein structures. We have previously shown that the differentiation of dental pulp stem cells is greatly affected by the substrate morphology of poly(4-vinylpyridine) (P4VP). It provides a perfect platform to study the additional effect of graphene on the cells. We found that graphene can be easily distributed into this system by electrospinning and spin coating process. The cell behavior and biomimralization and differentiation of DPSCs on the graphene-containing scaffolds are determined by multiple techniques, including SEM, Raman and RT-PCR. The results show that the cell-secreted ECM structure and biomimeralization on different scaffolds are affected by the addition of graphene in the original polymer matrices. The research was supported in part by the NSF (Inspire Award #1344267) program.

BM04.09.17

The Effects of Graphene in Different Morphologies of Polymer on Dental Pulp Stem Cells

BM04.09.18

Biomimetic, 3D Hydrogels to Investigate Effects of Microenvironment Biophysical Properties on Patient-Derived Glioblastoma (GBM) and Endothelial Cells (ECs)

Alireza Sohrabi, Jesse Liang and Stephanie Seidlits; University of California, Los Angeles, Los Angeles, California, United States.

Introduction: This study investigated how the mechanical microenvironment of glioblastoma (GBM) tumors may affect morphology and phenotype of patient-derived GBM and brain endothelial cells (ECs) – both critical components in the perivascular invasive niche.

Materials and Methods: Hydrogels were fabricated from thiolated hyaluronic acid (HA-SH) (0.5 w/v%) and 4-arm PEG-SH (varied), 8-arm PEG-norbomene (varied). Gelation occurred upon exposure to UV light (365 nm, 4 mw/cm²) for 15 s in the presence of a cytoocompatible photoinitiator LAP (Lithium Pehnyl (2, 4, 6-trimethylbenzoyle) phosphinate, 0.025 w/v%). Patient-derived gliomaspheres or single dissociated ECs were mixed with hydrogel precursors prior to gelation. Phase contrast images were acquired every 3 days to monitor cell migration. After 9 days, 3D cultures were fixed, and cells visualized with CellMask® Green (ThermoFisher) and Hoechst (nuclei). Cell survival following encapsulation was evaluated using a Live/Dead Assay (Life Technologies). A Leica LSP5 confocal microscope was used to image 3D cultures. Storage moduli (G′) of hydrogels were measured using shear rheometer (TA DHR-2) with an 8-mm flat plate geometry.

Results and Discussion: Hydrogel stiffness (G′) was controlled by varying Thiol content to achieve a range of 150–1500 Pa, which are representative of the normal brain and tumor microenvironments, respectively. Gliomaspheres and ECs cultured showed comparable survival 7 days post-encapsulation in both soft and stiff gels. Gliomaspheres cultured in stiff hydrogels remained did not migrate away from spheroids, while cells encapsulated in soft hydrogels exhibited robust migration. Our previous results showed that ECs residing in GBM perivascularute differently express high amount of integrin-binding sialoprotein (IBSP). Survival of ECs in hydrogels barring different biophysical properties is an appropriate platform to study the effect of stiffness on ECs protein expression.

Conclusion: Patient-derived GBM and ECs were successfully cultured in 3D HA hydrogels mimicking biophysical properties of brain or GBM tumor tissue. GBM cells cultured in stiffer environments were unable to migrate, but upon culture in soft environments were found to migrate up to 200 µm away from seeded spheroids within 9 days of cultures.

BM04.09.19

Tissue Engineered Scaffolds—Next Generation 3D Bone Mimetic Cancer Metastasis Testbeds

Kalpana Katti, MD Shahjahan Molla, Sumanta Kar and Dinesh R. Katti; North Dakota State University, Fargo, North Dakota, United States.

Tissue engineering through use of scaffolds is a very promising technology for replacement of tissues in regenerative medicine. A unique nanoclay based scaffold that enables mineralization of hydroxyapatite inside nanoclay galleries provides structural support and enables growth, proliferation and differentiation of human mesenchymal cells to form hierarchical mineralized collagen and ECM formation mimicking bone which is useful for regenerative medicine. In addition, it is known that breast cancer and prostate cancer have the propensity to metastasize to bone in the human body. The cancer at this stage of metastasis is incurable. Here we describe the use of tissue engineered bone as a humanoid testbed to create cancer tumors in vitro. We also demonstrate that this engineered test-bed duplicates the last stage of cancer metastasis as indicated by the gene expression and immunocytochemistry analysis of the tumors generated in the testbed. We also report the use of unique nanoindentation methodology to obtain elastic properties of tumors as they grow at the humanoid metastasis stage inside the bone scaffolds. FTIR experiments are also conducted during progression of tumor at metastasis and unique signatures of the DNA and protein contents during cancer progression are reported. Nanomechanical experiments on live tumors during their evolution and growth is related to the gene expression studies to bring mechanobiology as a new biomarker of the cancer progression. The engineering testbed can be used for personalized medicine as well as a screening tool for new anti-cancer drugs. Regenerative medicine thus provides unique opportunities to evaluate cancer metastasis.

BM04.09.21
Collagen is at once a main structural material and the most abundant protein in vertebrates. Collagen hydrogel reflects mechanical behavior of human tissues and is the most commonly used scaffold material and extracellular matrix in tissue engineering. As a structural material, it bears and loads stress and affects cell behavior depending on mechano-sensitivity of each cell type. Thus, providing prediction of cell response and mechanical reliability of collagen hydrogel presents significant challenge, so it is essential to understand mechanical properties of aforementioned material. However, soft collagen hydrogels were only tested shear, compressive and rheological properties because they have instability by gravitational forces and dehydrating issues at existing tensile testing methods. In addition, polymer network structure of collagen hydrogel varies under applied stress with showing non-linear stress-strain relationship and mechanism for the non-linearity was not proven yet. To predict hydrogels’ mechanical behavior completely, previously unavailable tensile data is required, and an alternative methodology is necessary to collect tensile properties of collagen hydrogel. In this study, we aim at investigating the mechanical behavior of collagen hydrogels under quasi-static tensile stress by suggesting a solution for tensile testing of soft collagen hydrogel and providing its mechanical response to tensile stress. Tensile testing on water surface imparts hydrating and free-standing environment to collagen hydrogels. Moreover, microstructure analysis of collagen hydrogels using SEM, and nano-scale 3D X-ray tomography demonstrates the mechanism of shown tensile properties. As the fiber diameter increases and the crosslink density decreases with decreasing gelation temperature, the tensile modulus due to the network structure change increases. In addition, the higher the collagen concentration, the more the crosslink density and the elastic modulus increase. After the first regime of mechanical behavior, the entropic deformation of the collagen network is completed and the enthalpic deformation of the network begins. These results illustrate that collagen hydrogels respond in complex manners to tensile stress, either as network or as fiber, which shows non-linear stress-strain relationship. Furthermore, we propose a new approach for tensile testing method for soft and hydrated materials that can be applied for bioengineering field.

**BM04.09.22**

Sphingosine-1-Phosphate-Bound High-Density Lipoprotein-Mimetic Nanoparticles Engineered to Protect Endothelial Functions in Cardiovascular Disease  
Hyun-Ji Park, Jwom Yom, Yoshiataka J. Sei and YongTae Kim; Georgia Institute of Technology, Atlanta, Georgia, United States.

Sphingosine-1-phosphate (S1P) is a natural signaling sphingolipid known to have important roles in regulating vascular and immune systems. In human plasma, S1Ps are associated with high density lipoprotein (HDL) of apolipoprotein A1 (ApoA1) and apolipoprotein M (ApoM) and leads to pleiotropic functions through specific receptors such as S1PR. Specifically, S1P-bound HDL (HDL-S1P) regulates several key biological functions in vascular system, such as endothelial nitric oxide (NO) production and vasodilatation. Plasma S1P levels are reportedly lower in patients with coronary artery disease, indicating that S1P is involved in the pathogenesis of atherosclerosis. However, the pathophysiological and molecular mechanisms leading to such disease-associated shifts in HDL-S1P remain elusive due to multiple reported arguments of the biphasic, pro- and anti-atherosclerotic properties. Here, we leverage out *in vitro* human carotid artery-mimicking model system to study the biological function of S1P using engineered HDL-mimetic nanoparticles (eHNP)s. Our advanced microvortex technology enhanced assembly of hydrophobic lipids (DMPC and/or S1P) and hydrophilic proteins (ApoA1 and ApoM) to continuously produce homogenous discoidal eHNPs, such as eHNP-A1, eHNP-A1-S1P, and eHNP-A1-M-S1P with the size range of 10 to 15 nm, which is consistent to the native HDL. These eHNP-s were endocytosed to human carotid artery-derived cells such as human carotid artery endothelial cells and smooth muscle cells. Moreover, the uptake efficiency of eHNP-A1 was enhanced by incorporating S1P into the eHNP-A1 (eHNP-A1-S1P). More interestingly, we successfully reproduced natural carotid arterial functions such as endothelial NO production and vasodilatation using our *in vitro* cardiovascular model system and investigated the physiological functions of eHNPs under pathophysiological conditions such as TNF-α stimulation or disturbed flow. This study helps to understand the mechanisms of endothelial effect of HDL and S1P and provides clues to improve HDL-based clinical studies of cardiovascular diseases. Our integrated approach using the designed eHNP complex and *in vitro* cardiovascular model system reported in this study are promising prescreening alternatives to costly animal model studies to study the structural and functional heterogeneity of HDL. Moreover, this study potentially leads to novel therapeutic measures that can prevent the progression of cardiovascular diseases such as atherosclerosis and coronary artery diseases.

**BM04.09.23**

Cardioprotective Effects of *Asparagus racemosus* Against Doxorubicin Induced Cardiotoxicity in Rats  
Manisha Chatterjee, Raj Kumar Goel, Manish Saxi, K.K. Saxena, Pinki Vishwakarma and Monica Sharma; Lalaji Lajpat Rai Memorial Medical College, Meerut, India.

Recently, herbal remedies have raised considerable research attention as they are safer, less expensive with fewer side effects than synthetic drugs. Here we report, the cardioprotective potential of medicinal plant *Asparagus racemosus* against cardiotoxicity induced by anticancer drug Doxorubicin. The comparison was done with the standard cardioprotective drug (Carvedilol) in albino rats. For this experimental study, the albino rats were divided into four different groups namely Control group (administered pellet diet and tap water for 21 days), Toxic control group (in addition to pellet diet and tap water this group was administered Doxorubicin in a single dose intraperitoneally on 21st day), and two Test groups (they were administered aqueous extract of *Asparagus racemosus* in doses 250mg/kg and 500mg/kg respectively for 21 days, followed by Doxorubicin in a single dose intraperitoneally on 21st day) and a Standard group (treated with Carvedilol per orally for 21 days followed by Doxorubicin in a single dose intraperitoneally on 21st day). All animals were sacrificed 48 hours after Doxorubicin administration. Blood samples were collected and different pathological tests like CK-MB, LDH, SGOT, and SGPT were performed. It was observed that the serum levels of CK-MB, LDH, SGOT, and SGPT were raised significantly in the Toxic control group, whereas these values were raised but to a lesser extent in the test group treated with *Asparagus racemosus* in dose of 250mg/kg, and these were within the normal limits in the test group treated with *Asparagus racemosus* in dose of 500mg/kg which was comparable to the standard group treated with Carvedilol. The histopathological tests of the dissected heart also confirm these observations. Collectively, these data indicate that *Asparagus racemosus* pretreatment could alleviate doxorubicin-induced cardiotoxicity.

**BM04.09.24**

CHANNELMAT—Controlling Mechanotransduction in Porous Biomaterials  
Mohammadreza Taale, Katharina Siemsen, Christine Arndt, Fabian Schutt, Rainer Adelung and Christine Sellhuber-Unkel; University of Kiel, Kiel, Germany.

Cells respond to external mechanical stimuli through a biological process called mechanotransduction. Mechanotransduction has great impact on cellular proliferation, migration and differentiation, as well as on cell adhesion. Likewise, diseases such as cancer and cardiac dysfunctions are also related to cellular mechanotransduction. Here we show data on controlling cells by an innovative 3D material that serves as a platform for controlling mechanotransduction by mimicking natural 3D cellular environments. Our material contains microporous structures represented by micron-sized channels that are embedded in a soft hydrogel matrix. For controlling mechanotransduction, the stiffness of the matrix is well-defined by the amount of cross-linker in the hydrogel. In addition we modify the hydrogel such that its surface is equipped with cell adhesion ligands, e.g. RGD and collagen. As the pores in the material provide a large and spatially controlled cell-surface contact area of up to 80%, the mechanical properties of the hydrogel environment will have
large impact on the cells. As an additional feature, we can also control the conductivity of the porous hydrogels by the targeted addition of carbon nanomaterials such as CNTs and graphene. We here show first data on the biocompatibility of the materials, on cell growth in the materials and how we can control the properties of cells by our materials.

**BM04.09.25 Efficient Excision of Proviral HIV-1 Genome in Human Primary Cells with Cell Penetrating TALEN Nanoparticles** Ming Zhao, Jing Wen and Yunfeng Lu; University of California, Los Angeles, Los Angeles, California, United States.

A critical step during human immunodeficiency virus (HIV) infection occurs when the complementary viral DNA is integrated into the host genome. This so-called “HIV provirus” becomes transcriptionally silent and sustains as a latent viral reservoir that can escalate new infections upon self-reactivation. Though the present anti-retroviral therapies could effectively suppress active virus replication, the latent HIV-1 reservoirs remain intractable and a tremendous risk to infected individuals. Therefore, a novel therapy that could abrogate proviral DNA is highly desirable but challenging. Genome-editing technologies whereby cellular genomic information is readapted have become increasingly utilized recently. Targets for gene modification, including the HIV-1 genome itself, have been investigated as a potential therapy for HIV-1 disease using the clustered regularly interspaced short palindromic repeat (CRISPR)/Cas9 endonuclease system and the transcription activator-like effector nucleases (TALEN), yet the off-target cleavage of the CRISPR/Cas9 remains a concern by many scientists. In contrast, TALEN possesses significant accuracy and robust nuclease activity for the targeted sequence. So far, cell-penetrating peptide (CPP) mediated TALEN delivery has been applied to knock down the HIV-1 co-receptor, CCR5, yet the working concentration of TALEN protein was excessively high (~μM). Likewise, transfection of TALEN mRNA abolishes HIV-1 proviral function drastically in T cell lines, which, however, is ineffective in disrupting proviral DNA in primary T cells. Herein, we report a proof-of-concept study that TALEN protein under the guidance of a pH-sensitive nanocapsule could be effectively delivered into the nucleus. The cationic surface charge and the acid-labile crosslinkers of the nanocapsule enable high-efficient transmembrane transportation, cargo release and avoidance of endosome/lysosome sequestration. As a result, the delivered TALEN demonstrated good gene-editing capability under an ultra-low working concentration. In particular, HIV-1 latent reservoirs in primary T cells were efficiently excised with this strategy, thereby providing a useful suggestion for developing anti-HIV drugs, particularly against integrated HIV genome in primary cells.

**BM04.09.26 Hierarchical Decoration of Eggshell Membrane with Polycaprolactone Nanofibers to Fabricate a Bilayered Scaffold for Full-Thickness Cutaneous Wound Healing** Prateek Gupta Ray, Pallabi Pal and Santana Dhara; BMTE, School of Medical Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, India.

The modern era of skin tissue engineering focuses on engineering and fabrication of scaffolds that can closely mimic the extracellular matrix and its microenvironment so as to facilitate cell adhesion and proliferation. The objective of the present study is to design and fabricate a porous, mechanically stable, biocompatible and non-immunogenic bilayered scaffold for wound healing applications. In order to do so, microfibrous eggshell membrane (ESM) along with nanofibers of Polycaprolactone (PCl) was deployed. In addition to a rich source of collagen, ESM also contains several growth factors and GAGs, essential for the regeneration process. A homogeneous blend of PCl was electrospun onto the ESM to decorate it with randomly arranged nanofibers (200 nm diameter), followed by cross-linking the same with microfibers (2μm diameter) using NHS/EDC coupling (EpN). The surface topography of the 1μm thick bilayered scaffold was explored using FE-SEM and AFM, while the porosity was evaluated using BET analysis. The spectroscopic analyses using FT-IR and XPS reveal successful crosslinking between the nanofibers of PCl and microfibers of ESM in the scaffold which corroborates to FESEM and AFM results. The matrix exhibits considerable enzymatic degradation after 27 days, 70% wettability, tensile strength of 15 MPa and substantial anti–microbial activity. In addition, MT, Rhodamine–DAPI assay and FESEM studies demonstrate excellent cell adhesion and proliferation of human dermal fibroblast (hDF) cells. Furthermore, the samples presented enhanced wound healing characteristics when grafted over a full thickness wound on a rat model. Moreover, the histopathological examination of the treated wounds at different time intervals revealed fast re-epithelization and collagen deposition in the extracellular matrix. Epi implanted wounds demonstrated complete wound closure within 14 days. Excellent physico-chemical properties and superior wound healing efficacy demonstrated by micro/ nano architected EpN mats make it a potential wound healing matrix for clinical skin regeneration.

**BM04.09.27 Terminal Autoclave Sterilization—Impact on Cryogel Properties and Injectableability** Sidi Benchetrit1, 2, 3, Pierre Villard1, Mahboobeh Rezaeeazad1, Kasturi Joshi Navare4, Colombani Thibault1 and Adnan Memee1, 4; 1Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; 2Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 3Sorbonne University, UTC CNRS UMR 7338, Biomechanics and Bioengineering (BMBI), University of Technology of Compiègne, Compiègne, France; 4Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia.

While effective sterilization is crucial for clinical utilization of biomaterials, maintaining both their structural and biological properties post-processing remain a challenge. One of the most popular terminal sterilization methods is heat sterilization and more particularly autocloving. Autoclaves use highly pressurized steam heated up to 134°C which is detrimental to many biomaterials including polymeric hydrogel scaffolds. Three-dimensional scaffolds are attractive for many tissue engineering applications due to their unique properties such as high-water content, tunable mechanical properties and biocompatibility. However, hydrogels typically get sanitized not sterilized, especially in an academic setting, as they are unable to survive the autoclave sterilization process.

Recently, we have developed a new class of more robust hydrogels with unique properties. These cryopolymerized hydrogels or cryogels do not only possess large and interconnected pores, and mechanical robustness sustaining up to 90% deformation, but also shape memory properties allowing their injection through conventional needles. A series of injectable cryogels prepared with various biopolymers have been autoclaved and tested not only for their degrees of sterilization but also for their physico-chemical integrity (i.e. injectability, physical properties, and retention of their intrinsic biological properties). Overall, our preliminary results suggest that unlike conventional hydrogels, injectable cryogels are resilient to the aggressive nature of steam sterilization and are well suited as safe and non-invasive biomaterials for a number of biomedical applications.

Acknowledgement: This work was supported by Northeastern University (Tier 1 Provost grant). Funds by the Thomas Jefferson Fund, FACE Foundation, and the Burroughs Wellcome Fund are acknowledged.

**BM04.09.28 Advanced Drug Delivery Platform—Silica Nanoparticles Engineered with Nanoscale Surface Roughness** Hao Song and Chengzhong Yu; The University of Queensland, Brisbane, New South Wales, Australia.

Recent advances in nanotechnology have greatly boosted the development of drug delivery systems, while the key challenge still lies in the rational design and fabrication of safe and efficient nano-carriers. It is noteworthy that the delivery performance could be possibly maximized by custom-designed nano-
carriers considering the configuration and surface textures of both cargo biomolecules and target cell/environment. Here, we showcase our recent progress on the development of silica-based advanced delivery platform by engineering the surface textures at the nanoscale. First, through a biomimetic approach, silica nanoparticles with an intrinsic spiky surface are fabricated.[1] The nanoscale surface roughness exhibits interesting surface properties at the microscale, enabling the nanoparticles with strong adhesion toward the hairy bacterial surface, thus leading to an efficient antimicrobial enzyme delivery. Then this novel delivery system is well extended for gene delivery.[2] Distinct from small drug or protein molecules, plasmid DNA possesses unique rope-like loop structures. The spiky nanotopography is here further demonstrated with great advantages at the nanoscale, acting as hooks to entangle the DNA loops and protect the gene molecules settled in the spiky layer against nuclease degradation. These spiky nanoparticles show excellent gene transfection efficacy, especially under harsh enzymatic conditions. The intriguing properties enabled by this unique nanoscale rough feature have been further explored in our recent studies. This rough nanoparticle-based novel delivery platform is of significant potential in practical biomedical translations, such as antibiotic-free animal feed and DNA vaccines.

BM04.09.29
pH Sensitive Nanoparticles to Study the Biofilm Interfacial Microenvironment Padryk Merkl and Georgios A. Sotiriou; Karolinska Institutet, Stockholm, Sweden.

Implant associated infections caused by biofilms are a major cause of implant rejection. One promising strategy to help combat biofilms are “smart” anti-biofilm release surfaces. These surfaces are often loaded with antibiotics or other antimicrobials and respond to the creation of a microenvironment characteristic of biofilms by releasing their cargo. One such characteristic biofilm microenvironment is low pH, whereas in healthy tissue the pH should lie close to 7.4 at the biofilm substrate interface the pH can decrease to 5 and below. These heterogeneous pH environments have been studied previously using electrodes and optical devices. However, here a novel ratiometric sensor which relies on the same processes for sensing as for antimicrobial release is presented in order to optically probe the interfacial biofilm surface pH. Calcium phosphate nanoparticles doped with europium were synthesised and directly deposited onto silicon wafer chips by flame spray pyrolysis, the deposited film was then further stabilised by in situ annealing. These phosphorescent nanoparticles exhibit pH dependent dissolution, with an associated decrease in luminescence intensity which provides a sensor response and known pH buffers were used to draw a calibration curve. A panel of clinically relevant biofilm forming bacteria of both the gram-negatives and gram-positives were selected to measure their interfacial pH. Both gram-negatives and gram-positives demonstrated low pH environments, however, differences between bacterial strains and species were observed. These pH responsive silicon chips can therefore be used to guide the development of anti-biofilm surfaces to target particular bacterial infections.

BM04.09.30
Engineering Vascularized Cardiac Tissue Using a Combination of Electrosprinning and 3D-Bioprinting Technologies Ibrahim Mostafavi and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Cardiovascular disease is one of the most leading causes of mortality in the USA. Fabrication of 3D large-scale cardiac tissue constructs with functional vascularization has been a great challenge in engineering tissues suitable for repairing injured heart tissue. To address this challenge, here a new combinatorial approach of electrosprinning and 3D bioprinting techniques is employed to make a functional cardiac tissue. First, we engineered highly elastic blood vessel made of gelatin methacryloyl (GelMA) and poly(e-caprolactone) (PCL) by using electrosprinning technique. The engineered tube was then endothelialized in vitro by using human umbilical vein endothelial cells (HUVECs) and perfused by culture media to form a functional blood vessel. In the next step, and a cell-laden GelMA-based hydrogel was 3D printed around the engineered GelMA/PCL vessel to form a vascularized cardiac tissue. Also, the effect of incorporation of Iron Oxide (Fe3O4) magnetic nanoparticles (MNPs) into both electrospin fibers as well as 3D printing GelMA bioink will be investigated to find out its influence on the cell growth, proliferation as well as the cardiac tissue regeneration. Our results revealed that the mechanical properties of the engineered GelMA/PCL vessels are comparable with small diameter porcine blood vessels. Moreover, the fabricated vessels by electrosprinning are suturetable and depicts high suture retention strength. The 3D printed cell-laden GelMA hydrogels exhibited high cell viability over 5 days (>90%) of culture as captured from fluorescent microscopy images using a commercial Live/Dead assay. The metabolic activity of 3D printed cell-laden GelMA hydrogel also increased consistently during 5 days of culture as measured by using PrestoBlue assay. In addition, the number of cells increased around 3-fold from day 1 to day 5, confirming cell proliferation within 3D printed hydrogels.

BM04.09.32
Silver Nanowire/Chitosan Nanocomposite Scaffolds for Tissue Engineering with Enhanced Durability Dilara Aydin1, Eda Ayse Aksoy2, Seyda Senel1, Husnu E. Unalan3 and Doga Doganay1; 1Pharmaceutical Technology, Hacettepe, Ankara, Turkey; 2Hacettepe University, Ankara, Turkey; 3METU, Ankara, Turkey.

We report on a successful scaffold based tissue engineering approach that aims to facilitate maximal cell seeding efficiency and subsequent cell proliferation using durable scaffolds with interrelated porosity with high surface area per volume and enhanced mechanical strength, durability. Among the biopolymers chitosan, which is a biodegradable, biocompatible cationic polysaccharide exerting bioactive properties (eg.antimicrobial, anti-inflammatory, hemostatic immunostimulatory etc) provides several advantageous as tissue scaffold. Previously we have shown antimicrobial activity of nanocomposite films of chitosan and silver nanowires (Doganay, 2017). In this study, silver nanowire/chitosan nanocomposite scaffolds were prepared via freeze-drying method and their durability were enhanced with αβ-glycerophosphate. Morphology and chemical nature of the nanocomposites were characterized by X-ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Mechanical strength, compression modulus, bioadhesion, porosity and water holding capacity of nanocomposite scaffolds were investigated. The scaffolds were observed to retain 35 to 65-fold water while maintaining their form and integrity. The nanocomposite scaffolds showed equilibrium swelling index compared to chitosan scaffold. Further mechanical analysis demonstrated that the incorporation of αβ-glycerophosphate enhanced the elastic modulus and tensile strength values of prepared scaffolds. These and other results obtained in this work revealed that the nanocomposite scaffolds can be mechanically and biofunctionally improved through tailoring the chitosan/αβ-glycerophosphate ratio and the amount of incorporated silver nanowires.

BM04.09.33

Shape-memory polymers (SMPs) are polymeric smart materials that have ability to return from a deformed state to their original shape by an external stimulus. Polycaprolactone (PCL) has properties of biocompatibility and biodegradable, therefore having a wide use in medical field such as drug delivery materials and biological tissue engineering. To make a shape – memory property in PCL, we proceed synthesizing poly(caprolactone-co-glycidylmethacrylate) (PCL-co-PGMA) which is network structure polymer by copolymerizing glycidylmethacrylate (GMA) with caprolactone (CL). PCL-co-PGMA was characterized by GPC, 1H-NMR. In addition, we controlled ratio of GMA in copolymer to set a melting temperature which is showing shape-memory property and DSC was performed.
The crosslinked poly(caprolactone-co-glycidylmethacrylate) network were prepared by photo-crosslinking with ultraviolet (UV) irradiation and using Irgacure 2959 by as the photoinitiating agent. The resultant crosslinked polymer was then characterized by DSC and dynamic mechanical analysis (DMA). Nitric oxide (NO) has many physiological functions such as vasodilation, neurotransmission, and angiogenesis in the human body. Especially, the nonthrombogenic properties of vascular surfaces are primarily attributed to NO generated from endothelial cells that line the inner walls of all blood vessels and Nitric oxide derived from endothelial cells regulates blood flow and pressure and inhibits platelet activation and aggregation under normal conditions. To enhance biocompatibility of shape memory polymer, Nitric oxide was introduced on the surface of shape memory polymer. After that, that was evaluated by cell toxicity test.

BM04.09.34 Preparation and Characterization of Poly(Glycerol-Sebacate-Stearic Acid) for Shape Memory Polymer Bo Keun Lee, Seol Jang and Woo Soon Jang; Future Bio Works Co., Seoul, Korea (the Republic of).

For past few decades, a new type of smart material, Shape Memory Polymer (SMP), has developed rapidly. Shape memory polymers can respond to changes in external conditions such as temperature, pH, and ionic strength. However, such as non-absorbable biomedical polymers can undergo undesirable reactions due to the physical or chemical properties of the surrounding biological components that can persist in vivo for a long period of time to cause toxic reactions in vivo. Therefore, these polymers may need to be removed from the body as a second surgery. Poly (glycerol-sebacate) (PGS) is a biocompatible and biodegradable elastomer that is used in a wide range of biomedical applications to manufacture microfluidic devices, vascular scaffolds, and other micro-tissue engineering systems. Polymers containing glycerol and sebacic acid have already been approved for medical use. While the porous form is preferred for the support to permit intracellular growth, PGS degradation has been studied primarily in non-porous form. Some papers describe their biocompatibility and biodegradation, but no studies have been presented on the shape memory effect of these polymers. The purpose of this study was to investigate shape memory properties, porosity and biocompatibility. Another way to strengthen this polymer is to impart new functionality such as poly (glycerol sebacate) -stearte (PGSS). PGSS based block copolymer with glycerol, sebacic acid and stearic acid by bulk polymerization. PGSS was successfully synthesized and characterized by 1H-NMR, GPC and DSC. The DSC was used to study the reversible movement required for temporary shape storage of shape memory materials. PGSS performed in vitro biocompatibility studies.

Characterization of PGSS is important when evaluating polymerization and future use of this biomaterial. The results confirm that PGSS is a shape memory material with a recovery rate of 99.5% or more. PGSS has also been found to be porous and biocompatible. Thus demonstrating that this material can be designed as a potential biomaterial in other applications where it interacts with pharmaceutical and biological systems.

BM04.09.35 Magnetic Hyperthermia Induced Liposomal Doxorubicin Release for Thermo-Chemotherapy Shan Zhao, Samuel Klein, James Petryk, Catalina Spatarella, Fridon Shabtideze, Zi Chen and Jack Hospes, Dartmouth College, Hanover, New Hampshire, United States.

The development of a targeted drug delivery system is an emerging approach to increase the targetability of anticancer agents. One of the most promising technologies to achieve high specificity is using a liposomal delivery system. In this work we developed a magnetic liposomal delivery system that combines magnetic nanoparticles (mNPs), the doxorubicin (Dox) and the application of an external alternating magnetic field (AMF). The mNPs are encapsulated in the hydrophilic core of liposomes and the Dox is embedded in the hydrophobic bilayer. Once the liposome is delivered into the tumor, then the AMF is activated. The AMF transfers the electromagnetic energy to the mNPs, which in return generates heat and increases the temperature locally in the surrounding ambral. When the temperature reaches the liposome melting temperature T_m, the Dox is released. To further increase the liposome’s targetability, in addition to the AMF-mNPs triggered Dox release approach, we have used a non-invasive, non-toxic external static magnetic field (SMF) to target the liposomes to the tumors. This combined AMF-SMF feature could reduce the non-specific side-effects and toxicity of encapsulated drugs, while ensuring a targeted, safe, high percentage Dox release and accumulation at the tumor site. An in vitro release experiment at 37°C showed that more than 80% of the encapsulated Dox was retained in liposomes after 6 hrs in PBS. Under the exposure of AMF (641 Oe, 170 kHz) for 10 mins, liposomes of 10 ug/ml displayed 80% of Dox release, indicating the high efficiency of this triggering technique. Mice inoculated with B16 murine melanoma cell, intradermal, rear limb, were assessed for Dox release and treatment efficacy when the tumors reached 120 mm³. Our preliminary in vivo study indicated that the external magnetic field demonstrated a notable increase of mNP when the STM was applied at the tumor site. 1 hour post-injection. The levels and distribution of Fe in tissue are examined via histopathology, TEM and ICP-MS. The concentrations of Dox in these biological samples (supernatants of tissue homogenates and plasma) are determined using the fluorescence spectrophotometer. This multimodal technology will allow for a safe, targeted, increase in Dox accumulation at the tumor site and ultimately an improvement in the therapeutic ratio and efficacy of Dox with radiation or other possible combinations of therapies.

BM04.09.36 Supercritical Carbon Dioxide Functionalization of Biomaterials with Antimicrobial Molecules Guillaume Nonglétou1,4, Clémentine Darpentigny1,4, Bastien Michel1,4, Pierre R. Marcoux1,4, Julien Bras1,4 and Bruno Jean1,4, 1CEA-Leti, Grenoble, France; 2CERMAT-CNRS, Grenoble, France; 3Grenoble INP-CNRS, Grenoble, France; 4Université Grenoble Alpes, Grenoble, France.

In a context where the need for innovative medical devices is increasing and the environmental issue is becoming a priority, the objective of this study was to develop “active” wound dressings with antimicrobial properties using a bio-inspired strategy and an eco-friendly solvent: supercritical carbon dioxide (SC-CO2). First, two different types of materials were studied: 1) nanocellulose-based aerogels or membranes and 2) polypropylene (PP), polyethylene terephthalate (PET) or polyamide (PA) plastic sheets as standard polymers used in biomedical applications. We choose to use nanocellulose derived from the biomass as biocompatible building blocks. Nanocellulose particles are a class of very promising bio-based material. In the biomedical field, their relatively low cost, low toxicity and biocompatibility have made them very attractive. They were assembled to prepare aerogels or surfaces with structural parameters controlled by the preparation process and the nanocellulose properties.

Then, the different materials were functionalized in SC-CO2 in an attempt to respect green chemistry principles. SC-CO2, considered as a non-toxic, eco-friendly solvent. The resultant functionalized polymer was then characterized by DSC and dynamic mechanical analysis (DMA). Nitric oxide (NO) has many physiological functions such as vasodilation, neurotransmission, and angiogenesis in the human body. Especially, the nonthrombogenic properties of vascular surfaces are primarily attributed to NO generated from endothelial cells that line the inner walls of all blood vessels and Nitric oxide derived from endothelial cells regulates blood flow and pressure and inhibits platelet activation and aggregation under normal conditions. To enhance biocompatibility of shape memory polymer, Nitric oxide was introduced on the surface of shape memory polymer. After that, that was evaluated by cell toxicity test.

Nitric oxide (NO) has many physiological functions such as vasodilation, neurotransmission, and angiogenesis in the human body. Especially, the nonthrombogenic properties of vascular surfaces are primarily attributed to NO generated from endothelial cells that line the inner walls of all blood vessels and Nitric oxide derived from endothelial cells regulates blood flow and pressure and inhibits platelet activation and aggregation under normal conditions. To enhance biocompatibility of shape memory polymer, Nitric oxide was introduced on the surface of shape memory polymer. After that, that was evaluated by cell toxicity test.

The detailed characterization of the structure materials and their chemical functionalization have been carried out using advanced technologies. The antimicrobial activity of the nanocellulose-based materials was assessed and correlated to the structure and chemistry. For impregnated molecules, the drug release kinetics and the zone of inhibition of growth were analyzed. For structures where antimicrobial agents were grafted, the contact killing activity was assessed and log-D reduction was measured against both bacteria and a eukaryote.
Carbon monoxide (CO), known for its toxicity, is a gaseous signaling molecule (gasotransmitter) endogenously produced through heme catabolism. CO is known to interact selectively with the soft metal centers of heme proteins and indirectly modulate other non-heme-containing targets through signaling pathways. This gasotransmitter participates in a variety of roles in mammalian pathophysiology and has been implicated in oxidative stress, cell proliferation, and apoptosis. In addition, CO has been shown to sensitize cancer cells to known chemotherapeutics, as well as induce dose-dependent eradication of malignant cells. The main difficulty with using CO as a therapeutic is its site-specific delivery in a controlled and sustained manner. Direct inhalation of CO requires continuous exposure to relatively high levels of this gas, lacking specificity and promoting negative effects. An alternate approach to deliver CO to tissue is to use CO-releasing molecules (CORMs). Photoactivated CORMs (photoCORMs), with a few exceptions, are metal carbonyl complexes that release CO upon illumination, allowing for the delivery of this gas with spatial and temporal control. Efforts have been made to impart desirable characteristics to these CO donors, such as visible light sensitivity, solubility, stability, and low toxicity. A wide variety of carriers have been used to deliver CO to biological targets. However, desirable delivery materials should retain the photoCORM or the CO-spent product, thus avoiding possible adverse side-effects. In this account, we describe a novel visible light active polyHEMA-based CO-releasing polymer (photoCORP-I). This hydrogel contains a manganese photoCORM ([Mn(CO)x(qbt)(4-vpy)]CF3SO3) co-polymerized to a hydroxyethyl methacrylate/ethylene glycol dimethacrylate (HEMA/EGDMA) backbone via use of a 4-vinylpyridine ancillary ligand. This covalent attachment ensures that the photoCORM as well as the CO-spent product remain inside of the bulk polymeric material. This robust yet flexible CO-releasing hydrogel can be molded, cast, or cut into any shape or form. Its high transparency and gas permeability allow for the rapid and sustained release of CO upon illumination with low power visible light. The release of CO can be visually tracked by the loss of the color arising from I. A fiber optic-based catheter using a photoCORP-Iip (CO-catheter) was constructed for use in light inaccessible cavities. The reported CO-catheter was successfully used to promote apoptosis in human colorectal adenocarcinoma (HT-29) cells by triggering CO photorelease under low power visible light. The easy application/removal of the CO-catheter from the malignant site circumvents toxicity arising from the photoCORM/photo-products while allowing for the delivery of controlled and sustained doses of CO at the target site. The use of this CO-releasing material coupled to a current endoscope can be used deliver required doses of CO to a colonic target.

Nanocellulose membranes and aerogels that exhibit lightweight and high specific surface areas were compared to determine the structure-functionalization-activity relationship. Impregnation

The mode of action and the lifespan of the newly designed antimicrobial materials were studied according to the incorporation process of bioactive molecules in supercritical carbon dioxide. Both impregnation and grafting can be used to impart antimicrobial properties and extend the shelf-life of the bioactive wound dressing. These bioactive materials will be used for the design of external wound dressings and implantable medical devices.

**BM04.09.37**

Eradication of HT-29 Colorectal Adenocarcinoma Cells by Controlled Photorelease of CO from a CO-Releasing Polymer (photoCORP-I) Triggered by Visible Light Through an Optical Fiber-Based Device

Miguel N. Pinto, Indranil Chakraborty, Cosme Sandoval and Pradip K. Mascharkar; University of California, Santa Cruz, Santa Cruz, California, United States.

Carbon monoxide (CO), known for its toxicity, is a gaseous signaling molecule (gasotransmitter) endogenously produced through heme catabolism. CO is known to interact selectively with the soft metal centers of heme proteins and indirectly modulate other non-heme-containing targets through signaling pathways. This gasotransmitter participates in a variety of roles in mammalian pathophysiology and has been implicated in oxidative stress, cell proliferation, and apoptosis. In addition, CO has been shown to sensitize cancer cells to known chemotherapeutics, as well as induce dose-dependent eradication of malignant cells. The main difficulty with using CO as a therapeutic is its site-specific delivery in a controlled and sustained manner. Direct inhalation of CO requires continuous exposure to relatively high levels of this gas, lacking specificity and promoting negative effects. An alternate approach to deliver CO to tissue is to use CO-releasing molecules (CORMs). Photoactivated CORMs (photoCORMs), with a few exceptions, are metal carbonyl complexes that release CO upon illumination, allowing for the delivery of this gas with spatial and temporal control. Efforts have been made to impart desirable characteristics to these CO donors, such as visible light sensitivity, solubility, stability, and low toxicity. A wide variety of carriers have been used to deliver CO to biological targets. However, desirable delivery materials should retain the photoCORM or the CO-spent product, thus avoiding possible adverse side-effects. In this account, we describe a novel visible light active polyHEMA-based CO-releasing polymer (photoCORP-I). This hydrogel contains a manganese photoCORM ([Mn(CO)x(qbt)(4-vpy)]CF3SO3) co-polymerized to a hydroxyethyl methacrylate/ethylene glycol dimethacrylate (HEMA/EGDMA) backbone via use of a 4-vinylpyridine ancillary ligand. This covalent attachment ensures that the photoCORM as well as the CO-spent product remain inside of the bulk polymeric material. This robust yet flexible CO-releasing hydrogel can be molded, cast, or cut into any shape or form. Its high transparency and gas permeability allow for the rapid and sustained release of CO upon illumination with low power visible light. The release of CO can be visually tracked by the loss of the color arising from I. A fiber optic-based catheter using a photoCORP-Iip (CO-catheter) was constructed for use in light inaccessible cavities. The reported CO-catheter was successfully used to promote apoptosis in human colorectal adenocarcinoma (HT-29) cells by triggering CO photorelease under low power visible light. The easy application/removal of the CO-catheter from the malignant site circumvents toxicity arising from the photoCORM/photo-products while allowing for the delivery of controlled and sustained doses of CO at the target site. The use of this CO-releasing material coupled to a current endoscope can be used deliver required doses of CO to a colonic target.

**BM04.09.38**

pH-Triggered Tumor Targeting Polymeric Micelles Loading with Dimeric Drug for FRET-Traceable Drug Release

Xing Guo1, 2, Lin Wang1, Kayla Duval1, Jing Fan1, Shaojing Zhou1 and Zi Chen1; 1Dartmouth College, Hanover, New Hampshire, United States; 2Southwest Jiaotong University, Chengdu, China; 3City College of New York, New York, New York, United States.

Trans-activating transcriptional activator (TAT), a cell-penetrating peptide, is extensively used for facilitating cellular uptake and nuclear targeting of drug delivery systems. However, the positively charged TAT peptide strongly interacts with serum components and undergoes substantial phagocytosis by the reticuloendothelial system, causing a short blood circulation in vivo. In this work, an acid-active tumor targeting nanoplatform DA-TAT-PECL was developed to inhibit the nonspecific interactions of TAT in the bloodstream. 2,3-dimethylmaleic anhydride (DA) is used to convert the TAT’s amines to carbonyl complexes that release CO upon illumination, allowing for the rapid and sustained release of CO upon illumination with low power visible light. The release of CO can be visually tracked by the loss of the color arising from I. A fiber optic-based catheter using a photoCORP-Iip (CO-catheter) was constructed for use in light inaccessible cavities. The reported CO-catheter was successfully used to promote apoptosis in human colorectal adenocarcinoma (HT-29) cells by triggering CO photorelease under low power visible light. The easy application/removal of the CO-catheter from the malignant site circumvents toxicity arising from the photoCORM/photo-products while allowing for the delivery of controlled and sustained doses of CO at the target site. The use of this CO-releasing material coupled to a current endoscope can be used deliver required doses of CO to a colonic target.

**BM04.09.39**

Comparative Study of Ampicillin-Loaded Melanin-Polycaprolactone Nanofibers Prepared by Single-Needle and Co-Axial Electrospinning Methods

Gözde Kabay1, 2, Gizem Ak3, Gizem Kaleli Can1 and Mehmet Mutlu3; 1Biomedical Engineering Division, TOBB University Of Economics and Technology, Ankara, Turkey; 2Biological Systems Engineering Department, University of Wisconsin–Madison, MADISON, Wisconsin, United States; 3Biomedical Engineering Department, TOBB University of Economics and Technology, Ankara, Turkey.

Melanin, natural consistent of human body, has attracted great attention in the last few years by being amorphous biopolymer with semiconducting, biodegradable, biocompatible and non-toxic, antioxidant and abundant biopolymer derived from natural sources 1, 2. Despite its great potential and ease on extraction, it has been rarely studied in pharmaceutical and biomedical fields. So that, in this study, it is decided to use natural melanin nanoparticles by incorporating into PCL solution to achieve controlled release of the ampicillin from electrosprun membrane by coaxial and single-needle electrospinning.

In the experimental setup, 10% (w/v) PCL was mixed with appropriate amounts of extracted melanin (0,001-0,1 g/ml) and ampicillin (0,01 g/ml) to prepare single-needle electrosprun membranes (S). For core-shell structures fiber production, 0,01 g Amp was mixed with 10% (w/v) PCL solution and used as a core solution, whereas 4% (w/v) PCL solution combined with melanin (0,001-0,1 g/ml) for a shell coverage, in turn. After spinnable solutions reached the nozzle tip, they were exposed to high voltage of 12 kV, while tip-to-collector distance was kept at 9 cm and nanofbers were produced. Drug release amounts of PCL-amp core (C), PCL-Mel-Amp single-needle and coaxialy electrosprun membranes (S and CS) were measured by Ultraviolet-Visible Spectroscopy at the wavelength of 203 nm and corresponded drug release profiles were analyzed.

For C membrane, 82% of the ampicillin was released within the first hour indicating burst release. The burst release can be due to the lower compatibility of ampicillin inside PCL fibers or the accumulation of the drug on fibers’ surface during spinning. Besides, in the presence of melanin, slower initial burst release compared to C was observed for the S membrane, which showed a burst release of 37%. In the same period, the release rate of the drug was only 7% for the CS membranes. It states that, more controlled drug release was achieved for CS nanofibrous membrane compared to the S membrane even if the melanin addition was carried out for both processes. This result would be attributed to the shell layer coverage that introduced an additional diffusion barrier.

In all, we first-time evaluated melanin-polycaprolactone composite as a drug nanocarrier, both in coaxial and monolithic forms. The findings of this
Dental Pulp Stem Cells (DPSCs), easily acquired from extracted wisdom teeth, are multipotent stem cells that can transform into osteoblasts, cardiac, and neuron cells and can thus provide cells resulting in an autologous implant. P4VP, a polymer shown to retain cell morphology, can help cells adhere to fibers, on DPSCs and their potential differentiation into neural cells.

Multiphase emulsion drops have wide applications such as in drug delivery and food industry because of their ability to encapsulate active ingredients and to release them in a controllable time. Recently, high-order multiphase emulsion drops have been successfully obtained by mass-transfer induced phase separation in microfluidic devices [1,2]. However, the ternary systems used in these studies always involve organic-solvents, such as oil and polar solvent, and few of them focus on the formation of high-order all-aqueous emulsions which are oil-free and highly biocompatible. Therefore, we propose a robust approach to form high-order multiple all-aqueous emulsions in a glass-based microfluidic device [3]. The proposed method is essentially based on the phase separation induced by the osmolality difference between the drop and the continuous phases. By varying the initial concentration of the drop phase, we also successfully achieve all-aqueous emulsions with different complexity and further summarize the complexity of the droplets into a phase diagram. Our method is simple, and the fabricated high-order all-aqueous emulsions could be templated as biocompatible capsules which are capable of encapsulating and releasing active components upon trigger.

References:

Utilization of P4VP and Graphene to Differentiate Dental Pulp Stem Cells into Functional Neurons

John Chen1, Zaiff Khan1, Linxi Zhang2, Kuan-Che Feng2, Rebecca Isseroff2, Marcia Simon1 and Miriam Rafailovich2; 1Lawrence High School, Cedarhurst, New York, United States; 2Dept. of Materials Science and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; 3Stony Brook University School of Dental Medicine, Stony Brook, New York, United States.

Currently, the central nervous system is unable to heal effectively by itself, leading to a search for ways to regenerate or grow neurons for replacement. Dental Pulp Stem Cells (DPSCs), easily acquired from extracted wisdom teeth, are multipotent stem cells that can transform into osteoblasts, cardiac, and neuron cells and can thus provide cells resulting in an autologous implant. P4VP, a polymer shown to retain cell morphology, can help cells adhere to a substrate, potentially eliminating the need for polyornithine. Graphene, known for its electrical conductivity, may prove useful in the differentiation of DPSCs into neurons, since neurons communicate through the electrical impulses of the synapses. This research compares the effects of thin film substrates of P4VP and P4VP+graphene, on DPSCs and their potential differentiation into neural cells.

Four experimental substrates were created: P4VP and P4VP+graphene thin films, as well as P4VP and P4VP+graphene electrospun into fibers. Two sets of each substrate were created; one set was coated with polyornithine and the other set was not coated. A positive control of tissue culture plastic was also plated with DPSCs.

Optical microscopy displayed that DPSCs grown on flat substrates of P4VP and P4VP+graphene grew into longer cells than those grown in the positive control. In addition, they had formed branches of axon-like structures from day 14, even without the use of polyornithine, suggesting that P4VP thin films allow cells to adhere on their own to the substrate. However, electrospun fibers did not show differences in cell growth from the positive control. Confocal Microscopy conducted after 21 days of culture confirmed that the cells directly attached to the P4VP and P4VP+graphene substrate had elongated, while the cells not attached were more round, but both types showed high confluency. Also, cells plated on electrospun fiber samples had the same shape and confluency as flat film samples, suggesting that fibers had similar effects as thin films on DPSC growth into nerve-shaped cells. No visible changes were seen with the addition of graphene. Further results were acquired with Scanning Electron Microscopy (SEM) and Real-Time Polymerase Chain Reaction (RT-PCR), determining whether the DPSCs were starting to undergo differentiation into neurons and thus showing promise that P4VP can provide a suitable scaffold for neuron cell development.

Micropatterning of TiO2 Nanotubes for High-Throughput Study

Qiaoling Huang1,2, Yanran Li1, Yuanjun Dong1, Ping Mu1, Xiang Yang Liu1,2 and Changqiang Liu1; 1Xiamen University, Xiamen, China; 2John A. Paulson School Of Engineering And Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 3National University of Singapore, Singapore, Singapore.

TiO2 nanotubes (TNTs) have attracted extensive attention by virtue of the similarity of their highly ordered nanotubular structure to that of cortical bone. Recent studies have indicated that titanium nanotubes are superior to pure titanium in terms of bone regeneration, blood compatibility and corrosion resistance. However, the optimal properties of TNTs for certain applications remain mystery. For example, the nanotube dimension ranges from several nanometers to hundreds of nanometers. The existing literature reports biological responses to confined dimensions owing to the technique difficulties in evaluating hundreds of TNTs with different properties at the same time. In this study, TNT gradients with different properties were fabricated and applied for high-throughput study. Results showed that TNT gradients provide facile platforms for high-throughput screening of biological responses, including cell responses, protein adsorption, bacterial adhesion, and et al.

References:

BM04.09.40

Phase-Separation Induced High-Order All-Aqueous Emulsions in Microfluidics

Youchuan Chao1,2, Sze Yi Mak1,2 and Ho Cheung Shum1,2; 1HKU-Shenzhen Institute of Research and Innovation (HKU-SIRI), Shenzhen, Guangdong 518000, China; 2Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China.
Mechanical Properties of Drawn Electrospun Polycaprolactone (PCL) Nanofibers

Katie Sun¹ ² and Vince Beachley³; ¹Rutgers, The State University of New Jersey, New Brunswick, New Jersey, United States; ²Rowan University, Glassboro, New Jersey, United States.

Introduction: Polycaprolactone (PCL) is a biodegradable polymer that has favorable structural, mechanical, thermal, and chemical properties which provide the necessary strength, rheology, porosity, biocompatibility, and flexibility to fulfill the role as a biological scaffold in musculoskeletal tissue engineering and repair. Significantly, PCL nanofibers have historically proved to be able to sustain large amounts of elongation before break. The method of electrospinning provides highly linear and aligned scaffolds like that of natural tissues, produces a favorable surface area to volume ratio, and protects the scaffold’s ability to provide a mechanical strength comparable to that of natural tissue. Thus, the post-draw of PCL nanofibers after electrospinning produces a product with mechanical properties that are correlated with strain rate.

Methods: An electrospinning device designed by our lab utilizes an adjustable frame and aluminum tape tracks controlled by a motor system to both electrospin PCL nanofibers while also post-drawing them to a desired draw ratio and improving alignment. The process of electrospinning 18wt% polycaprolactone (PCL) is protected and humidity-controlled in a polycarbonate enclosure. The electrospinning draw ratio was set at 2 for the PCL fibers. A scanning electron microscope (SEM) was utilized to analyze the fibers’ diameters, densities, and cross-links. The mechanical properties were tested under strain rates of 0.5mm/min, 5mm/min, and 50mm/min for nanofibers laid on a 10mm by 10mm testing square.

Results: The electrospun PCL nanofibers exhibited many trends after mechanical testing. The young’s modulus decreased with increased fiber number and with increased strain rate. The ultimate tensile strength increased with increased fiber number and increased more gradually with increased strain rates. The toughness shows increases correlated to fiber number and a strongly positive and steep correlation with a 0.5mm/min strain rate. The 5mm/min and 50mm/min testing rates and toughness show constant toughness regardless of fiber number. The ultimate tensile strain of the fibers varies little and thus is independent of testing strain rates.

Conclusion: Electrospinning while post-drawing proved to create PCL nanofibers that exhibit an inverse negative correlation to young’s modulus but direct positive correlation to ultimate tensile strength, toughness, and ultimate tensile strain. The increase in testing strain rate decreased the average-per-strain-rate young’s modulus, ultimate tensile strength, toughness, and ultimate tensile strain. This is due to the higher testing strain rates causing rapid plastic deformation. This prevents the PCL polymer chain alignments from accommodating new charge repulsions due to the elongation and movement of PCL fibers during mechanical testing, leading to failure. The data collected indicates that if further mechanical testing strain rates are tested, the same correlations will be exhibited.

Influence of Exposure to TiO₂ Nanoparticles on Staphylococcus aureus Infection

Fan Yang¹, Justin Zhou², Vincent Zhang¹, Jonathan Goldschlag⁴, Ethan Winkler⁵ and Miriam Rafaelovich⁶; ¹Stony Brook University, Stony Brook, New York, United States; ²Patchogue-Medford High School, Medford, New York, United States; ³Sachem High School East, Farmingville, New York, United States; ⁴Hebrew Academy of the Five Towns and Rockaway, Cedarhurst, New York, United States.

Titanium dioxide (TiO₂), commonly used in paints, toothpaste, sunscreen, cosmetics, pharmaceutics, and food additives, has been extensively studied for its anti-cancer and anti-bacterial applications when irradiated with UV light, but there is minimal data on its relative safety for normal human cells. In a previous study, HeLa cell exposed to TiO₂ nanoparticles showed an increased susceptibility to bacterial infection partially attributed to inhibition of enzymatic activity involved in membrane cholesterol distribution.[1] Since HeLa cells are an immortalized cell line derived from tumor tissue, they may not be representative of cells found in healthy human tissue. To investigate the influence on healthy tissue, we chose to focus on skin tissue, since skin is the first barrier to contact with various toxins. Dermal fibroblasts and keratinocytes were plated on tissue culture plastic for 24 hours and then exposed for another 24 hours to 0.1mg/ml of TiO₂. The results indicate that an increased susceptibility to bacterial infection is also present in healthy primary tissue cells. Since cells are also influence by their environment, we also investigated the role of the substrate on the toxicity to TiO₂ nanoparticles, as well as bacterial infection. Preliminary results indicate increased toxicity of the particles, when the cells are cultured on gelatin, and in particular collagen, which is commonly present in the skin tissue.


Preparation and Performance of Polycaprolactone Nanocarrier for the Controlled Release of Interferon-α for the Treatment of Malign Melanoma

Enes Celik, Gözde Kabay and Mehmet Muthu; Biomedical Engineering, Ankara, Turkey.

Melanoma is a type of skin cancer, results in higher mortality rates mostly in metastatic states which constitutes 80% of skin cancer deaths (Miller, A.J., et all. 2006). Because of being such a wild type of cancer, various therapeutic methods such as surgery, radiation therapy, chemotherapy, immunotherapy and targeted therapy are used to decrease the mortality rates. However, none of these procedures are enabled completely to remove the problems such as toxicity and efficacy. To overcome these problems, controlled drug release technology remains as a plausible approach.

Nanofibrous scaffolds designed for drug delivery purpose has various advantages compared to conventional drugs such as high loading and entrapment capacity, protection of therapeutic agent, controlling the release of the drug in a timely manner and accordingly preservation from any toxic effect. Several controlled drug release profiles such as sustained, burst, and delayed can be obtained by using electrospun nanofibrous membranes as carriers (Hui, X., et all, 2014). The ability to adhere the scaffold at the site of infection is another advantage of these systems compared to other drug delivery methods, which would be beneficial for the skin cancer types (Akduman, C., et all, 2016).

Based on the clinical problem defined above and the previous reports, we hypothesized that the good biocompatibility and biodegradability of polycaprolactone (PCL) makes it promising nanocarrier for drug release applications. Therefore, we developed a drug release platform combination of PCL and interferon-alpha-2B (INFα-2B) which is a therapeutic agent approved by the US Food and Drug Administration (FDA) and recently being used for the treatment of metastatic melanoma.

In the experimental setup, electrospun membranes combined of PCL and INFα-2B were produced by single and coaxial electrospinning setups. 10% (w/v) PCL was combined with INFα-2B by mixing with ratios of 5%,10% and 20% (w/w). System parameters such as applied voltage and tip-to-collector
distance were adjusted to 12 kV and 9 cm, respectively. Flow rates were varied between 0.5 and 1.0 ml/h for core and shell solution, in turn. The physical characterization of the electrospun membranes were achieved SEM and TEM analysis and chemical characterizations were carried out by FTIR spectroscopy. Moreover, in vitro drug release profile of INF α-2B from the electrospun membranes was sketched by calculating the concentration of INF α-2B released into the phosphate buffered saline solution (PBS, pH: 7.4) with UV–vis spectrophotometer (Hitachi U-5100, Japan) at 214 nm (Sultanova, Z., et al, 2016).

We showed that, coaxially electrospun INFα-2B loaded PCL nanofibrous membranes can be used to treat melanoma disease by providing controlled release of INFα-2B. The accurate adjustment of the drug release behavior of INFα-2B-loaded PCL nanofibers against tumor cells is currently under investigation.

**BM04.09.47**

**Characterization of Thermoreversible Hydrogels from Multiblock Poloxamers and Hybrid Hydrogels for an Application as Cell Barrier Layer**

Juyi Li1, Erica Inyoung Chui1, Christina Tong2 and Miriam Rafailovich1; Stony Brook University, Stony Brook, New York, United States; Fairview High School, Boulder, Colorado, United States; St. Paul’s School, Concord, New Hampshire, United States.

Periodontitis is a highly prominent issue in dental health today and the current solutions such as Guided Bone Regeneration (GBR), or the use of a barrier membrane to separate the alveolar bone and gums, have many shortcomings. These barrier layers can be composed of hydrogels, 3D cross-linked polymeric networks that are used for regenerative medicine; hydrogels are showing very promising applications in the biomedical field due to their biocompatibility and unique properties. Our previous work showed a promising hybrid gel synthesized with gelatin and poloxamer F127. Polymerized multiblock poloxamers maintain the thermo-reversibility but with an improved mechanical property. This study focused on characterization of the multiblock poloxamers PF127, PF108, and PF98 and synthesis/characterization of hybrid gels using these poloxamers to evaluate their potency. Rheology was used to characterize the poloxamer solutions and hybrid hydrogels, revealing that PF108 had a significantly higher elastic modulus compared to the other gels. The laser microscope imaging showed a unique, branching fiber structure of the PF108 hybrid gel, while the structures of the other hybrid gels displayed gelatin mesh networks. The PF108 hybrid hydrogel also showed significantly lower surface roughness. This is associated with decreased cell attachment, thus, gelatin-PF108 hybrid gel may possess promising characteristics to serve as a better cell barrier layer.


**BM04.09.48**

**Novel Collagen and Elastin Interlaced Composites for Heart Valve Tissue Engineering (HVTE)**

Sonia Hfehkar1, Colleen Lopez2, Jan Czernuszka1 and Carolyn Carr2; 1Department of Materials, University of Oxford, Oxford, United Kingdom; 2Department of Physiology, Anatomy and Genetics, University of Oxford, Oxford, United Kingdom.

Valvular Heart Disease (VHD) is an incurable disease that affects 2.5% of the population in the USA, this includes both congenital and acquired forms of VHD. Valve replacement is the most likely treatment when the valve is severely damaged resulting in stenosis and/or regurgitation. Prostheses used to replace damaged valves are predominantly of two types, biological or mechanical. Both types are temporary non-regenerative solutions that have drawbacks, these include a limited life-time and the prerequisite to take anticoagulants.

A tissue engineered substitute has the potential to overcome such limitations and could form a fully functional and viable heart valve, this is particularly advantageous for infants suffering from congenital VHD.

Heart valves are active, self-repairing tissues that can withstand tremendous magnitudes of pressure due to their unique architecture. They have an interconnected tri-layer structure made up of three distinct zones. Type I collagen and elastin are the two major components of the extracellular matrix (ECM). Elastin is a non-collagenous protein that is present in the form of a three-dimensional network with interconnected collagen fibres, together they provide the ability to bear high loads as well as be flexible and resilient.

Designing a scaffold to mimic the structure and function of native heart valves requires bioactive materials that can easily be processed and fabricated into scaffolds. Naturally based biomaterials are the most promising candidates to be used as the basis for rapidly regenerative scaffolds.

A combined microstructural, micromechanical and stem cell based approach is proving to be the most successful in terms of reproducibility, rapid generation of new ECM and changes to stiffness. Our work follows a biomimetic inspired approach, where we have designed novel scaffolds using ECM components to mimic the interconnected architecture of the heart valves closely. These unique compositions are the first step towards designing tri-layer structures to replicate the entire heart valve structure.
Weijia Zhang, Fudan University

Symposium Support
Allevi, Inc.
Biofabrication | IOP Publishing
MilliporeSigma
Wiley-VCH Verlag GmbH & Co. KGaA

* Invited Paper

SESSION BM05.02: Bioprinting Strategies for Tissue Modeling
Session Chairs: Akhilesh Gaharwar and Mario Álvarez
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Liberty C

1:30 PM *BM05.02.01
Chaotic Printing—Using Chaos to Fabricate Densely Packed Micro- and Nanostructure at High Resolution and Speed Grisell Trujillo-de Santiago1, 2, Maria Díaz-de León Derby1, 3, Carolina Chávez-Maduro1, 4, Mohammadali Samandari3, 4, Christian Carlos Mendoza-Buenrostro3, Gyan Prakash3, Sara Cristina Pedroza-González3, Brenda Giselle Flores-Garza1, Rute Fabiana Martins-Fernandes2, Yu Shrike Zhang3 and Mario M. Álvarez1; 1Centro de Biotecnología-FEMSA, Tecnológico de Monterrey, Nuevo León, Mexico; 2Departamento de Mecatrónica e Ingeniería Electrónica, Tecnológico de Monterrey, Nuevo León, Mexico; 3Imperial College London, London, United Kingdom; 4School of Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran (the Islamic Republic of); 5Department of Engineering in Medicine, Brigham and Women's Hospital, Harvard Medical School, Cambridge, Massachusetts, United States.

Nature generates densely packed micro- and nanostructures to enable key functionalities in cells, tissues, and other materials. Current fabrication techniques, due to limitations in resolution and speed, are far less effective at creating microstructure. Yet, the development of extensive amounts of surface area per unit of volume will enable applications and manufacturing strategies not possible today. Here, we introduce chaotic printing—the use of chaotic flows for rapid generation of complex, high-resolution microstructures. Here we use two classic mixing systems as models, the Journal Bearing (JB) flow and the Kenics mixer, to demonstrate the use of chaotic printing. In a miniaturized JB flow (miniJB) we induced deterministic chaotic flows in viscous liquids. These flows deform an “ink” (i.e., a drop of a miscible liquid, fluorescent beads, or cells) at an exponential rate to render a densely packed lamellar microstructure that is then preserved by curing or photocrosslinking. In a continuous version of chaotic printing, we created chaotic flows by coextruding two streams of alginate (two inks) through a printing head that contains an on-line miniaturized Kenics static mixer with multiple mixing elements (or sections). In this way, we continuously 3D-print multi-material lamellar structures with different degrees of surface area (as a function of the number of elements used) and full spatial control of the internal microstructure. The combined outlet stream is then submerged in a calcium chloride solution in order to crosslink the emerging alginate fibers and preserve the microstructure. We show that the exponentially fast creation of fine microstructure achievable through chaotic printing exceeds the limits of resolution and speed of the currently available 3D printing techniques. Moreover, we show that the architecture of the microstructure to be created with chaotic printing can be predicted using computational fluid dynamic (CFD) techniques. We present different proof-of-principle applications for this technology, including the development of densely packed biocatalytic surfaces and highly complex multi-lamellar and multi-component tissue-like structures for biomedical applications.

2:00 PM BM05.02.02
3D Bioprinted Mini-Brains as a Novel Tool to Study the Glioblastoma Microenvironment Marcel A. Heinrich1, Ruehi Bansal1, Yu Shrike Zhang2, 3, 4, Raymond Schifferels1 and Jai Prakash1; 1Department of Biomaterials Science & Technology, University of Twente, Enschede, Netherlands; 2Division of Engineering in Medicine, Harvard Medical School, Brigham & Womens Hospital, Cambridge, Massachusetts, United States; 3Division of Health Sciences & Technology, Harvard-Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, Massachusetts, United States; 5Department of Clinical Chemistry and Hematology, University Medical Center Utrecht, Utrecht, Netherlands.

Glioblastoma-associated macrophages (GAMs) play a crucial role in the progression and invasiveness of glioblastoma multiforme (GBM), however, the exact crosstalk between GAMs and glioblastoma cells is not fully understood. Furthermore, there is lack of relevant in vitro models to mimic their specific interaction in a dynamic and relevant environment. 3D bioprinting offers a promising approach to culture cells with well-defined structure and composition. In this study, we aim to develop novel bioprinted mini-brains that display in vivo-like behavior of both glioblastoma cells and GAMs. We bioprinted mini-brains (WxLxH: 4x6x3mm) comprised of either glioblastoma cells or macrophages or together to study their interaction in a realistic way. Both macrophages and glioblastoma cells remained viable in the mini-brains for at least 10 days. We observed an induction of glioblastoma-specific markers (e.g. Gfap up to 15-fold) compared to 2D cultures at mRNA level. Next, we studied whether tumor cells recruit macrophages to their site. To mimic that, we bioprinted mini-brains consisting of either macrophages or glioblastoma cells and cultured them in the same well. We found a 125-fold upregulation of Ccl2, a chemokine related to macrophages recruitment compared to 2D culture, indicating that tumor cells actively recruit macrophages in the 3D co-culture. Furthermore, we cultured mini-brains consisting of macrophages next to glioblastoma cells to confirm their migration. We found that macrophages significantly migrated towards the tumor site, indicating successful crosstalk between these cells. Next, we investigated the effect of direct cell-to-cell contact of tumor cells and macrophages in the 3D culture. We bioprinted mini-brains consisting of macrophages including a cavity containing glioblastoma cells mimicking the clinical situation. We investigated the gene expression of GAM-specific markers and observed a significant upregulation of markers for the GAM phenotype (Arg-1, Mmp2, Mmp9, Cad) and Gfap, indicating that tumor cells polarized macrophages towards GAMs. In addition, by resecting the tumor area from the mini-brains and investigate the expression of glioblastoma-related markers, we found that markers for tumor progression (Gfap, Chil1) and tumor invasion (Mmp9, Vimentin) were significantly overexpressed in the co-culture, displaying how GAMs support glioblastoma progression and invasion. To examine the clinical relevance of this model, we performed transcriptomic analysis of 159 GBM patients using available database, which showed a significant upregulation of highly relevant markers such as Mmp2, Mmp9 or Chil1. These data indicate that tumor cells induce recruitment of macrophages towards themselves and change their phenotype, as well as how GAMs support tumor progression and invasion. Altogether, our bioprinted mini-brains are a viable tool to study the interactions between different cell types and could potentially be used for drug screening purposes.
Tailoring a Functional Microbiotic Consortium via 3D Printing
Sudeep Joshi and Manu S. Mannoor; Stevens Institute of Technology, Hoboken, New Jersey, United States.

A characteristically well-diverse assemblage of myriad micro-organisms operating in a synergetic environment, constitutes a microbiotic consortium. It possesses a complex spatial and temporal microbial arrangement, which is self-sustained and perform multitudinous task by effective communicative functionality. The ability to custom-tailor a well-diversified microbiotic consortia permitting re-programmability of the microbial composition possess potential application prospects in bacteriology, drug-screening, clinical diagnostics, and therapeutic purposes. Additive manufacturing technique accomplished via 3D printing can serve as an efficient tool to realize such a functional microbiotic consortia. In the present article, we have utilized 3D printing technique to custom-tailor different genera of cyanobacterial cells within biofriendly hydrogel materials to realize a living microbiotic consortium. Moreover, these cyanobacterial colonies were seamlessly merged with abiotic nanomaterials for creating a functional microbiota capable of photosynthetic energy generation. Specifically, we demonstrate 3-dimensional interleaving of 2 genera of cyanobacteria (Anabaena and Nostoc Sp.) pre-seeded in a hydrogel matrix with electronic nanomaterial (graphene nanoribbons, GNRs) into various complex spatial geometries to enable harvesting of photosynthetic bio-electrons. Fluorescence and scanning electron microscopic studies were performed to examine the spatial distribution of cyanobacterial cells and their interaction with GNRs, respectively. Photo-electrochemical studies verified highly-conducting GNRs helped in efficient transfer of bio-electrons generated due to the water-splitting reaction during photosynthesis. UV-visible spectroscopy and standard plate counting methods were used to determine the growth of cyanobacterial cells in microbiotic consortium, hence confirming the cytocompatibility of hydrogel matrix. Significantly, the proposed 3D-printing strategy can organize cyanobacteria within complex arrangements to investigate the influence of spatial and environmental parameters on social behaviors for creating photosynthetically active microbiotic consortia.

Techniques developed in this research can also be extended to 3D print other genera of bacterial species with smart hydrogel materials to determine mutualistic relationships between bacteria, designing of synthetic systems, and post-biotic products. Taken together, our experimental efforts lead towards the better comprehension and understanding of complex microbial arrangement and associated functionality of a robust microbiota.

Numerical Simulation of Inkjet and Extrusion Bioprinting—Role of Resolution
Amir K. K. Miri1 and Iman Mirzaee2; 1Rowan University, Glassboro, New Jersey, United States; 2Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Since the emergence of the technology, 3D bioprinting has been applied to many areas of biomedicine such as creating customized devices, flexible bioelectronics, and scaffolds for tissue regeneration, novel therapeutic systems, prosthetics, and orthodontics. The macro-architecture of the generated construct can be as complex as the anatomical feature of the desired tissue, which necessitates proper printing fidelity. Printing resolution depends on the technical specifications of bioprinters and the physical properties of bioinks. In this work, a numerical model based on the method of volume of fluid (VOF) was created to obtain some insights on the droplet generation in inkjet bioprinting. Our simulations revealed the spatial and temporal features of the droplets before they impact the substrate, which is highly difficult to observe through experiments. The results further showed that high hydrophobicity of the substrate yielded a better printing resolution and lower stability for bioprinting. We then simulated the process of deposition from a sub-millimeter sized nozzle in extrusion bioprinting. In contrast to inkjet printing, the viscosity was found to be a dominant factor for flow properties inside the nozzle and after deposition. The viscosity dependency of shear rates also affects the surface deformation of the bioink when it leaves the nozzle and the combination of flow-induced stresses with surface tension forces dictates the form of the spherical residue formation. Based on our simulations, by selecting proper bioink properties, the resolution can be improved significantly in extrusion and inkjet bioprinting techniques.

Bioengineering Female Reproductive Tract Tissues
Monica M. Laronda1, 2; 1Stanley Manne Children's Research Institute, Ann & Robert H Lurie Children's Hospital, Chicago, Illinois, United States; 2Department of Pediatrics, Feinberg School of Medicine, Northwestern University, Chicago, Illinois, United States.

Hormones produced by the ovary support reproductive tract development and function, and are important for systemic health. The additional systems that are supported include brain, bone and cardiovascular tissues. There is a great need for mimics that represent the dynamic functionality of reproductive tissues in order to improve our understanding of normal function, function affected by disease or disease treatments and to improve current options for our patients. This includes restoring fertility and hormone function for survivors of childhood cancer who develop premature ovarian failure following their life-saving treatments. This particular population would benefit from hormone restoration in addition to new options for preserving and restoring gametes for future biological offspring, as they transition through puberty and may be put at significant risk of co-morbidities without normal ovarian hormones. The female reproductive tract is uniquely different from most model organisms and has forced researchers to develop creative ways to study the human condition. We have turned to engineering solutions to facilitate our quest for answers to these biological problems. This includes using new biomaterials or tissue reconstructed tissues to recapitulate normal female reproductive tract organs, simulating the paracrine and endocrine crosstalk that occurs among these tissues in a microfluidics system and 3D printing scaffolds to engineer follicle support in a bioprosthetic ovary that restored fertility and hormone function in sterilized mice. We continue to make improvements with these systems to impact reproductive biology research and fertility and hormone restoration for patients.

Glioblastoma (GBM), the most malignant brain cancer, remains deadly despite wide-margin surgical resection and concurrent chemotherapeutic and radiation therapies. Two pathological hallmarks of GBM are diffuse invasion along brain vasculature, and presence of therapy-resistant tumor initiating stem cells. Deciphering the underlying mechanisms of GBM-vascular interaction may add a new therapeutic direction to curtail GBM progression. However, the lack of proper 3D models that recapitulate GBM hallmarks restricts investigating cell-cell/cell-molecular interactions in tumor microenvironments. In this study, we created GBM-vascular niche models through 3D bioprinting containing patient-derived glioma stem cells (GSCs), human brain microvascular endothelial cells (hBMVECs) cells, pericytes, astrocytes and various hydrogels to model glioma/endothelial cell-cell interactions in 3D. Three GBM-vascular models were designed: Model A with large vessels and GBM spheroid; Model B with large- and micro-vessels, and GBM spheroid; Model C with large- and micro-vessels and dispersed GBM cells. Large channels were created by sacrificial 3D bioprinting. Microvessel network was formed through self-assembly of ECs and mural cells (fibroblast, pericytes, and/or astrocytes). Three GBM cell types were used in the study: SD02 and SD03 are GSCs;
U87MG is a commercially-available GBM cell line. GSCs cultured in these models maintained stemness and heterogeneity during the long-term cultures.

In Model A, GSCs actively invaded into the surrounding tissues (~Day26), initially regressed in response to the drug (~Day50), then developed therapeutic resistance and resumed aggressive invasion (~Day57). In Model B and C, three GBM types presented distinctive invasion patterns and EC-interactions. SD02 cells showed a spiky invasion pattern with elongated morphology. SD03 cells showed a more dispersed invasion pattern with many single cell migrations towards surrounding microvessels. U87MG cells showed a blunt invasion pattern, caused EC death in the spheroid form. In summary we have created GBM-vascular niche models that can recapitulate various GBM characteristics such as cancer stemness, tumor type-specific invasion patterns, and drug responses with therapeutic resistance. Our models have a great potential in investigating patient-specific tumor behaviors under chemo-/radio-therapy conditions and consequentially helping to tailor personalized treatment strategy. The model platform is capable of modifying multiples variables including ECMs, cell types, vascular structures, and dynamic culture condition. Thus, it can be adapted to other biological systems and serve as a valuable tool for generating customized tumor microenvironments.

4:15 PM BM05.02.07
Development of Strong and Biostable Nanocomposite Hydrogels Through Embedded Freeform 3D Printing Coupled with In Situ Precipitation Shenyang Chen, Tae-Sik Jang, Matthew Pan and Juha Song; Nanyang Technological University, Singapore, Singapore.

Embedded freeform 3D printing is an emerging 3D printing technique, where a hydrogel-based viscous medium provides support for extruded ink filaments during the printing process, allowing for omnidirectional printing of soft materials. One of the advantages of printing in a support bath is that the composition of the liquid medium can be modified to induce various chemical reactions in printed objects for solidification or functionalization of extruded ink filaments. Herein, we introduced a hybridization process to a 3D freeform printing system to achieve the direct fabrication of nanoparticle-reinforced composite hydrogels. In most composite hydrogel 3D printing systems, particles are preloaded in the ink prior to printing, which often reduces the printability of composite ink with little mechanical improvement due to poor particle-hydrogel interaction of physical mixing. In contrast, the in-situ incorporation of nanoparticles into a hydrogel during 3D printing achieves uniform distribution of particles with remarkable mechanical reinforcement, while precursors dissolved in inks do not influence the rheological behavior of pure ink materials. Therefore, we successfully fabricated hyaluronic acid (HAc)-calcium phosphate (CaP) nanocomposite scaffolds through 3D freeform printing of HAc, coupled with in-situ precipitation of CaP. Phosphate ions were dissolved in the hydrogel ink and calcium ions were added to the support bath for inducing the in-situ precipitation during 3D printing. The composite hydrogels demonstrated a significant improvement in mechanical strength, biostability as well as biological performance compared to pure HAc. Moreover, multi-material printing of composites of different CaP content was achieved by adjusting the ionic concentration of inks. Our method greatly accelerates the 3D printing of various functional or hybridized materials with complex geometries via the design and modification of printing materials coupled with in situ post-printing functionalization and hybridization in reactive viscoelastic matrices.

4:30 PM BM05.02.08
The Age of Applications for Bioprinting Ricky Solorzano; Allevi, Philadelphia, Pennsylvania, United States.

In an era where bioprinting continues to hold promise, sometimes its hard to understand why and how are they useful. What key applications will allow me to take my research to the next level and stay on the cutting edge. Come and listen to the key ways bioprinting is being most commonly used by researchers around the world.

4:45 PM BM05.02.09
Nanoengineered Inks for 3D Bioprinting Akhilesh K. Gaharwar; Texas A&M University, College Station, Texas, United States.

3D bioprinting is emerging as a promising method for rapid fabrication of biomimetic cell-laden constructs for tissue engineering. However, 3D bioprinting has hit a bottleneck in progress due to the lack of available bioinks with high printability, mechanical strength, and biocompatibility. We have developed multiple approaches to design highly printable bioinks for fabricating large scale, cell-laden, bioactive scaffolds. Specifically, we have introduced a family of bioinks including nanocomposite reinforcement, ionic-covalent entanglement (ICE), and nanoengineered ICE (NICE) based bioinks with excellent printability, mechanical properties, and shape-fidelity. These bioinks follow Herschel-Bulkley flow behavior, that shields encapsulated cells from excessive shear stresses during extrusion. The encapsulated cells readily proliferate and maintain high cell viability over 120 days within the 3D-printed structure, which is vital for long-term tissue regeneration. The unique aspect of these bioink is its ability to print much taller and higher-aspect ratio-structures than conventional bioinks without requiring secondary supports. We envision that these new family of bioinks can be used to bioprint complex, large-scale, cell-laden constructs for tissue engineering with high structural fidelity and mechanical stiffness for applications in custom bioprinted scaffolds and tissue engineered implants.

SESSION BM05.01: Biofabrication for Tissue Modeling
Session Chairs: Su Ryon Shin and Weijia Zhang
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Liberty C

8:00 AM *BM05.01.01
In Vitro 3D Tissue Construction by Microtissue Assembly Shoji Takeuchi; Univ of Tokyo, Tokyo, Japan.

In this presentation, I will talk about several Microfluidic-based approaches for the rapid construction of 3D cellular construct. Large-scale 3D tissue architectures that mimic microscopic tissue structures in vivo are very important for not only in tissue engineering but also drug development without animal experiments. We demonstrated a method of 3D tissue construction by using point, line and plane-type microtissues as cellular building blocks. For example, to prepare the point type building blocks, we used an axisymmetric flow focusing device (AFFD) that allows us to encapsulate cells within monodisperse collagen beads. By molding these cell beads into a 3D chamber and incubating them, we successfully obtained complicated and milli-sized 3D cellular constructs. As the line type building blocks, a cell-encapsulating core-shell hydrogel fiber was produced in a double coaxial laminar flow microfluidic device. When with myocytes, endothelial, and nerve cells, they showed the contractile motion of the myocyte cell fiber, the tube formation of the endothelial cell fibers and the synaptic connections of the nerve cell fiber, respectively. By reeling, weaving and folding the fibers using microfluidic handling, higher-order assembly of fiber-shaped 3D cellular constructs can be performed. Moreover, the fiber encapsulating beta-cells is used for the implantation of diabetic mice, and succeeded in normalizing the blood glucose level.

8:30 AM BM05.01.02
Tissue engineering holds great promise as an alternative therapy by creating functional tissue constructs that can reestablish the structure and function of injured tissue. However, a major challenge in tissue engineering is recapitulating the in vitro, three-dimensional (3D) hierarchical microarchitecture comprised of multiple cell types and the extracellular matrix (ECM) components of native tissues, along with achievement of continuous function and viability of engineered tissues after implantation. Specifically, survival of implanted cell-laden scaffolds is fully dependent on the oxygenation derived by its connection to blood circulation of the host body. The physiological process of angiogenesis is time-consuming, which results in the failure of clinically sized implants due to starvation-induced cell death, especially in thick and large constructs. Therefore, the incorporation of functional vasculature is important for maintaining thick and large complex tissue constructs, particularly in cardiac and skeletal muscle tissues that require highly vascularized networks to support the large metabolically activity in muscle cells. To address these challenges, 3D bioprinting is emerging as a powerful technique for the development of highly organized and complex 3D constructs. To achieve in vitro-like biological functions in 3D tissue constructs, ECM-based biomaterials are required to mimic biochemical and physical properties that will enhance the resulting tissue function. Furthermore, the bioprinted 3D tissue constructs can be used for toxicity assays based on organs-on-a-chip platforms, which have become increasingly important for drug discovery. The organs-on-a-chip system allows for the testing of cytotoxic effects of pharmaceutical compounds and nanomaterials on physiologically relevant human tissue models prior to moving forward with animal testing or clinical trials. To successfully establish organs-on-a-chip platforms, it is important to monitor the dynamic behaviors of human organ models interacting with drugs in situ for a long time. Furthermore, efficient methods for accurate analysis of the dynamic behaviors of human organ models are in urgent demand for improving the effectiveness of clinical predictions of human disease responses to different therapeutics. We introduce a microfluidic, label-free, biosensing technology combined with a 3D bioprinted human organ-on-a-chip system, which jointly allows for long-term and accurate measurements of the concentrations of the biomarkers secreted by tissues in response to drugs. The electrochemical biosensing chip will demonstrate a capability for regenerating its sensor surface, allowing for continual kinetic studies over extended periods of time. We believe that this novel platform technology may be further extended to a wide variety of applications in academia and pharmaceutics for personalized screenings of drug toxicity, efficacy, and pharmacokinetics in the future.

8:45 AM BM05.01.03
Applications of Multiphoton Polymerized Bio-Functional Platforms Bianca Buchegger1, Johannes Kreutzer1, Richard Wollhofer1, Jaroslaw Jacak1,2 and Thomas A. Klär1, 3 Johannes Kepler Universität Linz, Linz, Austria; 1 Upper Austria University of Applied Sciences, Linz, Austria.

Multiphoton polymerization (MPP) allows fabrication of arbitrary polymer structures in three dimensions with minimum feature sizes down to 100 nm and a lateral resolution around 200 nm. An excitation laser is focused into a photore sist consisting of a highly crosslinking acrylate and a photo-initiator. Adding a second laser beam which induces stimulated emission depletion (STED) of the photo-initiator in the outer rim of the excitation point spread function allows writing of even smaller structures with feature sizes below the diffraction limit.

Including functional groups other than the acrylate groups increases the versatility of the polymer structures, specifically for bio-functionalization. This can be either achieved by mixing of metal-oxo-clusters into the photosensitizers [1] or by using acrylate monomers with different functional rest groups such as thiols or carboxy groups enabling orthogonal functionalization [2]. The reactivity of the polymer structures was shown by covalent linkage of two different, chemically modified fluorophores. MPP scaffolds with bio-adhesive sites can also be used for 3 dimensional immunocaptives [3] and for physiological studies in microfluidic channels.

Using carboxy-acrylate polymer structures in combination with a biotin modified supported lipid bilayer enables orthogonal functionalization with two different fluorescent proteins. One sort of proteins is immobilized on polymer anchors via nickel-nitrilotriacetic acid / histidine interaction. The other one is freely moving within the lipid bilayer surrounding the structures which is enabled using biotin / streptavidin binding [4]. As mobility of proteins and lipids plays a major role in physiological processes, this platform is well suited for modelling of cell interactions with mobilized and immobilized proteins and studying cellular response.


9:00 AM BM05.01.04
Microengineered Human Blood-Brain Barrier Model with 3D Glia Network for Neuroinflammation Modeling and Nanomedicine Testing Song Il Ahn, Jiwon Yoon, Hyun-Ji Park and YongTae Kim; Georgia Institute of Technology, Atlanta, Georgia, United States.

The blood-brain barrier (BBB) is a unique barrier of the central nervous system (CNS) that has a highly selective barrier function that prevents most drugs from entering the brain, leading to a high failure rate in the development of therapeutics for the CNS diseases. Currently there is a large unmet need for the development of new therapeutics for the CNS diseases with an increasing death rate of patients with CNS diseases like Alzheimer’s disease (AD). One innovative approach to address this challenge is to develop a microengineered model of the human BBB that can mimick the pathophysiological conditions of the human brain. Yet, there is no physiologically relevant in vitro human BBB models that can incorporate shear stress, direct cell interactions, and 3D glial physiology of the human brain. Here we present a novel microengineered human BBB model designed to create a 3D co-culture of human brain endothelial cells (HBMECs), human brain vascular pericytes (HBVPs), human astrocytes (HAs) with the physiological morphology and interaction. Furthermore, we construct a neuroinflammation model with 3D incorporation of human microglia (HM) to understand the role of microglia-mediated neuroinflammation in AD pathogenesis.

Our microfluidic BBB model consists of two layers separated by a porous membrane to mimic the luminal and abluminal regions of the BBB. After growing HBVPs on the abluminal side of the porous membrane, HAs were cultured in the same channel. As HAs cultured in 3D Matrigel showed more physiologically relevant morphologies with lower expression of reactive markers compared to that in 2D, the abluminal layer of our model was filled with HAs that are embedded in 3D Matrigel. This Matrigel was confined by surface tension from the two side channels that are designed for culturing HMs.

HBMECs were cultured on the luminal side of the porous membrane and exposed to physiological shear stress that mimics blood flow in the brain microcirculation. As a result, our microengineered human BBB model showed a physiological network of the BBB cells with a polarized expression of aquaporin-4 to the luminal channel in astrocytic end-feet, highly specialized phenotypes of the brain endothelial cells with increased expressions of functional proteins and solute-carrier genes, and a significantly decreased permeability of the endothelial monolayer, as compared to the monoculture of HAs. Neuroinflammation model was constructed by adding HMs that were exposed to IFN-γ into the side channels of the stabilized human BBB model. HMs cultured in the side channels migrated into the Matrigel and showed a dynamic interaction with HAs, resulting in neurotoxic reactivities of HAs. Our microengineered BBB model can be utilized as a tool for the study of the pathological mechanisms of neuroinflammation and exploration of future therapeutic or preventive strategies for AD.
we discovered that even under prolonged UV irradiation (2.5-10 mins @ 18-19 mW/cm²), the viability of mammalian cells was preserved with the shielding effect of PP-alginate particles were thoroughly investigated with quantitative cell proliferation and LIVE/DEAD cell assays. Through our study, (PP) are especially suitable for encapsulation of cells due to the mild coating conditions required. Cell-laden alginate particles are generated followed by PP encapsulation of mammalian cells within cytoprotective polyphenol-alginate compartments before embedding them in photocurable bioinks. Polyphenolics and hIPSC derived neurons that show spontaneous epileptic seizure-like activity without any convulsant agent. This method can potentially provide a new simple yet novel and high-yield method to create polydimethylsiloxane (PDMS) confined scaffold-free 3D neuronal cultures from dissociated rat cortex or hIPSC derived neurons. It further shows significant differences of activity patterns between 2D and 3D cultures. Pharmacological experiments on these cultures showed that they can be reliably used as a powerful tool for high-throughput drug screening for AED development.

Results and Discussion:

- Application of TTX and KYNA abolished all burst activities, indicating the key-role of neuronal firing and glutamatergic network behind this phenomenon to entropic shielding and size exclusion factors.
- Test results showed that they can be reliably used as a powerful tool for high-throughput drug screening for AED development.

A patient-specific drug development system also becomes feasible with the integration of hIPSC with this technique.

Materials and Methods: We used PDMS to create 100 µm high micro-wells of different diameters (500-1500um). Dense solution of cells from neonatal rat cortex or hIPSC derived neurons was put into these PDMS micro-wells. Diluted solution of cells was also seeded outside the PDMS to create 2D cultures. Ca²⁺ indicator (R-GECO1) was applied to these cultures. Optical recordings were performed on both 2D and 3D cultures from day in vitro (DIV) 08 to DIV 21 to observe the spontaneous activity. Multi-electrode array was used to measure the extracellular field potential. Cultures were fixed and stained with antibody to NeuN at DIV21 for confocal imaging. tetrodotoxin (TTX), kynurenic acid (KYNA) and different concentrations of AEDs, phenytoin, carbamazepine, levetiracetam and topiramate were applied to 3D cultures created with rat and hIPSC derived neurons and the activity modulations were observed.

Acknowledgements: This work was supported in part by NIH/NIHNS R33 NS083858.

Biofabrication via Cytoprotective Polyphenol-Alginate Compartmentalization of Mammalian Cells in Photocrosslinkable Hydrogels Matthew Pan, Shengyang Chen, Tae-Sik Jung and Juhah Song; Nanyang Technological University, Singapore, Singapore.

Biofabrication technologies have endowed us with the capability to fabricate complex biological constructs at exceptional resolution and accuracy. Photocrosslinking is commonly coupled with biofabrication to produce stable cell-laden hydrogels due to precise control in the polymerization process, short crosslinking times, and minimal heat production. However, there are three major drawbacks: 1) deleterious effects of UV irradiation such as DNA damage or the cancerization of cells, 2) radicals generated during irradiation which react with cells either via direct contact or the formation of reactive oxygen species, and 3) cytotoxicity from unreacted double bonds of hydrogels functionalized with photoreactive groups such as acrylates and methacrylates. Herein, we implemented a cell protection strategy against harmful external stressors present during biofabrication, which involves the encapsulation of mammalian cells within cytoprotective polyphenol-alginate compartments before embedding them in photocurable biokins. Polyphenolics (PP) are especially suitable for encapsulation of cells due to the mild coating conditions required. Cell-laden alginate particles are generated followed by PP loading performed at various concentrations. The actual PP loading was quantified via UV-Vis absorbance spectrometry. The cytocompatibility and UV shielding effect of PP-alginate particles were thoroughly investigated with quantitative cell proliferation and LIVE/DEAD cell assays. Through our study, we discovered that even under prolonged UV irradiation (2.5-10 mins @ 18-19 mw/cm²), the viability of mammalian cells was preserved with the encapsulation of cells in PP-alginate particles. Lastly, in order to evaluate the applicability of our cytoprotective PP-alginate particles in biofabrication, we tested them with three photocrosslinkable hydrogels, Poly(ethylene glycol) diacrylate (PEGDA; 10, 15%), gelatin methacryloyl (GelMA ; 20%) and glycidyl methacrylate hyaluronic acid (GMHA; 4%). Hydrogel structures in the form of a thin substrate and a 3D printed scaffold were prepared at a particle to gel mass ratio of 2.3 and 1:3, respectively. The results clearly indicate that PP-alginate encapsulated cells exhibited higher viability under more stressful biofabrication conditions (extrusion-based 3D printing) and in more cytotoxic hydrogels such as PEGDA with high density of photoreactive side groups. The PP-alginate cell compartment acts not only as UV shield but also as diffusion barrier against harmful small molecules (photoinitiators) and larger macromolecules (polymer chains) as well as mechanical barrier against any external shear stresses. We envision this to be a technological breakthrough in biofabrication, maximizing mechanical stability of cell-laden scaffolds whilst minimizing damage to cells for any bioprinting or bioassembly processes.
A Fast and Simple Replication Technique for Biological and Artificial Surfaces with Superhydrophobicity Jing Xiang1, Hong Wang1, 2, Xun Zhu1, 2, Rong Chen1, 2, Yudong Ding1, 2, and Qiang Liao1, 2; 1Key Laboratory of Low-Grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing, China; 2Institute of Engineering Thermophysics, Chongqing University, Chongqing, China.

Advances in microfluidics technologies have stimulated the development of new materials and the design of surfaces which should require hydrophobic surfaces and interfaces with low adhesion. Biological surfaces are good and natural models for the development of functional surfaces, such as wettability, optical characteristics and water directional transmission. Therefore, learning the microstructure of biological prototype is meaningful for the design of surfaces. Here, a novel and fast molding method has been used to replicate the microstructures of different leaves, and cell-scaffold interaction play a vital role in tissue regeneration. Biomaterials can be either synthetic materials or natural materials and they are widely used to either substitute a living system or fabricate the scaffolds. Scaffolds can be designed in the computer environment and they can be fabricated in the laboratory environment. In this research, scaffolds were designed with Lindenmayer Systems (L-Systems) and they were fabricated with photolithography. L-systems are rewriting processes that are used to design the fractals. Firstly, a single strut was drawn with the L-Systems and it was printed out by a 3-D printer. Then a y-shape, a trunk with three branches and a trunk with four branches were designed by L-Systems and they were also printed out with a 3-D printer. In this process, the final product is a miniaturized repressor of polyethylene glycol (PEGDA) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) mixture and exposed to the UV light for about 4 minutes. Because of the interaction between U-shape, a trunk with three branches and a trunk with four branches were designed by L-Systems and they were also printed out with a 3-D printer.

Liquid overlay samples were prepared from MDA-MB-231 triple-negative breast cancer cells utilizing non-adherent, U-shaped 96-well plates, seeded either with (+) or without (-) the addition of 5% Matrigel growth factor (solubilized basement membrane from mouse sarcoma). The resulting cellular aggregates were imaged through maturity over a 4-day growth period via Optical Coherence Tomography (OCT) to assess construct morphologies. Molding is a fast, simple design of surfaces. Here, a novel and fast molding method has been used to replicate the microstructures of different leaves, and their surfaces decorated with Nano particles or wires by hydrothermal method, and eventually obtained the superhydrophobic property by silane treatment. Molding is a fast, simple and low-cost replication technique for biomimetic surfaces compared with other methods such as etching, lithography, electrochemical deposition and micromachining. The surface preparation process is as follows. At first, a negative is generated by molding. Then, we get the positive by filling the negative with liquid epoxy resins. In this way, we easily replicate the microstructure of various biologic surfaces, but the replicated surfaces just reach the hydrophobic degree after molding. Additionally, MCTSs formed via LDW were able to mimic this spherical morphology without the addition of exogenous factors. These findings have direct implications on the utility of direct-written MCTSs as in vitro tumor models for cancer research.
Microengineered Physiological Biomimicry—Human Organ-on-Chips

Dan Huh;

Human organs are complex living systems in which specialized cells and tissues are assembled in various patterns to carry out integrated functions essential to the survival of the entire organism. A paucity of predictive models that recapitulate the complexity of human organs and physiological systems poses major technical challenges in virtually all areas of life science and technology. This talk will present interdisciplinary research efforts to develop microengineered biomimetic models to reconstitute complex structural, dynamic microenvironment, and physiological function of living human organs. Specifically, I will talk about i) bioinspired microsystems that mimic the structural and functional complexity of the living human lung in health and disease, ii) an organ-on-chip microdevice that emulates the ocular surface of the human eye, and iii) microengineered physiological models of human reproductive organs.
Using light to manipulate liquid is a new approach for the actuation of microfluidic systems with contactless, spatial, temporal and precise control. Optical \cite{1,2} light modulation of electrical actuation \cite{3-5} or light-induced capillary forces \cite{6-8} are three advanced approaches to convert light energy to liquid motion. The last one has advantages over the first two in that it requires neither special optical set-ups nor complex microfabrication steps. Constructing microfluidic systems by photoresponsive materials is an efficient way to achieve light-induced capillary forces. Microfluidic liquid crystal polymers (LCPs) are polymers that show large and reversible deformation and allow temporal, localized, remote and isothermal triggering and actuation. \cite{9,10} Hence, LCPs are good candidates for microfluidic actuators through photodeformation.

In recent years, we have designed a new strategy to manipulate fluid slugs by photo-induced asymmetric deformation of tubular microactuators (TMAs), which induces capillary forces for liquid propulsion. Microactuators with various shapes (straight, 'Y'-shaped, serpentine and helical) are fabricated from a mechanically robust linear liquid crystal polymer. These microactuators are able to exert photocontrol of a wide diversity of liquids over a long distance with controllable velocity and direction, and hence to mix multiphase liquids, to combine liquids and even to make liquids run uphill. \cite{11,12}

Moreover, optofluidic chips were fabricated to integrate multifunctional liquid manipulation through this new strategy and realize micro-analysis and bio-reactions in them. The liquid transportation, combination, mixing, reaction and detection in the chip are all controlled by light, which successfully simplify the microfluidic system by avoiding the connection of external pumps. We anticipate that these optofluidic chips will achieve the portability and domestic use of microfluidics and open a new door to the microfluidic area.


\[5\] S. Park, M. Teteriell and P. Chiu, \textit{Lab Chip} 2010, 10, 1655.


9:30 AM BM05.03.03

\textbf{Recreating the Hematopoietic Microenvironment In Vitro Using Microfluidic-on-a-Chip Technology Enables the Study of Interactions of Normal and Malignant HSPCs with Specific BM Niches} \footnote{Julio Almeida-Portada\textsuperscript{1,2}, Samil K. George\textsuperscript{1}, Samuel Herberg\textsuperscript{1}, Christopher D. Porada\textsuperscript{1,2}, Aleksander Skradal\textsuperscript{1,2}\textsuperscript{,} and Graça Almeida-Portada\textsuperscript{1,2,3}; 1Wake Forest Institute for Regenerative Medicine, Winston Salem, North Carolina, United States; 2Virginia Tech-Wake Forest School of Biomedical Engineering and Sciences, Winston Salem, North Carolina, United States; 3Comprehensive Cancer Center at Wake Forest Baptist Medical, Winston Salem, North Carolina, United States.}

Under normal conditions, hematopoietic stem/progenitor cells (HSPC) reside within specific bone marrow (BM) niches. These are comprised of an array of different cell types located strategically to provide myriad chemical signals and physical interactions that maintain HSPC \cite{1,2}. In human myeloid malignancies, the BM niche is remodeled by malignant cells, which displace resident HSPC, and create self-reinforcing malignant niches that drive disease progression, chemoresistance, and relapse \cite{3}. Therefore, we engineered a microfluidic platform, inside of which are eight human hematopoietic niche constructs were patterned \textit{in situ} \cite{4}. The corresponding niches contained BM-derived mesenchymal cells (Stro-1\textsuperscript{+}, MSC), arterial endothelium (CD146\textsuperscript{+}/NG2\textsuperscript{-}; AEC), and sinusoidal endothelium (CD146\textsuperscript{+}/NG2\textsuperscript{-}; SEC), a fraction of the Stro-1\textsuperscript{+} cells were induced to undergo osteogenic differentiation, to generate osteoblasts (OB) for the fourth niche. U937 (lymphoma), MOLM13, and normal CD34\textsuperscript{+} cells were fluorescently tagged and independently perfused into the system. At 24h post-infusion, U937 cells already exhibited a marked predilection for AEC, and this persisted throughout the 5-day observation period, with roughly 4.5-times more U937 cells engrafting within the AEC niche than the SEC or MSC niches, and 3-times more U937 cells engrafting within the AEC niche than the OB niche. In contrast, MOLM13 cells exhibited a marked preference for the OB niche, and a moderate affinity for the AEC, SEC, and MSC niches. In contrast to malignant cells, normal CD34\textsuperscript{+} HSPC did not show a dominant engraftment within the niches, but exhibited moderate preferential engraftment within the OB niche.

In conclusion, our studies establish the feasibility of using microfluidic “on-a-chip” technology to recreate the various niches within the BM microenvironment, and prove proof that this novel system can be used to study the interactions of normal and malignant HSPC with distinct cells of the niche. We are currently using this system to delineate the signaling pathways responsible for the observed preferential HSPC niche cell interactions, with the ultimate goal of using this knowledge to develop more effective treatments for hematological malignancies and to enhance engraftment following HSC transplant.

9:45 AM BM05.03.04

\textbf{Microfluidic Fabrication of Dynamically Trigger-Responsive Microcapsules as Actively Manipulatable Microreactors} \footnote{Joerg Werner, Saraf Nawar, Zhang Wu, Brendan Deveney and David Weitz, Harvard University, Cambridge, Massachusetts, United States.}

Exploring and analyzing processes in small volumes such as droplets enables the screening of large parameter spaces with only small amount of materials, but active and selective control over the supply and removal of molecular matter in these systems is a missing feature. In droplet microreactors, critical parameters such as reagents and their concentrations can be screened over a wide range for their chemical and biological activities. In biological systems in particular, the confinement to aqueous microdroplets allows for the analysis of cellular behavior on the single-cell level. In aqueous emulsion drop systems, however, nutrients and reagents have to be included during the drop formation or added via coalescence events. Furthermore, the harvesting of products for analysis and further processing without the destruction of the drop is often unattainable. The active manipulation over molecular access to such droplets without changes to the microreactor space itself would enable increased control on the picoliter scale and single-cell level. A trigger-responsive and permselective membrane around the water drop that acts as a gate-keeper allows to turn diffusion to and from the microreactor on and off controllably, to supply new reagents and nutrients or harvest products when needed, while keeping the active species trapped within the droplet. Here we describe a number of polymer chemistries that allow for the synthesis of functional water-core microcapsules with tunable properties that are reversibly-responsive to various triggers. We employ microfluidic fabrication of double emulsion drops to synthesize trigger-responsive hydrogel membranes directly around water drops. These dynamic capsules can be repeatedly cycled between their permeable and impermeable state, enabling active control and manipulation over the accessibility of the capsule’s aqueous interior with molecular selectivity.
The endothelial resistance presents a critical barrier to molecular transport from blood to the interstitial space, hindering access of therapeutic proteins to their intended cellular targets. Understanding the physicochemical properties of protein therapeutics that affect transendothelial transport may aid development of therapeutic molecules with improved efficacy. Current in vitro methods that measure the distribution of these molecules are not representative of the complex human endothelial microenvironment and often yield results that are inconsistent with in vivo observations.

Our microfluidic platform addresses this problem, by utilizing a three-dimensional microvascular network with significant morphological similarities to in vivo capillaries that enables spatiotemporal control over solute measurements within a microfluidic device. These microvascular networks are self-assembled from human umbilical cord endothelial cells (HUVECs) and human lung fibroblasts within seven days, and are fully perfusable over a range of physiological fluid pressures. Molecular transport measurements can be made as a function of intravascular pressure for a variety of macromolecules. Quantification is achieved with fluorescently-labeled solutes using time-lapsed confocal microscopy. Furthermore, because the pressure difference between lumen and interstitium produces transendothelial flow, interstitial fluid is expelled from the device and can be collected for direct sampling. Good agreement is observed between transport measurements made within the device and with the direct sampling method.

We find that the endothelial resistance to the passage of both macromolecules and fluid are within the ranges observed in vivo. The mode of transport can be discerned between active and passive by considering the dependence of endothelial permeability on pressure. The approach we present allows for rapid measurement of physiologically-relevant transendothelial transport of labelled and unlabelled molecules. Therefore, this model system appears suitable to investigate the impact of physicochemical properties of therapeutic proteins on their relative biodistribution profiles.

**An Additive Manufacturing-Based Microfluidic System for Evaluation of Cancer Immunotherapies**

Ashley L. Beckwith1,2, Luis F. Velazquez-Garcia2 and Jeffrey T. Borenstein1; 1Biological Microsystems Group, Draper, Cambridge, Massachusetts, United States; 2Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Microfluidic models of the tumor microenvironment typically comprise cultured cells or spheroids embedded in matrix materials, and have shown wide utility in the study of key phenomena involved in cancer progression, including angiogenesis, metastasis and intravasation. However, the recent emergence of immune checkpoint inhibitor (ICI) therapies highlight the need for model systems that can incorporate the dynamics of immune cell interactions with tumors, imposing additional design requirements for microfluidic systems as well as the need for higher throughput systems. These requirements include the incorporation of biopsied tumor fragments rather than engineered spheroids to better recapitulate the influence of matrix and stroma, extended operation while maintaining tumor viability in perfused media, and the ability to investigate tumor killing mediated by drugs either introduced directly into the system following treatment of extrinsic immune cell populations in a separable and quantifiable manner.

Here we report on the demonstration of a customized microenvironment for testing cancer immunotherapies, built using additive manufacturing techniques in a monolithic manner that enables an accelerated design-fabrication-testing development cycle. The central element of the model is a tumor trapping scheme that captures a biopsied fragment at the junction of a network of flow streams, permitting controlled introduction and flow rate of media containing drug compounds and potentially circulating lymphocytes to study specific mechanisms of tumor killing. The microfluidic device, which contains a tumor trap, loading channels and circulating media and tumor-infiltrating lymphocyte (TIL) channels as well as a bubble trap, is constructed using a monolithic three-dimensional printing process with spatial resolution on the order of 25 microns. Materials and processes for generation of these devices have been selected on the basis of cytotoxicity and optical transparency considerations, and experiments run for several days confirm viability of tumor fragments across the duration of studies. Initial results presented here demonstrate the effect of ICI on human non-small-cell lung cancers, presumably mediated by the action of the ICI treatment on resident TIL populations present in the tumors. These results point the way toward mechanistic studies of immunotherapies, either singly or in combination with small molecules or other ICI antibodies, that extend far beyond current capabilities offered by existing animal or tumor microenvironment models.
Skeletal muscle has ability to repair due to the role of muscle satellite cells (MuSCs) in the regeneration but this capacity declines with aging. Recent in vivo studies using heterochronic parabiosis, in which two animals are surgically attached to share blood circulation, demonstrated that systemic factors in the blood of young animals can rejuvenate regenerative capacity of aged muscle. The exact mechanisms by which circulating youthful factors mediate the rejuvenating abilities of muscle stem cells, however, have yet to be elucidated. Due to the complexity of in vivo parabiosis and the dynamic nature of blood-borne factors, reliable identification of these humoral factors remains a major hurdle. To address this challenge, we leverage microengineering technologies to build 3D co-culture system of cells and tissues exposed to controlled biochemical cues with pathophysiological relevance. We first present microvascularized MuSC niche on a chip (VMoC) designed to harness key characteristics of the native muscle microenvironment where MuSCs are cultured on a myofiber-laden 3D hydrogel covered by a vascular endothelial cells (ECs). We then employ our VMoC devices integrated to mimic heterochronic parabiosis to identify potential rejuvenating factors that enhance myogenesis of MuSCs. Our VMoC was engineered using a double-layered microfluidic device that has 1) a top channel for the luminal side over a porous membrane, and 2) a bottom channel with a series of micropillars designed to confine the hydrogel. The primary MuSCs harvested from hind limb muscles of GFP-mice established multi-nucleated myotubes on the myofiber surface in the bottom channel, while immortalized mouse aortic ECs created a monolayer in the top channel. We first found that the MuSCs co-cultured with ECs significantly enhanced myogenic proliferation and differentiation as compared to the monoculture, while exhibiting similar differentiation to VEGF treatment to the monoculture. This result demonstrated that a biological paracrine effect of vascular ECs can be investigated in our chip 3D co-culture platform. We then found, more interestingly, that the administration of serum respectively isolated from young, old, and Sodl-/- (oxidative stress-accelerated model) mice showed distinct myogenic activities of MuSCs; those treated with old and Sodl-/- serum showed significantly lower myogenic differentiation. This result confirmed the more interestingly that the administration of serum respectively isolated from young, old, and Sodl-/- (oxidative stress-accelerated model) mice showed distinct myogenic activities of MuSCs; those treated with old and Sodl-/- serum showed significantly lower myogenic differentiation. This result confirmed the importance of the MuSC ECM in vitro to the 2D monolayer cultures which in no way represents the physiological tissue microenvironment in vivo. Therefore, preclinical and translational cancer research trends are moving toward organoid studies and 3D biomimetic models to provide more clinical relevance. Here, we set out to generate a biodegradable scaffold consisting of alginate, gelatin, and nano-crystal hydroxyapatite loaded with primary human osteoblasts and MSCs to produce a robust 3D bone-like microenvironment for studying human bone metastasis. A hydrogel (1% alginate; 7% gelatin) model for cancer cell-migration was modified to incorporate nanocrystal hydroxyapatite, primary human osteoblasts and primary human bone marrow derived stromal cells. Primary osteoblasts were isolated from vertebral bodies of organ donors and bone marrow MSCs were from Rooster Bio. The constructs were cultured for 28 days in either control medium (DMEM) or osteogenic medium (OM) with and without 0.5 mg/mL hydroxyapatite (HA). Live/Dead assays were performed to quantify viability and fixed frozen sections were stained with Alizarin red for calcified matrix deposition, and H&E to observe cells. High osteoblast viability in all conditions was observed after 28 days of culture: 91.3 ± 3.18 % for DMEM/HA+, 92.5 ± 2.5 % for DMEM/HA-, 88.6 ± 0.38 % for OM/HA+ and 85.9 ± 6.2 % for OM/HA-. MSCs showed approximately 85.1, 69.4, 87.8 and 90% viability in the same four conditions. Alizarin red staining showed that cells grown in DMEM without HA had the least amount of bone mineralized matrix. The combination found to have the most amount of bone mineralized matrix was OM/HA-.

Our data indicate that combination of 0.5mg/mL nano-HA with OM produces a favorable bone-like microenvironment for primary human osteoblasts and MSCs. Our preliminary work with low-cost bioprinting indicates this biodegradable scaffold is extrudable and will be ideal for screening therapeutics against patient-derived tumor cells cultured within a bone-like microenvironment. Ongoing work is assessing migration of fluorescein labeled tumor cells within this construct in the presence or absence of various chemotherapeutics. Furthermore, ongoing immunostaining for collagen type I, osteopontin and sclerostin will elucidate presence of bone matrix and osteocytes within the model. This work will allow better understanding of interactions between normal osteoblasts, stromal cells osteocytes and patient derived bone metastases cells while also placing higher clinical relevance on therapeutics screening.
tangentially, is imperative for determining foliar shape and size. While much is known about the genetic pathways involved in the GPC to GrC differentiation process, the effects on GPC differentiation and proliferation conferred by the mechanical stresses they experience during foliation is largely unknown.

In our present study, we employ a novel 4D printing technique to fabricate a rationally designed chip model of the Cerebellar cortex, which we use to simulate the foliation process in order to query the effects that mechanical compression and stretching has on the proliferation rate and differentiation potential of seeded GPCs. In order to simulate the gyration and sulcation processes of foliation in a biologically relevant manner in vitro, we have fabricated our chip construct using a novel, carbon nanotube (CNT) functionalized shape-memory polymer. Our shape-memory polymer can be printed into a convoluted shape with anatomical geometries, flattened, seeded with GPCs, and will then return to its original folded shape in a physiologically relevant time-course when thermally triggered at 37°C. We are able to achieve favorable cellular adhesion to our printed chip construct by coating it with CNTs, which functionally operate as artificial extra-cellular matrix scaffolding for adherent cells. The progressive restoration of the original folded shape of the polymer faithfully simulates the foliation process and can exert compressive and stretching stresses on resident GPCs that are comparable to that of developing Cerebellar tissue.

BM05.04.04

Biopsenised Silicification on Close-Packed Silica Bead Arrays by Liquid Phase Deposition

Yun Yeong Lee and Jin Seok Lee; Department of Chemistry, Sookmyung Women’s University, Seoul, Korea (the Republic of).

Organisms can biosynthesize hierarchically patterned three-dimensional (3D) biominerals, called as biomimeralization, such as calcium carbonate (mollusk shells), calcium phosphate (bone), and silica (diatom cell walls). The structural hierarchy in biominerals attributes strengths and stiffness, leading to protect themselves from natural environment. Especially, the process for production of silica into the living organism is known as biosilicification, which are often discovered in the diatom. Diatoms are complex and elaborated nano- and microstructured materials, whose architectures have numerous nanoscale pores with high porosity and high mechanical stability. Their extraordinary properties may have a potential for applications, such as sensors, molecular filters, and energy harvesting.

In this work, we explored the silicification on the arranged nanoscale-scaffold surface, such as the hexagonally close-packed silica bead arrays with porous structures, to mimic 3D hierarchical structures of diatoms by local liquid phase deposition. The energy and local concentration of silicic acid on the nanostructured surface are different; therefore, it is important to investigate the liquid phase deposition (LPD) on the nanostructure with diverse conditions to mimic and understand the mechanism of bioinspired morphogenesis. The different amount of water in LPD solution and reaction temperatures were used to investigate the effect of diverse environment because the biosilicification of diatoms occurs in the various surrounding environment such as concentration, temperature, and pressures. In addition, the silicification on the nanostructured surface deposited at the pinholes among the beads due to high local concentration, and this was monitored by Electrochemical Quartz Crystal Microbalance (EQCM).

BM05.04.03

Fabrication of Dome-Shaped Porous Alumina Microstructures and Their Applications for Drug Injector

Yoobeen Lee and Jin Seok Lee; Sookmyung Women's University, Seoul, Korea (the Republic of).

Nanostructures are promising candidates to inject and control of active agents such as drugs or biomaterials into cells. In particular, porous alumina is widely used as a template for nano-sized materials due to its high surface area. Many previous studies have been investigated injection of drugs using porous aluminum, carbon nanotubes and nanocapules as drug delivery systems. However, these drug delivery systems have some limitation to control the amount of injected drugs into cells.

In this work, we fabricated the dome-shaped porous alumina microstructures with hexagonal or cubic array, which are called simply ‘microdomes’, through the use of imprinting process on the initial surface over a large area with controllable diameter, thickness, and array. The different pitch of mold figure out the nanotopological effect on the morphology, which are range of 0 to 20 min. Furthermore, we investigated the amount of injected drugs into cells.

BM05.04.04

Optimization of Gold Nanostars Conjugated with Cell Penetrating Peptides for Intraoperative SERS Application

Tatiana Mironava1 and Bruce E. Cohen2; 1Stony Brook University, Stony Brook, New York, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

According to National Cancer Institute more than 12% of women in USA will develop invasive breast cancer during their lifetime. This project aims to develop imaging methodology based on SERS that combines sub-cellular resolution with ability to differentiate between normal and cancer cells. Amount of lipids in breast cancer cell is distinguishably different from the lipid content in normal and benign cells enabling cells distinction by means of Raman spectroscopy. Here we enhanced conventional Raman technique utilizing locally applied nanoparticles conjugated with cell penetrating peptides that ensure rapid nanoparticles penetration through the cell membrane. In this study normal and cancer breast cell lines - MCF-12 and MCF-7, respectively, were used. In addition, two types of nanoparticles - gold nanostars and nanospheres were conjugated to Tat-cell penetrating peptide for rapid intracellular delivery. Obtained results demonstrated sufficient differences in SERS spectra of cancer and normal cells providing the foundation for intraoperative cancer/normal tissue delineation by SERS imaging.

BM05.04.05

Engineered Phage-Based Immunostimulatory Materials for Virus Infectious Disease

Hyo Jung Lee and Hyo-Eun Jin; College of Pharmacy, Ajou University, Suwon, Korea (the Republic of).

Enterovirus 71 (EV71) is a contagious virus can cause hand-foot-and-mouth disease, severe neurological complications and death most commonly in infants and children under 5 years of age. Prophylactic vaccine and therapeutic agent against EV71 infection are not clinically available yet. Inactivated EV71 is under developing as a vaccine still now, however, safer immunostimulatory materials need to be developed for infants and children. Here, we developed filamentous bacteriophage (phage) as an immunostimulatory material to deliver enterovirus-specific protective immune responses for preventing EV71 infection. The engineered phage-based immunostimulatory materials could be a promising vaccine because it is generally regarded as safe to human and cost-effective owing to its property that infects only bacteria. Engineered phages displayed the identified epitopes of EV71 in high valency on the major coat protein and ligand for inducing mucosal immune response on the minor coat protein of phages. Following two dosages of immunization in 6-week C57BL/6 mice, EV71-specific immune responses including both T cell independent and dependent antibodies were induced by phage-based immunostimulatory materials without adjuvant, and all data were compared to experiments using EV71 subunit proteins with adjuvant. Our immunostimulatory materials showed high immunogenicity as preventing EV71 infection through EV71 challenge study. We expect that our

In recent years, many researchers have been interested in the physical and biological roles of topological defects in biological tissues [1,2]. One of the main issues faced by the study of these defects is the reproducibility with which they can be formed. Previous studies achieved the partial control of defect formation by culturing cells in a closed circular [1,2] or star-shaped [2] area. However, the position of the defects could not be precisely controlled, and no method has been established for designing the positions of defects in an arbitrarily shaped area. To solve this problem, this study proposes a systematic method for efficiently forming topological defects at specific points in a cell population by combining lithographic technology and computer-assisted design.

An overview of the proposed method is as follows. With our method, 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers are patterned on a glass substrate, and closed cell adhesion areas are formed on the substrate. The patterned cells spontaneously form topological defects by proliferation and spontaneous alignment along the boundary between the MPC patterned and non-patterned areas. The positions of the defects in the cell adhesion area can be predicted by extending the results of [1]. First, two topological defects are placed in certain positions, and a Poisson equation is solved numerically to obtain the cell alignment. Then, the elastic energy of the cell population is calculated from the calculated cell alignment. By changing the position of the defects, it can be predicted that the defects work together to minimize the elastic energy.

The proposed method was confirmed experimentally as follows. We fabricated MPC polymer coated glass substrates that had cell adhesion areas with ellipsoidal shapes (major axis length: 300 – 800 μm, ratio of major/minor axes: 1 – 2). Then, NIH-3T3 or HFF cells were cultured on the substrate. When the ratio of the major and minor axes was about 2 – 3, two topological defects were reproducibly formed near the major axis as predicted by the above computational calculations. With the HFF cells, the defects vanished when the lengths of the major and minor axes were 600 μm and 400 μm, respectively. Considering that the HFF cell was larger than the NIH-3T3 cell, this result suggests that the sizes of the cells and defects are important when estimating the defect positions.
Our results showed that the direction of the topological defects could be achieved by computational calculations and that it is possible to design the optimal boundary for an efficient defect direction without using a trial-and-error approach.

References

**BM05.04.10 Engineering Perfusionable Microscaffold for Meso-Physiological Systems Using Projection Micro Stereo-Lithography** Pierre Sphabmixay, Linda G. Griffith and Nicholas Fang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Current efforts in biomedical research are facing the necessity to improve in vitro systems towards more physiological and relevant models in order to recapitulate specific human in vivo mechanisms. The introduction of three-dimensional (3D) culture techniques have dramatically impacted our understanding of cellular biology and altered conclusions drawn from historically old two-dimensional in vitro models. The biggest challenge in the development of these 3D techniques remains the difficulty to sustain dense multi-cellular systems which requires to provide enough oxygen and nutrients deep within the tissue. In particular, the liver is one of the most difficult organs to culture in 3D in vitro, it constitutes only 2.5% of the total body mass but consumes 25% of the total cardiac output, making it unarguably the most oxygen and nutrient demanding organ of the human body, therefore requiring an extensively dense network of blood vessels in order to maintain its elevated metabolic activity. Furthermore, by being the central metabolizing organ in the human body, it is the organ most exposed to damage by chemicals and their metabolites entering the body. Pharmaceuticals pose a particular risk that can lead to drug-induced liver injury, whose mechanisms of actions are still poorly understood and are still the subject of controversy. For that reason, hepatotoxicity is a major cause for drug withdrawals from the market resulting in huge financial losses for the pharmaceutical industry. Therefore, tremendous efforts are being carried in order to improve current liver microphysiological systems (MPS) towards more predictive and physiologically relevant systems. Advances in micro/nano fabrication techniques offer promising solutions to tackle these challenges as they have enabled the development of devices and scaffolds capable of perfusing larger mass of cells, in combination with vascularization approaches in order to mimic the native microenvironment required for the cell function.

Here we have developed 3D perfusible scaffolds fabricated using Projection Micro-Stereolithography Apparatus (PuSLA) in order to provide improved 3D culturing techniques for liver MPS. Characterization of the fabrication technique allowed 3D printing of scaffolds with intricate architecture with resolution (3 microns) dramatically lower than the diffusion limit of oxygen (100 microns) therefore allowing efficient perfusion of dense tissue. Materials were engineered in order to feature favorable mechanical and biological properties for tissue formation and maintenance of mature phenotype. The designs of the scaffolds were engineered using a simulation approach by performing computational fluid dynamics in parallel with oxygen reaction simulation in order to predict viability of subsequent tissue in vitro. A commercially available bioreactor (Liverchip) was adapted in order to provide high flow rate and real time oxygen consumption monitoring.

**BM05.04.11 Novel Microfluidic In Vitro Intestinal Model for Studying Drug Transport and Metabolism** Haysam Ahmed1, Yang Li2, Igor Middel1, Nick Langerak1, Jos Maat1 and Rosalinde Masereeuw1; 1Utrecht Institute for Pharmaceutical Sciences, Utrecht, Netherlands; 2Orthopedics, Regenerative Medicine Utrecht, Utrecht, Netherlands; 3Physics, Institute for Theoretical Physics, Utrecht, Netherlands.

Caco-2 cells are widely used in pharmaceutical industry as a model to study intestinal absorption of drugs. Even though this 2D model provides enough insights into the intestinal absorption aspect, it lacks the metabolic functions that are exhibited in vivo (first-pass effect). In order to circumvent this shortcoming, a novel microfluidic device has been developed combining 3D printing, microfluidics and bio-functionalized hollow fiber membranes in one device. 3D printing is advantageous over the conventional soft lithography method for fabricating complicated structures, e.g., 3D flow chambers with hollow microchannels, microdevices with varying height in different locations. Moreover, it provides an alternative to polydimethylsiloxane (PDMS) that was shown to adsorb small molecules such as drugs hindering its use in a pharmaceutical setting. Here, we optimized the microfluidic design to allow for physiologically relevant shear stresses at low flow rates. The collagen-coated polyethersulfone hollow fiber membrane used in the developed device acts as a support for the cells and provides curvature to better mimic the in vivo microenvironment, thus providing both mechanical and dynamic signaling cues to Caco-2 cells to better differentiate into the various cell types observed in the human intestine.

The optimal shear stress rate was determined based on the cell differentiation (confirmed by immunofluorescent staining), villi formation, formation of a tight monolayer as a function of barrier function and more importantly enhanced metabolic function. In addition, it was shown for the first time that intestinal cells play a role in the generation of p-cresol metabolites, namely p-cresol sulfate and p-cresol glucuronide.

Taken together, this microfluidic gut device is a promising tool to study both the absorptive and metabolic functions of human intestine in pharmaceutical drug development compared to the currently used 2D models. Moreover, the modular design of the device allows for combining various organs to study not only the absorption but also metabolism (by connecting a liver device) and excretion (by connecting a kidney device).

**BM05.04.12 A Convenient and Effective Antibiofilm Coating on Vascular Catheters** Zheng Hou and M. B. Chan-Park; Nanyang Technological University, Singapore, Singapore.

Vascular catheters made from polyurethane (PU) are widely used in clinical settings and catheter-related infection are a serious clinical problem. It is mainly caused by the bacterial adhesion onto catheters’ surface. Once bacteria attach onto a catheter surface, they likely develop into biofilm that are hard to eradicate. Hence, it is important to develop a catheter surface with antibiofilm ability. In this project, a convenient method of modifying PU catheter surface was developed and optimized. A zwiterionic monomer was coated onto a 30-cm long catheter surface via a polymerization technique to form a hydration layer that retards biofilm formation. To demonstrate the feasibility of the coating method for industrial application, a 30cm PU catheter was coated by the same method.

PU catheter was treated with ozone to introduce peroxide group on surface. Different concentration of [2-(Methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (SBMA) was dissolved in water and isopropanol (IPA) mixture. The solution was purged with Argon for 30mins. The catheters were then put into the solution; polymerization was initiated by addition of ammonium iron(ii) sulfate and carried for 24hrs. The antibiofilm efficacy of the coating was tested by incubation of the coated catheter in bacteria inoculum at 37°C for 24hrs and shows >99.0% prevention of surface biofilm for both Gram-Positive Methicillin-resistant Staphylococcus aureus (MRSA) and Gram-Negative Pseudomonas aeruginosa (PAO1). The antibiofilm efficacy of coated 30cm PU catheter was tested with a intraluminal microbial biofilm model and shows >99.5% inhibition of MRSA growth.

**BM05.04.13**
Effects of Bioink Rheological Properties on Stability of Extrusion Bioprinting  Reza Avaz1, 2 and Amir K. K. Miri1, 2; 1Rowan University, Glassboro, New Jersey, United States; 2Bioengineering, University of California, Los Angeles, Los Angeles, California, United States; 1Institute for Computational Engineering and Sciences, University of Texas at Austin, Austin, Texas, United States.

3D Printing techniques have been flourished in the fabrication of advanced scaffolds for tissue engineering and regenerative medicine. For selected platforms, bioink formulation should be optimized for the desired application, in which it requires a deep understanding of bioprinting mechanism. The hydrogel-cell bioink is printed as a sol-state and then solidified following the deposition (or dispensing) process. This deposition process is occurred in extrusion-based bioprinting technique, which uses a cone-shape nozzle head to deposit the bioink. The deposition process ideally leaves spatially-controlled continuous strands of the bioink. However, mechanical issues can lead to instability of the deposited strands. The presence of mechanical instability can generate oscillatory forces and kinetics-related stress components that effect the behavior of cellular components within the hydrogel. This further hampers the printing resolution. A key factor in designing bioinks and selecting bioprinting parameters is to minimize instability of the bioink after leaving the nozzle. Although cell-laden bioinks often possess significant non-Newtonian properties, such as power-law and yield stress behaviors, the effect of such properties on the stability and spatial resolution of the fluid deposition has not been studied. In this work, assuming a slender flow model, we estimated the onset of instability as functions of the rheological properties of the fluid, such as rate-dependent viscosity and yield stress, as well as the geometry of the nozzle, such as size and bluntness. A moderate shear thinning behavior was found to stabilize the deposition process; in contrast, a high yield stress led to an unstable deposition of the bioink on a stationary substrate. The long-term goal of this work is to provide a simulation-assisted framework for high-fidelity 3D-printing of cell-laden bioinks.

BM05.04.14 Fabrication of Complex Vasculatures by 3D Printed Biomaterials  Terry T. Ching1, 2, 3, Yi-Chin Toh1 and Michinao Hashimoto1, 2; 1Pillar of Engineering Product Development, Singapore University of Technology and Design, Singapore, Singapore; 2Digital Manufacturing and Design Centre, Singapore University of Technology and Design, Singapore, Singapore; 3Department of Biomedical Engineering, National University of Singapore, Singapore, Singapore.

3D printing has enabled the fabrication of microfluidic devices, but it remains challenging to recapitulate the full complexity of the architecture in vasculatures. Despite several approaches used to print vascular-inspired features (such as surgical molding and embedded 3D printing), the complex hierarchical branching networks as seen in vivo is yet difficult to achieve by 3D printing. Herein, we proposed a design approach that enables existing commercial 3D printer to fabricate complex vasculatures in bio compatible hydrogels. Instead of directly printing the entire network as a unibody, our approach involved the decomposition of the system into simple and printable elements. We demonstrated to use two materials with different Young’s modules to fabricate such 3D networks—exterior elements printed in rigid polymers and interior elements printed in elastomeric polymers—to obtain tightly sealed 3D microchannels. The rigid elements served as an exterior shell to secure the interior elements in place while the elastomeric nature of the interior elements made conformal contacts when compressed, confining fluid in its intended space to form complex networks of microchannels. We used polymer jet (PJ) and stereolithography (SL) printers to demonstrate fabrication of vascular-inspired networks such as rectilinear lattice and helical networks of microchannels. Hierarchical branching of 1, to 4, to 16 channels with diameter of 850, 600 and 250 µm were achieved with the spacing between channels below 300 µm within the oxygen diffusion limit of 200 µm. The same strategy was applied to fabricate vascular-inspired networks in a bio compatible composite material. The assembled 3D microchannels were readily disassembled for imaging of different segments of the microchannels. Overall, we developed a design approach to enable 3D printing of complex vasculature-inspired architecture of microchannels. This is a general approach that can be demonstrated by most commercial 3D printers. To our knowledge, this is the first demonstration to fabricate 3D microchannels at this complexity (i.e. hierarchical branching) and the size scale (spacing between channels are maintain below 300 µm). Our current work opens opportunities to fabricate microchannels in a wide array of biomaterials. Devices created in this approach shall serve as effective in vitro model for vascularized tissue engineering, bioinspired surrogates for drug development, and regenerative medicine.

BM05.04.15 Engineering a Synthetic Analogue to the Nucleus Pulposus for Spinal Disc Repair Therapies  Juyi Li, Clement Marmorat, Yeshayahu Talmon, Raphael Davis and Miriam Rafailovich; Stony Brook University, Stony Brook, New York, United States.

The role of synovial fluids is to enable frictionless motion of joints and provide shock absorbance within the spinal cord for the central nervous system. Injury, disease, and even aging can degrade the structure and mechanical response of the fluid. Here we report on engineering a substitute for the nucleus pulposus, the viscous fluid within the spinal cord discs. Herniation of lumbar discs is a painful condition, which often requires surgical intervention, where the nucleus pulposus is removed and the disc space is fused. Recently hydrogels have been proposed as possible replacements. Here we report on the use of Pluronic physical gels, which we have successfully bioprinted, injected, and shown to prevent scarring and degradation in-vivo in dog trials. The results were very surprising since, despite their tremendous mechanical flexibility, these tri-block copolymers are very sensitive to fluid volume changes. We demonstrate, using SEM microscopy on gel cryo-sections, together with in-situ x-ray analysis, that in addition to the standard parameters defining the equilibrium state, the stability of physical gels is dependent on the dynamical aspects of the fluid medium. Using a specially constructed flow chamber, we show that for a Pluronic F127 physical gel, the degradation process can be greatly reduced under high fluid flow rate tangential to the gel surface. Since the physical gel is formed by an ordered crystal of micelles, stabilized by entanglements within their coronas, a simple model is proposed where swelling can occur only when the flow rate is less than the repuation time. Otherwise, rather than dissociating into individual micelles, the micelle gel responds collectively to the surface shear forces as an elastic solid, which deforms in a direction perpendicular to the flow in order to minimize stress. This aspect of the Pluronic triblock copolymer system greatly extends their application from an injectable drug delivery carrier to a structural component which is at once injectable, and yet able to sustain deformation and resist dissolution in physical fluids.

Poly(vinyl alcohol) (PVA) is a synthetic, biocompatible polymer that has been widely studied for use in bioengineered scaffolds due to its highly attractive properties, such as high strength, creep resistance, and porous structure. These properties can be fine-tuned by controlling the physical, non-covalent crosslinks through various techniques. Typically, PVA hydrogels are relatively brittle, non-elastic materials. Blending in gelatin, a natural collagen derivative, and using poly(ethylene glycol) (PEG) as a porogen for theta-gel formation, forms a highly organized, cell-instructive hydrogel with increased stiffness. Theta-gels are formed from the solidification and phase separation of high molecular weight gelatin and PVA from low molecular PEG during a decrease in temperature. To increase the stiffness and energy storage of PVA-gelatin theta-gels, the materials were additionally processed using cryo-gel techniques, which involved freezing theta-gels, lyophilizing and re-hydrating. The result was a stronger, more elastic material. Compressive rheological data suggest significant changes in the elastic modulus of PVA-gelatin theta-cryogels with increasing freeze-thaw cycles. The crystallinity as measured by Fourier transform infrared spectroscopy increased with increasing freeze-thaw cycles. Scanning electron micrographs showed an increased pore size of the PVA-gelatin theta-cryogels with increasing pore size, as expected from reports in the literature. Interestingly, however, the more crystalline materials demonstrated an increase in energy dissipation, which may be reflective of a higher water content. It is hypothesized that a stiffer material with larger pores may contribute to increased fluid flow, creating a tough yet resilient material for soft tissue repair.

Organoids, organ-mimicking multicellular structures derived from pluripotent stem cells or organ progenitors, have recently emerged as an important system for both studies of stem cell biology and development of potential therapeutics; however, a large-scale culture of organoids and cryopreservation for whole organoids, a prerequisite for their industrial and clinical applications, has remained a challenge. Current organoid culture systems relying on embedding the stem or progenitor cells in bulk extracellular matrix (ECM) hydrogels (e.g., Matrigel™) have limited surface area for mass transfer and are not suitable for large-scale productions. Here, we demonstrate a capsule-based, scalable organoid production and cryopreservation platform. The capsules have a core-shell structure where the core consists of Matrigel™ that supports the growth of organoids, and the alginate shell forms robust spherical capsules, enabling suspension culture in stirred bioreactors. Compared with conventional, bulk ECM hydrogels, the capsules, which could be produced continuously by a two-fluidic electrostatic co-spraying method, provide better mass transfer through both diffusion and convection. The core-shell structure of the capsules also leads to better cell recovery after cryopreservation of organoids probably through prevention of intracellular ice formation.

8:30 AM • BM05.05.03
Synthetic Human Embryo-Like Structures—A New Paradigm for Human Embryology Jianping Fu; Mechanical Engineering, University of Michigan, Ann Arbor, Ann Arbor, Michigan, United States.

Early human embryonic development remains mysterious due to drastic species divergences between humans and other mammalian models and limited accessibility to human embryo samples. Recent studies from my laboratory and others have shown that under culture conditions, human pluripotent stem cells (hPSCs) can undergo intricate morphogenetic events and self-organize to form patterned human embryo-like structures in vitro. These synthetic human embryonic tissues hold great promises for advancing human embryology and reproductive medicine. In this talk, I will first discuss a micropatterned hPSC-based neuroectoderm patterning model, wherein pre-patterned geometrical confinement induces emergent patterning of neuroepithelial and neural plate border cells, mimicking neuroectoderm regionalization during early neurulation. In the second part of my talk, I will discuss a hPSC-based, synthetic model of early human post-implantation development that recapitulates key developmental landmarks successively, including pro-amniotic cavity formation, amnion-epiblast patterning, primordial germ cell specification, and development of the primitive streak with controlled anteroposterior polarity. Together, our studies have developed powerful synthetic embryological platforms and provided new understandings of previously inaccessible but critical embryonic processes in human development.

Formation of Planar Intestinal Crypt with Distinct Proliferative and Differentiated Regions Raehyun J. Kim1, Yuli Wang2, Shee-Hwan J. Hwang2, Peter J. Atteyak1, Nicole M. Smiddy2, Christopher E. Sims1 and Nancy L. Allbritton1, 2; 1Joint Department of Biomedical Engineering, UNC at Chapel Hill and North Carolina State University, Chapel Hill, North Carolina, United States; 2Department of Electrical and Biomedical Engineering, University of Michigan, Ann Arbor, Ann Arbor, Michigan, United States.

A simple in vitro intestinal model system that recapitulates key aspects of the intestine in vivo can enhance our understanding on the physiology of the intestine and the impacts of drugs or biochemical stimuli such as metabolites and signaling molecules. We developed a planar platform recapitulating the segregation of the three-dimensional intestinal epithelial cells in vivo. A thin layer of collagen was overlaid onto microhole array made of an impermeable photoresist film, creating two distinct regions with different porosity and stiffness. When mouse primary colon epithelial cells were grown on the platform, the cells formed a monolayer across the microhole array with segregated cell populations: proliferative cells over the microholes and non-proliferative cells distanced from the microholes. Generation of growth factor gradients across the cells via the microholes resulted in in vivo-like cell behaviors where proliferative cells over the microholes migrated outward, differentiated as they migrated and then eventually reaching the end of their lifespan in regions apart from the microhole sources of growth factors. Short chain fatty acids, bacterial metabolites that are present in the colonic lumen, significantly influenced the proliferation and differentiation of the primary mouse colon epithelial cells as has been demonstrated to occur in vivo. With simple fabrication, ease of use, and low maintenance, this platform enables observation and quantification of proliferative and differentiated cells simultaneously and the interplay between these two cell zones. Access to both the luminal and basal sides of the polarized tissue permits the screening of drugs, metabolites and food stuffs for their impact on intestinal cell epithelium. This platform will be a valuable tool for to understand intestinal physiology in health and disease.

Folding Artificial Mucosa with Cell-Laden Hydrogels Guided by Mechanics Models Ruike Zhao1, 2, Hon Fai Chan1, German A. Parada3, Kam W. Leong1, Linda G. Griffith1 and Xuanze Zhao1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio, United States; 3Columbia University, New York, New York, United States.

The surfaces of many hollow or tubular tissues/organisms in our respiratory, gastrointestinal, and urogenital tracts are covered by mucosa with folded patterns.
The patterns are induced by mechanical instability of the mucosa under compression due to constrained growth. Recapitulating this folding process in the development of engineering of mucosa in various tissues/organisms. However, scant attention has been paid to address the challenge of reproducing mucosal folding. Here we mimic the mucosal folding process using a cell-laden hydrogel film attached to a pre-stretched tough-hydrogel substrate. The cell-laden hydrogel constitutes of human epithelial cell lining on stromal component to recapitulate the physiological feature of mucosa. Relaxation of the pre-stretched tough-hydrogel substrate applies compressive strains on the cell-laden hydrogel film, which undergoes mechanical instability and evolves into morphological patterns. We predict the conditions for mucosal folding as well as the morphology of and strain in the folded artificial mucosa using a combination of theory and simulation. The work not only provides a simple method to fold artificial mucosa but also demonstrates a new paradigm in tissue engineering via harnessing mechanical instabilities guided by quantitative mechanics models.

9:30 AM BM05.05.06
Alginate-Based Electrodeposition for On-Demand Fabrication of Tubular Structures for Applications in Vascular Tissue Engineering David Kingasley, Jared Capuno, Rachel Antmann, Cassandra Roberge and David T. Corr; Renssealaer Polytechnic Institute, Troy, New York, United States.

One of the major challenges in tissue engineering is the fabrication of tubular cell-loaded structures (e.g., blood vessels). This is due, in part, to the difficulties in generating a self-supporting luminal structure with an appropriate spatial distribution of loaded cells. Alginate - a polysaccharide derived from brown algae that gels in the presence of divalent cations, such as Ca²⁺ - has gained great traction as an exciting candidate material for biofabrication, due to its tunable mechanical properties, ease of gelation, overall biocompatibility, and ability to be gently resolved through reverse crosslinking. Typically, alginate structures are created through homogenous internal crosslinking systems in which insoluble CaCO₃ particles are suspended in an alginate solution, and the alginate slowly dissociates from the carbonate upon introduction of a weak acid (e.g., GDH), to crosslink the alginate network. Recently, electrolysis has been shown as an alternative method to generate crosslinked alginate gels. In this method, a current is run through an electrolyte solution to produce products of hydrogen and carbon dioxide, with a reaction byproduct of protons generated at the anode surface. These protons can be exploited to produce free calcium from CaCO₃ and cause local crosslinking when performed in an alginate solution. Herein, we utilize electrolysis to produce a pH change at a cylindrical copper anode surface, resulting in the radial deposition of an alginate gel around the anode wire. Furthermore, we investigate how alginate deposition is effected by key variables in the fabrication process, including: applied voltage, CaCO₃ particle size, anode wire diameter, alginate concentration, calcium concentration, and overall electrolysis duration. Within these experiments, the rate of alginate deposition increased inversely proportionately with CaCO₃ particle size (and therefore available surface area), however this effect appeared to diminish at longer deposition times. Furthermore, we observed that greater diameter anode wires were able to produce thicker gels, likely due to the available surface area for proton generation. Similarly, alginate and calcium concentration also affected the thickness of deposited gels on anode surfaces, and the overall robustness of the gels (qualitatively speaking). Last, we apply this technique to generate alginate tubular structures entrapping multiple layers of discretized cells. By performing sequential electrodeposition using two different alginate solutions, suspending either GFP or RFP labeled cells, we observe via fluorescent microscopy radial compartmentalization, i.e., the encapsulation of each cell line at different layers in the luminal thickness. Overall, within this work we demonstrate a novel, on-demand technique to fabricate alginate-based tubular structures with encapsulated discretized cells, using the principles of electrodeposition.

9:45 AM BREAK

SESSION BM05.06: Sensors for Monitoring Tissue Models
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Liberty C

10:15 AM BM05.06.01
Nanowire Arrays Restore Vision in Blind Mice Jing Tang; Materials Science and Engineering, Stanford University, Stanford, California, United States.

The restoration of light response with complex spatiotemporal features in retinal degenerative diseases towards retinal prosthesis has proven to be a considerable challenge over the past decades. Herein, inspired by the structure and function of photoreceptors in retinas, we develop artificial photoreceptors based on gold nanoparticle-decorated titania nanowire arrays, for restoration of visual responses in the blind mice with degenerated photoreceptors. Moreover, neurons in the primary visual cortex respond to light after subretinal implant of nanowire arrays. Improvement in pupillary light reflex suggests the behavioral recovery of light sensitivity. Our study will shed light on the development of a new generation of optoelectronic toolkits for subretinal prosthetic devices.

10:30 AM BM05.06.02
A Novel Technique for In situ Characterization of 3D Tissues Using MEMS Mohamed Elhebeary and Taher Saif; University of Illinois-Urbana Champaign, Urbana, Illinois, United States.

The development of multicellular tissues is highly dependent on the mechanical forces associated with cell-cell and cell-matrix interactions. Cellular forces are measured using Traction Force Microscopy (TFM) on 2D soft substrates. However, TFM cannot provide forces in 3D tissues. Also, the effect of cross talk between cells within the tissue microenvironment cannot be captured in 2D culture. Here, we propose a technology that introduces a new device and a new method that radically changes the way we form 3D biometric tissues, and study them in situ. The method exploits the advances in micro-fabrication and combines them with classical theories of capillarity to offer new functionalities, namely self-assembly and self-alignment of tissues on a sensor stage. Currently there is no technology available to measure tissue force (due to cells) and tissue stiffness simultaneously. The new device closes this gap for the first time. It not only provides a time lapse measure of both force and stiffness, it allows simultaneous inspection of the microstructure of the tissue in situ, thus linking tissue biophysics with pathophysiology. Such in situ quantitative inspection will offer new insights that cannot be achieved with existing methods.

A novel design of a silicon platform, that integrates a stretching and sample self-assembly mechanisms, is introduced. First, a mixture of collagen I solution and fibroblasts (3T3) is dispensed on the silicon platform at room temperature (500x500x200 μm³). After curing, the chip is imbedded in cell culture media within an incubation chamber. The small thickness of the chip (200 μm) makes it compatible with live cell microscopy and avoids any histological sectioning needed in the case of thick sample. The tissue forces are measured using an optical microscope by imaging the co-fabricated gauges on the chip and follow-up image analysis. An external 3D manipulator is used to stretch the tissue sample to measure its elastic modulus at different stages of tissue...
morphogenesis. Image analysis gives a displacement resolution of approximately 200 nm and a corresponding force resolution <1 µN. The proposed technology offers advantages over available techniques to study the biomechanical tissue due to the following reasons: no need to expose the sample to light which might affect its response, small size allows portability between different chambers during imaging and/or incubation, and ability to monitor the stiffness change along with microstructure development with time. Results from different cell lines showed the evolution of force with time after seeding cell/collagen mixture. Stiffness measurements of samples and effect of drugs on force relaxation are studied.

10:45 AM BM05.06.03 Improvement Performance of Ionic Liquid-Based Pressure Sensor for Integration into Body-on-a-Chip Yusuke Tsuji1, Yoshikazu Hirai1, Ken-ichiro Kamei1, Toshiyuki Tsuchiya1 and Osamu Tabata1; Kyoto University, Kyoto, Japan.

Body-on-a-Chip (BoC) platform holds a great potential for new pre-clinical tests in drug screening as in vitro human models by mimicking in vivo physiological and pathological conditions. Recently, the authors have reported a proof of BoC concept for recapitulation of the cardio-toxic side effects of an anti-cancer drug [1]; however, there is still a technological challenge to integrate a pressure sensor for monitoring or controlling pressure in BoC, leading to create cellular microenvironments close to in vivo physiological conditions in the BoC platform. Among existing polydimethylsiloxane (PDMS)-based pressure sensors, the sensor with ionic liquid (IL pressure sensor) [2] is promising due to allowing direct integration into a PDMS-based BoC platform by multilayer soft lithography. But previously reported sensors lack proper performance with respect to sensitivity and linearity. Here we propose a novel fabrication approach of an IL pressure sensor by using simulation-based three-dimensional (3D) lithography and show its improved sensor performance.

An IL pressure sensor is composed of a flow channel to circulate cell culture medium and an electro-fluidic (EF) channel filled with IL, and they are overlapped with separation by a PDMS microstructure (tens of µm). The pressure in flow channel can be measured by monitoring electrical resistance change of an EF channel induced by membrane deformation by pressure. Since the sensor performance such as sensitivity and linearity depend on cross-sectional shape of the EF channel, we focused to tune a cross-sectional shape of mold for EF channel.

To improve the sensor performance, the electrical resistance change of EF channel by deformation of PDMS membrane were simulated with FEM analysis for four sensors with different cross-sectional geometries (rectangle: 400, 600 µm width x 25 µm height, triangle: 400 x 25 µm², and semi-ellipse: 400 x 25 µm²). The triangular channel showed 10-time higher sensitivity than the rectangular channel.

Then, designed sensors were fabricated by digital micromirror device-based grayscale lithography [3] with a numerical process optimization, and resistance changes were measured by an impedance analyzer. The results on static pressure with the range of 0 to 12 kPa exhibited good agreement with the numerical simulation results. Moreover, to validate the performance to measure heart beating, the periodic pressures with a triangular wave were applied to the sensor. As the results, the sensor with triangular channel was able to follow at least pressure change at 1 Hz. We believe that our proposed approach and developed sensor will allow measuring pressures at the physiological levels.

References

11:00 AM BM05.06.04 Multiplexed Single-Cell Secretomic Profiling on 3D Scaffolds Yao Lu, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

Single cell barcode microchip (SCBC) has become an informative tool for comprehensive monitoring of the immune effector functions of single cells and has great value for quantifying cellular heterogeneity at the functional level in the complex biological systems such as the immune system or tumor microenvironment [1-4]. Despite its rapid progresses, efforts to control the three dimensional microenvironment for single cell measurements have been lacking [5]. We developed a simple method to incorporate three dimensional scaffolds with PDMS stencils into a multiplexed single cell secretomic analysis platforms to mimic the extracellular physical matrix and mechanical support for single cells [6]. Applying this platform to brain tumor cell line U87 to investigate single cell protein secretion behavior on different substrates, we revealed that single cell protein secretions were regulated differently in different microenvironments. The finding was further verified with intracellular cytokine staining, highlighting the significance of 3D single cell microenvironments. This new single cell biomimetic platform can be easily adaptable to other single cell assays and may become a broadly applicable three dimensional single cell analysis system to study the effect of microenvironment conditions on cellular functional heterogeneity in vitro.

References

11:15 AM BM05.06.05 Integrated Measurement of Cytosolic Proteins and Transcripts in Single Cells Alexander Xu1,2, Qianhe Liu1, Kaitlyn Takata1, Sarah Jeoung1, Yapeng Su1, Igor Antoschechkin1, Sisi Chen1, Matthew Thomson1 and James Heath1,3; 1California Institute of Technology, Pasadena, California, United States; 2Institute for Systems Biology, Seattle, Washington, United States.

Single cell measurements have revamped our understanding of biological tissues by resolving their single cell heterogeneity. New technologies such as droplet microfluidic transcriptomics and microchip proteomics provide better insights on how healthy tissues function, and how aberrant cells in the tissue cause disease. However, our understanding of how the single cells in a tissue perform their functions is limited by the types of information that can be captured from each cell. Here we present a method for measuring the whole transcriptome and cytosolic proteins in single cells on a microfluidic chip. By coupling single cell barcode chip (SCBC) proteomics and bead-based sequencing technologies, we capture multiple measurements of a single cell without splitting cell contents, and we use gold standard measurement modes – fluorescence sandwich immunoassays for proteins and sequencing for transcripts. This technology is enabled by a DNA labeling strategy that allows measurements to be taken independently and robustly, and linked after data processing.

We measure two cell types, showing that there is a unique molecular signature for both cell types in both protein and transcript data. The microfluidic chip is designed such that location barcodes scale geometrically and the chip can be readily scaled to produce larger single cell integrated datasets. This strategy...
for taking multiple measurements from single cells is unique in that it does not require either the protein or transcript signal to be converted from its native measurement mode. This is done in an effort to produce the best possible data using established technology. By using established technology, we are also able to further modify the integrated SCBC to capture metabolic measurements in the future. Ultimately, this technology presents a generalizable DNA encoding strategy to augment sequencing methods, as well as a powerful tool to better understand single cell biology by expanding the scope of their measurements.

11:30 AM BM05.06.06
Ultra-Small Biocompatible Iron Oxide T1 MRI Contrast Agents with Reduced Magnetic Coupling
Fabian H. Starsich1, Christian Eberhardt2, Kerda Keevend3, Andreas Boss2, Ann Hirt1, Inge Herrmann1 and Sofie S. Pratsinis1; 1ETH Zurich, Zurich, Switzerland; 2Institute of Diagnostic and Interventional Radiology, University Hospital Zürich, Zurich, Switzerland; 3Department Materials Meet Life, Swiss Federal Laboratories for Materials Science and Technology (Empa), Zurich, Switzerland.

Contrast agents are essential to magnetic resonance imaging (MRI) for the evidential visualization of soft tissue pathologies in regenerative medicine. MRI can be categorized into T1- and T2-weighted sequences that require as contrast agents paramagnetic and superparamagnetic materials, respectively. Typically, T1-weighted MRI is preferred over T2- due to the faster data acquisition using gradient-echo sequences and sharper image analysis. Commonly used and FDA-approved T1 contrast agents are based on highly paramagnetic Gd complexes. Although very efficient in terms of contrast enhancement, these complexes have been associated with nephrogenic systematic fibrosis due to Gd3+ release, especially in long and repeated exposure scenarios. Here, ultra-small iron oxide nanocrystals co-oxidized with SiO2 are investigated as a biocompatible alternative. By using SiO2 as a spacing material, the effective magnetic size of iron oxide is reduced resulting in significant T1 contrast enhancement due to minimized magnetic coupling. The nanocrystals are produced by scalable and sterile flame aerosol technology with potential production rates up to kg h-1. The optimized FeOx/SiO2 nanoparticles attain comparable relaxivities to harmful Gd-complexes, however, with no apparent cytotoxicity at clinically relevant concentrations tested in vitro against four different cell types (PC3, HepG2, THP-1 and red blood cells). With this, these flame-made ultra-small iron oxide nanoparticles offer safe and efficacious access to T1 contrast agents fulfilling major prerequisites for a future translation into clinics.


SESSION BM05.07: Breakthrough Technologies for In Vitro Tissue Modeling
Session Chairs: W. Swieszkowski and Yu Shrike Zhang
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Liberty C

1:30 PM *BM05.07.01
Infections and Inflammation-on-a-Chip—Neutrophil Swarming Against Fungi D. Irimia; Department of Surgery, Massachusetts General Hospital, Harvard Medical School, Boston, Massachusetts, United States.

Neutrophil swarms protect us from microbes by sealing off sites of infection. In the absence of swarming, microbes could invade into healthy tissues, and severe infections could progress. Recent observations in animal models have shown that neutrophil swarming is one essential immune response against large microbes and clusters of microbes. Although relevant, such models are low throughput and are also too complex to allow for the precise dissection of the innate immune actions that protect against infections. Large microscale arrays of targets for the study of human neutrophils during swarming ex vivo provide an attractive alternative and enable the observation of thousands of swarms at once against live-microbe. Moreover, the synchronized swarming in small volumes enables the detailed analysis of the amount and timing of mediators released during human-neutrophil swarming, responsible for the early activation and late resolution of the process. In the clinical setting, we compared the swarming behavior of neutrophils from patients following major trauma and healthy individuals and found various deficiencies that resolve over time. The new technologies for studying Infections and Inflammation-on-a-chip represents a valuable discovery and screening platform, which could lead to novel anti-inflammatory and anti-microbial treatment strategies.

2:00 PM *BM05.07.02
Biofabrication of Biomimetic 3D Models of Musculoskeletal Tissues W. Swieszkowski1, M. Constantini1,2, Chiara Rinoldi1, J. Idaszek1, A. Kosik-Kozio1 and E. Kijenska-Gawronska2; 1Faculty of Materials Science and Engineering, Warsaw University of Technology, Warsaw, Poland; 2Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

An innovative technique that may overcome current limits in reproducing complex structures of human tissues and organs is 3D biofabrication. This emerging fabrication technology relies on the simultaneous deposition of cells and biomaterials, mostly in a layer-by-layer fashion, to form 3D well-organized living heterogeneous porous structures that can mirror physiologically and morphologically relevant complex biological architectures. In this study, we present an innovative strategy to biofabricate biomimetic 3D models of musculoskeletal tissues, like muscle, tendon, or cartilage. Our 3D biofabrication approach is based on a microfluidic system coupled to a co-axial needle extruder for high-resolution computer-controlled 3D deposition of hydrogel fibers laden with different cells. By formulating tailored hydrogel based bioinks and precisely controlling the 3D spatial organization of the extruded hydrogel fibers, it was possible to biofabricate advanced engineered living constructs mimicking natural musculoskeletal tissues. Furthermore, the influence of mechanical loading and biochemical stimulation on proliferation, alignment, and differentiation of the cells as well as ECM deposition in 3D biofabricated constructs will be discussed. Additionally, the preliminary in vivo performance of selected 3D biomimetic 3D tissue models will be presented.

2:30 PM *BM05.07.03
Engineered Tumor Ecosystem for Personalized Anti-Cancer Therapy S. Sengupta; Division of Engineering Medicine, Department of Medicine, Brigham and Women’s Hospital, Harvard Medical School, Cambridge, Massachusetts, United States.

Being able to select the most effective therapy for each individual cancer patient remains the Holy Grail in cancer treatment. In today’s precision medicine, this selection is made based on molecular and genetic profiling of biomarker expression. However, a biomarker often does not translate into a successful
clinical response to the selected therapy. We have engineered a ‘micronized tumor ecosystem’ that conserves the patient tumor characteristics with high fidelity, and integrated with a novel machine learning algorithm can accurately predict anticancer drug responses. This talk will discuss how such a micronized tumor ecosystem can be used to choose the most effective therapy for a patient before initiation of treatment.

3:00 PM BREAK

3:30 PM *BM05.07.04
Origami Microfluidics for Biomimetic Organs on a Chip
C. Livermore1, 2, 3; 1Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States; 2Department of Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States; 3Northeastern University, Boston, Massachusetts, United States.

Fluid mechanics at the shortest length scales enables many functions of life, such as microcirculation in the human body and transpiration in plants. Ideally, we would be able to translate these properties directly into engineered tissues and organ on a chip systems, but there remains a significant gap between the materials and techniques of conventional microfluidics and the functions of the human body. For example, conventional organs on a chip can struggle to replicate the massively parallel flow and perfusion architecture of the liver. Origami-based microfluidics offer a new paradigm for addressing these challenges. Folding offers a low-cost, rapid means of creating flow structures to mimic vasculature. Multi-material architectures enable additional transport via diffusion, and directed assembly of cells offers hierarchical structure at the smallest length scales. This talk will present the enabling tools of origami tissue engineering, including the use of origami-based techniques to create multi-material, flow/perfusion microfluidic devices as a platform for scalable tissue engineering. In particular, the presentation will focus on the application of these multifunctional systems for the design, fabrication, and characterization of origami liver tissue units.

4:00 PM *BM05.07.05
Putting 3D Bioprinting to the Fabrication of Tissue Models
Yu Shrike Zhang; Division of Engineering Medicine, Department of Medicine, Brigham and Women’s Hospital, Harvard Medical School, Cambridge, Massachusetts, United States.

The talk will discuss our recent efforts on developing a series of bioprinting strategies including sacrificial bioprinting, microfluidic bioprinting, and multi-material bioprinting, along with various cytocompatible bioink formulations, in facilitating the fabrication of biomimetic 3D tissue models. These platform technologies, when combined with bioreactors and bioanalysis, are anticipated to provide new opportunities for constructing functional microtissues with a potential of achieving improved drug screening and precision therapy by overcoming certain limitations associated with conventional models based on planar cell cultures and animals.

SYMPOSIUM BM06

Plasma Processing and Monitoring for Bioengineering and Biomedical Engineering
November 26 - November 27, 2018

Symposium Organizers
David Graves, University of California, Berkeley
Emilio Martines, Consorzio RFX
Deborah O'Connell, University of York
Hajime Sakakita, National Institute of Advanced Industrial Science and Technology

* Invited Paper

SESSION BM06.01: Plasma Interaction with Living Systems and Liquids
Session Chairs: David Graves and Hajime Sakakita
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Independence West

8:45 AM *BM06.01.01
Plasma-Bio Interactions—Linking Plasma-Induced Liquid Phase Chemistry with the Biological Impact of Plasma
Peter Bruggeman; University of Minnesota, Minneapolis, Minnesota, United States.

Non-equilibrium atmospheric pressure plasmas interacting with biological matter offer a unique source of highly reactive chemistry beneficial for many applications including food decontamination, wound healing and cancer treatment. Many of these applications require controlled and selective interactions. For example, in decontamination processes, the inactivation of bacteria on healthy tissue or food samples needs to occur with minimized off target effects. Controlling selectivity requires a detailed understanding of the underlying plasma-bio-interaction mechanisms. As the majority of these plasma-bio interactions occur in an aqueous environment, linking plasma-produced reactive species in this environment with biological responses is of key importance to develop controlled and selective applications of plasmas in biomedical applications.

My group, in collaboration with microbiologists, has investigated the reactive species responsible for plasma-induced liquid phase processes such as the
inactivation of bacteria and virus and the interaction of plasma with mammalian cells using a well-characterized atmospheric pressure plasma jet with a known composition of the reactive species in the gas phase. As in several other reports we found the importance of long-lived species such as H2O2 and OCl-. However many results indicated the direct or indirect importance of short-lived species. We will discuss these results in detail illustrating the unique character of the plasma treatment and also outline the strong possible sensitivity of plasma-bio interactions on treatment modalities.

Acknowledgements
This work is partially supported by the United States Department of Energy, Office of Fusion Energy Science (DE-SC0001319 and DE-SC0016053), the National Science Foundation (PHY 1500135) and the US Department of Agriculture, National Institute of Food and Agriculture (2017-67017-26172).

9:15 AM *BM06.01.02
Investigation of Damage to Nucleic Acids Induced by Plasma Irradiation Hirofumi Kurita, Tomoko Nakajima, Kaori Sano, Saki Miyachika, Yoshito Uchihashi, Natsuki Haruta, Hachiro Yasuda, Kazunori Takashima and Akira Mizuno; Toyohashi University of Tech, Toyohashi, Japan.

Cold atmospheric pressure plasmas have been intensively studied due to growing interest in biological and medical applications. Especially the plasma has been considered as a promising tool for cancer therapy. One of the proposed molecular mechanism is DNA damage-associated cell death. Therefore DNA is one of the most important biomolecular targets for investigating the effects of exposure to the plasma. Over the last decade, many studies have attempted to characterize DNA damage and the associated cellular responses induced by plasma irradiation. In the early stage of the investigation, most of the reports used isolated plasmid DNA molecules in liquids and the analysis was based on gel electrophoresis. For example, it has been reported that oxidative damage is induced by exposure to the plasma, resulting in single-strand breaks (SSBs) and double-strand breaks (DSBs) separated by conventional agarose gel electrophoresis [1]. In recent years, the analysis of genomic DNA in the plasma-irradiated cells were reported. For example, the single cell gel electrophoresis assay, also known as the comet assay, is a versatile method for measuring DNA damage. Although gel electrophoresis is relatively inexpensive and easy to perform, it requires long run times. Therefore we have developed non-electrophoretic methodologies. Our first investigation is a single-molecule-based method for evaluating strand breaks in large linear DNA molecules that allows the length of individual DNA molecules to be measured [2]. In this investigation plasma-induced DNA breakages have been kinetically analyzed. However, the single-molecule method requires the acquisition and processing of many fluorescence images for reliable analysis. We have also investigated rapid detection of DNA strand breaks induced by plasma irradiation using a molecular beacon (MB) [3]. MBs are oligonucleotides that adopt a stem-and-loop structure and carry a 5'-fluorescent moiety and a 3'-nonfluorescent quenching moiety. Scission of the stem by plasma irradiation leads to separation of the fluorophore-quencher pair, resulting in an increase in fluorescence that directly correlates with the extent of DNA strand breaks. In addition, we reported that a plasma jet readily induced DNA strand breaks in synthetic models of tissue and cells, surprisingly without any significant rupture of the phospholipid membrane [4]. Furthermore, the feasibility of MB-based methodology for detecting intracellular DNA damage was investigated. Our novel methodology may allow investigations of the effects of atmospheric pressure plasma on DNA damage-associated cell death in plasma treatments.


9:45 AM BM06.01.03
Effects and Mechanism of Electric Stimulation Through Carbon Nanowalls Scaffold on Proliferation and Differentiation of Cultured Cells Hiroki Kondo1, Tomonori Ichikawa1, Kenji Ishikawa1, Hiromasa Tanaka1, Takayoshi Tsutsumi1, Keigo Takeda2, Makoto Sekine1, Masaru Horii1 and Mineo Hiramatsu2; 1Nagoya Univ, Nagoya, Japan; 2Meijo University, Nagoya, Japan.

In recent years, nanomaterials, such as carbon nanotubes, graphene nanoflakes, and so forth, have attracted much attention as a cell culturing scaffold. It has been reported that an introduction of nanometer level fine structures affects cell differentiation induction. Very recently, it has also been reported that an electric stimulation through conductive scaffold of resin containing carbon nanotubes can affect proliferation and differentiation of cultured cells. Based on these backgrounds, we have focused on carbon nanowalls (CNWs), in which multiple layers of graphene sheets are vertically grown on a substrate and form randomly intricate wall structures like maze. Due to their unique morphology, the CNWs have very high aspect ratio over 100 and high specific surface area. In addition, they also have high conductivity and robustness against chemical treatments. Therefore, the CNWs are promising as electrically conductive cell culturing scaffold with nanometer level fine structures. We have reported that the wall density and the chemical termination of CNWs influence the proliferation rate and morphology of HeLa cell. Furthermore, electric stimulation through the CNWs scaffold increased proliferation rate of human osteoblast-like cells (Saos-2) and suppress their ossification only if frequency of electrical stimulation was 10 Hz. In this study, the effects and mechanisms of such the electrical stimulation through the CNWs scaffold with the different wall densities were investigated. Proliferation rates and intra- and extra-cellular calcium amounts were measured for the Saos-2 cells cultured on the CNWs scaffold with the electric stimulation.

The CNWs were grown on Ti substrates by a radical injection type plasma excited chemical vapor deposition (RI-PECVD) system. In order to change the wall densities, the total pressures during the growth were controlled from 1 to 3 Pa, which realizes density controls of hydrogen and methyl radicals. According to scanning electron microscopy (SEM) images, distances between neighboring walls were 208 and 341 nm, when the total pressures were 1 and 3 Pa, respectively. Saos-2 cells were cultured on these CNWs scaffolds in an environment at 37°C and with CO2 concentration of 5%. Electric stimulation with a frequency of 10 Hz, square wave shape and a peak-to-bottom voltage of 226 mV was supplied for 24 hours after seeding the cells. Then, after culturing for a total of 100 hours, the number of cells and morphology were observed. A 58% increase in proliferation rate was observed on CNWs with a wall density of 341 nm, while that on the CNWs with a wall density of 208 nm hardly changed. At the same time, it was confirmed that aggregates of cells were formed only on the on the CNWs with a wall density of 341 nm. This suggested that an intercellular adhesion can be controlled by the electrical stimulation on the CNWs scaffold. These results could open the way of novel cell control system.

10:00 AM BREAK

SESSION BM06.02: Plasma Treatment toward Therapy and Pharmacology I
Session Chairs: Hirofumi Kurita and Deborah O’Connell
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Independence West

10:30 AM *BM06.02.01
Non-Thermal Atmospheric Pressure Plasma as a Tool to Control the Proliferation of Various Adult Stem Cells

Kiwon Song1, Jeongyeon Park1, Hyunyoung Lee2 and Jae June Lee2; 1Yonsei University, Seoul, Korea (the Republic of); 2Pusan National University, Pusan, Korea (the Republic of).

Non-thermal atmospheric pressure plasma (NTAPP) is described as a quasi-neutral mixture of charged particles and radicals in a partially ionized gas at atmospheric pressure. Recently, many researches attempted to take advantage of the low temperature of NTAPP for biomedical applications thanks to the controllability of plasma chemistry and kinetics. Adult stem cells can differentiate into various mature cell types within tissues or organs at specific conditions. Adipose-derived stem cell (ASC) is a kind of mesenchymal stem cell, which is able to self-renew and differentiate into adipocytes, chondrocytes, osteoblasts and neurons. In this study, we exposed ASCs to NTAPP generated in a helium-based dielectric barrier discharge (DBD) device 10 times, for 50 sec each time every hour, and incubated the cells till 72 h. NTAPP exposure increased the proliferation of ASCs by 1.57-fold on an average, compared with unexposed cells. NTAPP-exposed ASCs maintained their stemness, capability to differentiate into adipocytes but did not undergo the cellular senescence. In addition, the mRNA level of well-known pluripotent genes, Oct4, Sox2 and Nanog, was increased in NTAPP-exposed ASCs compared with that of the unexposed cells. Also, signaling pathways that activate the cell proliferation such as Akt, ERK1/2, and NF-κB were activated and the proliferating cell nuclear antigen (PCNA) was highly increased at 72 h in NTAPP-exposed ASCs. Studies using the scavengers for nitric oxide (NO) and reactive oxygen species (ROS) demonstrated that NO rather than ROS is responsible for the enhanced proliferation of ASCs following NTAPP exposure. Moreover, NTAPP induced the increased proliferation of bone marrow-derived stem cells (BM-MSCs) and hematopoietic stem cells (HSCs) by 80 % and 100 %, respectively. These results suggest that NTAPP can activate the proliferation of ASCs without affecting their stem cell properties. Taken together, this study supports that NTAPP would be an efficient tool to activate the proliferation of various adult stem cells for the medical application of stem cells both in vitro and in vivo. Currently, we are investigating the whole genome expression profile of NTAPP-exposed ASCs to understand the molecular mechanism of the activation of adult stem cell proliferation by NTAPP.

11:00 AM *BM06.02.02
Effectiveness and Safety of Plasma Activated Medium
Hiromasa Tanaka, Masaaki Mizuno, Kenji Ishikawa, Shinya Toyokuni, Hiroaki Kajiyama, Fumitaka Kikkawa and Masaru Horii; Nagoya Univ, Nagoya, Japan.

It is important to investigate effectiveness and safety for clinical applications of new therapeutic methods. Non-thermal plasma is pretty new technology which is expected to be applied for various medical applications such as blood coagulation [1], wound healing [2], and cancer treatments [3]. We have previously developed plasma activated medium (PAM) for cancer treatments [4]. We have also developed plasma activated Ringer’s lactate solution (PAL) for cancer treatments [5]. We would like to discuss effectiveness and safety of these solutions based on our accumulated knowledge through numerous studies.

PAM selectively killed glioblastoma brain tumor cells against astrocyte normal cells [4]. Selective killing of cancer cells by PAM have been reported in not only glioblastoma, but also ovarian, pancreatic, and other cancer cells. We have reported that PAL also selectively killed glioblastoma against normal keratinocyte cells and mammary epithelial cells. These in vitro experiments are good evidence to use PAM/PAL safely. Various in vivo experiments also demonstrated safety of PAM/PAL. For example, PAM inhibited ovarian cancer cell metastasis, resulting in prolonged survival in a mouse model, while PAM intraperitoneal injection exerted little influence on body weight [6]. Intravitreal injection of PAM suppressed laser-induced choroidal neovascularization, while PAM injection had no effect on regular retinal vessels, nor did it show retinal toxicity [7]. These in vivo experimental results are important evidences to use PAM effectively and safely.

To establish plasma medical science, understanding molecular mechanisms and effectiveness and safety tests are necessary. Since PAM was developed, many in vitro and in vivo experiments have demonstrated its effectiveness and safety especially in cancer treatments. Selective killing of cancer cells by PAM are good evidences for effectiveness and safety of PAM. These results suggest PAM therapy may be a promising treatment option.

Acknowledgements
This work was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Plasma Medical Innovation” Grant No. 24108002 and 24108008.

References

11:30 AM *BM06.02.03
Helium Plasma as a Tool for Interacting with Cells and Pathogens
Emilio Martines; Consorzio RFX, Padova, Italy.

This contribution reviews recent activity of the Padova group on the use of helium plasmas in plasma medicine. Following the initial emphasis on disinfection of the cornea [1], the research activity has developed along several research lines, which cover the topics of wound healing, cancer treatment and non-thermal coagulation.

Plasma source characterization from the physical and chemical point of view has been performed, comparing two different sources: a RF source for indirect plasma treatment [2] and a Dielectric Barrier Discharge jet for direct treatment, specifically designed for non-thermal blood coagulation applications. The comparison has included an assessment of disinfection properties. The specificity of helium as working gas has been emphasized by mass spectrometry measurements, which hint to the importance of metastable excited states.

The wound healing activity has seen a set of in vitro tests, which have shown the ability of a RF indirect treatment to stimulate cell proliferation and migration, processes which are related to an increase of intracellular ROS level [3]. Subsequently, an in vivo study on large animals (sheep) has been performed, showing the ability of the plasma treatment to significantly reduce bacterial charge on the wound, to reduce inflammation, to promote the regeneration of cutaneous annexes, such as hair follicles and glands, and to lead to an anticipated induction of blood vessel formation.

The work on cancer treatment has been carried out in vitro, using primary cells cultivated from tissue samples of patients affected by laryngeal and lung cancer. The plasma treatment has been shown to lead to an increased RONS level in cells, with a stronger effect observed in cancer cells than in healthy ones. As a consequence, apoptosis is induced in a remarkable fraction of cancer cells, with a preferential effect with respect to healthy ones. This result could be enhanced by combining the plasma treatment with incubation with a molecule known to increase the ROS level in cells.
Finally, the first results of a project on non-thermal blood coagulation induced by the direct interaction with a helium plasma jet will be reported. In vitro studies have shown that the applications of the plasma indeed accelerates coagulation. The result has been confirmed by in-vivo tests on animal models.

**References**


**11:45 AM BM06.02.04**

High Throughput Toxicity Assay on Cooperatively Ordered Single Cells with Individual Identity Qiuxuan Li and Ming Su; Northeastern University, Boston, Massachusetts, United States.

Cytotoxicity at single cell level plays an important role in understanding biological mechanisms, detecting diseases, and screening therapeutics. Since cell populations are heterogeneous, differentiating individual cells in large populations become very important. This abstract reports a single cell array where the identity of each individual cell can be determined from coordinators assigned to the cell. Cytotoxicity upon X-ray radiation exposure and drug treatment are determined through reactive oxygen species (ROS) signal in cells and quantified by fluorescent intensity with MATLAB. This method can provide toxicities of over thousands of cells with superior statistics power after different treatment. The heterogeneity of cells in response to chemical and physical stimuli can be easily obtained to allow deep analysis of obtained toxicity data.

**SESSION BM06.03: Plasma Processing of Biocompatible Materials**

Session Chairs: Tetsuji Shimizu and Kiwon Song

Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Independence West

**1:30 PM *BM06.03.01**

Plasma Processing of Liquid Media for Biology—An In Vitro Study of Chemical Actors and Biological Effects Elisa Sardella1, Valeria Veronica2, Francesco Fracassi3, Michele Casiolo1, Lucia d’Accolli1, Loris Grossi1, Francesco Cimina1, Pietro Favia1, Michael Schmidt2, R.D. Wilmann1 and Roberto Cristina1; 1Institute of Nanotechnology, CNR-NANOTEC, Bari, Italy; 2Department of Chemistry, University of Bari, Bari, Italy; 3University of Rimini, Rimini, Italy; 4Leibniz Institute for Plasma Science and Technology, Greifswald, Germany; 5University of Bari, Bari, Italy.

During the last 10 years atmospheric pressure plasmas have shown great promise for the treatment of wounds and cancer. All reported literature attests that the synergy between the plasma and liquid is critical to understanding the outcome of plasma treatment and envision targeted breakthrough in medical therapeutic approaches. In this work chemistry of cell culture liquid media was investigated after application of dielectric barrier discharges switched on at 6KHz with different gas feed: Air, Nitrogen, Oxygen and mixtures of them. A DBD closed system and a controlled gas environment were used in order to address important answers to the question: is the H2O2 really involved in promoting certain cell behaviors during in-vitro testing? Has the NO and its derivatives an active role in promoting some cell responses stimulated by a plasma activated biological media? Is there a clear role of biological molecules of cell culture media eventually modified by plasma in stimulating some biological responses? Plasma activated liquid media (PALM) have been analyzed by ESR, LC-MS and spectrophotometric quantification of reactive oxygen and nitrogen species. The chemical composition of such kind of plasma activated media show that [H2O2] increases while [NOx] species decreases with the percentage of O2 in the gas feed. Such results have been correlated to the biological characterization of plasma activated DMEM 10% FBS incubated for 2 hours with an osteoblasts cell line (SAOS2) and primary cells (BMSC). Cell growth of cells incubated with PALM have clearly shown that, the plasma processing with O2 (6KHz, 13kV, 25%DC, 1min) is more effective than that one carried out with N2 and air, performed in the same experimental conditions, in promoting a reduced cell adhesion, an absence of cell clusters and contemporary inhibiting cell growth of SAOS2 cell lines. Meanwhile, a different behaviors have been observed for the primary BMSC, with a less detrimental effect on cell adhesion and growth both on 2D and 3D growth. Two-dimensional (2D) cellular monolayers remain the standard for validation of several kind of biomedical and therapeutic approaches, even though 2D monolayers are unable to replicate the complicated environment and mechanisms of a tissue or a solid tumor and its growth. The production of three-dimensional (3D) in vitro models is now established as a much more accurate representation of in vivo conditions when compared to other in vitro models, such as the production of 2D monolayers. For these reasons the co-author of this paper will show the cell responses exposed to PALM both on 2D and 3D environment. The obtained results give important insight on plasma interfaced to biological liquids showing the potential for future application of plasma assisted approach both in regenerative medicine and cancer therapy.

**2:00 PM *BM06.03.02**

Cold Atmospheric Plasma Device for Decontamination of Space Equipment Hubertus M. Thomas1, Petra Rettbeg4, Gregor Morfill1, Julia Zimmermann1, Meike Mueller1, Markus Thoma1 and Tetsuji Shimizu1; 1DLR-Institute of Materials Physics in Space, Wessling, Germany; 2University of Giessen, Giessen, Germany; 3terraplasma GmbH, Garching, Germany; 4Institute of Aerospace Medicine, DLR, Cologne, Germany; 5National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Cold Atmospheric Plasmas (CAP) are commonly used in plasma medicine and plasma hygiene due to its sterilizing conditions. We are presenting a new device based on the circulation of the long-living species of an afterglow air CAP for the decontamination of space equipment. In space exploration the decontamination of equipment for the visit to other planets or moons is very strictly regulated through the planetary protection policies of the Committee on Space Research (COSPAR). Proven methods for the decontamination are using for treatment of the equipment dry heat or H2O2-gas, both having negative side effects in addition to the decontamination efficacy. In a first project we investigated the use of afterglow plasma produced in a CAP for the decontamination effects on bacterial spores [1]. The afterglow plasma contains only the long-living species like ozone, NO2, etc. which allows the treatment of very sensitive materials at room temperature. In a follow-on project the apparatus was completely redesigned to gain efficacy, stability and reproducibility.

Measurements of the decontamination efficacy combined with physical measurements of the produced reactive components (measured by FTIR and UV absorption spectroscopy) and their effect on treated materials allow a better understanding of the involved processes.

We will give an overview on the status of the plasma decontamination project funded by the Bavarian Ministry of Economics.
Superhydrophobic surfaces with hydrophilic patterns have great application potential in various fields, such as microfluidic systems and water harvesting. However, many reported preparation methods involve complicated devices and/or masks, making fabrication of these patterned surfaces time-consuming and inefficient. Here, we propose a high-efficient, simple and maskless micro-plasma jet (MPJ) treatment method to prepare hydrophilic patterns like dots, lines and curves on superhydrophobic Al substrates. Contact angles, sliding angles, adhesive forces and droplet impact behavior of the created patterns are investigated and analyzed. The prepared “dot” patterns exhibit high water adhesion, while the “line” patterns show anisotropic adhesion. Additionally, MPJ treatment does not obviously change the surface structures, which makes it possible to achieve repeatable patterning on one substrate. Adhesion behavior of these patterns could be adjusted using MPJs with different diameters. MPJs with larger diameters are efficient for creating patterns with high water adhesion, which can be potentially used for open channel lab-on-chip systems (e.g., continuous water transportation); while MPJs with smaller diameters are preferable in preparing patterns with low water adhesion for diverse applications in biomedical fields (e.g., loss-less liquid droplets mixing and cell screening).

Surface modification of microplates with plasma polymerization technique was achieved by low pressure plasma system. In this particular study, acrylic monomers included, the most significant anti-biofilm effect was shown for DP at 90W. In this study,Regardless of the monomers and plasma parameters used, biofilm formation was inhibited for all plasma modified microplate wells (p<0.000). Of all the different plasma powers (30, 60 and 90W), the most significant inhibition of biofilms was observed on DP coated microplate wells at 90W, for all cultures were inoculated in triplicates onto microplate wells. Individual strains isolated from patients as well as negative and positive controls were incubated for 48 hours. Biofilm formation on plasma modified and non-modified surfaces were evaluated both at 48 hours and two weeks after.

Evaluation was done using crystal violet (CV) binding assay. After staining with CV, the optical density (OD) of each well stained with CV was measured at 570 nm against the OD of negative controls (at 48 hours and at two weeks).

Surface modification of microplates with plasma polymerization technique was achieved by low pressure plasma system. In this particular study, acrylic acid (AA), 2–hydroxyethyl methacrylate (HEMA) and diethyl phosphite (DP) were assessed for their biofilm inhibition efficacy. On non-coated control surfaces 100% biofilm formation by Candida spp isolated from blood as well as two ATCC control strains (C. albicans ATCC 10231 and C. parapsilosis) were included in this study. Biofilm formation was determined as described by quantitative plaque assay method. Suspensions of Candida spp isolated from blood cultures were inoculated onto microplate wells. Individual strains isolated from patients as well as negative and positive controls were incubated for 48 hours. Biofilm production on plasma modified and non-modified surfaces were evaluated both at 48 hours and two weeks after. Evaluation was done using crystal violet (CV) binding assay. After staining with CV, the optical density (OD) of each well stained with CV was measured at 570 nm against the OD of negative controls (at 48 hours and at two weeks).

Surface modification of microplates with plasma polymerization technique was achieved by low pressure plasma system. In this particular study, acrylic acid (AA), 2–hydroxyethyl methacrylate (HEMA) and diethyl phosphite (DP) were assessed for their biofilm inhibition efficacy.

Regardless of the monomers and plasma parameters used, biofilm formation was inhibited for all plasma modified microplate wells (p>0.000). Of all the monomers included, the most significant anti-biofilm effect was shown for DP at 90W. In this study, in-vitro results indicated a potential for reducing biofilm associated Candida infections on selected plasma modified surfaces.

**SESSION BM06.04: Monitoring of Plasma for Biomedical Applications**

**Session Chairs:** Vittorio Colombo and Zdenko Machala

**Monday Afternoon, November 26, 2018**

**Sheraton, 2nd Floor, Independence West**

**3:30 PM** *BM06.04.01*

**Plasma Jet Delivery on Targets Relevant for Skin Treatments—Towards In Situ Monitoring and Loop Controlled Plasma Gun Based Device**

**Eric Robert**, Azadeh Valinattaj Omran, Giovanni Busco, Sébastien Dozias, Catherine Griffon, Jean Michel Pouveles and Loick Ridou; CNRS-Univ d'Orleans, Orleans, France.

We will first report on the key role of conductive targets mimicking biological samples (such as those involved during in vitro, ex vivo and in vivo skin or skin cells), on most of the plasma characteristics during non-thermal plasma treatments. Drastic mutual influence of plasma jet and targets has been shown to induce critical modifications of: reactive species balance and densities, current amplitude, temperature, gas flow features when comparing with the situation of the so called “free jet expansion” in ambient air. This strong interplay between plasma and targets has to be considered before (gas flow impingement before plasma ignition) and during plasma delivery as a dynamic feature. Both plasma and targets may indeed encounter various continuous evolutions during plasma treatment such as: plasma source feed gas purity, plasma kinetics, target humidity, target electrical conductivity, thermal load, on target charge deposition, cell microenvironment modulation (oxygen level, plasma induced permeabilization) … When translating results obtained during in vitro or preliminary skin sample experiments to clinical situation, one has also to account for the critical role of plasma nozzle to surface gap variation and of the skin specificity of individuals.
The first objective of our work is to try to achieve a safe, reproducible and individual-independent plasma delivery on human skin. This approach includes first the implementation of, as simple and user friendly as possible, diagnostics tools providing signals likely to be correlated with the plasma jet source operating parameters (voltage, repetition rate, gas distance). This requires to select the most sensitive in situ signals captured by diagnostics tools and then try to reach a "real time" modulation and loop controlled operation of the plasma source. This first task represents a prerequisite for the development of a safe and reliable plasma device likely to offer new opportunity for anti-aging issues or skin treatments in cosmetics or dermatology applications. This work is supported by the research project PlasmaCosm-ARD 2020 Cosmetosciences, Région Centre Val de Loire.

4:00 PM BM06.04.02
Ultrafast Laser Spectroscopy of Plasma Liquid Systems Stephan Reuter1, Benjamin Goldberg1, Yibin Zhang1, Arthur Dogariu1 and Richard Miles1,2; 1Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; 2Department of Aerospace Engineering, Texas A&M University, College Station, Texas, United States.

Non-thermal atmospheric pressure plasmas provide high reactivity at low gas temperatures, ideally suited for sensitive surface treatment. Recent studies have, for example, demonstrated that plasma jets in clinical use provide great potential for novel chronic wound therapies and cancer treatment. Plasma generates reactive oxygen and nitrogen species triggering biological responses that initiate healing processes. In order to target plasma-based therapy to a specific medical application, control over the plasma generated reactive oxygen and nitrogen species composition is required. First concepts in tailoring plasma reactivity for targeted therapies show exciting results. Controlling plasma requires in-depth knowledge of its parameters. Especially atmospheric pressure plasma jets pose a challenge to the diagnostics of reactive species and reaction processes due to small dimensions and high gradients in space and time. As mediator for the plasma interaction effect, liquid interfaces frequently play a major role. In plasma liquid systems, these liquid interfaces need to be taken into account for diagnostic studies. Methods based on laser spectroscopy have proven invaluable to study species generation and transport in atmospheric pressure plasmas. Our work focuses on the diagnostics of accurate flow profile measurements and determination of the electric field initiated by the ionization wave of plasma jets. The use of ultrafast lasers allows for a high time resolution together with space resolved measurements. Electric field induced second harmonic light generation (E-FISH) for electric field measurements and femtosecond laser electronic excitation tagging (FLEET) for flow profile measurements are presented for plasma jets that can be used in plasma liquid interaction: Plasma reaction kinetics is governed by the electron energy distribution function of the discharge, which can be controlled by the supplied electric field. We present 1D-electric field measurements, to study the electric field. To study the flow field of the plasma jet, we employ FLEET, which permits unseeded velocimetry in gas flows containing nitrogen and argon. A strongly focused femtosecond laser excites and ionizes nitrogen, which subsequently dissociates via electron ion recombination. Subsequent nitrogen recombination forms excited nitrogen species that can be tracked for flow field studies. Knowing electric field and gas flow development is of paramount importance for plasma tailoring. Single shot measurements allow to detect stochastic processes. The high resolution in space and time given by the described measurement techniques and the active probing by laser radiation advance insight into the reaction dynamics of plasma liquid systems.

SR acknowledges funding by Princeton University and the Alexander von Humboldt Foundation, YZ acknowledges funding through the Science and Engineering Graduate (NDSEG) Fellowship, 32 CFR 168a.

4:30 PM BM06.04.03
Emission Propagation in Low Energy Atmospheric Pressure Plasma Jet Hiromasa Yamada1,2, Tetsuji Shimizu1,3, Masanori Fujiwara1, Susumu Kato1, Jeoho Kim1, Sarae Ikehara2, Yuzuru Ikehara1,4, and Hajime Sakakita1,3; 1Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 2Nagano College, National Institute of Technology, Nagano, Japan; 3Graduate School of Medicine, Chiba University, Chiba, Japan; 4Biotechnology Research Institute for Drug Discovery, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Abstract
Atmospheric pressure plasma jet (APPJ) is attracting attention in many research fields such as biology and medicine. Low energy atmospheric pressure plasma (LEAPP) equipment specially designed by Sakakita et al. [1] is one of the APPJ. Stop bleeding accompanied with blood coagulation without thermal damage using the LEAPP has been confirmed as an attractive surgical procedure necessary for minimally invasive surgery [2]. To control the interactions between the plasma and treated targets such as blood, it is necessary to understand the plasma’s behavior. We have already reported several characteristics of the APPJ, such as dynamic gas-flow behavior [3], gas temperature [4], spatial distribution of reactive species [5], electrical characterization [6], and emission propagation phenomena [7]. In the emission propagation phenomena, a bullet-like emission [9] and a spatially continuous emission [10] were observed depending on the treated target conditions [8]. Moreover, striations have been also observed in the LEAPP [7, 8]. In this study, the characteristics of the emission propagation in the LEAPP under several experimental conditions were analyzed using a high-speed camera. All the observations were synchronized with the measurement of electrical characteristics such as the applied voltage, current and power consumption. As working gases, helium, argon, and neon gases were used. For the target, a copper plate was used and the emission propagation was measured with and without the target. In case with the target, the distance between the nozzle exit of the LEAPP equipment and target surface were changed. Furthermore, an optical emission spectroscopy (OES) was applied in order to identify the reactive species in the plasma. The experimental results are summarized and at the symposium, we discuss the mechanism of emission propagation associated with the characteristics of plasma such as electrical property and optical emission.

Acknowledgments
This study was financially supported by Grants-in-Aid for Scientific Research on Priority Area (24108006) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

4:45 PM BM06.04.04
Potential Formation on Insulator Film by Atmospheric Pressure Plasma Jet Tetsuji Shimizu1, Kazuya Kikunaga2 and Hajime Sakakita1; 1Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 2Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology, Tosu, Japan.

Biomedical applications using cold atmospheric plasmas (CAPs) have been studied extensively. At the beginning of this new field, sterilization and wound care were the main applications using CAPs because the plasma can supply reactive species similar to what the immune system produces. For sterilization,
CAPs can inactivate bacteria including antibiotics-resistant strains, fungi, and viruses in tens of seconds to minutes. Within a few years, biomedical applications by CAPs expanded to include cancer therapy, gene transfection, activation of cell functions, blood coagulation, and regenerative medicine. From CAPs, there are several agents reacting with targets such as reactive oxygen and nitrogen species, charged particles, UV photons, heat, and electric field. So far, the biomedically effects driven by CAPs have been discussed mainly in terms of reactive species. However, the charged particles can also play an important role in the biomedically effects because they can also initiate chemical reactions. Moreover, the accumulation of charge on the target can influence the production of CAPs and the transport of reactive species. In addition, the developed electric field by the accumulated charge themselves can cause a biomedically effect. In order to understand the behavior of the charged particles, we aim to investigate a potential formation on an insulator film by the CAP treatment in this presentation.

The used CAP device was an atmospheric pressure plasma jet specially designed for blood coagulation. This device has a dielectric barrier discharge plasma source driven by an AC high voltage power supply with low energy consumption. The frequency of the applied voltage was ca. 62 kHz, and the peak-to-peak voltage was 5–6 kV with sinusoidal waveform. As the working gas, helium, argon or those admixtures was used in order to control the distribution of ions species. A plasma flare was ejected from a quartz tube of 1.4 mm in inner diameter and the insulator film was exposed to the plasma flare. The surface potential distribution on the insulator film was observed by using a static electricity scanner system which can measure an area of 30 x 30 mm² at a spatial resolution of 1 mm within 3 s by scanning an object surface along a vibrating linear array sensor. This method allowed us to measure the potential distribution in a non-contact manner. For the plasma treatment, the insulator films were treated by the CAP for a certain period of time and the potential distribution was measured immediately after the plasma exposure. In the presentation, we discuss the potential profile developed by the CAP treatment and the charging mechanism by the charged particles from the CAP.

**References**

NO$_2^-$ and NO$_3^-$ as long-lived reactive species as well as ClO$_2^-$ and ClO$. The reason for focusing on ClO$_2^-$ and ClO$^-$ is that KCl is contained in the buffer solution (100 mm KCl, 25 mm HEPES, pH 7.4 (NaOH)). DOPC (dioleoylphosphatidylcholine) and RB-DOPC (rhodamine B dioleoylphosphatidyl-ethanolamine) were used as a lipid and fluorescent dye-labeled lipid, respectively, and SLB consisted of them. SLB was prepared in a buffer solution (pH 7.4) by the vesicle fusion method, and introduced into a DBD-plasma irradiator [1], which was settled in a glove box and filled with He. We applied AC high voltage at 15 kV for the DBD-plasma irradiation of DOPC-SLB with the electric energy in the range of 28 – 148 kJ/cm$^2$, which was standardized by electrode area. We observed the morphology of DOPC-SLB using an epi-fluorescence microscope (epi-FM) and atomic force microscope (AFM) [1].

Pack tests (RIKEN, Japan) were used for the measurement of H$_2$O$_2$, O$_2^-$, NO$_2^-$, NO$_3^-$, ClO$_2^-$ and ClO$^-$. In the liquid phase, O$_3$-3F (Kasahara Chemical Instruments Corp., Japan) was used for measurement of O$_3$ in liquid phase.

Measurement of the concentration of long-lived reactive species generated by the plasma showed that the main long-lived reactive species generated in this experimental system are H$_2$O$_2$, NO$_2^-$ and NO$_3^-$. These reactive species concentrations increased with increasing the electric power. We predicted that when DOPC reacted with these reactive species, the concentration in the suspension was lower than that in the buffer solution. However, concentrations of H$_2$O$_2$, NO$_2^-$ and NO$_3^-$ were higher when DOPC vesicle was exist. Therefore, it is suggested that these reactive species may not react with DOPC. From the above, it is considered that lipid oxidation causing pore formation in SLB is induced by short-lived active species.

References

BM06.05.03
Hemolysis and Coagulation by Plasma Treatment Kenji Miyamoto1, 3, 2, Sanae Ikehara2, 3, Hajime Sakakita4, 2, Tetsuji Shimizu2, Nobuyoshi Takeuchi2, Ken Wakaizumi and Yuzuru Ikehara2, 3, 4; 1Graduate School of Engineering, Yokohama National University, Yokohama, Japan; 2Graduate School of Medicine, Chiba University, Chiba, Japan; 3Biotechnology Research Institute for Drug Discovery, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 4Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

We are integrating the plasma technology of low-temperature at atmospheric pressure into the medical sciences through the development of hemostatic equipment.

The first report on blood coagulation using LTP was from Drexel University, which exclusively highlighted the effects on the natural blood coagulation process but for hemolysis or serum protein aggregation. On the other hand, we have focused on the plasma effects on hemolysis to form coagulation from red blood cells and on aggregation of serum proteins that were not involved in natural blood coagulation system [1]. It was the volume of erythrocytes and concentration of albumin that are much higher than platelets and fibrinogen. In our previous studies, we have observed and maximized the plasma effect that alters them to cellular and molecular “glue” in clot formation using the instrument to produce a plasma with a dielectric barrier discharge (66 kHz), sinusoidal peak-to-peak voltage of 6.0 kV applied to an electrode [1, 2].

In this study using the above setting, we monitored the clot formation, the input voltage onto the plasma generator, the gas flow rate, and the value of the current flowing through the conductor A by measuring system connected to the toroidal coil (Rogowski coil). The formed aggregations in serum proteins solutions (albumin and Immune globulins) and RBC solutions were analyzed by either histological, ultrastructural or protein biochemical methods [3].

Moreover, the threshold for hemolysis was much higher than for aggregation of albumin and hemoglobin [4]. RBC clot formation didn’t occur without exceeding a current limit for hemolysis [4]. Furthermore, the conductivity of the sample tray correlates with more active hemolysis. From the viewpoint of plasma physics and pathology, these findings that “electric current’s contribution to hemolysis” accelerates blood coagulation help to develop more effective hemostatic equipment by applying these results [1].

(MEXT/KSPS KAKENHI Grant Number 24108006, JSPS08413).

References

BM06.05.04
International Standardization of a Low Energy Ionized Gas Haemostasis Equipment Hajime Sakakita1, 2 and Yuzuru Ikehara1, 2; 1National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan; 2Chiba University, Chiba, Japan.

In the surgical procedure, surgeons conventionally control bleeding by cauterization, clipping, or ligation, depending on the types of blood vessel. Even in the bleeding case from capillaries and small vessels, cauterization has been used. Medical devices such as high-frequency electrical coagulator, ultrasonic wave equipment, laser, and high-temperature plasma induce cauterization, and produce smoke by the heat which is sometimes difficult to ensure the visual field during the operation. Moreover, cauterization causes prolonged postoperative disorder and scar tissue formation in the abdominal cavity. The scarring tissues are characterized as proliferation of fibroblast and blood vessels, so called as granulation tissue, which limits the performance of 2nd surgery. As a disorder caused by the digestive surgical operation, it is difficult to treat the subacute disorder by opioids [1]. Therefore, minimally invasive method to stop bleeding in capillaries is desired. It was reported that low temperature plasma treatment can reduce invasiveness under hemostasis, and risk of postoperative disorders [2,3]. Many of bleeding devices are already defined by international standards such as IEC 60601-2-2, 2016. Particular requirements for high frequency surgical equipment, but not for low temperature plasma. International standards on the basic performance and safety of medical plasma equipment for blood coagulation will accelerate and extend the usage of medical plasma equipment. To apply the plasma effectively, safety and reproducibly, it is necessary to certify the correlation between the plasma components and biological effects. To ensure the safety of medical plasma equipment, specifications such as current must be measured and evaluated. Recently (2018/4/10), IEC 60601-2-76: 2018, Particular requirements for the basic safety and essential performance of low energy ionized gas haemostasis equipment was published. In the meeting, detailed contents of this standard will be presented.

We thank to Profs. Y. Seto, N. Shimizu, M. Ichinose, T. Kaneko, Dr. K. Kurihara, Dr. T. Niwa, Prof. S. Hamaguchi, Mr. O. Shimoda, Mr. M. Hamanishi and Y. Seto. This study was financially supported by Strategic International Standardization Acceleration Projects, and R&D Guideline from the Ministry of Economy, Trade and Industry of Japan, and in part by Grants-in-Aid for Scientific Research on Priority Area (24108006) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Atmospheric-pressure plasma jets (APPJs) have recently attracted much interest not only for biomedical applications [1] but also for plasma physics [2]. One of the most interesting phenomena in APPJs is bullet propagation [3], which has been observed in experiments and analyzed by computer simulations [2,4]. Another is a striation phenomenon which widely appears in discharges [5]. A stratified emission was observed and analysed in a positive column of a neon gas discharge [6]. The striations between a nozzle exit and a conductive target plate were observed in neon plasma ejected from low-energy atmospheric-pressure plasma device [7]. It is not clear, however, how the bounded plasma is sustained in APPJs. Especially, the role of the excited state (metastable) are not clear even though it is believed to be an important role [8]. In order to elucidate the sustaining mechanism of striations of APPJs, optical emission or laser absorption spectroscopy are used [9].

In this paper, we proposed a simple kinetic model to analyse the optical emission from the atmospheric-pressure neon. The kinetic model includes only noble gas atom, metastable, some excited states, ion, dimer, dimer ion and electron reactions. The most of the optical emission consists of the transition from excited Ne(2p3p3p) states to Ne(2p3s). The Ne(2p3p) is dominantly generated by both the electron collisional excitation of metastable and ground state and the dissociative recombination of ion dimer [10]. In the atmospheric pressure, the collisional deactivation of the Ne(2p3p) become significant and comparable to the radiative decay [11]. The spectrum strongly depend on the plasma deactivation.

References


BM06.05.06


Agricultural applications using nonthermal atmospheric pressure plasmas have attracted much attention not only from plasma researchers but also from biologists. So far, we have found that seeds irradiated by a scalable dielectric barrier discharge (DBD) plasma show growth enhancement of the plants [1]. Three minutes plasma irradiation to Arabidopsis thaliana seeds shows 11% harvest time reduction and 56% crop yield enhancement [2]. The growth enhancement of plasma-irradiated plants is probably caused by eustress response. However, the details of the molecular mechanism involved in plasma-induced signal initiation and response regulation are unknown. Here we have evaluated the amount of reactive oxygen nitrogen species (RONSs) absorbed by seeds as a first step to understand the response regulation. First, we studied the relationship between growth of radish sprouts (Raphanus sativus L.) and a number density of seeds during the plasma irradiation using the scalable DBD device [2,3]. We arranged the seeds within 20x20 mm2 at the center of the electrodes at 3 mm below the electrodes. After 180 s plasma irradiation, 30 seeds for each number density were cultivated under dark condition for 3 days. We obtained seed number dependence of the averaged length of radish. While the growth is suppressed for the seed number of 3 and 5, the growth is enhanced for the seed number of 10, 15 and 30. The plant growth for 30 seeds is slightly less than that for 15 seeds. The results suggest that the dose of RONSs depends on the number of seeds, leading to the plant growth suppression and enhancement. We also measured the electron spin resonance (ESR) spectra of seeds to detect the radicals in seeds [4]. The signal intensity of radicals correlated with the biochemical compounds in seeds is increased by the plasma irradiation. Comparative study of the effects of seeds density using the ESR measurements will reveal RONS transport and absorption mechanism in seeds.

This work was partly supported by JSPS KAKENHI JP16H03895 and JAXA.

References


BM06.05.07

Porous Superstructural Raman Nanosensors for Ultrasensitive Biochemical Detection and Electrically Controlled Molecule Release Jianhe Guo1, Jing Liu1, 2 and Donglei (Emma) Fan3, 4; 1Materials Science and Engineering, The University of Texas at Austin, Austin, Texas, United States; 2Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, China; 3Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States.

It is highly desirable, while extremely difficult to actively control the release dynamics of molecules from nanoparticle-carriers and to monitor the release process in real time. In this work, we report the design, fabrication, and manipulation of a superstructural Raman nanosensor, offering integrated dual functions in ultra-sensitive biodetection and dynamic control in molecule release. The device has a designed porous superstructure, consisting of gold (Au) nanorod cores and silica shells embedded with arrays of nanocavities arranged in concentric layers in three-dimensions (3D), where high-density plasmonic silver (Ag) nanoparticles are grown both in the nanocavities and on the outer surfaces. The Ag nanoparticles provide substantially enhanced Raman sensitivity for detection of molecules, owing to the large number of hotspots, as well as the near-field coupling of Ag nanoparticles due to their 3D concentric arrangement. Furthermore, by controlling the external electric field, the release of molecules can be facilely controlled at tunable rates owing to the induced electrokinetics at the junctions of Ag nanoparticles. Finally, the biosensing-release-unibody devices can be readily motorized, including
transport and rotation, which opens new opportunities for single-cell bioresearch and precision medicine.

BM06.05.08
Preparation and Evaluation of Radiopaque and Biodegradable Microbeads Based on Lipiodol and Polycaprolactone for Transarterial Chemoembolization Yutaka Okamoto1, Kenta Hitoh1, Terumitsu Hasebe1–2, Shunto Maegawa1, Kosuke Tomita1, Tomohiro Matsumoto2, 1 and Atsushi Hotta1. 1Keio University, Yokohama-shi, Japan; 2Tokai University, Hochojo, Japan.

Surface modification by the molecular grafting of a biocompatible polymer on biomaterials is an attractive technique in several fields such as tissue engineering and drug delivery. Especially, the air-plasma treatment can readily modify a polymer surface under atmospheric pressure at low cost without using inactive gas and vacuum chambers. Using the air-plasma treatment, we modified the surface of the gel composed of an oil and a polymer, from which new drug-eluting beads (DEB) were made for transarterial chemoembolization (TACE). TACE is generally applied to liver cancer by embolizing arteries feeding tumors with DEB under fluoroscopy. During the embolization of the arteries, DEB are injected into the targeted tissue using a catheter. However, since the conventional DEB are not radiopaque in themselves, it is difficult to control an influx of the DEB in a blood vessel. An unintentional reflux into non-targeted blood vessels would end up in complicating diseases. Furthermore, since the conventional DEB are not biodegradable, problems would persist and become more serious.

Here, we focused on Lipiodol and polycaprolactone (PCL) to fabricate Lipiodol/PCL beads as new DEB. Lipiodol is an oil-based contrast agent, and PCL is one of the biomaterials actively studied owing to its excellent biocompatibility and biodegradability. However, Lipiodol/PCL beads agglutinate in water-soluble disperse media, which makes it hard to handle because of the hydrophobicity. Therefore, the air-plasma treatment was applied in order to graft gelatin molecules on the surface of the beads since gelatin is hydrophilic and biocompatible to prevent the beads’ aggregation. The surface chemistry was characterized using the X-ray photoelectron spectroscopy (XPS), and the gelatin existence was confirmed by observing the N1s peak derived from gelatin molecules. In order to evaluate the biodegradability, the beads were immersed in phosphate-buffered physiological saline (PBS) or 1 mg/mL of lipase/PBS solution at 37°C before and after the surface modification with gelatin. Furthermore, as angiography was performed with the soluble contrast agent, the beads were injected into a hepatic artery of a healthy rabbit through a catheter, after which CT scanning was performed. Our results indicate that the degradation of Lipiodol/PCL beads was promoted by lipase, and that the gelatin molecules grafted on the surface of the beads did not prevent the degradation. In addition, the surface-modified beads were successfully dispersed in soluble media. The embolization of the hepatic artery of the rabbit could be assessed by angiography, and the location of the beads in the rabbit could be recognized through the CT scan. Therefore, the Lipiodol/PCL beads were found to be a promising candidate for new DEB, and the success of the surface modification using air plasma on the beads indicated that the procedure was highly useful for the surface modification of the oil and polymer mixtures.

BM06.05.09
Enhanced Gas Sensing Performance by In2O3 Nanostructures Functionalized with Conducting Polymers Wang Wei Chien, Kuan-Wei Chen, Yu-Shan Hsu, Ying-Hao Pai and Chun-Hua Chen, National Chiao Tung University, Hsinchu, Taiwan.

A number of studies have demonstrated a strong correlation between exhaled breath components and specific diseases. Accurate detection of specific volatile organic compounds (VOCs) can thus provide essential information for screening and diagnostic tests. For instance, the acetone concentration in exhaled breath of diabetes is much higher than that of healthy people (below than 1.1 ppm) and the CO concentration of people who smoke a pack of cigarettes per day is ~20 ppm where a nonsmoker is only less than 8 ppm. In this work, we have successfully synthesized a series of conducting polymer functionalized In2O3 nanostructures for sensing low-concentration VOCs. To achieve the required sensing performance, a series of conducting polymers functionalized In2O3 nanostructures with a high surface-to-volume ratio and porosity were successfully synthesized through hydrolysis of InCl3 in NaBH4 aqueous solution at room temperature with the subsequent heat treatments. It was found that the novel organic-inorganic heterogeneous nanocomposites exhibit a high sensitivity and an excellent selectivity for specific VOCs, which evidently originated from the essential role of organic functional groups of the conducting polymer.

BM06.05.10
Accurate Point-of-Care Diagnosis of AIDS Based on Label-Free One-Step-Immunoassay Young-Eun Jang, Jounghyeok Kwon, Boram Lee, Ok Jeong Moon and Jeewon Lee; Chemical and Bioengineering, Korea University, Seoul, Korea (the Republic of).

We developed an accurate, rapid, simple, and label-free assay method for point-of-care diagnosis of AIDS, which quickly produces strong optical signals through one-step-immunoassay. The HIV proteins, gp41, p24, and/or gp120 were used as the probes to detect anti-HIV antibodies in AIDS patient sera. In particular, gp41 and p24 were genetically presented on the surface of engineered protein nanoparticles to prepare sensitive 3-dimensional (3D) probes. The 3D probes also present multi-copies of hexa-histidine peptide (His6) on their surface to chemisorb gold ions (Au3+), which is essential to producing strong optical signals. Point-of-care diagnostic performance of the developed one-step-immunoassay was compared with that of conventional lateral flow assay (LFA) using 30 AIDS patient sera. The sensitivity of LFA was only 63% when a single antigen (gp41) was used but enhanced to 90% when three different antigens (gp41, p24, and gp120) were used together as the assay probes. On the contrary, the one-step-immunoassay using gp41 only produced strong optical signals within 15 min without causing any false negative/positive signals, showing 100% sensitivity and 100% specificity. This technically advanced immunoassay method holds a promising potential as a clinical point-of-care diagnosis of AIDS.

BM06.05.12
Novel Nanoparticles as a Contrast Agent for In Vivo Computed Tomography Imaging for Vascular Inflammation Sun-Mi Lee and Kyung-Hwa Yoo; Yonsei Univ, Seoul, Korea (the Republic of).

Bismuth nanoparticle (Bi NPs) and gold nanoparticles (Au NPs) are a potential x-ray computed tomography (CT) contrast agent. We have designed multifunctional hybrid nanoparticles of targeting vascular cell adhesion molecule 1 (VCAM-1), which is up-regulated in numerous inflammatory processes in atherosclerosis. Early diagnosis of high-risk plaques using nanoparticles as CT contrasts may be useful for preventing ischemic events. One major hurdle in detecting high-risk atherosclerotic plaques in coronary arteries is the lack of an imaging modality that allows for the identification of atherosclerotic plaque composition with high spatial and temporal resolutions. Here we show that VCAM-1 in atherosclerotic plaques of ApoE−/− mice can be detected with a clinical CT scanner after the intravenous injection of a contrast agent. These novel VCAM-1 targeting Bi-Au nanoparticles may become an important adjunct to the clinical evaluation of coronary arteries with CT.

BM06.05.13
Immobilization of Antibacterial Monomer onto Dentin Substrate by Non-Thermal Atmospheric Plasma Qi Liu1, 2, Buling Wu1 and Yong Wang1. 1University of Missouri-Kansas City, Kansas City, Missouri, United States; 2Southern Medical University, Guangzhou, China.

The antibacterial effects of quaternary ammonium methacrylates (QAMs) included in adhesives are not sustainable due to their no/little interactions with
dentin substrate. In this first of its kind study, the use of non-thermal atmospheric plasma (NTAP) brush on immobilization of dimethylaminohexadecyl methacrylate (DMAHDM), a typical QAM, on dentin bonding substrate, and resulting antimicrobial activity against Streptococcus mutans were investigated. A bonding substrate with several-micron-decalcified layer was created from human dentin. DMAHDM was applied onto the demineralized layer with or without plasma exposure. SEM and FTIR spectroscopy were employed to verify immobilization/grafting of DMAHDM onto the substrate. Antimicrobial activity of the resulting substrate was assessed by using colony-forming unit (CFU) and confocal scanning laser microscopy. Effects of saliva pellicle treatment and aging process on the DMAHDM immobilized-substrate were also evaluated. The SEM and FTIR results demonstrated that plasma-treatment could induce DMAHDM immobilization onto dentin substrate, which was further verified via quantitative IR spectral analysis (i.e. 2925 cm⁻¹/1635 cm⁻¹, 1455 cm⁻¹/1635 cm⁻¹, DMAHDM/collagen ratios). Comparing with non-plasma-treated, the plasma-treated dentin bonding substrate, with CFU 4 log lower, exhibited much stronger inhibitory effects, which were minimally affected by saliva or aging. The DMAHDM-immobilized dentin substrate showed effective and sustained antibacterial characteristics.

In this proof-of-concept study, it was found that NTAP effectively induced immobilization of a quaternary ammonium methacrylate onto dentin bonding substrate within a clinically acceptable treatment time of 30s, generating an antibacterial surface with remarkable and long-lasting inhibitory function. Further investigations should be performed with respect to the NTAP/DMAHDM’s overall effect when incorporated into actual bonding procedures [1-2].

For example, by combining DMAHDM with a dental primer or adhesive, more systematic NTAP studies on antibacterial effects of dental restoration under clinically relevant settings are needed. It is expected that highly reactive particles from NTAP should also induce DMAHDM immobilization in presence of other monomers [1].

This work was supported by Research Grant R01-DE021431 from the National Institute of Dental and Craniofacial Research, National Institutes of Health, Bethesda, MD 20892, USA

References

BM06.05.14 Low-Energy Ion Dose Thresholds of DNA Double Strand Breaks P. Thopan1, 2 and L.D. Yu2, 3; 1Rajamangala University of Technology Isan, Khonkaen, Thailand; 2Chiang Mai University, Chiang Mai, Thailand; 3Thailand Center of Excellence in Physics, Chiang Mai, Thailand.

DNA double strands break (DSB) is the critical damage of DNA to induce cell mutation/cancer or death. Energetic ion irradiation of biological living systems can possibly result in DNA DSBs via both direct physical and indirect physical and biochemical interactions with DNA. To investigate the interactions separately for understanding the fundamental mechanisms, we focused our study in the direct interaction between ions and DNA. In this model study, we used ultra-low-energy ions generated and extracted from a plasma source and then decelerated for uniformly low ion energy which could be as low as a few eV/amu to bombard naked dry DNA so that physical and biochemical secondary effects could be avoided as much as possible. The plasma ion species used in the study included He, C, N and Ar, for He and Ar to investigate ion mass effect, for N to investigate ion activity effect when compared to He and Ar, and for C to investigate its effect in the medical application significance. The DNA used was plasmid pGFP which was a simple DNA model containing the green-fluorescence-protein character gene for easy detection of the DNA. The ion energy was ranged from 1000 eV down to 10 eV and the ion fluence was typically ranged in 1014 – 1016 ions/cm², and the dose could be converted from both energy and fluence. The DNA damage was observed using the gel electrophoresis which was operated after the ion bombardment of DNA. The electrophoresis could separate different DNA forms, including original supercoiled form, relaxed form which was normally caused by single strand breaks (SSBs) and linear form which was due to DSBs. We clearly observed that only under certain combinations of the ion energy and fluence which indicated a dose could DSBs start to occur. For He ions, the threshold was at the energy of 1,500 eV and the fluence of 2×1015 ions/cm², for Ar ion the threshold was at the energy of 1,000 eV and the fluence of 1×1015 ions/cm² or the energy of 750 eV and the fluence of 2×1015 ions/cm², for N ion the threshold was not found even at the energy as low as 26 eV and the fluence of 2×1015 ions/cm², indicating the threshold for the N ion case to be lower than this energy and fluence combination (which was already beyond the instrumental capability), and for C ion the threshold was at the energy of 50 eV and the fluence of 4×1015 ions/cm² or the energy of 100 eV and the fluence of 1×1015 ions/cm². The threshold was obviously dependent on the ion mass and activity, namely, the heavier the ion, the lower the threshold, and the more the ion activity, the lower the threshold. Why the DNA DSB has the threshold in such values is discussed in terms of the DNA double strand structure. There was a puzzle that the DSB dose threshold found here was considerably higher than the cell lethal dose. A discussion on the puzzle argued that our study implied cell death mostly caused by indirect interaction between radiation and cells.

BM06.05.15 Nanoscale Surface Engineering and Sterilization on Rice (Oryza sativa L.) Seed via Hybrid Nonthermal Discharge Plasma Siwapon Srisonphan; Department of Electrical Engineering, Kasetsart University, Bangkok, Thailand.

Well-controlled wettability and liquid spreading of seed surfaces can help achieve seedlings of better quality, especially in difficult-to-grow regions, including those affected by drought. Nonthermal (cold) atmospheric plasma (NAP) can provide the complex mixture of surface functionalities, leading to nanoscale surface modification and dramatically change in seed surface wettability. However, for coated biological objects, such as seeds, plasma interaction is not entirely understood. Herein, we employed atmospheric hybrid cold plasma (HCP) by combining the pulsed corona discharge plasma in conjunction with a dielectric barrier discharge (DBD) to elucidate how NAP fundamentally interacts with seed surfaces. Moreover, we applied HCP to inactivate microorganisms that commonly attach the rice (Oryza sativa L.) seed husk to elucidate seed surface modification and biological sterilization.

Overall results show that the HCP can provide NAP with low power consumption and high efficiency for surface activation. The cold plasma treatment modified the surface of the rice seeds, resulting in accelerated germination and enhanced water imbibition (WI). The HCP treatment completely inactivated pathogenic fungi and other microorganisms, enhancing the germination percentage and seedling quality without destroying the viable seed membrane. The SEM firmly indicate the nanoscale modification of the surface morphology and the decontamination of pathogen infestation. We also show that the modified surface was primarily attributed to the combined effects of physical ions-enhanced etching and chemical surface functionalization. The WI time of modified seeds is initially decreased as an exponential function of exposure time, and gradually reaching to the WI saturation time in which the absorption rate is constant. We explained such phenomena via electron-ions initiated impact ionization inducing the reactive species (RS) for surface functionalization.

Therefore, microcorona discharge on a single dielectric barrier provides a nonaggressive cold plasma that can be applied to organic materials without causing thermal and electrical damage, and open up new avenues for the NAP treatment for the surface sterilization and disinfection of organic and biological materials with large-scale compatibility.
Optical imaging is one of the most important techniques in biomedical studies. Recently, usage of near-infrared light has been extensively tried because of the higher transparency in biomaterials than the visible light. Single-walled carbon nanotubes (SWCNTs) are nanocarbon materials that show optical absorption and fluorescence in the near infrared (NIR) wavelength region. Especially, due to the bright fluorescence in NIR, SWCNTs have been expected as imaging probes.

In this talk, we first review the optical properties of SWCNTs and then show our recent results about the bio-application of oxygen-doped SWCNTs. Interestingly, covalent doping of the nanotube surface with a low concentration of oxygen atoms can create a new optically allowed defect state. Consequently, nanotube fluorescence is red-shifted and can be over 10 times brighter. Fluorescence vascular angiography and observation of the intestinal contractile activity of mice are demonstrated by using the produced oxygen-doped SWCNTs as infrared fluorescent labels and imaging agents. Further, the biodistribution analysis after the administration of the oxygen-doped SWCNTs in mice is also discussed by the resonance Raman spectroscopy and NIR fluorescence microscopy.

We obtained penetration depth for porcine tissues of fat, skin and muscle, and also obtained the increasing rate of local temperature at different tissue temperatures. These laser pulses were practically used as laser therapy in clinic treatment for recovering functions of muscle and cartilage from athletic injury.

Researchers have utilized infrared (IR) lasers as energy source for laser therapies for curing skin diseases and skin injuries with remarkable positive effects. Preliminary experiments also showed that high-intensity IR laser pulses could penetrate thick body tissues, resulting in remarkable effects for recovering from injuries in deep muscles and cartilage tissues. Yet for the deep-level IR laser therapies, it is not clear how much of the laser flux had penetrated the body tissues at certain depths, and which of the three major effects of laser irradiation, i.e., laser induced photo-chemical effect, photo-thermal effect and mechanical dragging effect, played the key role in the curing process. How to design a new applied device to measure the penetration effect about high-intensity infrared laser pulses through body tissues is our concern.

Here we developed sensitive micro-sized thin-film thermocouple (TFTC) arrays on freestanding SiN thin-film windows as sensors for laser flux and local temperature. These devices showed excellent linear response in output voltage to a laser flux of wavelength 325 - 1064 nm, and meanwhile indicated the local temperature at the laser spot. By using these devices we systematically measured the penetrating effect and thermal effect of near infrared, high-intensity Nd:YAG laser pulses passing through several kinds of thick porcine tissues. These laser pulses were practically used as laser therapy in clinic treatment for recovering functions of muscle and cartilage from athletic injury.

We obtained penetration depth for porcine tissues of fat, skin and muscle, and also obtained the increasing rate of local temperature at different tissue temperatures.
depth. Our results offered reliable references as the thresholds for maximum irradiation doses of IR laser in clinic treatments. The method also offered an alternative approach for measuring the flux and heat under laser irradiation. Therefore we think the novelty and technique presented in this work are valuable for the communities of medical applications of laser technology, health-care, sports biology and biophysics in tissues.

10:00 AM BREAK

SESSION BM06.07: Plasma Treatment toward Therapy and Pharmacology II
Session Chairs: Emilio Martines and Hiromasa Tanaka
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Liberty C

10:30 AM *BM06.07.01
Cold Atmospheric Pressure Plasma Treatment to Assist Bacterial Inactivation and Tooth Restoration in Endodontic Procedures Victorino Colombo1, Matteo Gherardi1, Romolo Laurita1, Emanuele Simoncelli1 and Riccardo Tonini2; 1Department of Industrial Engineering, Alma Mater Studiorum - Università di Bologna, Bologna, Italy; 2School of Dentistry, University of Brescia, Brescia, Italy.

In recent years, cold atmospheric plasma (CAP) - an ionized gas where the electronic temperature is much higher than the macroscopic plasma temperature - have raised great interest for the treatment of living tissue. A potential application of CAP is in the field of dentistry, where preliminary studies have demonstrated its potential use to improve osteointegration, dental instrument cleaning, adhesive polymerization, tooth bleaching, root canal disinfection and other purposes. The present study aims to investigate the use of an innovative and handheld DBD-jet plasma source, properly designed to be translated to the clinical environment and in a realistic endodontic procedure for the disinfection and restoration of root canals. Root canal disinfection experiments have been performed on tooth models and were designed to also address: i) the influence of the humidity of the root canal on the treatment efficacy ii) the possibility of employing plasma activated liquids with antibacterial properties as irrigants. On the side of endodontic restoration in the coronal region, the adhesive-dentin interface has been well recognized as the weaker area for dental composite resin restoration; the improvement, through the development of new materials and techniques, of its characteristic is essential to extend the longevity of dental restorations. To evaluate the enhancement of adhesive properties induced by CAP treatment of dentin, a push-out analysis is carried out on extracted teeth, where the shape of the root-canal has been standardized, using EDTA and phytic acid as etching reagents. Finally, the restoration of the apical region of root canal aims at avoiding a new bacterial colonization in the tooth apex. Filling materials such as gutta-percha, are generally used to completely seal the root apex, but they are characterized by low adhesive performances; thus, endodontic cements, known as sealers, are generally applied after their cytotoxicity to improve the adhesion with dentine. The present study investigates the enhancement of adhesion between these materials and apical dentine of ex-vivo teeth treated by a DBD-jet plasma source by means of pushout tests and confocal microscopy analysis. Although investigations on long-term stability of adherent monoblock to dentine surface and clinical studies are required, the present study supports the exploitability of cold plasma devices in real-life endodontic clinics.

V. Colombo et alii, “Cold Atmospheric Plasma (CAP) treatment to improve the bond strength of adhesive system in endodontic restoration,” Submitted to Dental Materials, 2018

11:00 AM *BM06.07.02
A Principle of Blood Coagulation Induced by Low-Temperature Plasma Treatment to Develop the Rational Medical Practices for Bleeding Control Yuuara Bekhari1,2*, Chiba University, Chiba, Japan; 1Biotecnology Research Institute for Drug Discovery, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 2Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

1. Introduction
The low-temperature plasma (LTP) technology at atmospheric pressure is being integrated into methodologies in the medical and biological sciences. Bleeding control using LTP was one of the applications to reduce the heat damages on hemostasis in surgery, based on the novel plasma effect to induce aggregation of soluble serum proteins. In my talk, I will introduce our concept of LTP use in hemostasis and illustrate our feature plan to integrate LTP technology into the biomedical manufacture.

2. Blood coagulation using LTP treatment
The first report on blood coagulation using LTP was from Drexel University, which highlighted the plasma effects on natural blood coagulation process, but for hemolysis or serum protein aggregation. On the other hand, we have focused on the plasma effects on hemolysis, and aggregation of albumin that was not involved in blood coagulation and the fibrogenesis system, because erythrocyte volume and albumin concentration are much higher than the amounts and levels of platelets and fibrinogen. To maximize the plasma effect that alters them to cellular and molecular “glue” in clot formation, we developed the instrument to produce plasma using a dielectric barrier discharge (66 kHz, sinusoidal peak-to-peak voltage of 6.0 kV applied to an electrode. In in vivo experiments, our plasma treatment succeeded to form clots solidly more than the naturally formed clot, and could generate aggregation on the solution that contained either albumin and immune globulins, resulting in the protein disc at 1-cm diameter with continuous contact with the plasma flare.

3. Significance in Medicine
A basic concept on the electronic surgical devices is to evaporate water components in tissue and to close bleeding points by shrinking the tissue, and the treatment using electronic surgical devices sometimes caused severe heat damage in parenchymal tissues. On the other hand, the LTP treatment is an innovative approach with minimal invasion because it can stop blood flow by sealing the bleeding point and creating a possibly favorable healing process. Moreover, the fundamental concept behind LTP hemostasis is to provide an essential method that can suppress excessive host inflammatory responses.

In other words, plasma treatment is a tissue-processing technology, insulating local inflammation to start the scar formation. Consequently, I believe that LTP will become a conventional processing technology in tissue and biomaterial engineering with the progression of plasma science. I hope that our results will serve as a stepping-stone for the advancement of plasma science.

Acknowledgments
I thank Dr. Sakakita for our collaborative research. I thank Dr. Sakakita for our collaborative research. Grant Numbers 24108006 and 15K08413 in MEXT/JSPS KAKENHI Grants-in-Aid for Scientific Research on Innovative Areas supported this study.
Investigations into plasma interaction with cysteine are currently limited to DBD1, COST-jet and kINPen3, and less directly via a DC plasma jet4. Remote modification of the beads by air plasma was useful to induce the mixture of oil and polymer. Confirmed that the beads were visible using the X-ray photoelectron spectroscopy (XPS), and the existence of gelatin was confirmed by the presence of the N1s peak coming from the gelatin. The surface modification by a biocompatible polymer such as PCL through molecular grafting on biomaterials is an attractive technique in tissue engineering. For the surface modification and the molecular activation for grafting, plasma treatments are widely used. It is expected that air-plasma treatment could easily modify polymer surface under atmosphere pressure at low cost without using reactive gases and vacuum chambers. Thus in this study, air-plasma treatment was studied to graft gelatin molecules on the bead surface, as gelatin is hydrophilic, biocompatible, and low cost, which may prevent the bead aggregation. Such Lipiodol/PCL beads may be applied to several parts in the drug-delivery system and the tissue engineering.

In this study the plasma induced interactions with cysteine are investigated using a remote RF plasma source containing He-H2O and isolated from atmospheric impurities in order to observe effects with a relatively simplified plasma chemistry. The liquid sample containing cysteine is located in the far effluent of the plasma source and the arrival species are predominantly H2O2 and OH. We also study the case of liquid exposure to the near effluent/afterglow region, where atmospheric gas impurities can be expected to influence the chemistry. This provides a reference to allow comparison with literature reports. We also present results using a droplet in plasma system whereby cysteine is passed through the plasma for ~100 μs and exposed to a high flux of electrons and OH as well as H2O2, H2O, etc. High rates of electron solvation and reduction reactions, similar to that found with radiolysis, has previously been demonstrated with this system. The corresponding modification of cysteine via each treatment method is analysed using FTIR and Raman spectroscopy. Differences in damage characteristics between individual methods and those previously published are detected and attributed to a change in the plasma induced chemistry. To aid the understanding of the plasma chemistry involved, buffer and radical scavenger solutions were also added. The droplet in plasma setup showed a significant increase in magnitude of cysteine modification in comparison to the other setups.


Preparation of a Radiopaque and Biodegradable Microbead Surface-Modified Using Air-Plasma Treatment for Transarterial Chemoembolization

Yutaka Okamoto1, Kenta Bito1, Terumitsu Hasebe1, 2, Shunto Maegawa1, Kosuke Tomita2, Tomohiro Matsumoto1, 2 and Atsushi Hotta1; 1Keio University, Yokohama-shi, Japan; 2Tokai University, Tokyo, Japan.

Drug-eluting beads (DEB), used as embolic agents for transarterial chemoembolization (TACE), are required to have radiopacity and biodegradability at the same time, to be visualized in a body under fluoroscopy and CT scanning, which should not lead to complicating disease. In this study, we fabricated radiopaque and biodegradable beads composed of Lipiodol (ethiodized oil) and polycaprolactone (PCL), a biocompatible and biodegradable polymer. However, since the Lipiodol/PCL beads were hydrophobic, they aggregated in water-soluble dispersive media, causing difficulty in handling. Therefore, the surface modification of the beads is necessary for the prevention of occlusion that is caused by the injected beads in catheters. The surface modification by a biocompatible polymer such as PCL through molecular grafting on biomaterials is an attractive technique in tissue engineering. For the surface modification and the molecular activation for grafting, plasma treatments are widely used. It is expected that air-plasma treatment could easily modify polymer surface under atmosphere pressure at low cost without using reactive gases and vacuum chambers. Thus in this study, air-plasma treatment was studied to graft gelatin molecules on the bead surface, as gelatin is hydrophilic, biocompatible, and low cost, which may prevent the bead aggregation. Such Lipiodol/PCL beads may be applied to several parts in the drug-delivery system and the tissue engineering. Lipiodol/PCL beads were first fabricated with a home-made microfluidic device. Then the beads were treated with air plasma to introduce -COOH groups on the surface, followed by the covalent grafting of gelatin molecules using carbodiimide as a coupling agent. The surface chemistry was characterized using the X-ray photoelectron spectroscopy (XPS), and the existence of gelatin was confirmed by the presence of the N1s peak coming from the gelatin molecules. The surface-modified beads were injected with water-soluble dispersive media into a hepatic artery of a rabbit, and the CT image of the liver confirmed that the beads were visible in vivo. Furthermore, the beads before and after the surface modification with gelatin molecules were immersed in phosphate-buffered physiological saline (PBS) or in 1 mg/ml of lipase/PBS solution at 37°C to analyze degradability by measuring the weight loss. It was found that the degradation of the beads was significantly promoted by lipase, and that the gelatin molecules grafted on the bead surface did not prevent the degradability. It was, therefore, concluded that the Lipiodol/PCL bead obtained in this study was a promising candidate for new DEB, and that the surface modification of the beads by air plasma was useful to induce the mixture of oil and polymer.

Preparation of a Radiopaque and Biodegradable Microbead Surface-Modified Using Air-Plasma Treatment for Transarterial Chemoembolization

Yutaka Okamoto1, Kenta Bito1, Terumitsu Hasebe1, 2, Shunto Maegawa1, Kosuke Tomita2, Tomohiro Matsumoto1, 2 and Atsushi Hotta1; 1Keio University, Yokohama-shi, Japan; 2Tokai University, Tokyo, Japan.

Drug-eluting beads (DEB), used as embolic agents for transarterial chemoembolization (TACE), are required to have radiopacity and biodegradability at the same time, to be visualized in a body under fluoroscopy and CT scanning, which should not lead to complicating disease. In this study, we fabricated radiopaque and biodegradable beads composed of Lipiodol (ethiodized oil) and polycaprolactone (PCL), a biocompatible and biodegradable polymer. However, since the Lipiodol/PCL beads were hydrophobic, they aggregated in water-soluble dispersive media, causing difficulty in handling. Therefore, the surface modification of the beads is necessary for the prevention of occlusion that is caused by the injected beads in catheters. The surface modification by a biocompatible polymer such as PCL through molecular grafting on biomaterials is an attractive technique in tissue engineering. For the surface modification and the molecular activation for grafting, plasma treatments are widely used. It is expected that air-plasma treatment could easily modify polymer surface under atmosphere pressure at low cost without using reactive gases and vacuum chambers. Thus in this study, air-plasma treatment was studied to graft gelatin molecules on the bead surface, as gelatin is hydrophilic, biocompatible, and low cost, which may prevent the bead aggregation. Such Lipiodol/PCL beads may be applied to several parts in the drug-delivery system and the tissue engineering. Lipiodol/PCL beads were first fabricated with a home-made microfluidic device. Then the beads were treated with air plasma to introduce -COOH groups on the surface, followed by the covalent grafting of gelatin molecules using carbodiimide as a coupling agent. The surface chemistry was characterized using the X-ray photoelectron spectroscopy (XPS), and the existence of gelatin was confirmed by the presence of the N1s peak coming from the gelatin molecules. The surface-modified beads were injected with water-soluble dispersive media into a hepatic artery of a rabbit, and the CT image of the liver confirmed that the beads were visible in vivo. Furthermore, the beads before and after the surface modification with gelatin molecules were immersed in phosphate-buffered physiological saline (PBS) or in 1 mg/ml of lipase/PBS solution at 37°C to analyze degradability by measuring the weight loss. It was found that the degradation of the beads was significantly promoted by lipase, and that the gelatin molecules grafted on the bead surface did not prevent the degradability. It was, therefore, concluded that the Lipiodol/PCL bead obtained in this study was a promising candidate for new DEB, and that the surface modification of the beads by air plasma was useful to induce the mixture of oil and polymer.
production of active species (e.g. O$_2$, NO, NO$_2$, and OH) in the gas and consequently the PAW properties can be controlled by the discharge regime and gas flow and liquid-flow parameters. Low power air corona discharge are dominated by O$_2$ production which enhanced the biocidal effects. In the higher power TS, dominant gaseous products are NO$_2$, that lead to significant NO$_2$ and NO$_3$ in the PAW and practically no O$_2$. Both discharges produce H$_2$O$_2$. The antibacterial action is then mainly due to the synergy of H$_2$O$_2$, NO$_2$ and acidic milieu (via ONOO$^-$ formation) and typically decays in time within several hours post plasma activation, depending on temperature and pH [1,2]. We use UV-VIS colorimetric and fluorescence methods for the analysis of RONS in the PAW.

PAW produced by TS air discharge has been tested for agriculture applications, such as enhanced plant growth (lettuce, radish, tomato, wheat) or seed germination rate. Testing various medical applications of PAW or plasma activated media in dentistry (periodontal biofilms, endodontics), wound disinfection, urinary tract infections, or cancer cells are under way.

In a similar concept, TS air discharge was successfully demonstrated to induce antimicrobial effects in fresh fruit juices to extend their shelf lifetime without thermal pasteurization and without reducing their composition and nutrition/vitamin qualities. Potential effects of cold plasma on chemical changes of pH, degradation of organic acids, polyphenols, sugars) and sensory juice properties (color, taste) were carefully tested and it was shown that the juice quality was not significantly affected.

This work was supported by Slovak Grant Agency VEGA 1/0419/18 and Slovak Research and Development Agency APVV-0134-12 and APVV-17-0382.


2:00 PM *BM06.08.02

Innovative Agricultural Productivity Improvement Using Atmospheric Pressure Plasmas Kazunori Koga and Masaharu Shiratani; Kyushu Univ, Fukuoka, Japan.

Seeking for low energy consumption and high productivity processes for biomass and harvest is an important topic on agriculture. The conventional improvement methods of the agricultural productivity are irrigation, fertilization, and crop protection. Atmospheric pressure nonthermal plasmas can contribute to such methods by various ways such as sterilization, fertilization, water treatment and purification, soil treatment, seed treatment, storage improvement, insecticide, pre-harvest treatment, and post-harvest treatment. Nonthermal atmospheric plasmas are attractive for agricultural applications because they provide a large amount of reactive oxygen species (ROSs) and reactive nitrogen species (RNSs) with a little thermal damage to plants, crops, and fruits [1-8]. So far, we developed a scalable dielectric barrier discharge (DBD) device [5]. Using the device, we found that plasma-irradiated seeds of Arabidopsis thaliana show 11% reduction in a first harvest period from sowing and 56% increase in seed yield [1]. Plasma irradiated seeds of Sorghum, which is a strong candidate of biomass plants to produce ethanol [9], show 74 % increase in the volume of the plant. The energy consumption of 4.7MJ/ha for plasma irradiation corresponds to only 0.14% of 3.3 GJ/ha for cultivation and harvesting. The energy gain by plasma irradiation is 43.2 GJ/ha, in other words, the energy leverage is a quite high value of 1x104. Thus, atmospheric pressure nonthermal plasma offers an innovative agricultural productivity enhancement method with a high impact on our society.

This work was partly supported by JSPS KAKENHI JP16H03895 and JAXA.


2:30 PM BM06.08.03

Optical Diagnostics of Atmospheric-Pressure Microwave-Excited Plasma Jets Jaeho Kim and Hajime Sakakita; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Non-equilibrium air plasmas at atmospheric pressure have been attracting special attentions for practical applications in various industrial fields including sterilization, decontamination, pollution control, surface materials processing, aerodynamics, high-speed combustion, microwave propagating, and lighting discharge control. Recently, their medical applications such as blood coagulation, bleeding control, and wound healing have been also reported [1-6]. Natural air is a mixture of gases including N$_2$, O$_2$, Ar, CO$_2$, H$_2$O, and so on. Air plasmas can provide molecular radicals such as OH, NO, CN, atomic radicals such as H, O, N, and other active species.

In this work, we have developed a minimalized microwave-exited plasma source using a 2.45 GHz magnetron source. The plasma source produces stable air plasma jets even at atmospheric-pressure. We have considered their materials processing applications as well as biological and medical applications. Optical diagnostics were carried to better understand the fundamental properties of the plasma jets for the applications using an optical emission spectroscopy. The kinds of air plasma-induced radicals were identified with a variety of operation conditions. Temperature properties of a plasma jet were also investigated by measuring rotational temperatures and vibrational temperatures of nitrogen molecules. In the conference, we will present these experimental results.


2:45 PM BREAK
SESSION BM07.01: Flexible, Stretchable Active/Passive Materials/Devices for Health Monitoring
Session Chairs: Sahika Inal, Christian B. Nielsen, Tsuyoshi Sekitani and Benjamin Tee
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Constitution B

8:00 AM BM07.01.01
Bioinspired Wet/Dry Adhesion for Bioelectronics
Changhyun Pang1, 2; 1School of Chemical Engineering, Sungkyunkwan University, Suwon-si, Korea (the Republic of); 2Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Korea (the Republic of).

Recently, extraordinary performances of natural creatures living in various conditions have been explored to understand their reversible dry/wet adhesion, including gecko feet, insect secretion, mosquito needles or endoparasitic worm’s proboscis, octopus suction cups, and slug’s footpad with viscous mucus. Extensive studies on the adhesive properties of such animal skins have revealed various multiscale architectures inducing various physical interactions. The attachment phenomena of various hierarchical architectures found in nature have extensively drawn attention for developing highly biocompatible adhesive on skin or wet inner organs without any chemical glue. Structural adhesive systems have become important to address the issues of human-machine interactions by smart outer/inner organ-attachable devices for diagnosis and therapy. Breakthroughs in flexible and conductive materials have accentuated the development of wearable or organ-attachable bioelectronics for stable biosignal monitoring and drug delivery. For such medical applications, the devices need to manifest conformal contact on human skin even under dynamic movements, as well as repeatable, long-term attachment without skin irritations or chemical contaminations. Here, we investigated an artificial reversible wet/dry adhesion systems biologically inspired by the suction cups of octopi and amphibian’s pad. Our biologically inspired architectures exhibit strong, reversible, highly repeatable adhesion to silicon wafers, glass, and rough skin surfaces under various conditions. Applying these bioinspired architectures to interfacial adhesive layers can attribute to developing skin-attachable or implantable bioelectronics for health diagnosis, controlled drug therapeutics, and achieving multifunctional integrated devices for ubiquitous-healthcare systems.

8:15 AM BM07.01.02
Nanocellulose Printed Circuit Boards for Human Monitoring
Jonathan Yuen1, Dan Zabetakis1, Lisa Shriver-Lake1, Md Qumrul Hasan2, David A. Stenger1, Scott A. Walper1 and Gymama Slaughter2; 1Naval Research Laboratory, Washington, District of Columbia, United States; 2Computer Science and Electrical Engineering, University of Maryland, Baltimore County, Baltimore, Maryland, United States.

Flexible and ultrathin substrates supporting microelectronic components have the potential to spur the development of pervasive healthcare and the internet of things by providing sensors and bioelectronics that can provide seamless and imperceivable integration. We will describe our ongoing work to develop sensing electronics on microns-thin bacterial nanocellulose for human monitoring applications. The porosity and hydrophobicity of nanocellulose sheets offer advantages that typical plastics cannot provide, such wicking of analytes and absorption of inks. We have developed a printing method to form nanocellulose printed circuit boards (PCBs), and created a simple low temperature soldering process to form circuit structures using standard surface-mount components on our nanocellulose PCBs. This has been used to create nanocellulose decals that measure human body temperature and perform pulse oximetry. We have also developed self-powered electronics for sensing of bioanlytes, such as glucose. For all applications, the fabrication processes are solution-based and requires only ambient processing, and therefore simple, potentially low-cost, and can be aimed for a wide range of applications.

8:30 AM BM07.01.03
Intrinsically Stretchable Polymer Semiconductors and Electronics as an Emerging Platform for Bioelectronics
Sihong Wang; Institute for Molecular
The vast amount of biological mysteries and biomedical challenges faced by human provide a prominent drive for seamlessly merging electronics with biological living systems (e.g. human bodies) to achieve long-term stable functions. Towards this trend, the main bottlenecks are the huge mechanical mismatch between the current form of rigid electronics and the soft biological tissues.

In this talk, I will first describe a new form of electronics with skin-like softness and stretchability, which is built upon a new class of intrinsically stretchable polymer materials and a new set of fabrication technology. As the core material basis, intrinsically stretchable polymer semiconductors have been developed through the physical engineering of polymer chain dynamics and crystallization based on the nanoconfinement effect. This fundamentally-new and universally-applicable methodology enables conjugated polymers to possess both high electrical-performance and extraordinary stretchability [1]. Then, proceeding towards building electronics with this new class of polymer materials, the first polymer-applicable fabrication platform has been designed for large-scale intrinsically stretchable transistor arrays. [2] As a whole, these renovations in the material basis and technology foundation have led to the realization of circuit-level functionalities for the processing of biological signals, with unprecedented mechanical deformability and skin-conformability. Equipping electronics with human-compatible form-factors has opened a new paradigm for wearable and implantable bio-electronic tools for biomedical studies, personal healthcare, medical diagnosis and therapeutics. [3]


BM07.01.06
Human Inspired Bio-Electronic Sensor Skins Benjamin C. Tee1, 2, 3; 1Materials Science and Engineering, National University of Singapore, Singapore, Singapore; 2Biomedical Institute for Global Health Research and Technology, National University of Singapore, Singapore, Singapore; 3Institute of Materials Research and Engineering, Agency for Science Technology and Research Singapore, Singapore, Singapore.

Human sensory organs such as the skin have evolved to have excellent sensing performance and ultra-robustness. Electronic versions of skin have witnessed tremendous interest and development over the last decade. Functional soft, flexible and stretchable materials are crucial to the continued evolution of skin-like sensor applications in emerging robotic systems, new human-machine interfaces and life-like prostheses.

Here, I will discuss our recent work in next generation technologies for bio-electronic skins using an integrated hybrid materials approach that synergizes the best qualities of organic and inorganic materials. For example, recent developments in self-healing polymeric systems have propelled the exciting notion that electronic systems can repair themselves when damaged. Bio-inspired digitization of analog signals have also enabled us to develop artificial mechanos-receptors that optically interfaces with neurons. These sensor and materials technologies would be extremely applicable in an increasingly advanced cybernetic and Artificial Intelligence (AI) robotics future.


BM07.01.05
Fully Printed All-Polymer Tattoo/Textile Electronics for Electromyography Eloise Bihar1, Timothee Robert2, Jozina De Graaf2, Mohamed Saadaoui3, Esma Ismailova4, George G. Malliaras4, Khaled Salama1 and Sahika Inal5; 1King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Aix Marseille Université, Marseille, France; 3École des Mines de Saint Etienne, Gardanne, France; 4University of Cambridge, Cambridge, United Kingdom.

Driven by the ever-growing needs for developing portable, easy-to-use, noninvasive diagnostic tools, biomedical sensors that can be integrated on textiles or even directly on human skin have come to fruition. Wearable sensor technologies that seamlessly interface electronics with human skin can be especially promising for detecting a wealth of biologically relevant signals ranging from neuro-muscular activity, to electrophysiology, even to metabolite profiles.

In this work, we present a simple and low cost platform fabricated on a tattoo paper used for on-skin electromyography (EMG) measurements. The electrodes comprising the conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) are directly inkjet-printed on the tattoo paper. Addressing the integration challenge common for stretchable electronic devices, we connect the tattoo electrodes to the acquisition system through a textile in the form of a wristband comprising of printed PEDOT:PSS contacts. While the textile wristband conforms around the “tattooed” skin, it enables a reliable contact with the electrodes beneath due to its conformability around the limb. We show that this tattoo/textile electronics system, which does not rely on gels or expensive metallic materials, is able to detect the biceps activity of the arm during muscle contraction for a period of seven hours, with comparable performance to conventional wet biopotential electrodes. Combining the tattoo electronics with the electronic system, which does not rely on gels or expensive metallic materials, is able to detect the biceps activity of the arm during muscle contraction for a period of seven hours, with comparable performance to conventional wet biopotential electrodes.

BM07.01.06
Fabrication of Fabric Biomedical Electrode Array with Printable Electronic Ink and Hot-Melt Film for Electromyography Seiichi Takamatsu and Toshihiro Itoh; The University of Tokyo, Kashiwa City, Japan.

We have developed fabric biomedical electrode array where silver paste, conductive polymer and ionic liquid gel are printed and insulation layers are formed with hot melt film on the fabric substrate. Recently, wearable electronic devices such as Microsoft Hololens, google glass, sportband, or other tools have been developed and commercialized for human healthcare monitoring and information tools. Among wearable electronic devices, wearable ECG or EMG electrodes are promising for human motion sensing tools. Especially for monitoring human hand or foot motion sensing, the biomedical electrode array which is made of fabric is necessary.

To make biomedical electrodes array, new fabrication process of fabric multilayer electrodes which consists of biomedical electrode parts to contact human skin and the wiring parts from biomedical electrodes parts to the amplifiers are required. Previous study (S. Takamatsu et al., "Direct patterning of organic conductors on knitted textiles for long-term electrocardiography," Scientific Reports, vol. 5, 15003(7pp), Oct 2015.) reports single layer fabric electrodes, but the multilayer electrodes has not been fabricated on the fabric and the biomedical electrode array has not been achieved. The most difficult fabrication
The developed fabrication process of fabric biomedical electrode array with printable electronic ink and hot-melt film for Electromyography is following and can combine several layers of functional fabric and films.

1. Patterned urethane film is attached on the knit fabric with hot melt film. 2. Laser cut hot melt film is placed on the electrode and heated. 3. The patterned urethane film is attached on the knit fabric with hot melt film. 4. Conductive polymer of PEDOT PSS and ionic liquid gel is patterned on another knit fabric for making biomedical electrode part. 5. Wiring part fabric and biomedical electrode fabric are attached by hot melt film and glue. By using our process, the 2x5 array biomedical electrode which has 1cm² biomedical electrodes parts and 0.5 mm wide wiring can be successfully fabricated. The impedance between electrodes and human skin is less than 1 MOhm, which is useful for EMG monitoring. Thus, our process will useful for wearable multi array of EMG measurement.

9:45 AM BM07.01.07
Sub-300 nm Thin-Film Au/Parylene Dry Electrodes for Motion Artifact-Less sEMG and sECG Monitoring Robert A. Nawrocki1, 2, 3, Hanbit Jin1, Sunghoon Lee1, Tomoyuki Yokota1, Masaki Sekino1 and Takao Someya1, 4; 1Univ of Tokyo, Tokyo, Japan; 2Purdue University, West Lafayette, Indiana, United States; 3Birck Nanotechnology Center, West Lafayette, Indiana, United States; 4Thin-Film Device Laboratory & Center for Emergent Matter Science (CEMS), Wako, Japan.

Accurate, imperceptible and long-term monitoring of vital biopotential signals promises to revolutionize healthcare industry by shifting from costly and uncomfortable hospital visits to in-home usage. Currently available wearable electronics are typically rigid with non-conformal skin contact resulting in poor data quality, necessitating the integration of such bioelectronics [1] directly onto the skin [2]. Increasing the conformity of the artificial electronic skin to the soft, irregular and stretchable human skin typically results in improved signal quality and user comfort [3].

We report on the fabrication of self-adhesive and conformable to highly irregular three-dimensional soft surfaces, sub-300 nm thin dry electrodes that produce biopotential (sEMG and sECG) recordings of excellent quality (SNR). The electrodes are based on thermally evaporated thin film (100 nm) of Au, sandwiched between two layers (100 nm each) of CVD-deposited biocompatible parylene (parylene/Au/parylene). They are fabricated on glass substrates, with fluorinated polymer (85 nm) and poly(vinyl alcohol) (PVA, 5 µm) sacrificial layers used for delamination and ease of handling. Parylene is etched away at the skin-interface side, allowing for direct Au contact with the skin. Following delamination, electrodes are placed on pre-stretched human skin and sprayed with H2O to remove PVA, forming a skin/Au/parylene structure. The skin is then dried and relaxed, with the ultra-thin film conforming to the skin grooves via van der Waals forces [4], without any additional adhesives.

These simple-to-fabricate and use, ultra-thin sensors show single-day electrical and mechanical stability of up to ten hours. Their bending stiffness was calculated to be comparable to stratum corneum, the uppermost layer of human skin, at ~0.33 pN/m², which is over two orders of magnitude lower than the bending stiffness of a 3.0 µm thick sensor. Compared with the thicker sensor, its impedance also decreased by almost two orders of magnitude. Laminated on a pre-stretched elastomer, the sensor forms wrinkles with a period of 17 µm and amplitude of 4 µm, agreeing with theoretical calculations.

In contrast to wet adhesive Ag/AgCl electrode, with skin vibrations of up to ~15 µm, the sensor demonstrates motion artifact-less sEMG monitoring. Additional impedance and sEMG measurements reveal that the decrease of impedance, as well as the motion artifact-less operation, is likely due to improved skin adhesion of the sub-300 nm thin sensor.

With compatible fabrication to our previously demonstrated sub-300 nm thin electronics [5], this demonstrates a path for integration of skin-laminated systems consisting of sensors and electronics.


10:00 AM BREAK

10:30 AM BM07.01.08
Multifunctional Silk Adhesive for Epidermal Electronics Ji-Won Seo, Hyojung Kim and Hyunjoo J. Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

In order to improve the signal accuracy and long-term monitoring of electronics on biological skin, it is essential to achieve a conformal and robustly adhered electronics/biological skin interface. Here, we suggest a biocompatible calcium (Ca)-modified silk adhesive for robust epidermal electronics on biological skin. At optimized weight ratio of silk:CaCl₂ of 70:30, the silk adhesive shows strong adhesion force (> 600 N/m) through enhanced mechanical interlocking at interface. The physical mechanism facilitates a high adhesion on various substrates and a reusability of silk adhesive. Moreover, a water-degradability of silk adhesive shows the easy detachment without any high external force. With the multifunctional characteristics such as reusability, biocompatibility, and water-degradability, we fabricate the practical epidermal electronics: strain sensor, touch sensor, and long-term drug delivery system to demonstrate the potential of the proposed silk adhesive.

10:45 AM BM07.01.09
Deformable Electronic Materials for Two-Way Communication with Biological Systems Darren J. Lipomi; University of California, San Diego, La Jolla, California, United States.

The goal of this project is to create a class of electronic materials that can measure signals and interface with the nervous system for two-way communication with biological systems. The project is exploring two classes of materials. (1) Metallic nanosilands on single-layer graphene for cellular electrophysiology and wearable sensors. We have used these materials to measure the forces produced by the contractions of cardiomyocytes using a piezoresistive mechanism. Separately, we have developed orthogonal methods of stimulating myoblast cells electrically while measuring the contractions optically (a modality we nicknamed as “piezoplasmic”). We have also used these sensors to measure the swallowing activity of head-and-neck cancer patients who have received radiation therapy and are at risk of dysphagia arising from fibrosis of the swallowing muscles. The combination of strain sensing, surface electromyography, and machine learning can be used to measure the degree of dysphagia. (2) We have developed ionically conductive
organogels for haptic feedback. Medical haptic technology has myriad potential applications, from robotic surgery and surgical training, to tactile therapy for premature infants and patients with neurological impairment.

**11:00 AM • BM07.01.10**

**UltraSoft, Bio-Compatible Electronic Systems for Neuroscience** Tsuboshi Sekitani, Osaka University, Osaka, Japan.

We present an implantable sheet-type flexible electronic sensor system for long-term simultaneous monitoring of an electrocorticogram (ECoG) from the brain surface and local field potential (LFP) from the deep brain. UltraSoft gel electrodes provide a minimally invasive interface consisting of highly conductive nano-conductive materials including Ag-based nanowires, thermoplastic polymers, and bio-compatible gels. The gel composite shows conductivity greater than 10,000 S/cm and can be stretched more than 100% without any reduction to its electrical and mechanical performance. Hence, it can be stretched across arbitrarily curved surfaces, including the ultra-soft brain surface.

By integrating ultraSoft gel electrodes, an ultraflexible amplifier, and a wireless Si-LSI platform with a thin-film battery, we intend to demonstrate the applications of long-term implantable wireless sheet sensors, including 64-channel sheet-type electric potential monitoring systems. This wireless system with soft gel electrodes can measure biological signals of less than 1 µV. Taking full advantage of this system, simultaneous signals from the cerebral cortex in the ECoG and LFP have been wirelessly measured in animal experiments including non-human primates for over a month. Long-term bio-compatibility, electrical performance, and mechanical stretchability and durability are discussed for the integration of nanomaterials and processes and wireless low-noise sheet-type systems.

This research is partially supported by the Brain Mapping by Integrated Neurotechnologies for Disease Studies (Brain/MINDS) from Japan Agency for Medical Research and development,AMED.

**11:30 AM BM07.01.11**

**Flexible Biosensors for Non-Invasive Medical Diagnostics** Agostino Romeo¹, Paul Eduardo David Soto Rodriguez², Ana Moya², ³, Gemma Gabriel², ³, Rosa Villa², ³, Rafael Artuch², ³ and Samuel Sanchez², ³, ¹Institute of Bioengineering of Catalonia, Barcelona, Barcelona, Spain; ²National Centre of Microelectronics - Microelectronics Institute of Barcelona, Barcelona, Barcelona, Spain; ³Research Networking Center in Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Barcelona, Spain; ⁴Instituto Carlos de Recerca i Estudis Avançats (ICREA), Barcelona, Spain; ⁵CIBER-ER (Biomedical Network Research Center for Rare Diseases), Instituto de Salud Carlos III, Madrid, Spain; ⁶Laboratory of Hereditary Metabolic Diseases, Hospital Sant Joan de Déu, Barcelona, Spain.

In the last few decades the quality of life has significantly improved due to the achievements of biomedical technology. Innovative healthcare solutions contributed to these advances by decreasing costs and making health assessment easier and more accessible. Versatile bioelectronic sensors targeted to health biomarkers and bioanalytes (metal ions, proteins, amino acids, glucose, lactate, etc.) can non-invasively monitor the health status of the user by analyzing external body fluids (sweat, saliva, tear fluid) alternative to blood.[1,2] On-demand biosensing is envisaged due to the versatility of sensing platforms that can adapt to specific needs in terms of target biomarkers and health issues to monitor. To this regard, several recognition systems, including antibodies, enzymes, and inorganic nanomaterials can be used to modify the sensors to achieve high selectivity towards target analytes. In this scenario, recent advances in microfabrication, sensor technologies and data transmission led to the developments of point-of-care (PoC) diagnostics.

Here we present few examples of biosensors for painless and on-demand self-assessment of health conditions. In particular, we describe a non-invasive electrochemical sensor for the non-enzymatic analysis of tear glucose.[3] Electrochemical sensing is chosen among other types of transduction because it is well suited for simple, rapid, and cost-effective personalized medicine devices. Electrodes are fabricated on soft and flexible materials using inkjet printing and then modified with CuO microparticles (CuO-µPs) to carry out non-enzymatic detection of glucose. This detection mechanism is based on the CuO-catalyzed electro-oxidation of glucose in alkaline environment, due to the electrochemical conversion of CuO into strong oxidizing Cu(II) species such as CuOOH or Cu(OH)₄⁻. Glucose detection is achieved by CA, with an excellent linearity observed in the 3–700 µM range, matching typical glucose levels in tears. A sensitivity of 850 µA mM⁻¹cm⁻² and a limit of detection (LOD) of 2.99 µM are calculated. This sensor shows good selectivity, reproducibility, and life-time, resulting in a reliable tool for painless and non-invasive self-assessment of diabetes, as confirmed by tests on tear samples.

Personalized and non-invasive sensing technologies allow to easily and frequently monitor the health status of an individual as often as needed. This helps make early-stage detection simpler and more convenient, thus enhancing the efficacy of therapeutic treatments. Rapid and cheap PoC diagnostics also allows improving the life style of patients, by interfering in low or negligible extent to their daily activities.

References

**11:45 AM BM07.01.12**

**Highly Durable, Ultrasensitive Nanoscale Crack Based Mechano-Sensor for Bio-Signal Monitoring Inspired by Spider’s Sensory Organs** Byeonghak Park¹, Daeshik Kang¹ and Tae-il Kim¹; ¹Sungkyunkwan Univ, Suwon, Korea (the Republic of); ²Ajou University, Suwon, Korea (the Republic of).

With increasing demand for the detection of delicate bio-signals for medical electronics, the Internet of Things (IoT), E-skin and flexible integrated circuit (IC) devices, an enhancement in sensitivity has become a major issue in flexible mechanosensors, however, overcoming the limited sensitivity remains problematic. Here, we introduce mechanosensors inspired by spiders having an ultrasensitivity, durability. For ultrasensitivity and durability, we considered the geometrical effects in cracks and self-healable polymers. By controlling crack depth by simple propagating process, the sensitivity of our sensor shows ~15,000 in 2% strain, which is the world best sensitivity value. Due to the high sensitivity, the signal-to-noise-ratio is 6 times higher than before, up to ~35 so that it can be used in sensing human voice clearly. Also, self-healable polymer helps to recover the crack gaps after 25,000 cycles. We introduce the possibility of semi-permanent uses over 1,000,000 cycles in our sensors. The spider inspired sensory system with high sensitivity and durability would provide versatile novel applications such as E-skins, devices for medical applications, and IoT applications etc.
1:30 PM *BM07.02.01/EP05.02.01
Interacting Ion and Electron Currents

Paul Meredith; Swansea University, Swansea, United Kingdom.

Ionic and electronic conduction mechanisms are underpinned by fundamentally different physics [1]. For example, ions diffuse through a conducting matrix via centre of mass transport that can be described by classical processes. Electrons and holes are quantum mechanical entities characterised by delocalisation, tunnelling or hopping. These fundamental differences impose radically different length-and-time-scales on ionic and electronic conduction – and generally speaking the solid-state physics of ions and electrons have remained two very different fields requiring different skill sets [2]. However, bioelectronics, where a central challenge is the transduction between ion and electron currents, is a scientific collision point between the two worlds.

In my talk I will summarise the major differences between ionic and electronic solid state electrical conduction. I will also describe methods that can probe the relevant time-and-length scales in order to identify and disentangle the native signatures of each carrier type [3, 4]. A number of model systems and devices will be exemplified that allow the study of ion and electron conduction processes, and indeed provide a means to test prototypical concepts in transduction and bioelectronic logic interfaces [5, 6].


2:00 PM BM07.02.02/EP05.02.02
The Device Physics of Organic Electrolytic Photocapacitors—From the Nanoscale to the Single Cell Level

Vedran Derek1, Marie Jakosova1, Tobias Cramer2, Marek Havlicek3, David Rand4, Yael Hanein5, Daniel Simon5, Magnus Berggren6, Fredrik Elinder4 and Erik D. Glowacki5; 1Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, Sweden; 2Department of Physics and Astronomy, Università di Bologna, Bologna, Italy; 3Department of Nanometrology and Technical Length, Czech Metrology Institute, Brno, Czechia; 4School of Electrical Engineering, Tel Aviv University, Ramat-Aviv, Tel-Aviv, Israel; 5Department of Clinical and Experimental Medicine, Linköping University, Linköping, Sweden.

We have recently developed the organic electrolytic photocapacitor (OEPC), a nanoscale optoelectronic device for eliciting action potentials in neurons. Herein, we cover in detail the physical mechanisms behind the charge generation and dynamics of charging and capacitive coupling in these devices using optoelectronic/electrochemical measurements combined with simulation and modeling. Electrochemical impedance measurements allow corroboration of these models, and reveal the nature of photocapacitive and photofaradaic effects in the devices. Using scanning probe microscopy techniques, we have evaluated the mechanical properties of the nanocrystalline films, finding relatively low Young’s moduli in the range of 500 MPa. In order to take a reductive approach compared with previous measurements of neurons and electrolytic tissues, we have validated the performance of OEPCs using nonexcitable cells, *xenopus laevis* oocytes. We find rapid membrane potential changes in the range of tens to hundreds of millivolts are induced by OEPC devices, showing extremely effective capacitive coupling and explaining previous findings of action potential generation. The overall result of our work is a fully physical and mechanistic understanding of this novel device platform, and a roadmap for guiding future development.

2:15 PM BM07.02.03/EP05.02.03
The Design of Air Stable, Redox Active Conjugated Polymers and Their Applications in Accumulation Mode OECTs

Alexander Giovannitti1, Reem Rashid2, Jenny Nelson1, Iain McCulloch1 and Jonathan Rivnay2; 1Imperial College London, London, United Kingdom; 2Northwestern University, Chicago, Illinois, United States.

Organic electrochemical transistors (OECTs) are receiving a great deal of attention due to the ability to efficiently transduce biological signals. The working principle of OECTs relies on the modulation of the conductivity of an organic semiconductor, which can be modified by applying a potential at the gate electrode and driving electrochemical redox reactions in aqueous solution (doping/de-doping of the organic semiconductor). OECTs can either be operated in accumulation [7] or depletion mode [8] where the operation in accumulation mode has the advantage of lowering the operational voltage and therefore improve the power consumption of the device (device is in an off state rather than an on state when no gate voltage is applied). Recently, high performing OECT materials have been reported based on electron rich alkoxybithiophene copolymers which show low oxidation potentials in aqueous electrolytes and enable OECT operation at low voltages [9]. However, one drawback of these easily oxidizable polymers is that the copolymers can become oxidized by reactions with oxygen from ambient air. This result in the formation of p-doped polymers and superoxide anions (O2−) where the latter is a reactive radical and might cause harm to biological systems or degrade the organic semiconductor. As a result of this oxidation reaction, a constant gate voltage would need to be applied to keep the material in its neutral state (and the device off).

We will present the development of an air-stable conjugated polymers based on donor-acceptor type copolymer. The copolymer shows reversible redox reaction at potentials below 0.3 V vs Ag/AgCl. When exposed to aqueous ambient conditions, the polymer does not become oxidized. Long-term stability tests were carried out where devices were exposed to ambient conditions for more than 6 months with no sign of degradation. The polymer shows a good stability when charged with up to one hole per repeat unit (polaron) with transconductances in the range of 80 S/cm (at -0.7 V). This work demonstrate the importance of chemical design strategies for the development of accumulation mode OECT materials to mitigate reactions with oxygen in aqueous electrolytes and ambient conditions.

This talk will give an overview about our recent activities on electronic and ionic conductivity in conjugated and redox polymer thin films with different molecular architectures. Preparation of films is done either by electropolymerization or solution deposition followed by morphology tuning, e.g. by solvent vapor annealing.[1]

We are particularly interested in three-dimensional architectures based on branched monomers such as terthiophenes (3T) or triphenylamines (TPA). TPA redox moieties are useful to allow for electrochemical or chemical crosslinking of as-deposited films. Both, with TPA redox polymers[2] and with polymers which bear TPA as pending redox moieties of linear polythiophenes[3] we could perform successful crosslinking and simultaneous doping of polymer films. The films provide very high stabilities with high electronic conductivities as evidenced by cyclic voltammetry coupled with in-situ conductance measurements and four-probe measurements. In the case of 3T we have reported on homopolymer and copolymer films of 3T and ethylenedioxythiophene which allow polymer-analogous reactions to induce ionic functionalities, thereby creating branched conjugated polyelectrolyte films.[4],[5]

To get a better understanding on mixed conductivity in polymer films, we have recently performed a study on electronic and ionic conductivity of linear conjugated polyelectrolytes by impedance spectroscopy and dc-measurements.[6] The clear dependence of the conductivities as function of humidity and degree of doping will be discussed in the talk in more detail.


4:00 PM *BM07.02.06/EP05.02.06
Soft Electronic and Ionic Neural Interfaces
Klas Tybrandt,1,2, Dion Khodagholy,1, Flurin Stauffer3 and Janos Vörös3; 1Department of Science and Technology, Linköping University, Norrköping, Sweden; 2Institute for Biomedical Engineering, ETH Zürich, Zurich, Switzerland; 3Department of Electrical Engineering, Columbia University, New York, New York, United States.

Two-way communication between electronics and neural tissue is key for advancing diagnosis and therapies for neurological diseases and disorders, as well as providing detailed information about brain signaling. Establishing such neural interfaces is a major challenge, as the tissue response to implants can have a detrimental effect on the signal quality and functionality of the implant. Also, electrical stimulation is inherently limited in its stimulation of neural tissue, in comparison to the sophisticated chemical signaling processes within biological tissue. Here, I present our efforts in addressing two critical technological aspects for the creation of versatile neural interfaces: the matching of mechanical properties of tissues and electronics, and the development of fast and low-leakage chemical interfaces. Soft electronic biomedical implants have a demanding set of requirements, including biocompatibility, mechanical and electromechanical properties, long-term stability and electrode performance. To meet these requirements, we have developed a high-performance, long-term stable soft and stretchable composite for neural electrodes. Based on this composite, high-density soft electrode grids were developed and implanted onto brain surface of rats. The electrodes provided high-quality recordings during three months of implantation. Next, I will outline our strategy for creating high-speed low-leakage chemical neural interfaces, by discussing the relationship between delivery delay and leakage, and then present an iontronic approach to achieve low leakage and small delay simultaneously.

4:30 PM BM07.02.07/EP05.02.07
Organic Electronics for Neuromorphic Computing
Yvoert van de Burgt; Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands.

Neuromorphic computing could address the inherent limitations of conventional silicon technology in dedicated machine learning applications. Recent work on silicon-based asynchronous spiking neural networks and large crossbar-arrays of two-terminal memristive devices has led to the development of promising neuromorphic systems. However, delivering a parallel computation technology, capable of implementing compact and efficient artificial neural networks in hardware, remains a significant challenge. Organic electronic materials offer an attractive alternative to such systems and could provide neuromorphic devices with low-energy switching and excellent tunability, while being biocompatible and relatively inexpensive.

This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them1. We demonstrate a novel concept based on an organic electrochemical transistor2 and show how some challenges in the field such as stability, linearity and state retention can be overcome2.

Furthermore, we investigate chemical doping mechanisms in the active material for improved material functionality and demonstrate that this device can be
entirely fabricated on flexible substrates, introducing neuromorphic computing to large-area flexible electronics and opening up possibilities in brain-machine interfacing and adaptive learning of artificial organs.

1 van de Burgt et al. Nature Electronics, 2018
2 van de Burgt et al. Nature Materials, 2017
3 Keene et al. J Phys D, 2018

4:45 PM BM07.02.08/EP05.02.08
Anisotropic Conducting Polymer Films for Bioelectronics Patricia Iastrewska-Perfeci, Georgios Spyropoulos, Jennifer Gelinis and Dion Khodagholy; Columbia University, New York, New York, United States.

Anisotropic conductive films, which consist of electrically conductive particles dispersed in nonconductive media, are increasingly being applied to establish high-density electrical bonds between electronic boards and chips. However, current anisotropic composites utilize metallic particles, often nickel and epoxy-based media, that require high thermocompression energy for bonding. Therefore, they have limited applicability in thin-film, conformable, and plastic-based devices that are used in bioelectronic applications. Furthermore, these materials are not biocompatible, significantly limiting their use in biological systems. We hypothesized that replacing the metallic particles with conducting polymer particles combined with a biocompatible nonconducting matrix would address this limitation. We developed a novel anisotropic conducting polymer (ACP) consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) conducting polymer particles dispersed in a matrix of crosslinked chitosan (CS). To determine the permeability of PEDOT:PSS to CS, we characterized the resistances of thin CS-based films sandwiched with PEDOT:PSS and gold pads. We investigated the particle size, structure, density and distribution of pure PEDOT:PSS particles and PEDOT:PSS-coated CS particles. The anisotropy was defined by the ratio of horizontal and vertical impedance between interconnects. We benchmarked the anisotropy of the developed ACPs by geometrically varying an array of gold electrodes. The final ACP, which was created at 70°C with minimal pressure, yielded anisotropy of 10^5-10^6. The ACP was then used to maintain precise connections between a high density conformable implantable neural probe and back-end electronics. It enabled complete chronic in vivo implantation of these electronics with minimal encapsulation layers, highlighting applicability for use in bioelectronic and clinical devices

SESSION BM07.03: Neural Interfacing/Implantable Devices I
Session Chairs: Jurgen Kosel, Duygu Kazum and Roisin Owens
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Constitution B

8:00 AM BM07.03.01
Toward Biocompatible and Degradable Electronics—A Comprehensive Material Approach Ashkan Shafighi, Elham Ghadiri, Kunzhao Li and Anthony Atala; 1 Institute for Regenerative Medicine, Wake Forest School of Medicine, Winston-Salem, North Carolina, United States; 2 Chemistry Department, Wake Forest University, Winston-Salem, North Carolina, United States; 3 Biology, Wake Forest University, Winston-Salem, North Carolina, United States.

Over the past 10 years, regenerative medicine has witnessed a significant technological and scientific advancement. For instance, numerous revolutionary progress in stem cell science as well as additive manufacturing, namely 3D printing, have opened up new horizons in research and brought them closer to reality than ever before. However, for more sophisticated indications, fabrication of biological structures such as human tissues and organs may require an optimized procedure to obtain the impeccable final product. Therefore, the need for biocompatible electronic devices is a focus of attention in academia and industry. Moreover, biodegradable electronic devices for healthcare applications can also produce a revolution in the electronics industry and reduce electronic waste products. Currently, thousands of tons of silicon that is used to manufacture computers, cell phones, and other devices are discarded into the environment annually. It is critical that such waste be curtailed. Here, we report a systematic investigation on finding biocompatible/degradable functional electronic materials. To address this aim two different approaches were employed: 1-study the electronic properties of biomaterials, 2- study the biocompatibility of functional electronic materials. Materials with energy band gap between 1 to 3 eV are categorized as semiconductors and bigger than 3 eV as insulators. Various biomaterials were sought in terms of energy band diagram. Most biomaterials showed energy band gap bigger than 3 eV confirming them as insulators, for example, fibrinogen, glycerol, and gelatin showed 3.54, 3.02, 3.0 eV. Meanwhile, a few biomaterials were found as semiconductors such as phenol red in the cell culture medium with 1.96 eV energy band gap. On the other hand, the biocompatibility of organic semiconductors, such as P3HT and PCBM for different cell types such as satellite cells were examined. The cells were exposed to the thin layer of films prepared with the organic materials, and essential biomarkers (Desmin and MF20) were used to determine the consequence effect on the cells, their functionality, proliferation, and differentiation. The outcomes of this research can be used to fabricate biocompatible/degradable electronic devices for medical applications.

8:15 AM BM07.03.02

Deciphering complex neural circuits relies on the developments of neural interface devices with good biocompatibility, mechanical compliance, high spatial resolution, and high quality recording. There has been significant development in neural interface devices in the past decades, mostly based on silicon and metal electrodes or contact printed film electrodes. More recently, thermally drawn polymer fibers have been utilized as neural recording probes which exhibit good flexibility and biocompatibility. However, due to the low conductivity of conventional polymer electrodes, the size of a polymer fiber probe is typically much larger compared to the size of a single neuron in order to have the overall impedance fall in the recordable range, resulting in a poor spatial resolution of these probes. Therefore, it is of great importance to reduce the impedance of the polymer electrode while maintaining the miniaturized footprint in order to increase the spatial resolution and minimize the brain damage. In this study, we deposited metallic nanostructures on the tip of the polymer fiber probe to enhance the electrical properties as well as the electrophysiological recording performance. Soft nanolithography patterning technique was utilized to create dense vertical 3D nanopillar nanoelectrodes on the small area of the flexible polymer fiber tips via gold nanohole array masks. Because of the large surface area of the nanopillar nanoelectrode structure, the resulting impedance of the modified electrode has been reduced to be able to capture neural signals. The power density of local field potential (LFP) from both the modified and unmodified electrode showed the better recording performance of the modified one. Finally, we evaluated these nanoelectrode integrated polymer fiber probes in terms of chronic recording and long term tissue response. These results show that nanoelectrode-based surface modification can significantly reduce the impedance of polymer electrodes, thus increase the spatial resolution and improve the electrophysiology recording performance of polymer fiber probes.
As our understanding of the brain’s physiology and pathology progresses, increasingly sophisticated materials and technologies are required to advance discoveries in systems neuroscience and develop more effective diagnostics and treatments for neuropsychiatric disease. Localizing brain signals may assist with tissue resection and intervention strategies in patients with such diseases. Precise localization requires large and continuous coverage of cortical areas with high-density recording from populations of neurons while minimizing invasiveness and adverse events. We describe a large-scale, high-density, organic electronic–based, conformable neural interface device (NeuroGrid) with embedded integrated circuitry capable of simultaneously recording local field potentials (LFPs) and action potentials from the cortical surface. We demonstrate the feasibility and safety recording with such devices in anesthetized and awake subjects. Highly localized and traveling physiological and pathological LFP patterns were recorded, and correlated neural firing provided evidence about their local generation. Application of NeuroGrid technology to disorders such as epilepsy may improve diagnostic precision and therapeutic outcomes while reducing complications associated with invasive electrodes conventionally used to acquire high-resolution and spiking data.

Adhesion quality and biocompatibility are the main obstacles to a successful use of conducting polymers coatings on metal microelectrodes for recording and stimulation. Such microelectrodes have very small dimensions, resulting in a high impedance. One way to address this problem is to deposit a conducting polymer, PEDOT, on their electroactive area to lower the impedance and reduce the foreign body reaction [1]. However, the small size of such microelectrodes and the poor adhesion of conducting polymers on most inorganic substrates remain practical difficulties for large scale production. In our recent experiments using electrochemical polymerization, we explored the influence of different solvents (acetonitrile, propylene carbonate) [2] and electropolymerisation methods (potentiodynamic, galvanostatic, pulsed deposition) on the adhesion of an electropolymerized thin layer of PEDOT:BF4 on platinum electrodes. We also investigated the use of a diazonium salt as an anchoring layer for PEDOT on platinum [3]. We evaluated the stability of our PEDOT-coated electrodes ex vivo by passive aging in physiological solutions and under repeated electrical stimulations, similar to those used for deep brain stimulation. Finally, we investigated in vivo aging to hopefully gain more insights on the stability of our PEDOT coating in contact with living tissues.


9:15 AM *BM07.03.03
Large Scale Integrated Organic Transistors for High-Resolution Electrocytography of the Human Brain Dion Khodagholy; Columbia University, New York, New York, United States.

9:30 AM *BM07.03.06
Graphene-Based Neural Interfaces for Probing Brain Activity Yichen Lu, Xin Liu and Duygu Kuzum; University of California, San Diego, La Jolla, California, United States.

The complexity of neural activities has challenged both neuroscience research and clinical practice for decades. Understanding neuronal dynamics and information processing performed by neural populations requires advanced technologies with high-resolution sensing and stimulation capability. Clinical neuromodulation therapies widely used for neurological disorders also depend on the ability to manipulate the dynamics of neural circuits. Conventional neural interfaces offering electrical, optical, or chemical signals have greatly advanced our understanding of neural functions, however, most of these technologies are based on a single functionality. Combining multiple functionalities in a single system has recently been pursued as an integrative approach in new neurotechnology development. Graphene has recently emerged as a neural interface material offering several outstanding properties, such as optical transparency, flexibility, high conductivity, functionalization and biocompatibility. The unique combination of these properties in a single material system makes graphene an attractive choice for multi-modal probing of neural activity. In this talk, I will present our recent work on graphene-based neural interfaces, highlight key applications, and finally discuss future directions and potential advances for graphene-based neurotechnologies in both basic neuroscience research and medical applications.
A soft, fully biocompatible, stretchable strain sensor device based on ultra-thin stretchable electronics is reported. The sensor is able to monitor stretch of the bladder wall, via a resistive strain sensing approach. The stretchable sensor is used to determine bladder stretch, and hence volume, without the need for complex and invasive surgical procedures used currently, enabling the development of new safer and cheaper treatment options for various urological conditions. Such instances where a means to monitor bladder stretch could be invaluable are for sufferers of overactive bladder syndrome (OAB), urinary incontinence or after spinal cord injury.

Thermally evaporated Cr/Au thin films (~150 nm) on compliant, stretchable polyurethane (PU) film (~50 μm), were deposited to produce resistive sensors. The sensors were patterned into a ‘dogbone’ design by laser patterning, with sensor W and L dimensions on the mm scale. The sensors display a linear response as a function of strain from 0 to 50 %, and as sensor length increases, sensor sensitivity as a function of strain increases. We show that the sensitivity is highest for L = 6 mm, at 3.18 Ω-%-strain, which is around 15 times higher than the sensitivity for L = 2 mm, at 0.21 Ω-%-strain. Furthermore, cycling tests performed on sensors of various length reveal that the devices display good stability, with virtually no hysteresis.

The highest sensitivity sensors were subsequently tested in vitro on an isolated pig bladder. The sensors were attached onto the external wall of the bladder using a biocompatible hydrogel adhesive. The bladder was repeatedly filled and emptied using a syringe system designed to mimic natural bladder behaviour. As bladder volume changes, the sensor changes resistance as a function of stretch, and displays very good repeatability over several bladder filling/emptying cycles. We found a maximum sensitivity of 0.1 Ω/ml for the most sensitive device. Our sensors pave the way towards completely implantable health monitoring systems of the future.
population ages. Response to medications for these conditions has plateaued, paving the way for a revolution in implantable devices as the next wave of effective treatments for these “brain network disorders.” Key to developing these new devices are advances in computation, batteries, sensors and closed loop algorithms. New and more versatile materials is one of the main requirements and drivers of innovation in new medical devices and technologies. In this lecture I will outline major applications in the area of neurodevices/brain computer interfaces, present unmet needs, and discuss the path to clinically translate innovations from the laboratory to patients. I will give examples from our own research and other labs on this path, touch on common failure modes and novel tools for collaboration, bringing engineers, clinicians and industry together to advance clinical care.

SESSION BM07.04: Neural Interfacing/Implantable Devices II
Session Chairs: Dion Khodagholy and Stephanie Lacour
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Constitution B

1:30 PM BM07.04.01
Highly Stable PEDOT-CNT Nanotube as Neural Electrode Coating Nuan Chen1, 2, Baiwen Luo2, Nitish Thakor2 and Seeram Ramakrishna1; 1Department of Mechanical Engineering, National University of Singapore, Singapore, Singapore; 2Singapore Institute for Neurotechnology (SINAPSE), National University of Singapore, Singapore, Singapore.

During the past decades, neural electrodes have been developed as promising interface technology for direct communication with the neural tissues for diagnosis of the nervous disorders and treatment of the injury. Considering the significant material mismatch between the external implant and native tissue, a thin coating is employed on the electrode sites as an intermediate layer to bridge the difference. However, great challenges still exist regarding the long-term performance of the electrode coating in vivo.

In this study, a tubular electrode coating made of poly(3,4-ethylenedioxythiophene) (PEDOT) and carbon nanotube (CNT) was designed, targeted to long-term neural recording. The PEDOT-CNT nanotube coating was fabricated and showed compatibility with flexible polyimide electrode. The coating exhibited a 3D network-like structure made of hollow tube with an outer diameter of ~70nm and wall thickness of ~90nm. The electroactivity of the PEDOT-CNT coating was investigated using electrochemical impedance spectroscopy and cyclic voltammetry. The coated electrode sites showed significantly decreased impedance and increase charge storage capacity compared to bare site, which would allow more charge transfer at the interface and increase the sensitivity during neural recording. To test the mechanical adhesion of the PEDOT-CNT nanotube coating, ultrasonic treatment was employed in the study. The PEDOT-CNT nanotube could sustain 20min sonication with less than 20% delamination area while the PEDOT-PSS nanotube showed more than 60% delamination area after 5min treatment. The incorporation of CNT significantly reinforced the nanotube structure and improved the mechanical durability against sonication which would address the delamination issue of PEDOT coating and support chronic recording. We have also studies the different deposition condition and their effects on the morphology, electrical property and mechanical property of the coating. In vitro culture of neurons showed positive neuron attachment and neurite extension on PEDOT-CNT nanotube immobilized with poly-lysine and laminin.

1:45 PM BM07.04.02
Conducting Polymers for Stretchable and Healable Electronics Fabio Cicoira1, Yang Li1, Shinning Zhang2, Floriane Miquet-Westphal3 and Leslie Liu4; 1Ecole Polytechnique de Montreal, Montreal, Quebec, Canada; 2University of California, Los Angeles, Los Angeles, California, United States.

Organic electronic devices, apart from consumer applications, are presently paving the path for key applications at the interface between electronics and biology. In such applications, organic polymers are very attractive candidates, due to their distinct properties of mechanical flexibility, self-healing and mixed conduction.

My group investigated the processing conditions leading to high electrical conductivity, long-term stability in aqueous media as well as robust mechanical properties of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) and polystyrene sulfonate (PEDOT:PSS) [1-3]. We have demonstrated that stretchable PEDOT:PSS films can be achieved by adding a fluorosurfactant to the film processing mixture and by pre-stretching the substrate during film deposition. We have achieved patterning of organic materials on a wide range of substrates, using orthogonal lithography and pattern transfer [4-5]. Recently we have discovered that PEDOT:PSS films can be rapidly healed with water drops after being damaged with a sharp blade [6] or show autonomous self-healing if processed in presence of certain additives.

My talk will deal with processing, characterization and patterning of conducting polymer films and devices for flexible, stretchable and healable electronics. I will particularly focus on the strategies to achieve films with optimized electrical conductivity and mechanical properties, on unconventional micro patterning on flexible and stretchable substrates, on the different routes to achieve films stretchability and self-healing.


2:00 PM BM07.04.03
Multimodal Characterization of Soft Bioelectronics Stephanie P. Lacour; Ecole Polytechnique Federale de Lausanne, Geneva, Switzerland.

Soft bioelectronics incorporates all the functional attributes of conventional rigid electronics in formats that enable reversible mechanical loading and, in the case of implantables, performance under physiological conditions. Understanding the underlying mechanisms of stretchable materials and establishing the performance boundaries of such devices under the multiple operation conditions are fundamental to research efforts in the field. The biomimetic context also imposes a challenging experimental environment that is difficult to replicate or predict. There is an unmet need for experimental set-ups that combine multiple modes of loading e.g. mechanical, thermal, electrical, biological, and provide real-time, concurrent probing of the devices.

This talk will describe our recent efforts in constructing multimodal experimental set-ups and establishing standardized tests and experiments that can clearly define the reliability and lifetime for soft bioelectronics. Using stretchable metallization integrated in wearable sensors and spinal implants as test vehicles for the new characterization platforms, we will report on failure modes, repeatability, robustness, and reliability. These metrics are often underestimated in academic research yet critical to advance the translation of soft bioelectronics.
Bioelectronics with Nanocarbons—From Transparent to Fuzzy Interfaces

2:30 PM BM07.04.04
Chronic and Acute Stress Hormone Monitoring/Stimulation in Adrenal Gland
Yiel Jae Shin¹, SungHyuk Sunwoo² and Tae-il Kim¹; Sungkyunkwan University, Suwon, Korea (the Republic of); ²Seoul National University, Seoul, Korea (the Republic of).

Living organisms mainly use nervous and endocrine systems to control the body and maintain homeostasis independently. Endocrinal signal based on the flow of special chemicals called hormone affects the body chronically and massively. When stress is applied to human body, hypothalamus releases corticotropin-releasing hormone (CRH) to the pituitary gland that generates adrenocorticotropic hormone (ACTH) which flows into the adrenal cortex, especially adrenal zona fasciculata (AZF) cell in adrenal gland. The adrenal cortex then produces cortisol, a stress hormone that rebalances body functions and performances of neural and muscular system. However, repeated and chronic stress can cause malfunctions in cortisol releasing endocrine system. Chronic stress involves accumulation of excessive and unnecessary cortisol that eventually cause several diseases such as amnesia, depression, fatigue, anxiety. It is necessary to continuously monitor the cortisol concentration to prevent such diseases which caused by chronic stress. Recently, it was revealed that the electrophysiologic (EP) signal induced by ion flux through cellular membrane was responsible for hormone releasing process in connection endocrine organs. We assumed that accurate recording of electric signal representing physiological activities of endocrine cells could be applied to characterize cortisol change. Here, we introduce a long lasting, implantable Anchor - like flexible probe that can be used to quantify relationship between cortisol releasing level and electrophysiologic (EP) signals from adrenal gland based on flexible EP sensors. This anchor – like probe penetrated through Adrenal Gland, which ensured minimal invasion to organs and stability, low impedance increment over 13 weeks. Through our research, we identified EP signal Frequency was increased in AZF cells, only induced by acute stress or ACTH injection. Thus, our team successfully determined activities of hormonal cells and relative change of cortisol hormone level under stress environment in in vivo animal model. Next, we hypothesized that electrical stimulation of surface of adrenal gland could improve or suppress activity of adrenal gland. We designed elastomer based, conformally attaching stretchable serpentine electrodes. It is known that cortisol secretion is also increased by not only stress but blood loss, therefore we extracted small doses of blood from inferior vena cava (IVC) of rat with every 5 minutes to suppress artificial hemorrhage. By comparing Cortisol concentration of Non - electrical stimulated rat with electrically stimulated showed us that high frequency electrical stimulation tend to suppress activity of AZF cell. However, low frequency electrical stimulation improved AZF cell activity, which showed higher cortisol concentration then standard cortisol concentration. This research of Adrenal gland could provide fundamental knowledge to medical applications such as stress regulator.

2:45 PM BM07.04.05
Design of Conductive Gel for Sensing Weak Biosignals with High S/N Ratio
Yuki Noda¹, Naomi Toyoshima¹, Teppei Araki¹,², Shusuke Yoshimoto¹, Takafumi Uemura¹,² and Tsyoshi Sekitan¹,²; ¹Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Japan; ²Advanced Photonics and Biosensing Open Innovation Laboratory, Suisa, Japan.

Conductive gel enabling precise measurement of weak electrical signals are desired for the detection of biomedial signals such as an electroencephalogram (EEG) or a fetal electrocardiogram (ECO). Since these signals are intrinsically weak less than 100 µV, the noise level has to be lowered to acquire signals with the high S/N. In general, one strategy for obtaining the high S/N ratio signal is to increase the electrode area to lower the contact resistance between skin and electrode or to shorten the length of the wiring to prevent invasion an external noise, however, we propose another option to detect signals with high quality by modifying gels on electrode. Here, we designed the biocompatible conductive gel to obtain weak EEG signals with the high S/N ratio by reducing the contact resistance and mains hum intensity.

The developed gels are based on Amylopectin contained in rice and NaCl. By just printing and heating the precursor solution on a noble metal, conductive gel can be fabricated. The impedance spectrum of gels shows almost frequency-independent characteristics through a range of 0.1 Hz to 100 kHz lower than 1kΩ. Hydrogen-bonded network of Amylopectin gives sufficiently strong adhesive force to the skin with its strength comparable to adhesive plasters. Other components enable to suppress mains hum that is one of the origin of lowering the S/N ratio of EEG signals. By combining the developed gels and the wireless measurement system, we successfully obtained EEG signals from forehead. As with Ten20 conductive paste that is commonly used to measure EEG signals in hospitals, the developed gels can also detect representative brain wave like alpha waves that appears at 10 Hz when eyes are closed. Additionally, the intensity of mains hum appeared between 50-60 Hz are effectively suppressed to about 50% against that of Ten20 conductive paste.

3:00 PM BREAK

3:30 PM *BM07.04.06
Bioelectronics with Nanocarbons—From Transparent to Fuzzy Interfaces
Tzahi Cohen-Karni², ¹; ¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; ²Biomedical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene (3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular spatial resolution (~5μm) and jsec temporal resolution. Last, we have developed a unique transparent graphene-based electrical platform that enables concurrent electrical and optical investigation of ES-derived cardiomyocytes' intracellular processes and intercellular communication. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science, and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

4:00 PM BM07.04.07
Bioinspired Nanowire Devices Utilizing Perylene Diimides
Kuo-Yao Lin¹, Andrew Bartlett², Alon Gorodetsky² and Jason D. Slinker¹; ¹The University of Texas at Dallas, Richardson, Texas, United States; ²Chemical Engineering and Materials Science, The University of California-Irvine, Irvine, California, United States.

Despite remarkable examples of difficult-to-produce isolated molecular devices, the scalable nanomanufacturing of such electronics remains at a standoff due to fundamental roadblocks associated with the synthesis of large quantities of modular nanoscale circuit elements. We have introduced a methodology for rapid, scalable production and facile purification of nanowire devices. We have synthesized organic semiconductor moieties, perylene-3,4,9,10-tetracarboxylic diimides (PTCDIs), within DNA-like scaffolds, leveraging the rapid, efficient, and precise coupling afforded by traditional DNA bioconjugate chemistry. These DNA-inspired nanowires enable the self-assembly of active, nanoscale circuit elements at patterned electrodes. The
assembly and electrical performance of these arrayed devices have been characterized through scanning microscopy techniques and custom, automated electrical test equipment. Further characterization under controlled environmental and temperature conditions revealed absolute currents of fully well matched duplexes incorporating perylene units were enhanced by twofold over such nanowires incorporating two C-A mismatches and 4.4 fold over conventional DNA nanowires. Temperature dependence revealed a sharp current drop with temperature consistent with the dissociation of the modular duplex. Our unique and economically viable approach offers a new paradigm for the fabrication of nanoscale electronic circuits.

4:45 PM *BM07.04.08
Ink-Jet Printed 3D-Microelectrode Arrays for Neuroelectronic Interfaces and Sensing Applications - Sourad Adly1, Leryo Grob1, Philipp Rinklin1, Sabine Zips1, Lennart Weiss1, Hideaki Yamamoto3, Ayumi Hirano-Iwata4, and Bernhard Wolfraum2; 1Neuroelectronics - Munich School of Bioengineering, Department of Electrical and Computer Engineering, Technical University of Munich, Garching, Germany; 2Institute of Complex Systems ICS-8, Forschungszentrum Jülich GmbH, Jülich, Germany; 3Advanced Institute for Materials Research, Tohoku University, Sendai, Japan; 4Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

Microelectrode arrays are used in a variety of sensing and stimulation applications including electrochemical biosensor platforms and neuroelectronic interfaces. Typically, these arrays are produced with state-of-the-art fabrication methods such as photolithography or electron beam lithography, which provide high-resolution capabilities to include thousands of electrodes on a single chip. However, these methods are expensive and restricted to certain substrate or electrode materials. Thus, they are not ideally suited for low-cost rapid prototyping of devices with alternative geometric features or materials.

4:45 PM BM07.04.09
Ti3C2 MXene Neural Electrodes for Sensitive Detection of Neuronal Spiking Activity - Nicolette Driscoll1, 2, Andrew G. Richardson1, 4, Kathleen A. Malecki1, 4, Babak Anasori1, 2, Oladayo Adewole1, 2, Pavel Lelyukh1, 4, Lila Esfendro1, 2, D. K. Cullen1, 2, Timothy H. Lucas1, 2, Yury Gogotsi1, 4, Flavia Vitali1, 2, 4, and Dennis A. Jaklevic1, 2, 4; 1Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Center for Neurotrauma, Neurodegeneration, and Restoration, Corporal Michael J. Crescenz Veterans Affairs Medical Center, Philadelphia, Pennsylvania, United States; 3Center for Neuroengineering and Therapeutics, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 4A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; 5Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 6A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; 7Department of Chemical Engineering, Cornell University, Ithaca, New York, United States; 8Department of Neurology, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

High-resolution neural interfaces are essential tools for studying neural circuits underlying brain function and disease. As electrodes are miniaturized to achieve high spatial resolution and resolve individual neuronal spiking activity, maintaining low impedance and high signal quality becomes a significant challenge. Nanostructured materials have the potential to address this challenge by offering a combination of unique electrical and mechanical properties and the ability to interact with biological systems on a molecular scale. Ti3C2 MXene, a recently discovered 2D nanomaterial, possesses remarkably high volumetric capacitance, conductivity, surface functionality, and processability in aqueous dispersions, making it unique among 2D nanomaterials. In this work, we seek to evaluate the recording performance of MXene for detection of neuronal spiking activity in vivo. We employed a high-throughput microfabrication process for micropatterning MXene onto flexible, parylene-C substrates, and fabricated a 16-channel laminar probe. The laminar probe has 5 sets of side-by-side MXene and gold (Au) electrode contacts (25 μm diameter) arranged in a stereotrode configuration to enable direct comparison of signal quality between the two materials during in vivo recording. Electrochemical impedance spectroscopy revealed that the MXene electrodes in the array exhibit remarkably low 1 kHz impedance compared to their Au counterparts: 219 ± 31 kΩ vs. 865 ± 125 kΩ, respectively. The MXene electrodes have a rough and layered surface morphology (Ra = 32 nm), which likely contributes to their ~4x improvement in impedance properties compared to Au. We performed acute recording experiments in anesthetized rats and recorded multiunit neuronal spiking activity on adjacent MXene and Au stereotrode contacts implanted in sensorimotor cortex. Spikes that occurred simultaneously on adjacent MXene and Au electrodes were considered to have been generated by the same neuron, and their signal-to-noise ratios (SNR) were computed and compared. We found that MXene electrodes recorded neural spiking activity with significantly higher SNR than Au electrodes. We also found that MXene electrodes recorded more spikes overall than the Au electrodes, and that the spikes unique to the MXene electrode in a stereotrode pair tended to be low amplitude, suggesting that MXene electrodes have a larger “seeing distance”, allowing them to resolve spiking activity from a larger volume of tissue. Finally, we assessed the neuronal biocompatibility of Ti3C2 MXene in vitro and found that neurons cultured on MXene films proliferated, showed axonal growth, formed synaptic connections, and were as viable as control cultures. This work highlights the suitability of Ti3C2 MXene for high resolution neural interfaces and suggests that MXene has significant potential to enhance the performance of neural microelectrodes beyond current capabilities.

SESSION BM07.05: Poster Session I: Bioelectronics—Fundamentals, Materials and Devices
Session Chairs: Sahika Inal, Christian B. Nielsen and Rosisin Owens
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

BM07.05.01
With the advent of the hyperconnected era, visual IoT devices attracted great interest. Flexible displays are powerful candidates for interactive visual communication. Inorganic-based micro light-emitting diodes (μLEDs) have been regarded as key technologies in RGB micro LED TVs due to their excellent electrical/optical properties, fast response, long lifetimes and high stability in harsh environments. Several groups have studied various inorganic LED materials for various applications. Despite previous reports of flexible micro LEDs, GaN f-VLEDs on plastic substrates have not yet been demonstrated due to the difficulty of vertical GaN interconnections. Flexible energy sources for f-LEDs are also required for practical applications of flexible optoelectronic systems.

Herein, we report a flexible 30x30 GaN VLED array through a simple manufacturing process. The GaN LED chip was separated from the sapphire wafer by the ILLO process. Stand-alone micro LEDs are isolated by biocompatible layers and are interconnected vertically with AgNW-based conductors by resolving the high step coverage of f-VLEDs. Ultra-thin, transparent and flexible GaN VLEDs are attached to the human nail in a conformal structure with high light output of 30 mW mm⁻². The lifetime of the f-VLED was experimentally investigated by a high accelerated stress test (HAST) and theoretically estimated by simulation. In addition, our f-VLEDs exhibited excellent mechanical durability during cyclic bending cycles. A wireless power supply system for human skin has been successfully demonstrated by delivering electrical energy to the f-VLED. Finally, the blue f-VLED successfully emitted blue light into the mouse brain without severe tissue damage.

BM07.05.02
Metal Nanoparticles-Grafted Functionalized Graphene Coated with Nanostructured Polyaniline ‘Hybrid’ Nanocomposites as High-Performance Biosensors Sanjiva Gupta and Romney Meek, Western Kentucky University, Bowling Green, Kentucky, United States.

We report on the development of next-generation chemical, electrochemical and biological sensors from nanocomposites with broader electrical conductivity and anticipated linear time response, specificity and stability. We synthesized metal nanoparticles-grafted functionalized graphene nanosheets with nanostructured polyaniline (PANI) ‘hybrid’ nanocomposites for ascorbic acid (AA) sensing. The versatility of the nanocomposite performance was corroborated by altering the size and areal density of metal nanoparticles (AgNP, AuNP and AgNP) on the graphene-family nanomaterials, GFNs namely, graphene oxide (GO); GO, thermally reduced GO; rGO, and nitrogenated functionalized graphene; NFG. In addition, the globular surface morphology and charge density of electropolymerized polyaniline (PANI) onto GFNs can also influence the biosensor performance. The noble metal nanomaterials are selected due to their higher electrical conductivity, facile synthesis, easier processability, antimicrobial applicability and scalability. The as-synthesized multilayer architectures (PANI|AgNP|GFN and PANI|AuNP|GFN) on fluoride-doped tin oxide (FTO) coated glass, graphite foil (GF) and graphene rod (GR) electrodes increased the electrical conductivity of the electrodes significantly and reduced the charge transfer resistance dramatically promoting localized orbital re-hybridization and heterogeneous integration with PANi. We all contribute toward enhanced electroactivity and ensure rapid charge transfer and ion conduction. These multilayer ‘hybrid’ nanocomposite electrodes are also useful as advanced electroanalytical platforms for platinum-free electrocatalysis, electrodes for energy storage pseudocapacitors and enriching biofuel cell development. This work is supported in parts by NSF EPSCoR Grant and WKU Graduate School Fellowship.

BM07.05.03
Biosensor for the Simultaneous Monitoring of Breath Isoprene and Acetone Jan van den Broek, Amy Wang, Andreas T. Günnter and Sotiris E. Pratsinis; ETH Zürich, Zürich, Switzerland.

Volatiles from the human body, especially from breath, contain a wealth of physiological and pathological information. Chemo-resistive metal-oxide gas sensors stand at the interface to the human biosystem as they specifically interact with such biomarkers and are capable to measure their concentrations even at the lowest parts-per-billion (ppb) levels. This way, individual emanating volatiles can be monitored to infer and better understand metabolic states and processes. In specific, breath isoprene has been suggested to be an indicator for the efficacy of blood cholesterol-lowering therapy and cardiac output, while acetone is an established biomarker for fat metabolism. Thus, online monitoring of these two gases simultaneously by a portable device can be a promising tool to optimize effective weight loss through physical exercise and diet planning.

Here, we present a sensor system for the simultaneous detection of isoprene and acetone in complex breath mixtures. It consists of nanostructured films of inorganic metal-oxides designed by flame aerosol synthesis to selectively interact with these biomarkers on a molecular level, resulting in a detectable electrical signal. The resulting biosensor can detect acetone and isoprene simultaneously down to 5 ppb in real time at breath-related relative humidity. It has high selectivity to other major breath markers like methanol, ethanol and ammonia. The biosensor is also tested in vivo by direct sampling of breath through a breath sampler and simultaneously cross-validated by state-of-the-art mass spectrometry. All the components utilized can be readily miniaturized and integrated into a portable device enabling monitoring of these important metabolic tracers.


BM07.05.04
Transparent, Flexible Deep-Well Micro-Structured PEDOT:PSS/Au Nanorods Based Electrode Array for Neural Recording Yeounguk Cho and Ki Jun Yu; Electrical and Electronics Engineering, Yonsei University, Seoul, Korea (the Republic of).

Neural interfaces offer an insight into the mechanism of nervous system by recording signals from neurons. Conventional neuro-electrodes are made of metal that may occur clinical image distortion by its inherent opacity. Electrode transparency is ultimately important factor, because electrical artifacts from light stimulation for opto-genetics hinder the neural recording and interfere with the pinpoint control of neural activity. Ultrathin metal based devices for neural recording have been reported as alternatives with transparency, but the relatively low transmittance rate (<40%) requires novel materials and micro/nanopatterning techniques that offer significant enhancement of signal to noise ratio (SNR) of electrophysiological signals while maintaining its transparency.

Biocompatibility is also important factor to be considered for electrodes that are used for implantable neural arrays. Numerous materials for biocompatible implantable devices with the outstanding electrical properties have been discussed for the electrophysiological recordings or stimulations. However, only small number of reported such electrodes satisfy the conditions where multiple characteristics such as high transparency, flexibility, and high SNR, together with credible bio-stable property require, thereby enabling conformal electrical and optical neural recording simultaneously. Conducting polymers
are excellent material choice for the neural electrodes that satisfy the characteristics mentioned above. Recently, poly(3,4-ethylenedioxythiophene)(PEDOT) as the representative conducting polymer is widely used for the neural electrodes due to the good conductivity with a high degree of an optical transparency.

Herein, we present a facile fabrication of deep-well structured PEDOT:PSS/Au nanorods array that can greatly improves SNR of neural recordings compared to the conventional PEDOT:PSS based electrodes. In our work, Au nanorods with three-dimensional(3D) deep-well microstructures by self-assembly are exploited as particles that can greatly enhance electrode conductivity while maintaining its optical transparency. Au nanorods are also suitable for the implantable neural interface design because of its well-known biocompatibility. Electrical and optical characterizations were conducted on both the deep-well microstructure and the plain surface-based PEDOT:PSS/Au nanorod electrode as a point of comparison. These experimental results show the much lower impedance plot and higher optical transparency with the deep-well surface structure compared to that with the planar device. Conducting cytotoxicity and implantation experiments on animal models also support its good biocompatibility. We expect this novel microstructure electrode array to be the unprecedented candidates for electrodes in a field of biomedical engineering such as an implantable cell regulating device or neural interface.

**BM07.05.05**

**Sensing Applications of Remote-Gate Field-Effect Transistor Combining Polymer Sensing Membrane**

From 1ug/ml to 1 mg/ml in contact with the P3HT layer. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the membranes. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before sensor, pH sensor, and dopant monitoring sensor. All of these sensors share the same detection system but use different remote polymer sensing membrane, not the FET, crucially determines sensitivity, specificity, and characters of the sensing platform.

The remote gate geometric approach. P3HT was deposited on the remote gate structure and the dopant, F4TCNQ, was dissolved in acetonitrile and exposure was compared for each individual polymer. In our last application, we demonstrate new way to quantify dopants concentration on polymers using intrinsic pH sensitivity of polystyrene, poly(methyl methacrylate), and PSMA, by ranging the pH from 3 to 11. The long and short-term pH sensitivity exposure was compared for each individual polymer. In our last application, we demonstrate new way to quantify dopants concentration on polymers using the remote gate geometric approach. P3HT was deposited on the remote gate structure and the dopant, F4TCNQ, was dissolved in acetonitrile and deposited onto the P3HT layer. We were able to quantify and evaluate the deposition from solutions with varying concentrations of dopant which ranged from 1ug/ml to 1 mg/ml in contact with the P3HT layer.

**BM07.05.06**

**Eco-Friendly Biodegradable Thin-Film Transistor and Floating Gate Memory Using Indigo Organic Semiconductor**

From 1ug/ml to 1 mg/ml in contact with the P3HT layer. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the membranes. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before sensor, pH sensor, and dopant monitoring sensor. All of these sensors share the same detection system but use different remote polymer sensing membrane. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before coating the modified polymer on the remote gate. The embedded structure of the anti-cortisol in the polymer allowed cortisol molecules to bind near the membrane-substrate interface. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the intrinsic pH sensitivity of polystyrene, poly(methyl methacrylate), and PSMA, by ranging the pH from 3 to 11. The long and short-term pH sensitivity exposure was compared for each individual polymer. In our last application, we demonstrate new way to quantify dopants concentration on polymers using the remote gate geometric approach. P3HT was deposited on the remote gate structure and the dopant, F4TCNQ, was dissolved in acetonitrile and deposited onto the P3HT layer. We were able to quantify and evaluate the deposition from solutions with varying concentrations of dopant which ranged from 1ug/ml to 1 mg/ml in contact with the P3HT layer.

**BM07.05.07**

**Ternary Metal Chalcogenide (Ni, Co)0.85Se for Biosensing Applications**

From 1ug/ml to 1 mg/ml in contact with the P3HT layer. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the membranes. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before sensor, pH sensor, and dopant monitoring sensor. All of these sensors share the same detection system but use different remote polymer sensing membrane. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before coating the modified polymer on the remote gate. The embedded structure of the anti-cortisol in the polymer allowed cortisol molecules to bind near the membrane-substrate interface. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the intrinsic pH sensitivity of polystyrene, poly(methyl methacrylate), and PSMA, by ranging the pH from 3 to 11. The long and short-term pH sensitivity exposure was compared for each individual polymer. In our last application, we demonstrate new way to quantify dopants concentration on polymers using the remote gate geometric approach. P3HT was deposited on the remote gate structure and the dopant, F4TCNQ, was dissolved in acetonitrile and deposited onto the P3HT layer. We were able to quantify and evaluate the deposition from solutions with varying concentrations of dopant which ranged from 1ug/ml to 1 mg/ml in contact with the P3HT layer.

**BM07.05.08**

**Antagonism D1 Agonism and Antagonism**

From 1ug/ml to 1 mg/ml in contact with the P3HT layer. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the membranes. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before sensor, pH sensor, and dopant monitoring sensor. All of these sensors share the same detection system but use different remote polymer sensing membrane. In cortisol sensors, the polymer sensing membrane was made by linking poly(styrene-co-methacrylic acid) (PSMA) with anti-cortisol before coating the modified polymer on the remote gate. The embedded structure of the anti-cortisol in the polymer allowed cortisol molecules to bind near the membrane-substrate interface. A limit of detection of 1 ng/mL was shown in lightly buffered artificial sweat. In the second application, we investigated the intrinsic pH sensitivity of polystyrene, poly(methyl methacrylate), and PSMA, by ranging the pH from 3 to 11. The long and short-term pH sensitivity exposure was compared for each individual polymer. In our last application, we demonstrate new way to quantify dopants concentration on polymers using the remote gate geometric approach. P3HT was deposited on the remote gate structure and the dopant, F4TCNQ, was dissolved in acetonitrile and deposited onto the P3HT layer. We were able to quantify and evaluate the deposition from solutions with varying concentrations of dopant which ranged from 1ug/ml to 1 mg/ml in contact with the P3HT layer.
Screening methodologies of potential G-protein-coupled receptor (GPCRs), which transfer external signals into the cell, drugs has been developed for several decades. Recently, the field-effect transistor (FET) has been used in the development of diagnostic tools, leading to high-performance biosensors, especially liquid-ion gated FET biosensors. Therefore, the FET platform can provide the foundation for the next generation of analytical methods. A principle application of GPCRs is screening new drugs, so the development of a GPCR-conjugated analytical device is highly desired. In this study, we firstly proposed a new approach for studying receptor agonism and antagonism by combining the FET and GPCR roles in a dopamine receptor D1 (DRD1)-conjugated FET system, which is a suitable substitute for conventional cell-based receptor assays. DRD1, for the first time, was reconstituted and purified to mimic native binding pockets that have highly discriminative interaction toward DRD1 agonists/antagonists. The real-time responses from the DRD1-nanohybrid FET were highly sensitive and selective for dopamine agonists/antagonists, and their maximal response levels were clearly different depending on their DRD1 affinities. Moreover, the equilibrium constants ($K_a$) were estimated by fitting the response levels. Each $K_a$ value indicated the variation in the affinity between DRD1 and the agonists/antagonists: greater $K_a$ value corresponds to a stronger DRD1 affinity in agonism, whereas a lower $K_a$ value in antagonism indicates a stronger DA-blocking effect.

BM07.05.09
High-Performance Biosensor Using Multi-Channel System Graphene Field Effect Transistor (GFET) Microfluidics for the Rapid Bacteria Detection
KyoungHo Kim and Oh Seok Kwon; Korea Research Institute of Bioscience & Biotechnology (KRIBB), Daejeon, Korea (the Republic of).

Over the past of decades, bacteria monitoring is critical in detecting bacteria from contaminated drinking water and food. A various kind of bacteria detection methods such as electrical or optical sensor has been developed. Nevertheless, although many studies with bacteria detection sensors have been reported for high performance detecting properties, the development of the bacteria sensor still remains as challenge. Herein, we study the demonstration of graphene field-effect transistor (GFET) microfluidics using single-layer graphene micropatterns and characterize its monitoring capacity in bacteria detection. The GFET microfluidics had excellent mechanical/electrical properties in fluidics and showed high sensitivity and selectivity for a target in bacteria mixture. Based on those results, our GFET microfluidics can provide potential applications in the field of disease diagnostics at early stage.

BM07.05.10
Field Effect Transistor Based In Vitro Dopamine Aptasensor
Jiyoon Lee and Oh Seok Kwon; Korea Research Institute of Bioscience and Biotechnology, Yuseong-gu, Korea (the Republic of).

In this study, ultrasensitive and precise detection of a representative brain hormone, dopamine was pursued and demonstrated using functional conducting polymer nanotubes modified with aptamer. The produced aptasensor was composed of a micropatterned gold electrode, carboxylated polypyrrole nanotubes, and specific aptamer molecules. The sensor was constructed by sequential deposition of the PPy-COOH nanotubes and aptamer molecules on the electrode. The sensitivity and selectivity of this sensor were monitored using field effect transistor type measurements. In addition, real dopamine released from PC12 and SH-SY5Y cells induced by high concentration potassium ion (K+) stimulus were also analyzed and compared with the data obtained from the sensitivity (1 nM) and selectivity tests. This article can provide the feasibility for practical use of simple and efficient field effect transistor type aptasensor.

BM07.05.11
Traditional Conjugated Polymer as Efficient Mixed Conductors for High-Performing Electrochemical Transistors
Priscila Cavassin and Gregorio C. Faria; Universidade de São Paulo, São Carlos, Brazil.

Organic electrochemical transistors have garnered attention for applications in biological interfacing, logic circuits and neuromorphic devices. [1] Despite recent advances in device fabrication and materials development, however, only a narrow class of polymers have been found to stably operate in these new applications. To this end, we have developed general guidelines that allow for the fabrication of OECTs with semiconducting polymers that do not uptake water efficiently. The methodology produces devices that operate stably at room temperature, exhibits excellent transistor characteristics, (e.g., transconductance and volumetric capacitance), and is versatile, making it possible to fabricate OECTs with virtually every conjugated polymer synthesized to date. Using the general guideline here proposed, we have successfully fabricated high-performing OECTs using standard conjugated-polymers, such as, poly(3-hexylthiophene) (P3HT). Additionally, by fitting the transient curve response and transfer curves of our OECTs, we are able to extract key fundamental properties of both the device and the active channel materials, including the volumetric capacitance ($C_v$), the intrinsic hole/electron mobility ($\mu$), as well as the product $\mu*C_v$, which has been used as the benchmark for comparing OECT device. [2] We have used such benchmark to compare our OECTs performance with previously reported materials and show that some of our devices are the best published to date. Furthermore, we showed applications of these devices in biosensing.

References:

BM07.05.12
Anion-Dependent Doping and Charge Transport in Organic Electrochemical Transistors
Lucas Q. Flagg, Rajiv Giridharagopal and David S. Ginger; Chemistry, University of Washington, Seattle, Washington, United States.

We study the effects of different dopant anions on mixed ionic/electronic transport in organic electrochemical transistors (OECTs) based on poly(3-hexylthiophene-2,5-diyli) (P3HT). We show that the electronic transport properties depend on the anion present in the electrolyte, with greater transistor currents resulting from the use of polyatomic anions such as such as trifluoromethanesulfonilimide (TFSI) as compared to halide anions. Using spectroelectrochemistry, we show the maximum doping level at a given bias is also anion dependent. Furthermore, we find that the average electronic carrier mobility depends on the identity of the compensating counterion. We investigate this effect further using electrochemical quartz crystal microbalance (EQCM) measurements, showing the solvation shell of the dopant anions within the polymer varies drastically depending on the type of anion. Surprisingly, we find that the doping kinetics in these OECTs is faster for larger anions. Lastly, we use electrochemical strain microscopy (ESM) to resolve ion-dependent differences in local swelling on the nanoscale, providing further insight into the interplay between local polymer structure and ion uptake. These measurements show that the chemical properties of the compensating ion are an important design consideration for polymer materials with mixed ionic/electronic conductor applications.

BM07.05.13
Liquid-Ion Gated Field-Effect Transistor (FET) with Human Dopamine Receptor Integrated-Multidimensional Conducting Polymer Nanofiber for Dopamine Detection
Seon Joo Park and Oh Seok Kwon; KRIBB, Daejeon, Korea (the Republic of).

Dopamine (DA) has been studied in the field of nervous and cardiovascular systems. Abnormal levels of dopamine is an indicator of neurological
disorders, resulting in Alzheimer's and Parkinson's diseases. Therefore, dopamine is a clinically useful diagnostic sign and requires a novel approach with high sensitivity, selectivity and a rapid response. Various sensors have been developed, such as high-performance liquid chromatography (HPLC), mass spectrometry, and spectrophotometry. However, they are limited by their high cost, low sensitivity, and variable label response.

The field-effect transistor (FET) has been used in the development of diagnosis for several decades. It is gated by changes of charge carrier density in the channel induced by the binding of target molecules, leading to high-performance biosensors. In addition, the FET platform has attracted due to their low cost, easy operation, fast response, label-free operation, parallel sensing as well as high sensitivity.

In this article, we introduced a high performance dopamine sensor based on FET assay. Multidimensional carboxylated poly(3,4-ethylenedioxythiophene) (MCPEDOT) NFs membrane was utilized as the conductive channel of sensor in the FET system. Interestingly, it provided high performance sensing due to enhanced interaction from high surface area and gate-potential modulators. Moreover, hDRD1, G protein-coupled receptors (GPCRs) as the recognition elements, was first expressed in Escherichia coli and modified with the surface of MCPEDOT NFs, leading to high selectivity. As a results, the hDRD1-MCPEDOT NF-based FET exhibits a rapid real-time response (~2 s) with high dopamine selectivity and sensitivity performance (approximately 100 FM).

BM07.05.14

Nanoionic Electronic Nose with Human olfactory Receptor-Functionalized Graphene Micropatterns for the Analysis of the Spoiled Odor, Trimethylamine Sung Fun Seo and Oh Seok Kwon; Korea Research Institute of Bioscience and Biotechnology, Daejeon, Korea (the Republic of).

Trimethylamine(TMA), a odor from the spoiled meat, is a positive proof that we can decide if the food is spoiled or not. We demonstrated the nanoionic electronic nose using the human olfactory receptor(hOR) functionalized graphene field-effect transistor (GFET). At first, the hOR is prepared from the Escherichia coli (E. coli) for the sensing of the real food sample’s TMA. The nanoionic electronic nose was characterized by SEM, TEM, I-V and transfer curve. The real-time responses under liquid-ion gated system showed that the bioelectronics nose with hOR-conjugated GFET had higher selectivity and specificity compared to conventional electronic noses without bio-receptors. Moreover, the nanoionic electronic nose could provide the effective criteria to judge the food’s freshness. The most advantage of this research is the quantitative analysis of the popular fish. Moreover, it can be utilized to any other real food samples with only the reactive receptor.

BM07.05.15

High Molecular Density Bio-Electronic Sensor Based on 2D Crystalline Interface and QTY Modified GPCR Proteins Rui Qing1, Andreas Breuwiesser2, Giovanni Azellino1, Mantian Xue1, Jiuyuan Zhao1, Uwe Sleytr1, Jing Kong1 and Shuguang Zhang1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2University of Natural Resources and Life Sciences Vienna, Vienna, Austria.

Bio-electronic is an emerging interdisciplinary subject which utilizes biomolecules in electronics or mimics biological architectures. One important aspect of the field is to fabricate sensors for biomolecules detection, i.e. ligands. Researchers previously designed sensors based on metal-oxide-semiconductor (MOSFET), polymers and inorganic crystalline materials which produce decent sensitivity but lacks selectivity. Recent efforts are devoted on directly connecting biological receptors with electronic systems. G protein-coupled receptors (GPCR), are the largest family of membrane receptors that detects information (molecules and lights) and transduce to cell internal signals to regulate body functions. There are nearly 1000 types of GPCR proteins in human body, each one being highly specific to a particular signal, which make them suitable candidates as sensors in bio-electronic devices. Based on our previous reported novel approach of QTY modification on GPCR proteins, we were able to obtain water soluble receptors active to their natural ligands without adding any detergent. Recombinant SbpA S-layer proteins can reproduce ordered 2-dimensional crystalline monolayer in vivo and were employed as the intermediate layer between biomolecules and electronic substrates. By fusing –Fc region of human IgG protein to GPCRQTY and Protein G onto SbpA, we successfully formed GPCR-S-layer complex and anchor them onto the electronic active surface, i.e. Si wafer, graphene, etc. SbpA proteins also helped to guide the orientation of attached GPCRQTY proteins and expose their active binding sites. The assembly yields functional molecule monolayer density as high as 2.37-4.73*1012 molecule/cm2. 

BM07.05.16

The Charge Carrier Modulation in PEDOT:PSS Films via Chemical Crosslinking with PVA Ji Hwan Kim and Myung-Han Yoon; School of Materials Science and Engineering, Gwangju Institute of Science & Technology (GIST), Gwangju, Korea (the Republic of).

Recently, the charge carrier modulation in semiconducting polymer films has drawn much attention, but there exist a relatively small number of studies on the charge carrier modulation in highly conductive polymer films despite their potential for energy storage and bioelectronics applications. In this work, we report the charge carrier modulation of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) films and its application to organic electrochemical transistors (OECTs) with finely-tuned threshold voltage characteristics by crosslinking with polyvinyl alcohol (PVA) as a de-dopant. PVA was blended with an aqueous solution of PEDOT:PSS and the PEDOT:PSS-PVA blend films were chemically crosslinked in the solid state. The electrical characterization revealed that the crosslinking with PVA significantly lowered the conductivity from 1800 to 80 S/cm, the volumetric capacitance form 100 to 1 F/cm, and the hole concentration from 3.3 × 1017 cm−3 to 7.5 × 1016 cm−3 in the PEDOT:PSS-PVA hybrid films. Despite the inclusion of electrically insulating polymer in the conductive material, however, the resultant OECT devices exhibited relatively high on-current (~1 mA), large current on/off ratio (>104), and excellent transconductance (>2 mS), which are acceptable for bioelectronic sensors with the customized electrical/electrochemical properties. In addition, the concurrent threshold voltage shift from 0.5 to 0.3 V upon PVA crosslinking suggests that the PEDOT:PSS-PVA hybrid channel can offer finely tunable threshold voltage characteristics to OECT devices without the significant degradation in OECT performance.

BM07.05.17

Nano-curvature Effect on Electrical Properties of Conductive Polymer Thin Films for Bioelectronics Applications Grazia M. Messina, Nunzio Tuccitto, Giovanni Li Destri and Giovanni Marletta; University of Catania, Catania, Italy.

The use of conducting polymers has a great deal in the last decades. It is mainly due to the possibility to employ them in tissue engineering, neural probes, biosensors, drug delivery and bioactuator in order to create an interface with living cells and tissue. Electrical stimulation (ES) is one of the agents that may modulate the interaction at the interface, in particular at the bioactive interface. The optimization of the CP bioactive interface is crucial since the first contact between biological systems and biomaterials is done at interface. In this study we investigate the preparation and modification of thin film of P3HT and PEDOT:PSS, in view of tuning their electrical properties by appropriate surface nanostructuring. In particular, we have studied the effect of nano-curvature of the electrical properties on the conductive layers of the polymer films. Controlled modification of the nano-curvature of conducting polymer film has been obtained by preparing hexagonally packed arrays of colloidal nanoparticles of different diameter and using these nanostructured surfaces as substrates for the deposition of the conducting polymer thin films. Interdigitated electrodes, having strips 5μm width, have been used as structure for the electrical measurements. The nanostructured surfaces have been
Highly Sensitive Lactate Sensors Based on Carbon MEMS (CMEMS) Shafrad Forouzanfar, Chunlei Wang and Nezih Pala; Florida International University, Miami, Florida, United States.

L-Lactic acid is one of the important metabolites produced during the anaerobic phase of glycolysis, making its precise determination highly important in various fields such as clinical diagnosis, sport, and military activities. Lactate plays a crucial role in several areas of human health, including heart failure, hepatic dysfunction, shock, respiratory insufficiency and systemic disorders. In sports medicine, knowledge of optimal blood lactate levels is vital to ensuring the maximum performance of an athlete during intensive exercise and endurance-based activities. Various methods have been developed for determining lactate levels, such as optical, nuclear magnetic resonance, liquid chromatography, fluorimetry, and amperometry. Among these methods, electrochemical ones possess advantages such as simple instrumentation, low detection limit, and wide dynamic range, as well as high selectivity and stability. A Carbon-microelectromechanical system (CMEMS) is one in which Carbon is synthesized through pyrolysis of micro patterned photore sist polymer in an oxygen-free environment under high temperatures. Carbon possesses various remarkable properties such as a wide electrochemical window, low non-specific adsorption of biomolecules, excellent biocompatibility, and low cost. Furthermore, carbon-based materials exhibit good electrical conductivity, as well as good tolerance toward bio-fouling. The surface of the carbon can be functionalized efficiently via various physical, chemical, or electrochemical treatments. CMEMS devices circumvent the major drawbacks associated with commercialized screen-printed carbon electrodes such as low resolution and miniaturization.

We developed an electrochemical CMEMS-based sensing platform to detect L-Lactic Acid. The sensing platform of the biosensor—interdigitated carbon micro fingers—was synthesized by pyrolysis of photo-patterned photoresist polymer in oxygen-free and high-temperature conditions. The surfaces of the fingers were functionalized by an oxidation pretreatment technique involving oxygen reactive ion etching (RIE) to form –COOH on glassy carbon. Taking advantage of having high concentrations of this carboxylic group on the surface of the carbon, we immobilized Lactate Oxidase (LOx) on the surfaces of the interdigitated carbon micro fingers without any other surface pretreatments. We employed various analytical characterization methods such as Fourier-transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) for material characterization. Sensing capabilities were measured by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS). The carbon capacitive sensor demonstrated detection of lactate over a wide dynamic range of 50 nM-5 mM for the electrode area of 0.5×0.5 cm². The sensitivity of this linker-free lactate sensor was found to be 40 nM/cm², making it the first carbon capacitive L-lactate sensor with such high sensitivity.
Microfiber-Based Organic Electrochemical Transistors for Channel Dimension-Independent Single Strand Wearable Sweat Sensors Youneseok Kim¹, Seong-Min Kim¹, Taekyung Lim², Sanghyun Ju³ and Myung-Han Yoon¹; ¹Gwangju Institute of Science and Technology, Buk-gu, Korea (the Republic of); ²Kyunggi University, Suwon, Korea (the Republic of).

Herein, we report conjugated polymer microfiber-based organic electrochemical transistors (OECTs) for single strand fiber-type channel dimension-independent wearable sweat sensors. The highly conductive microfibers were fabricated by simple wet-spinning of aqueous poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solutions, and PEDOT:PSS microfiber-based OECTs were successfully constructed showing high on-current (>5 mA), current on/off ratio (>10³), and transconductance (> 80 mS). Owing to excellent electrical/electrochemical characteristics and aqueous stability of PEDOT:PSS microfibers, the resultant OECT devices exhibited the linear response to aqueous cations at the large dynamic range (10⁻⁴ - 10⁻² M) as well as the high device fabrication reproducibility. Moreover, the proposed method for extracting the ion concentration sensitivity is independent of microfiber channel dimensions (e.g., length, width, diameter), leading to the definition of the suitable figure-of-merit even at arbitrary channel dimensions. Finally, we developed single strand fiber-type wearable sweat sensors, and demonstrated that the resultant sensors can perform real-time repetitive measurements of ion concentrations in human sweat samples.

Simultaneous Co-Electrodeposition of Plasma Protein/Iridium Oxide Hybrid Film for Electrically Controlled Drug Release Applications Fu-Erh Chen¹, Zheng-Ting Tang², Pochun Chen¹ and Wei-Chen Huang²; ¹National Taipei University of Technology, Taipei, Taiwan; ²Taipei Medical University, Taipei, Taiwan.

Implantable neurostimulation devices have been attracted considerable attention recently. When a neural stimulating electrode is implanted in vivo, neural disorders can be treated by electrostimulation. Additionally, electrically controlled drug release has been particularly attractive for bioelectronics because the electrical signal is portable and controllable on-demand, without the requirement of large or special equipment. However, protein-based bioactives such as growth factors or antibodies are easily denatured to lose their bioactivity in response to external stimulation. It is challenging to develop a bioelectrode system that permits the electrically responsive release of proteins without damage. In this study, a facile co-electrodeposition method has been developed to form a hybrid film of iridium oxide and plasma protein. We carried out a cyclic voltammetry approach to co-electrodeposit iridium oxide and plasma protein on ITO-coated glass substrates. We characterized and evaluated the hybrid electrolytes and deposited films for bio-electrode applications. We also demonstrated the releasing behavior triggered by an electric field. In addition, the biocompatibility of the hybrid films was also investigated by testing the cell viability.

Development of Highly-Conductive Crystallized PEDOT:PSS Microfibers for Wearable Bioelectronics Applications Myung-Han Yoon; Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Despite the great potentials of polymer microfibers toward human-friendly wearable and implantable bioelectronics, most of the previous polymeric electronics have been limited to thin film-based devices due to the practical difficulties in preparing conductive microfibers with desired characteristics and fabricating free-standing fiber or woven textile devices. Herein, we report highly conductive polymer microfibers prepared by wet spinning and their application to microfibrillar bioelectronics. First, we developed the simple wet-spinning process to form highly conductive crystalline poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) microfibers. PEDOT:PSS microfibers with various cross-sectional areas, compositions, and crystallinity could be prepared by varying wet spinning conditions such as needle size, injection speed, coagulation bath, etc., while the corresponding mechanical, electrical, electrochemical properties were carefully examined. The resultant microfibers showed very high conductivities (~1000 S/cm) and capacitances (~70 F/g) with decent mechanical strength (~1 GPa), which exceed the metrics of PEDOT:PSS microfibers reported in the previous literature. Finally, we successfully proved the potential of conducting polymer microfiber-based bioelectronics by demonstrating the PEDOT:PSS microfiber-incorporated textile for wearable electrolymography sensor and the PEDOT:PSS microfiber organic electrochemical transistor for cation concentration sensor in human sweat.

Organic Bioelectronic Fibers and Capillaries Magnus Berggren, Daniel Simon, Eleni Stavrinidou and Roger Gabrielson; Linköping University, Norrköping, Sweden.

Organic electronic materials offer mixed ion electron conduction and signal processing and can be manufactured into various flexible and soft device configurations using solution-based processing protocols. While bridging the biology-technology signaling gap, to record and regulate biological functions, it is crucial to develop a bioelectronic form factor that enables signal translation at high spatiotemporal resolution, close proximity and at minimal invasiveness. Fiber and capillary structures are natural and common structures of most biological systems, they serve as confined transportation highways of biological components, biochemicals and signals. Here, developments of organic bioelectronic fibers and capillaries are reported. Conductors, electrodes, transistors and electronic ion pumps have been manufactured into capillary and fiber structures to enable non-invasive integration and high-quality signal translation across the biology-technology gap. For instance, organic electronic ion pumps have been manufactured inside glass capillary structures, with an outer diameter of 60 micrometers, and has been applied to various biological systems to deliver signal substances at high spatial resolution. Conductors, electrodes and transistors have been manufactured or have been applied into or onto the vasculature or fibers, of living system, resulting in passive and active bioelectronics for recording and sensing of physiology and bio-signaling. The resulting technology, which utilizes the twinning of living biological components and organic bioelectronic materials, to form active devices have been applied to various biological settings to for instance monitor action potentials and to form small scale bioelectronic circuits.
The efficiency of devices for bioelectronic applications, including neuronal stimulation, is heavily dependent on the scale and the performance level. With miniaturization of stimulation electrodes, achieving a sufficiently high current pulse to elicit action potentials becomes an issue. We have developed the organic electrolytic photocapacitor (OEPc) for stimulation of light-insensitive retinas, previously achieving pixels of 100 μm in diameter. In the work herein, we report on our approach of arranging pixels of photocapacitors vertically in order to substantially increase the photovoltage and charge density without sacrificing lateral area. The tandem devices are created by stacking vertically p-n junctions made of semiconducting organic small molecules with 1 nm recombination layers of gold in between. These devices still do not exceed a total thickness of 300-500 nm. These devices represent a substantial improvement over previously-reported single p-n junction OEPcs, and are able to generate five-times higher voltages and at least double the charge densities. We have tested the efficacy of tandem devices using measurements of xenopus oocytes, where we find substantially enhanced stimulation of K+ channels relative to single-junction devices. Finally, we have used the tandem approach to microfabricate optoelectronic stimulation pixels (< 50 μm) for retinal prosthesis, validating their performance by measuring light-insensitive retinal extracts. These results corroborate the conclusion that OEPc technology not only has achieved parity with state-of-the-art silicon devices, but can exceed them in miniaturization and performance.

9:30 AM BM07.06.06
Photosynthetic Bacteria-Based Biohybrids for Organic Bioelectronics Gianluca M. Farinola1, Francesco Milano1, Roberta Ragni1, Marco Lo Presti1, Simona la Gatta1, Livia Giotta2, Angelo Agostiano1-3 and Massimo Trotta1,1University of the Studi-Bari Aldo Moro, Bari, Italy; 2Dipartimento di Chimica Universitá degli Studi di Bari “Aldo Moro”, Bari, Italy, CNR IPCF UOS BARI, Bari, Italy; 3Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Ecotekne, Monteroni, Lecce, Italy.

The photosynthetic bacterial Reaction Center (RC) is a specific transmembrane multi-subunit protein complex which photogenerates charges to fuel the photosynthetic process [1]. The RC exhibits a conversion efficiency of photons to electrons close to 100%. The possibility of taking advantage of such excellent photoconversion efficiency to create functional nanomaterials and bio-hybrid devices is very attractive [2]. We recently demonstrated that the light harvesting capability of the native RC in the visible spectral region is increased by covalently affixing different tailored molecular antennas, thus obtaining hybrid systems which outperform the native protein in solar light absorption and photogeneration [3,4]. The RC integration in bioelectronic devices is an appealing challenge that has recently been explored. It demands for proper approaches to implement the biological photoconverter in either nanocostructs and/or bio-integrated devices. The lecture will discuss chemical routes to hybrid RC-based materials, focusing on: i) retainment of perfectly unaltered functions of the RC photoenzyme in confined environments [5]; ii) creation of functional interfaces between the biological structure and the electrodes’ surface. Highly selective chemical strategies to address these systems at the interfaces with electrodes in bioelectronics devices will be presented. The role of organic synthesis and self-assembly techniques in bridging the gap between the biotechnological production of materials and engineering of the devices will be highlighted.

References
recently combined fiber-based fabrication with direct tough-hydrogel integration. These probes exhibited tunable mechanical moduli allowing for deep-brain implantation without adverse tissue response and permitting tracking of identifiable action potentials for 6 months. In addition to enabling neural activity, fiber-based devices can guide nerve growth. To produce biocompatible nerve guidance scaffolds, we have developed porous fibers, where the pores were established via salt-leaching following thermal drawing. This process allowed for control over the pore sizes in fibers produced from arbitrary polymers with a range of dimensions and cross-sectional geometries.

11:00 AM BM07.06.09
Effective Weight Control via an Implanted Self-Powered Vagus Nerve Stimulation Device Xudong Wang1, Guang Yao2,3, Weibo Cai1 and Lei Kang1,2,1 University of Wisconsin-Madison, Madison, Wisconsin, United States; 2Peking University First Hospital, Beijing, China; 3University of Electronic Science and Technology of China, Chengdu, China.

In vivo vagus nerve stimulation holds great promise in regulating food intake for obesity treatment. Here we present an implanted vagus nerve stimulation (VNS) system that is battery-free and spontaneously responsive to stomach movement. The VNS system comprises a flexible and biocompatible nanogenerator that is attached on the surface of stomach. It generates biphasic electric pulses in response to the peristalsis of stomach. The simulated other electrical stimulation strategies. This work also provides a new concept in therapeutic technology using artificial nerve signal generated from (VNS) system that is battery-free and spontaneously responsive to stomach movement. The VNS system comprises a flexible and biocompatible nanogenerator that is attached on the surface of stomach. It generates biphasic electric pulses in response to the peristalsis of stomach. The simulated other electrical stimulation strategies. This work also provides a new concept in therapeutic technology using artificial nerve signal generated from

11:15 AM *BM07.06.10
Miniature, Wireless Neural Stimulation Using Magnetoelectric Materials Jacob T. Robinson; Rice University, Houston, Texas, United States.

Wireless neural stimulation is important for implantable bioelectronic devices, and neuroscience experiments in freely moving animals; however many wireless stimulators require batteries or large receiver coils, that limit the ability to make miniature implants. Here we present a new approach for wireless neuromodulation that uses a material to convert magnetic fields that freely penetrate the brain into electric fields that stimulates nearby neurons. Because these materials do not rely on electromagnetic waves for power harvesting, they can be made millimeter sized while retaining high power conversion efficiencies. To create these biocompatible “magnetoelectric” materials we fabricated a film of a piezoelectric material polyvinylidene fluoride bonded to a magnetostriuctive film of Metglas. We then encapsulated the final films to make them biocompatible. We find that these magnetoelectric films can generate voltages above ten volts using alternating magnetic fields with an amplitude of about 1 mT. We also demonstrate that a simple film is able to stimulate cellular activity in vitro in excitable HEK cells and acute brain slices. We also show that light-weight millimeter-scale films enable wireless activation of neural activity in freely-moving rats. Overall, our results show that magnetoelectric materials offer great promise for wireless electrical stimulation of specific brain areas. The basic understanding of magnetoelectric neural stimulation can also be used to develop novel magnetoelectric materials (such as nanoparticles or nanofibers) to achieve even more targeted and less invasive wireless neural stimulation technologies.

11:45 AM BM07.06.11
Wireless Magnetoelectrical Neural Stimulation Mediated by Magnetic Nanodics Alexander Senko, Danijela Greguric, Ian Tafel, Pooja Reddy, Dekel Rosenfeld, Siyuuan Rao, Michael G. Christiansen, Po-Han Chiang, Seongjun Park and Polina Anikeeva; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

A new technique has been developed for magnetic nanoparticle-based neural stimulation. Unlike magnetothermal neural stimulation, which is based on the transfection of neurons to sensitize them to heat, this magnetoelectromechanical approach does not rely on transgenes, making it potentially safer for clinical applications. In contrast to previously reported magnetomechanical stimulation techniques, in which neurons are typically hundreds of microns or less from a magnetic field source, the field required for this technique (1–50 mT, 1–20 Hz) is produced at the scale of an entire rodent model using a simple solenoid and a 200 W audio amplifier. This advantage in stimulated volume is enabled by magnetic nanodics with volumes hundreds of times larger than conventional magnetic nanoparticles, but which have favorable colloidal properties due to their disc shape. These magnetic nanodics possess a spin vortex state, which nearly eliminates stray field and results in less inter-particle attraction compared to isotropic magnetic particles of similar volume. The neural stimulation technique enabled by these magnetic nanodics has also demonstrated to robustly induce calcium influx in sensory neurons in rat dorsal root ganglion (DRG) explant cultures and enhance rat expression of an immediate early gene c-fos in DRGs of adult rats. This technique may find applications in basic studies of neural circuits as well as pave the way for future neuromodulation therapies.

SESSION BM07.07: Electronic Actuators/Novel Architectures II
Session Chairs: Mehmet Kanik and Jacob Robinson
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Constitution B

1:30 PM BM07.07.01
On-Demand Generation of Chemical Signals with Electromagnetic Fields for Neuronal Modulation Jimin Park1,2, Junsang Moon1,2, Po-Han Chiang1, Dena Shahbazi1, Atharva Sahasrabudhe1, Siyuuan Rao1, 2 and Polina Anikeeva1, 2; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The development of electromagnetic tools for neuronal stimulation can significantly enhance our understanding of signaling pathways in the brain and enable treating neurological disorders. To date advances in the design of neural probes and magnetic nanoparticles have provided promising opportunities for electrical and mechanical stimulation of neurons under electromagnetic fields. However, robust chemical stimulation of neurons has not yet been achieved with these systems due to difficulties in generating chemical signals under electromagnetic fields. Here, we developed two material systems that formed either protons or reactive-oxygen-species (ROS), which are both important chemical species in the nervous system, under electromagnetic field and demonstrated their utility for chemical stimulation of neurons. In the first system, a polymer-magnetic nanoparticle nanohybrid was designed that released protons upon exposure to an alternating magnetic field. Hysteretic heat dissipation by magnetic nanoparticles accelerated the degradation process of biodegradable polymer matrix within the nanohybrid, which in turn led to the release of protons and
change in pH of solution. The proton release kinetics from the nanohybrid was regulated by adjusting material properties, synthesis method, and magnetic field conditions. The ability to optimize nanohybrid system indicated its potential for wireless magnetic-field driven stimulation of acid-sensitive ion channels.

The second material system composed of transition-metal based nanoparticles that generated ROS. Inspired by biological enzymes interacting with ROS, an iron-based nanocatalyst, which has a crystal structure and material properties similar to those of these enzymes were designed. Through combined electrochemical and spectroscopical analyses, we confirmed that the catalyst could convert soluble precursor ions to ROS in solution in the presence of electric field. It is noteworthy that, by changing electric field conditions, such as current or voltage, ROS releasing behavior from the catalyst was quantitatively controlled. In vitro tests suggested that this system could stimulate ROS-sensitive channels, which may be a potential method to differentiate the roles of ROS in the nervous system.

We envision that these material systems can broaden the current palette of electromagnetic approaches for neuronal stimulation.

1:45 PM BM07.07.02

A Bioelectronic Solution for a Health Problem—An Implantable Integrated System to Treat Neurogenic Underactive Bladder

Faezeh Arab Hassanini1, 2, Chengkuo Lee1, 2 and Ninath V. Thakur1, 2; Singapore Institute for Neurotechnology, National University of Singapore, Singapore, Singapore; 2Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore.

Bioelectronics shapes a new era aiming to solve the health problems by merging the electronics, and biology science [1]. Incomplete emptying of the bladder may happen due to the atrophy of the detrusor muscle, or disease or damage to the afferent nerve system, i.e. neurogenic underactive bladder (UAB) [2]. For neurogenic UAB patients, the nerve stimulation maybe a solution, however, it may lead to several complications [3]. Using of catheters is the other treatment for these patients, but this treatment is not without shortcomings [2]. Therefore, we proposed a device that could physically contract the bladder muscle to void [4-6]. The recently proposed device, is an implantable integrated system that consists of a sensor to detect the fullness status of the bladder, and an actuator to initiate assisting the bladder muscle for the consequent voiding [6].

The shape memory property of shape memory alloy (SMA) components allows the voluntary activation and voiding of the bladder by patient. The actuator was designed by using of two flexible polyvinyl chloride (PVC) sheets as the substrate for the SMA components. A spring SMA with the transition temperature of 45°C was the main component for the actuation that resulted in a bi-stable bending of the PVC sheet during one 20 s cycle of activation. Two compression and restoration phases was designed for the device for multiple activations. We have designed, fabricated, and experimentally tested various designs and configurations for the actuator on anesthetized rat animal models [4-6]. The recent SMA spring-based actuator provided a substantial voiding percentage of about 80% with the reduced total energy consumption compared to the originally proposed devices. We have tested various types of sensors for the integration with the actuator from commercial piezo-resistive force sensors [5], quantum tunnelling composite-based sensors [7], and finally triboelectric energy harvesting (TENG) sensors [6]. The wet sponge-based TENG sensor consists of water and polydimethylsiloxane (PDMS) as the two materials with different electron affinities. The output triboelectric voltage can be used as a feedback control signal to the patient for initiating the activation of the actuator and voiding.

The integration of a sensor with the actuator is necessary for neurogenic UAB patients. However, the integrated sensor should be flexible enough not limiting the voiding capability of the actuator, and at the same time provide repeatable output signal to the patient. Our future work, is focusing on designing new solutions to assist the lost sensation of neurogenic patients.


2:00 PM *BM07.07.03

Nanostructures as Electromagnetic Bio-Transducers

Jürgen Kessel1, Aldo I. Martinez Banderas1, Ainur Sharip1, Antonio Aries Trupote2, Nofa Alsharif1, Aitziber Lopez Cortajarena1, Jasmeen Merzaban1 and Timothy Ravasi1; 1King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2IMDEA Nanociencia and Nanobiotechnology Unit associated to Centro Nacional de Biotecnología (CNB-CSIC), Campus Universitario de Cantoblanco, Madrid, Spain; 3CIC BiomaGUNE, Parque Tecnológico de San Sebastián, San Sebastian, Spain.

Unique features of magnetic nanowires render them attractive materials for biomedical transducer applications. Due to the high aspect ratio, they are characterized by single magnetic domain properties, which can be exploited by electromagnetic interrogation. This allows utilizing such nanowires as remotely operated nanorobots, i.e. induce motion, produce heat or sense their location. Their versatility is further enhanced by surface functionalization, making them cell-specific targeting agents or drug delivery vehicles. Magnetic nanowires are fabricated by a facile and efficient method using electrodeposition into nanoporous membranes. Iron nanowires are highly biocompatible, and they can be further optimized by annealing, resulting in nanowires with an iron core, an iron oxide shell and tailored magnetization. In combination with polymer matrices, nanowires are employed as ultra-low power flow sensors, for realizing bioinspired artificial skins with tactile sensing capabilities, or to trigger remotely controlled drug delivery particles. Magnetic nanowires are readily internalized by cells via phagocytosis. When applying an alternating magnetic field, they kill cancer cells by a magnetomechanical effect. When further functionalizing the nanowires with drugs, they deliver these drugs into cells, and a combined treatment effect can be obtained together with a magnetic field and/or laser irradiation. The later exploits a photo-thermal effect, that utilizes the near infrared light absorption of iron oxide. Surface coating with antibodies give nanowires specific targeting capabilities, as will be shown for the case of anti-CD44 antibodies to target leukemic cells. The nanowires also have excellent properties as magnetic resonance imaging contrast agents, providing high transverse magnetic relaxivities. This enables high-resolution cell tracking in combination with their manipulation. Nanostructured substrates for cell growth can be produced, when partially releasing the nanowires from the nanoporous membranes. Due to mimicking the mechanical properties of cellular environments, stem cells growing on top of such substrates show alterations in their differentiation behavior. Thereby, nanowire dimensions modify the stiffness of the cellular environment, affecting the cells’ behavior. A mechanical stimulus can be applied via activating the substrate by an electromagnetic field, providing means for additional manipulations of the cell fate. Differentiation of mesenchymal stem cells into osteoblasts can be achieved on such substrates by electromagnetically induced mechanical stimuli within a few days. With the growing relevance of nanomaterials in biomedical applications, multifunctionality of nanoprobes is being discovered and exploited. Combining a high capacity for functionalization, with diagnostic capabilities and therapeutic functions, iron nanowires are ideal candidates for these theranostics approaches.

2:30 PM BREAK
An important aim of regenerative medicine is to restore tissue function with implantable, laboratory-grown constructs that contain tissue-specific cells that replicate the function of their counterparts in the healthy native tissue. In this talk I will describe our recent work in the development of materials for bioelectronics including polymers and functionalised nanoneedles. I will also describe our new imaging technologies for monitoring and elucidating the cell-material interface.

Complicated real-world tactile information is efficiently processed by the biological mechanosensory system. The basic building blocks of the biological mechanosensory system are mechanoreceptors, neurons, and synapses. We fabricated flexible organic devices to emulate the building blocks and the signal processing of a biological mechanosensory nerve. Our organic artificial mechanosensory nerve [1] consists of pressure sensors, organic ring oscillators, and organic synaptic transistors. A cluster of pressure sensors receive pressure inputs, which are converted to voltage pulses by a ring oscillator. A synaptic transistor integrates the voltage pulses from multiple ring oscillators. We used our artificial mechanosensory nerve to detect movement and large-scale textures of an object and distinguish braille letters. Also, our artificial mechanosensory nerve and biological motor nerves in a detached insect leg formed a hybrid reflex arc to actuate the muscles of the leg. Our flexible organic artificial nerve can be used in neurorobotics and neuroprosthetics.

An important aim of regenerative medicine is to restore tissue function while bone marrow stem cells (BMSCs) can differentiate into Schwann cells under appropriate conditions. We have investigated the differentiation of BMSCs into Schwann cells on scaffolds comprised of electrosprun nanofibers. We changed the alignment, diameter, and surface properties of the fibers to optimize the differentiation efficiency. The uniaxial alignment of fibers not only promoted the differentiation of BMSCs into Schwann cells but also dictated the morphology and alignment of the derived cells. Coating the surface of aligned fibers with laminin further enhanced the differentiation and thus increased the secretion of neurotrophins. When co-cultured with PC12 cells or chick dorsal root ganglion, the as-derived Schwann cells were able to promote the outgrowth of neurites from cell bodies and direct their extension along the fibers. Furthermore, we constructed a multi-tubular conduit with a honeycomb structure from the electrosprun fibers by mimicking the anatomy of a peripheral nerve. A bilayer mat of electrospun fibers was rolled up to form a single tube, with the inner and outer layers comprised of aligned and random fibers, respectively. Seven such tubes were then assembled into a hexagonal array and encased within the lumen of a larger tube to form the multi-tubular conduit. By introducing an adhesive to the regions between the tubes, the conduit was robust enough for handling during surgery. The seeded BMSCs were able to proliferate in all the tubes with even circumferential and longitudinal distributions. Under chemical induction, the BMSCs were transdifferentiated into Schwann-like cells in all the tubes. The cellular version holds great promise for the potential repair of large defects in thick nerves peripheral nerve repair.
Self-Assembling Peptide-Based Tissue-Like Hydrogel for Highly Effective Neural Interface

Jinyoung Nam,1 Hyung-Kyoung Lim,2 Minah Suh1 and Yong Ho Kim1,2,3
1SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Korea (the Republic of); 2Center for Neuroscience Imaging Research, Institute for Basic Science (IBS), Suwon, Korea (the Republic of); 3Department of Biomedical Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

The biomechanical dissimilarity between rigid electrodes and soft neural tissues is a recurring problem in recording neural activity from the live brain, yet the development of stable neural interfaces that enable a complete biointegration remains a challenge. Self-assembling peptide has great advantages in developing a new biomaterial because along with its inherent biocompatibility, chemical and physical properties in macroscopic level can be controlled by sequence modulation. However, unwanted proteolytic degradation of α-peptide based material imposes challenges on chronic utilization. Here, we present a new, biocompatible, and bioactive neural interface with a peptidomimetic foldamer-based biopolymer hydrogel which forms a complex with carbon nanotubes (CNTs). We utilized a β-peptide as a molecular building blocks to form the hydrogel because it has not only the ability to mimic natural peptides, but excellent structural and proteolytic stability. To endow conductivity into β-peptide-based hydrogel, hierarchical assembly of β-peptide was designed to self-assemble into nanofiber that associate with carbon nanotubes (CNTs). Transmittance electron microscopy images revealed the end-to-end assembling of β-peptide nanofibers and tight wrapping of the nanofibers around CNTs. The mechanical properties of β-peptide/CNTs hydrogel was found to completely mimic the viscoelastic behavior of neural tissue. The intercortical and epidural neural signal recorded with the conductive hydrogel were found to be augmented, especially in high frequency range, due to increased contact area and tight coupling with neural tissues. We expect the tissue-like hydrogel-based neural interface will suggest many possibilities for developing advanced neural implants with secured signal reliability and recording sensitivity.

Shape-Reversible Magnetic Hydrogel Drug Carriers for Remote Neural Modulation Cindy Shi, Siyuan Rao and Polina Anikeeva
1Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Simons Center for Social Brain, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Minimally invasive magnetothermal technology that uses heat dissipation from magnetic nanoparticles (MNPs) in the presence of an alternating magnetic field offers the convenience of remotely controlling heat-sensitive processes. We applied this remote control capability of MNPs to enable an on-demand release of pharmacological substances to modulate neuronal activity. Thus, we developed a magnetic hydrogel that permitted local drug release with reversible shape contraction triggered by the heating of MNPs under an external magnetic field. By adjusting the composition of the MNPs and the hydrogel, drug loading capacity and release efficiency were optimized. When preloaded with clozapine-N-oxide, a substrate for the designer receptors exclusively activated by designer drugs (DREADDs), the magnetic hydrogel enabled the remote manipulation of neural activity in DREADD-expressing neurons upon exposure to magnetic field. The biocompatibility and chemical stability of the thermally responsive hydrogel were investigated. The introduced magnetic hydrogel drug carrier provides the remote release of pharmaceutical drugs for neural modulation with a long-lasting carrier lifetime and can potentially be expanded to other chemicals and pharmacological agents.

Electrical Performance after Mechanical Stress of Hafnium Oxide Capacitors on Deformable Softening Polymer Substrate Ovidio Rodriguez Lopez1,2, Gerardo Gutierrez-Heredia3,4, Alexander J. Polednik1, Adriana C. Duran-Martinez1, Edgar Guerrero1, Aldo Garcia-Sandoval2 and Walter Voit1,5
1Department of Electrical and Computer Engineering, The University of Texas at Dallas, Richardson, Texas, United States; 2Department of Biomedical Engineering, The University of Texas at Dallas, Richardson, Texas, United States; 3Centro de Investigaciones en Optica, Leon, Mexico; 4Department of Material Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States.

Recently, the microfabrication of thin film devices on flexible substrates has attracted great interest due to the broad field of applications where they can be used. In particular, the biomedical field has taken advantage of this technology for the development of chronic and implantable devices based on stimulating and recording electrodes. However, its commercial production remains elusive because of the rigorous demand of these applications. High performance, reliability, stable behavior, and resilience to the periodic mechanical stress of the electronic circuits are some characteristics needed for the fabrication of these devices. Therefore, further research on electronic components such as transistors, diodes, and capacitors among others devices is needed to develop reliable complex circuits on flexible substrates. This work presents the electrical performance of hafnium oxide (HfO2) thin-film capacitors on a softening polymer, as a flexible substrate. The softening polymer used as the substrate is a shape-memory polymer (SMP), which has been previously used for implantable devices. It is well known that SMP has the capability to retain a certain shape after being deformed and return to its original state when an external stimulus is applied. The metal-insulator-metal capacitors were fabricated using gold as top and bottom contacts and HfO2 as a dielectric, deposited by atomic layer deposition (ALD) at 100°C. This study centers on the electrical characterization after a mechanical stress of the HfO2 capacitor fabricated on SMP. Different HfO2 thicknesses were used. Capacitors of each thickness (20, 30, 40 and 50 nm) were measured and compared with capacitors fabricated on silicon with the same structure. The devices were evaluated after 102, 104, 106 and 108 cycles of bending with a 5 mm bending radius. Electrical parameters such as capacitance density, dielectric constant, leakage current and breakdown voltage of these devices were evaluated. This research might pave the way towards the fabrication of complex circuitry based on thin film devices using SMP as softening substrate, and assist in the development of implantable electronic, where mechanical resilience is required.

Improving the Compatibility of Semiconducting Polymers for Biological Interfacing David Ohyun1, Weiyuan Du1, Sahika Inal1 and Iain McCulloch1,2
1KAUST, Thuwal, Saudi Arabia; 2Imperial College London, London, United Kingdom.

Organic semiconductor polymers have been extensively used as efficient bio-transducers thanks to their unique mixed ionic and electronic conductivity. Their applications include biosensors, drug delivery, neural interfaces, etc. Nonetheless, if these semiconductor materials are able to translate biological signals from cells, the translation is not always easy and sometimes not as efficient as it could be. The main limitation of organic polymers in bioelectronic tissue-like hydrogel-based neural interface will suggest many possibilities for developing advanced neural implants with secured signal reliability and recording sensitivity.
are promising to use such biofunctionalized polymers to record/stimulate neural signals more effectively as the cells adhere directly to the protein-like surfaces.

**BM07.09.05**
**Inkjet Printed Stretchable Organic Electrochemical Transistor with Petal-Molded Substrate**  
Yuanzhe Li, Naixiang Wang, Anneng Yang and Feng Yan; Hong Kong Polytechnic University, Hong Kong, China.

Organic electrochemical transistor (OECT) modifies its channel current by injecting ions from the electrolyte. The employment of organic polymer as the channel material is so central to OECT that it deeply affects most all aspects of the device. It gives OECT excellent biocompatibility and contributes to its successful application as biological interfacing. The organic nature also provides space for solution processing, where powerful patterning method such as inkjet printing can be introduced and therefore realize the high-throughout, roll-to-roll fabrication of OECT.

However, the benefit of organic channel still hasn’t been exploited to its limit. When we have device-level integration with rigid metal electrode, for instance, gold, the intrinsic stretchability of organic polymer is greatly wasted. The poor mechanical performance of gold electrode is now a bottleneck and may risk the device being missed as an effective solution for wearable electronics, which are widely considered as next generation of human-computer interaction medium.

Encouragingly, efforts have been made in various aspects to bypass the limit imposed by rigid electrodes. Both prestretching of substrate and laser-patternning of electrodes achieve considerable improvements by creating buffer for electrodes so that the device is practically not deformed even under great strain.

The place we cut into is when this inevitable deformation finally occurs, and more and more cracks are tearing the electrodes into pieces. We propose with periodic ridge morphology, it is possible to suppress the expansion of the crack and make it stay at the ridge of each nearest pit. To make this kind of periodic structure, we no longer use expensive and complicated photolithography techniques, but instead turn to nature for inspiration and find the petals as an ideal mold for replicating its honeycomb structure. Gold electrodes and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) channel are then deposited on molded polydimethylsiloxane (PDMS) substrate by magnetic sputtering and inkjet printing respectively. Fabricated devices show stretchability up to 30% under multi-axial strains.

Given that the proposed principle works at different stages of device deformation and there is no conflict in the manufacturing process, it should function well as an augment to existed solutions, paving way for devices with even higher stretchability by adopting hybrid strategies.

References:

**BM07.09.07**
**Progress Towards a Silicon-Based Cochlear Nucleus Hearing Prosthesis**  
Nicholas Nolta, Pejman Ghelich and Martin Han; University of Connecticut, Storrs, Connecticut, United States.

Over the past decade, we have developed a silicon-based neural recording and stimulation electrode array for a cochlear nucleus hearing prosthesis. The current design and fabrication process are presented and published in vivo results are summarized. The materials used in the array include the silicon and silicon oxide of the silicon-on-insulator wafer, titanium/platinum/gold for the interconnects, silicon oxide and silicon nitride for passivating layers, and titanium/iridium for the electrode sites. Deep reactive ion etching defines the shape of the array, with the burried oxide layer in the silicon-on-insulator wafer serving as the etch stop. Backside thinning with an SF6-based dry etch precedes manual release of the array from the wafer. Mechanical grinding sharpens the tips of the array’s shanks into sharp points rather than a vertical wedges. Finally, the arrays are cleaned, packaged, and sterilized. In vivo testing in cat auditory brainstem demonstrates the viability of the array. The array’s physical sharpness and stiffness allowed for successful implantation into cochlear nucleus and inferior colliculus, which are considered deep and difficult-to-reach targets, using an inserter tool. Once in tissue, the array’s 3D multi-shank layout allowed for tonotopic stimulation in different tissue volumes throughout the cochlear nucleus. The electrode and passivation materials proved to be sufficiently long-lasting and biocompatible to allow for in vivo recording and stimulation for over one year. Other applications include any situation in which mechanical robustness, a 3D multi-shank layout, and stable long-term stimulation and recording performance are desired, such as in the spinal cord or for deep brain stimulation. In the future, we plan to push this device towards human clinical use as an alternative hearing prosthesis to the cochlear implant for patients with ossified cochleas or damaged auditory nerves.

**BM07.09.08**
**Controlled Corrosion for Electrochemically Modified Surfaces in Nanofabrication Process**  
Francis McEachern and Geraldine Merle; Surgery, McGill University, Montreal, Quebec, Canada.

Pseudomonas aerugenosa (PA) is a ubiquitous and drug-resistant bacteria responsible for approximately 27% of hospital-acquired infections (Alatraktchi et al, 2016). Current diagnostic standards rely upon labor-intensive bacterial culturing, which demand multiple measures over several days for conclusive results. Fortunately, the development of electrochemical biosensors proves an encouraging avenue for further diagnostic advance. Biosensors are small, relatively simple to fabricate, easily implantable and can provide real-time measurements with excellent spatial and temporal resolution. Pyocyanin (PYO) is a redox-active toxin uniquely expressed by PA, and stands as a novel biomarker for PA infection. Due to its unique oxidation window (at 0.59 V), PYO proves to be a viable target to which we may tailor future electrochemical diagnostic tools (Alatraktchi, 2016). Previous studies have indicated that PYO can be clinically isolated from patient samples and validated effectively via square-wave voltammetry (Simaet et al, 2017).

Our research focuses on tuning everyday medical tools to powerful analytical devices to provide a dichotomous yes/no response to the presence of biomarkers in real-time. Minimally invasive, low-cost stainless steel acupuncture needles (AN) were modified via a two-step process: 1) controlled corrosion microfabrication, and 2) polymer free deposition of carbon nanoparticle (CNP). Following physical, electrical and chemical characterization of the probe (AFM, CV, SEM, microCT, EIS, compressive strength testing with Instron), we validated this electrochemical detection needle with in vitro and in vivo measurements of PYO.

We successfully developed a well-controlled corrosion environment that produces reproducible and robust pitted needles. These pitted needles exhibit high capacitance, increased SSA, and a homogeneous porosity with the presence of large voids. Despite the porosity, the structural integrity of the pitted ANs remained high according to the compressive strength analysis using the ballistic gel simulating human tissue. Adding CNPs on the surface of the pitted needles enhances drastically the electron transfer, and maximize the signal to noise ratio. PYO has been successfully detected in vitro and clinically viable
concentrations (2-100μM), and the testing on clinical isolates from patients has yet to be applied (Alatraktchi, 2016). This finding potentially removes one of the remaining obstacles to highly efficiency point-of-care diagnostics and the ability to tailor antibiotic therapy using inexpensive materials and equipment.

References

BM07.09.09
Multi-Frequency Assessment of the Electrical Impedance Myography Parameters on 3D Malignant Breast MD Nurul Anwar Tarek1, Ahmed H. Jalal1, Fahmida Alam2 and Mohammad Ahad1; 1ECE, Georgia Southern University, STATESBORO, Georgia, United States; 2ECE, Florida National University, Miami, Florida, United States.

Electrical properties such as conductivity and permittivity of biological material have notable dependency on frequency. These frequency dependent changes in biomaterial properties can play a prominent role in impedance signature of Electrical Impedance Myography (EIM). EIM is a non-invasive and painless four electrode measurement tool, measuring the impedance based on the response of the low amplitude alternating current. In this study, multifrequency Electrical impedance Myography assessment was performed using an applied range of frequencies for getting valuable insight of the biomaterials. In this paper, the objective of our study is to explore the effects of different sized malignant tumor in female breast tissue on the multifrequency signature of EIM. In this study, a finite element model of a female breast has been developed based on electro-biophysical data for each malignant tissue within a frequency range of 2 GHz to 3 GHz and log frequency vs resistance and log frequency vs reactance of EIM have been analyzed for various sized tumor on breast. It is found that the slope of log reactance vs. frequency and resistance vs log frequency decrease with increasing tumor size. For instance, the percentage deviation of log reactance slope for 8 mm tumor and 6mm tumor from 2 mm (1mm radius) tumor size is 4.12% and 0.412% respectively. The study provides evidence that evaluation of the frequency dependent impedance data can provide rich assessment of the abnormal biological tissue.

BM07.09.10
Biomimetic Modification of Biopolymers for Electrochemical Synthesis of Organic-Inorganic Composites Amanda Clifford and Igor Zhitomirsky; Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada.

A conceptually new approach has been developed for the fabrication of organic-inorganic composite films for orthopaedic coatings and biosensors, using cathodic electrophoretic deposition (EPD). This technique is based on the biomimetic modification of biopolymers such as chitosan (CHIT), and poly-l-lysine (PLL) with a catechol containing moiety, 3,4-dihydroxybenzaldehyde (DHBAla), utilizing a Schiff base reaction. CHIT is a naturally occurring biopolymer, which has been used for a variety of biomedical applications due to its structural similarity to glycosaminoglycan, which is the primary component in the extracellular matrix of bone and cartilage. The surface morphology and roughness of PLL allow for remarkable cell adhesion, and as a result it has been used in the past as a coating agent to promote cell adhesion as well as for drug delivery applications. Benefits of biopolymer modification with catechol group include superior adhesion to inorganic nanoparticles, as well as tissue adhesion in the presence of body fluid. Catechol modification also imparts redox-activity upon the coating, which is useful for in-situ reduction of metallic nanoparticles and biosensing applications. These unique properties allow catechol modified biopolymer films to be used as reducing, capping, charging, dispersing and film forming agents for the fabrication of advanced nanocomposite films utilizing cathodic EPD. In the following work, catechol-modified CHIT polymer was used for the in-situ reduction of Ag+ to silver nanoparticles, and the unique redox properties were utilized for the development of photovoltaelectrochemical (PEC) DNA biosensors. Modified CHIT and PLL were both used for fabrication of nanocomposite coatings, containing advanced functional biocarriers such as hydroxyapatite (HA) and rutile (TiO2), to improve osseointegration for orthopaedic and dental applications. Preliminary cell testing revealed that composite PLL-DHBA films containing HA and TiO2 promoted cell proliferation due to its hydrophilic nature and rough surface morphology. These techniques pave the way for the continued development of biomimetic materials processing, and the fabrication of advanced multi-functional materials for use in a variety of biomedical applications, from orthopaedic coatings to DNA biosensors.

BM07.09.11
Following Anticancer Drug Activity in Cell Lysates with DNA Devices Dimithree Kahanda1; 2, Naveen Singh1, David Boothman1 and Jason D. Slinker1; 1The University of Texas at Dallas, Richardson, Texas, United States; 2Department of Biosciences, Rice University, Houston, Texas, United States; 3Department of Biochemistry and Molecular Biology, Indiana University Simon Cancer Center, Indianapolis, Indiana, United States.

There is great need to follow the selectiveness of anticancer drug activity and to understand the mechanisms of biological activity. Here, multi-electrode chips with DNA monolayers are used to track anticancer drug activity in cellular lysates and correlate cell death activity with DNA damage. Cells were prepared from the triple-negative breast cancer (TNBC) cell line, MDA-MB-231 (231) to be proficient or deficient in expression of the NAD(P)H:quinone oxidoreductase 1 (NQO1) enzyme to represent cancerous and control cells. Cells were lysed and added to chips, and the impact of β-lapachone (β-lap), an NQO1-dependent DNA-damaging drug, was followed with DNA electrochemical signal changes arising from drug-induced DNA damage. Devices showed a 3.7-fold difference in the electrochemical responses to NQO1+ over NQO1− cell lysates, as well as 10 to 20-fold selectivity to controls deactivating DNA damaging pathways. Concentration dependence study revealed that 1.4 μM β-lap correlated with the onset of cell death from viability assays and the midpoint of DNA damage on the chip, and 2.5 μM β-lap correlated with the mid point of cell death and the saturation of DNA damage on the chip. Results indicate that these devices could inform therapeutic decisions for cancer treatment.

BM07.09.12
DNA Sizing and Quantification Using Multi-Frequency Impedance Cytometry Jianye Sui1, Neeru Gandotra2, Pengfei Xie1, Zhongtian Lin1, Curt Scharfe2, Mehdi Javanmard1 and Hemanth Maddali1; 1Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Yale University, New Haven, Connecticut, United States.

In recent decades, DNA quantification has attracted substantial research efforts due to its significance in disease diagnosis and analysis. A number of DNA quantification methods have been established. Traditional methods to quantify nucleic acids usually use fluorescent labels or dyes and require bulky instruments for excitation. Previously, Saleh et al. demonstrated quantification of biomarkers through resistive pulse sensing using a DC measurement to
detect changes in particle diameter due to analyte binding on the surface of a bioactivated colloid [1]. In this work, we proposed a new approach for label-free nucleic acid strand recognition by using multi-frequency impedance flow cytometry.

The process begins by amplifying (PCR) and biotinylating target DNA, and immobilizing the DNA onto streptavidin coated magnetic beads. The cytomter consists of a pair of electron-beam deposited gold electrodes on glass wafer, with a Polydimethylsiloxane (PDMS) microfluidic channel embedded on top. Various quantities of DNA on the surface of the bead will affect the surface conductance, permittivity, and charging profile and thus modulate the frequency-dependent impedance response. When a bead flowed through the sensing region, it partially blocks ions conducted between two electrodes. Thus, there is a frequency-dependent impedance increased. By probing peak intensities at different frequencies, beads coated with differing quantities of DNA can be differentiated from each other. The impedance response is captured in real-time at 8 frequencies using a multi-frequency lock-in-amplifier.

Different beads immobilized with a series of DNA quantities (ranged from 0.1 ng to 1000 ng) to the surface were investigated using impedance flow cytometry. The bare magnetic streptavidin coated beads that had no DNA captured were used as a negative control. We implemented multi-frequency analysis, which provides a more comprehensive result, since the impedance response of different samples at single frequency may not be separable. The peak intensity increased as frequency increased from 100 kHz to 5 MHz and then decreased as frequency increased to 15 MHz. Results showed that using multi-frequency analysis, we can differentiate beads with different concentrations of DNA. In addition, a study on the effect of different DNA lengths on impedance responses was performed. We demonstrated that as the length of DNA increased, the impedance responses increased linearly. The results of these studies suggest that this approach can be applied for DNA quantification using small sample volumes using a miniaturized electronic chip.


BM07.09.13
Artificially Well-Designed Biomonolayer for Prevention of Nonspecific Electrical Signal
Shohei Himori, Shoichi Nishitani and Yoshiya Sakata; The University of Tokyo, Bunkyo-ku, Japan.

[Introduction]
An artificially well-designed biointerface is required for a new strategy of biosensor such as an enzyme-free glucose sensor. A solution-gate field-effect transistor (FET) is based on the potentiometric measurement of intrinsic ionic or biomolecular charges at the gate surface of the FET without enzymatic reactions. Moreover, an extended-Au film-gate FET enables a highly-sensitive detection of small biomarkers, because the Au film exhibits a strong catalytic action, resulting in the oxidation of organic compounds such as uric acid and glucose. However, the selective detection of small biomarkers, which involves a signal to noise ratio, with the Au film electrode is not sufficient for a real sample containing impurities. In this study, we have designed a Au film/solution interface for the selective detection of small biomarkers and investigated the effect of diazonium monolayer on the prevention of nonspecific signals based on non-targeted small biomarkers.

[Methods]
An Au(Cr) film was fabricated by sputtering on a glass substrate. The Au electrode was modified by nitro group-terminated aryldiazonium monolayer in acetonitrile including 1 mM 4-nitrobenzenediazonium tetrafluoroborate (NBD), 25 mM tetrabutylammonium hexafluorophosphate (nBuPF6), and 2 mM DPPH via cyclic voltammetry (CV), which was in the potential range of +0.3 V to -0.7 V at the scan rate of 50 mV/s. The immobilization density of NBD monolayer was controlled via CV treatment. On the other hand, the same method was applied for the modification of NBD multilayer in the solvent without DPPH. The change in the surface potential was monitored using the NBD-grafted FET. In particular, uric acid was used as a small biomarker and introduced onto the Au film electrode with the different densities of NBD monolayer or NBD multilayer. The concentration of added uric acid was changed in the range of 5 µM to 1 mM. The thickness of diazonium film was analyzed by laser microscope. Besides, the surface coverage was calculated by reduction from nitro group of NBD to amino group.

[Results and Discussion]
The uric acid response for the NBD monolayer-grafted FET was smaller than that for the NBD multilayer-grafted FET. That is, the NBD multilayer-grafted FET suppressed the nonspecific electrical signal based on the interaction of uric acid with the Au film. This is because the surface coverage by the NBD multilayer was insufficient, that is, there were some vacancies among the grafted NBDs, through which uric acid approached to the Au surface. On the other hand, the grafting density of NBD monolayer on the Au film was higher than that of NBD multilayer. Moreover, the effect of NBD multilayer on the prevention of nonspecific signal was enhanced with increasing potential cycles via CV method, resulting in the increase of immobilization density.

[Conclusions]
Our work suggests a new strategy of selective detection of small biomarkers using the extended-Au film-gate FET biosensor.

BM07.09.14
Observation of Local Ionic Concentration at the Hippocampal Neuron with Nano-Pipette
Jong Wan Son1; Tomohide Takam1, Woong Sun2 and Bae Ho Park1; 1Konkuk Univ, Seoul, Korea (the Republic of); 2Kogakuin University, Hachioji, Japan; 3Korea University, Seoul, Korea (the Republic of).

Selected cationic currents at the cell membrane inside and outside of hippocampal neuron were measured using nano-pipette probes. A polyvinyl chloride film was prepared in the nano-pipette probes, and the film contains each cation ether ligands that collector of potassium, sodium or calcium cations. The currents of the collected cations were detected through a silver wire electrode and the currents were recorded with a sub-picoampere current measurement system, developed from the techniques of TΩ-gap impedance scanning tunneling microscopy. Depending on the position of the nano-pipette probes, the local ionic concentration at hippocampal neuron is measured as the selected cationic currents. We also demonstrate the progress of our work about real-time measurements of ionic concentration when stimulate the hippocampal neurons.

BM07.09.16
Magnetocochemical Technique for Remote Manipulation of Neurons
Siuyan Rao1, 2, Ritchie Chen2, Ava LaRocca3, Michael G. Christiansen3, Alexander W. Senko1, Cindy Shi1, Po-Han Chiang1, George Varnavides2, Seongjun Park2, Junsang Moon3 and Polina Anikeeva1, 3; 1Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Simons Center for Social Brain, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Targeted delivery of neuromodulators within the brain is essential in linking the activity of their molecular targets to behavior. However, existing delivery methods are often non-specific, e.g. intravenous and peritoneal systemic administration, or invasive, e.g. implantation of microfluidic devices. To facilitate spatially-restricted and remotely-controlled delivery of neuromodulators to neural circuits of interest, we sought to gate the release of small molecules
using non-invasive stimuli. Here, we coupled weak alternating magnetic fields (AMFs) in the low radiofrequency range to trigger the release of chemical compounds encapsulated within liposomes loaded with magnetic nanoparticles. Multiple micro-doses with minimal leakage could be delivered upon liposome permeabilization through localized heating of magnetic nanoparticles. When combined with chemogenetic neuromodulation approaches, we find that the activation times can be decreased from hours to seconds at multiple time points within genetically-defined neural populations. This scheme was also applied to control over endogenous receptor function using magnetochemical delivery of known antagonists and agonists, demonstrating applications of this approach to various ligand-receptor pairs. We anticipate that the magnetochemical tools will facilitate investigation of neural circuits during behavioral experiments and enable neuromodulation studies in rodent models incompatible with permanently implanted hardware.

BM07.09.17
Nanowell Array Impedance Platform for Multiplexed Label-Free Quantification of Cytokines in Serum at Femtomolar Level Detection Limits Pengfei Xie, Tuan Le and Mehdi Javanmard; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Protein microarrays, on which thousands of discrete proteins are printed, provide a valuable platform for functional proteomic analysis. A protein microarray provides a multi-functions platform for the comprehensive and high throughput studies. Label-free techniques avoid interference due to the tagging molecules, which is the fundamental preparation for the labeling based detection methods. Detection of proteins in blood using label-free impedance based techniques is difficult due to high salt concentration of the matrix, which results in screening of the charge of the target proteins. In this work, we describe a novel sensing configuration where sensitivity benefits from the high salt concentration of the matrix, and demonstrate robust performance through testing in rat serum. To be exactly, we developed a platform with nanowell array sensor, which can monitor multiplexed cytokines in serum at femtomolar level. The nanowell impedance sensor involves the fabricating the micro-wells array patterned electrodes with nanometer level gap, and the continuous impedance measurement using lock-in amplifier based automatic monitor platform. And we have demonstrated the ability of the platform with 100 femtomolar level cytokines detection of mouse TNF-alpha, IL6, IL10 and CXCL2. The titration curves of all 4 cytokines ranging from 10 fM up to 1 nM are also plotted in this work.

BM07.09.18
Electronic Quantitative Surface Markers for Cancer Cells Based on Bead-Cell Aggregate Sizing and Multi-Frequency Impedance Spectroscopy Zhongtian Lin1, Siang-Yo Lin2, Pengfei Xie3, Joseph Bertino1 and Mehdi Javanmard3; 1Cancer Institute of New Jersey, Rutgers University, New Brunswick, New Jersey, United States; 2Department of Electrical and Computer Engineering, Rutgers University, Piscataway, New Jersey, United States.

Rapid analysis of surface markers on the membrane of cancer cells can be used for point-of-care device for monitoring patient’s response to various cancer treatments. Here, we introduced a microfluidic sensor for quantification of proteins on membrane of cancer cells using multi-frequency impedance cytometry. To demonstrate proof-of-concept, we successfully detected “activated” matrigel on the surface of cultured breast cancer cells. Activated matrigel is overexpressed in most epithelial cancer cells. In order to target the cancer cells, magnetic beads were coated with an anti-matrigel monoclonal antibody (M69) that recognizes activated matrigel. The beads then form aggregation with cancer cells as a result of expression of matrigel on the cells’ membrane. The magnetic beads and the bead-bound cancer cells were extracted from the test sample via immuno-magnetic separation. Multi-frequency electrical impedance cytometry was applied to the bead-cell mixture which enable differentiating between unbound beads, non-target cells and bead-cell aggregates. This method can be used for detection and quantification of membrane bound protein (i.e. matrigel) levels, as the concentration of matrigel expressed on the cancer cells is related to the size and quantity of peaks from bead-cell aggregates.

The biochip consists of two microelectrodes on a glass substrate with a PDMS micro-channel above it. Gold electrodes were fabricated using standard photolithography, electron beam evaporation, and lift-off processing. The micro-channels are 400 µm wide and 20 µm high connecting to a sensing region which is 100 µm wide and 20 µm high. M69 coated 2.8 µm sheep anti-mouse IgG beads were mixed with cancer cells off chip. A portion of the beads bind together with cancer cells in the positive assay which form effectively large aggregates compared to the negative control assay where beads were not treated with M69. The mixture is then injected into the inlet of micro-channel. As beads and bead-cell aggregates pass over the microelectrodes that is connected to a multi-frequency lock-in amplifier and AC voltage source, a frequency dependent increase in impedance was detected. The amplitude of the current peak is proportional to particle size. Utilizing simultaneous multiple frequencies measurement of peak intensity, we can demonstrate the quantification of the number of bead-cell aggregates which allows for estimation of matrigel expression levels.

BM07.09.19
Conducting Polymers for Axonal Regeneration—Effect of Surface Topography on Modulation of Axonal Growth Martin Antensteiner, Anthony M. Kisucky and Mohammad Reza Abidian; Biomedical Engineering, University of Houston, Houston, Texas, United States.

Nerve injuries in the peripheral nervous system caused by trauma (i.e. nerve lesions) or debilitating disorders such as Parkinson’s disease have affected more than 20 million people and are estimated to account for 2.8% of all trauma cases in the United States. Autografts are the clinical gold standard for the treatment of nerve gaps, the disadvantages of which include a limited supply of donor nerve, inability to reconstruct complex nerve gaps, sensory deficits in the distribution of the donor nerve, painful dysesthesias following sensory nerve harvest, and structural-ultrastructural nerve mismatch. To overcome these limitations, artificial conduits have been widely investigated to bridge nerve gaps. However, functional recovery after nerve injury remains a challenge.

Biocompatible Conducting Polymers (CP) can be utilized to guide neurons and eventually repair nerve injuries such as nerve gaps due to their unique electrical, physical, and chemical properties. However, few works address the effect CP roughness has on axonal regeneration. In this work, we have investigated two common biocompatible CPs, poly(pyrrole) (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT), fabricated using galvanostatic (GSTAT) and potentiostatic (PSTAT) methods, and characterized the surface roughness of these two polymers. While PPy is well-known for its electrical conductivity and physical stability, PEDOT displays superior chemical stability and electrical conductivity, making it an ideal candidate for artificial conduits.

Electrodeposition was performed on microfabricated Au electrodes using a solution of EDOT or Py monomer and poly(styrenesulfonate) under GSTAT (0.1 to 1.5 mA/cm²) or PSTAT (0.5 to 0.95 V) deposition modes over intervals ranging from 1 to 10 minutes. Each surface was analyzed with materials confocal microscopy (MCM) to measure the CP film thickness and surface roughness. Additionally, the impedance and charge storage capacity (CSC) of the films were measured with impedance spectroscopy and cyclic voltammetry, respectively. Preliminary data suggests a dual dependence of all measured properties (roughness, thickness, impedance, and CSC) on both deposition time and applied charge. For example PPy/GSTAT films on Michigan neural electrodes, roughness (Rq) increased from 2.1±0.25 nm to 12.0±0.84 nm; CSC also increased from 5.7 mC/cm² to 98.7 mC/cm²; finally, impedance at 100 Hz decreased from 8.94±2 Ω to 3.83±2 Ω. These measurements were taken from films deposited at 1 min, 0.1 mA/cm² and 10 min, 1.5 mA/cm² respectively. PPy properties exhibited generally linear trends, and PEDOT properties tended to display nonlinear trends. Dorsal root ganglion (DRG) cells will be cultured on these CP films and neurite outgrowth will then be assessed as a function of surface roughness. These results can be leveraged to improve the control of regenerating axons via surface cues.
Organic semiconducting polymers hold great potential to act as electrically active materials at the interface with a biological environment due to their biocompatibility, soft nature and ability to support both ionic and electronic transport. Recently, functionalization with polar ethylene glycol chains of thiophene-based polymer backbones led to p-type materials with high transconductance and stability in accumulation mode organic electrochemical transistors (OECTs). When a similar side-chain engineering strategy was employed for n-type OECT materials based on naphtho[2,3-b:6,7-b′]dithiophene-4,5,9,10-tetracarboxylic-diimide (NDTI) units, a high stability for n-type doping in aqueous solution and a high volumetric capacitance were observed. However, the overall performance of the device was limited by the poor electron mobility of the material. In search of n-type OECT materials with improved electron mobility, we report the design and synthesis of a series of copolymers containing more planar and rigid naphtho[2,3-b:6,7-b′]dithiophene-4,5,9,10-tetracarboxylic-diimide (NDTI) units as the electron acceptor building block. The properties of these copolymers will be discussed in the context of OECTs.
in comparison with the ND1 analogues, elucidating strategies for backbone engineering in order to develop high-performance electron transport materials for bioelectronic applications.


8:15 AM BM07.10.02
Novel P-Type Small Molecules for Organic Electrochemical Transistors Zachary S. Parr1, Benjamin Poggi1, Jonathan Rivnay2 and Christian B. Nielsen1; 1SBCS, QMUL, London, United Kingdom; 2Biomedical Engineering, Northwestern University, Chicago, Illinois, United States.

Conducting and semiconducting organic materials have existed for over forty years and have seen a broad range of applications from transistors to photovoltaics to logic circuits to OLEDs and more recently biosensors. Among the biosensing devices developed in recent years the most promising has been the organic electrochemical transistor (OECT). Much of the research into OECT’s has mainly involved PEDOT:PSS which has proved itself a champion material for biosensors. Very recently, it has been demonstrated that traditional p-type conducting polymers can be modified with polar ethylene glycol sidechains to allow for mixed ionic and charge conductance affording a polymer with higher transconductance than comparable PEDOT:PSS devices with this design methodology also affording the first n-type biosensing device1–3. Ionic conductance or capacitance combined with charge mobility are the two critical material properties required to achieve high transconductance ($g_m$), the figure of merit of an OECT. With this in mind, we have investigated the potential of small molecule semiconducting materials which often display very high charge mobility in OFETs as materials for OECTs via modification of the conjugated small molecule with ethylene glycol side chains.

We have designed and synthesised a series of molecules primarily based on EDOT oligomers via direct arylation end capped with phenyl groups functionalised with tri-ethylene glycol side chains. The molecules have been fully characterised structurally, electrochemically and optically and exhibited repeatable, stable redox behaviour in aqueous environment with low onsets of oxidation as well as strong electrochromism in thin films. Finally, the molecules have been characterised operationally in the OECT regime. We have achieved OECT devices which can be solution deposited and promising OECT performance is achieved for a number of the molecules. This promising initial result opens an avenue to achieve scalable synthesis of attractive materials for OECTs based on small molecules which with some further structural modification and optimisation of side chain length and solid state morphology are likely to compete with the properties of reported OECT polymers as well as afford access to significantly more varied processing methodologies than for polymer systems.


8:30 AM *BM07.10.03
Organic Mixed Conductors for Bioelectronic Devices Jonathan Rivnay; Northwestern University, Evanston, Illinois, United States.

Polymeric materials capable of ionic-to-electronic signal transduction are important for enhancing bi-directional communication in bioelectronics. Prototypical conducting polymers such poly(3,4-ethylendioxythiophene):poly(styrenesulfonate), PEDOT:PSS, have enjoyed prolonged success as organic bioelectronic mainstays, but they are challenging to study, and may suffer from stability issues and other potentially disqualifying drawbacks. Studying the strengths of PEDOT-based systems, we are able to establish design rules in order to develop new conjugated mixed conductors. Introducing glycolated side chains to carefully selected semiconducting polymer backbones, for example, has produced a class of high performance bioelectronic materials that feature high volumetric capacitance, and enabled electrochemical transistors with transconductance >10mS (device dimensions ca. 10um), and steep subthreshold switching characteristics. A sub-set of these materials outperform PEDOT:PSS and show significant promise for low power, biocompatible devices for implantable bioelectronics. These materials and devices have led to enhanced sensing circuits with the potential for hybrid integration with inorganic transistors.

9:00 AM BM07.10.04
Imaging Ion Dynamics on the Nanoscale with Time-Resolved Electrostatic Force Microscopy Jeff Harrison1, Dean Waldow2, Phillip Cox1 and David S. Ginger1; 1Chemistry, University of Washington, Seattle, Washington, United States; 2Pacific Lutheran University, Tacoma, Washington, United States.

Ionic transport processes govern performance in many classic and emerging devices, ranging from battery storage to modern mixed-conduction electrochemical transistors. Here, we study local ion transport dynamics in polymer films using time-resolved electrostatic force microscopy (trEFM). We compare time-domain behavior using both local trEFM and macroscopic electrical impedance spectroscopy (EIS). We use poly(exo-(2-(2-methoxyethoxy)ethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide)(Poly-ONDI) films doped with lithium bis(trifluoromethane)sulfonimide (LiTFSI) as a model system. Our results show that the local polymer response measured in the time domain with trEFM follows stretched exponential relaxation kinetics, consistent with the Havriliak-Negami relaxation we measure in the frequency-domain EIS data for macroscopic samples of the same polymers. Furthermore, we show that trEFM data correlate with bulk samples in EIS—changes in ion dynamics with increasing temperature, increasing salt concentration, and increasing volume fraction of ethylene glycol side chains in the polymer matrix evolve with the same trend in both measurement techniques. We conclude from this correlation that trEFM data reflect, at the nanoscale, the same ionic processes probed in conventional EIS at the device level. Finally, as an example application for emerging materials syntheses, we use trEFM and infrared photoduced force microscopy (PiFM) to image a novel diblock copolymer electrolyte for next-generation solid-state energy storage applications.

9:15 AM BM07.10.05
The Influence of Water on the Ion-to-Electron Transduction of Organic Semiconductors Achilleas Savva1, Camila Cendra Guinassi2, Alberto Salleo2, Jonathan Rivnay1 and Sahika Inal1; 1Biological and Environmental Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Department of Materials Science and Engineering, Stanford University, Santa Clara County, California, United States; 3Department of Biomedical Engineering, Northwestern University, Evanston, Illinois, United States.

Organic electrochemical transistors (OECTs) comprised of organic (semi)conductor channels operate in aqueous, biological media and translate low
magnitude ionic fluctuations of biological origin into measurable electrical signals. The growing technological interest in these bio-transducers makes the fundamental understanding of the ion-to-electron conversion extremely important for the design of new materials and devices. One crucial aspect that has been so far disregarded is the water taken up by the film during device operation. Here we show the influence of water taken up by a p-type organic semiconductor film on the efficiency, reversibility and speed of charge generation induced by electrolyte anions, penetrating inside the film. The efficiency of ion-to-electron transduction is linked to the performance of the accumulation mode OECTs comprising the polymer in the channel. We find that when less water is incorporated into the polymer film alongside the dopant anions, the OECT ON current is higher, the device is more reversible, stable and switches faster. This work gives insights into the impact of a swollen channel material on the performance of OECTs and lays the foundation for future materials design for efficient ion-to-electron transduction.


9:30 AM BM07.10.06
Low Voltage Current-Driven Organic Electrochemical Transistor for Biomedical Applications Leona V. Lingstedt1, Matteo Ghittorelli2, Fabrizio Torricelli2, N. Irina Craciun1, Paschalis Gkoupidenis1 and Paul W. Blom1; 1Max Planck Institute for Polymer Research, Mainz, Germany; 2Information Engineering, University of Brescia, Brescia, Italy.

Detection of ion concentrations plays a fundamental role in biomedical diagnostics, health and environmental monitoring, water and food controlling, as well in the security and agriculture industry. Here we show an organic electrochemical transistor (OECT) in a current-driven configuration providing highly sensitive ion detection at low voltages. The ion sensitivity normalized to the supply voltage is larger than 1200 mV V⁻¹ dec⁻¹, which is the highest value ever reported for ion-selective transistors. The bias current determines the range of ion concentration and the sensitivity is not limited by the supply voltage, thus overcoming the fundamental limit. A potential application is demonstrated by the integration of the current-driven OECT with an ion-selective membrane, exhibiting a sensitivity of 1035 mV V⁻¹ dec⁻¹, normalized to the supply voltage.

We were able to extend this concept by interfacing organic electronics with biological systems. The integration of OECTs with human cells, enables the assessment of barrier tissue layer properties in a non-invasive and label-free method. Measuring the paracellular transport provides information about the integrity and function of the barrier tissue as disruption or dysfunction can be an indicator for disease or toxicity. The OECT, resembled in the inverter-like topology, is sensitive to cell coverage and shows minute-respons to toxins due to barrier rupture. Pushing this technology to greater sensitivity, this proposed approach may open opportunities in toxicology, drug delivery, disease diagnostics and fundamental research in molecular biology.


9:45 AM BM07.10.07
Polymer OFET Biosensors with High Performance and Stability Mark Nikolka1, 2, Amir Foudeh1 and Zhenan Bao1; 1Stanford University, Stanford, California, United States; 2University of Cambridge, Cambridge, United Kingdom.

Due to their ease of processing, conjugated polymers are promising candidates for a range of optoelectronic applications ranging from flexible displays and light emitting diodes (OLEDs) to organic photovoltaics (OPV). Recently, surprisingly high levels of performance and stability have been demonstrated especially for low disorder conjugated polymers exhibiting charge carrier mobilities well above 1cm²/Vs and operational stability compatible with demanding state-of-the art OLED displays [1,2]. However, these advancements so far have not been translated into the emerging field of biosensors where similar performance and stability requirements prevail. Here we demonstrate how high mobility, low disorder polymers can be utilized in platforms for PH-sensing and bio-sensing. In particular, we demonstrate a highly stable sensors platform based on the dual-gate mechanism. In this architecture a sensing signal is transduced and amplified by the capacitive coupling between a low-k bottom-dielectric and a high-k ionic elastomer top-dielectric that is in contact with an analyte solution. We show that our platform design exhibits a high stability in various aqueous environments of different salt concentrations making it particularly interesting for biosensing applications where high selectivity is desired.


10:00 AM BREAK

SESSION BM07.11: Biosensors—Analytical
Session Chairs: Sahika Inal, Dania Mawad and Bernhard Wolfrum
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Constitution B

10:30 AM *BM07.11.01
Physical Biology at the Semiconductor-Based Biointerfaces Boshil Tian; University of Chicago, Chicago, Illinois, United States.

Although there are numerous studies on either semiconductors or biological components, our understanding of the fundamentals at the semiconductor-based biointerfaces has been limited. As different types of energy (such as electrostatic, mechanical, thermal, and chemical energies) display diverse scaling behaviors and can converge, an appropriate selection of the length scale is critical for promoting new scientific discoveries. My group integrates material science with biophysics to study several semiconductor-based biointerfaces. We synthesize new forms of semiconductor materials and use them to probe biological dynamics, with particular focus at the sub-micrometer and sub-cellular length scales. In particular, we have recently identified a biology-
of these devices is unique and therefore outperforms other OECTs despite the absence of an electron mediator. We show that by tuning the device operation parameters, the sensitivity and dynamic range of the device is controlled, demonstrating possible applications for biosensing.

Nanoparticles for Improving Performance of Enzymatic Electrodes

Organic Electrochemical Transistors (OECTs) are devices which find growing interest in the field of biological and chemical sensing. Although the OECT transduction is based on electrochemical reactions, the transistor architecture offers several advantages with respect to amperometric sensors, such as signal amplification, the use of easy and cheap readout electronics, low supply voltage (usually < 1 V), low power operation (< 100 μW), bio-compatibility. Moreover, OECT configuration does not require freestanding reference electrodes used in conventional electrochemical setups and offers design freedom in terms of device geometries and substrates (flexible). In addition to their inherent robustness, versatility and ease of integration, OECTs can be miniaturized and fabricated with low-cost materials [1], on any kind of substrate, including textile and plastic. Our research group has reported the fabrication of OECTs wherein the channel and all the electrodes are made by PEDOT:PSS (polystyrene sulfonate) and their use as chemical sensors for a wide class of analytes. The selectivity and sensitivity to the target analyte can be given by a proper functionalization of the gate material and/or acting on the transistor operation mode. This contribution describes our most recent results on OECT based chemical sensors exploiting the functionalization of the gate PEDOT electrode, as assessed by the following two applications:

1. The first application is the use of PEDOT doped with pH dyes (BTB and MO, i.e. Bromothymol Blue and Methyl Orange, respectively), as the gate electrode to develop an OECT sensor for pH monitoring. The developed sensor can reliably operate with a super-Nernstian sensitivity, that can be reached thanks to the amplification offered by the transistor architecture. The optimised configuration was realised on a PET substrate and the performance of the resulting flexible OECT was assessed in artificial sweat within a medically relevant pH range.

2. The second application is the design and synthesis of a new composite material based on Ag/AgCl nanoparticles (NPs) and PEDOT:PSS that allowed us to fabricate a novel kind of OECT-inspired sensor, integrating an Ag/AgCl gate electrode into the semiconductor polymer in the form of NPs. Such sensor combines an intrinsically amplified response associated to the transistor design with a simple two terminal electrical connection, which offers great advantages in terms of read-out electronics, adaptability to new and unconventional geometries and faster response time. The efficacy of such a simple connection has been demonstrated through the development of a textile sensor for real-time sweat monitoring.

References


Direct Metabolite Detection with an Accumulation Mode Organic Electrochemical Transistor

We describe the influence of gold nanoparticles (AuNPs) and nanoclusters (AuNCs) on the mechanism of bioelectrocatalytic reactions. Below a certain size the monolayer-protected AuNPs show a series of oxidation states and a clear HOMO-LUMO gap [1]. We propose that AuNPs can change their role in the bioelectrocatalytic processes when their size decreases below 2nm. Fructose dehydrogenase (FDH) used here is a heterotrimERIC membrane-bound enzyme complex, insensitive to oxygen, consisting of three domains. Subunit I is the catalytic dehydrogenase domain containing FAD as the cofactor. Subunit II contains 3 paramagnetic heme C moieties acts as an electron acceptor to subunit I [2].

We show that AuNCs ca. 1nm in size lead to larger FDH catalyzed currents of fructose oxidation and smaller overpotentials which reflects improved electronic communication between the electrode and the active sites [3]. The catalytic wave appears at a potential close to that of the beginning of clusters.
HOMO-LUMO gap. The effect of the smallest gold clusters is of special interest and features such as low-coordination sites, adsorptive properties of the AuNC surfaces, thiol monolayer organization have to be considered in the discussion of the improved catalytic current densities and lower overpotentials. Such behavior may be also understood as mediation of the enzymatic processes by the AuNCs as opposed to larger, plasmonic AuNPs, for which direct ET process (DET) is observed. Controlled switch from DET to mediated MET mechanism of electron transfer by decreasing AuNPs to cluster sizes might be considered for other oxidoreductases as well.

We also show that under influence of magnetic field superparamagnetic iron oxide NPs interact with paramagnetic heme centers of FDH subunit II leading to suitable orientation of the enzyme molecule and enhancement of DET. Closer approach of heme sites to the support results in the decreased fructose oxidation overpotential and Michaelis–Menten constant. Improved performance of enzymatic electrodes achieved through use of Au clusters or magnetic NPs holds great promise for third generation biosensors and biofuel cells.

Thus, by establishing a direct relation between presence of adhered cells and electrical output, we demonstrate that carbon-based electrolyte-gated transistors constitute a promising technology to perform large-scale and cost-effective monitoring for toxicology and drug development. Real time monitoring for toxicology and drug development applications, able to perform measurements with enhanced sensitivity and temporal resolution compared to standard electrochemical cell-substrate impedance spectroscopy and other well-established optical probes. Although this approach has proved to be useful in different applications, it does require complex read-out electronics, as well as non-trivial signal processing and analysis for data interpretation, being based on impedance spectroscopy techniques.

In this work, we propose carbon-nanotube based electrolyte-gated transistors as a novel tool to electrically monitor cell adherence and proliferation, able to operate consistently in aqueous environment and in conjunction with more established optical techniques. By exploiting the changes in the capacitive coupling occurring at the electrolyte/semiconductor interface as cells adhere on the active material, information on proliferation and detachment can be easily extracted from the quasi-static variation of the drain-source current in time, without any need for electrochemical spectroscopy or other frequency-dependent techniques. This particular sensing approach is validated by monitoring over a time span of three days the adhesion and growth of several cell lines via quasi-static measurements, and corroborated by means of standard and fluorescence optical microscopy. Indeed, in all instances the behaviour of the output current follows the expected changes in interfacial impedance that result from cell-proliferation on the active layer, corresponded by a full recovery of the initial currents upon inducing cell detachment from the device.

By establishing a direct relation between presence of adhered cells and electrical output, we demonstrate that carbon-based electrolyte-gated transistors constitute a promising technology to perform large-scale and cost-effective in vitro monitoring for toxicology and drug development applications, able to operate complementarily to state-of-the-art optical and electrochemical techniques.

Integrating Native Cellular Membranes with Organic Transistors Anna-Maria Pappas1, Han-Yuan Liu2, Charalampos Pitsalidis1, Rohit Singh2, Alberto Salles1, Susan Daniel1 and Roisin Owens1; 1Cambridge University, Cambridge, United Kingdom; 2Cornell University, Ithaca, New York, United States; 3Stanford University, Palo Alto, California, United States.

Cellular membranes represent an obvious, yet relatively neglected target for developing new drugs. Using membrane models (e.g., supported lipid bilayers, SLBs) for sensing and drug screening is limited by incompatibility at the biotic/abiotic interface, lack of molecular complexity, and lack of integrated functionality to transduce at the molecular level. We have recently demonstrated that SLBs are compatible with electroactive materials able to transduce molecular interactions of toxins with a model membrane. In parallel our teams have developed methods to assemble complex (native) membrane structures into planar supported bilayers on solid supports, using materials directly harvested from live cells. By using hydrated polymer-based transducers, instead of solid supports one can achieve a fluid environment- close to the physiologically relevant environment- i.e., facilitating mobility of the transmembrane proteins, which is essential for such native plasma membrane systems. These features enhance the native structural and functional properties of the membrane and ensure the credibility of our platform to be physiologically relevant and predictive of membrane molecular interactions. In this work, we demonstrate the formation of native SLBs on top of the conducting polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) transistors. We characterize the native SLBs using both optical and electronic methods. Real time monitoring of the native SLB formation reveals useful information regarding dynamics of membrane fusion and allows for sensitive detection of minute changes on the membrane properties. This work is a first step towards the use of native plasma membranes with highly-sensitive, label-free and fast electrical readout to transduce membrane-compound interactions, essential for diagnostics and drug discovery applications.

Biosensor Prototype Based on Carbon Nanotubes for Detection and Hyperthermia Treatment of Cervical Cancer Cells Giovanni S. Caro1, André Marra1, Darinel Ortiz2, Ismael Jiménez2, Javier Avalos2, Gerardo Morell2 and Brad R. Weiner2; 1University of Puerto Rico at Rio Piedras, San Juan, Puerto Rico, United States; 2University of Puerto Rico, Bayamón, Puerto Rico, United States.

Current treatments for cancer include surgery, chemotherapy, and radiation, as well as combinations of these. Although widely utilized, these treatments are not entirely effective. Our primary aim is to develop a non-invasive radiofrequency-based biosensor that is able to detect cancerous cells as well as provide therapy using localized heat with the aid of nanotechnology. This wireless radiofrequency (RF) sensor employs carbon nanotubes (CNTs) to enable the detection of cancer cells and the selective treatment via hyperthermia. The sensor is a gold resonant coil LRC circuit for wireless transmission and in its capacitive component contains CNTs that were deposited and functionalized. The detection relies on the phase change of the RF signal in the presence of...
Organic Electrochemical Transistors for Electrical Cell-Substrate Impedance Sensing with Single Cell Resolution
Sven Ingebrandt1, Felix Hempel2, Jessica Ka Yan Law3, Fabian Brings1 and Xuan Thang Vu1; 1Institute for Materials in Electrical Engineering, RWTH Aachen University, Aachen, Germany; 2Informatics and Microsystems Technology, University of Applied Sciences Kaiserslautern, Zweibrücken, Germany.

Electrical Cell-substrate Impedance Sensing (ECIS) is a well-established technique in the field of bioelectronics and several commercial platform technologies are available. We developed a similar technique, which is using ion-sensitive field-effect transistors (ISFETs) as transducer elements and we coined the term Field-Effect Transistor Cell-substrate Impedance Sensing (FETCIS) [1]. In early works we utilized different designs of silicon ISFET arrays. However, they are very tedious to fabricate and devices are opaque. Nevertheless, we applied our ISFETs in practical cell assays such as adhesion, migration, wound healing, apoptosis and toxicological influences with single cell resolution [2-4].

Recent years organic thin-film transistors (OTFT) gained a lot of attention in the field of biosensing. Their versatility, easy fabrication and their biocompatibility make those devices a new and exciting alternative for cell-sensing applications [5]. We developed arrays of electrochemically-gated OTFTs (OECTs) out of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) scaffold. OECTs offer a completely novel, ionic gating mechanism compared to the classical, purely capacitive coupling to silicon ISFETs. We realized a wafer-scale fabrication protocol for OECTs. Devices out of PEDOT:PSS scaffold, coined the term Field-Effect Transistor Cell-substrate Impedance Sensing (FETCIS) [1]. In early works we utilized different designs of silicon ISFET arrays. However, they are very tedious to fabricate and devices are opaque. Nevertheless, we applied our ISFETs in practical cell assays such as adhesion, migration, wound healing, apoptosis and toxicological influences with single cell resolution [2-4].

In recent years organic thin-film transistors (OTFT) gained a lot of attention in the field of biosensing. Their versatility, easy fabrication and their biocompatibility make those devices a new and exciting alternative for cell-sensing applications [5]. We developed arrays of electrochemically-gated OTFTs (OECTs) out of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS). OECTs offer a completely novel, ionic gating mechanism compared to the classical, purely capacitive coupling to silicon ISFETs. We realized a wafer-scale fabrication protocol for OECTs. Devices exhibited excellent sensor characteristics with transconductance values exceeding those of our silicon ISFETs [2]. Sensors were optimized to a frequency level of 1-10 kHz. We present FETCIS assays with individual HEK 293 cells and with tight junctions forming MDCK cells [6]. An extended FETCIS model including the ionic gating mechanism of OECTs can explain the recorded frequency spectra and can be utilized to extract cell-related parameters from the bioassays. In future OECTs could be produced such cheap that sensing in disposable standard plastic dishes would be possible. This could be a very interesting alternative to the classical sensor types in ECIS.

References:

SESSION BM07.13: Biosensors—Performance
Session Chairs: Sven Ingebrandt and Christian B. Nielsen
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Constitution B

3:00 PM BM07.13.01
Integrated Biosensor for Point-of-Care Sepsis Diagnosis
Joaha Min1, Maria Nothing2, Georg F. Weber3, Cesar Castro1, Filip K. Swinarski1, Hakho Lee4, and Ralph Weissleder1,2, 4
1Center for Systems Biology, Massachusetts General Hospital, Boston, Massachusetts, United States; 2Systems Biology, Harvard University, Boston, Massachusetts, United States; 3Cancer Center, Massachusetts General Hospital, Boston, Massachusetts, United States; 4Radiology, Massachusetts General Hospital, Boston, Massachusetts, United States; 5Surgery, University of Erlangen-Nuremberg, Erlangen, Germany.

Sepsis is an often fatal condition that arises when the immune response to an infection causes widespread systemic organ injury. A critical unmet need in combating sepsis is the lack of accurate early biomarkers that produce actionable results in busy clinical settings. Here, we report the development of a point-of-care platform for rapid sepsis detection. Terned IBS (integrated biosensor for sepsis), our approach leverages i) the pathophysiological role of cytokine interleukin-3 (IL-3) in early sepsis, and ii) a hybrid magneto-electrochemical sensor for IL-3 detection. The developed platform produces test results within 1 hour from native blood samples, and detects IL-3 at a sensitivity of <10 pg/mL, this performance is >5-times faster and >10-times more sensitive than conventional enzyme-linked immunoassorbent assays, the current gold standard. Using clinical samples, we show that high plasma IL-3 levels are associated with high organ failure rate and thus greater risk of mortality, confirming the potential of IL-3 as a sepsis diagnostic biomarker. With
further system development (e.g., full automation, data security measures) and rigorous validation studies, the compact and fast IBS could become a practical clinical tool for timely diagnosis and proactive treatment of sepsis.

DOI: 10.1021/acsnano.7b08965

3:15 PM BM07.13.02 Nanopatterned Bulk Metallic Glass Biosensors. *Emily Kinser*, 1, 2, 3 and Themis Kyriakides1; 1Yale University, New Haven, Connecticut, United States; 2IBM T.J. Watson Research Center, Yorktown Heights, New York, United States; 3IBM Corporate Research Lab, Maple Grove, Minnesota, United States.

Nanopatterning as a surface area enhancement method has the potential to increase signal and sensitivity of biosensors. Platinum-based bulk metallic glass (Pt-BMG) is a bio-compatible material with electrical properties conducive for biosensor electrode applications, which can be processed in air at comparably low temperatures to produce nonrandom topography at the nanoscale. Work presented here employs nanopatterned Pt-BMG electrodes functionalized with glucose oxidase enzyme to explore the impact of nonrandom and highly reproducible nanoscale surface area enhancement on glucose biosensor performance. Electrochemical measurements including cyclic voltammetry (CV) and amperometric voltammetry (AV) were completed to compare the performance of 200 nm Pt-BMG electrodes vs Flat Pt-BMG control electrodes. Glucose dosing response was studied in a range of 2 mM to 10 mM. Effective current density dynamic range for the 200 nm Pt-BMG was 10-12 times greater than that of the Flat BMG control. Nanopatterned electrode sensitivity was measured to be 3.28 µA/cm²/mM, which was also an order of magnitude greater than the flat electrode. These results suggest that nonrandom nanopatterography is a scalable and customizable engineering tool which can be integrated with Pt-BMGs to produce biocompatible biosensors with enhanced signal and sensitivity.

3:30 PM BM07.13.03 Stimuli-Responsive Polymer-Graded Gate Field-Effect Transistor for Bioanalytical Sensor. *Akeo Fujita*, 1 Tsukuru Masuda1, Aya M. Aikimoto2, Taira Kajisa1, Ryo Yoshida1 and Toshiya Sakata2; 1School of Life Science and Technology, Tokyo Inst. of Tech., Tokyo, Japan; 2School of Engineering, The University of Tokyo, Tokyo, Japan; 3PROVIGATE Inc., Tokyo, Japan.

Bioanalytical tools such as biosensors are being developed for in situ monitoring of biological phenomena. As one of them, a biologically coupled gate field-effect transistor (FET) is based on a potentiometric detection of the changes in ionic charges induced by biomolecular recognition events and cellular activities in a real-time, label-free, and noninvasive manner. Meanwhile, poly(N-isopropylacrylamide) (PNIPAAm) is one of the most widely studied thermoresponsive polymers, and exhibits hydrophilic/hydrophobic phase transition in aqueous media across the lower critical solution temperature (LCST). Thanks to the thermo-responsivity, PNIPAAm-modified surfaces can exhibit hydrophilic/hydrophobic changes in response to temperature, and they have been studied for various applications including flow control, bioseparation, and cell culture dishes. Here, we hypothesized that the PNIPAAm-modified surface would be useful as a signal transduction interface in the semiconductor-based biosensor. In this study, we clarified the dynamic electrical behavior of a thermoresponsive PNIPAAm film on the gate of FET device [1]. Our findings will be useful for the application of semiconductor-based biosensors.

PNIPAAm was modified by atom transfer radical polymerization (ATRP) on the Ta2O5 gate of FET devices. At first, the ATRP initiators were modified on the Ta2O5 surfaces with hydroxyl groups by silane coupling method, and then the PNIPAAm chains were grafted on them by surface-initiated ATRP. The phase transition behavior of the grafted-PNIPAAm film induced by the temperature change from 25 °C to 40 °C was analyzed from the electrical properties of the FET device. Moreover, the phase transition time of the grafted-PNIPAAm film was measured in real time using the PNIPAAm-grafted FET device. The surface potential of the PNIPAAm-grafted FET became more negative than that of the non-grafted FET, as the temperature increased from 30 °C to 35 °C. This is because the phase transition of the grafted-PNIPAAm film from a hydrated state to a dehydrated state occurs across LCST, which is 32 °C in aqueous media. In this case, the capacitance of the grafted-PNIPAAm film should be altered because water has high permittivity. Thus, the change in the electrical characteristic of FET device can exhibit hydrophilic/hydrophobic changes in response to temperature, and they have been studied for various applications including flow control, bioseparation, and cell culture dishes. Here, we hypothesized that the PNIPAAm-modified surface would be useful as a signal transduction interface in the semiconductor-based biosensor. Moreover, we have found that the surface-modified polymer needed several hours to complete the phase transition using the PNIPAAm-grafted FET. Our work suggests a new strategy of bio-interface based on a stimuli-responsive polymer for the semiconductor-based biosensor.


3:45 PM BM07.13.04 Mechanism of Label-Free, Potentiometric Sensing of Neuropeptide-Y in Artificial Skin Using Graphene Field Effect Transistors. *Ahmad E. Ismail*, 1, 2, 3, Rhett Martineau1, 2, Cameron M. Crasto1, 2, Hyunil Kim3, 4, Michael Brothers3, 4, Rahul Rao5, 6, Ariana Nicolini1, 2, Cameron M. Crasto1, 2, Hyunil Kim6, 7, Benji Maruyama1 and Lawrence F. Drummy1; 1Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States; 2UES, Inc., Dayton, Ohio, United States.

Label-free, potentiometric bio-sensing is an emerging method for rapid, specific and sensitive detection of biomarkers to probe a wide range of physiological conditions. Neuropeptide Y (NPY) is one such biomarker, which is involved in regulation of important biological and pathophysiological functions such as food uptake, energy homeostasis, circadian rhythm and cognition. NPY is also an indicator of susceptibility to stressful or threat-related events. We have recently shown PM sensitivity for NPY detection in artificial sweat using graphene field effect transistor (GFET) functionalized with a peptide-based bio-recognition element (BRE). We used in-operando Transmission Electron Microscopy (TEM) imaging to examine the structure of NPY and its interfacing with BRE and graphene. We visualized the operation of the sensors in real-time to optimize their performance.

Here, we expand our understanding of NPY sensing by thoroughly analyzing the electrical and optical responses of graphene using electrolyte-gate GFET and Raman spectroscopy measurements. In particular, we study the GFET responses in an artificial sweat environment formulated using a range of salt concentration (~ 10-100 mM) and pH (~ 4.5-7.0), as measured in sweat [1]. In these pH ranges, the charged states of BRE and NPY are away from their isoelectric points (as calculated using Henderson-Hasselbalch equation). This charged states result consistent changes in the Dirac point and mobility of graphene after the BRE functionalization and after adding NPY at different concentrations (~ 1 pM - 10 µM); this covers the range of NPY measured in depressive disorder patients [2]. In addition, a two-dimensional plot of the shifts in the graphitic G and G' peaks (generally observed at ~ 1600 cm⁻¹ and ~ 2700 cm⁻¹, respectively) obtained from Raman spectroscopy [3] confirms the magnitude of the Dirac point shift measured electrically and suggests changes in strain on the graphene layer after attachments of BRE and NPY. Overall, these complimentary electrical and optical measurements reveal the mechanism of NPY sensing using graphene through potentiometric sensing and suggest pathways for sensing of other biomarkers that have similar charged states and isoelectric points.

The latest Zika virus (ZIKV) pandemic caused great international concern from explosively proliferating throughout the Americas. This arbovirus is primarily transmitted through the bite from an infected mosquito, but infection has also been spread through perinatal transmission, sexual contact, blood transfusion, and physical contact. Although asymptomatic, ZIKV became a major health crisis due to the link with the steep rise in cases of microcephaly and Guillain-Barré syndrome with infection. With no viable vaccine or reliable and economically feasible diagnosis in sight, the World Health Organization has called for rapid development of flavivirus diagnostics. Unfortunately, antibody-based detection systems can result in false positive results and RNA-based detection systems are costly, time-consuming, and impractical for testing in remote regions. In this study, a potential point-of-care (POC) diagnostic system was developed using a chip-based potentiometric sensor to detect flaviviruses using a 3D molecular imprinting technique. The co-adsorption of ZIKV and alkanethiols formed a crystalline self-assembled monolayer (SAM) on the surface of the gold chips. The crystalline SAM was verified using cyclic voltammetry. The removal and re-adsorption of the targeted virus was verified using electrochemical impedance spectroscopy supporting the molecularly wired mechanism. This chip-based potentiometric sensor system was able to detect 10^3 PFU/mL ZIKV in a buffered solution under 20 minutes without any sample manipulation. This sensor was tested against Dengue virus at clinical viral loads and showed no sign of cross-reactivity. When tested against human saliva samples containing clinical viral loads, this sensor was able to detect 10 PFU/mL ZIKV among the pool of bio-macromolecules. The high sensitivity and high selectivity demonstrated here proved that this lab-on-a-chip diagnostic has the potential to become a POC detection system for rapid and accurate screening of flaviviruses. This work was supported by the NSF. Inspire #1344267. This work was performed in part at the Advanced Science Research Center NanoFabrication Facility of the Graduate Center at the City University of New York.


The need for rapid, sensitive, and reliable pathogen detection is of utmost importance on the global scale from food safety, biomedical diagnostics, homeland security to environmental monitoring. With the emerging technology of Internet of things/everything and flexible/wearable electronics, thin film transistor-based bacterial biosensors employing conducting polymer materials could hold promise to offer ubiquitous bacteria detection with low-cost and high-performance. Organic electrochemical transistors (OECTs) represent a very promising class of organic thin film transistors (OTFTs) that have recently fueled scientific interest as performing transducers in sensing applications. OECTs offer the advantages of simple electrical readout, low operation voltage, inherent signal amplification, straightforward miniaturization, and ease of fabrication on flexible substrates including paper. Therefore, they are excellent candidates for disposable biosensors. However, the commonly used conducting polymer poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) PEDOT:PSS lacks of functionality and non-fouling properties, which limits the application as the active layer for OECT biosensors. In this work, we develop the presentation of zwitterionic carbobxyatene PEDOT conducting polymers (PEDOT-CB) and print it on paper or PET substrate to form a planar OECT. PEDOT-CB offers both functionality to chemically link antibody to the sensor surface and non-fouling properties to allow direct detection in complex media. We synthesized EDOT-CB monomer and chemically polymerized to PEDOT-CB. The UV-Vis absorption spectroscopy and electron spin resonance (ESR) spectroscopy measurements were conducted to determine polaron and bipolaron populations in the oxidized PEDOT-CB. The conductivity of the PEDOT-CB:PEDOT thin films was measured using the four-probe approach. We printed planar OECTs on paper and PET substrate using inkjet printing method. Small molecules were added to further increase the conductivity and to improve the microstructure to allow efficient link antibody. Surfactant was added to improve the adhesion of PEDOT-CB:PEDOT on paper (or PET) substrates. The dimension of channel length/width and gate length were optimized to achieve high transconductance under certain gate voltage (V_G) and source-drain voltage (V_DS). The anti-E-coli antibody was immobilized on PEDOT-CB:PSS gate via the NHS/EDC chemistry. The drain current (I_D) was recorded with time after a certain concentration of targeted ZIKV to the cavities yielded surface charging on the chips which was measured in real-time potentiometrically. The formation of these crystalline SAM was verified using cyclic voltammetry. The removal and re-adsorption of the targeted virus was verified using electrochemical impedance spectroscopy supporting the molecularly wired mechanism. This chip-based potentiometric sensor system was able to detect 10^3 PFU/mL ZIKV in a buffered solution under 20 minutes without any sample manipulation. This sensor was tested against Dengue virus at clinical viral loads and showed no sign of cross-reactivity. When tested against human saliva samples containing clinical viral loads, this sensor was able to detect 10 PFU/mL ZIKV among the pool of bio-macromolecules. The high sensitivity and high selectivity demonstrated here proved that this lab-on-a-chip diagnostic has the potential to become a POC detection system for rapid and accurate screening of flaviviruses. This work was supported by the NSF. Inspire #1344267. This work was performed in part at the Advanced Science Research Center NanoFabrication Facility of the Graduate Center at the City University of New York.
of the resistive sensors and scaling laws to facilitate rapid, noninvasive thermal measurements on broad classes of biological and non-biological soft materials, as well as the opportunity to further study skin injury in clinically relevant settings.


4:45 PM BM07.13.08
Fully Organic, Flexible and Biodegradable Components for Bioinspired Electronics Meng Xu, Ramendra Pal, Sayantan Pradhan and Vamsi K. Yadavalli; Chemical and Life Science Engineering, Virginia Commonwealth Univ, Richmond, Virginia, United States.

The integration of naturally derived and synthetic polymers provides exciting opportunities to develop physiologically compliant bioelectronic systems and functional scaffolds for tissue regeneration. The combination of protein biomaterials and intrinsically conducting polymers enables the formation of functional bio-composites with properties different from conventional silicon or metal-based paradigms. In particular, silk proteins can provide mechanically strong, optically transparent, bio-compatible, and biodegradable matrix materials. Conducting polymers such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT: PSS) can provide electrical/ionic conductivity, electrochemical properties and chemical stability in biological environments. Coupled together, our group has demonstrated photopatternable, water-based conductive inks comprising PEDOT: PSS and in-house synthesized photoactive silk proteins that can be used in facile, room-temperature, aqueous techniques to form flexible substrates and sensors.[1, 2] Here we will discuss recent results that show how these composite inks can function as the starting point to develop diverse components of flexible, fully organic bioinspired electronics. These include electroactive coating materials for conventional electrodes, flexible electrodes, biosensors, and energy storage devices.[3-5] These systems in multiple formats are formed without the use of metals or other charge collector support materials, making them programmably, and completely biodegradable. The use of proteins as the matrix of the composite improves interfacing with biological surfaces. Electroactive biomolecules such as ascorbic acid and dopamine, and analytes such as glucose can be detected sensitively and selectively using enzymes. For the first time, we demonstrate how even large biologically relevant macromolecules such as vascular endothelial growth factor (VEGF) can be detected \textit{in situ} in a flexible, conformable format [6]. We discuss the mechanical, biochemical and electrochemical characterization and microfabrication. Such systems can provide applications towards real-time health monitoring of disease in addition to the measurement of biophysical parameters. Utility of these elements as bio-sensors, opto-electronic devices and flexible energy storage systems are envisioned.

References:
The extracellular domain of Human epidermal growth factor receptor type 2 (ECD-HER2) is a well-known biomarker to prognosis various kind of metastatic cancer such as breast, ovarian, and gastric cancer. Investigating the ECD-HER2 in serum has been used antibody-based detection method called the enzyme-linked immunosorbent (ELISA), which is using costly many processing steps such as adding a binding buffer, exchanging washing buffer, and dilution steps for quantitative analysis the ECD HER2 protein level in serum. Also, antibody-based ELISA should be conducted in certain conditions due to its denaturation property depending on heating and pH in the buffer.

Oligonucleotide-based recognized aptamers have been widely studied for substituent molecules of antibody because the aptamers have not only highly specific binding property to target molecules but also thermal and pH stability [3]. Gold nanorods (GNRs) have been widely used as optical sensors which retain its unique extinction spectrum within the visible range. This is because the electrons at the surface of gold nanorods oscillate collectively corresponding to light injection named localized surface plasmon resonance. Furthermore, this extinction spectrum is easily tunable in dealing with the morphological transformation of GNRs, chemical coatings and refractive index changing around the vicinity. In here, we developed anti-HER2 aptamer-based surface plasmon resonance sensors (HER2-APlaS) with robustness by a simple drop-coating method to detect ECD-HER2 in serum. To immobilize the GNRs on substrates with homogeneously, we introduced surface microscale grooved patterning on a polymeric substrate for controlling the dispersivity. Also, dopamine, well-known chemically adhesive materials, was used as inhibiting the aggregation of GNRs, enhancing immobility on the substrate, and giving the covalently binding available site to anti-HER2 aptamers. We used as pyrimidine modified third generation aptamers which have high stability in serum. Assembled all these advantages of described materials, HER2-APlaS was conducted real-time binding kinetic experiments in a

BM07.14.04

Wireless Injectable Microsystem for Programmable In Vivo Pharmacology and Optogenetics Yi Zhang1, Philipp Gutruf2, Catro Daniel2, Michael Bruchas3 and John A. Rogers3; 1Biomedical, Biological, and Chemical Engineering, University of Missouri, Columbia, Missouri, United States; 2Washington University School of Medicine, St Louis, Missouri, United States; 3Northwestern University, Evanston, Illinois, United States; 4University of Arizona, Tucson, Arizona, United States.

BM07.14.05

Testing the Viability and Reusability of Hemoglobin Biosensors Utilizing SAM Surface Molecular Imprinting and Natural Surface Roughness Indices Yehoshua Auerbach1, Nicholas Clayton2, Miguel Hulyalkar3, Andrew Todt4, Rebecca Isseroff2, 1, Vincent Ricotta2 and Miriam Rafaelovich1; 1Lawrence High School, Cedarhurst, New York, United States; 2Dept. of Materials Sciences and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; 3South Side high School, Rockville Centre, New York, United States; 4Lake Oswego High School, Lake Oswego, New York, United States.

We have shown that molecular imprinting (MI) technology, together with potentiometric detection, can be used to produce sensitive, yet robust, biosensing systems with real-time electrochemical readout that can be utilized for point of care diagnostics. Real time detection of biomarkers is essential when rapid, critical decisions need to be made, such as during medical procedures when cancer is suspected, or when public health is threatened, as in the recent Zika virus epidemic or in dealing with a suspected attack by biological agents. The biosensor that we developed was tested against standard methods, such as ELISA, and was found to have comparable or better sensitivity, with sample sizes which were at least an order of magnitude smaller. Furthermore, the results from the technique are obtained within minutes, using inexpensive potentiometric readout technology which can even be wirelessly transmitted. These biosensors utilize surface molecular imprinting of a self-assembling monolayer (SAM) of hydroxyl-terminated alkanethiol chains that are able to form a crystalline ‘lock-and-key’ structure around a target analyte; this allows the sensors to detect and differentiate between bio-macromolecules of similar size and shape with high selectivity and sensitivity. Therefore, they can be used as a quick yet accurate analysis of many chemical and biological processes, such as stem cell differentiation. The sensors are also very versatile, and can be used to detect molecules with sizes ranging over several orders of magnitude, and of widely varied chemical composition and structure.

In order to fully exploit the advantages of these biosensors, especially in remote, economically disadvantaged areas, it is important to understand and quantify the durability and reusability of the sensors. Polished and unpolished biosensor chips were created to A) test the viability of hemoglobin detection using molecular imprinting techniques, and B) to test if these sensors can be washed and reused after adsorption testing. The successful readsoption of hemoglobin even after washing indicates that these biosensors can be reused, extending the life and usefulness of the device. Further work is in progress to determine the number of uses for the device, and the optimal method for storage. Preliminary work seems to show that vacuum sealing of the sensors with a commercial device is adequate, indicating that convenient long-term packaging of the sensor can be achieved, in turn enabling shipping and storage.

BM07.14.06

Magnetic Nanodiscs for Simultaneous Mechanical and Thermal Neuronal Stimulation Daniela Gregorec1, Alexander W. Senko1, Andrey Chuvilin2, Pooja Reddy1, Ashwin Sankarakaram1, Po-Han Chiang1, Dekel Rosenfeld1, Francisco Garcia1 and George Varnavides1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2CIC nanoGUNE, San Sebastian, Spain.

Wireless schemes based on hysteretic heating of magnetic isotropic nanoparticles in high-frequency alternating magnetic fields (AMFs) have already permitted modulation of neural activity. We present a novel approach for neuronal modulation based on magnetite nanodiscs (MNDs). These anisotropic iron oxide nanoparticles exhibit a characteristic vortex alignment of magnetic spin with zero net magnetization in the absence of external magnetic field.
Such magnetic configuration fosters the colloidal stability in physiological solutions essential for applications in biomedicine. We synthesize a geometric palette of MNDs from 40 nm to 250 nm in diameter. Consistent with geometry, MNDs exhibit direction-dependent hysteresis loops and their specific loss power (SLP) at frequencies of 75-150 kHz up to 1000 W/g is comparable to the spherical magnetite nanoparticles, but at 5-10 times lower particle count owing it to the size of MNDs. Targeted activation of heat-gated channels is thus permitted at high frequency AMFs.

Furthermore, the magnetization in the presence of weak magnetic fields assumes an “in-plane” orientation revealing a large magnetic moment that allows MNDs to transduce magnetic fields to mechanical torques at slow-varying magnetic fields. We show how the mechanical torques are further transduced to the mechanical stimuli of neuronal cells. These stable, biocompatible MNDs robustly mediate calcium influx in mechanosensitive sensory neurons from rat dorsal root ganglia (DRGs) upon application of weak (23 mT), slow-varying (1-5 Hz) magnetic fields.

Finally, MNDs allow for multiplexed stimulation of neurons by selectively activating mechanoreceptors at 1-5 Hz magnetic fields, while heat dissipation and consequent activation of heat-gated ion channels is allowed at frequencies of around 100 kHz.

8:00 AM BM07.15.01
Nanostraw Platform for Intracellular Delivery into Fungal Cell
Exyam Souihel and Nicholas A. Melosh; Stanford University, Stanford, California, United States.

Major advances in nanotechnology have facilitated the development of powerful tools to study biology at the cellular level. Here, we report a nanostraw platform providing an intracellular access to introduce exogenous components such as nucleic acids, proteins and synthetic molecules directly into the cell. This platform is composed of a cargo reservoir, a polymer membrane with protruding nanostraw and a cell culture reservoir. Cargo delivery is performed by electrical pulse allowing the cargo diffusion through the nanostraw to reach the intracellular compartment. This technology allow an access into the cell without perturbing vital functions and promise high transfection efficiency of mammalian cell. Nanostraws with different dimensions i.e. length and diameter can be optimized to interface with different cell types. In this study we evaluate the ability of the nanostraw platform to delivery of exogenous components into fungal cells.

Fungi are described to be responsive of human and plants diseases and also widely used in industrial process to produce antibiotic compounds, enzymes and recombinant proteins. In all of these research areas, genetic modification using exogenous DNA is widely used to study these organisms. However fungal cells are different from mammalian cells as they are surrounded by cell walls which serve as barriers reducing the delivery of exogenous compounds into the cell. The most commonly used techniques to delivery DNA into fungal cells require the production of protoplasts (cell whose cell wall has been removed) and result in low transformation efficiency in many strains. In this context, nanostraw technology is a promising tool to increase fungal transformation efficiency and develop genetic engineering of fungi.

8:15 AM BM07.15.02
Surface-Initiated Hydrogel Adhesives for Seamless Cell-Electronics Integration
Han N. Nguyen, Huan-Hsuan H. Hsu and Xiaocheng Jiang; Tufts University, Medford, Massachusetts, United States.

The electronic detection and interpretation of cell-derived signals represents an important approach to understanding, interrogating, and directing many biologically significant processes. The intrinsic mismatch in biophysical and biochemical properties between living systems and artificial electronics, however, has made it challenging to establish a compatible bioelectric interface for effective signal coupling and transducing, thus limiting many potential applications. Here, we report the use of biocompatible and photo-crosslinkable hydrogels as surface-initiated “adhesives” for seamless cell-electronics integration, where nanometer-thick hydrogels are grown directly from device surface to immobilize living cells with intimate proximity and minimal invasiveness. A custom-built projection stereolithography system is used to spatially control the visible light irradiation and precisely program cell “placement” with diffraction-limited resolution. In particular, we have demonstrated the technique’s capability to incorporate living cells with different nano-electronic platforms, including both passive (microelectrode arrays) and active (field-effect transistors) type of transducers. By designing and modulating the hydrogel structure at the device interface, highly-localized, device-specific microenvironment can be created, allowing real-time, ultrasensitive bioelectrical and biochemical detection at single-cell level. A variety of cell types, including adherent (HL175 and HL1), floating (Jurkat and human white blood cells) and bacterial cells, have been reliably immobilized without compromising cell viability and functionality. Additionally, a broad range of biomaterials, including photo-crosslinkable polyethylene glycol, gelatin, hyaluronic acid, and silk have been tested and optimized as cell adhesives, which helps module interface biochemical/biological properties to overcome limitations posed by challenging material requirements of many applications. Lastly, we have demonstrated the possibility to integrate multiplex cells with large-scale, addressable device arrays, which enables high-spatiotemporal resolution studies of signal propagation at network levels. The current work represents a strategic approach to overcome the intrinsic mismatch at traditional bioelectronic interfaces and is expected to open up new opportunities for a wide range of applications in biomedical sensing, prosthetics, and hybrid information processing.

8:30 AM *BM07.15.03
Organic Bioelectronics—Addressing the Interface Challenge
Dania Mawad; School of Materials Science and Engineering, Centre for Advanced Macromolecular Design, Australian Centre for NanoMedicine and ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, University of New South Wales, Sydney, New South Wales, Australia.

Bioelectronics is considered the future of medicine as it is not only contributing to the basic understanding of biological systems but also to clinical diagnostics and therapeutics through tissue-electronics interfaces. A major challenge facing their successful medical applications is the development of compatible and functional interface technologies that enable biological to electronic signal transduction. This central consideration is driving the “rise of organic bioelectronics” [1]. Critical to this rise has been the incorporation of conducting polymers (CPs) as the electrically active component. CPs are soft, flexible and mechanically tunable; thus more compatible with tissue than inorganic electronics. The attractive properties of CPs have largely been demonstrated in in vitro applications while their in vivo application is limited to coatings for inorganic electrodes to allow for more intimate electronic contact between the device and the tissue [2]. Examples of the challenges that have been hindering the translation into the complex physiological environment include electronic stability and integration with the host tissue. A lack of versatile chemistries for functional CPs underpin these challenges. By manipulating the chemistry of CPs and employing controlled design strategies, we develop novel bioelectronics that address the aforementioned
limitations. New generation CPs are synthesized with demonstrated biocompatibility and ease of processability [3-6]. Conductive constructs such as a hydrogel doped with large polyelectrolyte or free standing patch dopel with small anion were fabricated. Functionized CPs allowed the fabrication of conductive hydrogels that not only possessed tailored physical properties, such as swelling ratios and mechanical properties, but also displayed electroactivity dependent on the chemical composition of the network. Incorporated as the active material in organic electrochemical transistor, these functional CPs exhibited good transconductance and provided surface functionalization with relevant biomolecules. In simple fabrication processes, we introduced porosity in a conductive patch and demonstrated its electronic stability in response to cyclic stretching mimicking the contraction cycle of the heart as well as its stability in the oxidized form after 2 weeks implantation in vivo. By modifying the chemistry of CPs, these macromolecules could be fine-tuned into functional materials opening the way for the development of novel multifunctional bioelectronics capable of effectively electro-coupling with biological tissues.


9:00 AM BM07.15.04
Molecularly Engineered Conducting Polymers with Biomimetic Properties Jadranka Travas-Sejdic1, 2; 1Polymer Electronics Research Centre, The University of Auckland, Auckland, New Zealand; 2MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand.

With the vision of mimicking the many functions found in nature, such as stretchability, healing and sensing, the next-generation applications including organic electronics, tissue engineering and bioensors will require new electronic materials with biomimetic features. The main challenges in developing biomimetic materials for such applications concern mechanical compliance of such material with soft biological interfaces. Organic electronic materials, notably conjugated polymers, offer many advantageous properties - the most valuable being versatile synthesis by molecular design, ease of chemical functionalisation and solution processability.

Herein, we demonstrate that the valuable biomimetic properties can be expressed through molecular design and side chain functionalisation of conjugated polymers. The simple yet versatile synthetic procedure we present enables one to fine-tune the electrical and mechanical properties without disrupting the electronic properties of the conjugated polymer. We exemplify various biomimetic properties, including stimuli-responsiveness,1 bio-sensing,2 anti-fouling,3 intrinsic stretchability and self-healing,4 by grafting polymeric side chains that affords such properties.

References

9:15 AM BM07.15.05
Dimensionality Explored at the Nanoscale in Bioelectronics Francesca Santoro, Fabrizio A. Pennacchio, Leonardo Garma and Laura Mattino; Istituto Italiano di Tecnologia, Napoli, Italy.

The interface between biological cells and non-biological materials has profound influences on cellular activities, chronic tissue responses, and ultimately the success of medical implants and bioelectronic devices. For instance, electroactive materials in contact with cells can have very different composition, surface topography and dimensionality. Dimensionality defines the possibility to have planar (2D), pseudo-3D (planar with nano-micropatterned surface) and 3D conductive materials (i.e. scaffolds) in bioelectronics devices. Their success for both in vivo and in vitro applications lies in the effective coupling/adsorption of cells/tissues with the devices’ surfaces. It is known how a large cleft between the cellular membrane and the electrode surface massively affects the quality of the recorded signals or ultimately the stimulation efficiency of a device. However, this field is hindered by lack of effective means to directly visualize in 3D cell-material interface at the relevant length scale of nanometers. In this work, we explored the use of ultra-thin plasticization technique to cells for the first time on materials which differ in dimensionality, particularly those with biological tissue.

In this work, we explored the use of ultra-thin plasticization technique to cells for the first time on materials which differ in dimensionality, particularly those with biological tissue. However, this field is hindered by lack of effective means to directly visualize in 3D cell-material interface at the relevant length scale of nanometers. In this work, we explored the use of ultra-thin plasticization technique to cells for the first time on materials which differ in dimensionality, particularly those with biological tissue.

References

9:30 AM BM07.15.07
Characterising Material Properties and Biological–Material Interactions for Conducting Polymer Biomaterials Paul J. Molino1, 2, Michael Higgins1, 2 and Gordon Wallace1; 1ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Wollongong, New South Wales, Australia; 2ARC Research Hub for Australian Steel Manufacturing, University of Wollongong, Wollongong, New South Wales, Australia.

Conducting polymer materials have attracted considerable interest for a suite of biological applications due not only to their ability to transfer charge, but the ability to tailor a suite of material properties that mediate biological interactions. Polymer morphological, chemical, electrochemical and mechanical properties can easily be tuned by varying the monomer, dopant species, and polymerisation conditions and method, providing an avenue to adapt and optimise polymer properties for particular applications. This presentation will focus on the ability to use quartz crystal microbalance (QCM-D) and atomic force microscopy (AFM) to not only characterise the polymer physical and mechanical properties, but to also provide critical information on the nature of protein and cell interactions with the nanostructured conducting polymer surfaces.

QCM-D provides a highly sensitive measurement of the mass and viscoelastic properties of protein in real-time, providing a temporal study of the dynamic process of protein binding and organisation on nanostructure conducting polymer surfaces. This approach has been used to identify variations in protein mass and viscoelastic properties on conducting polymers as a function of surface nanoroughness, the identity and loading of the dopant anion in the polymeric film, and the redox state of the polymer film. More recently advances in high speed atomic force microscopy (HS-AFM) has enabled the dynamic interactions of individual protein molecules on nanorough conducting polymer films and in aqueous buffer to be studied at near video rate.
imaging speeds (i.e. 10 images/s). This approach is now being used to obtain new information relating to dynamic protein interactions with surfaces and nanoparticles, providing structural details not possible using other optical techniques. Finally the ability to use QCM-D to study cell – surface interactions will be discussed, demonstrating its ability to present information relating to the physical interaction between the cell and surface, which provides complimentary information to optical microscopy methodologies.

10:00 AM BREAK

10:30 AM BM07.15.07
Precise Control of ERK Activation in Epithelial Cells by Local AC Electric Fields

Quan Qiong1, Houpu Li1, Liang Guo2, Yuan Wang1, Min Zhao2 and John Albeck1,2; Arizona State Univ, Tempe, Arizona, United States; 2University of California, Davis, Davis, California, United States.

Different types of electric fields (EF) have demonstrated great potential to trigger the extracellular-signal-regulated kinase (ERK) signaling pathway. However, it remains difficult to precisely modulate both the amplitude and frequency of the ERK activities by EF with high spatial and temporal resolution. In addition, to date the mechanism of how EF couples with ERK has been generally complicated by EF induced change of membrane potential, permeability of ions such as Ca2+, or exogenous chemical signals such as pH, and reactive oxygen species (ROS). Here we used customized planar microelectrode arrays and a dynamic single-cell reporter of ERK to demonstrate non-invasive ERK activation with precise timing by bipolar symmetric AC EF pulses with no Faradic processes involved. The ERK activities can be repeatedly synchronized and modulated in localized region close to the electrodes. We show that the ERK activation was initiated directly by EF-induced EGFP-independent phosphorylation of epidermal growth factor receptor (EGFR), and did not involve changes in pH, Ca2+ or ROS. Our results on EF coupling to ERK signaling pathway enable precise synchronization and modulation of ERK activities with single-cell resolution, and can serve as a new platform for a wide range of biomedical applications.

10:45 AM BM07.15.08
Biological Model Membranes Supported on Organic Electrochemical Surfaces

Han-Yuan Liu1, Anna-Maria Pappa2, Charalampos Pitsalidis3, Rohit Singh2, Alberto Salles3, Rosin Owens1 and Susan Daniel2; 1University of Cambridge, Cambridge, United Kingdom; 2Cornell University, Ithaca, New York, United States; 3Stanford University, Palo Alto, California, United States.

Supported lipid bilayers (SLB) are emerging as a model system for investigating the function of membrane proteins, and protein-lipid interactions, and for developing new biotechnology for biosensing applications. So far, most of them have been shown on hydrophilic and smooth surfaces, such as silica based surfaces, due to the ease of vesicle fusion and SLB formation. Even though silica based surfaces serve well for SLB assembly, they have several drawbacks, as the material is electronically insulating, inflexible, and causes protein denaturation because of the interactions with the surface. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), is a promising surface for SLB formation because it possess electronic transducer properties, which is unlike the typical inorganic substrate. PEDOT:PSS can not only allow the transduction of signal, but also preserve transmembrane protein function. However, it is challenging to induce vesicle fusion because of surface structures and physicochemical properties. There are a variety of stimuli for triggering the vesicle fusion (pH, osmotic shock, temperature) even under unfavorable circumstances. In this work, we systematically investigated lipid vesicle interactions with conductive polymer, PEDOT:PSS. Recently, we further leveraged native cell membrane vesicles derived directly from live cells as an intermediate to incorporate native membrane species (lipid, membrane protein, etc.) into a SLB on PEDOT:PSS. The platform presented here, which is a biological model membrane supported on an organic electrochemical material with functional proteins, can be applied towards a myriad of technological purposes from drug discovery to pathogen detecting. This study is likely to pave the way for the next generation of bioanalytical sensor interfaces.

11:00 AM BM07.15.09
Engineering M13 Bacteriophage Platforms for Synthesis of Nanotheranostics and Novel Materials

Uyanga Tsedev, Fred C. Lam, Ching-Wei Lin, Alan Ransil and Angela Belcher; MIT Koch Institute, Cambridge, Massachusetts, United States.

Here, we are expanding on the functionality of M13 bacteriophage as an engineerable biomaterial. M13 bacteriophage, a naturally monodisperse, multifunctional nanostructure, is especially well-suited for active material templating and assembly. The phage consists of thousands of distinct protein subunits organized in a high aspect ratio, filamentous viral capsid; approximately 900nm in length and 6nm in diameter. Both the major and minor coat proteins are amenable to mutation, and thus can be chemically tuned for such capabilities as programmable assembly; the binding, nucleation, and capping of inorganic nanoparticles; chelation of metal ions; and expression of targeting ligands or even enzymes. All of these characteristics have made the M13 bacteriophage a competitive biomaterial—we have previously demonstrated its versatility in the formulation of nanofoams, aerogels, and hydrogels for novel inorganic material synthesis as well as its use as a tumor specific vehicle for the delivery of imaging agents to ovarian cancer models. Now, to further improve on the medical and material applicability of M13, we first describe the blood brain barrier (BBB) crossing of M13 with peptide display on the capsid of M13; and second, the assembly of M13 of smaller sizes, termed ‘inho’ phages.

BBB targeting optimizes for the in vivo trafficking properties of the phage nanoparticles and allows delivery past the BBB; functionalizing the phage as a nanotheranostic for medical imaging and therapy applications, particularly in the case of difficult to reach disease sites associated with glioblastoma and neurodegenerative illnesses. Second window near infrared (NIR-II) imaging of glioma targeted phage, complexed with single walled carbon nanotubes (SWNT) or small molecule NIR-II dyes such as IR1050, reveals localization of the phage to glioma, and opens up the possibility for phage based shutting of high drug loads to the tumor cells and simultaneous, inexpensive NIR-II tracking of the therapy progression. Metal nanofoams can also be synthesized using an M13 bacteriophage template. For the first time, we demonstrate that the properties of metal nanofoams can be tuned by altering the length of M13 with inho-phage of sizes ranging from 50nm to 980nm. The morphology of metallized foams made from differing inho-phage struts reveals optimal lengths and concentrations for the crosslinking of the foam material and the resulting porosity. Batteries made using these foams can vary in ion transport capability, giving us biological control over their electrochemical properties. This can be extended to catalysis and other fields where nano-structured materials could provide significant impact including filtration and desalination, tissue or antimicrobial scaffolds, electromagnetic composites, hydrogen storage, wearable energy devices, and more.

11:15 AM BM07.15.10
Silicon Nanowire and Electrospun Nanofibre Polymer Interfaces and Devices to Alter Non Excitable Brain Cell Morphology and Functionality

Emmanuel Saracino1, Ana I. Borrachero-Conejo1, Luca Mao1o, Davide Polese1, Francesco Formaggio1, Grazia P. Nischia1, Maria G. Mola1, Marco Caprin2, Michelle Muccini3, Luigi Ambrosio1, Roberto Zamboni1, Vincenzo Guarino1, Annalisa Convertito1, Valentina Benfenati3 and Guglielmo Fortunato1; 1CNR-Consiglio Nazionale delle Ricerche, Bologna, Italy; 2FABIT, University of Bologna, Bologna, Italy; 3Bioscience, Biotecnologie e Biofarmaceutica, University of Bari, Bari, Italy.

Nanostructured interface capable to modulate structural, molecular and functional properties of brain cells has a huge potential to improve our understanding of the central nervous system. Astrocytes, that are the majority of non neuronal brain cells, are key players in brain physiology and pathology. Nonetheless, the astrocytes/material interaction needs to be considered in engineering implants targeting the brain, as they are the first cells
reacting to brain injury. Here we define and validate the use of innovative nanostructured materials interface based on gold coated silicon nanowires (Au/SiNws) and electrospun nanofibers made of biodegradable polymers such as polycaprolactone (PCL), as substrates where to culture and to study astrocytes physiology in an in-vivo-like morphological and functional phenotype. Nonetheless, the possibility to modulate and record astrocytes electrophysiological properties by Au/SiNws and PCL interface based device. We performed cell viability assays, fluorescent and confocal imaging, revealing that astrocytes adhere and grow on Au/SiNws and PCL nanofibers without need of additional coating. Au/SiNws mashed nanowires induce morphological stellation of astrocytes and arborisation of processes. PCL nanofibers substrate topography promotes elongation of process sprouting from astrocytes cell body. Analyses of gliotic markers indicates that both substrates are not inducing inflammatory reactions. The functional properties of cells grown on Au/SiNws and PCL nanofibers were defined. Notably, Au/SiNws based device enable recording extracellular signals from astrocytes unreported previously and not recordable on Au/Si flat device. Our results validate PCL nanofibers and Au/SiNws as novel glial interfaces that enable the growth, differentiation and recording of astrocytes in vitro. These glial interfaces are representing the first class of devices enabling to dialogue with non excitable brain cells. This work is supported by AFOSR projects ASTROMAT, FA9550 16 1 0502 and ASTRONIR, FA9550-17-1-0502 and 3D NEUROGLIA.

SYMPOSIUM BM08

Materials-to-Devices for Integrated Wearable Systems—Energy Harvesting and Storage, Sensors/Actuators and Integration
November 26 - November 30, 2018

Symposium Organizers
Renkun Chen, University of California, San Diego
Woochul Kim, Yonsei University
Luigi G. Occhipinti, University of Cambridge
Choongho Yu, Texas A&M University

* Invited Paper

SESSION BM08.01: Wearable/Flexible Electronics and Sensors/Actuators
Session Chairs: Yunqi Liu and Tse Nga Ng
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Grand Ballroom

8:00 AM *BM08.01.01
Organic Field-Effect Transistors Based on Polymeric Semiconductors Yunqi Liu, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Great interests have been aroused in flexible functional electronics and photoelectronics, such as artificial skin, non-volatile memories, photosensors and health monitoring systems. Packed up through van der Waals interactions, organic/polymeric materials have advantages of intrinsic mechanical flexibility. During the past several years, impressive progresses have been made in organic field-effect transistors (OFETs), particularly in conjugated polymer-based FETs. A few high-performance polymers-based FETs have been developed with a remarkable mobility of more than 10 cm² V⁻¹ s⁻¹, which provides a promising opportunity for applications in flexible displays and wearable devices.

In this presentation, we report an organic photosensor by three-component integration: an organic light-dependant resistor (OLDR), an organic resistor (OR) as a load resistor, and an OFET as readout element. The photosensor is transconductance type instead of conductance, thus giving a higher photo to dark on/off ratio. In addition, as a mimicry and spectral extension of human visual system, we present an integrated, retina-like optoelectronic device for filter-free near-infrared (NIR) imaging and memory purposes. The device transforms NIR signals into grey scale nonvolatile resistance states, enabling a NIR-to-memory capability. We also demonstrate color differentiation between NIR and visible incidents with preferred NIR selectivity. Due to circuit design, our retinal system accommodates a bi-modal operation with respect to incident wavelengths. It functions as nonvolatile memory under NIR (850 nm) with a dynamic range of 62 dB and 86 dB photoswitch under green light (550 nm). On the other hand, we report the design and synthesis of some copolymers with D-A structures exhibiting p-type, n-type and ambipolar behavior as well.

Highly Sensitive Flexible Pressure Sensors Based on Printed Organic Transistors with Three-Dimensionally Self-Organized Organic Semiconductor Microstructures June Ah Lim; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Highly sensitive flexible pressure sensors are at the forefront of the development of future mobile applications, such as rollable touch displays, health monitoring, and electronic skin. Recently, monolithic organic field-effect transistors (OFETs) combined directly with pressure-sensitive components have been demonstrated as actively workable pressure sensors due to cost-effectiveness, good flexibility, and large-area solution processing, which effectively enables conformal large-area contact with a surface. Despite many pioneering efforts, the low cost and easy fabrication of OFET devices cannot be fully exploited without the development of OFET-based pressure sensor printing processes. In this presentation, we will introduce a highly sensitive pressure sensor based on a printed OFET with centro-aperically self-organized organic semiconductor microstructures. Unlike previously reported OFET-based pressure sensors prepared with a top microstructured dielectric layer, we designed a unique OFET bottom layer consisting of semiconductor channels positioned at the highest summit of printed cylindrical microstructures, referred as “3D OSC”. This unique microstructure was achieved simply by printing an organic semiconductor and a polymer blend, which self-organized after deposition without additional process. The proposed 3D OSC OFET pressure sensors demonstrated a high pressure sensitivity of 1.07 kPa⁻¹ and a rapid response time of <20 ms with a high reliability over 1000 cycles. We demonstrated that our sensors are applicable to the real-time monitoring of radial artery pulse waves and as touch sensors for use in realistic prosthetic hands.

8:45 AM BM08.01.03
Colloidal Dispersion Supported Ionic Liquid Gels for New Transistor Geometries Rachel E. Owyeung, Matthew J. Panzer and Sameer Sonkusale; Tufts University, Medford, Massachusetts, United States.

Intimate monitoring of physical and chemical patient data is changing the health industry. Real-time monitoring devices, such as implantable and wearable tools for diagnostics, need truly flexible transistors for advanced electronics and elegant sensors. Previous reports have realized flexibility through geometric patterning[1] or intrinsically stretchable semiconductors[2]. For gate dielectric insulators, researchers have utilized elastomeric matrices and polygon electrolyte systems to achieve flexibility. Ionic liquid-based gel electrolytes offer high capacitance, a large electrochemical stability window, and are nonvolatile. Typical demonstrations of these ion gels use block copolymers[3] or chemically crosslinked in situ polymerization to add support, though some have demonstrated that colloidal particles dispersed in ionic liquids can result in gels[4].

In this work, we differ from previous reports of ionic liquid-based transistors (IL-OFETs) by using a colloidal dispersion of silica nanoparticles to support the ionic liquid. This scaffold is advantageous over existing triloblock copolymers or chemically crosslinked gels because of its facile fabrication for conformal gel formation. Specifically, triloblock copolymers have complex chemistry and in situ methods require additional crosslinking steps, such as UV treatment to form a gel, which could be difficult to apply to certain substrate types and geometries. Contrarily, these silica dispersion gels are easily applied after gelation for a conformal coating.

We employ 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as the ionic liquid and poly(3-hexylthiophene) as the organic semiconductor, both well studied materials in regards to IL-OFETs[5]. We achieve OFET performance assessed by output and transfer characteristics. Use of this ion gel results in an on-off ratio of 10⁶, threshold voltage of -1.65V, an operating window of 0 to -2.7V, and allows for transistor development on softer, more flexible substrates than typical silicon or glass. For demonstration, we employ our transistor on a linen thread, which could offer a route to 3D monitoring of health in the form of smart sutures and transdermal implantations. These transistor systems have shown an on-off ratio of 10⁴, threshold voltage of -2.8V, and an operating window of 0 to -4V. These preliminary results validate this proposed material selection and design as ideal for electronics and sensors on both 2D and 3D flexible substrates.


9:00 AM BM08.01.04
High ON-Current Vertical Quantum Dot Transistors as a Novel Platform for Flexible and Wearable Electronics Jeongkyun Roh, Hyeong Jin Yun and Victor I. Klimov; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Colloidal quantum dots (QDs) have gained tremendous attention as a new class of nanomaterials that can potentially enable the next-generation solution-processible electronic and optoelectronic devices (Science 353, aa5523, 2016). Owing to their superior optical properties, intense studies on QD-based color converters, light-emitting diodes (Nature 515, 96, 2014, Nat. Photon. 12, 159, 2018) and solar cells (Nat. Nanotechnol. 13, 456, 2018) have been underway leading to successful commercialization of the QD-display technology. The next frontier is exploration of electronically coupled QD solids in the context of prospective applications in solution-processable flexible electronics toward wearable electronic and sensing systems. One existing challenge in this area is low mobility of QD films, which limits performance characteristics of QD-based field-effect transistors (FETs) that represent basic building blocks of electronic circuits. Low mobilities lead to low ON-currents of typical QD-FETs. Increase in the current is possible by reducing the FET channel length, however, this would require the use of expensive and nonscalable patterning methods such as e-beam lithography. Here, we demonstrate high ON-current QD p-type FETs by employing a vertical architecture, which is a vertical stack of a gate electrode, a gate insulator, a source electrode, semiconducting transport layer, and a drain electrode. Using this approach, we reduce a channel length down to submicron-meter scale, and as a result, achieve an unprecedented ON-current of ~0.1 A/cm², which is three orders of magnitude higher than in standard lateral FETs. This notably increases the performance of an electric semiconductor and a polymer blend, which self-organized after deposition without additional process. The proposed 3D OSC OFET pressure sensors demonstrated a high pressure sensitivity of 1.07 kPa⁻¹ and a rapid response time of <20 ms with a high reliability over 1000 cycles. We demonstrated that our sensors are applicable to the real-time monitoring of radial artery pulse waves and as touch sensors for use in realistic prosthetic hands.

9:15 AM BM08.01.05
Towards Low-Cost Electronics on Three-Dimensional Substrates Tong Yang1, Jeremy S. Mehta2, Alexander M. Haruk3, Jiayi Xu, Shan Yan3, Jin Luo1, Chuan-Jian Zhong4 and Jeffrey M. Mativetsky1, 2; 1Materials Science and Engineering, Binghamton University, Binghamton, New York, United States; 2Department of Physics, Applied Physics and Astronomy, Binghamton University, The State University of New York, Binghamton, New York, United States; 3Department of Chemistry, Binghamton University, The State University of New York, Binghamton, New York, United States.

Solution-based electronic material deposition holds promise to enable the low-cost fabrication of wearable electronics, soft robotics, and energy harvesting technologies. Conventional deposition and patterning processes for electrically-active materials, however, are only compatible with flat substrates, while
future technologies will integrate circuitry into three dimensional platforms, such as prosthetics, car windshields, or contact lenses. In this presentation, we will introduce methodologies for depositing and patterning functional materials on three-dimensional substrates. The processes are simple, scalable, and use minimal quantities of starting material, opening new possibilities for device integration.

Decanethiolate-capped gold nanoparticles were deposited and laser-sintered to pattern micron-resolution electrodes on cylindrical substrates with diameters as small as a human hair. We will show how this platform enables new approaches to local pressure and chemical sensing, while balancing the need for simple processing and high performance. In addition, stripes of high-performance organic semiconductor crystallites (6,13-Bis(trisopropylsilylethynyl)pentacene,TIPS-pentacene) were deposited at targeted locations on folded flexible substrates and complex three-dimensional objects. Preferential crystallite alignment led to anisotropic charge transport, with a hole mobility of up to 0.83 cm²V⁻¹s⁻¹ along the crystallite axis. These experiments lay the groundwork for the low-cost integration of electronic function into arbitrary non-planar substrates for sensing, energy harvesting, and display applications.

9:30 AM BREAK

10:00 AM BM08.01.06
Flexible Organic Sensors for Biomechanical Measurements Zhenghui Wu, Moran Amit and Tse Nga Ng; University of California, San Diego, La Jolla, California, United States.

Photosensors responsive to the short wavelength infrared (SWIR) spectra are used in a variety of applications including environmental monitoring and medical diagnosis. However, conventional SWIR sensors are limited by complex die transfer and bonding processing. Here we are advancing SWIR photodiodes by using a new generation of narrow bandgap conjugated polymers that are processed by solution processing techniques and allow simple direct deposition. The polymers are processed into bulk heterojunction photodiodes with photoresponse up to wavelength of 1.8 micron. The performances of devices with different polymer structures were compared through metrics including detectivity, quantum efficiency, response time and rectification ratio. Example applications including blood pulse measurements and spectroscopic identification will be demonstrated.

In addition to optoelectronics, I will also show an example of an instrumented glove for augmenting movement disorder assessments. The system is based on capacitive pressure sensing, and the validation allows an objective, repeatable metric that improve resolution over the current best practices. The glove measures the power required to move a patient’s arm and shows reduced inter- and intra-rater variability. Our approach using wearable sensors offers an objective route for the characterization of movement patterns, which would permit the effective evaluation of intervention outcomes, as well as provide a platform for novel motor interventions in the future.

10:30 AM BM08.01.07
Enhancing the Sensitivity in Capacitive-Type Strain Sensors Using Thin Au Film Electrodes Roka Nur, Naoji Matsuhisa, Zhi Jiang, Md Osman Goni Nayeen, Tomoyuki Yokota and Takao Someya; The University of Tokyo, Tokyo, Japan.

Wearable sensors are a vital component in wearable electronics, since they are responsible for transducing external stimuli into electronic signals. In particular, strain sensors are needed for applications involving motion detection and the monitoring of vital bio-signals. Capacitive-type strain sensors are excellent candidates for practical applications due to their excellent linearity, high stretchability, and low hysteresis. However, a huge limitation of this sensor is its low sensitivity due to the constraints of the parallel-plate capacitor structure under applied strain operations. At best due to theoretical limitations, this structure can achieve a gauge factor (sensitivity) of 1. Here, we present a design technique to enhance the sensitivity in capacitive-type strain sensors through using thin Au film electrodes. We achieved a best gauge factor (GF) slightly above 3 over a high stretchability of 140% strain with great linearity and negligible hysteresis. We further found that the gauge factor of this strain sensor is tunable through varying the film thickness of the electrode. The enhanced sensitivity in capacitive-type strain sensors allows for the opportunity to distinguish subtle motions more sensitively for reliable and practical wearable applications.

10:45 AM BM08.01.08
Flecography Printing of Liquid Alloy-Based Stretchable Electronics Shuo Zhang, Bei Wang, Jiajun Jiang, Kang Wu and Zhigang Wu; Huazhong University of Science & Technology, Wuhan, China.

This work presents a rapid method to selectively print liquid alloy circuits on soft substrate at ambient environment using a laser-treated stamp, by tuning the liquid alloy wettability on different surfaces. This technology has the advantage of efficient as it only need inking and imprinting in just two steps. It can compatibility with existed industrial line equipment for complex and volume automation production easily.

Room temperature liquid alloy has been widely used in stretchable and flexible electronics because of high adaptability, fluidity and high conductivity. Numerous approaches were developed for pattern, such as injection, masked deposition, directly writing, and so on. However, these processing techniques are lack of compatibility to fit existing production lines directly. A simple way with more excellent portability is still being sought. In this work, a stamp was fabricated by selectively laser treatment on the surface of carbon filled PDMS (cPDMS). The laser processed cPDMS demonstrated an alloy-photonic behavior which could attach and then transfer liquid alloy to target substrate easily, while the left parts show an alloy-philic behavior. The difference of adhesion can be characterized quantitatively by measuring the bias of advancing and receding contact angles and calculating theoretically. After inked on stamp, the liquid alloy was printed on target substrate by gently pressing the stamp on target substrate. The liquid alloy would attach on both stamp and target substrate because of adhesion effective and surface oxide layer, and the liquid alloy would separate during lifting off because of Rayleigh-Taylor instabilities. Therefore, liquid alloy could be theoretically left on both stamp and target substrate. Since the oxide layer of liquid alloy exhibits adhesion on sorts of materials, this technique could be widely used on universal substrates, such as pure PDMS, Ecoflex, vinyl tape, glass, polyethylene glycol terephthalate (PET) and so on. Additionally, the method was proved to print arbitrary liquid alloy patterns with resolution as fine as 30 μm with excellent repeatability.

Further, a 64-LED-matrix with bistratal typography with a developable surface stamp were fabricated and demonstrated by this technique.

11:00 AM BM08.01.09
Controlling Thermoplastic Elastomer Optical Properties by Mechanical Processing—Materials for Stretchable Fiber Optic Sensors Margaret Campbell, Paramjot Singh, Kunal Kate and Cindy K. Harnett; University of Louisville, Louisville, Kentucky, United States.

We demonstrate that changing the extrusion speed of thermoplastic elastomer (TPE) fiber can modify its optical transmission by a factor of more than 100. Recently, we created stretchable fiber optic sensors from commercial urethane elastomer fibers that could detect muscle activity when sewn into textiles [1]. By extruding fiber from pellets at slow speeds, optical transmission increased beyond that of the commercial material, potentially leading to sensors that measure deformation on the meter scale instead of cm scale.
Thermoplastic elastomer pellets (Versaflex CL40, PolyOne Corp.) were dehydrated overnight at 60°C, then extruded at 190°C at rates between 0.005 and 0.3 mm/s. The 0.005 mm/s specimen appeared clear upon extrusion while successively faster speeds appeared hazier. Optical transmission was measured with a photodiode and light source. Stress-strain testing showed that the fast-extruded filaments had a greater ultimate tensile strength than filaments extruded at slower speeds.

Wavingguiding in a stretchable optical fiber requires a stretchable cladding with lower refractive index than the core. Our previous silicone coating approach worked with the new extruded cores. However, the silicone claddings peeled under extreme strain (>100%). Therefore, we investigated whether solvents could improve cladding adhesion, wavingguiding and light-coupling properties of the fibers. Soaking the fibers in NMP (n-methyl-2-pyrrolidinone), then stretching the fibers while the solvent dried, turned out to modify the cladding in a way that solvents alone did not. The clearest, slowest-extruded cores were relatively unchanged by the NMP “soak-and-stretch” treatment, while the faster-extruded cores developed a porous, textured cladding with a uniform thickness.

The differing optical properties, mechanical properties, and response to solvents are likely caused by a transition from amorphous polymer at low extrusion speeds, to crystalline at high extrusion speeds. The microstructural properties of urethane based TPEs are known to involve pseudo-crosslinks, which are not chemical bonds but rather physical connections between the monomers of the block co-polymer [2], and which may be disrupted by the soak-and-stretch process. Further investigations with differential scanning calorimetry and FTIR spectroscopy were conducted to identify changes in fiber microstructure at different extrusion speeds.

Varying extrusion speed at constant temperature may tune optical properties along the axis of a fiber, for example creating absorbent regions that are sensitive to length and diameter changes, surrounded by more transmissive segments that carry the signal over long distances. The work also has implications for 3D printing soft optical structures from thermoplastic elastomer.


11:15 AM BM08.01.10

**Inkjet-Printed Graphene/ZnO Ammonia Sensor for Personal Healthcare Monitoring**

Tien-Chun Wu1, Andrea De Luca2, Thomas Albrow-Owen1, Guohua Hu1, Florin Udrea1 and Tawfique Hasan1; 1Cambridge Graphene Centre, University of Cambridge, Cambridge, United Kingdom; 2Department of Engineering, University of Cambridge, Cambridge, United Kingdom.

Early diagnosis of diseases with smartphone/wearable devices is at the forefront of intelligent personal healthcare monitoring system. Analysis of components in exhaled breath is a practical and non-invasive approach. We focus on the detection of exhaled ammonia (NH₃) level which is a critical biomarker associated with hepatitis, kidney failure, and stomach cancer.

We present a novel and industrially scalable inkjet-printed graphene-based sensory system that is integrated onto a miniaturized CMOS MEMS platform. We inkjet-printed nano-composite sensing layer of graphene/ZnO which is synthesized by a cost-effective solution-processing approach. The approach involves liquid phase exfoliation (LPE) of graphite and mixing of ZnO nanoparticles, producing uniformly decorated nanoparticles in a network of graphene flakes.

Our device outperforms conventional metal oxide semiconductor (MOS) sensors via improved gas adsorption ability at materials interface. Moreover, thanks to precisely-controlled thin-film inkjet deposition technologies, we achieve consistent readings among the fabricated devices (<1% variation in response among four devices).

The device is ideal for implementation in smartphones due to its compact size (1mm²) and its ultralow power consumption (5mW). Coupled with rapid temperature modulation of the built-in micro-hotplate, we achieve ultrahigh response of 1600% at 10 ppm of NH₃ (compared to N₂) at a low operating temperature (150 °C) with fast rise and fall time (30s and 45s, respectively).

The versatile technologies enable multi-analyte sensors to be fabricated reliably and cost-effectively, offering new routes towards the development of multi-disease diagnostics platforms.
A Novel, Low Cost, Rapid, Disposable, Enzyme-Free and Colorimetric Paper-Based Platform for Point-of-Care Testing on Glucose Sensing in the Physiological Range Elvira Fortunato 1, 2 and Rodrigo Martins 1, 2; FCT-UNL, Caparica, Portugal; 3CEMOP-UNINOVA, Caparica, Portugal.

Diabetes mellitus is currently one of the most serious and prevalent diseases in the world, affecting million people worldwide and the rate of new cases is expected to continue increasing. Therefore, the development of cheap and simple methodologies for point-of-care glucose sensing is of paramount relevance for an effective diagnosis and management of patients, mostly in underdeveloped and developing countries where the access to medical infrastructures is limited and cost-effect and simplicity are of major concerns. Due to its properties, paper represents an alternative in the performance of point-of-care tests for colorimetric determination of glucose levels, providing simple, rapid and inexpensive means of diagnosis. In this work, we report the development of a novel, rapid, disposable, inexpensive, enzyme-free and colorimetric paper-based platform for point-of-care glucose detection. This method is based on the synthesis of gold nanoparticles (AuNPs) by reducing of a gold salt precursor in which glucose is the reducing agent. Different concentrations of glucose present during the reduction process result in the formation of AuNPs of different size, to which color changes of the sensor are associated. The developed platform was tested and calibrated using different physiological concentrations of glucose from 1.25 to 50 mM and the obtained results were examined and digitally analysed through an image analysis software. It was also compared the colorimetric results obtained with a commercial scanner and with a smartphone camera, concluding that both methods are viable alternatives in the digital analysis of the sensor. The colorimetric sensor revealed sensitivity to determination of glucose levels in samples, in a simple, rapid, inexpensive and eco-friendly way.

2:15 PM BM08.02.03
Truly Stretchable and Transparent Smart Contact Lenses for the Diagnosis of Diabetes Jihan Park, Joohye Kim, Seoyeong Ju and Jang-Ung Park; Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea (the Republic of).

Recent developments in wearable electronic devices integrated with wireless technologies, which can perform health monitoring, will help to advance the medical applications. Among the advanced wearable platforms, smart contact lenses are one of candidates to provide real-time, noninvasive medical diagnostics from the physiological information on the eye and tear fluid. Especially, the eyes always contain the tear fluid, so the smart contact lenses can monitor the physiological status continuously.

Previously reported smart contact lenses exploited opaque and rigid electronic components for the operations of electronic devices. Therefore, these devices could interfere with the user’s vision and be potentially dangerous to the eyes. Furthermore, the bulky equipment with an excessive cost to monitor the signals from the smart contact lens could restrict the user’s activities. These limitations reduce the convenience and features of the smart contact lenses. Therefore, we propose smart contact lenses which can detect the glucose concentrations in tear fluid. For the superior stretchability and transparency, the smart contact lenses are fabricated using silver nanowire (AgNW) networks and graphene which have stretchable and transparent properties. Therefore, the resulting smart contact lens can provide a clear vision. In addition, the antenna composed of AgNWs enables the wireless communication, so the results of glucose sensor in smart contact lens could be wirelessly monitored. These sensor platforms based on AgNWs and graphene can be exploited as not only smart contact lenses but also internet of things (IoTs) for the environment monitoring.

Furthermore, the smart contact lens integrated with wireless display can exhibit the sensing results through the display pixel and exclude the use of bulky measurement equipment which reduces user convenience. Therefore, we believe that the smart contact lenses suggest a promising strategy towards wearable electronics for the diagnosis of diabetes.

2:30 PM BM08.02.04
Towards a Flexible and Biocompatible Implantable Sensor for Wireless Monitoring of Human Bladder Volume Filippo Melloni, Giorgio Ernesto Bonacchini, Mario Carioni and Guglielmo Lanzani; Istituto Italiano di Tecnologia, Milan, Italy.

The incidence of pathologies related to bladder dysfunction is clinically relevant, these including spinal injuries and neurological disorders. A considerable part of these illnesses is associated to urinary incontinence, which is not only cause of severe discomfort for patients, but in cases of poor or erroneous treatment it could lead to infections and tissue lacerations, with serious threats for health. A number of therapies are currently available for micturition control, however a definitive solution for real-time and adequate monitoring of bladder volume is still not available. Such a solution would allow the continuous probing of the filling state of the organ, thus avoiding the insurgence of two complications, i.e. excessive expansion of the bladder and its incomplete evacuation. This aid could work in cooperation with a wearable unit or also as feedback for already existing systems apt to urinary stimulation.

We herein propose an innovative design for a capacitive strain gauge, fabricated with a hybrid process that exploits organic and flexible materials as scaffold, metallic conductive layer as electrodes and an electrical insulator coating as protective and dielectric layer. The main challenge for this application is the design of a strain gauge able to match the high elasticity of the sensor and the considerable elongation that the device undergoes during bladder filling and emptying. For this reason, we designed a strain gauge made up of two different dielectric layers with different dielectric constants, obtaining a stepwise varied dielectric constant that allows for a linear response of the sensor to the deformation of the bladder.

The proposed design allows for a distributed strain analysis exploiting a principle similar to a linear encoder, and embeds contactless communication through an integrated RF antenna. In our work, we operate the system on an artificial bladder model, demonstrating contactless data read-out via a passive communication system, and thus paving the way towards testing on more realistic ex vivo and in vivo models.

The sensing system proposed in this work thus aims at providing a novel approach to the long-standing issue of bladder volume measurements, by advancing a design that could in principle allow for easy and reliable monitoring, not achievable with current technologies. Further developments of this approach could lead to the coupling of such device to implantable stimulating ones, hence helping to restore the original bladder functionality in patients, as well as enable direct data communication and control though smartphones or other handheld devices.

2:45 PM BM08.02.05
Bioinspired Multifunctional Nanostructures Integrated in Micro-Optical Sensor for Translational Implants Radwanul H. Siddique1, Vinayak Narasimhan1, Jeong-Oen Lee1, Shailabh Kumar1, David Srtavan1 and Hyuck Cho1, 2; California Institute of Technology, Pasadena, California, United States; 3University of California, San Francisco, San Francisco, California, United States; 4Samsung Institute of Advanced Technology, Suwon, Korea (the Republic of).

While numerous multifunctional antifouling nanostructures on insect wings have been previously studied and replicated, their potential incorporation into implantable medical devices remains unexplored. We have demonstrated the use of multifunctional bioinspired nanostructured membrane inspired by transparent butterfly wings for intraocular pressure (IOP) sensing in vivo. [1]

We investigated the multifunctional properties of the biophotonic nanostructures found on the wings of the longtail glasswing (C. faunus) butterfly. The APM, SEM, optical, and biological characterizations have revealed that two groups of dome-shaped nanostructures with different periodicity co-exist on the transparent wings of the C. faunus: (1) angle-independent anti-reflective nanostructures with periods of 140-180 nm in the postdiscal areas; and (2) angle-independent transmissive light-scattering nanostructures with periods of 200-300 nm in the basal areas. In vitro testing has revealed both regions displayed antifouling properties based on physically-induced cell lysis. We have (1) adapted the coherence-preserving angle-independent transmissive light-scattering nanostructure as the sensing platform for the IOP sensor, and (2) fabricated the sensor as a passive and wireless micro-photonic sensor and demonstrated the ability to sense IOP in vivo. We have also validated the sensor in vivo in two different models using a standard and a custom fabricated device.
property of the basal nanostructures that could make optical sensors such as Fabry Perot (FP) resonators more angle-independent; and (2) by further engineering the basal nanostructures, created bioinspired nanostructures (BINS) that would prevent cell lysis and suppress inflammation. To produce BINS with periods of 385-505 nm on a Si$_3$N$_4$-membrane, we used a polymer-phase-separation process following the nature’s way of forming nanostructures [2,3]. Angle-resolved transmission spectroscopy showed that the light transmission of the BINS-integrated membrane was twice more angle-independent than a flat Si$_3$N$_4$-membrane. In a series of in vitro studies, the BINS-integrated Si$_3$N$_4$ surface displayed remarkable anti-biofouling properties against proteins (albumin and streptavidin, ***P ≤ 0.001), prokaryotes (E. coli, **P ≤ 0.01), and eukaryotes (HeLa cells, **P ≤ 0.001) when compared to flat Si$_3$N$_4$ and control (glass) surfaces.

Finally, we integrated BINS onto the FP-resonator-based IOP sensor that was recently developed in our lab [4]. However, its practical applications were limited by its narrow readout angle inherent to FP-resonators and infrequent but severe biofouling observed after long-term implantation. The BINS integration onto the IOP sensor led to a 2.5-fold improvement in readout angle allowing easy handheld monitoring and in a one-month in vivo study conducted in rabbits, showed a 3-fold reduction in IOP error and 12-fold reduction in tissue encapsulation and inflammation, compared to an IOP sensor without BINS.

References
Portable Respiration Sensor Using Nanoparticle Film for Monitoring Respiratory Condition

Shinya Kano and Minoru Fujii; Kobe University, Kobe, Japan.

Respiration is one of the important vital signs of human in daily life. Respiratory signals including the information of rates, patterns, and phase are highly related to condition of respiratory organs and activity of exercise. Monitoring respiration rates helps us to find a risk of respiratory disorders such as sleep apnea, asthma, and chronic obstructive pulmonary disease. Conventional respiratory monitoring system, such as transthoracic impedance plethysmography, mainly records respiration of subjects at rest because motion of a target person can affect the observation of respiration. Therefore, wearable respiration sensors using various sensing mechanisms have been intensively studied. In this study, for monitoring human respiratory condition during exercise, we develop a portable respiration sensor with a humidity-sensitive nanoparticle film. We adopt surface-oxidized silicon-based nanoparticle (silicon nanocrystal, silica nanoparticle) thin films as a humidity-sensitive film. The thin films are solution-processed on flexible polyimide films by using the colloidal nanoparticle solution. Interdigitated electrodes on the polyimide films have 100 μm spacing. Fabricated devices work as a respiration sensor which detects water vapor in exhaled air. Response of the respiration sensor is fast enough to fully monitor human respiration condition up to 1.7 Hz. Patterns and phase of respiration can be analyzed by using the signal of the sensor. We also demonstrate a portable sensor using a portable data logger and a humidity-sensitive film for monitoring human respiration during running. This sensor can track and assess respiratory information during exercise easily.


4:45 PM BM08.02.10
Thread-Based Wearable Multiplexed Sensor for Real-Time Sweat Monitoring
Trupti Teese, Zimple Matharu, Meera Punjia, Boyang Lyu and Sameer Sonkusale; Department of Electrical and Computer Engineering, Tufts University, Medford, Massachusetts, United States.

A wearable thread based sensor patch for continuous multiplexed analysis of sweat is reported. This sensor performs real-time, simultaneous, on-body measurements of important sweat markers such as electrolytes (sodium and ammonium ions), metabolites (glucose and lactate), sweat pH and body temperature. Low cost and flexible polyester threads coated with conductive inks were used as sensing electrodes. Selective potentiometric detection of electrolytes and pH was achieved by an ion-selective membrane and pH-sensitive polyaniline coating on threads respectively. Whereas threads functionalized with enzymes were used in the amperometric detection of glucose and lactate. The selectivity and sensitivity of these sensors in detecting the known concentration of target analyte were studied. The array of these selective thread sensors were further integrated on a patch that can be worn on the skin with readout electronics for real-time sensing. The real-time data was recorded by placing the sensor on the human volunteer during strenuous exercise condition. This sensor device can also be integrated with wireless data communication and storage for real-time data analytics. Proposed thread based sensing platform truly offers a great avenue for simple, low cost, flexible and stretchable wearable sensor development which can be sewn, woven or sutured on any substrate including body tissues.

SESSION BM08.03: Poster Session I: Materials-to-Devices for Integrated Wearable Systems—Energy Harvesting and Storage, Sensors/Actuators and Integration

Session Chairs: Jinhye Bae and Choongho Yu
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

BM08.03.01
Self-Healable, Transparent and Stretchable Pressure-Sensitive Capacitor Using Light-Induced Curable Polymer Based on Dynamic Reversible Urea Bonds
Sun Ok Kim2, Cheul-Ro Lee2, Youngmin Kim1 and Jang-woong Kim2; 1Korea Electronics Technology Institute, Seongnam Gyeonggi, Korea (the Republic of); 2School of Advanced Materials Engineering, Chonbuk National University, Jeonju, Korea (the Republic of).

Since the functionalization of the pressure sensor is basically based on contact with external objects and mechanical deformation of the sensor, efforts to render the pressure-sensitive devices robust and durable to withstand mechanical damages have led to development of various self-healable polymers. Considering that polymers are susceptible to be damaged which would severely weaken the mechanical properties and lifetime of materials, the integration of the pressure sensing functionalities with the ability to self-heal would be highly beneficial to all the domains of their application. One of the most prominent self-healing approaches is Diels–Alder (DA) reaction, which utilize reversible covalent bond formation. Previous studies have revealed that in polymeric materials based on multi-furan and multi-maleimide synthesized via the DA reaction, the inter-monomer linkages disconnect at temperatures above 120 °C (corresponding to the retro-DA reaction) and subsequently reconnect upon cooling. It was revealed that the DA adducts can be used in fabrication of self-healable and stretchable substrate due to their impressive healing performance and mechanical softness. However, DA-based elastomeric polymers are not considered to be suitable as a material for fabricating a pressure sensor because of their insufficient toughness and strength. Recently, the urea bonds with bulky substituents have drawn much attention as the linkages for the self-healing polymers because they were reversibly transformed to their starting materials of isocyanate and amine groups in the mild condition. Furthermore, the Young’s moduli of the polymers with the dynamic urea bonds can be enhanced when they were produced through the UV curing process due to the high density in crosslinking. Inspired by this, we have synthesized the UV-curable urethane acrylate and monomer featuring the dynamic urea bonds. The mechanical properties and the self-healing capabilities were adjusted by mixing the urethane acrylate and the monomer. Based on this, we fabricated a self-healable, stretchable and transparent pressure-sensitive capacitor by embedding Ag nanowire (AgNW) patterns just underneath the surface of the polymer. A simple tandem compound electrode was patterned on AgNW electrodes, allowing a capacitance to be formed between the parallel electrodes, which varies with the gap. The resulting sensor was mechanically stable to several bends or stretches, and was highly sensitive to the direct contact pressure or its deformations. Most interestingly, many artificially formed scratches by steel brushes on AgNW electrodes were instantaneously removed by irradiations of intense-pulsed-light (IPL). The scratches formed at the surface of the electrode were healed and electrical conductivity was efficiently recovered by the photo-thermal effect. The scratching and healing were repeatedly demonstrated at the same location for several times.

BM08.03.02
Multimodal Resistive Pulse Analysis
Makusu Tsutsui1, Kazumichi Yokota1, Akihide Arima1, Wataru Tonomura2, Masayoshi Tanaka2, Mina Okochi2.
Masateru Taniguchi¹, Takashi Washio³ and Tomoji Kawai¹; ¹Institute of Scientific and Industrial Research, Ibaraki, Japan; ²Tokyo Institute of Technology, Tokyo, Japan.

A nanoscale hole sculpted in a thin solid membrane, so-called nanopore, has been extensively studied as an ultrasensitive sensor device for detecting and identifying particles and molecules of variety of sizes from cells to polynucleotides. It measures temporal blockade of the ionic current flowing through the nanochannel, via an individual object passing through there. Height of the thus acquired electrical signals, which is in a form of a resistive pulse, serves as a useful index to measure the size of the object as the amount of ion exclusion scales with the size of the object. Compared to this conventional single-modal approach, I will present our recent research on multimodal resistive pulse analysis for identifications of single-particles through leveraging machine learning algorithm to pattern-analyze the single-particle signatures in a high-dimensional feature space.

Our device consists of a nanopore formed in a thin Si₃N₄ membrane. Here, the channel depth was designed to be much thinner than the diameter. This low-thickness-to-diameter aspect ratio architecture renders exceptional sensitivity of the ionic blockade to not only the size of analytes but also several other features including their shape and surface charge status (M. Tsutsui et al., ACS Nano 10, 803-809 (2016)). Using the ultrathin nanopores, we obtained resistive pulses for several kinds of bacteria and viruses. Each pulse waveform, which contains wealth of information about the detected bioparticles, was then interrogated by the ensemble learning method (M. Tsutsui et al., Sci. Rep. 7, 17371 (2017)) with multiple feature parameters such as the width and pulse bluntness. We demonstrated single-bacteria discriminations of resembling shape and size by the multimodal resistive analysis method with better accuracy than the conventional single-modal approach (M. Tsutsui et al., Sci. Rep. 7, 17371 (2017); Anal. Chem. 90, 1511-1515 (2018)). In my presentation, I will also show our recent results on a use of the machine learning based single-particle analysis for influenza typing in a functionalized nanopore.

BM08.03.03
Soft Electromagnetic Actuators
Stanley Doerger and Cindy K. Harrett; University of Louisville, Louisville, Kentucky, United States.

The prevalence of textiles in our everyday lives, from clothes to upholstery to carpets, means we are surrounded by flexible and wearable surfaces that can support functional fibers—including current-carrying wires. In this work, we use machine embroidery to embed fine, insulated copper magnet wire into flexible fabrics, producing soft electromagnetic actuators. We show that consumer-level embroidery machines are capable of making thin, flexible cm-scale electromagnets that exert forces and torques on permanent magnets. Beyond textiles, we discuss a path to transfer these electromagnetic actuator sheets into soft silicones and 3D printed robotic parts [1].

Our soft electromagnetic actuators use currents in the 100-500 mA range and voltages in the 1 V range. To produce linear motion, pairs of coils are driven by a sequenced pair of square waves that create a travelling magnetic field, driving a permanent magnet along the length of the device; alternatively the soft coils can move atop a stationary magnet array [2]. The magnets move in discrete steps related to the distance between segments of the embedded coils.

Using experiments and simulations, we examine the effect of magnet size and material, wire gauge, current, loop density and coil shape on the output force. We also investigate an embroidery-specific tradeoff: how to maximize the magnetic field gradient by creating flux overlap from multiple coils, while preventing the sewing needle from striking previously-placed wires and maintaining flexibility of the finished device. These embroidery-specific coil pattern generators are available for others to use.

Further investigations look at the maximum speed at which permanent magnets can be driven, the maximum height the magnet can be above the surface for successful actuation, and currents induced by externally moving a permanent magnet in the presence of the flexible coils. Potential applications of this technology include energy harvesting using stretchable materials, wearables with integrated actuators that can open vents, create folds and move flaps in fabrics, precision positioning on flexible surfaces, and electromagnetic actuator sheets that can be dropped into 3D printed robotic mechanisms.


BM08.03.04
Performance Optimization of Thermoelectric Measurement Based on Wearable Materials
DanHong Han, Gang Li and Shengyong Xu; Key Lab. for the Physics and Chemistry of NanoDevices Department of Electronics Peking University, Beijing, China.

Along with the development of nanotechnology, wearable devices and “Internet of Things”, substrate materials using for wearables include PET, parylene, PDMS and less conventional substrates, such as papers [1, 2]. Polyethylene terephthalate (PET) has been broadly used as the substrate for fabrication of flexible electronics owing to that its optimal thermoelectricity is beneficial to slow down the device performance degradation. Parylene has not only the well electrical properties, protective performance, but also the bio-compatibility, which is listed as a long-term implantable biological medical materials in the body. We can measure changes on physiological state like the surface and internal micro-scale temperature changes in living organisms through this flexible material. How to optimize the performance of a thin-film thermocouple array using for monitoring the body temperature at times on the flexible material is our concern.

Here we will introduce a kind of cascaded devices with a single layer of metal thin-film thermocouple (TFTC) [3]. A single layer metal thermocouple is similar to a conventional bimetalic thermocouple, but the two beams of the sensor are of different widths and composed of the same metal thin film, which leads to that the sensitivities of the single-metal TFTCs were all around 1 μV/K or less. In view of this situation, we developed the cascaded array of single metal thin film thermocouples, which consist of a 5μm narrow stripe and a 100μm wide stripe. We have got a 64-cascaded thermocouple achieved a Seebeck coefficient of up to 55.69 μV/K, which is much higher than that of a commercial type-K thermocouple, 39.60 μV/K. Furthermore, we have fabricated this cascaded array on flexible substrates - parylene-C, making it potentially useful in practical applications such as measuring arm surface temperature, as seen in Figure 1.

Due to the simple fabrication process and remarkable temperature sensing ability, the cascaded thermocouples could be integrated easily into the flexible electronics and wearable devices, as well as find potential applications in monitoring temperature of body surface and interior in real time under various conditions, which would be beneficial to public health and care.

BM08.03.05
Magnetically Actuated Hydrogels as a Remote-Controlled, Robust and Wearable Drug Delivery Platform Ayomide Perera, Richard Jackson, Mark Modownik and Marc-Olivier Coppens; University College London, London, United Kingdom.

Polymer hydrogels incorporated with magnetic nanoparticles (MNPs) have vast potential in various biomedical applications such as treatment of cancer and cardiovascular diseases, and in regenerative medicine. The advantages of having MNPs in such platforms are that they can be remotely triggered by various methods, such as hyperthermia, pH and chemical changes, to release drugs or other desired molecules. Actuation of a drug-carrying platform by an external magnetic field (i.e., magnetic actuation), is another such possible pathway to trigger drug release in a controlled manner. This technique has tremendous potential as a non-invasive, safe and precise approach to drug delivery, for both in vivo and ex vivo applications.

We have developed a novel technique to fabricate polymer hydrogels incorporated with Fe₃O₄ MNPs. These gels are biocompatible, and can be actuated via an external magnetic field. The porosity and mechanical properties of the gels can be readily customized. Various drug molecules can be mixed into the polymer-MNP solution, prior to gel formation, to generate gel patches infused with known drug quantities. Using acetaminophen as a model drug, we demonstrate that these gels can be actuated with external magnetic fields for drug release. The amount of acetaminophen released can be controlled by customizing the physicochemical properties of the gels by varying the amount of either polymer or MNP concentrations.

The macro-structure of the magnetic gels can be tailored to optimise their mechanical properties. We have used a nature-inspired approach, by utilizing the structural and functional features of mollusc nacre (i.e., the inner shell layer) to improve the compressibility and strength of the gels. 3D printed templates were employed to develop hexagonal moulds that were used to assemble the gel into various layer-by-layer structures. This technique allowed the Young’s modulus of the layered gels to be increased up to 5 times, compared to the non-layered material.

The biocompatibility, customizable properties and robustness allows for these materials to be used as wearable drug release devices for both external and sub-epidermal applications. The magnetic component allows for remote control actuation, as well as the possibility to be activated via hyperthermia. Such a platform can potentially lead to significant improvements in targeted drug delivery, with minimal invasive procedures.

BM08.03.06
Low Voltage, Core-Shell Electrospinning Patternning of Submicron Silver Fibres Wenya Wang, Xia Li and Yan Yan Shery Huang; Engineering Department, University of Cambridge, Cambridge, Cambridge, United Kingdom.

Ultrathin, meso-scaled metallic fibres possess unique mechanical, electrical and optical properties, such as high aspect ratio, transparency, and lightweight. These properties will enable a wide range of novel applications such as fibre-based circuitry, and flexible and transparent electrodes. Due to their low bending stiffness, meso-scaled metallic fibres produced by existing fabrication techniques are restricted to applications where the fibres were bound to a supporting substrate. Such a configuration inevitably compromises the unique attributes of the meso-scaled fibre structure, as the mechanical and optical properties of substrate can dominate the performance of final products. Herein, we introduce a novel one-step printing technique to synthesis and pattern conductive silver meso-fibres under mild temperatures and atmospheric conditions. We demonstrate spanning silver core-shell fibre arrays with an average diameter of ~1μm and best conductivity of 1.8×10⁶ S/m. A rapid line writing speed of 600 mm/s is achieved, where fibres can span across a distance of up to 10mm with both ends making direct electrical contact with external circuits. No post-processing such as annealing is required in this process. Based on this technique, ‘floating’ electronic structures are demonstrated with LEDs and photodiodes. Unlike traditional transparent or flexible electrodes confined to a substrate, in our work, electronics can be mechanically suspended and electrically connected by the meso-fibre array alone. Tensile test shows that the mechanical property of the fibres is similar to human skin, indicating potentials for artificial skin and wearable sensors. Overall, we demonstrate an efficient and rapid silver meso-fibre patterning technique, and its applications in facilitating facile circuitry connection for unconventional, floating electronic structures.

BM08.03.07
A Novel and Rapid Single Step Approach Toward Fabrication of Piezoelectric Sensors Chithra Parameswaran and Dipti Gupta; Indian Institute of Technology Bombay, Powai, India.

Sensors for biomedical applications have become indispensable for their signal detection and simplicity. Various fabrication techniques are being explored for fabrication of cost effective and high sensitive piezoelectric sensors, both capacitive and resistive in nature. For this purpose elastomers sponges have been targeted due to their skin conformity and bio-friendly nature. Here we introduce a leavening agent mediated process for obtaining PDMS sponges over large area. These are then realized in capacitive sensors over a wide range of pressure from finger touch to pulse sensing with better sensitivity (0.756 kPa⁻¹ to 5kPa) to the best of our knowledge. This approach is further extended in obtaining resistive pressure sensor by bringing a variant in the synthesis. The hydrophilic sponge is made resistive using a dip-and-dry method in a commercially available ink. A compression induced in the sponge decreases the resistance providing an electrical equivalent of the applied mechanical stimulus providing an efficient resistive sensor with good cyclic response and sensitivity. The approach presented here paves way for huge feasibility in obtaining desired sensitivity and porosity during the in-situ fabrication process which is a first report in literature.

References:

BM08.03.08
Broadband LED and Piezo-Phototronics Enhanced Photodetector on CMOS Compatible Flexible Si Platforms Arijit Sarkar, Ajit K. Katiyar, Amal K. Das and Samit K. Ray; 1S.N. Bose National Centre for Basic Sciences, Kolkata, India; 2Advanced Technology Development Centre, Indian Institute of Technology Kharagpur, Kharagpur, India; 3Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur, India.

Development in mechanically flexible optoelectronic devices on Si platforms, compatible with conventional CMOS technology are encouraging for future integrated wearable and flexible optical sources, detectors, displays and solar cells. Typical flexible devices based on organic semiconductors are fabricated on plastic substrates. These devices have the disadvantages of thermal and chemical degradation as well as low mobility of carriers and low efficiency compared to Si based devices. Therefore, optoelectronic devices fabricated on mechanically flexible Si substrates are very promising in this regard. Here we report the fabrication of flexible Si membranes (3-5 μm thick) acting as a substrate to develop a low power consuming broad band visible light emitting diode (LED) and a high responsive photodetector, sensitive to both UV and visible photons. The p-Si membranes are fabricated by simple and
cost effective chemical etching method followed by n-ZnO thin film (~180 nm) deposition by RF sputtering method forming a p-n heterojunction. The n-ZnO/p-Si membrane heterojunction exhibits very good rectification behaviour and broad band electroluminescence (EL) in the 400-850 nm wavelength range at room temperature under forward bias condition. The minimum operating voltage of the fabricated flexible LED is 3.19 V which is lowest on comparing with other reported results on similar device structure. The EL from the device appears to be yellowish white to naked eye in a dark room. The flexibility of the device was tested by recording EL spectra at different bending conditions, from relaxed to bend to a semi-circle. In all the cases the EL spectra exhibited no significant change in intensity or emission feature. This confirms that the fabricated flexible LED performed brilliantly under different mechanical bending conditions.

Similar n-ZnO/p-Si membrane heterojunction was also developed into a flexible and high responsive photodetector which demonstrated enhanced photosresponse in UV and visible wavelength range utilizing piezo-phototronic effect. A peak responsivity of 0.20 AW⁻¹ with detectivity of 4.8 × 10¹³ cm Hz⁻¹/₂ W⁻¹ has been obtained without applying any external bias. The high mechanical flexibility of the Si membranes and the inherent piezoelectric property of ZnO thin film have been utilized to enhance the performance of the device via piezo-phototronic effect. On application of external tensile strain, piezo-potential developed in piezoelectric ZnO thin film has been exploited to modulate the transport property of the photo generated carriers thereby enhancing the device performance. Photocurrent has increased by 22% with gradual increase in the applied tensile strain. Thus the fabricated mechanically flexible n-ZnO/p-Si membrane heterojunction based low power consuming broad band visible LED and piezo-photodetector is very promising for future wearable optoelectronic applications such as flexible displays and CCD devices.

BM08.03.09
DNA-Inspired Supercoil Fiber for Superelastic, Weavable Supercapacitors Changsoon Choi¹ and Younghoon Kim²; ¹Division of Smart Textile Convergence Research, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea (the Republic of); ²Convergence Research Center for Solar Energy, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea (the Republic of).

Stretchable and electrically conductive one dimensional fibers are important for diverse applications. Here we report the DNA supercoil structure inspired composite fibers which are highly stretchable, and electrically conductive. Carbon nanotube wrapped sheath on commercially available spandex core fibers were fabricated and giant twist was inserted for supercoiling. The resulting supercoiled composite fibers show highly ordered and compact structures along fiber direction, which enable superelasticity (up to 1300%). The supercoiled fiber exhibited stretch-invariant electrical property that very low resistance increase is observed for a fully stretch, when especially overcoated by passivation layer. Moreover, by incorporating pseudocapactive MnO₂ active materials on the supercoiled fibers, we demonstrated the superelastic supercapacitors with high linear and areal capacitances, which are highly retained when reversibly deformed in the fiber direction.

BM08.03.10
Graphene Oxide Modification for Machine Learning-Based Multisensor Systems Feder S. Fedorov, Alena Alekseeva, Stanislav Evtushin, Vladislav Kondrashov, Maxim Panov, Alexander Shafeev and Albert Nasibulin; Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

Monitoring of temperature, air humidity, concentration of CO₂ and CO air pollutants (NOₓ, SOₓ), and volatile organic compounds requires new sensor systems which would combine enhanced selectivity and low detection limit. Among criteria to be fulfilled, we could outline low power consumption what requires room temperature operation, simple manufacturing protocols and long-term performance that generally determines the cost of the final product [1]. Thus, the key element of the sensor is a sensing material whose properties should be properly tuned to enable good performance. Here we propose a single material sensor platform based on graphene oxide (GO)/reduced graphene oxide (rGO) which is a unique material sensitive to humidity, pollutants and other gases [2]. The material also responds well to temperature changes. GO/rGO shows good response, stability, reversibility at ambient conditions, though, lacks the selectivity. To approach the selectivity, we combine several sensors based on GO/rGO material in an array whose vector signal is processed by pattern recognition algorithms to get a “fingerprint” of the gas mixture at defined temperature, following known multisensory concept. Sufficient variation of the sensor properties enables successful discrimination of the environment changes. Such variation we create by partial reduction GO by laser under developed treatment protocols [3]. Particularly, we will discuss the results on sensor arrays fabricated by irradiation of GO by laser to transform it to rGO tuning the ratio between GO/rGO areas what allows us to get different response for each sensor element in the array. The reconstruction of the environment changes from property variations is realized by modern machine-learning algorithms what we illustrate by successful determination of both the humidity (from 5% to 95% RH) and the temperature (up to 60 °C). The authors acknowledge MIT Skoltech Next Generation Project.


BM08.03.11
Stretchable Substrate for Body Attachable Systems Minwoo Nam, Myung Sub Lim, Young Hyun Son and Kyung Cheol Choi; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Development of stretchable electronic devices has been perceived as a key technology to meet interest in making more functional devices. Compared with recently-commercialized electronic devices, which are mechanically robust because they are based on rigid substrates such as wafers or glass slides, stretchable electronic devices that can withstand a variety of mechanical stress conditions like bending, twisting and folding can be integrated with wearable or fashionable electronic clothing and biocompatible medical devices.[1-2] The ability of stretchable electronic devices to undergo stretching and compression to various degrees will enable people to move more freely when the devices are worn or even placed on the skin. To realize stretchable electronics, the flexibility limitations of plastic and glass substrates have to be overcome and stable operation performance is needed on the substrate when elongated. Here, we have developed design and fabrication technology for stretchable substrates with structures yielding mechanical stress isolation and relief for body attachable systems.

In this study, we fabricate a stress-relief stretchable substrate by structure change of substrate with general materials and demonstrate its feasibility, with the further aim of developing a soft patch for an obstructive sleep apnea monitoring system. The stretchable substrate used in this study consists of two parts, one, PDMS, which gives elasticity to the substrate and another, SU-8 (negative photoresist), consisting of rigid planar plates on which chips and devices are operated. Patterned with bridges and plates, SU-8 can be stretched and tied up on top of the protruding PDMS pillar arrays. The PDMS column array disperses the mechanical stress applied to the SU-8 plates when the substrate is elongated and makes devices more stable. Transfer-based integration
of thinned chips onto stress-relief stretchable surface allows us to realize sensors and devices that can remain stable under tensile and compressive stress. We fabricated different colors of organic-light emitting diodes, which are applied to a sleep apnea monitoring system on stress-relief substrates using thermal evaporation without the addition of a process like pre-straining of the substrate; devices were found to work stably under stretch-release test.

In conclusion, we present stress-relief stretchable substrates essential for realization of body attachable systems applicable to non-planar and arbitrarily shaped surfaces. Integrated circuits and sensors can be operated when the patches are stretched with stress-relief substrates, reducing stress on devices. This substrate is expected to provide a key base technology for wearable electronic devices as well as medical patch systems.


BM08.03.12
Encapsulation of Single Nanoparticle in Fast-Evaporating Micro-Droplets in PDMS for Photocatalysis and Other Applications Xinjian Shi and Xiaolin Zheng; Stanford University, Stanford, California, United States.

This work describes the use of fast-evaporating micro-droplets to finely disperse nanoparticles (NPs) in a polymer matrix for the fabrication of nanocomposites. Agglomeration of particles is a key obstacle for broad applications of nanocomposites. The classical approach to ensure the dispersibility of NPs is to modify the surface chemistry of NPs with ligands. The surface properties of NPs are inevitably altered, however. To overcome the trade-off between dispersibility and surface-functionality of NPs, we develop a new approach by dispersing NPs in a volatile solvent, followed by mixing with uncured polymer precursors to form micro-droplet emulsions. Most of these micro-droplets contain no more than one NP per drop, and they evaporate rapidly to prevent the agglomeration of NPs during the polymer curing process. As a proof of concept, we demonstrate the design and fabrication of TiO2 NPs@PDMS nanocomposites for solar fuel generation reactions with high photocatalytic efficiency and recyclability arising from the fine dispersion of TiO2. Our simple method eliminates the need for surface functionalization of NPs. Our approach is applicable to prepare nanocomposites comprising a wide range of polymers embedded with NPs of different composition, sizes, and shapes. It has the potential for creating nanocomposites with novel functions.

BM08.03.13
Development of Electrochemical Biosensors with Alternative Inorganic Framework Structures Burcu Akata Kurc1, 2, Sergei Dzyadevych3 and Berna Ozansoy1; 1Micro and Nanotechnology Department, Middle East Technical University, Ankara, Turkey; 2Central Laboratory, Middle East Technical University, Ankara, Turkey; 3Laboratory of Biomolecular Electronics, Institute of Molecular Biology and Genetics, Kiev, Ukraine.

An electrochemical biosensor is a self-contained integrated device, which is capable of providing specific quantitative or semi-quantitative information about the composition of a liquid or gaseous sample. Nowadays the development of biosensors is an actual challenge. The biosensors characteristics essentially depend on the conditions of biomaterial immobilization on the transducer surface. Thus, the improvement of methods of immobilization is very important. Recent progress in the synthesis of nanomaterials is a ground for the development of new immobilization methods. It is expected that the application of nanoparticles for biomaterial immobilization will improve sensitivity, linear range, stability, and other analytical characteristics of biosensors. Zeolites as being potential alternative nanomaterials for immobilization are micro- and nanoparticles based on a crystalline lattice structure containing a highly ordered structure with a complex pore and canal system. They have a large surface area, on which various substances can be adsorbed, and are widely used in various fields as adsorbents. In the current work, zeolites were added to the biorecognition elements of the biosensors and served as additional components of the biomembranes or adsorbents for enzymes. Three types of biosensors (conductometric, amperometric and potentiometric) were studied and developed biosensors were compared with similar traditional biosensors without zeolites. The biosensors contained the following enzymes: urease, glucose oxidase, glutamate oxidase, and acetylcholinesterase and were intended for the detection of urea, glucose, glutamate, and acetylcholine, respectively. Furthermore, a biosensor for the sucrose determination contained a three-enzyme system (invertase/mutatorase/glucose oxidase), immobilized by a combination of adsorption on silicalite and cross-linking via glutaraldehyde; such combined immobilization demonstrated better results as compared with adsorption or cross-linking separately. The analysis of urea and sucrose concentrations in the real samples was carried out. Methods to obtain these zeolitic films on flexible substrates will be discussed. Accordingly, results obtained with biosensors were shown to have high correlation with the results of traditional analytical methods, thus the developed biosensors are promising for practical applications.

BM08.03.14
Self-Cleanable, Stretchable and Transparent Ionic Communicators Based on Triboelectricity Younghoon Lee and Jeong-Yun Sun; Seoul National University, Seoul, Korea (the Republic of).

Human-machine interfaces have been highlighted with the advent of wireless sensor networks and the internet of things; it may require wearable/attachable electronics exhibiting stretchability, biocompatibility, and even transmittance. Furthermore, due to limited weight and volume for wearability, energy efficient and even self-powered devices are required. Here, we report practical approaches for a stably self-cleanable, transparent and attachable ionic communicator based on triboelectric nanogenerators. It can be easily applied on human skin due to its softness and chemically anchored robust layers. It functions as a means of real-time communication between humans and machines. Surface functionalization on the communicator by (Heptadecafluoro-1,1,2,2-tetrahydrodecy)trichlorosilane improves sensitivity and makes the communicator electrically and optically stable due to the self-cleaning effect without sacrificing transmittance. This research will be a foundation for potential development of attachable ionics, self-powered sensor networks, and monitoring system for biomechanical motion.

BM08.03.15
Integrating Deep Learning into Wearable Stretch Sensors Ben Oldfield2, Richard Jackson1, Peter Smitham1 and Mark A. Miodownik1, 3; 1Mechanical Engineering, University College London, London, United Kingdom; 2CoMPLEX, University College London, London, United Kingdom; 3UCL Institute of Orthopaedics & Musculoskeletal Science, Royal National Orthopaedic Hospital, London, United Kingdom; 4Institute of Making, University College London, London, United Kingdom.

There is a growing need for flexible stretch sensors to monitor real time stress and strain in wearable technology. However developing stretch sensors with linear responses is difficult due to viscoelastic and strain rate dependant effects. Instead of trying to engineer the perfect linear sensor we take a deep learning approach which can cope with non-linearity and yet still deliver reliable results. We present a general method for calibrating highly hysteretic resistive stretch sensors. We show results for 1D and 2D textile and elastomeric stretch sensors however we believe the method is directly applicable to any physical choice of sensor material and fabrication, and easily adaptable to other sensing methods, such as those based on capacitance. Our algorithm does not require any a priori knowledge of the physical attributes or geometry of the sensor to be calibrated, which is a key advantage as stretchable sensors are generally applicable to highly complex geometries with integrated electronics.
requiring bespoke manufacture.

The method involves three-stages. The first stage requires a calibration step in which the strain of the sensor material is measured using a webcam while the electrical response is measured via a set of arduino-based electronics. During this data collection stage, the strain is applied manually by pulling the sensor over a range of strains and strain rates corresponding to the realistic in-use strain and strain rates. The correlated data between electrical resistance and measured strain and strain rate are stored. In the second stage the data is passed to a Long Short Term Memory Neural Network (LSTM) which is trained using part of the data set. The ability of the LSTM to predict the strain state given a stream of unseen electrical resistance data is then assessed and the maximum errors established. In the third stage the sensor is removed from the webcam calibration set-up and embedded in the wearable application where the live stream of electrical resistance is the only measure of strain - this corresponds to the proposed use case.

This rapid desktop method requires less than one hour of data collection followed by a fully automated calibration routine based on LSTM. Highly accurate stretch topology mapping (within 5-15% errors) is achieved for the sensor skins tested including three different commercially available flexible sensor materials (Medtex P130, Technitex P130B, and Adafruit conductive rubber) as well as a bespoke printed composite silicone stretch sensor.

We discuss the application of our approach to various real-world use scenarios in emerging wearable technology sectors including prosthetics and assistive technology.

BM08.03.16
Integrating MXene Electrochemical Microsupercapacitor with Triboelectric Nanogenerator as a Wearable Self-Charging Power Unit Qiu Jiang1, Changsheng Wu2, Zhengjun Wang3, Aurelia C. Wang4, Jr-Hau He5, Zhong Lin Wang6 and Husam N. Alshareef7; 1King Abdullah University of Science & Technology, Thuwal, Saudi Arabia; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

One aspect that has been poorly studied in the field of wearable electronics is the integration of energy harvesting and storage devices. By using silicone to encapsulate TENG device and solid-state microsupercapacitor into a single monolithic device, a power unit made of a single-electrode-mode TENG and 2D MXene-based solid-state microsupercapacitor can sufficiently convert and store mechanical energy of human biomechanical motions into electrochemical energy, while maintaining long life time and high mechanical flexibility.

The device can utilize and store the random energy from human activities in a standby mode and provide power to electronics when active. As a result, our microsupercapacitor delivers a capacitance of 23 mF/cm² with 95% capacitance retention after 10,000 charge-discharge cycles, while the triboelectric nanogenerator exhibits a maximum output power of 7.8 µW/cm². Given the simplicity and integrated nature, our device can be integrated with a variety of electronic devices and sensors.

BM08.03.17
Facilely Prepared Layer-by-Layer Graphene Membrane-Based Pressure Sensor with High Sensitivity and Stability to Detect Human Motions Liu Tao; City University of Hong Kong, Hong Kong, Hong Kong.

With the prospering development of artificial intelligence, medical diagnostic and electronic skins, wearable electronic devices have drawn much attention in our daily life. Flexible pressure sensors with high sensitivity, especially in a large pressure range regime are highly required in the past decades.

In this work, graphene membrane with a layer-by-layer structure has been successfully prepared via a facile self-assembly & air-drying (SAAD) method. Air-drying the graphene hydrogel contributes to the uniform and compact layer structure in the obtained membrane. Owing to the excellent electrical and mechanical properties of the prepared graphene membrane, the pressure sensor based on several layers of membranes has high sensitivity and repeatability in the pressure range of 0-20 kPa. What’s more, the pressure sensor shows desired results in wearable applications to detect human motions. We demonstrate it can be used for pulse monitoring, breathing detection as well as various intense motion recording such as walk, run and squat et al.

We hope the facilely prepared layer-by-layer graphene membrane-based pressure sensor will have great potentials in the fields of smart electronics for medical health, human movements and even artificial intelligence and robot technology development.

BM08.03.18
Flexible InO/Al2O3 Hetero-Interface Diode Using PEALD for Active-Matrix Tactile Sensor Array Platform Hye-In Yeom, Guk-Jin Jeon, Steve Park and Sang-Hye K. Park; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

With a rapid development in Internet of Things (IoT), intelligent terminals including smart wearable devices, humanoid robotics, and artificial electronic skins (E-skin) have attracted huge attention. For those advanced applications, it is necessary to develop a proper tactile sensor array system. Especially for our targeted application (E-skin), we have to consider the low-pressure regime (1-10 kPa), a common but crucial range, covering a pressure on a daily activities. Resistive type sensors are often used due to their simple structure and easy read-out system. So, they offer significant advantages over other types of pressure sensor in terms of integration with other circuit system. Also, backplane can be one of the key component for the tactile sensor array, enabling precise sensing contrast with low noise level and low power consumption. As a switching device in each pixel, organic thin-film transistor (OTFT) has usually been adopted in resistive sensor array, however, they often suffered from environmental degradation and poor electrical performance.

Herein, we demonstrate highly stable and sensitive tactile sensor array platform using flexible InO/Al2O3 hetero-interface diode using plasma-enhanced atomic layer deposition (PEALD). As a starting step, we had to carefully consider proper diode structures according to their environmental stabilities, on/off-ratio, and on-current level. Then, the metal/oxide semiconductor (OS)/insulator/metal (MSIM) structure was adopted and was successfully developed with the ultra-thin indium oxide layer(<3nm) and alumina layer(<20nm) using PEALD, showing outstanding rectifying performance as a switching device. The on-to-off ratio is over 10⁷ and off-current density is lower than 100 nA/cm². There could be several reasons for the fairly stable current flowing phenomenon through the interface between OS and insulator. One plausible cause is enhancement of electron injection from cathode to insulator through thin OS layer, thereby electron can easily flow to anode under forward bias. Thus, on the basis of our active-matrix sensor array platform, any kind of resistive sensor can be integrated with it. The 8x8 matrix arrays were fabricated by photolithography process and top anode was patterned as interdigitated electrode. Then, a microstructured PDMS sheets coated with MWCNT would be integrated on them. We will further discuss about electrical properties and sensing performance.

BM08.03.19
Development of Highly Stretchable Printed Circuit Board Towards Reliable Integration of Electric Components Minsong Kim1, Kyuyoung Kim2, Hyuneul Lim3 and Inkyu Park1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

We developed stretchable printed circuit board (PCB) which can easily integrate electric components with high electrical and mechanical reliability. To surely apply techniques of stretchable electronics to wearable devices, it is necessary to realize totally stretchable device including complex interconnections between electric components. Stretchable PCB is the one of the most promising solution to achieve the all-stretchable electronics. We
chose most suitable elastomeric polymer as a substrate of the PCB by conducting electromechanical tests. Also metal film and highly conductive nanomaterials were used as conductor lines, buried in the substrate. Under the stretched state, metal film was strongly-adhered to the substrate and metallic nanowire act as electrical anchor and bridge respectively. Not only this hybridization effect but serpentine patterns of conductive materials attribute to improvement of the performances of stretchable PCB in terms of stretchability and strain-insensitivity. Additionally, other electric components can be easily integrated onto the opening of substrate occurring electrical/mechanical contact with buried conductor line, which is similar with surface mount technology of conventional PCB. The integration region includes tiny parts of rigid film to minimize stress applied to the mounted components, leading reliable integration. Finally, we show electromechanical characteristics of the fabricated stretchable PCB, and demonstrate the integration performance of which additional components are negligibly affected by the strain of the PCB.

BM08.03.20
Epidermal Multiple-Stimulus Electroluminescence Sensor for Human Activity Monitoring
Eunhyuk Kim, Hyowon Han and Cheolmin Park; Yonsei University, Seoul, Korea (the Republic of).

Wearable human-interactive electronics require the stimuli-responsive sensor that can detect stimuli in human body with vital signals of health-monitoring in epidermal skin through several sensing mechanisms. Here, we describe an epidermal electronic electroluminescence based multiple-stimuli sensor that allows for both monitoring and visualization of human-readable response. This “epidermal multiple-stimulus electroluminescence sensor” (EMES) is capable of human activity monitoring including internal body information and external stimuli. Our device consists of stacked bilayers of sensing layer on two transparent electrodes separated by an in-plane air gap on single side and the epidermal skin itself pressure and conductance sensing architecture. Simultaneous sensing and visualization of human monitoring is achieved to field induced between two separated electrode and skin is controlled by the capacitance change or impedance change of the sensing layer on epidermal skin. The utility of the EMES for human activity signal has been successfully demonstrated by touch, blood pressure, respiration, motion behaviour, fingerprint recognition, heat/cold, and humidity. Our multiple-stimuli sensor devices provide potential advantages in terms of simplicity, functionality, and broad applicability compared to previous wearable sensor based highly flexible and ultrathin substrate that involve conformal attachment of active elements onto skin.

BM08.03.21
The Effect of Interfacial Interaction on the Conformational Variation of poly(vinylidene fluoride) (PVDF) Chains in PVDF/Graphene Oxide (GO) Nanocomposite Fibers
Jeong-Eun Lee, Sojeong Heo, Youngho Eom, Sang-Ha Hwang and Han Gi Chae; Ulsan National Institute of Science and Technology (UNIST) U Plan Lab, Ulsan, Korea (the Republic of).

Polymers such as poly(vinylidene fluoride) (PVDF), and its copolymers with hexafluoropropylene (HFP), trifluoroethylene (TrFE) and chlorotrifluoroethylene (CTFE) are known to possess electroactive properties and have been studied for decades, enabling them one of the most promising candidates for wearable and smart textile applications. Nonetheless, the practical applications are still limited and are in the early stage of development because of poor mechanical integrity. In the current study, we have prepared PVDF/graphene oxide (GO) nanocomposite fibers by dry-jet wet spinning method at the GO concentrations of 0, 1, and 2 wt% with respect to the polymer weight. The as-spun fibers were drawn in the draw ratio (DR) range of 2 to 6.5, and the correlation between the PVDF chain conformation and the mechanical properties of the fibers upon drawing has been studied by 2D correlation spectroscopy (COS) of Fourier-transformed infrared (FTIR), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and tensile testing. The PVDF/GO nanocomposite fibers exhibited that the mobile PVDF crystals were nucleated because it was based on the conformational defects and kinks due to the polar interaction between PVDF chains and functional groups of GO, whereas the control PVDF fiber showed the conventional conversion of crystal polymorphs (α and γ phases to β phase). As a result, the nanocomposite fiber showed dramatically improved toughness (enhanced by 1123% at a DR of 2 and 120% at a DR of 6.5) as compared to that of the control fiber. Furthermore, the tensile strength and modulus of the PVDF/GO (2 wt%) fiber were 394 MPa and 4.6 GPa, respectively, while those of the control PVDF fiber were 295 MPa and 3.9 GPa.

BM08.03.22
Stretchable Ultrasonic Transducer Arrays for Three-Dimensional Imaging on Complex Surfaces
Hongjie Xu, Xuan Zhu, Chonghe Wang, Lin Zhang, Francesco Lanza di Scalea and Sheng Xu; University of California, San Diego, San Diego, California, United States.

Ultrasonic imaging has been implemented as a powerful tool for noninvasive subsurface inspections of both structural and biological media. Current ultrasound probes are rigid and bulky and cannot readily image through nonplanar three-dimensional surfaces. However, imaging through these complicated surfaces is vital because stress concentrations at geometrical discontinuities render these surfaces highly prone to defects. This study reports a stretchable ultrasound probe that can conform to and detect nonplanar complex surfaces. The probe consists of a 10 × 10 array of piezoelectric transducers that exploit an “island-bridge” layout with multilayer electrodes, encapsulated by thin and compliant silicone elastomers. The stretchable probe shows excellent electromechanical coupling, minimal cross-talk, and more than 50% stretchability. Its performance is demonstrated by reconstructing defects in 3D space with high spatial resolution through flat, concave, and convex surfaces. The results hold great implications for applications of ultrasound that require imaging through complex surfaces.

BM08.03.23
Strongly Correlated Oxides as Electric Field Sensors for Haptics
Zhen Zhang, Derek Schwanz and Shriram Ramanathan; Purdue University, West Lafayette, Indiana, United States.

Advancing sensing modality to monitor bio-matter and chemical signatures in water-containing environment is of great importance in emerging fields of haptics and robotics. However, sensing multiple properties with the same material is often impossible due to instability when exposed to water. On the other hand, elasmobranch marine organisms such as sharks have evolved to naturally detect their environment through various electroreceptors, positioning them as apex predators. In this work, we will discuss how perovskite nickelates such as SmNiO₃ can directly mimic the functionality of the gel-like Ampullae of Lorenzini electroreceptor organs in sharks. Such sensing behavior of nickelates is enabled by an electric-field-driven Mott phase transition in aqueous environment which is accompanied by large nonlinear electrical resistivity increase and visible color change. These unprecedented properties of metastable oxide materials introduce a new sensing modality for environmental sensing that may be adapted to wearables and autonomous systems that operate in unstructured environments.

BM08.03.24
A Novel Straightforward Wet Pulling Technique to Fabricate Carbon Nanotube Fibers
Mariia Goncharova¹, Eugene Shulga¹, Sergey Shandakov², Ivan Sergeichev¹, Evgenia Gilshteyn¹, Anton Anisimov¹ and Albert Nasibulin¹; Skolkovo Institute of Science and Technology, Moscow, Russian Federation; ¹Kemerovo State University, Kemerovo, Russian Federation; ²Canatu Ltd, Helsinki, Finland.

The growing demand for wearable electronics requires flexible and stretchable conductive materials. Among them, carbon nanotubes are recognized for their outstanding mechanical, electrical, optical properties and chemical stability. Although CNTs possess remarkable properties, the devices made of
individual CNTs are quite challenging in fabrication. CNTs are usually used in the form of fibers, arrays, or films. In this work, we introduce a novel technique of rapid fabrication of both active and passive flexible electronic components. A tactile sensor, a pulsometer and an electrical circuit are fabricated for the demonstration of their applicability. We expect this new approach to simplify the production of functional carbon nanotube fibers and to enlarge their usage in diverse applications.

This work was supported by MIT Skoltech NGP Program (Skoltech-MIT joint project).

BM08.03.25
A Bandage-Type, Wearable and Luminescent Sensor for Monitoring Transcutaneous Oxygen Pressure Changjin Lim, Soyeon Lee and Jin-Woo Park; Yonsei University, Seoul, Korea (the Republic of).

We present a new concept for a wearable oxygen (O2) sensor for transcutaneous O2 pressure (tcpO2) monitoring by combining the technologies of luminescent gas sensing and wearable devices. O2 monitoring has been exhaustively studied given its central role in diagnosing various diseases. The ability to quantify the physiological distribution and real-time dynamics of O2 from subcellular to the macroscopic level is required to fully understand mechanisms associated with both normal physiological and pathological conditions. Despite its profound biological and clinical importance, few effective methods exist for noninvasively quantifying O2 in a physiological setting. The wearable sensor developed here consists of three components: a luminescent sensing film attached onto skin, an organic light-emitting diode (OLED) as a light source, and an organic photodiode (OPD) as a light detector. The green OLED was fabricated to excite the sensing film in accordance with absorption spectrum of oxygen sensitive material, 2,7,12,13,17,18-octaeethyl-2H,3H-porphyrin, platinum(II), (PtOEP) changing the ratio of PL intensity (sensitivity, L/I30) in relation to O2 concentration. After energy excitation of luminophores by absorption from OLED, the PL emission intensity decreases by energy transfer from PtOEP molecules to surrounding O2 molecules which is called quenching effect. P3HT:PCBM bulk heterojunction based OPD precisely detects the red PL intensity change from the O2 sensing film. All the components are solution-processable and integrated on a plane in a bandage-like configuration. To verify the performance, tcpO2 variations by pressure-induced occlusion were measured in the lower arm and a thumb by the wearable sensor, and the results were comparable to those measured by a commercial instrument. Due to its noninvasive and flexible features, the wearable bandage-like O2 sensor proposed in this study can monitor the tcpO2 in any part of the body, even when a person is exercising or working, which is currently beyond the restrictions of existing commercially available monitoring systems. Our wearable, bandage-like O2 sensor opens new possibilities for the continuous monitoring of not only patients during surgery and recuperation but also out-patients suffering from Raynaud disease, diabetic ulcers and similar ailments.

BM08.03.26
Electroactive Polymer-Electrolyte-Composite Artificial Muscles of Greatly Enhanced Strength Zachary A. Goodwin1, Michael Eikerling2, Hartmut Lowen3 and Alexei Kornyshev1; 1Imperial College London, Cambridge, United Kingdom; 2Chemistry, Simon Fraser University, Vancouver, British Columbia, Canada; 3Theoretical Physics, Heinrich Heine Universität Düsseldorf, Düsseldorf, Germany.

There is great interest in developing artificial muscles for soft robotics.1 Such electroactuators, composed of polymer-electrolyte films with bulky mobile cations, confined between two electrodes, curve in response to an applied voltage between the electrodes (forward actuation). On the other hand, upon bending an output voltage or current can be generated (reverse actuation). Both of which, forward and reverse actuation, involve the redistribution of the mobile cations and solvent. To further understand and develop these much-desired devices, we present a unified theory that describes both forward and reverse actuation with flat and porous electrodes.

Forward actuation with flat electrodes has a limited response from an applied voltage because stressful regions only develop in a minor part of the hydrated fibers with desired properties. To vary by parameters of the CNT fibers, we demonstrated the possibility to control the strength of the SWCNT fibers from 300 to 700 MPa and their resistance from 60 to 300 Ohm (for 1 cm long fiber). The method is also easily adaptive to different kinds of carbon nanotubes and allows rapid fabrication of both active and passive flexible electronic components. A tactile sensor, a pulsometer and an electrical circuit are fabricated for the demonstration of their applicability. We expect this new approach to simplify the production of functional carbon nanotube fibers and to enlarge their usage in diverse applications.

This work was supported by MIT Skoltech NGP Program (Skoltech-MIT joint project).

BM08.03.27
Printed Integration of High-Performance Intrinsically Stretchable TFTs with Soft Sensors for Mass Customization of Wearable Electronics Byeongmoon Lee, Jiseok Seo, Hyeon Cho, TaeHo Kim and Yongtaek Hong; Department of Electrical and Computer Engineering, Inter-University Semiconductor Research Center, Seoul National University, Seoul, Korea (the Republic of).

Soft electronics has become the driving force of innovation in the way that the electronic systems maintain their performance under harsh deformation and are conformably attached on arbitrary-shaped surfaces, thus realizing stretchable display, skin-patch devices, and implantable biomedical electronics. As core components in electronic systems, thin film transistors (TFTs) also need to be soft, in order to give the soft electronic system sophisticated functions without hindering its softness. For this reason, intrinsically stretchable TFTs have attracted great research attention in recent years. Several leading groups have realized this soft basis by exploiting 1-dimensional materials such as single-walled carbon nanotube (SWCNT) as semiconductors and electrodes.
Another novel idea has been reported to make polymer semiconductors stretchable through forming nanoconfined morphology. In spite of these remarkable achievements, there are still many challenges in integrating stretchable TFIs with active components such as silicon-based integrated circuits into wearable electronics. Most of the previous work has focused on fabricating polymer-free devices, and the challenge is to integrate stretchable electronics into wearable systems. In this work, we report a facile and low-cost fabrication strategy based on ink-jet-printing for high-performance intrinsically stretchable TFIs. The materials are carefully selected in order to achieve both high electrical performance and stretchability. We exploit high-K elastomeric dielectrics for gate insulators, SWCNT for active layers, and highly conductive silver nanowire (AgNW)-based stretchable conductors for gate/source/drain electrodes. The components including the gate/source/drain electrodes and the active layers are ink-jet-printed so that all layers of the device are fully customizable. The fabricated devices show mobility of $5-10 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$, on/off ratio over $10^4$, low operation-voltage under $5\text{V}$, and stretchability over $50\%$, which imply the feasibility of our devices for applications in wearable integrated circuits. Furthermore, our ink-jet-printing-based fabrication strategy enables not only facile integration of the soft TFIs with printing-based soft sensors, but also mass customization of the integrated wearable systems. For proof of concept, we demonstrate a series of ink-jet-printed active matrix sensor arrays with various layouts. We believe that this work contributes to the effective integration of soft components into functional wearable systems. The detailed methods and results will be discussed later.

This work was partly supported by Institute for Information & Communications Technology Promotion (IITP) grant funded by the Korea government (MSIP) (No.2017-0-00048, Development of Core Technologies for Tactile Input/Output Panels in Skintronics (Skin Electronics)) and the Center for Advanced Soft-Electronics grant funded by the Ministry of Science, ICT and Future Planning as Global Frontier Project (CASE-2015M3A6A5065309).

**References:**


**BMO8.03.28**

**Principles of Multi-Layer Encapsulant Design for Wearable and Implantable Systems**

Soumen Saha, Bhaskar Mitra and Madhusudan Singh; Electrical Engineering, Indian Institute of Technology Delhi, New Delhi, India.

Wearable and implantable electronic devices are enabling in a new generation customized healthcare real-time monitoring system [1]. Some of the most sophisticated systems involve silicon MOSFETs as the basis for active sensors as well as digital and analog circuits, in a thin, flexible form [2][3]. Protecting these transistors in a harsh fluidic environment is relatively difficult because the requirement of wearability demands biocompatible encapsulation with low flexural rigidity. The charged ions (such as Na+) from the biofluids are capable of diffusing rapidly through the thin encapsulation layer and destabilize the entire system. Moisture is another problem since the water molecules could either penetrate through or dissolve the encapsulation layer at a temperature-dependent rate. The optimization of the encapsulation layer is, therefore, a critical challenge for the development of wearable/implantable system design.

In this work, we describe the design principles of stacks of encapsulation layers as biofluid barrier for flexible electronic implants. The multi-layer encapsulation can be conformally coated on both sides of a flexible electronic platform with an array of NMOS transistors. The threshold voltage shift of the NMOS ($\Delta V_{th}$) transistor indicates the level of performance degradation. Accelerated soaking experiments show that (1) thermally grown SO$_3$Se$_2$N$_6$, bilayer block the passage of ions [4][5], (2) HIO$_4$ coated thermal SiO$_2$ slows down both moisture diffusion and dissolution of the encapsulation layer by orders of magnitude [6]. Systematic theoretical investigations reveal the details associated with encapsulant material property [7]. In this context, both numerical and analytical models describe the ion penetration as well as the moisture assisted dissolution process. Coupled with the device physics of MOSFET, our model predicts that $\Delta V_{th}$ follows accelerate growth over time due to the coupled effect of ion transport and encapsulant dissolution. The predictions are well validated by results of the accelerated soaking experiment. Our physics-based model serves as the basis for lifetime projection for MOSFET-based wearable/implantable electronics under different operating conditions in a harsh biological environment. Ion and moisture penetration through encapsulant is a generic problem, therefore our results are also relevant for encapsulation of electronic, mechanical, and chemical systems.

**References:**


**BMO8.03.29**

**Compositional Dependence of Electromechanical Response in Lead-Free Piezoelectric Thin Films for Wearable Electronics**

Raininder S. Deol, Soumen Saha, Bhaskar Mitra and Madhusudan Singh; Electrical Engineering, Indian Institute of Technology Delhi, New Delhi, India.

Wearable sensors and other electronic devices require reliable autonomous power generators that are compact and can scavange mechanical vibration energy sourced from various movements of the human body. While lead zirconium titanate (PZT) and its derivatives are usable in compact piezoelectric devices, the presence of lead limits their use due to health and environmental concerns. Thus, lead-free high-performance piezoelectric materials are uniquely needed for wearable sensor applications. Further, piezoelectric materials can be used to sense human movement through time variation of stress. The highest piezoelectric response in one such material, potassium sodium niobate (KNN), is expected at the morphotropic phase boundary (MPB) systems.

This work was partly supported by Institute for Information & communications Technology Promotion (IITP) grant funded by the Korea government (MSIP) (No.2017-0-00048, Development of Core Technologies for Tactile Input/Output Panels in Skintronics (Skin Electronics)) and the Center for Advanced Soft-Electronics grant funded by the Ministry of Science, ICT and Future Planning as Global Frontier Project (CASE-2015M3A6A5065309).

**References:**


**BMO8.03.30**

**Upconversion Nanoparticles/Graphene—Opening New Windows for Highly Sensitive Photodetection**

Monika Kataria1,2, Wei-Hua Wang1,2 and Rajinder S. Deol; 1Department of Physics, National Taiwan University, Taipei, Taiwan; 2Department of Physics, National Central University, Chung-Li, Taiwan; 3Department of Physics, National Taiwan University, Taipei, Taiwan.

References:

With recent technological advancements engulfing the world and making it a better place to live, wearable transparent electronics definitely have a crucial role to play. Plentiful studies on upconversion mechanism observed in lanthanide doped core-shell upconversion nanoparticles (UCNPs) have successfully marked their presence in the ongoing research fields of displays, solar cells, etc. The lanthanides doped core-shell UCNPs are capable of sequentially absorbing two or more photons of higher wavelength leading to an emission of photons of lower wavelengths. Graphene is a 2D material which is famous for its high carrier mobility, short carrier life time, flexibility and its optical transparency. Since graphene has a low density of states around the Dirac point therefore its conductance is influenced by external perturbations from allied materials. Therefore placing core-shell UCNPs in close vicinity of graphene opens a new window for highly sensitive photodetector. In this work we demonstrate a very novel approach towards lanthanide doped core-shell UCNPs and graphene hybrid rippled structure photodetector. The 4th electronic configuration of lanthanides contributes for a multi-energy sublevels which eventually results in longer excited state lifetime for photogenerated charge carriers due to the presence of metastable states when subjected to laser illumination. This unlocks a new regime for ultrahigh sensitivity in lanthanide doped core-shell UCNPs (NaYF4:Yb:Er:Nd@NaYF4:Nd) and graphene hybrid rippled structure photodetector. The device fabrication process includes the usage of core-shell structured UCNPs and monolayer graphene on pre-strained poly(dimethylsiloxane) (PDMS) substrate which was later released to get a core-shell UCNPs/rippled graphene structure hybrid wearable photodetector. Under 808nm laser illumination, core-shell UCNPs/rippled graphene hybrid structure exhibits the highest responsivity of the order of ~31 AW⁻¹ among core-shell UCNPs based hybrid photodetectors based on the upconversion transitions of the several energy sublevels of core-shell UCNPs. Also, the rippled graphene structure helps to increase the optical absorption of photons for core-shell UCNPs. The graphene ripples accelerate light trapping due to multiple scattering, which adds on to increase the responsivity for the hybrid rippled structure photodetector. Also, we have demonstrated that the core-shell UCNPs and graphene hybrid rippled structure photodetector works effectively under 100 % longitudinal strain. The rippled graphene and UCNPs hybrid photodetector on PDMS substrate exhibits superb wearability and durability. This innovative design, nominal low cost fabrication, large-area, and its ability to function at lower powers of illumination makes this highly flexible, stretchable, transparent hybrid rippled structure photodetector most suitable for our day to day optoelectronics applications for.

BM08.03.31

Starch-Cellulose-Based Triboelectric Nanogenerator Obtained by a Low-Cost Cleanroom-Free Processing Method
Robert Ccorahua, Alexandra Cordero, Juan Huaroto, Maria Quintana and Emir Vela; Universidad Peruana Cayetano Heredia, Lima, Peru.

Triboelectric nanogenerators (TENGs) have become one of the most sustainable ways to scavenge blue energy from mechanical movements. However, fabrication of TENGs often requires use of expensive instruments. Some attempts to reduce costs, using biomaterials of cellulose and chitosan, were reported. Nevertheless, to date only few low-cost bio-based materials have been reported to be useful as TENGs but they still keep employing costly nanofabrication techniques. Herein, we report on a new bio-based starch-cellulose TENG fabricated without using complex equipment is reported for the first time. Chopped samples of peruvian potato (Solanum tuberosum: yellow variety) were homogenized in a blender, sieved and left for decantation. After 4 h, supernatant was discarded and the precipitate was degreased by resuspension in a solution of 1:1 metanol/water. The obtained starch was dried at 60°C for 24 h. Starch films were prepared by casting. Dried starch was diluted in distilled water to form a 5% (w/w) starch solution. This solution was partially hydrolyzed in dilute hydrochloric acid (0.1 N) adjusting pH to 2.0. Glycerol was added at ratio of 2:5 (glycerol:starch (dry basis)). The starch solution was homogenized by stirring for 15 min at 95°C. Then, the solution was neutralized in dilute sodium hydroxide (0.1 N) adjusting the pH to 10 to stop hydrolysis. Finally, the starch solution (7% (w/w)) was poured on Petri dishes containing substrates of sand paper (grit #400) and placed in an oven at 40°C. After 48 h of drying, films of about 50 to 200 μm in thickness were obtained. For the complementary dielectric film, a microfiltration membrane of 47 μm of pore size was used. The surfaces open to the air (upper part) of the films were covered with a thin layer of commercial aluminum foil by using double sided adhesive tape. The resulted TENG was electrically characterized by using a linear motor as a vibrating external source at forces up to 6 N. Surprisingly, despite both dielectric films inside the TENG were made of biomaterials, the electrical output was considerably higher than other biomaterial-based TENGs reported to date. Our results showed that, depending on the film thickness, electric outputs varied from 60 mV to 300 mV per 4 cm² area. The thicker the film, the lower the electrical outputs, and vice versa. Moreover, FTIR-ATR analysis also showed that no chemical modification was made on the surface of starch after casting. Therefore, starch remained unmodified at the time of characterization, being this performance proper of a pristine starch. In addition, though organic starch isolation, fabrication of the proposed TENG was entirely handmade, thus avoiding use of complex equipment of nano- and micro-fabrication which resulted in the development of an eco-friendly TENG with very good performance according to the state-of-the-art.

BM08.03.32

Development of a Sheet-Like pH Imaging Sensor with Polyelectrolyte Multilayered Thin Films
Shinji Takeoka, Daichi Someya, Satoshi Araiz and Toshihito Fujie; Waseda University, Tokyo, Japan.

We developed flexible and physically adhesive polymer thin films (nanosheets) for biomedical or bioelectronic applications. Recently, we reported a temperature sensor nanosheet responding to the external NaCl stress. The pH sensor nanosheet will be useful for biology or medicine if it is combined with the apoplastic ion milieu of plants. Here we report a new pH sensor nanosheet to be used for biosensing applications. We developed flexible and physically adhesive polymer thin films (nanosheets) for biomedical or bioelectronic applications. Recently, we reported a temperature sensor nanosheet of peruvian potato (Solanum tuberosum: yellow variety) was homogenized in a blender, sieved and left for decantation. After 4 h, supernatant was discarded and the precipitate was degreased by resuspension in a solution of 1:1 metanol/water. The obtained starch was dried at 60°C for 24 h. Starch films were prepared by casting. Dried starch was diluted in distilled water to form a 5% (w/w) starch solution. This solution was partially hydrolyzed in dilute hydrochloric acid (0.1 N) adjusting pH to 2.0. Glycerol was added at ratio of 2:5 (glycerol:starch (dry basis)). The starch solution was homogenized by stirring for 15 min at 95°C. Then, the solution was neutralized in dilute sodium hydroxide (0.1 N) adjusting the pH to 10 to stop hydrolysis. Finally, the starch solution (7% (w/w)) was poured on Petri dishes containing substrates of sand paper (grit #400) and placed in an oven at 40°C. After 48 h of drying, films of about 50 to 200 μm in thickness were obtained. For the complementary dielectric film, a microfiltration membrane of 47 μm of pore size was used. The surfaces open to the air (upper part) of the films were covered with a thin layer of commercial aluminum foil by using double sided adhesive tape. The resulted TENG was electrically characterized by using a linear motor as a vibrating external source at forces up to 6 N. Surprisingly, despite both dielectric films inside the TENG were made of biomaterials, the electrical output was considerably higher than other biomaterial-based TENGs reported to date. Our results showed that, depending on the film thickness, electric outputs varied from 60 mV to 300 mV per 4 cm² area. The thicker the film, the lower the electrical outputs, and vice versa. Moreover, FTIR-ATR analysis also showed that no chemical modification was made on the surface of starch after casting. Therefore, starch remained unmodified at the time of characterization, being this performance proper of a pristine starch. In addition, though organic starch isolation, fabrication of the proposed TENG was entirely handmade, thus avoiding use of complex equipment of nano- and micro-fabrication which resulted in the development of an eco-friendly TENG with very good performance according to the state-of-the-art.
patient’s everyday life remains an open challenge. We have successfully screen-printed piezoelectric P(VDF-TrFE) sensors with versatile geometries on 25 µm thin, stretchable substrates suitable for a skin conformal attachment. The stretchable piezoelectric transducer allows for a versatile sensing, ranging from whole body motion down to tiny pressure variations originating from the human blood flow or heartbeat. Additionally, vibro-acoustic sensing allows for the detection of various physiological signals such as speech, snoring, or respiratory auscultation. Rigid islands for the incorporation and connection of read-out electronics, as well as electrical shielding for signal improvement were all fabricated by means of screen-printing. We thus present a printed, entirely stretchable, low-cost sensor patch for various medical applications.

8:30 AM *BM08.04.02

**Triboelectric Nanogenerators for Powering Portable, Wearable and Body-Implantable Devices**

Sung-Woo Kim; Department of Advanced Material Science and Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Energy harvesting systems based on piezoelectric and triboelectric nanomaterials are in great demand, as they can provide routes for the development of self-powered devices which are highly flexible, stretchable, mechanically durable, and can be used in a wide range of applications. Our recent research interest mainly focuses on the fabrication of piezoelectric and triboelectric power generators based on various kinds of nanomaterials. Flexible generators exhibit good performances and are easy to integrate which make it the perfect candidate for many applications, and therefore crucial to develop. In this presentation, I firstly introduce the fundamentals and possible device applications of triboelectric power generators, including their basic operation modes. Then the different improvement parameters will be discussed. As main topics, I will present a couple of recent achievements transparent flexible graphene triboelectric generators, textile-based wearable triboelectric power generators, etc. The recent research and design efforts for enhancing power generation performance of generators to realize self powering of portable and wearable sensors and electronics will also be discussed in this talk. In addition, I will address a high performance inertia driven triboelectric nanogenerator based on body motion and gravity. The packaged device has successfully harvested around 144 mW during day time in preclinical test, and real-time output voltage data is monitored via Bluetooth low energy information transmit system.\[1\]

9:00 AM BM08.04.04

**Soft, Stretchable, Conductive Metal-Polymer Composites as Nonlinear Springs for Broadband Vibration Energy Harvesting**

Zining Yang and Seek Kim; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Energy harvesting from ambient vibrations is widely considered as a solution for the most prominent obstacle towards the commercialization of internet of things (IoT), which is the expenses and human efforts invested in battery replacement for millions of wireless sensor nodes. Unfortunately, ambient vibrations are generally distributed over a low-frequency domain with wide bandwidth, which renders most microscale vibration energy harvesters unpractical for real-world applications. Here, a vibration energy harvester with both low operation frequency and a broadband response is achieved by using a resonator with soft and nonlinear springs. A soft, deformable, and electrically conductive metal-polymer composite is employed as the spring material, not only to obtain a low spring constant using a compact clamped-clamped beam design but also to trigger the broadband behavior by harnessing the geometric nonlinearity of the doubly clamped beam at large deflection. A highly miniaturized (footprint < 1 cm2) capacitive vibration energy harvester with low operation frequency (resonant frequency 73Hz), broad bandwidth (28% of the resonant frequency), and high power density (171 μW/cm3 at resonant frequency) is realized using the soft spring resonator. The energy harvesting device is also used as a wearable, self-powered acceleration sensor with a voltage sensitivity of around 0.78 V/g.

9:15 AM BM08.04.05

**Textile Based Triboelectric Nanogenerator with Fully Stretchable Knitted Fabrics**

Sung Soo Kwak, Jihye Kim and Sang-Woo Kim; Sungkyunkwan Univ, Suwon-si, Korea (the Republic of).

Harvesting human-motion energy for power-integrated wearable electronics could be a promising way to extend the battery-operation time of small low-power-consumption electronics such as various sensors. For this purpose, a fully stretchable triboelectric nanogenerator (S-TENG) that has been fabricated with knitted fabrics and has been integrated with the directly available materials and techniques of the textile industry is introduced. This device has been adapted to cloth movement and can generate electricity under compression and stretching. We investigated plain-, double-, and rib-fabric structures and analyzed their potentials for textile-based energy harvesting. The superior stretchable property of the rib-knitted fabric contributed to a dramatic enhancement of the triboelectric power-generation performance owing to the increased contact surface. The present study shows that, under stretching motions of up to 30 %, the S-TENG generates a maximum voltage and a current of 23.50 V and 1.05 µA, respectively, depending on the fabric structures. Under compressions at 3.3 Hz, the S-TENG generated a constant average root-mean square power of up to 60 µW. The results of this work show the feasibility of a cloth-integrated and industrial-ready TENG for the harvest of energy from human biomechanical movements in cloth and garments.

9:30 AM BM08.04.06

**Super-Stretchable and Mechanically-Durable Triboelectric Nanogenerator for Wearable Energy Harvesting and Self-Powered Tactile Sensing**

Ying-Chih Lai and Zhong Lin Wang; 1Materials Science and Engineering, National Chung Hsing University, Taichung City, Taiwan; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

In this presentation, we demonstrate a mechanically durable and resilient triboelectric nanogenerator (MDTENG) with unprecedented features of ultrahigh omnidirectional stretchability and capability to produce energy in different extreme mechanical deformations. The innovative nanogenerator can be adaptive on various desired non-planar and irregular objects, including human bodies, spheres, and tubes, etc., and act as power sources for other electronic components. The MDTENG was realized through composed of intrinsic stretchable and durable components that enable the device to generate electricity from tapping or skin touching despite under various deformations. Based on the durable materials, the triboelectric nanogenerator is omnidirectionally stretchable over 300% strain. Even experiencing severe tearing damages, the device can still function as an effective power source for the load. Moreover, the energy produced has been demonstrated to be able to sustainably power a commercial smart watch. Based on the stretchable and durable nanogenerators, we further demonstrated the first fully autonomous and self-powered adaptive e-skin system that can map touch by responding to visual light-emitting diode (LED) signals without the need of external power supply. The work presented here are timely and beneficial for the development of wearable, deformable electronics and self-powered electronic and sensing systems.

[Ref]


9:45 AM BREAK

10:15 AM *BM08.04.07

**Triboelectric Nanogenerator as a Power Source and Self-Powered Sensor**

Zhong Lin Wang; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States.
United States; 2Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

Triboelectrification is an effect that is known to each and every one probably ever since the ancient Greek time, but it is usually taken as a negative effect and is avoided in many technologies. We have recently invented a triboelectric nanogenerator (TENG) that is used to convert mechanical energy into electricity by a conjunction of triboelectrification and electrostatic induction. As for this power generation unit, in the inner circuit, a potential is created by the triboelectric effect due to the charge transfer between two thin organic/inorganic films that exhibit opposite tribo-polarity; in the outer circuit, electrons are driven to flow between two electrodes attached on the back sides of the films in order to balance the potential. Ever since the first report of the TENG in January 2012, the output power density of TENG has been improved for five orders of magnitude within 12 months. The area power density reaches 500 W/m², volume density reaches 490 kW/m³, and a conversion efficiency of ~50% has been demonstrated. The TENG can be applied to harvest all kind of mechanical energy that is available but wasted in our daily life, such as human motion, walking, vibration, mechanical triggering, rotating tire, wind, flowing water and more. Alternatively, TENG can also be used as a self-powered sensor for actively detecting the static and dynamic processes arising from mechanical agitation using the voltage and current output signals of the TENG, respectively, with potential applications for touch pad and smart skin technologies. This presentation will focus on TENG for wearable electronics.


10:45 AM BM08.04.08
Body Implantable Triboelectric Nanogenerator Driven by Inertia for Powering Implantable Medical Device Hanjun Ryu and Sang-Woo Kim; Sungkyunkwan University, Suwon (the Republic of Korea).

Body-implantable bioelectronics devices that monitor and modulate abnormalities in patients are highly sophisticated technologies, and long-term operation of such in vivo devices has faced a major technological challenge. Currently, medical implant devices require high-risk repeat surgery to replace used devices; permanent operation of body-implantable bioelectronics devices will reduce the patient’s risk of surgery, including device removal and replacement. Notwithstanding that a variety of in vivo energy harvesters using near-field or mid-field electromagnetics, thermal gradient, and mechanical movements of organ have been proposed, in vivo power generators are still limited, which are lack of power to charge storage device as energy sources for bioelectronics devices. Especially, the metal package of in vivo devices interferes with energy transfer, resulting in low energy conversion. In addition, in vivo energy transfer systems require external energy transmitters that can be inconvenient for the user. Thus, while the only possible and promised energy source for implantable medical devices is batteries, batteries with limited dimensions, capacity, or stability have a finite lifespan.

We demonstrate a high-performance inertia-driven triboelectric nanogenerator (I-TENG) based on body motion and gravity. We also successfully operated the in vivo I-TENG in a preclinical test and collected real-time output-voltage data via a Bluetooth low-energy (BLE) information-transmitting system. A synchronous shock structure, which achieves current waveform superposition, can step the peak current value up without additional components, so that, the I-TENG generated 7.3 mWpeak and 90 μWRMS in laboratory experiment, and harvested around 144 mW during the daytime in the preclinical testing in a synchronous stack structure, which achieves current waveform superposition, can step the peak current value up without additional components, so that, the source for implantable medical devices is batteries, batteries with limited dimensions, capacity, or stability have a finite lifespan.

11:00 AM BM08.04.09
Adding a Stretchable Deep-Trap Interlayer for High-Performance Stretchable Triboelectric Nanogenerators Dong Wook Kim, Ju Hyun Lee, Insang You, Jin Kon Kim and Unyong Jeong; Pohang University of Science and Technology, Pohang, Korea (the Republic of). The main approach to enhancing the electrical output performance of triboelectric nanogenerators (TENGs) has been focused to increase of triboelectric charge generation. However, there have been few studies on achieving effective electrostatic induction and conserving the triboelectric charges. This study reports that an interlayer containing deep charge traps of large trap density can conserve the surface charges for long period of time and increase the surface potential that can be obtained. This study suggests polydimethylsiloxane (PDMS) added between a charge generation layer and an electrode as an effective material candidate for the interlayer. The PDMS interlayer greatly enhanced the output power density of TENGs (20.8 W/m² by gentle tapping), which is 173-fold increase compared to TENGs without the interlayer. Surprisingly, the PDMS interlayer resulted in triboelectric performance even between identical surfaces, which is owing to the enhanced charge conservation by the interlayer. This study demonstrates a high-performance stretchable single-electrode TENG (S-TENG) which shows stable high performance at 50% uniaxial strain during repeated stretch cycles. The results in this study provide insight to material design for achieving high-performance stretchable self-powered electronic systems.

11:15 AM BM08.04.10
Increasing Surface Charge Density by Intrinsic Charge Layer Inclusion for High-Performance Triboelectric Nanogenerator Devices Aravind Ravichandran and Marc Ramuz; EMSE-CMP, Gurdanne, France.

With the rapid development of wearable electronics and sensor networks, batteries cannot meet the sustainable energy requirement due to their limited lifetime, size and degradation. With miniaturization leading to high-power and robustness, triboelectric nanogenerators(TENGs) have been conceived as a promising technology by harvesting mechanical energy to power small electronics and wearables. The main issues associated with TENGs are their very low output power leading to low output charge density and high impedance matching.

In this work, a state of the art multilayer flexible structure is devised which not only increases the charge density but also provides a high average(RMS) power output. Thin-film organic flexible materials are deposited to trap the charges from the triboelectrification process, allowing the acceptance of more charges from an electrode and thereby increasing the power output. Material work function provides better understanding towards charge transfer process.

A proof of concept wearable device is conceptualized for use in a highly efficient self-powered sensor network system, converting ambient mechanical energy to electricity with a 1.2kV peak amplitude and a charge density of 1000 μC/m². This device structure makes the TENGs attractive to charging applications for wearables and large-scale harvesting without massive volume. By this technique, we have overcome numerous friction-based operation challenges including lack of uniform contact, material loss through wear, high sensitivity to humidity, and output power storage.

By considering these merits of simple fabrication, outstanding performance, robust characteristic and low-cost technology, we believe that TENGs can
open up great opportunities not only for powering small electronics but can contribute to large-scale energy harvesting through engineering design being complementary to existing energy sources.

SESSION BM08.05: Circuits, Integration and Communications

Session Chairs: Seunghyun Baik and Unyong Jeong
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Grand Ballroom

1:30 PM *BM08.05.01
Thermoplastic Elastomer-Based Stretchable Devices Unyong Jeong; Pohang University of Science and Technology, Pohang, Korea (the Republic of)

The Folding and stretching will be the key characteristics in the next-generation electronic devices. The stretchable electronics have motivated scientists to develop deformable materials for use in electrodes, semiconductors, bio-interfaces, and sensors. To realize fully stretchable electronic devices, each component of the device must maintain its performance up to a critical strain. This talk will present recent developments of stretchable polymeric conductors and semiconductors, and stretchable devices that are based on thermoplastic elastomers. Special focuses will be put on the thermoplastic block copolymer composites for their uses as substrates, electrodes, interfacial adhesives, and circuits. This talk presents a generalized platform that can be used for a variety of stretchable devices and several stretchable devices will be demonstrated including real-time a long-term use heart sensor, haptic device, display, energy harvesting, and stretchable transistors.

2:00 PM BM08.05.02
High-Performance Flexible Carbon Nanotube Complementary Electronics for Integrated Sensor Systems Li Xiang, Heng Zhang, Lian-Mao Peng and Youfan Hu; Peking University, Beijing, China.

The long-time vacuum of high-performance complementary metal-oxide-semiconductor (CMOS) technology on plastics is a non-negligible obstacle to the applications of flexible electronics with advanced functions, such as continuous health monitoring with in situ signal processing and wireless communication capabilities, in which high speed, low power consumption, and complex functionality are desired for integrated circuits (ICs). Here, we report the implementation of carbon nanotube (CNT)-based high-performance CMOS technology and its application for signal processing in an integrated sensor system for human body monitoring on ultrathin plastic foil with a thickness of 2.5 μm. The performances of both the p- and n-type CNT field-effect transistors (FETs) are excellent and symmetric on plastic foil with a low operation voltage of 2 V: width-normalized transconductances (gm/W) as high as 4.69 μS/μm and 5.45 μS/μm, width-normalized on-state currents reaching 5.85 μA/μm and 6.05 μA/μm, and mobilities up to 80.2 cm²V⁻¹s⁻¹ and 97.1 cm²V⁻¹s⁻¹, respectively, together with a current on/off ratio of approximately 10⁵. The devices were mechanically robust, withstanding a curvature radius down to 124 μm. Utilizing these transistors, various high-performance CMOS digital ICs with rail-to-rail output and a ring oscillator on plastic surface with an oscillation frequency of 5 MHz were demonstrated. Furthermore, an ultrathin skin-mounted humidity sensor system with in situ frequency modulation signal processing capability was realized to monitor human body sweating.

2:15 PM BM08.05.03
Super-Elastic Electronic and Photonic Fiber Devices via Thermal Drawing Fabien Sorin1, Yunpeng Qu1, Dang Tung Nguyen1, Alexis Page1, Wei Yan1, Tapajyoti Dasgupta1, Rene M. Rossi2 and Nicola Bartolomei1; 1Ecole Polytechnique Federale de Lausanne, Switzerland, Lausanne, Switzerland, 2Empa-Swiss Federal Laboratories for Materials Science and Technology, Saint-Gallen, Switzerland.

Stretchable optical and electronic fibers constitute increasingly important building blocks for a myriad of emerging applications, such as in robotics or medical implants. They are particularly suitable for wearables and smart textiles as seamlessly integrated devices that can bring high added values in monitoring and energy harvesting. Fibers can indeed integrate complex sensing and actuating functionalities such as light, heat, chemicals or pressure sensing, as well as piezoelectric actuation. They can also be used for energy harvesting from heat, light or mechanical movement. Yet, it remains challenging to fabricate efficient and advanced soft fiber-base devices that can undergo significant mechanical deformation in a simple and scalable way. Conventional fiber manufacturing methods, such as wet and dry spinning, or extrusion, are not well adapted to fabricate multi-material functional fibers. The preform-to-fiber thermal drawing technique on the other hand is an emerging powerful platform to fabricate multi-material fibers with complex architectures and functionalities. Thus far however, this fabrication approach has been restricted to rigid thermoplastic or glass fibers, preventing their use for mechanical sensing or actuation, and rendering difficult their use in wearable approaches or within textiles.

In this contribution we will show how we could revisit the selection criteria for cladding materials compatible with the thermal drawing process, and fabricate super-elastic fibers with advanced optical and electronic functionalities. We will demonstrate how, thanks to a deeper rheological characterization, we could identify thermoplastic elastomers that could be drawn from a solid preform at high viscosity. Subsequently, we will demonstrate that thermoplastics, liquid metals, and conductive polymer composites could be co-drawn with prescribed architectures within thermoplastic elastomer cladding. This allowed us to successfully fabricate stretchable optical and electronic fibers that are used as precise and robust pressure, strain or more generally deformation sensors, as well as soft and stretchable waveguides. This work was just published (Advanced Materials, 2018, 201707251) and highlighted in several news media (here is a video highlighting this recent breakthrough: https://actu.epfl.ch/news/an-elastic-fiber-set-to-revolutionize-smart-clothes/). As we will show via concrete examples, the ability to thermally draw soft multi-material fibers open new opportunities in robotics as well as fiber integrated devices and wearable technologies. These results open opportunities not only for exploring new academic research directions, but also in industrializing fiber-based flexible and stretchable devices for applications in sensing, health care, robotics, wearable devices and smart textiles.

2:30 PM BM08.05.04
Integrated Wearable Electronic System with Stretchability, Modularity and Self-Healability Jiheong Kang and Zhenan Bao; Stanford University, Stanford, California, United States.

Electronic skin devices capable of monitoring physiological signals and displaying feedback information through closed-loop communication between user and electronics are being considered for next-generation wearables and Internet-of-Things. Such devices need to be ultrathin to achieve seamless and conformal contact with our human body, to accommodate strains from repeated movement such as bending, and, more importantly, be comfortable to wear. However, ultrathin materials are inevitably more susceptible to our daily wear and tear processes. Recently, self-healing chemistry has driven important advances in deformable and reconfigurable electronics, particularly with self-healable electrodes as the key enabler. Although polymer substrates are self-healable due to its dynamic nature, the disrupted conducting network is unable to recover its stretchability after damage. In addition, commonly used self-
constructing p-n junctions in a single planar polymer film

Hong Wang; Frontier Institute of Science and Technology, Xi'an, China.

Constructing p-n junctions with a single planar polymer film will not only largely reduce the fabrication cost but also largely increase the integration density of organic electronic devices. However, it is very challenging to build Schottky barriers or p-n junctions in only one organic material because diffusion of the counter-ion dopants renders such structures very unstable. Here we show a rectifying curve obtained from a single planar polymer film with a high current density of 2-3 orders higher than conventional organic rectifiers. The structure was built by converting half of the film from p-type into n-type using a chemical reaction other than a doping method. This approach is expected to be extended into other polymers. We hope our work could open the door for designing flexible and portable organic devices with high integration level.

Constructing p-n junctions will not only largely reduce the fabrication cost but also largely increase the integration density of organic electronic devices. However, it is very challenging to build Schottky barriers or p-n junctions in only one organic material because diffusion of the counter-ion dopants renders such structures very unstable. Here we show a rectifying curve obtained from a single planar polymer film with a high current density of 2-3 orders higher than conventional organic rectifiers. The structure was built by converting half of the film from p-type into n-type using a chemical reaction other than a doping method. This approach is expected to be extended into other polymers. We hope our work could open the door for designing flexible and portable organic devices with high integration level.
Organic light-emitting devices have become a big topic in modern research and are often discussed as a future leading technology because of their light weight, flexibility and solution-processability. Here we refer to a further advantage of this technology, namely the possibility of producing biodegradable/biocompatible devices, which will open the pathway to a whole new field of future applications ranging from healthcare and medicine to smart packaging, disposable and wearable electronics.

In this work we present the fabrication of light-emitting electrochemical cells (LECs) comprising a non-halogenated bio-friendly solid-polymer electrolyte (poly-(ε-caprolactone-co-trimethylene carbonate) plus tetrabutylammonium bis-oxalato borate) on biodegradable cellulose di-acetate substrates by industrially relevant printing techniques. [1] By using a biocompatible electrode system consisting of PEDOT:PSS and ZnO we could produce functional devices comprising up to 99 vol% of biocompatible materials. The devices are semi-transparent and flexible even under operation. A maximum luminance of over 200 cd m\(^{-2}\) is achieved significant for display and lightning applications. The relatively short lifetime on the timescale of some minutes can be compensated by a fully-printed production process utilizing inkjet printing and blade coating, relevant for an industrially cost-efficient production of biodegradable-transparent electronics.

References:

Binder Jetting Fabrication of Graphene Composite Structures for Printed 3D Electronic Devices

Xuechen Shen and Hani E. Naguib; University of Toronto, Toronto, Ontario, Canada.

Carbon-based nanomaterials see ubiquitous usage in research and industry as structural reinforcement in composites. Aside from excellent mechanical properties, carbon-based nanomaterials also demonstrate desirable electrical properties. Graphene has current carrying capacity several magnitudes higher than copper, able to achieve a current density on the scale of 10\(^9\) Acm\(^{-2}\), compared to the current density of copper at 10\(^6\) Acm\(^{-2}\). The improved current density of graphene over traditional conductive materials is significant for reducing the size of electronic devices to meet demands for higher device density. Furthermore, graphene has high affinity for compositing with polymer materials, enabling the fabrication of flexible and conductive composites. Such graphene-polymer composites are highly suitable for wearable electronics and soft robotics applications. Developing additive manufacturing techniques for 3D carbon nanomaterial structures could lead to manufacturing processes that facilitate rapid prototyping and promote more ubiquitous usage of nanomaterials in flexible sensors, actuators, and energy devices.

Graphene oxide (GO) is a popular material choice in 2D circuit printing due to its ease of processability. As GO, the material disperses well in water, and aligns readily when extruded from thin micronozzles, which enhances mechanical and electrical properties over bulk material. GO inks need to be reduced to graphene after printing to recover conductive properties.

In an ongoing study, we investigate the use of principles from 2D inkjet printing of GO in a binder jetting process to additively manufacture 3D electronics including actuators, sensors, energy storage, and integrated electronic systems. In this system, a GO/water dispersion is used as binder. The dispersion is jetted onto a polymer or metal powder to temporarily bind adjacent particles. Dropping binder to define 2D patterns over stacked layers of powder builds a...
3D object. Following post-processing procedures, the final product is a 3D printed composite material of graphene and the polymer or metal powder.

Our first study investigates Polyvinyl alcohol (PVA) as powder because it dissolves in water and forms a flexible plastic when dried. This property gives PVA powder high affinity with a graphene oxide/water binder, which is a well-studied material. The effect of adding Intrinsically Conductive Polymers (ICP) such as poly(pyrrole)s or polyanilines mixed with PVA is investigated to increase conductivity of the graphene composite without significant increase in cost.

Our second study investigates Copper as powder to fabricate PVA to increase conductivity. The resulting structure is significantly less flexible compared to a polymer composite, but it exhibits high electrical conductivity and density, forming a metal-graphene composite with exceptional electrical properties.

BM08.06.02
Integrated Energy Devices for Smart Textiles and Electronic Skins Xiong Pu; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

Rapid advancements in wearable smart textiles and stretchable/multifunctional electronics impose the challenge on corresponding power devices that they should possess comparable flexibility, stretchability and functionalities. Here, we briefly summarize our recent progresses on wearable energy storage and harvesting devices, especially energy devices aiming to power smart textiles and artificial electronic skins. Both yarn or textile-based electrochemical energy storage devices and textile-based triboelectric nanogenerators (TENGs) have been developed; meantime, self-charging systems have been achieved by integrating them so that energies harvested from daily human motions can be stored simultaneously. It is even more challenging to provide power sources for electronic skins or soft electronics/robotics. We report a soft skin-like triboelectric nanogenerator that enables both biomechanical energy harvesting and tactile sensing by hybridizing elastomer and ionic hydrogel as the electrification layer and electrode, respectively. Ultra-high stretchability and transparency are achieved simultaneously for an energy-harvesting device. Our work provides new opportunities for soft power sources and potential applications in soft/wearable electronics.

BM08.06.03
Flexible Drug Delivery Device for Controlled Administration Sang Hyun Sung and Keon Jae Lee; KAIST, Daejeon, Korea (the Republic of).

We report flexible drug delivery microdevices (f-DDM) that are capable of controlled administration. The unique structure of the f-DDM consisting of freestanding gold membranes over the microreservoirs was enabled by reversing the fabrication order of the reservoir and sealing membrane. We optimized the design of the f-DDM by a finite element analysis (FEA) to prevent thermal damage during the laser transfer process. The required current density for reliable drug release operation was determined through an electrochemical analysis. The f-DDM was conformally implanted on the curved cerebral cortex, and localized drug delivery was confirmed by the diffusion of two different types of fluorescent neurotracers. Finally, in vivo therapeutic treatment using the f-DDM was demonstrated by the controlled release of an anti-epileptic drug into the mice.

BM08.06.04
Study of Long-Term Biocompatibility and Bio-Safety of Implantable Nanogenerators Jun Li, Lei Kang, Yanhao Yu, Yin Long, Justin Jeffery, Weibo Cai and Xudong Wang; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Since the first demonstration of ZnO nanowire-based implantable nanogenerator (i-NG) in 2010,[1] i-NGs have been consistently investigated and developed as self-sustainable implantable power sources and real-time healthcare monitoring sensors.[2,3] One of the most essential requirements for i-NG development is the long-term bio-compatibility and bio-safety considering years-long lifespan of most implantable medical devices (IMDs). Although earlier work on NG development has demonstrated extensively long working cycles of the piezoelectric functional components which is sufficient for in vivo operation of NG over 5-10 years in theory,[4, 5] long-term assessment of i-NG in biological systems has not been investigated. Meanwhile, considering the potential risks of immune reactions and infections over a long period of time, biological influence of i-NG also needs to be fully evaluated to justify their implantation feasibility. To fill the gap and address this critical issue, herein we present a systematic study of polydimethylsiloxane (PDMS) and PDMS/Parylene-C packaged polyvinylidene fluoride (PVDF) NGs implanted inside female ICR (Institute of Cancer Research) mice for up to six months.

The packaged PVDF NG had a stable in vitro output of 0.3 V when bended for 7200 cycles. After i-NGs were implanted between the skin and muscle of mice at lower right back, multiple advanced imaging techniques, including computed tomography (CT), ultrasound, and photoacoustic were used to characterize the embedded i-NGs in vivo. These techniques not only demonstrated that the i-NGs kept excellent adhesion to the adjacent muscle surface and exhibited intactness without damage but also observed the real-time motion of packaged i-NGs in response to muscle movements. While no signs of toxicity or incompatibility were found from the surrounding tissues based on complete pathological analyses, the whole body functions of mice kept normal evidenced by the blood and serum test. Moreover, all devices exhibited stable electrical output during the entire examine period and packages were also able to effectively insulate the i-NG in biological environment with negligible stray currents at a pA scale.

These series of in-vivo and in-vitro studies confirmed the high biological feasibility of using i-NG in vivo for biomechanical energy harvesting, and thereby further enables self-powered capability of practical IMDs bypassing the requirement of batteries. This research provided the first cornerstone for the future intelligent self-powered IMD system implantation.

References:

BM08.06.05
Sensitivity Controllable, Printed Flexible Vibration Sensor Daisuke Yamamoto1, Takayuki Arie1, Seiji Akita1 and Kuni Takei1, 2; 1Osaka Prefecture University, Sakai, Japan; 2JST PRESTO, Chiyoda, Japan.

Trillion sensor concept requires many sensors on everywhere including humans and infrastructures to monitor a lot of information. One of the important
information is to monitor infrastructures such as strain and vibration. Vibration can be often monitored by inflexible acceleration sensor. Although few demonstrations about flexible acceleration sensor have been reported, the detail study of the printed flexible acceleration sensor has yet to be conducted. This study printed flexible acceleration sensors to control the sensitivity and demonstrates a vibration monitoring. By optimizing the device size and materials, we successfully monitored small vibrations. This technique can be monitored infrastructure vibration mapping by attaching the sensor sheet on the objects.

The flexible acceleration sensor consists of 4 beam structure with various beam length (L) and width (W). Strain sensors formed by Ag nanoparticles and carbon nanotube inks were printed on three beams, and Ag ground electrode was printed on another beam on PET film. The strain sensor is resistive-change sensor. First, real-time resistive change of a sensor was monitored by applying different acceleration directions. The results explain that resistance change is different depending on the acceleration directions, which are in good agreement with simulation results. To observe the size dependence, acceleration dependences of different beam length and width were characterized. The results show that the sensor with longer length and narrower width has lower threshold acceleration. Based on the results, threshold acceleration is proportional to $-L^{-2.7}$ and $-W$. To support these experimental results, finite element method simulation to extract the force for 1 mm displacement with three different beam lengths and widths was conducted. These suggest that the trends of length and width dependences were well matched between them. Based on the results, it can be concluded that mechanism of strain distribution for flexible acceleration sensor is explained by the standard spring mechanism. For mechanical flexibility of the acceleration sensor, the normalised sensitivity change as a function of bending radius is studied. At smaller bending radius, the sensitivity increases (decreases) when the bending direction is along (perpendicular to) the beam. This is most likely due to spring constant change depending on the bending directions. For reliability of long time use, this can be withstood for more than 500 times strong acceleration ($\approx 29\ m/s^2$). As the first proof-of-concept of vibration detection, the sensor sheet was attached on a smartphone and applied a vibration by calling the phone. The results clearly show the vibration detection, which is also good agreement with a commercially available acceleration sensor.

In summary, we studied the device size dependence of the printed flexible vibration sensor, and the results may be good advances for the future flexible electronics.

BM08.06.06 Enhanced Polarization of CaCu$_3$Ti$_4$O$_{12}$ Composite Layer Induced by Triboelectric Field for High-Performance Triboelectric Nanogenerator Ilhye Kim and Sang-Woo Kim; School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-Si, Korea (the Republic of).

Triboelectric nanogenerator (TENG), which can harvest energy from various resources in our living environment such as wind, wave, raindrops, and human motions, has gained great attention thanks to their relatively high output power and simple device structures by comparison to other energy harvesting devices. To date, numerous studies are being conducted to control and design the inside of the dielectric layer for sustainable and high triboelectric output power. For instance, performance enhancements of TENGs have been reported by aligning the dielectric polarization by applying an external electric field to the dielectric composite structure. However, this research also has the limitation that the external electric field is needed and the stability of polarization and output power over time is significantly reduced.

In this work, we utilized a high dielectric constant material, CaCu$_3$Ti$_4$O$_{12}$ (CCTO), to improve the triboelectric output power of the Butylated Melamine Formaldehyde (BMF) resin based composite layer by enhancing the polarization of dielectric layer induced by the triboelectric field, which always occurs during friction. We investigated the triboelectric output performance depends on the dielectric constant of the composite layer by using Al$_2$O$_3$, TiO$_2$, and CCTO particles. Evidently, the triboelectric output enhanced as the dielectric constant of dielectric layer increased; BMF-CCTO based TENG produced higher RMS output voltage (270 V) and current (26 mAm$^{-2}$) than those of pure BMF, BMF-Al$_2$O$_3$, and BMF-TiO$_2$ based TENG. And the Polarization-electric field (P-E) curves show that a larger polarization is formed in the BMF-CCTO composite layer than in the pure BMF layer, when the same strength electric field is applied. In addition, we found that the triboelectric output increases until the concentration of CCTO reached 1 wt%, and decreased with larger CCTO concentration above 1 wt% due to the charge concentration effect. The introduction of particles in the polymer matrix generally introduces defects in the system causing centers of charge concentration leading to the leakage current. Furthermore, there is no limit to the dielectric matrix material because the high dielectric constant particles, CCTO, always enhances the triboelectric output regardless of the direction of the triboelectric field that changes depending on whether the dielectric matrix material is positive or negative. Since CCTO increases the triboelectric output without an external electric field, BMF-CCTO composite based TENG has the output sustainability and stability, which is always maintained over time.

BM08.06.07 Nanomaterial-Based Wearable Electrochemical Sensor for Glucose and pH Monitoring in Human Sweat Seungyoon Oh and Jeong Sook Ha; Korea University, Seoul, Korea (the Republic of).

Along with the increased efforts in developing wearable healthcare devices for monitoring and managing physiological and metabolic information, electrochemical sensors have been also extensively investigated. Especially, electrochemical sweat sensor capable of measurements of the glucose level and pH in sweat can serve as disease diagnosis device because glucose level and pH in human sweat provide rich information about our health condition. To apply a sweat sensor to human skin, it should be stretchable, and patchable onto a non-planar skin surface so that it can keep the stable performance even under body movement.

In this work, we report on a facile fabrication of a nanomaterial-based wearable electrochemical sensor for detecting glucose and pH in sweat. Our conductive electrode is fabricated via filtration of gold nanosheet (AuNS), and the AuNS forms the percolation network on a stretchable polymer substrate to make intrinsically stretchable sensor without serpentine or island-bridge structure. Our working electrodes for glucose and pH detection are based on CoWO$_3$/CNT and polyaniline/CNT nanocomposite coated on CNT-AuNS electrode, respectively. Also, solid-state stretchable reference electrode is prepared via chlorination of silver nanowires. Encapsulation of the stretchable sensor with silbione as sticky polymer leads to a conformally skin-attachable sensor. Our wearable glucose and pH sensors were evaluated using real human sweat samples, and we confirmed that the sensors can measure glucose and pH in real human sweat with good linearity ($R^2 = 0.999$).

The work demonstrates the high potential for the application of our wearable electrochemical sensor to health management as a healthcare wearable device.

BM08.06.08 Control of Mouse Behavior via Flexible Vertical Light-Emitting Diodes on the Cortical Surface Jung Ho Shin, Seung Hyun Lee, Han Eol Lee and Keon Jae Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

The stimulation of targeted neural regions in the brain is one of the attractive technology in neuroscience for controlling physical movement, and long-range interactions. Recently biomedical implants now employ flexible light-emitting-diodes combined with optogenetic mouse models to generate the neural signals in high resolution. However, most conventional devices are fabricated to stimulate functional regions through blue-light driven channelrhodopsin. In this report, we introduce flexible AlGaInP vertical light-emitting diodes (VLEDs) for the stimulation of functional cortical regions in the mouse brain. Micro-sized VLED chips effectively captured the conductive particles in anisotropic conductive film (ACF) inducing red light emissions with high optical
power density, which are high enough to modulate motor neurons deep below layer III from the cortical surface. Stable operation of pulsed red light from f-VEGs produces strong body movements and electromyogram (EMG) signal changes. The expression of chrimson, red-shifted channelrhodopsin, enables red-light excitation of targeted functional cortical regions. This demonstration opens new opportunities for sophisticated cortical mapping, analyzing the interactions between different motor regions in the mouse brain.

**BM08.06.09**

**Thermally Invisible Optoelectronic Patch for the Skin**

Han Hee Jung and Kyung In Jang; DGIST (Daegu Gyeongbuk Institute of Science and Technology), Daegu, Korea (the Republic of).

Nowadays, as wearable sensor technologies have surpassed the limits of technologies such as electronics, healthcare system and medical devices, which have been in the past, the interest of necessity measuring the physiological signal actively and accurately is critical for prophylaxis and prediagnosis. There are many devices that can easily check the conditions of the body, and pulse oximetry is the most commonly used in daily life and clinics for monitoring the vital signal. By virtue of pulse oximetry, it is convenient to check and readily predict health condition by observing cardiac and cerebral activities by monitoring heartrate and dynamics of blood flow. Although the applications of modern optoelectronic devices have been extended and provided practical tools for seamless real-time monitoring of blood flow dynamics, there are still prominent challenges in thermal management for optoelectronic devices due to undesired thermal energy originated from light source. The optoelectronic device exhibits very high surface temperature compared to that of neighboring biological epidemris layer, which resulting skin integrity issues and deterioration of the light-emitting diode functionality. In this study, we propose heterogeneous integration of the light-emitting diode, photodetector and thin metallic heatsink element embedded in the optoelectronic module which can provide an attractive architecture for sustainable in-situ spatiotemporal measurement of blood flow dynamics with excellent thermal management. Experimental and computational analysis clearly explain that the proposed optoelectronic device with heatsink element has excellent heat dissipation and long-term usability with thermally safe operating condition to the skin in virtue of high thermal conductivity and thin film geometrical design of the embedded heatsink. The biomedical demonstration envisions that the proposed optoelectronic device with metallic heatsink is an ideal blood flow monitoring system, which is mechanically and thermally compliant to the skin and offer opportunities for long-term clinical applications, such as sleep study for insomnia patients.

**BM08.06.10**

**Structural Design and Optimization of Wearable Thermoelectric Generator System**

Jeong Hun Kim¹, Junsoo Kim², Jong-Pil Im¹, Jaewoo Lee¹, Solye Im¹ and Seungeon Moon¹; ¹Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); ²Harvard University, Boston, Massachusetts, United States.

A thermoelectric generator (TEG) is promising energy harvesting device that can convert heat generated from power plant, furnace and combustion engine to electric energy. A TEG can use various heat sources not affected by weather, interests are growing by its stable energy generation property. In this paper, we not only have measured heat resistance of human body also optimized the structure of the thermoelectric element (TE) and TEG. From this result, we fabricated wearable TEG system and show the application using electrical energy converted from body heat. As a TE for fabrication of TEG, we used BiTe-based material which is most widely used for TEG system. The surface area and height were fixed as 1 mm² and 3 mm respectively from our previous research and the module size was 22 mm x 36 mm. Then the numerical simulation about the temperature difference of hot and cold side, open circuit voltage (OCV) and output power of the module have been conducted as the number of TE pairs are increased. For the TEG module fabrication, we assembled 31 pair of TE on the PCB substrate using metal jig. Because the general PCB substrates for fabrication of TEG are rigid, though metal PCB is facile material to make high performance TEG, but it cannot suitable for the wearable energy harvesting system. To solve this problem, we adopted two kinds of flexible PCBs which are made from polyimide and epoxy/silica composite. The polyimide PCB (PI-PCB) is very promising platform because of its flexibility, thin structure and thermal resistance. But in the TEG system, the temperature difference between hot and cold side that concludes the output power decreases from its low thermal conductivity, therefore, other materials have to be considered. The composite PCB consists of epoxy/silica shows higher thermal conductivity, and we could make up for the weakness of the PI-PCB. As over time, the temperature difference would decrease if heat dissipation at the cold side is not sufficient. Though metal fin is most widely used structure for the heat sink, but it is not suitable for wearable system because of the rigidity and bulky structure. We proposed novel bio-inspired heat sink system composed of polymer micro structures. Our heat sink is not only flexible also able to change structures by temperature modulation by the characteristic of Poly(N-isopropylacrylamide) (PNIPAm) that can shrink under 32 °C and expands over 32 °C. Likewise sweat gland of human body, this bio-inspired heat sink can prevent evaporation of water in low temperature via structural expansion, but in the high temperature, heat sink releases the heat of the TEG through water evaporation opened region by shrinkage of the active polymer. The TEG module using our heat sink show two times higher output power than using the metal fin. The optimized TEG module components were integrated for wearable energy harvesting system and we could demonstrate turning on a light emitting diode via body heat.

**BM08.06.11**

**Functionalised Nanoporous Gold as a New Biosensor for Quantitative Detection in Ultra-Low Concentrations**

Paola Rizzi; Federico Scaglione, Eugenio Alladio, Francesco Turci, Cristina Giovanni, Silvia Bordiga and Livio Battezzati; Università di Torino, Torino, Italy.

The development of a new generation of ultra-sensitive sensors for analytical and bio-diagnostic devices requires a strong signal in front of a very small quantities of material. Taking advantage of peculiar plasmonic properties of nanoporous gold (NPG), a promising sensor for selective detection of Human Serum Albumin (HSA), as a proof of concept, has been prepared by a proper functionalization of the substrate. NPG has been synthesized by chemical de-alloying an amorphous precursor, Au₅₅Cu₄₅Ag₉. Pd₁₀S₂₅, starting from melt spun ribbons. A fully de-alloyed ribbon with ligaments of around 60 nm was obtained after 4 h of de-alloying in proper conditions of temperature and concentration of the electrolyte. This material is self-standing and mechanical resistant and then well-versed for applications. At this stage, NPG is SERS active toward probe molecules (i.e. pyridine, bi-pyridine, rhodamine) even in very low concentration, but not specific for other complex molecule of interest such as HSA. Ad hoc functionalization is then required for this purpose. Bare NPG has been bound with a selective ligand i.e. a target-directed antibody (anti-Human Serum Albumin, Ab anti-HSA) covalently grafted onto the gold surface and then tested by Surface Enhanced Raman Spectroscopy (SERS) measurements as a function of HSA concentration. Data analyses in junction with a chemometric approach have successfully demonstrated that the NPG sensor is able to perform HSA quantitative detection in ultra-low concentrations.

**BM08.06.13**

**Non-Invasive Monitoring of Ketosis for Improved Therapy of Epilepsy with Breath Acetone Sensors**

Julia F. Kompalla, Andreas T. Günther and Sofinis E. Pratsinis; ETH Zurich, Zurich, Switzerland.

By implementing healthcare sensors into portable or even wearable devices, continuous monitoring of the patient’s physiological state is possible. Chemo-
resistive gas sensors based on semi-conductive metal-oxides could give such continuous feedback by analyzing exhaled breath. This could enable routine and personalized dietary monitoring needed for the treatment of drug-resistant epilepsy affecting 15 million people worldwide. More specifically, breath acetone detection could be a non-invasive and cost-effective way to monitor ketogenic diets (KD; high fat at low carbohydrate and protein intake). Here, a portable breath acetone sensor based on flame-made Si-doped WO3 was used for non-invasive ketosis monitoring of 20 volunteers following a 36-hour KD. This sensor could accurately follow the ketosis level over a wide acetone concentration range (0.4 – 30 ppm) relevant for this application. Furthermore, the individual metabolic responses of the volunteers could be easily distinguished by this sensor as validated by parallel capillary blood BOHB. As a result, this portable non-invasive sensor embodies a reliable device for non-invasive monitoring of enhanced ketosis during KDs enabling routine and personalized dietary monitoring and epilepsy treatment. With the potential for compact size and low power consumption of this sensor fabrication technology, this sensor could be readily incorporated into integrated health monitors.


BM08.06.14
Metabolic Monitoring from Breath with Portable Acetone Sensors Stéphanie Schon, Andreas T. Güntner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Wearable health devices enable cost-effective, user-friendly and continuous personalized healthcare at any time and place. For this, biological fluids such as sweat or breath are attractive as they are readily accessible providing a non-invasive insight into human metabolism. For instance, tracing exhaled acetone, a volatile by-product of ketosis, could enable close monitoring of the interplay between fat and glucose metabolism thus enabling individual customization of physical activity and dietary regimes towards optimal performance and fat loss. Chemo-resistive gas sensors are appealing for breath acetone sensing as they feature high miniaturization potential, low power consumption. When based on Si-doped WO3 nanoparticles, acetone can be detected down to 20 ppb with high selectivity to interfering analytes. Such sensors have been applied already successfully on 20 volunteers to measure their individual fat burn rates during and post exercise. As current technologies to monitor the interplay between fat and glucose metabolism are either invasive (e.g. blood assay) and/or too expensive for widespread application (e.g. indirect calorimetry) such sensors might be ideal for personalized metabolic monitoring. Here, a portable breath acetone sensor consisting flame-made Si-doped WO3 films is presented that can follow individual changes between fat and glucose metabolism in real-time. We applied this sensor on 11 healthy volunteers in a test course first stimulating ketogenesis by exercise (i.e. 3 × 30 min of cycling) and thereafter rapidly inhibiting fat metabolism by an oral glucose tolerance test (i.e. intake of 75 g glucose). The sensor clearly followed breath acetone concentrations during the test course in good agreement to bench-top mass spectrometry. Thereby, the sensor correctly identifying a shift from fat to glucose metabolism for all volunteers even recognizing individual dynamics between the subjects, as validated by parallel capillary blood β-hydroxybutyrate (BOHB) and glucose measurements. In the long run, this sensor is highly promising for integration into wearable devices to guide daily diet and exercise routines towards optimal performance or fat loss.


BM08.06.15
A Bio-Inspired Mineral Hydrogel as a Mechanically Adaptable Ionic Skin for Highly Sensitive Pressure Sensing Zhuyue Lei1 and Peiyi Wu1,2. 1Department of Macromolecular Science, Fudan University, Shanghai, China; 2Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China.

Human skin is soft, robust, self-healable and able to sense subtle environmental differences like a gentle breeze, which has stimulated numerous studies of artificial skin-like materials, especially electronic skins or soft sensor devices. However, profound challenges remain in terms of imitating natural skins because of their unique combination of mechanical and sensory properties. Currently, there are three major approaches to stretchable electronic skins: (1) buckling flexible electronic devices, (2) patterning discontinuous stiff components, and (3) developing intrinsically stretchable materials. While for the purpose of biomimetic and medical applications, materials that are flexible and/or stretchable are not sufficient. A soft artificial skin needs to be mechanically compliant and durable for practical applications, i.e., plastically deformable to fully match curved and dynamic surfaces and autonomously self-healable, mechanically compliant to curved and dynamic surfaces, and exhibit relatively high sensitivity. The hydrogel-based ionic skin can sense subtle pressure changes, such as a gentle finger touch, human motion or even small water droplets. This work may not only show the great potential of physically-crosslinked hydrogels as novel intelligent skins, but also enrich the design of artificial skins for future large-scale Internet of Things applications.

BM08.06.16
Highly Stretchable, Transparent and Biocompatible Gelatin-Supported Deep Eutectic Solvent Gels for Strain and Pressure Sensors Huan Qin and Matthew J. Panzer; Tufts Univ, Medford, Massachusetts, United States.

There is a growing demand for flexible and soft electronic devices in the past two decades because of their broad applications in personal healthcare, human motion detection, and soft robotics. Hydrogels have been intensively investigated and utilized for multiple sensing applications due to their high ionic conductivity, good biocompatibility and tunable stretchability and toughness. However, the long-term use of hydrogel-based devices is limited by the dehydration of most hydrogels in ambient conditions. Ionogels based on ionic liquids with relatively lower ionic conductivity and nonvolatility have attracted considerable attention in sensing applications, but their high cost and toxicity make them unlikely to replace hydrogels. Deep eutectic solvents
(DESs) with similar physical properties (e.g. moderate ionic conductivity and low volatility) are generally low cost and environmentally-friendly, which could be scaled up with a great potential for sensor applications. Herein, we present the first example of DES gels as ionic conductors for multiple capacitive-type sensor prototypes. A DES based on choline chloride and ethylene glycol has been prepared and transparent DES gels have been synthesized in a facile manner using the coil-helix transition process of gelatin. AC impedance spectroscopy and tensile tests are used to characterize the ionic conductivity and stretchability of DES gels containing different amount of gelatin. A DES gel containing 22 wt.% gelatin could be stretched up to 400% without breaking while retaining a decent room temperature ionic conductivity of 2.5 mS/cm. Further stress-strain and strain cycling tests have been performed on the 22 wt.% gelatin gel. There is no obvious hysteresis response up to a strain of ~130% and the elastic modulus decreased slightly (27 kPa to 23 kPa) over 10 cycles at a strain of ~130%, indicating its excellent durability. Therefore, the DES gel with 22 wt.% gelatin was selected to be incorporated into capacitive-type sensor prototypes, where a stretchable tape was inserted as an insulator between two layers of DES gel. A relative capacitance change of 33% was obtained via bending a finger attached to a sensor. Tensile testing has also been carried out for the device and a good linearity between capacitance vs. strain was obtained over ~130% strain with a gauge factor close to 1, which is the theoretical limit of capacitive-type strain sensors. A pressure sensor prototype has also been fabricated and could measure pressures as low as 1 kPa. These promising device results and the low volatility of the DES gel prove that these materials could be an ideal alternative to hydrogels in multiple sensing applications and offer a novel solution to the development of soft electronics.

BM08.06.17

Gold Nanoparticles Decorated on Single Layer Graphene Applied for Electrochemical Ultrasensitive Glucose Biosensor Shifeng Hou; Shandong University, Jinan, China.

A glucose biosensor was fabricated by glucose oxidase (GOD) immobilized on gold nanoparticles decorated on single layer graphene (Au/SLG) modified glassy carbon electrode, with 6-(ferrocenyl)hexanethiol (Fc-C6H12-SH) as electron transfer medium (Fc/GOD/Au/SLG/GCE). The free-standing Au/SLG was obtained by sputtered gold nanoparticles on CVD-generated monolayer graphene. The good dispersion and clean surface of gold nanoparticles on graphene promote immobilization of GOD. The synergistic effect of graphene and electron mediator facilitates electron transfer process which account for the enhanced electrochemical performance with the detection limit of 0.1 nM (S/N = 3). The CVD-generated monolayer graphene has lower background current and good ductility, with free polymer transfer process bring clean surface, which is suit as platform for ultrasensitive detection of glucose. The biosensor was further studied for real perspiration test with attractive feasibility, which has potential application in large-scale production and perspiration-based wearable glucose detection.

BM08.06.18

Development of Biocompatible Microbatteries Aimed at Ingestible Sensors Using MEMS-Fabrication Processes Sven Staube1, Shinya Yoshida2,3, Tsutomu Nakamura4, and Itaru Honma1; 1Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; 2Graduate School of Engineering, Tohoku University, Sendai, Japan; 3Innovation Center for Creation of a Resilient Society, Tohoku University, Sendai, Japan.

Biocompatible microbatteries hold promise for a wide range of applications, especially for health care devices and environmental sensors. One specific example where biocompatible batteries can be employed is in ingestible devices, which can be used for regular monitoring of vital body functions, drug release, or for controlling medication adherence. Currently, ingestible sensor devices are often powered by large batteries that contain electrode materials that are toxic, requiring special encapsulation to ensure their safe use. This leads to bulky systems that are difficult to swallow and also expensive. Moreover, fabrication processes of the batteries are based on conventional methods and therefore possess only limited potential for miniaturization and eventually mass production, to lower the cost of the devices. We have developed biocompatible microbatteries that use gastric fluid as an electrolyte and which can be realized using existing microfabrication processes.

The microbatteries consisted of essentially two main parts: An Si substrate, that contained microstructures acting as passive, biomimetic capillary pumps, and electrodes of the microbatteries which were deposited on glass wafers containing W-vias for connecting front and backside electrodes. Microfluidic reservoirs containing the capillary pumps were realized in Si by standard photolithography and deep reactive ion etching, to depths ranging between 100–200 μm. The capillary pumps enabled more controlled filling of the microreservoir with electroyte, reducing the risk of trapping gas bubbles which could prevent operation of the microbatteries.

For the microbatteries, electrodes with nominal footprints of 0.7 x 3.2 mm² and consisting of about 3 μm thick AgCl cathodes and Zn anodes were fabricated by sputtering using shadow masks. The AgCl cathodes were then formed by electrochemical oxidation of the sputtered Ag films in 0.1 M KCl solutions.

Finally, the Si and glass wafers were bonded together and diced to chips of 5 x 5 mm². The microbatteries were characterized by galvanostatic testing in simulated gastric fluid at current levels ranging from 1 to 100 μA. The cell output reached values of the order of 0.9V, close to the theoretical value 0.984 V of the AgCl/Zn redox couple. The operation time of the microbatteries was limited to about 5–8 minutes, but it is expected that by using thick film techniques, that the operation time can be increased.

It is also anticipated that the use of Si-compatible MEMS fabrication will enable further size reduction of the microbatteries and thereby facilitate their integration in future sensor devices aimed at medical and environmental applications.

BM08.06.19

Interfacial Adhesion Improvement Between Stretchable PDMS and EcoFlex Layers with Nanoparticles for Electrodeposition Robot Gripper Application Lim Hanhuyu1,2 and Baejin Kim1; 1Yonsei University, Seoul, Korea (the Republic of); 2Green Chemistry and Materials Group, Korea institute of Industrial Technology, Cheonan, Korea (the Republic of).

The polymer layers could be easily deformed by external force because of its intrinsic elasticity. In the case of multi-layered polymer thin films, however, it could bring a certain problem. If the adhesion between the interfaces isn't sufficient, slip may be occurred. Particularly, the nanoparticles such as TiO₂, SiO₂, Al₂O₃ and BaTiO₃ dispersed polymers are further modified and affects to the adhesive force. Therefore, it is necessary to predict the relationship among deformation, composisites and interfacial adhesion. In this study, the modulus and interfacial strength of whole layers were measured by Universal Test Machine (UTM) in the ASTM-638. Based on this result, the maximized interfacial adhesion value was confirmed less than 10 N with 200 μm thickness. For the test, the pristine polymer and NP embedded polymer were spin coated to form bilayer shape with single layer tail. As a result, the NP coated polymer showed similar mechanical strength with double error range 1 N compared to the pristine polymer's modulus. Furthermore, we also introduced an adhesive layer such as primer and polyethylene imine (PEI) added PDMS to improve the interfacial adhesion. With NP/PDMS composites, we applied to electrodeposition (EA) robot gripper. NPs have higher dielectric constant than polymer so that it can increase EA force in the same potentials. Furthermore, the critical parts of robot gripper are skin layer and EA layer. Both of skin and EA layers are composed of stretchable polymers so that our achievement could be used for it. As a result, highly adhesive EA gripper was investigated by solving interfacial adhesive problem.

BM08.06.20
High-Performance Energy Devices Based on Amphiphilic Core-Sheath Structured Fibers Xuemei Fu, Hao Sun, Songlin Xie, Limin Xu, Zhuoer Li and Huisheng Peng; State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai, China.

Owing to the lightweight, flexibility and adaptation to various curved surfaces like our bodies, fibrous energy devices are widely studied to revolutionize electronic fields. Numerous efforts have been made to develop high-performance fibrous electrodes which demonstrate high mechanical strength, electrical conductivity and electrochemical activity. As a candidate, carbon nanotube (CNT) fibers have attracted extensive attention but the poor electrochemical activities need addressed. Plasma treatment has been thus adopted to obtain hydrophilic oxygenated CNT (OCNT) followed by introducing active materials. However, the defects formed during treatment largely decrease the mechanical strength and electrical conductivity. The balance between these two aspects requires to be struck for realizing high-performance fibrous energy devices.

Herein, a novel family of amphiphilic core-sheath structured fiber is developed as high-performance fibrous electrode. The hydrophobic CNT core provides high mechanical strength and electrical conductivity while the hydrophilic OCNT sheath acts as platform depositing electrochemically active materials. When the core-sheath fiber used as counter electrode for fibrous dye-sensitized solar cell, a power conversion efficiency of 10% has been achieved, representing the highest power conversion efficiency among all kinds of fibrous solar cells. Further, upgraded core-sheath fibers are applied to fibrous supercapacitors which show excellent capacitance of 324 F/cm² retained at 79% as current density up to 50 A/cm². The structure design can be generalized to other high-performance energy devices.

Reference


BM08.06.22

Highly Sensitive Crack Based Strain Sensor Using Microsphere Expansion Young Jung1,2 and Hanchul Cho1; 1Korea Institute of Industrial Technology, Seoul, Korea (the Republic of); 2Mechanical Engineering, Pusan National University, Buan, Korea (the Republic of).

In recent years, the needs for flexible and wearable electronics have rapidly increased. Among them, strain sensors based on polymer such as PDMS, Ecoflex, Dragon Skin play an important role in the human motion monitoring, electronic skin, etc. Most of these strain sensors with high sensitivity have cracks on the conductive layer, which maximizes the sensitivity of the sensors. However, there is a limitation that the process of making such micro/nano cracks is difficult to manufacture in a large area and the productivity is low. In this work, we suggest new crack fabrication method on the conductive layer using thermal expandable microsphere (THEM). The microsphere is consists of thermoplastic resin and hydrocarbon like a balloon. THEM expands 5~7 times at operating temperature. The cracks are formed by expanding of microsphere in the PDMS/Microsphere composite. Owing to its unique structure and mechanism, strain sensors can have high sensitivity in the 10 percent strain range, good mechanical property, fast response time and high durability in the cyclic tests. We verified the crack propagation using in-situ scanning electron microscopy (SEM) when microsphere was expanded and the sensors were strained. We compared with experimental results and theoretical strain range. Furthermore, we confirmed the expansion ratio of thermal expandable microsphere by adjusting the temperature, which affected the size and total length of cracks. Sensitivity of the fabricated sensor could be tuned by controlling the temperature for the various strain range. The sensors showed significant performance to detect very tiny human body motion like a finger, wrist and neck.

BM08.06.23

Development of a GaN Based Liquid Sensor Using FIB Milling Technique Inas Tahar1,2, Nitu Rajput1, Tomas Palacios2, Mustapha Jouidi1 and Daniel Choi1; 1Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Gallium nitride (GaN) has the advantage over many other semiconductor materials in sensor applications at high temperature environment because of its high temperature stability. Moreover, it has potential capability in sensing polar liquids due to its high internal piezoelectric polarization and chemical stability. Water adsorbs dissociatively on the GaN surface with a sticking coefficient ≥ 0.45 [1]. Dissociation of the water molecules is an exothermic reaction (-44 kcal/mole); therefore, it is thermodynamically favored. Through a reaction chain, oxygen can eventually bound to Ga, and hydrogen desorbs into the gas phase in the form of H₂. High activation energies are achieved by hydrogen desorption from Ga-H bonds and breaking of hydroxyl groups (Ga-OH). Thus, these processes are expected to occur only at higher temperatures [1]. In this work, we report the fabrication of single crystal p-type GaN lamella using focused ion-beam (FIB) milling technique for liquid sensing applications. Two-terminal metal contact geometry was fabricated by depositing Ti/Al on a Si/SiO₂ substrate using electron-beam evaporation. The effect of polar molecules was monitored using Agilent B1505A curve tracer and 2-terminal metal contact geometry was fabricated by depositing Ti/Al on a Si/SiO₂ substrate using electron-beam evaporation. The effect of polar molecules was monitored using Agilent B1505A curve tracer and Agilent B1505A curve tracer by adjusting the temperature, which affected the size and total length of cracks. Sensitivity of the fabricated sensor could be tuned by controlling the temperature for the various strain range. The sensors showed significant performance to detect very tiny human body motion like a finger, wrist and neck.

Reference


BM08.06.24

Interconnection of Flexible NAND Flash Memory via Roll-to-Plate Transfer Method Taelin Kim, Do Hyun Kim and Keon Jae Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Roll-based fabrication has received large attention for the mass production of unconventional soft electronics. Recently, a number of research groups have shown innovative methods in roll-to-roll (R2R) processing such as graphene fabrication, nanotexturing, nanoimprint lithography, and transfer of oxide thin-film transistors (TFTs). However, fully packaged flexible large-scale integrated circuits (LSI) for the computational application should be accomplished in roll-based technology to utilize fully operational roll-based flexible electronic systems. In this work, our group demonstrated the ultrathin silicon-based flexible NAND flash memory (f-NAND) fabricated by highly-productive roll-based flip-chip packaging technology. The roll-to-plate thermo-compression bonding enables the interconnection of the f-NAND on a flexible printed circuit board (FPCB), realized by non-linear elastic deformation of the anisotropic conductive film (ACF). The ACF packaging materials exhibits high compatibility with the continuous roll-transfer process and excellent flexibility even after the interconnection. To confirm non-linear deformation during the roll-based ACF transfer bonding, finite element analysis (FEA) was carried out. The reliable circuitry operation of the 16×16 f-NAND is observed through addressing and bending tests, enabled by the high flexibility of ACF.
interconnections. This work suggests a significant breakthrough toward the mass commercialization of roll-based advanced f-LSI integration technology.

BM08.06.25

All-Soft and Liquid-Phase Supercapacitors Based on CNT-Integrated Liquid Metal Electrodes Min-su Kim1,2, Byeongyong Lee1, Seung Woo Lee1 and Oliver Brand1,2; 1School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2Institute for Electronics and Nanotechnology, Georgia Institute of Technology, Atlanta, Georgia, United States; 3George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Soft energy storage systems are a core technology for powering wearable and skin-mountable electronics. Supercapacitors are considered promising energy storage components for these applications because of their ultrafast power supply and long cycle life; however, their relatively low energy density compared to Li-ion batteries is the major limitation. Moreover, conventional supercapacitors are manufactured from hard and brittle materials, which fail at less than 2% strain. Therefore, interfacing failure between soft skin and rigid electronics is the major limiting factor for wearable and skin-mountable electronics. As a result, a key consideration for realizing all-soft supercapacitors is that each electrode component must be soft and conductive without sacrificing electrochemical performance. The use of liquid-phase conducting materials, such as eutectic Ga-In alloy (EGaIn), can open a new path for all-soft, deformable, and self-healing electronics because of its low melting temperature (<15°C), non-toxicity, favorable electrical conductivity (~3.4×10⁶ S/m), and unlimited mechanical stretchability. In addition, nanocarbon materials, such as carbon nanotubes (CNT), have been actively investigated for improving the energy density.

This paper presents all-soft and liquid-phase supercapacitors based on CNT integrated with EGaIn electrodes. Soft and stretchable CNT-integrated liquid metal electrodes are enabled by i) large area EGaIn thin-film patterning on polydimethylsiloxane (PDMS) substrates using an additive stamping process and ii) functionalization of EGaIn with CNT via a layer-by-layer (LbL) adsorption technique. The additive stamping approach provides large area (~cm²) and uniform EGaIn patterning with a lateral resolution of 500 μm at film thicknesses of ~1.5 μm. The EGaIn patterns will serve as the electron transport channel and support for CNT adsorption. The oxygen functional groups on the CNT enhance the energy density of the electrodes as well as interaction with native oxide (Ga₂O₃) on the surface of EGaIn, resulting in a 3D network on the EGaIn surface with strong adhesion even at 50% applied strain. To demonstrate supercapacitors with a parallel-plate configuration, CNT-integrated EGaIn electrodes were vertically integrated with a soft separator, comprising a porous PDMS structure filled with ionic liquid. The ionic-liquid-filled soft separator enables physical separation between the two electrodes for all-soft and liquid-phase supercapacitors. Our preliminary data show that the areal capacitance increases almost linearly with the number of LbL adsorption steps with a measured areal capacitance ≈15 mF/cm² with 30 LbL steps. Moreover, the specific capacitances remain nearly unchanged for >2000 cycles, which indicates excellent electrochemical stability. The demonstrated all-soft and liquid-phase supercapacitors overcome the limitation of rigid supercapacitor configuration and could enable fully-integrated wearable and skin-mountable electronics.

BM08.06.26

Advanced MEMS Vibrating Ring Gyroscope for Miniaturized Space Attitude Control System Daniel Choi1,2, Boo Hyun An1, Mariam S. Mansouri1, Wajih Syed1, Zakriya Mohammed1 and Ibrahim Elfadel1; 1Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2UAE Space Agency, Abu Dhabi, United Arab Emirates.

Extremely miniaturized, very low power, navigation-grade attitude control systems are an enabling technology for a number of civilian and defense systems, including miniature, autonomous sensors, navigation systems for satellites and unmanned air vehicles (UAV), ground and underwater robotic systems, and defense and law-enforcement systems for widely dispersed surveillance and precision targets. Space systems employing an attitude control system should include the control and processing appropriate electronics to provide the most direct method for sensing inertial angular velocity. While micro-electromechanical systems (MEMS) are playing a growing role in safety critical applications, in the harsh and remote environment of space, reliability is still the crucial issue, and the absence of an accepted qualification methodology is holding back MEMS from wider use.

In this study, we develop an innovative, affordable, miniature, low-power, navigation-grade integrated gyroscope for the attitude control system that applies MEMS technology to achieve the performance, size, power, sensitivity, and cost objectives of space and other commercial applications. We have designed physical model of MEMS gyroscope investigated using Finite Elements Method (FEM) simulation by improving previous developed vibrating ring gyroscope (VRG) designs. Design parameters and elements are modified to narrow down bandwidth and improve shock resistance. To meet the requirements of MEMS gyroscopes for space application, the proposed model of MEMS VRG is designed with shock resistive dual spring structure and multiple ring structure for increasing shock resistance and Q factor. The MEMS VRG is designed in 5 x 5 mm device with 3 mm diameter of the vibrating structure.

BM08.06.27

MEMS Accelerometer Based on GaN for Harsh Environment Daniel Choi1,2, Boo Hyun An1, Menguang Yuan2, Tomas Palacios2, Inas Taha1, Nitu Rajput1, Hamad Al Yass1, Mihai Sanduleanu1, Tawaddod Alkindi1, Mariam S. Mansouri1 and Maryam Almuhayyan1; 1Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Inertial sensing technologies in high temperature environments over 500°C are in great demand in aerospace, power plants and material processing applications. However, conventional micro-electromechanical systems (MEMS) sensors still cannot be operated at such high temperature and need to be isolated in controlled environment.

Gallium nitride (GaN) is very promising for high power devices, high temperature electronics and microsystems due to their wide energy bandgap with low intrinsic carrier density at high temperature over 500°C. Capacitive inertial sensors which consist of two separated electrodes can be operated by detecting capacitance changes between the electrodes upon applied stress. Capacitive inertial sensors have lower thermal drift, high resolution and good noise performance compare to piezoresistive sensors.

In this study, we develop MEMS accelerometer as part of the smart sensor system that will be utilized for monitoring the catalysts inside of the high temperature furnace for the oil refining process. We will discuss a design of MEMS accelerometer using GaN as structure layer, grown epitaxially on aluminum nitride/silicon substrate. The resonance frequency of the designed accelerometer is found to be 2.235 kHz and bandwidth is around 1.2 kHz. Modeling and simulation results of the GaN accelerometer will be discussed and characterization of the fabricated devices would be presented.

The chainmail fabric is made by selective laser sintering (SLS) nylon. These 3D prints have high inherent porosity, and easily take up a fluid containing magnetic nanoparticles through capillary action in post-processing. When dried, the magnetic nanoparticles coat the interior of the porous material, such that it becomes uniformly magnetically functionalised. We show that the location and strength of magnetic actuation can be controlled at the scale of individual links in the chainmail. Therefore, our chainmail fabric can be regarded as a functional chainmail mesh for the swine heart. The mesh monitors cardiac activation signals from ventricles and stimulates at any sites in the ventricles without being hindered by anatomical obstacles.

Intrinsically stretchable conductors form a vital component of advanced bioelectronics. And novel nanocomposites based on conductive nanomaterials have been used in diverse areas including wearable and implantable bioelectronics. Among many nanomaterials for the composites, silver (Ag) nanowires are popular because they are highly conductive and the ultralong nanowires form highly percolated conductive networks in the elastomeric media. However, achieving highly conductive and soft composites is challenging because current methods produce materials that are either highly conductive or soft but never both. Furthermore, because bioelectronics is necessarily exposed to biofluids, preventing Ag nanowire oxidation and Ag ion leaching are significant challenges. And we have achieved a highly conductive, biocompatible, and soft nanocomposite by using silver-gold (Ag-Au) core-sheath nanowires and polystyrene-butadiene-styrene (SBS) elastomer. We synthesized ultralong Ag nanowires encapsulated with a smooth and uniform Au sheath and then mixed them with the polymer. Phase separation of Ag-Au NWs and SBS occurs, which forms microstructures in the composite, reduces Young’s modulus, and increase softness and conductivity of the composite, allowing it to be stretched up to ~266% whilst maintaining a conductivity of 41,850 S/cm. By increasing the content of Ag-Au nanowires, the nanocomposite can achieve conductivity up to ~72,600 S/cm. Using the heat-rolling-press, stretchability of the nanocomposite can be further increased up to 840%. We used the Ag-Au nanocomposite to develop a wearable device for recording electrophysiological signals through the human skin and delivering electrical and thermal stimulations that respond to sensor signals. We also designed and fabricated a customized multi-channel soft cardiac mesh for the swine heart. The mesh monitors cardiac activation signals from ventricles and stimulates at any sites in the ventricles without being hindered by anatomical obstacles.

At some point in our lives, many of us, either through injury, chronic disease or old age, will have to rely on technologies to mechanically assist and support our bodies. Current solutions tend to rely on robotics which often involve cumbersome electronics and heavy power packs. One new approach is the use of soft robotics using pneumatic actuators, which is proving fruitful but usually requires the provision of compressed air through a tether. Actuating smart materials are a potential lightweight and low-power alternative but until recently, their reliable integration into wearable technology has proved difficult. However, recent advances in the field of 3D printing of smart materials (so-called 4D printing), has led to growth of both the hardware and software available for successful integration of these materials into biomedical devices. Here we report on our progress using 4D printing to create active chainmail fabrics for use as wearable exoskeleton supports.

This paper describes the characterisation and processing parameters of magnetically functionalised chainmail fabric that can be used as a biomedical device with controllable stiffness. The use of 3D printing techniques to fabricate the device allows it to be digitally designed by clinicians to exactly fit a patient’s needs. The magnetic actuation results in an on/off state for each controllable link in the chainmail making stiffness a tailored metaproperty of the device, which can be controlled by the clinician.

The chainmail fabric is made by selective laser sintering (SLS) nylon. These 3D prints have high inherent porosity, and easily take up a fluid containing magnetic nanoparticles through capillary action in post-processing. When dried, the magnetic nanoparticles coat the interior of the porous material, such that it becomes uniformly magnetically functionalised. We show that the location and strength of magnetic actuation can be controlled at the scale of individual links in the chainmail. SLS printing is well-suited to making the complex geometries required for wearable fabrics. The functional chainmail reported can be regarded as a mechanical metamaterial, since its design at the macroscale directly influences its mechanical properties. The smallest elements of mechanical metamaterials have become known as melexs (mechanical pixels). In this case, our melexs are individual links in the chainmail. Through our 4D fabrication process they can be designed to be in one of two states – locked or unlocked – and a magnet can be used to flip between them. We show that when all melexs are in the locked state this corresponds to an overall rigid fabric, whereas melexs in the unlocked states renders the material flexible. By design, there are a large number of states in-between fully rigid and fully flexible which is what gives this approach so much potential for wearable exoskeleton support garments.

Monitoring of central blood pressure (CBP) waveform from deeply embedded vessels, such as the carotid artery and jugular vein, has significant clinical values due to their proximity to the heart. The CBP waveform has a direct relationship with the cardiovascular status such as the atrial, ventricular, and valvar activities on both left and right sides. The most accurate method for measuring CBP, namely cannulation, is too invasive to allow frequent measurements, even though it is crucial for many conditions related to all-cause cardiovascular mortality prediction. Existing non-invasive solutions, including photoplethysmography (PPG) and tonometry, have significant challenges to provide accurate and reliable measurements on blood vessels that are deep underneath the skin. Here, we demonstrate a skin-integrated conformal ultrasonic device that overcomes all these limitations by combined strategies of material design and advanced microfabrication. This conformal probe has an ultrathin profile (240 μm in thickness), a high reversible stretchability (60%), and a comparable axial resolution (400 μm) with commercial transducers. This study demonstrates the first conformal electronics capable of launching ultrasonic waves that penetrate into deep biological tissues (~4 cm) in a gel-free manner, and acquiring accurate CBP waveforms at deeply embedded arterial and venous sites to monitor cardiovascular events. Also, this is the first conformal device that enables observing the prominent pressure amplification caused by progressive increase in vessel stiffness along the arterial tree, by comparing the captured peripheral blood pressure (PPB) with the CBP waveforms. Additionally, this device allows correlating the blood pressure (BP) waveforms at different locations of the body with a simultaneous electrocardiogram (ECG) to evaluate arterial stiffness along conduit arteries. Collectively, this opens up extensive opportunities for continuous and accurate deep tissue diagnosis and prognosis using non-invasive wearable electronics.
This talk describes materials and device designs for soft, skin-compatible, battery-free platforms that offer unique capabilities in quantitative capture, storage and in situ chemical analysis of microfluidic volumes of sweat. These systems have options in integration of enzymatic biofuel cells, microfluidic networks, colorimetric chemical reagents and near-field communication (NFC) electronics for readout. A demonstrator includes a reusable NFC electronic module with reversible magnetic connection to a single-use soft, flexible microfluidic component for simultaneous tracking of sweat rate, total sweat loss and pH and of concentrations of lactate, glucose and chloride using biofuel cell and colorimetric approaches. Detailed benchtop studies and field tests on human subjects establish quantitative correlation of data collected using these devices with those obtained by nuclear magnetic resonance spectroscopy, chloridometry and pH measurements.

9:30 AM BM08.07.05
Highly Sensitive and Robust Soft Pressure Sensor Using 3D-structured Microchannel and Liquid Metal for Wearable Applications 

Kim1, Yongrok Jeong1, Jacho Park1, Minseong Kim1, Yong Suk Oh2 and Inkyu Park1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Northwestern University, Chicago, Illinois, United States.

In this study, we have developed a highly sensitive and robust soft pressure sensor for wearable applications using 3D-structured microchannel and liquid metal. Liquid metal is used as a stretchable conductor because of its high conductivity and high adaptability to the mechanical deformation. First, the 3D-structured microchannel was fabricated using 3D-printed dissolvable molds. Using fused deposition modeling (FDM) 3D printing, 3D-printed molds with micro-bumps were fabricated and removed after casting into an elastomer. Then, the liquid metal was inserted into the prepared microchannel using vacuum filling method. It is a competitive fabrication method for its simplicity and cost-effectiveness for not using conventional photolithography. When the pressure is applied, the cross-sectional area of the microchannel decrease draws the resistance of the sensor increases. The high sensitivity of the pressure sensor is achieved by two strategies. First, conventional microchannels fabricated with photolithography were not able to have different thickness of the channel in Z-direction. Using 3D printing technology, we fabricated the 3D-structured microchannel. It is more advantageous for them to close the channel against the small pressure compared with those with uniform thickness. Second, liquid metal reservoirs fabricated at the ends of the sensor acted as a buffer zone for liquid metal flow. Since there was enough room for liquid metal flow, the sectional area of the microchannel could change in respect to the given pressure.

In our study, the pressure sensors with different styles were tested with corresponding finite element method (FEM) simulation results. The geometry and the stiffness of the bumps were controlled. On the other hand, it is ideal for the pressure sensor signal not to be disturbed by other external inputs such as strain. Also, the initial signal level has to be maintained after the deformation. To demonstrate the robustness of the proposed sensor, we performed various complex deformation modes including stretching, folding, twisting, stretching + folding, stretching + twisting, and so on and observed the change of the signal. As wearable applications, we implemented five pressure sensors into the textile and monitored the pressure distribution during sitting and lying. For the real-life wearable applications, it is important for the sensor to be robust and reliable. The proposed pressure sensor has a high sensitivity and robustness having a long life cycle and a simple and cost-effective fabrication process. It is expected to be applied to various applications such as wearable devices, electronic skins, and soft robotics.

9:45 AM BREAK

SESSION BM08.08: Flexible and Wearable Thermal Energy Harvesting/Storage Materials/Devices

Session Chairs: Woowul Kim and Choongho Yu

Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Grand Ballroom

10:15 AM #BM08.08.01
Large Low Temperature Thermoelectric Power Factor from Completely Organic Nanocoatings on Textiles 

Jaeheon Cho1, 2 and Choongho Yu1; 1Texas A&M University, College Station, Texas, United States; 2Wonkwang University, Jeonbuk, Korea (the Republic of).

In an effort to create a paintable/printable thermoelectric material, comprised exclusively of organic components, polyaniline (PANI), graphene, and double-walled carbon nanotubes (DWNT) were alternately deposited from aqueous solutions using the layer-by-layer assembly technique. Graphene and DWNT are stabilized with an intrinsically conductive polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). A 1 μm thick film, composed of 80 PANi/graphene-PEDOT:PSS/PANI/DWNT-PEDOT:PSS quads (QL) exhibits electrical conductivity (σ) of 1.88 X 10^5 S/m and a Seebeck coefficient (S) of 120 μV/K, producing a thermoelectric power factor (σS^2) of 2710 μW/(mK^2). This is the highest value ever reported for a completely organic material measured at room temperature. Furthermore, this performance matches or exceeds that of commercial bismuth telluride. These outstanding properties are attributed to the highly ordered structure in the multilayer assembly. The thermoelectric power output increased with the number of cycles deposited, yielding 8.5 mW at 80 QL for ΔT = 5.6 K. A simple thermoelectric generator was prepared with selectively-patterned, fabric-based system. The electric voltage generated by each TE device increased in a linear relationship with both ΔT and the number of TE legs, producing ~ 5 mV with just five legs and a ΔT of 9.5 K. This unique TE coating system is water-based and uses only organic components. For the first time, there is a real opportunity to harness waste heat from unconventional sources, such as body heat to power devices in an environmentally-benign way.

10:45 AM BM08.08.02
Large Volume Change in a Conjugated Polymer with Polar Side Chains During Electrochemical Doping 

Eleni Stavrinidou1, Johannes Gladisch1,2, Alexander Giovanitti3,4, Daniel Simon1, Iain McCulloch4,5 and Magnus Berggren1; 1Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, Sweden; 2Printed and Organic Electronics, RISE ICT/Acreo, Research Institutes of Sweden, Norrköping, Sweden; 3Department of Physics, Imperial College London, London, United Kingdom; 4Department of Chemistry, Imperial College London, London, United Kingdom; 5Physical Sciences and Engineering Division, KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.

Conjugated polymers can be doped or de-doped electrochemically by exchange of ions with an electrolyte under the influence of an electric field. Their ability to conduct both electronic and ionic carriers in a tightly coupled fashion makes them attractive materials for bioelectronic and energy applications. During electrochemical doping dimensional changes occur in the polymer film due to ion and solvent movement but also changes in the polymer chain
Thermoelectrics for Harvesting Body Heat in Wearable Devices—Optimizing the System-Level Problem

Kedar Hippalgaonkar1, 2, 3
1Institute of Materials Research and Engineering, Singapore, Singapore; 2Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore. 3Institute of Molecular and Materials Engineering, Nanyang Technological University, Singapore, Singapore.

Thermoelectric (TE) materials are able to transform heat into electrical power. Design and manufacturing of new materials for energy harvesting of low-grade waste heat have different design principles than traditional high temperature, high power applications. For example, low power wearable and Internet-of-Things (IoT) devices such as wireless sensors can benefit greatly from ambient power harvesters, where TE can play a key role. Especially interesting is the opportunity to provide a non-intermittent source of power, which only depends on the existence of a temperature gradient. In this talk, I will describe the state-of-the-art innovation in such low-power applications and demonstrate an energy-harvesting system that is integrated with energy storage. Further, such devices in the low temperature application space will have to rely on next-generation inorganic-organic materials and I will describe progress in understanding and designing such materials for high performance thermoelectrics. Finally, I will end by describing a new approach using Machine Learning (ML) algorithms coupled with novel experimental techniques that can provide a diagnostics tool for TE materials to determine not only Seebeck, electrical conductivity and thermal conductivity, but the underlying performance-limiting bulk and interface properties.
volume fraction (10%) of polymer as a binder for Bi$_2$Te$_3$-based n- and p-type micrograins. The thermoelectric performance of these threads was quantified using a home-built in-situ conductivity/Seebeck vise for calibrated temperature gradient and voltage drop with a pressure-control function to study the effect of lateral pressure on thread operation. The resulting threads showed electrical conductivity only 1 order of magnitude lower than the annealed sintered micrograin samples. A particle boundary model was introduced to explain the resulting energy barrier for charge transport as a consequence of charge depletion at the boundary. The threads showed a thermopower very close to that of the annealed sintered samples. To demonstrate the potential applications of the thermoelectric threads, woven thermoelectric fabric is designed to vertically harvest heat flux. Both n-type and p-type thermoelectric threads have been successfully fabricated in air ambient from 3D-inks made from thermoelectric semiconductor powders (Bi$_2$Te$_3$) embedded in a polymer matrix and extruded. A new double-sided insulating/conducting ribbon will be developed to interconnect a weave of such threads to create the thermoelectric fabric. Textile fabrication is inherently scalable, and weaving fabrics from looms of such thermoelectric threads will drive down manufacturing costs for large-scale production.

2:30 PM BREAK

3:30 PM *BM08.09.04/TP03.09.04
High Power Density Mico-Thermoelectric Generators for Powering Wireless Sensor Nodes Jian Zhang, Wenhua Zhang and Dongyan Xu; The Chinese University of Hong Kong, Shatin, Hong Kong.

Thermoelectric generators (TEGs) are promising for harvesting waste heat from the environment to power wireless sensor nodes in smart buildings. In this talk, I will share our recent research effort on developing non-flexible micro-TEGs by integrating pulsed electroplating with microfabrication processes. We systematically studied the effects of the pulsed electroplating conditions on the composition, microstructure, and thermoelectric properties of the electroplated Bi$_2$Te$_3$ thin films. Our results show that the thermoelectric figure of merit of the electroplated Bi$_2$Te$_3$ films can be enhanced by increasing the pulse off-to-on ratio, which is mainly due to the reduced thermal conductivity and the increased Seebeck coefficient. A maximum $ZT$ of 0.16 is obtained at the pulse off-to-on ratio of 50 at room temperature. Based on the fundamental materials research, we further developed cross-plane micro-TEGs on a SiO$_2$/Si substrate. The device consists of a total of 127 pairs of n-type Bi$_2$Te$_3$ and p-type Sb$_2$Te$_3$ thermoelectric pillars embedded in a SU-8 matrix. Both thermoelectric pillars and interconnectors are formed by electroplating, which is advantageous because of low parasitic electrical resistances. The micro-TEG we developed demonstrates a maximum power of 3 mW at a temperature difference of 52.5°C, corresponding to a power density as high as 9.2 mW cm$^{-2}$. The power density of our TEG is more than two times the highest value reported for the electroplated TEGs in the literature, which can be attributed to the low internal resistance and high packing density of thermoelectric pillars.

4:00 PM BM08.09.05/TP03.09.05
Compliant and Stretchable Thermoelectric Coils for Energy Harvesting in Miniature Flexible Devices Kewang Nan$^1$, Stephen D. Kang$^{2, 3}$, Kan Li$^4$, Yonggang Huang$^2$, Jeffrey G. Snyder$^2$ and John A. Rogers$^{6, 8}$; 1Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States; 3Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 4Mechanical Engineering, Northwestern University, Evanston, Illinois, United States; 5Civil and Environmental Engineering, and Mechanical Engineering, Northwestern University, Evanston, Illinois, United States; 6Materials Science and Engineering, Biomedical Engineering, Neurological Surgery, Chemistry, Mechanical Engineering, Electrical Engineering and Computer Science, Northwestern University, Evanston, Illinois, United States; 7Simpson Querrey Institute and Feinberg Medical School, Northwestern University, Chicago, Illinois, United States; 8Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

With expediting trends in electronic device miniaturization, thermoelectric energy harvesting becomes increasingly valuable, especially in wearable technologies and sensors for the internet-of-things. However, it has been impossible to match the device thermal impedance with the natural heat gradient using the thin-film thermoelectric materials much needed for device miniaturization. This limitation has prevented thermoelectrics from competing as a harvester at small scale. Here, we propose and demonstrate an architectural solution to this dilemma, where thin-film thermoelectric materials are mechanically assembled into three-dimensional (3D) coil architectures. This approach not only allows thermal impedance matching but also multiplies the heat flow through the harvester, thus increasing the efficiency for energy conversion. We design and fabricate thermoelectric coils with silicon as the active material that achieve flexibility, scalability, and durability. An array of such coils produces a power of 2 nW, with calculated projections showing the orders-of-magnitude improvement up to a few µW by replacing silicon with state-of-the-art thermoelectric materials. Demonstrations of the idea open up long-waited paths to utilize thermoelectric thin films and provides strategies to interface hard thermoelectric materials with soft harvesting environments, such as those of the human body.

4:15 PM BM08.09.06/TP03.09.06
Flexible Photo-Thermoelectric Nanogenerators Based on MoS$_2$/Nanocomposites for Energy Harvesting Yannan Xie$^1, 2$; 1Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, China; 2College of Energy, Xiamen University, Xiamen, China.

With the rapid growth of economy, the fossil fuel consumption has been sharply increasing to satisfy the energy demand, which results in global warming and environmental pollution. It is crucial to develop clean and renewable energy technology for the sustainable development of human society. Targeting at scavenging thermal energy, thermoelectric effect has been utilized to develop thermal energy harvesting technology. Compared to the pyroelectric energy harvester which has little energy output, thermoelectric devices have been widely recognized as more effective and efficient technologies which has been utilized in practical applications. However, how to harvest thermal energy by using thermoelectrics when the environmental temperature is spatially uniform without any gradients is still a crucial issue and needs to be conquered. The key challenge is to create a significant temperature difference ($\Delta$T) across the device which can act as driving force of thermoelectric generators.

In our living environment, in addition to the direct heat source, light source (such as the infrared light) can also provide thermal energy through the photothermal effect. Based on the photothermal effect and Seebeck effect, photo-thermoelectric generator has been rapidly developed for converting photo energy into electricity without a spatial temperature gradient in the environment. To generate a necessary $\Delta$T, the conventional approach is utilizing various bulky components such as a vacuum enclosure, condenser lens, and heat sink. Nevertheless, these extra modules will not only increase the weight and size of thermoelectric generators but also are unfavorable for the flexibility of the whole devices which is of great importance for wearable electronics. Therefore, developing novel photothermal materials and device structure is essential for the photo-thermoelectric nanogenerator (PTENG).

In this work, we report on a flexible photo-thermoelectric nanogenerator (PTENG) by hybridizing MoS$_2$/PU photothermal layer with tellurium (Te) nanowire based thermoelectric device. The MoS$_2$/PU film which is flexible and transferable exhibits excellent photothermal characteristics due to exceptional surface-area-to-mass ratio of MoS$_2$ nanoclusters. Te nanowire is chosen for the thermoelectric nanogenerator because of its reported outstanding thermoelectric properties, such as low thermal conductivity and a wide temperature range. By integrating the photothermal layer with thermoelectric device, the PTENG can absorb infrared light to form a temperature difference across the device. With this, a potential difference between
two electrodes can be established and used for electrical energy generation. Therefore, the PTENG can generate electricity without a spatial temperature gradient. Furthermore, the PTENG which is flexible and shape-adaptive can demonstrate great practical application of photo-thermoelectric energy harvesting for wearable electronics and implantable electronics.

4:30 PM BM08.09.07/TP03.09.07
Low-Cost Flexible Energy Harvesters Based on Transverse Thermoelectric Effects Radhika Prabhakar and Je-Hyeong Bahk; Electrical Engineering and Computer Science, University of Cincinnati, Cincinnati, Ohio, United States.

Considerable thermal energy is available for energy harvesting from diverse sources in our environment like industrial machines, heat engines and human bodies. This heat, otherwise wasted, can be converted to electrical energy by a thermoelectric energy generator and used to meet daily energy needs like battery charging, powering smart wearable devices or even enabling the Internet of Things. State of the art thermoelectric generators (TEGs) make use of the Bi$_2$Te$_3$ (bismuth telluride) thermoelectric alloys, which are inorganic, brittle, non-flexible, and require expensive processing. The TEGs are typically based on a longitudinal p-n structure, which is complex, both in terms of electrical connections and manufacturing. Moreover, such TEGs often feature a bulky heat sink to maintain high temperature differences between the hot and cold sides. These reasons limit their large scale use in ambient energy harvesting.

In this work we report a low cost, flexible TEG based on transverse thermoelectric effects. A transverse TEG consists of tilted multi-layers made of alternating metal and semiconductor materials. In such a device, a thermoelectric voltage can be generated in the direction perpendicular to the vertical temperature gradients, which makes the transverse structure suitable for planar devices. For our transverse TEG we use aluminum or nickel as the metal layers and carbon-nanotube (CNT)-polydimethylsiloxane (PDMS) composites as the semiconductor layers. Both materials are inexpensive with the TE composites being solution processable. For device fabrication the polymer composite solution is cast in between 3D-printed metal layers followed by air drying to obtain the transverse device. By filling the metal layer gaps partially with the polymer composite solution the upper portions of the metal layers are directly exposed to air at the cold side, thus acting as a fin type heat exchanger for lowering the cold side temperature by air convection. The use of flexible composites as the semiconductor material imparts flexibility to the TEG in one direction. It can therefore make good thermal contact with curved surfaces like hot water pipes, solar reflectors and even human skin, thus enabling TE energy harvesting from such surfaces. Transverse TEG architecture provides a number of degrees of freedom like the layer thickness, tilt angle, fin length, which can be varied to study the power generated. We present detailed thermoelectric properties of the CNT-PDMS polymer composites as well as its performance under bending tests. We also present a full range of experimental results of the fabricated transverse TEGs augmented with finite element simulations to optimize the device design for maximum power output.

4:45 PM BM08.09.08/TP03.09.08
Development of N-Type Single-Walled Carbon Nanotube Sheet with Excellent Air Stability Tsuyoshi Fujigaya1, 2; 1Kyushu University, Fukuoka, Japan; 2JST, Saitama, Japan.

Thermoelectric (TE) conversion is one of the most promising methods for the generation of cost-effective electricity. TE devices have applications in many fields especially microelectronics devices due to their simple device structures. TE generation using Seebeck effect requires both n-type and p-type TE materials for the efficient conversion; however, deterioration of n-type nature due to air oxidation has been the critical issue. Recently, we reported single-walled carbon nanotubes (SWCNT) sheet doped by 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzimidazole (o-MeO-DBMI) showed n-type property and remarkable air-stability[1] We chose o-MeO-DBMI because of the following reasons; i) o-MeO-DBMI is stable under atmospheric conditions, ii) the cationic form of o-MeO-DBMI is also stable and, iii) n-doping of the other carbon materials such as fullerene and graphene has already been reported.[2,3] Here, we study the mechanism of the air stability of o-MeO-DBMI-doped SWCNT films by changing the doping level.

eDIPS (Meijo Nano Carbon, EC1.5) was used as SWCNT. SWCNT films were dipped in the 0.01, 0.1, 1.0, 10 and 50 mM ethanol solution of o-MeO-DBMI for 10 min and dried in vacuum at room temperature for 12 h. The time course of Seebeck coefficient of the SWCNT films doped with various concentration of o-MeO-DBMI solution was studied. It is noted that the films were kept under air condition at room temperature to evaluate the air stability of the o-MeO-DBMI-doped SWCNT films. Positive value of Seebeck coefficient for 0.01 and 0.1 mM doped films indicated n-type, and negative value for 1.0, 10 and 50 mM doped films showed n-type nature of the films. Interestingly, we found that Seebeck coefficient of 1.0 mM doped film changed to positive, while 10 mM doped film showed stable negative value. From above results, we conclude that the mechanism of the air-stabilization of n-doping is the passivation effect by the formation of o-MeO-DBMI layer onto the surface of SWCNT films.

storage at room temperature. This all-polymer “smart multisensor” fully printed on paper advances on the next generation low cost, disposable, noninvasive, multianalyte sensing wearable biomedical devices.

BM08.10.02 Porous Polymer Microneedles for the Sensing of Subcutaneous Interstitial Fluid Hiyuki Kai, Kumata Hiroki and Matsuhiro Nishizawa; Tohoku University, Sendai, Japan.

The microneedle array, a two-dimensional array of needles of a few hundred micrometers, penetrates skin in a minimally invasive manner, and they have been applied to transdermal drug delivery and sampling and analysis of subcutaneous interstitial fluid. Microneedles with different materials have been developed such as hollow silicon microneedles, hydrogel microneedles, and dissolvable microneedles. We have previously developed a porous polymer microneedle array using a polymer monolith of poly(glycidyl methacrylate). It combines continuous internal micropores to absorb water quickly and sufficient mechanical strength and tip sharpness to penetrate skin.

In this work, we fabricated proof-of-concept microneedle sensors using the porous polymer microneedles. We adopted two different strategies to integrate sensors into the micropores of the microneedles. (1) Electroless gold plating was applied to the surface of the micropores to obtain a porous microneedle electrode, and redox enzymes were immobilized on the electrode surface to conduct amperometric sensing. (2) Hydrogel that contains a boronic acid-based fluorescent glucose sensor was filled into the micropores to optically quantify glucose concentration of an analyte. These designs enable the sensors to quickly interact with analytes absorbed into the micropores. In addition, they do not require an extra step of measurement following the removal from skin, which potentially makes the continuous readout from the outside of the skin feasible.

BM08.10.03 High-Performance Triboelectric Nanogenerators Using Visco-Poroelastic Ion Pump Joo Sung Kim1, Heejae Hwang2, Han Wool Park3, Eunsong Jee1, Dukhyun Cho2 and Do Wun Kim1, Hanyang Univ., Seoul, Korea (the Republic of); Kyung Hee University, Yongin, Korea (the Republic of).

Recently, many attempts have been made to implement stretchable triboelectric nanogenerators (TENGs) that can be energy harvesting systems and self-powered electronic devices. There are several kinds of soft materials to enhance the power efficiency and power density of TENGs. Especially, ionic materials such as ionic hydrogels, which are capable of achieving electrical double layer (EDL) phenomena and polarization of ions, are regarded as a new platform to achieve high-performance and stretchable TENGs. A similar concept has been reported by using ionic materials as conductor and electrification layer. However, since free ions contained in the ion materials are able to carry electric charges, unlike conventional tribo-materials having dielectric characteristics, it is required to consider electrical characteristics and electrochemical properties of ionic materials.

In this talk, we describe a highly deformable and visco-poroelastic ion pump as a potential triboelectric channel with high power density and its impact on mechanical characteristics, it is required to consider electrical characteristics and electrochemical properties of ionic materials.


The family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides known as MXenes have received considerable attention for energy storage applications due to their favorable and tunable electronic and physical properties. MXenes have high specific capacitances1 due to their redox-active transition metal surfaces and when MXenes are fabricated into binder free, free-standing films they have high electric conductivity (>8000 S/cm).2 In addition to the intrinsic electrochemical properties of MXenes, their hydrophilicity allows formulation of functional inks that can readily be printed, spray-coated, or spin cast in any desired pattern, enabling the creation of MXene thin-film coatings that are ideal for applications that require microscale energy storage devices.

However, the traditional methods used to create electrodes from 2D materials for energy storage applications, namely vacuum assisted filtration, result in densely restacked films. This electrode architecture impedes electrolyte infiltration and transport in thick films (>10 μm), which has put a limit on the practical implementation of not only MXene electrodes, but other 2D materials like graphene and transition-metal dichalcogenides. For this reason, developing new methods for fabricating thick films using 2D materials is desirable, and in a recent study we have developed a technique for vertically aligning the 2D flakes of MXenes to create rapid, directional ion transport.3 By mechanically shearing a discotic lamellar liquid crystal phase of titanium carbide MXene (Ti3C2), we can produce electrode films that are hundreds of microns in thickness that show thickness-independent specific capacitance. Our approach for aligning 2D materials is not limited to MXenes and energy storage applications, this method can be modified to suit any 2D material and can be extended to any application where directional transport is desirable, e.g. catalysis and filtration systems.


BM08.10.05 A Finite Element Design of a Kirigami-Based Wearable Device for Human Joints Antonio Avila; Mechanical Engineering, Univ Federal-Minas Gerais, Belo Horizonte, Brazil.

Human skin of elbows, ankles and knees undergo considerable deformations during the body motion. Therefore, wearable devices (WD) for such regions shall be capable of sustaining these deformations while remaining into the elastic regime. Silicone rubber, e.g. polydimethylsiloxane (PDMS), is a natural candidate to be used as a substitute for such wearable devices. Unfortunately, most of PDMS have a limitation regarding the total elastic strain, which is in the
200-300% range. Moreover, due to these body part’s morphologies, these wearable devices not only have to undergo extreme large strains but they are also inhomogeneous. To be able to design a stretchable wearable devices for human joints, the ancient Japanese art of paper cutting, often known as Kirigami is applied to PDMS thin films doped with carbon nanotubes. The multi-walled carbon nanotubes were placed into the PDMS surface’s to create a conductive network. The Kirigami configuration is analyzed by a finite element method, where the hyper-elastic second order Ogden model is employed. The wearable device design two main constraints must be fulfilled, i.e. the large stretchability and the MWNT network continuity. Based on these conditions a finite element analysis was performed, where boundary conditions, such as number of cuts, its length and spatial distributions were varied. The main objective was to obtain a near optimum design. The numerical simulations indicate that elastic strains up to 900% can be achieved with effective elastic stress around 75% of the ultimate stress. From the Fracture Mechanics perspective, the Kirigami configuration introduces a increase on local stress field near the cut/crack tip. The MWNT surface distribution not only induces a local inhomogeneity but it also changes the stress intensity factors around the cut/crack tips. Experimental data and the ones obtained from the numerical simulations are in good agreement.

BMO8.10.06  Flexible Ferroelectric Electronic Skins with Ultrahigh Pressure Sensitivity and Linear Response over Exceptionally Broad Pressure Range Youngho Lee, Jonghwa Park, Soowon Cho, Young-Eun Shin, Changgi Baig and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Flexible pressure sensors with a high sensitivity and linear response over a broad pressure range can simplify the wearable sensing systems without additional signal processing for the linear output, enabling device miniaturization and low power consumption. Here, we demonstrate a flexible ferroelectric sensor with ultrahigh pressure sensitivity and linear response over an exceptionally broad pressure range based on the material and structural design of ferroelectric composites with a multilayer interlocked microdome geometry. Due to the stress concentration between interlocked microdome arrays and increased contact area in multilayer design, the flexible ferroelectric sensors could perceive static/dynamic pressure with high sensitivity (47.7 kPa⁻¹, 1.3 Pa minimum detection). In addition, efficient stress distribution between stacked multilayers enables linear sensing over exceptionally broad pressure range (0.0013 – 353 kPa) with fast response time (20 ms) and high reliability over 5,000 repetitive cycles even at extremely high pressure of 272 kPa. Our sensor can be used to monitor diverse stimuli from low to high pressure range including weak gas flow, acoustic sound, wrist pulse pressure, respiration, and foot pressure with a single device.

BMO8.10.07  Triboelectric Energy Generator for Powering Implantable Electronics Hong Joon Yoon and Sang-Woo Kim; Sungkyunkwan Univ, Suwon, Korea (the Republic of).

A great challenge in research for powering or being self-powered implantable electronics, scavenging very limited biomechanical energy such as pulse by heart, respiration, circulation, is to generate extremely low electrical energy. Without technological breakthrough, energy harvester would not supply sufficient power to operate not only in vivo medical gadget, but charging rechargeable battery. Here, we demonstrate the use of external mechanical energy as non-invasive kinetic energy to transmit through human skin and trigger oscillation. We first show external mechanical energy driven very tiny oscillation inside the body is enough to induce micrometer scaled displacement of a biocompatible membrane and to generate electrical energy by contact electrification. Generated voltage and current values are 10 V and 500 μA which is almost 100 times higher than previously reported triboelectric generators. In addition, we use this approach to charge commercial Li-ion battery, resulting in charging rate of about 50 μC/s. Our results establish external kinetic triggers as powerful energy harvesting method in biomedical electronics research.

BMO8.10.08  Calculation of Polarization and Bound Charge Density Inside a Dielectric Material in Triboelectric Nanogenerators—Analytical and Numerical Study SeongMin Kim¹, Yohan Jeong² and Sang-Woo Kim¹; Sungkyunkwan University, Suwon, Korea (the Republic of).

We analytically calculated polarization and bound charge density inside the dielectric material in metal-to-dielectric–mode triboelectric nanogenerators (TENG) where the transferred charges are collected on the bottom metal via electrostatic induction from the triboelectric charges that are generated by frictional contact. This bound charge density is associated with the surface density of states (DOS), N(E). Two cases are considered here: i) for N(E) >> 1, it is calculated that the bound charge density is proportional to the dielectric constant and the work function difference between the two materials, but inversely proportional to the thickness of the dielectric material, the bound charge density is mostly proportional to the work function difference between the materials, and inversely proportional to the thickness of the dielectric material.

BMO8.10.09  Highly Sensitive Transparent and Flexible Pressure Sensors Based on ZnO Nanocrystals by All Solution-Process Hong Joon Yoon and Sang-Woo Kim¹; Sungkyunkwan University, Suwon, Korea (the Republic of).

Applications of pressure sensors have increased in popularity as they are used to measure human motion and monitor the industry. However, complicated and expensive processes and/or low sensitivity remained challenging issues. Herein, a simple and inexpensive process using Silver Nanowire (NW) and ZnO Nanocrystals (NCs) without lithography is developed to fabricate a transparent pressure sensor. ZnO NCs guarantee the transparency of the device and improve the sensitivity of the device while it is rugged on the surface. Device performance analysis with structural, chemical, and electronic characterization and conductive atomic force microscopy study reveal that hybrid nanostructure-based pressure sensor shows a sensitivity of higher than 90 kPa⁻¹, reliability and stability. Finally, we demonstrate that all sensors can be easily applicable to many fields such as wearable or attachable sensors by sensing a wide range of pressures.

BMO8.10.10  Flexible, Fiber-Shaped Supercapacitors with Roll-Type Assembly Seongil Yu and Heejoon Ahn; Hanyang University, Seoul, Korea (the Republic of).

A fiber-shaped supercapacitor with a unique roll-type configuration is developed by simply rolling polyaniline-coated carbon fiber bundle electrodes and using an H₃SO₄/polyvinyl alcohol gel electrolyte. The electrochemical performances of this device are characterized and compared with those of a twist-type fiber-shaped supercapacitor. The roll-type polyaniline-coated carbon fiber supercapacitor exhibits four times higher capacitance retention than the twist-type fiber-shaped supercapacitor at a high scan rate of 100 mV s⁻¹ and shows a gravimetric energy density of 2.97 Wh kg⁻¹ at a power density of 4 kW kg⁻¹, which is almost three orders of magnitude higher than that of the twist-type fiber-shaped supercapacitor (0.004 Wh kg⁻¹). The enhanced performance of the roll-type fiber-shaped supercapacitor is attributable to its unique roll-type configuration, which creates a short and consistent distance between the electrodes. The capacitance and voltage are tripled by simply connecting three roll-type fiber-shaped supercapacitors in parallel or series, respectively. In addition, the roll-type fiber-shaped supercapacitor shows excellent mechanical stability. The excellent performance of the roll-type fiber-shaped supercapacitor suggests its potential as a flexible energy storage device in portable and wearable electronics.
Textile-Permeable Conductive Inks for Electrophysiological Sensors on Garments

Textile-Permeable Conductive Inks for Electrophysiological Sensors on Garments

It is important to make soft and stretchable circuits for wearable biometric sensors, since human body has a curvilinear surface which dynamically moves and deforms. Textile is one of the ultimate wearable platform because of their mechanical flexibility, thermal properties and breathability originated from their porous structure. A seamless integration of electronics into the textile has been researched and it became a field of technology, so-called E-textile. Recently, researchers have achieved highly conductive and stretchable wiring on the textile by using metal plating and weaving, although those methods have challenges in patterning which are crucial for electronic circuits. Printing is an alternative method for fabricating conductive wirings on textile. However, it is difficult to achieve high stretchability more than 30% strain since the textile is porous and significant contours on the surface which make printed film susceptible to the cracking. In this work, we propose textile-permeable stretchable conductor which resulted in significant improvement of stretchability and cyclic durability of printed wiring. Specifically, a new type of ink that easily permeates textile substrate was developed, initial sheet resistance of printed wiring on textile was 0.06 ohm/sq, and increased only 70 times after stretching 450%. And resistance change after 100 cycles at 30% strain was less than 10 times while the resistance of printed trace on elastomer film increases 10^5 times. The ink is comprised of silver flakes, fluoroelastomer, and slow evaporating solvent (2-butoxyethoxy ethyl acetate). The key idea to realize stretchable wirings in textile is building conductive pathways inside of the fiber bundles by permeating ink deeply, instead of forming a thick film on the surface of the textile. We systematically investigated penetration of ink by changing evaporation speed and viscosity of ink, also optimized the composition of the ink. Finally, we demonstrate 8-channel EMG monitoring garment which can monitor muscle activity of upper body during the pitching motion of baseball pitcher and transmit the data wirelessly.


Electronic skins (e-skins) with high sensitivity to multidirectional mechanical stimuli are crucial for healthcare monitoring devices, robotics, and wearable sensors. Previously, numerous e-skins have been successfully demonstrated to improve the tactile sensing performance using various microstructure arrays. However, there have been no systematic studies of the effects of the microstructure geometry on force-induced microstructure deformation and the resulting force sensitivity and selectivity in response to multidirectional mechanical stimuli. To investigate the geometrical effects of microstructure arrays on force-sensing capabilities, we here present three kinds of piezoresistive e-skins based on carbon nanotube/elastomer composites with different surface microstructures (i.e., dome, pyramid, and pillar). In addition, we compared the experimental piezoresistive properties and finite-element simulations of changes in the contact area and localized stress distributions in the microstructures. Depending on the microstructure geometry, distinct variations in contact area and localized stress distribution are observed under different mechanical forces (i.e., normal, shear, stretching, and bending), which critically affect the force sensitivity, selectivity, response/relaxation time, and mechanical stability of e-skins. As proof-of-concept demonstration in healthcare monitoring applications, our e-skins are used for detecting various bio-signals including acoustic waves, breathing, and human artery/carotid pulse pressures. Unveiling the relationship between the microstructure geometry of e-skins and their sensing capability provides a platform for the future development of high-performance microstructured e-skins.

Smartphone Based Phage-Colorsensor to Detect Ovarian Cancer

Smartphone Based Phage-Colorsensor to Detect Ovarian Cancer

We developed phage-based colorimetric sensors to diagnose ovarian cancer. Ovarian cancer is known as a “silent killer” because its symptoms are minimal or very rare. The 5-year relative survival rate of ovarian cancer is higher than 90% if detected early, whereas drastically lowered to 40% when detected after stage III. Therefore, early diagnosis is critical for treatment and survival of the ovarian cancer. It has been known that serum and salivary CA125 and HE4 biomarkers were correlated in ovarian cancer patients. Therefore, we developed phage-biosensor to detect the CA125 and HE4 ovarian cancer biomarkers in saliva. We identified highly specific phages to CA125 or HE4 through high-throughput phage display technique. We then genetically engineered the phages to express CA125 and HE4 receptors on the major coat protein. Using the resulting engineered phages, we fabricated self-assembled matrices composed of quasi-ordered fiber bundle structures to exhibit tunable colors by self-templating assembly approach. Upon exposure of different concentrations of biomarkers, the multi-color phage matrices exhibited distinct color changes that can be correlated to colorimetric measurement. Furthermore, we used home-designed smart phone app to detect the biomarkers selectively and sensitively from the human saliva. We believe that our phage-based ovarian cancer biomarker detection approach will be useful for early detection of ovarian cancer and increase of the survival rate.

All Transparent-Stretchable Electrochromic-Supercapacitor Wearable Patch Device

All Transparent-Stretchable Electrochromic-Supercapacitor Wearable Patch Device

Electrochromic devices, that control transmittance of ultraviolet and visible light by electrochromism due to charge transfer, have been applied to low emission mirrors and energy saving systems by suppressing the internal temperature rise of the smart building system. Furthermore, electrochromic device can be used as a wearable healthcare device that detect harmful substances in human body as electric signals. For example, wearable electrochromic-chemical sensor technology have been developed by integrating a chemical sensor that detects resistance change by a target chemical component and an electrochromic device that generates a color change by electron movement. Wearable electrochromic devices have attractive functions and development possibilities that can be applied in everyday life however, the limitations of conventional electrochromic devices based on ITO-glass, which is brittle and required external electrical input did not overcome. All transparent-stretchable electrochromic-supercapacitor wearable patch devices with high electrochemical and electrochromic performance was fabricated to overcome the limitations of conventional electrochromic devices. All transparent-stretchable wearable patch device was consisted of transparent-stretchable low density silver nanowire embedded PDMS substrate, electrospunned WO₃ nanotube-PEDOT.PSS thin layer composite and transparent-stretchable Li ion-poly acrylamide based hydrogel electrolyte. Especially, the contact efficiency of WO₃, nanotube is considerably increased by even employing low density silver nanowire current collector. In addition, PEDOT.PSS thin overlayer was introduced to prevent the delamination of
WO₃ nanotube and offer enhanced coloration efficiency by dual electrochromic coloration. As a result, electrochemical energy capacity, electrochemical cycle reliability and electrochromic coloration efficiency were enhanced 20.6%, 7.0%, 12.0% by using WO₃ nanotube-PEDOT:PSS active materials. The electrochromic-supercapacitor wearable patch device capable of stretching-bending deformation and simultaneously electrochromic coloration-electrochemical energy storage with enhanced electrochemical-electrochromic properties was operated by integrated hydrogel electrolyte with high ionic conductivity, transparency and more than 80% elongation. Therefore, the fabricated all-transparent-stretchable electrochromic-supercapacitor wearable patch device is highly suitable for wearable electronic applications.

BM08.10.15
Polymer-Based Wearable Throat Microphone with High Sensitivity and Flat Frequency Response Singyoung Lee, Hyungsuk Lim, Woong Sung, Sangsik Park and Kilwon Cho; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Flexible and skin-attachable vibration sensors have been researched for wearable mechanosensors to recognize human voice, the most important bio-signal for communication. However, the reported sensors so far have shown low sensitivity and non-flat response. In this work, we present polymer-based wearable throat microphone that detects the neck skin acceleration, which has high and linear correlation with the voice pressure. Our device exhibits a high sensitivity over 4 V/Pa with flat frequency response over the voice band, which results from the polymer with low stiffness and low damping constant, and the hole-patterned diaphragm structure: Our device has superior skin conformity due to polymer-based ultrathin structure (< 10 μm). We successfully demonstrated voice security authentication and voice-controlled system notwithstanding ambient noise or use of mouth mask. This development enhances the utility of voice recognition application in human machine interface and Internet of Things area. In addition, the device enabled vocal healthcare monitoring conveniently even in noisy work places, by measuring quantitatively phonation time, voice frequency and pressure. This diagnostic application can provide a valuable monitoring approach for more than one-third of the working population, who use their voice as the primary tool.

BM08.10.16
Polymer Functionalized Carbon Nanomaterials for Flexible Tactile Sensors S. Ramaprabhu1, Krishnan Balasubramanian2, Vetrivel S1 and Ashwin Namb1; 1Department of Physics, Indian Institute of Technology Madras, Chennai, India; 2Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai, India.

In biomedical applications, sensors play a critical role in detecting and monitoring the human activities. In particular, tactile sensors are useful in detecting the external stimulus which is highly required in designing the biofunctional prosthetic system. In real time, prosthetic system may undergo different kinds of motion like bending, twisting and rotating. Functioning of tactile sensor in all these circumstances, demands high flexibility along with robustness. To design such system, fabrication of polymer nanocomposite is one of the ideal solutions. In this regard, researchers have started exploring novel nano materials like carbon nanotubes (CNT), graphene, nanowires and nanoparticles. Due to the exceptional electrical, mechanical and thermal properties, CNT and graphene can be used as nano-fillers in the polymer matrix substrate to enhance the electrical characteristics of the polymer nano-composites. Due to the high surface energy of the nano-fillers, it gets easily agglomerated in the polymer matrix and reduces the electrical conductivity of the film. Hence, it is essential to functionalize the nano-fillers to enhance the dispersion in the matrix and hence the electrical conductivity. In the present work, we analyzed the effect of two selective polymer functionalisation of multiwall CNT and hydrogen exfoliated graphene (HEG) fillers in a suitable polymer matrix and investigated the electrical conductivity of the polymer composites. The polymer functionalisation enhances the dispersion of the nano-fillers without introducing the defects in the structure and enhances the electrical conductivity. When force/strain is applied on the polymer nanocomposite, the established conducting networks is affected which leads to change in resistance, which is used as an electrical readout signal for actuating the prosthetic system. This sensor can be extended to the different applications like wearable electronics, robotics and structural health monitoring.

BM08.10.17
Surface Roughening with Iron Nanoparticles for Promoted Adhesion of Spin Coated Microsupercapacitor Electrodes Aarin Vyas, Fabio Cornaglia, Qi Li, Mazharul Haque, Volodymyr Kuzmenko, Anderson D. Smith, Per Lundgren and Peter Enoksson; Chalmers University of Technology, Gothenburg, Sweden.

In order to be able to use autonomous (wireless) miniaturized sensor nodes as part of the Internet of Things, integrating CMOS compatible sensor manufacturing technology with energy harvesting and energy storage devices would be a significant advantage. Supercapacitors are devices which store energy by charge accumulation (and/or transfer) at an electrode-electrolyte interface. Previous attempts at manufacturing microsupercapacitor electrodes for microsystem integration have required techniques such as laser scribing, doctor blade coating, or reactive chemical growth for their deposition. Replacement of these techniques with a simple CMOS compatible spin coating technique is therefore highly desirable. Although previous investigations establish fabrication of microsupercapacitors through spin coated graphene oxide (GO) layers, the non-uniformity in the spin coating of the electrodes remained a critical issue. Moreover, poor adhesion of the carbon material to the metal contact pads leads to the risk of low electrode retention in subsequent fabrication steps – resulting in low output power and energy performance. In this work, we present a CMOS compatible electrode deposition process for reduced graphene oxide (rGO) using spin coating. Additionally, we report improvements in adhesion and surface uniformity by employing surface roughening through Fe nanoparticle formation. A 4 nm thick Fe layer was evaporated on the bare Si/SiO₂ surface and then annealed at 500°C for 2 min, which magnifies the average mean surface roughness from 0.175 nm to 1.45 nm. After comparison with a sample without the Fe deposition and annealing, we see more than 300% improvement of surface coverage of the electrosynthesized rGO (from 19% to 79% of the surface covered), which was performed by image processing in MATLAB (ver. R2015b). A 1.80 µm thick electrode was deposited on the roughened surface, compared to the 1.01 µm accumulated on the non-roughened sample. A 40 sec sonication test of the spin coated electrodes revealed a 62% GO mass retention on the roughened sample in comparison to only 18% retention on the non-roughened device. We believe that these characteristics will directly translate to better electrochemical performance for the final microsupercapacitor devices which will be demonstrated at the conference.

BM08.10.18
A Solution Processable Conjugated Polymer for Direct Metabolite Sensing and Energy Powering Device Georgios Nikiforidis, David Ohayon and Suhika Inal; KAUST, Thuwal, Saudi Arabia.

Biosensors and biosensing protocols can detect a wide range of compounds, sensitively and selectively, with their application range extending from security and health care for point-of-care analyses of diseases to environmental safety. Since the first implantation of a pacemaker in 1960, tremendous efforts have been made to develop small power-supply medical devices for environmental safety, healthcare monitoring, neural disorders and hearing loss. Amongst them, biofuel cells have attracted significant attention due to their ability to convert the energy of metabolism into electricity. Unlike other conventional fuel cells, biofuel cells find their substrate directly in biofluids, where the metabolite of choice is abundant, cost efficient and offers a clean source of energy.
Herein, we present a novel enzymatic biofuel cell design, based on an n-type semi-conducting polymer where the anode creates current in the presence of metabolites in the solution. Due to the specific design of the polymer structure, enzymes are able to adsorb on the surface of the polymer film, avoiding the tedious processes of enzyme immobilization and leading to a mediator-free system. Moreover, since the power output of the cell is directly dependent on the metabolite concentration, the enzymatic biofuel cell acts itself as a biosensor. The polymer based (i.e biocompatible) membrane-less biofuel is simple and scalable. The power output of this novel n-type polymer-based biofuel cell (626 mW cm⁻²) outperforms other systems reported. Finally, the power delivered from the proposed biofuel cell can be collectively implemented to measure multiple analytes. This design paves the route of self-powered multi-analyte sensors for continuous healthcare monitoring.

BM08.10.19
Aloe Vera-Based Conducting Polymer Electrodes for Transcranial Electrical Stimulation Jeremy Savarir1, Georgios Spyropoulos1, Jennifer Gelinas3, Eleni Stavrinidou2 and Dion Khodagholy1; 1Columbia University, New York, New York, United States; 2Laboratory of Organic Electronics, University of Linköping, Linköping, Sweden.

Transcranial electrical stimulation (TES) is an emerging neurostimulation technique. It is minimally invasive and utilizes electrodes on the surface of the skin or skull, avoiding damage to brain tissue. However, the poor mechanical contact combined with high electrochemical impedance of the metal-body interface mandates high power stimulation protocols for effective interventions. As a result, TES has poor spatial resolution and anatomical specificity. We hypothesize that improving the interface between the stimulating electrode and body would result in lower stimulating power and better localization of electric stimulation. We developed TES electrodes that consist of a standalone composite film based on aloe vera hydrogel and poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS). The aloe vera hydrogel matrix provides unique properties to the film including conformability, softness when in a hydrated state, and strong adhesion with the surface of the skull after dehydration. In parallel, PEDOT:PSS ensures high conductivity and a low skull-electrode interface impedance, enabling efficient ion-to-electron conversion. The hydrogel-based electrodes were implanted on the surface of the rat skull, where SEM images of the skull-electrode interface demonstrated a conformable contact, highlighting its efficient mechanical interface. The effect of film composition and surface area on the electrochemical impedance were characterized and compared to a conventional TES electrode, and a significant reduction in impedance and increase in charge capacity was observed. The hydrogel-based electrodes did not require any additional adhesive to attach to the surface of the rat skull, forming an in vivo TES-based, closed-loop system for detection and stimulation of interictal epileptiform discharges (IED). Efficacy and stimulation thresholds were determined in vivo electrochemical impedance spectroscopy and power titration, and comparison was made to conventional metallic electrodes. Overall, such films demonstrated high stability, biocompatibility, and spatial resolution for transcranial stimulation and hold a great promise in improving the efficacy of TES as a non-invasive intervention for neuropsychiatric disorders.

BM08.10.20
Patternable Nano-Cracked Strain Sensor Based on One-Step Laser Heat Encapsulation Chan Park, Hyunsuk Jung, Hyunwoo Lee, Hong Sung Uk, Hyonguk Kim, Seong Kyung Hong and Seong Jin Cho; Department of Mechanical Engineering, Chungnam National University, Chungnam, Korea (the Republic of).

Skin mountable or wearable electronic devices have recently grown in popularity due to their numerous advantages in the context of human–machine interactions. Despite the improved performance of recently developed flexible and stretchable strain sensors, performance degradation caused by a change in external environmental conditions such as humidity and dust is a critical barrier to practical use. Here, we report a benefits of highly stable crack-based strain sensor using a novel laser heating encapsulation method optimized for thin film structure. first, unlike other encapsulation methods such as liquid polymer, multi-layer, resin, bar sealing, and laser sealing, it is possible to fabricate the patternable, cutting, and bonding of sensors without complicating one-step. Second, the novel encapsulation process is an economical process because it does not require any additional materials such as PDMsPoly(dimethylsiloxane), resin, film. Third, it does not adhere directly to the metal thin film, so the performance does not deteriorate. Since the part to be bonded is the edge to which the laser is irradiated, there is no influence on the metal. Finally, we evaluated the performance of the sensor after inserting sensor in water, and confirmed the possibility of encapsulation by comparing the performance of the sensor encapsulated in dust state and detergent state and the bare sensor. We believe that our sensor and encapsulation process will be useful in environments that need to be controlled by shape, and in environments such as underwater conditions motion monitoring where there are many foreign substances.

BM08.10.21
MXene Enables Wearable Energy Storage Shayan Sevedin1, 2; Si (Alex) Qin1, Jizhen Zhang1, Zhiyu Wang1, Raquel Ovalle-Robles1, Ray H. Baughman1, Yury Gogotsi2 and Joselito Razal1; 1Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia; 2A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; 3Nan-Science & Technology Center, Lintec of America, Richardson, Texas, United States; 4Alan G. MacDiarmid NanoTech Institute, The University of Texas at Dallas, Richardson, Texas, United States.

A recently discovered family of 2-D early transition metal carbides or carbonitrides called “MXene” has presented a distinct combination of metallic conductivity, outstanding electrochemical properties, and hydrophilic behavior. MXenes have been used to prepare films, papers, and composites with electrical conductivity of up to ~10,000 S cm⁻¹ and volumetric capacitance of up to ~1,500 F cm⁻³, rivaling existing materials for energy storage applications. To date, however, approaches for preparing MXene-based fibers or yarns for wearable applications have been relatively unexplored. Small sheet size (<2 µm), weak inter-sheet interactions, and lack of efficient processing have made it challenging to fabricate MXene-based fibers or yarns. Here, we present strategies to achieve fibers or yarns from the most prominent member of MXene family (Ti₃C₂). We first demonstrate MXene’s potential in fabricating high-performance yarn supercapacitors by coating MXene on conductive carbon fiber bundles. The MXene-coated yarn supercapacitor device (at mass loading of 2 mg cm⁻²) showed a high length capacitance of ~123 mF cm⁻² which is higher than the literature reports (typically lower than 100 mF cm⁻²). We then produce MXene-based fibers using a wet-spinning technique by taking advantage of the templating role of liquid crystalline (LC) graphene oxide (GO). We show that the favorable interactions of GO and MXene flakes result in the preservation of the LC property of the GO dispersion at an extremely high MXene content of ~88 wt. %, a key to its fiber processing. The MXene-based fiber demonstrates excellent flexibility and a high volumetric capacitance of ~341 F cm⁻³. By employing a bisscaling technique that traps MXene nanosheets within carbon nanotube yarn scrolls, we achieve yarns that are predominantly composed of MXene (containing up to ~98 wt. % MXene). This MXene-based yarn provides an areal capacitance of as high as ~3,188 mF cm⁻² (volumetric capacitance ~1,083 mF cm⁻³), which exceeds the previously recorded performance for any fiber or yarn supercapacitor electrode. When fabricated into a yarn supercapacitor device, the asymmetric electrode configuration reach a maximum energy and power densities of ~61.6 mWh cm⁻³ and ~5,428 mW cm⁻³ respectively. We show that the MXene-based fibers and yarns are useful for powering small electronic devices when knitted or woven into a textile. The MXene fibers and yarns developed in this work, introduce new classes of fibers and yarns from an emerging family of 2-D nanomaterials, and are excellent candidates for integration with textile-based electronics to meet the energy demands of future wearable devices.

BM08.10.22
Chemically/Biochemically Enhanced Nanoelectronic Gas Sensor for Airmen Performance and Protection Yen Ngo1, 2, Taneka Littlejohn1, Michael
Air Force interest in wearable sensors for continuous force protection and human performance monitoring require airborne chemical/biochemical sensors with high sensitivity, selectivity and specificity. Additionally, these sensors must be both portable and energy-efficient for continuous deployment. Sensors with all of these attributes are currently unavailable in commercial off-the-shelf sensors. Of these challenges, specificity is particularly challenging, especially in the presence of the large number of non-specific analytes found in human/environmental field samples. Increasing the affinity and/or specificity of the Chemical Recognition Elements (CREs) will benefit the sensor response to the target, leading to a corresponding enhancement of not only the signal to noise ratio, but also a significant reduction in sensor response time and non-specific interferences. Based on nature’s olfactory receptor-like concept, we demonstrated how a bio-inspired CRE acts as the “sensing material” which can selectively bind to the target chemical. The CRE’s influence on enhancing the sensitivity and selectivity of a nanoelectronic/electrochemical sensor is discussed in this talk. In addition, we will discuss other, future detection strategies we are pursuing for an airborne simulant chemical warfare agent.

BM08.10.23

Highly Sensitive Pressure Sensor Based on Baking-Like Foaming Process for Wearable Human Activity Monitoring Device

In this study, we present highly sensitive pressure sensor fabricated by simple and fast baking-like foaming process. The mixture of PDMS and Ecoflex is used to form an elastomeric insulator of pressure sensor. In order to introduce microporous structure in the insulator, NaHCO₃ and CH₃COOH are blended as pore precursors in PDMS/Ecoflex. Since NaHCO₃ and CH₃COOH are used even for food, they are biocompatible and easy to use. While curing the elastomeric mixture, NaHCO₃ and CH₃COOH chemically react and produce CO₂ gas. All the process to fabricate the insulator are completed within 1 hour. Flexible electrodes are made of PDMS coated with AgNW, and two electrodes are separated by the insulator. The pressure sensors will be electrically characterized by a capacitance versus pressure measurement system.

BM08.10.24

Integrating Optically Actuated Liquid Crystal Elastomer Fibers into Textiles

Flexible physical sensors that can replace human skin or interface human to robots have been attracting many interests over last several decades, as revealed by the outstanding developments in various applications, such as artificial electronic textile/skin, motion monitoring, and personal healthcare. Such physical sensors are classified mainly by the signal to be measured, such as pressure, strain, temperature and humidity. Among the various physical sensors, the pressure sensor can detect the pressure generated by human-body activity, which is distributed in low-pressure regimes (<10 kPa) and medium-pressure regimes (10-100 kPa). The pressure can be detected typically by three types of transduction mechanisms, such as piezoresistivity, piezocapacitance and piezoelectricity, converting pressure stimuli into electrical signals. The piezocapacitive pressure sensors are normally composed of an elastomeric insulating polymer, such as polyurethane, polydimethylsiloxane (PDMS) and Ecoflex, sandwiched between the two conducting plates, and preferred to detect wide pressure range up to about 100 kPa. When the pressure is applied to the surface of sensors, the thickness of insulator is reduced, causing the increase in capacitance. Therefore, it is necessary for the elastomeric insulator to be deformed sensitively according to the external pressure. For that intention, microstructured, porous, or air-gap embedded form have been typically suggested for high sensitivity at the low-pressure regime. However, although those sensorsshave excellent sensitivity, they have a relatively narrow pressure sensing range. Porous structures were conventionally fabricated by hard-template/etching and phase separation, which are highly time-consuming processes. In this study, we present highly sensitive pressure sensor fabricated by simple and fast baking-like foaming process. The mixture of PDMS and Ecoflex is used to form an elastomeric insulator of pressure sensor. In order to introduce microporous structure in the insulator, NaHCO₃ and CH₃COOH are blended as pore precursors in PDMS/Ecoflex. Since NaHCO₃ and CH₃COOH are used even for food, they are biocompatible and easy to use. While curing the elastomeric mixture, NaHCO₃ and CH₃COOH chemically react and produce CO₂ gas. All the process to fabricate the insulator are completed within 1 hour. Flexible electrodes are made of PDMS coated with AgNW, and two electrodes are separated by the insulator. The pressure sensors will be electrically characterized by a capacitance versus pressure measurement system.

BM08.10.25

Inkjet Printing E-Textiles for Flexible Electronics and Wearable Devices

The use of printed electronics on textile platforms have led new advancements in wearable technology, becoming one of the most appealing routes for e-textile fabrication. However, limitations are remained in high processing cost, low resolution in pattern designs, and undesirably significant change in surface characteristics of the textile materials. Albeit inkjet printing is an alternative technique to solve the aforementioned challenges in fabricating e-textiles, nozzle clogging is one of the most significant challenges in terms of printing nano- and micro-particle based inks due to small nozzle diameters.
<100 μm in the inkjet system. In this study, we introduce a novel technique of inkjet printing e-textiles for wearable technology applications utilizing particle-free, reactive silver inks. The reactive silver inks minimized nozzle clogging in the inkjet system with low viscosity around 17 cps, requiring subsequent annealing process to reduce silver ions and form thin layers around 100 nm on fiber substrates. Multiple layers of ink deposition passes and in situ annealing process provides a unique method for tailoring the electrical conductivity, from >10KΩ/sq to 0.1 Ω/sq for up to 15 print passes on polyethylene terephthalate (PET) single-jersey knit textiles. Wash fastness of the inkjet printed e-textiles was tested based on AATCC TM61, and the result showed electrical conductivity maintained until 25 wash cycles without further encapsulation, implying enhanced performance compared to previous studies on e-textiles. In addition, unique structural characteristics of textiles were utilized to understand the use of this process toward wearable strain sensors. For example, conductive patterns printed as course direction showed higher electrical conductivity than wale direction, derived from the different geometrical structures of the knit loops. The electrical resistance of the sensors decreased with increase in strain and recovery of electrical resistance was measured with release from elongation. This study demonstrates novel materials and processing technologies in inkjet printing e-textiles for wearable technology applications.

BM08.10.26

**Nanoparticle Sensitized Direct Conversion Organic-Inorganic Hybrid X-Ray Sensors**

Imalka Jayawardena1, Hashimi Thirimanne1, Andrew Nisbet1,2, Indrachapa Bandara R M1, Chris Mills1 and Ravi Silva1; 1University of Surrey, Guildford, United Kingdom; 2Department of Medical Physics, Royal Surrey County Hospital NHS Foundation Trust, Guildford, United Kingdom.

X-rays are a critical tool which finds applications in a number of different sectors including medical diagnostics and treatment, homeland security and non-destructive evaluation among many others. The modern genre of detectors or imagers used in this regard are based on a flat panel architecture whose geometric restrictions necessitates either complicated arrays of X-ray sources or a significant level of post-computational activities. For example, cadmium telluride or even single crystal perovskites often requires high quality single crystals that are several millimetres thick.

Organic semiconductors have emerged as a route towards enabling system that have the potential to address factors such as cost and geometric restrictions placed by conventional semiconductor systems. However for X-ray detecting applications, the X-ray attenuation or stopping power enabled by organics is significantly low for satisfactory X-ray detection.

Herein, we introduce a direct conversion X-ray sensing architecture[1] based on the incorporation of high Z bismuth oxide nanoparticles within a ~20–30 μm thick organic bulk heterojunction system consisting of hole transporting polymer [mainly, poly(3-hexylthiophene) or P3HT] and electron transporting small molecule [mainly, [6,6]-Phenyl-C71-butyric acid methyl ester or PC70BM]. These hybrid detectors demonstrate high sensitivities of ~1.7 mC mGy⁻¹ cm⁻² when irradiated under a 50 kV X-ray source which are ~1-2 orders of magnitude higher in terms of sensitivity obtained using other emerging and enabling X-ray sensing materials such as perovskites. We also expand the application of these hybrid X-ray sensors to the Hard X-ray energy range by carrying our measurements under a medical Linear Accelerator (LINAC). Noticeably, this hybrid detector architecture enables a sensitivity of ~ 60 μC mGy⁻¹ cm⁻² which exceeds previous reports on direct and scintillator based X-ray detectors [2,3]. Notably, such high sensitivities are enabled at low bias voltages of ~10V which indicates the potential of this new detector architecture for real time radiation monitoring in a real world environment.

References


BM08.10.27

**Applying the Double Network Principle on the Macroscale to Toughen Soft Materials**

Takashi Nakajima1, 2, Takayuki Nonoyama1, 2, Takayuki Kurokawa1, 2, and Jian Ping Gong1, 2; 1Graduate School of Life Science, Hokkaido University, Sapporo, Japan; 2Faculty of Advanced Life Science, Hokkaido University, Sapporo, Japan; 3Soft Matter GI-CoRE, Hokkaido University, Sapporo, Japan.

Double Network (DN) gels possess high toughness and strength, in significant contrast to traditional gels which are brittle and weak. DN gels have a structure that consists of two interpenetrating networks, where the “1st network” is hard and brittle, while the “2nd network” is soft and ductile. When force is applied to the DN gel, the 1st network fractures, prior to global fracture of the composite structure. The 1st network structure therefore contributes sacrificial bonds, which break efficiently to dissipate energy and avoid stress concentrations. This results in the dramatic increase in toughness seen in DN gels. This toughening mechanism can be generally referred to as the DN principle, and the DN principle is known to hold without depending on chemical species. The goal of this research is to understand the breadth of the DN principle, and attempt to make macroscale composites which match the design principles of DN gels. We aim to reproduce the sacrificial bonds of the 1st network by changing the material and the scale, and we have designed various structures that greatly influence the energy dissipation of the composites. Samples were fabricated by first 3D printing a rigid grid that acts as the 1st network, and embedding it in silicone rubber (matrix) which is used as the 2nd network. The mechanical properties and internal fracture behavior of the obtained composites were evaluated by uniaxial tensile tests. Despite different materials and scale, we can see influence of the DN effect on the mechanical properties. Specifically, we see increased stiffness and energy dissipation. When the composite is stretched, the 1st network is loaded imparting high stiffness, but quickly fractures at low strain. The stress then transfers to the 2nd network, which builds force with increased stretching, until the 1st network again fractures. This cycle is repeated until all sacrificial bonds are consumed. This indicates that the sacrificial bonds can be reproduced on the macroscale. From this work, we find that the internal fracture behavior of composite changes as the fracture force relationship between the grid and the matrix varies. Our results show that when the fracture force of the matrix exceeds that of reinforcing grid, multistep internal fracture occurs, dissipating significant energy. When the fracture force of the reinforcing grid exceeds that of the matrix, brittle fracture occurs, resulting in minimal energy dissipation, even less than the neat matrix without reinforcement. Understanding these design parameters will help develop new composite materials useful for future applications in biomaterials and soft robotics.

SESSION BM08.11: Flexible/Wearable Energy Storage I
Session Chair: Renkun Chen
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Grand Ballroom
Reduced Graphene Oxide—Aramid Nanofiber Capacitors for Structural Energy and Power. Jodie Lutkenhaus1, James Boyd1, Dimitris Lagoudas1, Micah Green2 and Haleh Ardebili2; 1Texas A&M University, College Station, Texas, United States; 2University of Houston, Houston, Texas, United States.

Structural energy and power systems offer both mechanical and electrochemical performance in a single multifunctional platform. These are of growing interest because they potentially offer reduction in mass and/or volume for aircraft, satellites, and ground transportation. The long-term vision is to combine the mechanical properties of structural composites with the energy storage properties of batteries or capacitors. However, there is a natural tradeoff between mechanical and energy storage properties, such that it remains difficult to synergistically optimize both. To this end, flexible graphene-based supercapacitors have attracted much attention due to their extraordinary mechanical and electrical properties, yet they suffer from poor strength. This problem may be exacerbated with the inclusion of functional guest materials, often yielding strengths of less than 15 MPa. Here, we show that reduced graphene oxide paper supercapacitor electrodes containing aramid nanofibers as guest materials exhibit extraordinarily high tensile strength (100.6 MPa) and excellent electrochemical stability (Kwon, S. et al. ACS Nano 11 (7), 6682-6690 (2017)). This is achieved by extensive hydrogen-bonding and π-π interactions between the reduced graphene oxide sheets and aramid nanofibers. Aramid nanofibers are the nanoscale version of Kevlar, which is known for its exceptional mechanical properties and use in bullet-proof vests. The tradeoff between capacitance and mechanical properties is evaluated as a function of aramid nanofiber loading, where it is shown that these electrodes exhibit multifunctionality superior to that of other reduced graphene oxide-based supercapacitors. We anticipate these composite electrodes to be a starting point for structural energy and power systems that harness the mechanical properties of aramid nanofibers. Our future work, which includes an informatics-driven assessment of the system as well as functionalization effects of the reduced graphene oxide sheets will also be discussed.

Flexible All Organic Batteries Based on Conducting Redox Polymers. Christian Strietzel, Rikard Emanuelsson, Maria Stromme and Martin Sjödin; Nanotechnology and Functional Materials, Department of Engineering Sciences The Ångström Laboratory, Uppsala University, Uppsala, Sweden.

Batteries consisting of naturally occurring organic materials can be envisioned as sustainable alternatives to conventional metal-based batteries, thus avoiding the negative environmental impact associated with the production and recycling of the latter. In this way the negative environmental impact of the constantly increasing demand for secondary batteries can be decreased. Apart from being fully organic, such batteries also open up for flexible battery designs as they can be produced in a roll-to-roll process and are anticipated to be viable in a broad range of applications as energy supplies in innovative flexible electronics designs. In the current work, fully organic batteries are realized utilizing conducting redox polymers (CRPs) as electrode materials. CRPs combine the high charge storage capacity of a redox active pendant group (PG) with the conduction properties of a conducting polymer (CP) backbone, both to reduce the need for addition of conductive carbon black and increasing the stability of the PG redox conversion in a battery setup. The first results from a fully organic, aqueous battery based on CRP electrode material are presented. Challenges and possibilities of this type of battery in flexible battery designs are discussed.

Reduced Graphene Oxide—Aramid Nanofiber Capacitors for Structural Energy and Power. Jodie Lutkenhaus1, James Boyd1, Dimitris Lagoudas1, Micah Green2 and Haleh Ardebili2; 1Texas A&M University, College Station, Texas, United States; 2University of Houston, Houston, Texas, United States.

It is critically important to develop miniature energy storage and conversion devices in modern electronics, e.g., for portable and wearable electronic facilities. Here a novel family of energy storage and conversion devices as well as their integrated devices in 1D configuration are carefully discussed with unique and promising advantages such as lightweight and weaveable compared with the conventional planar architecture. For the energy conversion devices in 1D configuration, fiber-shaped dye-sensitized solar cells, polymer solar cells and perovskite solar cells are covered. For the energy storage devices, fiber-shaped electrochemical capacitors, lithium ion batteries, lithium sulfur batteries, lithium air batteries and zinc air batteries are carefully investigated. The main efforts will be made to highlight the recent advancement in the electrode material, device structure and property extension.

Thermally Chargeable Supercapacitors with Charging and Discharging Cycles for Wearable and IoT Electronics. Angela Mohammed Abdul Mageeth, Myunghwan Jeong and Choongho Yu; Texas A&M University, College Station, Texas, United States.

Thermally chargeable planar supercapacitors are good candidates for energy harvesting and storage in wearable and internet-of-things (IoT) electronic devices. We report a graphene oxide based supercapacitor which can be thermally chargeable and has good areal capacitance and charge storage capability in conjunction with a shape memory polymer (SMP) to create a device operating in a cyclic manner having thermal charging and discharging cycles. The supercapacitor has reduced sulfate graphene oxide electrodes fabricated by laser irradiation on a film of graphene oxide over PET substrate using a 3D printer with laser diode assembly. Graphene oxide with H2SO4 acts as separator/electrolyte for the super capacitor. The fabricated supercapacitor employs the Soret effect as the transport mechanism, which results in high thermoelectric voltage. The shape memory polymer was prepared from EPON 826 resin with neopentyl glycol diglycidyl ether (NGDE) added at 1:1 molar ratio to have a glass transition temperature just above room temperature. The SMP after fabrication was casted onto a rubber mold of desired shape made by 3D printing and cured to impart the final shape. An array of supercapacitor specimen modules were placed over the SMP film connected in series or parallel depending on the voltage and current requirements of the device application. Temperature gradients applied across the two ends of the SMP film were used for thermal charging, and a shape change was utilized for discharging when the applied temperature gradient raised the temperature of the SMP. The mechanism developed here can be easily integrated into various devices operating intermittently with low power consumption.

Design of A Flexible and Stretchable Full-Cell Lithium-Ion-Battery Based on Hydrogel Electrolyte and Polymer Composite Current Collector. Xi Chen, Long Pan, Huijian Huang and Markus Niederberger; Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich, Zurich, Switzerland.

We designed a flexible and stretchable thin film battery with potential application in wearable devices and flexible electronics. A polymer electrolyte is prepared by utilizing the swelling behavior of a cross-linked hydrogel, which allows the water contained in the network structure of the polymer chains to be replaced by the concentrated aqueous solution of the lithium salt. A high ionic conductivity of 10^{-1} S/cm is achieved at room temperature, which is comparable to the typical liquid electrolyte and about 100-1000 times higher than the conventional polymer gel electrolytes. The outstanding flexibility and stretchability of the hydrogel are also preserved after the salt incorporation. The ultra-high lithium salt concentration successfully broadens the stability voltage window of the hydrogel electrolyte to about 3.0 V, ensuring a good energy density of the battery. Being limited by this window, a rational material screening process is performed and LiMn2O4-Fe2O3 is selected as a proper electrode pair which can reach the optimized performance. Instead of using copper or aluminum foil, a flexible and stretchable current collector is fabricated with adequate conductivity to ensure the realization of the overall targeted
MXene-Coated Cellulose Based Yarns for Wearable Supercapacitor Applications

Ti$_3$C$_2$ MXene, the most widely studied MXene in the family to date, has been incorporated into yarn fibers to provide the pathway for the electrons, and carbon black (CB) particles that lie around the joint location of the CNT can benefit the preservation of the electronically connected status of the CNT network while stretching. A phase-inversion membrane forming process is conducted to prepare the composite film with a porous structure, which can further enhance the conductivity upon strain. In-situ tensile and resistance tests show that the composite possesses a high Young's modulus as well as a low sheet resistance of about 80 Ω/sq at the strain-free status, which increases to only 200 Ω/sq at 100% strain. The active materials are directly deposited onto the porous surface of the current collector membrane to achieve a strong adhesion without any powder peeling off during stretching. To fabricate the full cell, the hydrogel electrolyte and the current collector deposited with anode and cathode powders are sandwiched and treated with a moderate heating process that results in a good contacting. The laminated thin film is then sealed inside a PDMS packaging. The charge/discharge cycling and impedance of the full cell are tested in bent, rolled, folded, twisted and stretched (up to 200% elongation) states, respectively.

9:45 AM BREAK

SESSION BM08.12: Functional Materials and Devices with Energy Harvesting and Storage I

10:15 AM BM08.12.01
MXene Fibers for Wearable Energy Storage, Harvesting and Sensing
Simge Uzun1, Ariana S. Levitt1, Mohamed Alhabeb1, Genevieve Dion2 and Yury Gogotsi3; 1Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Design, Drexel University, Philadelphia, Pennsylvania, United States.

Two-dimensional (2D) metal carbides, known as MXenes, have recently attracted much attention due to their unique combination of properties, including high metallic conductivity (up to 10,000 Scm$^{-1}$ as a free-standing film), excellent mechanical properties, electrochemical activity, and chemical stability. As such, MXenes are promising for a diverse range of wearable applications, including energy storage, harvesting, sensing, and electromagnetic interference (EMI) shielding. These applications require the development of highly conductive fibers that are well-suited for dynamic environments, meaning that the fibers are light-weight, flexible, and durable.

Ti$_3$C$_2$ MXene, the most widely studied MXene in the family to date, has been incorporated into yarns via a variety of methods, including dip-coating, drop-casting, and electrospinning. Using these fiber-processing methods, MXene fibers can be produced with tunable properties, such as fiber diameter, which can range from the nano-scale via electrospinning to the micro-scale, via wet-spinning. Not only have MXenes demonstrated unique properties on their own, but they have also been incorporated into a variety of polymer matrices and mixed with other nanomaterials, such as carbon nanotubes (CNTs) and graphene oxide (GO) and processed into composite fibers. These MXene composite fibers have shown enhanced mechanical, thermal, and electrochemical properties. This talk, an overview of the methods developed to process MXenes into fibers will be presented, in addition to their electrochemical, electronic, and mechanical properties. The potential applications of these fibers in wearable applications, such as energy storage, will be discussed.

10:45 AM BM08.12.02
Colloidally Synthesized Nanomaterials as Building Blocks for Functional Fibers
Vida Jamali1, Farnaz Niroui1, Matteo Pasquali2 and A. P. Alivisatos2; 1University of California, Berkeley, Berkeley, California, United States; 2Rice University, Houston, Texas, United States.

Smart fabrics that combine traditional clothing with functional devices are a topic of a growing field of research with a broad range of applications in areas including healthcare, sports and internet of things development. Two common approaches for producing smart fabrics are 1) to adhere fabricated devices on top of a pre-woven fabric, and 2) to develop devices in form of fibers that can be then integrated into large area textile. The latter approach allows us to combine fibers with different functionalities into a large area fabric showing a collective complex functionality. Functionality of the fibers can be tuned using a large library of nanomaterials as building blocks. Here, we propose a layer by layer assembly process to fabricate functional fibers using colloidally synthesized nanomaterials. As an example, we will discuss fabrication of solution-processable, flexible, and wearable light emitting fibers with a potential to be incorporated into light-emitting fabrics.

11:00 AM BM08.12.03
MXene-Coated Cellulose Based Yarns for Wearable Supercapacitor Applications
Simge Uzun1, Ariana S. Levitt1, Mohamed Alhabeb1, Genevieve Dion2 and Yury Gogotsi3; 1Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Design, Drexel University, Philadelphia, Pennsylvania, United States.

In this work, we demonstrate a scalable dip-coating approach for fabricating high-performing supercapacitor yarns using low-cost, commercial cellulose-based yarns. Since MXenes are processible in various solvents [3], it can be incorporated into conventional yarns using a simple dipping and drying procedure. Concentration and flake size distribution of MXene solutions were tailored to ensure effective penetration of MXene flakes into the individual fibers and under the yarn surface without sacrificing adhesion to the fiber substrate. The high porosity of cellulose-based yarns offers a large surface area for MXene uptake and electrolyte exposure to facilitate charge transport. Finally, the knittability of the electrode yarns into full fabrics on industrially used machines will be discussed. This study provides insight into the processing requirements for coating cellulose-based yarns. Furthermore, the effect of MXene flake size on coating uniformity, yarn conductivity, and supercapacitor performance was investigated. Our findings suggest the potential use of MXene for achieving large-scale and cost-effective production of high-performance supercapacitors as energy storage devices for powering wearable electronics.

11:15 AM BM08.12.04
Waterproof, Skin-Like, Electronics-Enabled Microfluidic Systems for Sweat Collection, Biomarker Analysis and Digital Thermography in Aquatic Environments Jonathan Reeder1, Jungil Choi1, Yeguang Xue1, Justin Hanson1, Philipp Gutruf2, Mark Liu1, Tyler R. Ray1, Amany Bandodkar2, Rauldel Avila1, Wei Xie3, Siddharth Krishnan4, Shuai Xu4, Roozbeh Ghaffari4, Yonggang Huang1 and John A. Rogers1; 1Northwestern University, Evanston, Illinois, United States; 2University of Illinois at Urbana-Champaign, Champaign, Illinois, United States.

Non-invasive, in situ biochemical and biophysical monitoring of sedentary, ambulatory, and exercising people could enable new forms of healthcare diagnostics and personalized hydration strategies. Present sweat collection and sensing strategies are not applicable to aquatic or arid environments due to unique challenges in eliminating interference/contamination from surrounding water, maintaining robust adhesion in the presence of viscous drag forces and/or vigorous motion and preventing evaporation of collected sweat. This talk introduces materials and device architectures for waterproof, skin-like, microfluidic and electronic systems that adhere to the skin to enable capture, storage and analysis of sweat, even while fully underwater. A method of forming ultrathin, low modulus epidermal microfluidic systems and a scheme for using physically patterned, skin-safe adhesives enable reliable operation during swimming for two hours, or more, with minimal influence of the surrounding water or of biological effects such as compensatory sweating. The combination of an elastomeric polymer with excellent barrier properties and computationally guided design of microfluidic channel geometries prevents contamination from environmental water and minimizes evaporative loss of collected sweat during dryland studies. Field trials demonstrate the functionality of these devices during cycling and swimming in controlled, indoor conditions and in open water swimming in the ocean. Wireless, digital measurements of skin temperature via integration of systems that operate via near field communication protocols not only elucidates differences in the thermal response of the skin during exercise in aquatic and dry environments but also, more generally, illustrates the ability to co-integrate electronics into these platforms. A demonstrator device leveraging all of the key materials and design strategies introduced here enables quantitative in situ measurements of chloride concentration, total sweat loss (and sweat rate), and skin temperature during vigorous physical activity in aquatic environments.

SESSION BM08.13: Functional Materials and Devices with Energy Harvesting and Storage II
Session Chair: Jodie Lutkenhaus
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Grand Ballroom

1:30 PM *BM08.13.01
Energy Harvesting, Energy Storing and Comfort Adjusting Yarns and Textiles Ray H. Baughman; The University of Texas at Dallas, Richardson, Texas, United States.

The design, fabrication, and performance of multifunctional yarns and fibers for energy harvesting, energy storage, and actuation in textiles, as well as for other applications, will be discussed. Our bisscrolling technology can be used to trap up to 95 wt % of a functional guest in the helical corridors of nanofiber yarns that are weavable, braidable, sewable, and knot-able without sacrificing guest functionality. One application area is in comfort adjusting clothing that automatically opens and closes porosity depending upon the temperature or the presence of perspiration. When used as large-stroke artificial muscles, these yarns are twisted until they fully coil, and in this coiled state they can deliver tensile strokes exceeding 40% and generate contractile stresses, gravimetric work densities, and gravimetric power densities that are 230, 65, and 95 times that of natural muscle, respectively. Depending upon the relative chirality of yarn and coil, homochiral and heterochiral muscles are obtained, which respectively contract and expand when yarn volume increases. Related electrochemical twistron mechanical energy harvesters will also be described, which are electrochemical muscles operated in reverse. Without requiring an external power source to provide a bias voltage, these twistrons can generate 250 watts per kilogram of peak electrical power when cycled up to 30 hertz, as well as over 41 joules per kilogram of electrical energy per mechanical cycle, when normalized to harvester yarn weight. All solid-state twistrons will be described that are woven into textiles to generate electricity from body movement.

2:00 PM BM08.13.02
Ultraflexible Organic Photovoltaic Diodes Combined with Organic Light-Emitting Diodes for Self-Powered Wearable Indicators Hiroaki Jinn1,2, Kenjiro Fukuda1, Xiaomin Xu2, Sungjun Park2, Tomoyuki Yokota2, Itaru Osaka3 and Takao Someya1,2; 1The University of Tokyo, Tokyo, Japan; 2Riken, Wako, Japan; 3Hiroshima University, Higashi-Hiroshima, Japan.

For continuous operation of wearable sensors for the Internet of Things (IoT), ultraflexible organic photovoltaics (OPV) are the most promising among all existing energy harvesting power sources because of their exceptional flexibility, environmental stability, and high efficiency [Ref 1, 2]. Since sufficiently high output power (typically ranging from 1-10 mW) is necessary to operate external circuitry, sensors, and displays, making OPVs as module devices with series and/or parallel connection to achieve high current and/or voltage output is necessary for practical applications [Ref 3]. Moreover, to our knowledge, there are no examples of ultraflexible self-powered devices integrated with ultraflexible light-emitting diodes (LEDs). Here, we show ultraflexible and efficient OPV modules with various series and/or parallel connections to achieve high current and/or voltage output. The OPV modules are based on an inverted structure with an active layer of a D–A polymer with quaterthiophene and naphtho[1,2-c:5,6-c’]bis[1,2,5]thiadiazole (NTz) (PNTz4T) and [6,6]-phenyl C71-butyric acid methyl ester (PC71BM). The module with 10 series connections features high open circuit voltage up to 6.8 V and short circuit current of 0.61 mA on 1-μm-thick foil. At the maximum power point of the OPV module, the module shows an output power of 2.78 mW. We achieved large-area OPV modules with 5 parallel connections, each containing 3 single cells in connected in series. The module exhibited an output voltage of 2.01 V and a short-current of 4.81 mA, resulting in a maximum power of 5.54 mW. Additionally, inverted structure ultraflexible OLEDs with yellow-orange emission were fabricated. The ultraflexible OLED shows an external quantum efficiency of 1.3%, which is sufficiently high enough to be detected by the human eye. Finally, we demonstrated a self-powered indicator for imperceptible wearable devices consisting of an ultraflexible OPV module with 8 series connections connected to an OLED. These results highlighted the potential advantage of ultraflexible OPVs for IoT device applications.
In recent decades, research and development of flexible and wearable electronics has attracted significant interest and attention for applications in flexible displays, smart textiles, electronic skin, etc. To achieve these applications, much work has been focused on the development of electric circuit fabrication on polymer substrates. However, in most cases, either the input is externally applied or the output is externally measured; thereby, forgoing a fully integrated stand-alone device. Here, we have developed an integrated flexible self-powered display, which harvests the energy of human motion to actuate a display. The development of the power source is done in conjunction with reducing the power requirements of flexible displays. Our printable thin film energy harvester generates output voltage up to 10s of V and output current up to μAs. It is used to power both a polymer dispersed liquid crystal (PDLC) display and an electrophoretic display with slight finger motions. This development will enable direct operation of stand-alone low power flexible electronics without external circuitry and holds potential for harvesting large-scale mechanical energy.

Prepared by LLNL under Contract DE-AC52-07NA27344.
devices are rigid, bulky, and heavy, making them not suitable for wearable applications. On the other hand, fibres are materials that have been worn by human beings for more than a thousand years. Fibres are flexible, lightweight, conformal, and highly manufacturable. This talk will introduce how our research group makes use of fibre for wearable electrochemical energy storage devices including supercapacitors and lithium batteries. These fibre-based devices can maintain the flexibility, lightweight, permeability, processibility, and even washing ability like textiles. In addition, we also show that fibrous materials can significantly improve the electrochemical properties of the devices.

4:00 PM BM08.14.02
Ultra-Tough Ion Conducting Elastomers for Stretchable Lithium-Ion Batteries **David Mackanie**¹, **Yi Cui**² and **Zhenan Bao**³; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²Materials Science and Engineering, Stanford University, Stanford, California, United States.

Batteries for wearable electronics should be safe, flexible, and robust. Solid-state batteries based on either solid or gelled polymer electrolytes have the potential to fulfill these criteria. However, many current electrolyte architectures in solid-state batteries utilize polymers that are either weak or easily deformable. Herein, we employ rational polymer design and synthesis to create a series of extremely tough elastomers with remarkably high lithium-ion conductivity. The catalogue of ion conducting elastomers (ICEs) are created by varying the strength of polymer-polymer interactions within the electrolyte. In their optimal configuration, the gelled ICEs can be stretched elastically to over 30x their original length and have an ionic conductivity of 2E-4 at 25 °C. By tuning the strength of polymer-polymer interactions, we develop insights into the effect of mechanical strength on the chemical, electrochemical, and ion transport properties of a series of ICEs. It is observed that controlling polymer-polymer interactions allows for de-coupling of ion transport from the mechanical robustness of the films. We also demonstrate the application of ICEs in a quasi-solid-state battery configuration. In this setup, ICE is used as both a solid electrolyte and a binder for the electrodes. Intermolecular interactions help adhere the battery layers, leading to an integrated all-stretchable battery stack. The interfacial interactions also minimize interfacial impedance, leading to improved cycling. Successful operation of such a battery is demonstrated at conditions that mimic those of wearable electronics.

4:15 PM BM08.14.03
A Novel Strategy of One Device Achieves Two Functions—Energy Storage and Temperature Sense Multi-Functions Device Based on Graphene Planar-Structure Supercapacitor **Ziyu Yue** and **Chunyang Jia**; University of Electronic Science and Technology of China, Chengdu, China.

Multi-functions devices attract much attention due to their great potential and large demands in wearable electronics. Besides some practical applications of integrated different functional devices as one, there is a novel strategy to fabricate multi-functions devices, that using one device to achieve two or more functions. Herein, we report the energy storage and temperature sense dual function device based on graphene planar-structure supercapacitor. Combining the supercapacitor and electronic components on one flexible printed circuit board, the obtained device could detect environmental temperature by measuring the change of leakage current of supercapacitor. The temperature sense function exhibits a high resolution of 0.0588 °C due to the 0.0407 μA precision of leakage current measurement, and the high accuracy of 1 °C comparing with temperature sensor chip. Meanwhile, as an energy storage device, the supercapacitor presents excellent electrochemical performance with the areal capacitance of 118 μF cm⁻² at scan rate of 0.1 V s⁻¹. This work demonstrates the feasibility of using one supercapacitor to achieve energy storage and temperature sensing dual function simultaneously.

4:30 PM BM08.14.04
2D Auxetic Reentrant Graphene Nanostructures for Stretchable Energy Storage Electrodes **Jeong Gon Son**; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Stretchable electronics, which require the flexibility and stretchability necessary to endure complex motions from humans, have recently attracted considerable attention because of the increasing demand for bio-implantable and wearable devices. To accommodate large applied strains without fracturing the materials, structure-assisted stretchability, which provides brittle materials with the stretchability, can be an ideal approach. In this talk, we suggest self-assembly based approaches for structure-assisted stretchable energy storage electrodes. A source of electricity is necessary to operate the stretchable devices, and the power supply for an energy storage unit should be integrated into the stretchable device. Therefore, the energy storage device should also be deformable/stretchable and retain these attributes under various deformations. Herein, we introduce novel 2D reentrant cellular structures of porous graphene/CNT networks for omnidirectionally stretchable supercapacitor electrodes. Reentrant structures, with inwardly protruded frameworks in porous networks, were fabricated by the radial compression of vertically aligned honeycomb-like rGO/CNT networks, which were prepared by the directional crystallization method. Unlike typical porous graphene structures, the reentrant structure provides self-assisted stretchability, such asaccordion and biaxial structures, to otherwise unstretchable materials. The 2D reentrant structures of graphene/CNT networks maintained excellent electrical conductivities under biaxial stretching conditions and showed a slightly negative or near-zero Poisson’s ratio over a wide strain range because of their structural uniqueness. For practical applications, we fabricated all-solid-state supercapacitors based on 2D auxetic structures. Radial compression process up to 1/10th densified the electrode, significantly increasing the areal and volumetric capacitances of the electrodes. Additionally, vertically aligned graphene/CNT networks provided a plentiful of surface area and induced sufficient ion transport pathways of the electrodes. Therefore, these exhibited high gravimetric and areal capacitance values of 152.4 F g⁻¹ and 2.9 F cm⁻², respectively, and had an excellent mechanical resilience while maintaining high room temperature ionic conductivity. A solid-state lithium metal/LiFePO₄ full cell with this resilient electrolyte can operate at room temperature with a high cathode capacity of 152 mAh g⁻¹ for 300 cycles and can maintain operation even after being subjected to intense mechanical impact testing. Our new dual crosslinking design provides robust mechanical properties without decreasing the ionic conductivity and opens a route toward stable, high-performance operation of solid-state batteries even under extreme abuse.

4:45 PM BM08.14.05
Dual-Crosslinking Design for Resilient Lithium-Ion Conductor **Jeffrey F. Lopez**¹, **Yongming Sun**², **Yi Cui**² and **Zhenan Bao**³; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²Materials Science and Engineering, Stanford University, Stanford, California, United States.

Solid-state electrolyte materials are attractive options for meeting the safety and performance needs of advanced lithium based rechargeable battery technologies because of their improved mechanical and thermal stability compared to liquid electrolytes. However, there is typically a tradeoff between mechanical and electrochemical performance. Here we describe an elastic Li-ion conductor with dual covalent and dynamic hydrogen bonding crosslinks to provide high mechanical resilience while maintaining high room temperature ionic conductivity. A solid-state lithium metal/LiFePO₄ full cell with this resilient electrolyte can operate at room temperature with a high cathode capacity of 152 mAh g⁻¹ for 300 cycles and can maintain operation even after being subjected to intense mechanical impact testing. Our new dual crosslinking design provides robust mechanical properties without decreasing the ionic conductivity and opens a route toward stable, high-performance operation of solid-state batteries even under extreme abuse.
BM08.15.01
Diagnostic Redox Biosensors Based on Immobilized Aptamer Scaffolds
Nancy Nguyen, Jessica Anderson, Amira Gee and Mehnaaz F. Ali; Chemistry, Xavier University of Louisiana, New Orleans, Louisiana, United States.

Applications of detection systems at the nanomedicine regime require highly sensitive, quantitative and selective analysis platforms for the real-time multiplexed monitoring of target analytes. Developing biosensors with an electrochemical output allows for the sensitive detection of analytes with an inherent amplification system that can be easily amenable to bioelectronic devices. Our work focuses on sensing relevant small-molecules and biomarkers through the design of aptamer scaffolds that are bound to a redox trigger. The aptamer scaffolds allow for allosteric binding of both the redox signaling trigger and the clinical target. We use a redox trigger within a double-surface electrochemical approach where target recognition is performed at a different surface from that enabling signal transduction. This strategy allows for independent optimization of the target recognition and electrochemical detection steps. We have demonstrated the use of such systems for clinically relevant molecules such as miRNA’s and small molecules such as ATP. Current studies demonstrate the design of an adaptable aptamer scaffold, which is utilized for the detection of biomarkers for prolonged concussion symptoms. Isothermal titration calorimetry is used to elucidate the affinities of the signaling trigger to a newly designed set of aptamer scaffolds. Specific parameters to optimize binding of the electrochemical trigger to the binding loops within the aptamer are explored. This body of work is important for the use of aptamer based sensing systems within an adaptable electrochemical device. Such diagnostic mechanisms are aimed at enhancing selectivity and sensitivity of the detection of clinically relevant biomarkers.

BM08.15.02
Development of a Micro-Supercapacitor with Tannins Enhanced Capacitance
Julien Lemeux and Clara Santato; Engineering Physics, École Polytechnique Montréal, Montréal, Quebec, Canada.

At a time when the number of both independent power sources and environmental issues are increasing, electrodes based on tannins could enable environmentally friendly storage devices on a flexible substrate. Tannins, a family of polyphenol molecules from secondary metabolites of higher plants, exhibit many redox moieties and metal binding properties via their catechol and galloid units, investigated in order to produce efficient micro-supercapacitors. We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of tannin-based pseudo-supercapacitor (where electrostatic and redox processes both contribute to accumulate charge). Santato’s group has already demonstrated that eumelanin, an organic pigment ubiquitous in flora and fauna, can be used in micro-supercapacitors [1].

Here we report on the energy storage properties of three different molecules of tannins, tannic acid (TA), Pyrogallol (PG) and Catechin (Ctn). PG and Ctn molecules have been selected as they are basic units of all the tannins molecules and TA is a complex of esterified gallo with a glucose already used in a number of technologies. Ctn and galloid moieties are the building blocks of most of the tannins and they proved to be able to form uniform coatings [2]. Mukhopadhyay et al. [3] combined tannins and polypyrrole and Oh et al. [4] used a metal-phenolic network on carbon nanotubes to create supercapacitors.

On the other hand, in this work we used a technique similar to Geissler et al. [5] and Ball et al. [6] for the deposition of tannins on carbon paper to reduce the quantity of heavy metals and keep an easy processing route, both on a glass and on a flexible plastic substrates. Besides cyclic voltmetry and galvanostatic charge-discharge cycles, XRD, AFM, SEM and XPS measurements have been performed in order to understand the physicochemical properties of the tannin coating and extract sound structure-properties relationships.


BM08.15.03
Two-Dimensional Titanium Carbide (MXene) in Accommodating Lens Design
Emma J. Ward1, 2, Susan Sandeman1, Joseph Lacey2 and Yury Gogotsi1; 1School of Pharmacy and Biomolecular Sciences Huxley Building, University of Brighton, Brighton, United Kingdom; 2Rayner Intraocular Lenses Limited, Worthing, United Kingdom; 3A. J. Drexel Nanomaterials Institute, Philadelphia, Pennsylvania, United States.

Intraocular lenses (IOLs) have been under development to treat cataracts since the late 1940s[1]. Whilst significant changes in materials and design have enhanced IOLs, there still remain several deficiencies linked to poor biocompatibility and failure to mimic the refractive properties of the natural lens. One approach is to incorporate transparent, electrically conductive, biocompatible materials. A new class of two-dimensional metal carbides, known as MXenes have increased considerably. With approximately 20 variations of MXenes being synthesised, the most studied being titanium carbide (Ti3C2)[5,6].

We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of supercapacitors. We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of supercapacitors. We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of supercapacitors. We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of supercapacitors. We made the hypothesis that the presence of the redox moieties and the chelation properties of the material allows the development of supercapacitors.

As a result of our research involving MXenes, the biological evaluation of toxicity remains largely understated evaluated[5]. Optoelectronic properties of Ti3C2 were optimised and fully characterised. In vitro cell models were used to measure the suppression of oxidative stress, cell adhesion and inflammatory response of Ti3C2 thin films.

Flexible electronics is a branch of electronic fabrication that allows increasingly ergonomic devices. However, its production still requires multi-step, expensive and time-consuming processes. Laser direct writing (LDW) is a clean and low-cost alternative technique to produce electronics on flexible substrates with high resolution, without the need of masks or direct contact with the device. Laser induced graphene (LIG), a particular type of LDW, is a technique where by the irradiation of polypyrrole (PPy) films with a pulsed CO2 infrared laser a photothermal reaction occurs, which leads to the formation of stacked graphene structures. LIG emerges thus as a rising substitute to produce graphene-based devices. This work consists in the development and optimization of flexible UV sensors with zinc oxide nanostructures as the active layer for the UV detection, PI as the substrate and its respective LIG as electrodes. The nanostructures with higher area-volume ratio, synthesized through a microwave assisted hydrothermal method, were selected and deposited by drop casting onto the electrodes that in turn were optimized to enhance electrical properties by varying the laser parameters. The assembled sensors were able to successfully detect the UV radiation with a responsivity of 92 and 2 mA/W for 1 V bias for the PI substrate. In addition, the PI sensor has shown to be capable of working under strain and to be stable after several hours of constant cyclic operation.

Flexible Electrodes Towards Low Cost Flexible Electronics and Its Applications to Sensors

Flexible electronics combines the materials chemistry with the conventional printing technology resulting in high throughput fabrication of cheap and light-weight electronic devices. The work described here demonstrates printing of PEDOT:PSS onto flexible nonwoven polyester (PET) textile as well as stretchable spandex fabric. Firstly, an optimization study was carried out to determine the relationship between number of printing layers and resistance of printed PEDOT:PSS. PEDOT:PSS based organic wires on PET was shown to have current carrying capacities approaching that of copper. To demonstrate the practical applicability of the printed wires, PEDOT:PSS wires connected to Ag/AgCl electrodes was shown to recording electrocardiogram (ECG) signal. Secondly, PEDOT:PSS wires were then combined with PEDOT:PSS electrodes on PET and ECG signal were recorded at rest in both dry skin conditions and with a moisturizing lotion on skin. Lastly, a prototype shirt was also developed with PEDOT:PSS electrodes for measuring ECG signal under exercise avoiding the need of hydrogel and adhesive around the electrode. The signal was recorded in dry skin conditions which showed an increase in amplitude because of transpiration of water vapor from the skin. The prototype was shown to record signal even after 1 month of fabrication and also after three wash cycles. The above work focuses on designing prototype device for health monitoring from commercially available sources using a conventional screen printing process rendering it industrially scalable. The applications of this prototype could be extended beyond healthcare into military and gaming industry.
BM08.15.09
High-Gain Low-Power Active-Load Monolithic Amplifier Based on Depletion-Mode Organic Field Effect Transistor (OFET) for Health Monitoring Applications Chenxi Xu and Ni Zhao; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Wearable technologies have been developed rapidly recently, from tracking of personal sweat chemicals during exercise to daily cardiovascular monitoring for prevention of chronic diseases. Wearable electronics are designed to achieve high fidelity and ease of use. However, the poor signal-to-noise ratio of the measurement circuitry often limits the devices from picking up small physiological signal variations at the device-skin interface. In-situ amplification of sensor signals could be an effective way to minimize the wiring-induced noise and greatly reduce the stringent requirement of rear-end amplification circuit, and it calls for a device technology that can be easily integrated with the sensor fabrication.

Organic transistors are a suitable candidate for this application owing to their fabrication versatility, mechanical flexibility and tunable amplification gain via material engineering. In this work, we introduce a novel monolithic active-load amplifier (MALA) based on threshold-voltage-tunable depletion mode OFET, which can achieve a gain up to $34dB@17Hz$ with a battery voltage source. This MALA also holds a great potential to be optimized towards a fully flexible in-situ pre-amplifier utilized in biomedical signal sensing such as ECG/EMG, which will highly enhance the simplification of data acquisition circuit for wearable electronics. In this presentation I will mainly focus on the design principles of the device structure, the achievement of tunable gain via composition tuning of the active material and the implementation of MALA-assisted ECG measurement.

BM08.15.10
Glucose Responsive Nanogel-Immobilized Silk Hydrogel Microneedle and Light-Stimulated Monitoring Hyojung Kim, Ji-Won Seo and Hyunjoon J. Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

A continuous glucose monitoring (CGM) system that tracks glucose concentrations in real-time is important as it provides abundant data to devise effective treatments for diabetic patients. Being developed fluorescent nanogel-based CGM systems which measure glucose concentration intuitively and no any skin irritation or electric interference compared with amperometric-based CGM systems, it still has inadequate problems like immobilization to apply the CGM system in vivo. Here, we propose a new CGM system based on a biocompatible silk fibroin hydrogel which is immobilized with glucose responsive fluorescent nanogels. In addition, glucose responsive silinked silk hydrogel in a microneedle array structure allows easily tracking glucose level through epidermis without painful implantation. We found that functionalized poly(N-isopropylacrylamide) (pNIPAM)-bounded silk fibroin hydrogel microneedle array showing high sensitivity ($<1mM$), fast response ($<100sec$), reversibly and continuously measure change of glucose concentration through epidermis. This preliminary study shows the potential for real-time, chronic glucose monitoring.

BM08.15.11
Low-Voltage Operational, High-Performance Wearable Fibriiform Organic Field-Effect Transistors via Twist Assembly Micro-Fiber Electrodes Soo Jin Kim,1-3, Ho Won Jang1 and Jung Ah Lim1; 1Institute of Science Technology, Seoul, Korea (the Republic of); 2Seoul National University, Seoul, Korea (the Republic of).

As a new platform for wearable device, fiber-shaped devices for electronic textile(E-textile) have been demonstrated with flexibility, light weight, low-cost and comfort to wear. Especially, fibriiform organic field-effect transistors (OFETs) are essential component for realizing circuit integration based on E-textile. In the practical wearable device, fibriiform OFETs require high performance with low-power consumption. In this study, we have demonstrated high-performance fibriiform OFETs with new device configuration which is capable of high output current under low voltage. With this structure, channel length and width could be easily controlled by thickness of semiconductor film and length of fiber. In particular, utilization of ion-gel as a gate dielectric allows low-voltage operation due high capacitance. We found that nanostructure control of organic semiconductor layer plays a critial role to improve the mechanical durability as well as charge carrier mobility. The resulting fibriiform OFET show high performance with good on/off ratio of 10^5 and on-current level of 10mA at 1.5 V which is proper to operate the current-driven LED devices. It was confirmed that these device performance almost remains even after weaving process with the common threads and repeated of bending deformations.

BM08.15.13
Ultra-Sensitive, Highly-Selective, Real-Time Chemical Wearable Sensors Based on Hydrogel Interferometer Xinmin He1, Mo Sun1, Ruobing Bai2 and Zhiqiang Suo2; 1University of California, Los Angeles, Los Angeles, California, United States; 2Harvard University, Cambridge, Massachusetts, United States.

The fast development of wearable sensors has been promoted by the broad needs for real-time monitoring the bodily functions and air quality. Interests in many wearables electronic sensors however have seen a decrease over time, due to the needs of frequent charging of batteries in practical usage. Wearable colorimetric sensors, using optical read-out signals under ambient light without any electronic components, become highly advantageous. Here we report an adaptive colorimetric sensing platform based on a bulk structure of covalently bonded hydrogel thin film-substrate system. External stimuli from the analytes can rapidly change the thickness of the hydrogel film, resulting in an instant color change. The soft and highly stretchable robust synthetic hydrogel materials can form a highly compliant contact to human epidermis and has good self-recovery capability, as an ideal candidate for soft matrices of wearable devices. Also, this colorimetric sensing platform allows for in situ quantitative analysis by naked eye or camera via analysis app, as a wireless wearable sensing component for the next-generation textile. We have shown this customizable adaptive platform can detect a large variety of analytes including cations for hydration and other physiologic metabolic state monitoring. Cu2+ for Wilson's disease prescreening, glucose for diabetes monitoring, and sulfur dioxide and nitrogen dioxide for air quality detecting. This sensing platform showed a high performance on the sensitivity and response time. The limit of detection for Cu2+ could reach as low as 10.0 pM with only 1-2 second. Such high performance is attributed by this unique chemo-mechano-optical signal transduction mechanism, which effectively amplifies the nm-scale hydrogel thickness change to a greater and more detectable optical spectrum change. This will lead to a broad platform of a new class of wearable sensors with superior performance at low cost.

BM08.15.14
Crack-Based Strain Sensor with High Sensitive and Low Hysterisis for Pulse Wave Monitoring Hyeonsuk Jung, Chan Park, Hyunwoo Lee, Hong SungUk, Hyonguk Kim and Seong Jm Cho; Chungnam National University, Daejeon, Korea (the Republic of).

Measuring pulse wave technology has received great attention because it indicates the status of the heart and blood vessels. For measuring precise pulse wave, high sensitivity (gauge factor $>$500) at low deformation ($<$1% strain) and repeatability are necessary. Because pulse of blood causes micro-scale deformation of skin, high sensitivity sensor is required to measure the small deformation. In addition, repeat measurements are required for using as clinical application. However, other studies are low sensitivity under 1% strain and poor hysteresis that makes unreliable repeatability. Here, we have fabricated strain sensors which has high sensitivity (gauge factor $>$6,000) at 1% strain and can measure micro deformation ($<$1% strain) for pulse wave measurement. Our sensors also exhibited excellent hysteresis and repeatability (100,000-cycle test).
For high sensitivity and low hysteresis, we optimized nanocracking structure's shape, thickness and substrate's characteristics. Sensing performance of the sensors depends on morphology of substrates, material property of sensing layer and interfacial property such as adhesiveness. We studied their effects on the sensing performances and resulted optimal conditions for pulse wave measurement. In addition, we developed a novel pre-strain process to improve hysteresis and sensitivity. By applying the optimal pre-strain, the hysteresis was significantly reduced at low strain range (<1%), and the gauge factor (gauge factor=6,000) was be increased up to 100times, compared to the conventional sensors. Through optimization and pre-strain process, we successfully developed a crack-based sensor with a high sensitivity (gauge factor=6,000), low hysteresis and repeatability (100,000-cycle test). Considering the outstanding performances, we believe that our sensor is highly suitable strain sensor for accurate pulse wave monitoring.

BM08.15.15
ZnO Nanostructures Based Flexible FET for Immuno-Sensing Applications Syed K. Pasha, Fahmida Alam, Mubarak Mujawar, Nezih Pala and Shekhar Bhanusali; Florida International University, Miami, Florida, United States.

Zinc oxide (ZnO) nanostructures serve as an ideal substrate for binding bio-recognition molecules viz., antibodies, aptamers, enzymes, microorganisms etc. Biocompatibility, ease of deposition and low cost makes it an ideal material for application to biosensing. The binding of biomolecules to ZnO is facilitated by the difference in the isoelectric points of the bioreceptor molecules (~5) and ZnO (~9). Using this strategy, construction of bio-functionalized field effect transistors (FETs) is proposed here for linker-free and label-free detection of biomarkers. ZnO thin film/nanostructure-based FETs with channel length 2, 1, 0.5 mm and width as 4mm were fabricated on both rigid (Si/glass) and flexible (PET) substrates. The ZnO films were deposited using sputtering and sonochemical method. The thin film thickness varied between 30 - 100nm after deposition, the films were characterized using SEM, XRD and Raman spectroscopy. Electrical properties of the FET devices were measured using semiconductor parameter analyzer. The surface of the ZnO nanostructures was functionalized with cortisol-specific antibodies without any linker molecules for label-free detection of cortisol. Cortisol, the stress hormone is chosen as a model biomarker because of its importance in health-related disorders.

BM08.15.16
Assessment of the Chemical Properties of the Supported Monolayer CVD Grown Graphene Using a Hybrid Substrate Towards Biosensing Applications Ayaz Hassan and Frank N. Crespiolho; USP, Institute of Chemistry of Sao Carlos, Sao Carlos, Brazil.

Graphene, a 2D material exhibits exceptional electronic, thermal and mechanical properties and due to these unique properties, graphene-based materials have gained a widespread attention in various applications, including electronics, optoelectronics, semiconductors, energy storage and many others. However, to properly exploit the use of graphene in these devices, a chemical functionalization is usually required, because this approach allows the proper understanding of the electron transfer properties of these electrodes, exploitation of their physical and chemical properties and finally their use in various applications. The main approach to functionalize monolayer graphene on substrate is the covalent functionalization through diazonium chemistry. Nevertheless, due to single atomic layer, the chemical properties and hence the reactivity of supported graphene depends on various factors, including the number of layers of graphene, shape of graphene and nature of the substrate, the last one of fundamental importance in diazonium chemistry. Though several substrates have been used to evaluate the electronic properties of the graphene, in all the previous studies the graphene is mostly supported on one substrate or other. Here in this work, we proposed a hybrid substrate, based on the modification of the surface of SiO2/Si substrate with some metallic film, such as Au, Pt, Cu etc, which is lithographically decorated on SiO2/Si and then supported with monolayer chemical vapor deposition (CVD) grown graphene. The metallic substrate beneath the graphene is expected to further enhance the electronic properties of the graphene as compared to the graphene supported on SiO2/Si. This was initially observed in the diazonium chemistry, where a surface coverage of 4.3 x 10⁴ mol.cm⁻² was achieved for the graphene, supported partially on the metal and partially on the SiO2/Si, as compared to the surface coverage of 2.3 x 10⁻⁹ mol.cm⁻² obtained for the graphene supported only on SiO2/Si; almost 20 times enhancement was achieved for the attachment of the molecules to the surface,. The chemical functionalization of the graphene was confirmed through micro-FTIR spectroscopy and FTIR chemical imaging, as well as through micro-Raman spectroscopy on both kinds of substrate. The charge transfer properties of the fabricated graphene device were further evaluated through various electrochemical techniques, where a 2-3 fold enhancement in the electron transfer kinetics was achieved for the graphene supported on M-SiO2/Si (M= Au, Pt, Cu) substrate as compared to the substrate without the presence of metal i.e SiO2/Si. Our developed device may thus find potential applications in the ultra-fast and sensitive sensing of biomolecules in the biosensors and biodiodes.

BM08.15.17
Multifunctional Electrospun Multilayered Separator for Flexible Battery Applications Wisawat Keaswejareansuk and Jianyu Liang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Lithium-ion battery (LIB) is highly demanded in rapidly developing smart and connected livings, sensorization, and wearable electronics. While the battery safety is a visible challenge beside the numerous efforts to increase electrochemical performance, the flexibility in shape and size is an important factor for moving toward those applications. A separator is an electrochemically inactive component and essential for providing safety to the battery. It is known as the weakest component because of an anisotropic characteristic of the primary commercial separator, polyolefin. Electrospinning is a simple and efficient process to create the continuous fibers at nanoscale and fabricate the high porous membranes with high surface area to volume ratio. The electrospun, nonwoven mats are lightweight with spaces between the mesh for electrolyte uptake and surface functionalization. The membrane’s characteristics and properties are customized by simultaneously adjusting material parameters. In this work, the electrospun separators with multilayers of different types of polymer are created with good physical affinity. The multilayered separators offer multifunction owing to the material properties of different polymers. In this presentation, we will discuss the material selections, material and process parameters of the electrospinning, the electrospinning routines, and the characteristics of the fabricated electrospun multilayered separator, which has enhanced battery safety, increased ionic conductivity, and provided shape flexibility.

BM08.15.18
Intrinsically Stretchable Organic Electrochemical Transistors Yang Li¹, Shiming Zhang² and Fabio Cicora³; ¹Department of Chemical Engineering, Polytechnique Montreal, Montreal, Quebec, Canada; ²California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California, United States.

Stretchable electronics show great significance for emerging biomedical sensing and wearable healthcare application, since it can allow intimate contact with soft objects. Recently, organic electrochemical transistors (OECTs) become suitable candidates for biological interfacing and logic circuitry applications due to the synthetic tunability, facile fabrication and bio-compatibility. However, intrinsic stretchable OECTs, which enable simple fabrication process and low cost, haven’t achieved intrinsic stretchability, due to the brittleness of conducting polymer and metal electrodes. This talk focuses on intrinsically stretchable OECTs, which can be stretched up to 30% strain while maintaining identical transistor characteristics. The intrinsic stretchability is obtained by synergistically optimizing the processing conditions during device fabrication through which we can control the formation of microcracks in
the device with a pre-set strain. These microcracks maintain the current stable while being stretched. This work paves the way for OECTs applications as conformable biosensors and its integration with wearable electronics.

**BM08.15.19**

Low-Cost, Mass-Manufacturable Microfluidic Systems for Wearable Diagnostic Devices

Amber Bouitteau, Matthew Talbot, Bailey Corless, Chris Toothaker and Caitlin Howell; Department of Chemical and Biological Engineering, University of Maine, Orono, Maine, United States.

The use of microfluidics in wearable diagnostics presents multiple opportunities for sophisticated, continuous monitoring. However, many of the most popular microfluidic components used today are typically made of materials that are expensive and difficult to manufacture on a large scale. In this work, we use an existing roll-to-roll release paper manufacturing process to create precisely patterned sheets of flexible acrylated channels on a paper backing. The channels are used to direct capillary or pressurized fluid flow, mix in reagents, and direct the final sample to a detection zone. Proof-of-concept tests and theoretical modeling examining the efficacy of these systems toward applications in “smart” bandages and diapers are presented.

**BM08.15.20**

Transferring Microelectromechanical Devices to Breathable Fabric Carriers with Strain-Engineered Grippers

Canisha Ternival, Mohammad S. Islam, Jasmin Beharic and Cindy K. Harnett; University of Louisville, Louisville, Kentucky, United States.

We demonstrate a path to transfer microelectromechanical systems (MEMS) from silicon wafers to soft, porous, fiber-based materials using strain engineering to wrap micro-fabricated grippers around fibers in a target mesh. Applications include sensor integration into breathable, high conduction flow-through structures like tissue engineering scaffolds, bandages, and air filters.

Grippers were made from thin-film bilayers on a silicon substrate, typically a metal on a thermal oxide, using a self-aligned lift-off and etch process to define bilayer beams with lengths in the 0.2 -1 mm range. The patterned silicon substrate was loosely covered with a fiber mesh by taping it down at the edges. A xenon difluoride (Xactix Inc) dry silicon etcher exposed the substrate to 3 Torr XeF₂ for 20 cycles, undercutting the grippers through holes in the mesh. The compressively-stressed oxide layer caused the MEMS grippers to curl from the surface and interact with the mesh fibers. The grippers’ radius of curvature was set by the thickness and elastic modulus of the layers [1].

We were able to release bilayer structures underneath 100% nylon mesh with 0.5mm to 1mm diameter openings and fiber diameters of ~50 microns. We investigated which planar layouts and curvatures worked well as grippers in this range of fiber diameter and mesh hole spacing. Because the goal is to transfer large-area integrated circuits to porous carriers, we also investigated serpentine structures to connect multiple grippers into a continuous circuit that could survive the transfer process.

Stretchable electronics fabrication generally relies on fine-tuning adhesion forces, putting some restrictions on what the carrier layer can be. In contrast to adhesion, mechanical tangling makes more kinds of carrier materials available. Antibacterial, conductive, heat-responsive and other functions can be brought in by fiber networks as long as they are compatible with the highly selective silicon etch process. The grippers can also bring electronic contacts from one side of a mesh to the other, which is difficult to do on continuous thin films of other soft materials like silicone or polyimide. Our solution produces large arrays of redundant contacts that could potentially be used for connecting soft circuits without alignment [2]. When used with a stretchable mesh, this surface micromachining method provides a route for MEMS and integrated circuits to move from a small-diameter wafer to a larger surface area.


**BM08.15.21**

Conductive Silk Material Produced from Silk Fibroin and Waste Biomass

Diego López Barreiro1, Zaira Martin-Moldes2 1, Francisco J. Martin-Martinez1, David Kaplan2 and Markus Buehler1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Tufts University, Medford, Massachusetts, United States.

Silk fibroin (SF), a protein obtained from Bombyx mori cocoons, can be used to manufacture biocompatible and biodegradable materials with outstanding flexibility and mechanical properties. Activated carbons (ACs) derived from biomass are nanostructured porous materials with highly aromatic structures populated with doping elements (mainly nitrogen), and with good electron conductivity. The polar nature of the ACs facilitate their interaction with SF. Thus, combining ACs and SF to manufacture conductive silk-based materials is a promising approach to develop environmentally matched and biocompatible biomaterials where silk provides flexibility and strength, and ACs provide conductivity and mechanical reinforcement. These materials can be of interest for the biomedical field, to develop wearable sensors or conductive coatings, among other biomaterials. In this work, we present the mechanical properties, cytocompatibility and nanostructures of SF-AC biomaterials, such as membranes or hydrogels, using a synergic approach of experimental synthesis and computational modeling.

**BM08.15.22**

Ultrathin, Stretchable, and Flexible Structural Color Filters Based on a Metal-Dielectric-Metal Structure

David D. Ordinario, Hiroaki Jinno, Md Osman Goni Nayeem, Yutaro Tachibana, Tomoyuki Yokota and Takao Someya; University of Tokyo, Tokyo, Japan.

Color filters are a simple yet highly relevant device in today’s increasingly technology-driven world and can be found in a large number of applications such as displays, sensors, and photovoltaics. For flexible electronics, a flexible color filter would be suitable for a wide range of potential uses where an unusual form factor is required, or even integration with wearable devices. One important factor to consider is conformal adhesion to a complex surface while preserving filter effectiveness. Increased adhesion while preserving filter effectiveness would be highly conducive for any future applications. Here, we demonstrate ultrathin, stretchable, and flexible structural color filters based on a simple MDM (metal-dielectric-metal) structure on a 1.3 µm-thick ultrathin substrate. We first fabricate and characterize the basic optical and mechanical characteristics of the flexible color filters. We next investigate how effective they are at both passing the desired wavelengths and blocking the undesired wavelengths both before and after mechanical deformation. We also describe their angular sensitivity and assess its overall impact on filter performance. Remarkably, we find that the performance of the filters is not greatly
impacted by repeated mechanical deformation. Overall, our findings represent a potential strategy for making adhesive color filters with compatible mechanical properties to current flexible and/or wearable technologies without sacrificing functionality.

**BM08.15.23**

**Patternable Ionic Gels for Tactile Sensors**

Yoon Ji Seo, Heecheon Lee, Hyemin Lee and Hyunsik Yoon; Seoul National University of Science and Technology, Seoul, Korea (the Republic of).

Wearable electronics and robotics have received attention because of potential applications such as health monitoring and rehabilitation. For the devices, there are many components which should be developed, for example, power sources, actuators, and sensors. Ionic gels have been studied to be harnessed as wearable sensors due to their stretchability, biocompatibility and conductivity. However, when we synthesize the ionic gel in water environment, the modulus is too small to be constructed in microscale. Moreover, it is almost impossible to deposit metal films onto the gel in a vacuum condition. In this work, we present a method to prepare ionic gels without water environment to construct microscale structures, such as pillars, lines, prisms and pyramids. We fabricate tactile sensors with ionic gels with various structures and conditions and compare the electrical characteristics. Furthermore, we use a model to explain the difference and find an optimum condition.

**BM08.15.24**

**Electrochemical, PCR-Mediated Biosensor for the Detection of pks Genomic Island in E. coli Samples Utilizing Custom Gold Flexible Electrodes**

Nadia E. Solis Marcano1, Marjorie Lopez-Nieves1, Ramon Gomez-Moreno2, Dina Bracho-Rincon1 and Carlos R. Cabrera1; 1University of Puerto Rico, Rio Piedras Campus, Carolina, Puerto Rico, United States; 2University of Puerto Rico Medical Science Campus, San Juan, Puerto Rico, United States.

The use of custom sensing platforms, such as electrodes, allows for the selection of optimum characteristics for the system such as: size, robustness, flexibility and biocompatibility, among others. ColicinB is a genotoxin produced by the polyketide synthase multienzyme (pks genomic island) encountered in the human gut microbiota. Many studies link colibactin production to different kinds of cancers, therefore making it a molecule of interest in the biomedical research field. More specifically, certain strains of *Escherichia coli* have been found to harbor pks genomic island that induced DNA damage. Here, we developed a PCR mediated-electrochemical protocol to successfully identify the presence of the pks genomic island in DNA samples utilizing a custom gold electrode platform. For this, pks and non-pks containing *E. coli* DNA were impedimetrically analyzed before and after amplification through polymerase chain reaction (PCR) protocol. Custom DNA primers where synthesized in order to selectively amplify a specific 400 base pair sequence from the cibN gene from the pks island. Impedance data showed a 97% increase in charge transfer resistance after the protocol was applied for the pks containing samples as opposed to the 15% increase for the non-pks containing DNA samples. Overall, effective identification of the pks genomic island was achieved.

**BM08.15.25**

**Dispersion Methods of Nanoparticles in Stretchable PDMS and Their Dielectric Constant to Fabricate Electroadhesion Gripper**

Hanwhu Lim1,2 and Baekjin Kim2; 1Yonsei University, Seoul, Korea (the Republic of); 2Green Chemistry and Materials Group, Korea Institute of Industrial Technology, Cheonan, Korea (the Republic of).

Polymer/nanoparticle (NP) composite is well known methodology to improve physical and chemical properties depending on its polymerization conditions and kind of NPs such as TiO2, SiO2, Al2O3, and BaTiO3. However, when we applied high amount of NPs, the aggregation was occurred due to its dispersion. To overcome this problem, we optimized the dispersion by choosing the suitable dispersion method according to the viscosity of composites. In less than 10,000 CPS, homogenizer and Ultrasonicator were used to mix NPs into polymers. Higher than 10,000 CPSs, however, it is almost impossible to mix NPs into polymer so we changed mixer to plenary machine in the high viscous condition. As a result, a well dispersed polymer/NP composite was fabricated with higher than dielectric constant of 4 via its equipment and observed by HR-SEM and TEM. Furthermore, the high dielectric constant layers were applied to an electrical adhesion robot gripper comprised of robot arm, skin layer and EA layer based on stretchable polymer. The gripper was controlled with voltage ON/OFF to attach and detach target materials.

**BM08.15.26**

**A Soft Self-Powered Microfluidic Sensor for Heavy Metal Ions Detection**

Peiwi Song2,3, Guang Yang2 and Ken-Tye Yong2; 1School of Physics, Huazhong University of Science and Technology, Wuhan, China; 2School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore.

The detection of heavy metal ions is of great significance in healthcare, environmental monitoring and drinking water safety. The current states of strategies for heavy metal detection in water are mainly focusing on electrochemical and optical techniques, which are restricted to laboratory testing due to the bulky and expensive instrument involved. The emergence of the microfluidics technology coupled with flow-induced electrochemistry has boosted the development of innovative self-powered micro-sensors. We here demonstrate a soft self-powered microfluidic sensor mainly constructed by PDMS. The working mechanism of the sensor is based on liquid-solid contact electrification between the testing liquid sample and the sensing microfluidic channel that is modified with chelating molecules for metal ions coordinating. When flowing samples into the sensor, their electrification potentials can be determined by measuring the static induction current over an electrode patterned on the channel's outer surface. Once metal ions from the sample are captured onto the channel surface, the flowing electrification effects would be alerted due to the changes of surface potentials, which are highly sensitive to ions concentration. Only a small amount of liquid samples (< 30 μL) is needed in this method. By choosing different chelating molecules, the as-developed sensor shows excellent performance in the sensing of common heavy metal ions, such as Pb2+ and Cd2+, in a sensing range of 10 ppb to 100 ppm, with the sensitivity of 10 ppb. For selective sensing, we coat glutathione on the sensor as chelating molecule, under the same testing condition, the electrification potential generated from Pb2+ solution is more than 2.5 times larger than that from Cu2+, Zn2+ and Al3+, indicating selectively sensing capability of the sensor. This method can also be applied in detecting ions other than heavy metals (e.g. Na+ and K+) by coating certain coordinating agents such as crown ether onto the sensing layer, which will greatly broaden the sensor's applications. It is also worth noting that, the whole sensing process is self-powered which requires no external power source but only a current signal read-out. The sensor made by PDMS is soft, stretchable and biocompatible, making it suitable to be used in wearable or even implantable sensing applications.

**BM08.15.27**

**Small Molecules-Based, Water-Resistant Stretchable Organic Light-Emitting Diodes with Ag-Nanowire Elasticomer Substrates**

Chang Min Lee, Daekeun Choi, Dong Hyun Kim, Hassan Hafeez, Justin Jesuraj Periyanayagam and Seung Yoon Ryu; Korea University, Seoul, Korea (the Republic of).

Recently, the fabrication of stretchable organic light-emitting diodes (SOLEDs) has drawn a great attention due to development in the field of biomedical
devices and wearable electronics. Much of the device efficiency and stability investigations have been realized with polymer-based device layouts on plastic substrates. Even though polymer-based OLED is demonstrating a good mechanical stability, it suffers with low device efficiency due to large triplet-exciton loss. Moreover, even though the recently introduced small-molecule based, geometrically wavy-buckled SOLEDs approach demonstrated a high device efficiency, however revealed a shift in the emission color coordinates (CIE) in wavy form (without stretch) as compared to flat form (with stretch). This makes it difficult to achieve the luminance in an identical CIE (wavelength) region for the same device under different strain conditions.

In this work, we present the fabrication of small-molecule-based intrinsic (flat-form) SOLED capable of performing under various bend and strain values with a small decrease in efficiency. Silver nanowires (AgNW) embedded poly (urethane) (PU) was utilized as an anode, which maintained a high conductivity (low sheet resistance of 20 Ω/sqr) up to a strain of 50%. A degassing step was performed by annealing the AgNW-PU electrode at 120 °C for 2 hours, which removed the absorbed oxygen/moisture, and improved the stability of the device. The sandwiched OLED device was fabricated with small-molecules based layers (HAT-CN/NPB/TCTA/CBP+Irppy3/TPBi/LiF/Al) maintaining a strong advantage in terms of their processing in vacuum condition, with a small decrease in efficiency. Silver nanowires (AgNW) embedded poly (urethane) (PU) was utilized as an anode, which maintained a high conductivity (low sheet resistance of 20 Ω/sqr) up to a strain of 50%. A degassing step was performed by annealing the AgNW-PU electrode at 120 °C for 2 hours, which removed the absorbed oxygen/moisture, and improved the stability of the device. The sandwiched OLED device was fabricated with small-molecules based layers (HAT-CN/NPB/TCTA/CBP+Irppy3/TPBi/LiF/Al) maintaining a strong advantage in terms of their processing in vacuum condition, which provides uniform, high quality films with low triplet-exciton loss. The resulting SOLED devices demonstrated a current efficiency, quantum efficiency and power efficiency of 25 cd/A, 7% and 24 lm/W respectively, which is considerable in terms of small-molecule based intrinsic stretchable devices. (H.-B. Sun, group presented small molecule based geometrical, wavy SOLED with ~70 cd/A current efficiency). Due to the absence of any wavy/buckled structures and intrinsic form of SOLEDs, no shift in electroluminescence peak was observed demonstrating a stability in the emission CIE. Moreover, the polyurethane (PU) encapsulation was performed on the SOLED devices, which enabled it to be water-resistant and the device’s operation was confirmed in liquid atmosphere.

The approach mentioned in this work has the high potential to realize small molecule-based intrinsic water-resistant SOLEDs, which can provide high performance under strain without any shift in the CIE.

BMO8.15.28
Soft Knee-Exoskeleton System Using Variable-Stiffness Magnetorheological(MR) Gel to Reduce the Energy Cost of Human Walking
JungHwan Youn1, YunSoo Back2 and KiUk Kyung1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Department of Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of); 3Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Soft Knee-Exoskeleton System Using Variable-Stiffness Magnetorheological(MR) Gel to Reduce the Energy Cost of Human Walking

Wearable and Luminescent Oxygen-Sensing Films with Improved Sensitivity Based on Light Scattering by TiO2 Particles
Changjin Lim and Jin-Woo Park; Yonsei University, Seoul, Korea (the Republic of).

Dissolved oxygen (O2) is an essential element for energy production and cellular respiration in a human body. Insufficient O2 delivery can cause peripheral artery diseases (PAD) such as cancers, diabetic foot ulcer, and Raynaud’s disease. Based on the fact that transcutaneous oxygen pressure (tcpO2) is proportional to O2 concentration of tissues, research for measuring tcpO2 in real-time and in a large area have been done to diagnosis and monitor PAD. As a golden standard for sensing tcpO2, Clark electrode has been extensively used, which operates based on electrochemical reaction. However, this method is an invasive technique accompanying pain and consumes O2 during the measurement. Recently, luminescence-based O2 sensing mechanism has been studied as non-invasive method and for a large-area mapping of O2 distribution. The new concept of luminescent tcpO2 sensor consists of an O2 sensing film, a light source, and a photodiode as the photoluminescence (PL) detector. The luminescent oxygen sensors can be based on either the photoluminescence intensity or light-quenching lifetime of the sensing films. The ratiometric method based on the intensity analysis approach has been introduced to provide a low-cost technique capable of quantitatively and accurately measuring the oxygen distribution over large areas. However, to utilize the ratiometric method,
the sensitivity of intensity-based methods to ambient light, photobleaching, and self-quenching of dye molecules should be minimized for accurate analysis. To improve the signal-to-noise ratio and sensitivity ($I_{ph}/I_0$) of the oxygen sensor, in this study, we investigated the effects of embedded titanium dioxide (TiO$_2$) nanoparticles on the photocurrent and sensitivity of luminescent oxygen-sensing films based on platinum octaethylporphyrin (PtOEP), which is an indicator dye. The effects of the particle size and $n$ of the photocurrent and $I_{ph}/I_0$ of the oxygen sensor were investigated based on Mie light-scattering theory. The diameter and $n$ of the TiO$_2$ nanoparticles were varied by the simple processes of laser irradiation and thermal annealing. Finally, an integrated sensing platform (luminescent sensor) was made with the sensing film with TiO$_2$, and it was confirmed that the photocurrent and sensitivity of the oxygen-sensing films were greatly improved with increases in the size and refractive index ($n$) of the embedded TiO$_2$ nanoparticles. Furthermore, the improvements in the photocurrent and sensitivity of the oxygen-sensing films allowed the fabrication of a high-resolution oxygen-sensing film that can detect the oxygen distribution over large areas.

BM08.15.31
Fabrication of Flexible and Wearable Thermoelectric Fibers with Micro- and Nanoscale Structures Based on Laser-Induced In-Fiber Capillary Instability
Zing Zhang, Ting Zhang and Lei Wei; School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore.

High-performance flexible and wearable thermoelectric (TE) devices are increasingly needed in many applications for thermal energy conversion. Well-designed thermoelectric devices open a path to recycle waste heat energy owing to its intrinsic capacity. Unfortunately, existing TE devices with high energy conversion efficiency are mainly constituted by inorganic TE materials, making those devices inflexible and bulky. Thus they are unsuitable for using on heat sources with irregular or curved surfaces. To bridge the gap, we develop a flexible and ultralong TE fiber with precisely patterned micro- and nanoscale in-fiber structures. The fabrication process that takes advantages in thermal drawing process and laser-induced in-fiber capillary instability phenomenon is designed and realized in this study.

Our process begins with the fabrication of a macroscopic preform, next we scale down the preform into micro- or nanoscopic fibers by thermal drawing. The prior issues in multi-materials fiber thermal drawing process are to match the melting/softening temperatures and the linear thermal expansion coefficients of the fiber core and cladding materials. Herein, we choose p-type Bi$_2$Sb$_3$Te$_6$ and n-type Bi$_2$Se$_3$ as the TE fiber core and the borosilicate glass as the fiber cladding. To achieve mechanical protection, a polymer layer is also coated onto the fiber outer surface. We calculate the thermal conductivities of 0.839 W/m K for the n-type fiber and 0.844 W/m K for the p-type fiber and obtain the ZT values of 0.23 for the n-type fiber and 1.25 for the p-type fiber at room temperature.

Furthermore, TE fibers with multiple functionalities and energy-storage capabilities could be achieved by patterning designed structures in fibers with functional materials such as metals and semiconductors. To avoid mixing and disrupting the device structures during the fiber thermal drawing process, we introduce a method that utilizes the in-fiber capillary instability phenomenon to define the inner structures of multi-functional TE fibers. A CO$_2$ laser serves as heating source induces the capillary instability occurring at certain positions of the fiber. The instability transforms continuous fiber core into designed and periodic micro- and nanoscale structures, such as spheres, rods, and spindles by carefully determining the laser treatment parameters. This step brings TE functional materials to interact with other materials (such as metal and semiconductors) in a precisely controlled procedure, forming a ladder-like structure in fiber. This structure makes energy conversion much feasible and efficient in the TE fiber. More importantly, the combination of fiber thermal drawing process and utilizing in-fiber capillary instability phenomenon could offer more design spaces and finally lead to high-performance, micro- and nanoscale, flexible and wearable TE devices to be available in the near future.

BM08.15.32
Highly Sensitive Flexible Capacitive E-Skins with Biomimetic Ionic Gel
Jingyi Yang and Chuanfei Guo; Southern University of Science & Technology, Shenzhen, China.

Flexible electronic skins (e-skins) with high sensitivity and low-cost fabrication have been intensively desired in human motion detection, health monitoring, soft robotics, etc. Capacitive type flexible e-skins usually improve sensitivity though introducing surface microstructures, but the change of the dimensions in dielectric layer is quite limited thus the improvement is also limited. Herein, we demonstrated a low-cost and highly sensitive flexible capacitive e-skin with biomimetic ionic gel (BIG). The BIG film with uniform cone-like microstructures, is templated from a Calathea zebrina leaf though soft lithography. Both the top and bottom electrodes are fabricated via spraying AgNWs onto a colorless polyimide (CPI). The device is in framework of CPI/AgNWs/BIG/AgNWs/CPI. Owing to the electrical double layer contributed by BIG film, this device exhibits a ultralow limit of detection around 0.1 Pa, and a ultrahigh sensitivity of 54.31 kPa$^{-1}$ in low pressure regime (0.5 Pa), and a strong response of larger than 1 kPa$^{-1}$ over a wide range of pressure from 0.1 Pa to 115 kPa. Such high performance e-skins have great potential in motion monitoring, health monitoring and human-machine interaction, etc.

BM08.15.33
Implanted Battery-Free Direct-Current Micro-Power Supply from In Vivo Breath Energy Harvesting
Jun Li, Lei Kang, Yin Long, Hao Wei, Weibo Cai and Xudong Wang; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Majority of current IMDs are powered by conventional primary or secondary batteries that contribute up to 90% weight and volume of the entire device. [1,2] While replacement of or recharging the batteries requires substantial surgical or technical efforts, introducing additional suffering and complexity to the patients, other batteries potential issues such as overheat and leakage of toxic electrolyte further prohibit the advancement and miniaturization of IMDs. Therefore, increasing efforts are now being focused on the innovation of designated IMD power sources. Implantable nanogenerators (i-NGs) have been designed to convert biomechanical energy into electricity. [3,4] In spite of their numerous merits, the outputs of state-of-the-art i-NGs are always in a form of largely discrete pulses. Although their theoretical output power could be sufficient for IMDs, battery component is still needed in the i-NG design to produce a steady and useable direct current (DC) output. Moreover, most i-NGs are non-stretchable with incompatible mechanical properties compared to soft biological tissues, which further challenges their practical applications.

In this work, we reported an ultra-soft stretchable i-NG system that could function as a battery-free DC micro-power supply. The i-NG consisted of ultrafine micro-scale interdigital electrodes (IDEs) and multi tribo-active layers with a small working area (approximately 2 cm$^2$), packaged by biocompatible silicone elastomer. While the micro IDEs support the output of high frequency electricity (1 μA at 70 Hz) driven by slow mechanical stimulation, the silicone elastomer and an embedded cavity design enable i-NGs with extremely low Young’s Modulus (46 kPa), exactly matching the mechanical property range of most soft biological tissues. By implanted inside the abdominal cavity of Sprague Dawley (SD) adult rats, the i-NG could convert slow diaphragm movement during normal breath into stable high-frequency electrical spikes, which were readily transmitted into a continuous ~2.2 V DC output on a LED load after being integrated with a basic electrical circuit (rectifier and capacitor) for a relatively long period of time.

This electric output could continuously power the LED without any observable power decay, successfully demonstrating a constant operation of small electronics DC power free of the battery component. This solely biomechanical-energy driven DC micro power supply offers a very promising solution for
the development of self-powered IMDs in the near future.

References:

BM08.15.34
Bio-Inspired Structural Designs for Bendable, Foldable and Stretchable Lithium-Ion Battery with High Energy Density Xiaoñbiao Liao1, Guoyu Qian2, Yuan Yang2 and Xi Chen2; 1Columbia University, New York, New York, United States; 2Earth and Environmental Engineering, Columbia University, New York, New York, United States.

Flexible batteries are attractive for wearable devices for various applications, such as health care. It is challenging to achieve high energy density and high mechanical flexibility simultaneously. In this work, we propose feasible and scalable strategies to fabricate flexible lithium-ion batteries, which can concurrently obtain high energy density and mechanical flexibility, including bendability, foldability, twistability and stretchability. Inspired by the structure of animal spine, the vertebræ-like hard segments with multiple layers of conventional anode/seperator/cathode stack to offer energy storage are interconnected by the soft components as marrow with the monolayer stack to provide flexibility. Its nonoptimized energy density of 242 Wh/L can be over 85% of a standard prismatic cell. It should be emphasized that the bioinspired design allows the battery to sustain stable electrochemical performance even upon continuous dynamic mechanical deformation including twisting and bending (Guoyu Qian, Bin Zhu, Xiangbiao Liao, et al. Advanced Materials 30.12 (2018): 1704947). Additionally, a wrinkling structure replacing the flat interconnector in between two hard segments is introduced to realize stretchability up to 50%. To further improve energy density and mechanical stability, we minimize the width of soft components by asymmetrically folding one long strip of electrode stack, where complex fabrication process of winding and cutting is not needed. Thanks to this improved design, the battery exhibits excellent mechanical and electrochemical stability upon up to 180 degree folding. Our facile and scalable designs of flexible lithium ion battery potentially play an important role in wearable electronics.

BM08.15.35
Applicable Phase Transition Capsule to Smart Fabric for Thermal Energy Storage Youngkwon Jung1, Taegu Do1, Youngsang Chun1 and Young Gun Ko2; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2KAERI, Daejeon, Korea (the Republic of).

The need for the manufacturing of innovative fabric product has been required for using the waste heat. Fiber and fabric which have automatic acclimatising properties have recently attracted more attention. The phase transition capsules (PTCs), which can storage the thermal energy using the latent heat from solar heat and body temperature, have been highlighted. In order to apply the PTCs to industrial fields, the metallic, inorganic, or polymeric shell coated PTCs had been studied. However, metallic and inorganic shell is corrable in aqueous liquid such as water and perspiration, and polymeric shell has low thermal conductivity. Furthermore, because the previously studied capsules have low core content, the capsules have low thermal energy capacity. In this work, we used Pickering emulsion based encapsulation method to enhance the core content for high thermal energy capacity, and encapsulated the phase transition material (PTM) with water-absorbable polymeric shell to enhance the thermal conductivity. Paraffin wax was used as core thanks to its high heat storage capacity and nontoxic properties. And the poly[2-hydroxyethyl methacrylate] (pHEMA), a water-absorbable polymer, was used as a shell because the pHEMA can show high thermal conductivity after absorbing a water. The thermal conductivity of pHEMA were measured according to the water content by LFA, and the thermal conductivity of fully hydrous pHEMA was measured to be 0.45 W/m K which is far higher than the other polymers. The manufactured PTC showed good durability owing to the flexibility and elasticity of hydrous pHEMA. The thermal storage properties of the PTC were measured by DSC, and the thermal storage capability of the PTC was calculated to be 99.7%, which is higher than previously researched other PTCs thanks to its high core content.

Our study demonstrates that the PTCs with water-absorbable polymer are an attractive material for effective thermal storage and delivery. In addition to the use of the PTCs as thermal energy carrier, the PTCs can become an attractive material for various heat sensitive industrial fields, such as wall materials of buildings or houses, refrigerator vehicles, and outdoor wear by storage and release thermal energy.

BM08.15.36
Mapping Strain/Pressure with ZnO Nanowire Arrays by Piezotronic and Piezo-Phototronic Effect Caofeng Pan1, Xiaojia Zhang1 and Zhong Lin Wang2; 1University of Chinese Academy of Sciences, Beijing, China; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

Emulation of human senses via electronic means has long been a grand challenge in research of artificial intelligence as well as prosthetics, and is of pivotal importance for developing intelligently accessible and natural interfaces between human/environment and machine. In this talk, we present a novel design of ZnO nanowire arrays, which can be used to directly record the strain distribution by piezotronic and piezo-phototronic effect. First, we have reported large-area three-dimensional (3D) circuitry integration of piezotronic transistors based on vertical zinc oxide nanowires as active taxel-addressable pressure/force-sensor matrix for tactile imaging with a high resolution of 100 μm3. The device matrix has been demonstrated for achieving shape-adaptive high-resolution tactile imaging and self-powered, multi-dimensional active sensing. However, the signal of the piezotronic transistors array is the change of the resistance of each NWs, which can only be measured in a series way. That means such piezotronic transistors array can only mapping a static strain. Different with the electrical signal, the optical signal can be measured in a parallel way. In our previous work, we have demonstrated how the piezo-phototronic effect can be effectively utilized to enhance the emission intensity of an n-ZnO/p-GaN NW LED. Here, we extend the single NW device to NW LEDs array, for pressure/force sensor arrays for mapping strain with a resolution as high as 2.7 μm. Such sensors are capable of recording spatial profiles of pressure distribution, and the tactile pixel area density of our device array is 6250000/cm2. When the device is under pressure, the images unambiguously show that the change in LED intensity occurred apparently at the pixels that were being compressed by the molded pattern, while those were off the molded characters showed almost no change in LED intensity. Instead of using the cross-bar electrodes for sequential data output, the pressure image is read out in parallel for all of the pixels at a response and recovery time-resolution of 90 ns. This may be a major step toward digital imaging of mechanical signals by optical means, with potential applications in touch pad technology, personalized signatures, bio-imaging and optical MEMS.

Furthermore, our recent studies achieve such piezo-phototronic effect induced strain mapping in a flexible n-ZnO NWs/p-polymer LEDs array system composed of PEDOT:PSS and patterned ZnO NWs with a spatial resolution of 7 μm for mapping of spatial pressure distributions. The emission intensity of the LED array sensor matrix is dominated by locally applied strains as indicated by piezo-phototronic effect. Therefore, spatial pressure distributions are immediately obtained by parallel-reading the illumination intensities of LED arrays based on electroluminescence working mechanism. A wide range of pressure measurements from 40 MPa to 100 MPa was achieved through controlling the growth conditions of ZnO nanowire array.

BM08.15.37
Flexible all-solid-state supercapacitor is highly desired for integration with flexible electronic products. However, most current flexible supercapacitor electrodes show mediocre performance, especially for high mass loading electrodes. Herein, we report high performance chlorine-doped (Cl-doped) graphene films with either low or high mass loading prepared by a facile hydrothermal method. Benefiting from the enhanced electroconductivity and electrochemical activity resulted from Cl-doped effect, the film electrode with 1.06 mg cm^{-2} shows a high gravimetric capacitance of 210 F g^{-1} at 1 A g^{-1} and the capacitance of the electrode still remains 71.2% (149.5 F g^{-1}) at 100 A g^{-1}. Moreover, when the mass loading of the film increases to 10.1 mg cm^{-2}, the gravimetric capacitance can retain 92% (193.2 F g^{-1}) at 1 A g^{-1}, showing little decrease compared with that of low mass loading film. Besides, the film shows a high areal capacitance of 2110 mF cm^{-2} and 1487 mF cm^{-2} at 1 mA cm^{-2} and 50 mA cm^{-2}, respectively. Furthermore, a symmetric flexible all-solid-state supercapacitor is assembled by two films with 11.0 mg cm^{-2} mass loading. The flexible all-solid-state supercapacitor shows almost the same capacitance under different bending angles and can retain 98% capacitance after bending 500-time. The flexible all-solid-state supercapacitor also shows a high areal energy density of 160.7 μWh cm^{-2}. All the above results demonstrate Cl-doped graphene electrode is a promising material for flexible all-solid-state supercapacitor.

Flexible Ferroelectric Nanocomposite Film for Enhanced Triboelectric Effect

Hedong Zhu, Yucan Zhu, Xingke Ye, Ziyu Yue, Zhongquan Wan and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

Supercapacitor is regarded as the ideal power source in wearable electronic device, the electrode materials of which are always research focus due to it is a key component in the supercapacitor. Among numerous electrode materials, graphene has attracted significant attention for its outstanding electrochemical performance and mechanical properties, which endows graphene films with great potential of applications in future flexible electronics. Therefore, effective preparing methods of graphene films were researched and reported extensively in recent years. Herein, we fabricate a novel graphene oxide (GO) film with excellent mechanical properties via foam film method. Its thickness can be simply regulated by changing the concentration of the surfactant. After chemical reduction, the reduced GO (rGO) films exhibit impressive electrical conductivity of ~172 S cm^{-1}. The supercapacitors based on the fabricated rGO films exhibit satisfied capacitive performance of ~56 mF cm^{-2} at 0.2 mA cm^{-2} with 6 M KOH solution. Furthermore, the flexible all-solid-state supercapacitors (FSSCs) based on the rGO films also show great volumetric capacitance of ~2810 mF cm^{-3} at 12 mA cm^{-3} (~1607 mF cm^{-3} at 613 mA cm^{-3}) with polyvinyl alcohol-KOH gel electrolyte, which indicates great rate performance of solid-state devices. Besides, the supercapacitor also show great cycling stability and flexibility: after 10000 cycles and continuously bent to 180° for 300 times, the volumetric capacitance of the FSSC remains at 81.4% and 90.4% of its initial capacitance value, respectively. All the results demonstrate the free-standing rGO films prepared via foam film method in this study could be considered as promising electrode materials for high performance flexible supercapacitors.

Chlorine-Doped Graphene Film for High Mass Loading Flexible All-Solid-State Supercapacitor

Jiang Hedong, Yucan Zhu, Xingke Ye, Ziyu Yue, Zhongquan Wan and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

We introduce a strategy of materials synthesis, characteristic evaluations and manufacturing process for a mechanically elastic, biologically safe silicon-based dopamine detector that is designed to be completely transient, i.e. dissolved in the brain and/or other body organs after a desired period of operation. Dopamine is an electroactive neurotransmitter released by the brain, playing critical roles in the mammalian central nervous system. Abnormal lack of dopamine levels in the brain has been implicated in chronic neurological disorders such as Parkinson’s disease, Attention deficit hyperactivity disorder (ADHD), schizophrenia. Therefore, rapid and sensitive detection of dopamine has been required for accurate diagnosis and monitoring of such diseases. A fundamental mechanism responsible for dopamine detection is that dopamine molecules are adsorbed onto the CPPy surface of the hybrid NPs (Fe^{3+}-CPPy NPs) via pi-pi interactions and oxidized to form dopamine-derived quinone, i.e. dopamine-o-quinone, catalyzed by a number of transition metal (Fe) NPs. As a result, generated electrons from the reactions transferred to highly p-doped Si NMs-based electrodes contributed to modulations in electrical characteristics. Use of inexpensive, bioresorbable iron (Fe) nanoparticles (NPs) is one of attractive choices for efficient catalytic oxidation of dopamine as an alternative for noble, non-transient platinum (Pt) nanoparticles, based on extensive studies of synthesized materials and catalytic reactions. Arrays of transient dopamine sensors validate electrochemical functionality to determine physiological levels of dopamine and to selectively sense dopamine in a variety of neurotransmitters, illuminating feasibilities for a higher level of soft, transient electronic implants integrated with other components of overall system.

Free-Standing Graphene Films Prepared via Foam Film Method for Impressive Performance Flexible Supercapacitors

Zhu Yucan, Xingke Ye, Hedong Jiang and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

In the present work, we have prepared a flexible nanocomposite film of polyvinylidene fluoride (PVDF) with hydrothermally synthesized ZnO nanorods embedded inside it. The flexible nanocomposite film shows an enhanced triboelectric effect. The triboelectric nanogenerator fabricated by coupling ZnO-PVDF flexible nanocomposite film with polytetrafluoroethylene (PTFE) shows a much enhanced triboelectric output of voltage of ~119 V and short circuit current of ~1.6 µA. The device gives an instantaneous output power of ~10.6 µW/cm². The instantaneous power is 65.6% more as compared to PVD/PTFE based TENG. Upon analysing the possible factors contributing the enhanced triboelectric effect of PVDF with the incorporation of ZnO into it, it is found that the enhancement in the triboelectric effect is due to (1) the increase in β-phase content of PVDF, which increases the polarizability of PVDF (2) increase in surface roughness and (3) increase in hydrophobicity of PVDF. Therefore, by embedding ZnO into the PVDF matrix, we achieved enhanced triboelectric effect of PVDF. This is a simple and novel approach for enhancing the triboelectric effect.

References

3. X. He, Q. Wen, Y. Sun, and Z. Wen, Nano Energy 40, 300 (2017).

Flexible Ferroelectric Nanocomposite Film for Enhanced Triboelectric Effect

Huidrom Hemojit Singh and Neeraj Khare; Department of Physics, Indian Institute of Technology Delhi, New Delhi, India.

Triboelectric nanogenerators (TENGs) are the devices which can convert low-frequency mechanical vibrations into electrical energy. These devices can be used for sustainable energy source as there are abundant mechanical vibrations like muscle contraction, body movement, vehicular movements, ocean waves, etc.[1-3] Moreover, these devices are easy to fabricate, robust and not costly. However, there is a need to enhance their output power so that it can be used effectively for driving the electronic devices.[1][4] In the present work, we have prepared a flexible nanocomposite film of polyvinylidene fluoride (PVDF) with hydrothermally synthesized ZnO nanorods embedded inside it. The flexible nanocomposite film shows an enhanced triboelectric effect. The triboelectric nanogenerator fabricated by coupling ZnO-PVDF flexible nanocomposite film with polytetrafluoroethylene (PTFE) shows a much enhanced triboelectric output of voltage of ~119 V and short circuit current of ~1.6 µA. The device gives an instantaneous output power of ~10.6 µW/cm². The instantaneous power is 65.6% more as compared to PVD/PTFE based TENG. Upon analysing the possible factors contributing the enhanced triboelectric effect of PVDF with the incorporation of ZnO into it, it is found that the enhancement in the triboelectric effect is due to (1) the increase in β-phase content of PVDF, which increases the polarizability of PVDF (2) increase in surface roughness and (3) increase in hydrophobicity of PVDF. Therefore, by embedding ZnO into the PVDF matrix, we achieved enhanced triboelectric effect of PVDF. This is a simple and novel approach for enhancing the triboelectric effect.
Highly Conductive and Flexible Composite Integrated with Personal Earphone for Simple, Wireless, Real-Time Monitoring of Electrophysiological Signs

Suk-won Hwang1, 1KU-KIST Graduate School of Converging Science and Technology, Korea University, SEOUL, Korea (the Republic of); 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2Kookmin University, SEOUL, Korea (the Republic of); 1Biomedical Engineering, Korea University, SEOUL, Korea (the Republic of).

Electroencephalogram (EEG) is one of most important noninvasive brain signal measurement method to diagnose various brain diseases on the scalp. With the advance of science and technologies, diverse EEG applications have been developed in various areas such as ubiquitous (U)-healthcare and brain computer interface (BCI). In addition, simple and insensible recording of EEG is highly required for EEG applications. Therefore, many different wearable EEG sensors have been developed for simple and comfortable EEG recording. However, conventional EEG sensors still have limitations such as ugly wearing, unreliability and inconvenience.

We introduce optimized elastomeric conductive electrodes using a mixture of silver nanowires (AgNWs) with carbon nanotubes/polydimethylsiloxane (CNTs/PDMS), to build a portable earphone type of wearable system that is designed to enable recording brain activities as well as listening to music at the same time. A custom-built, plastic frame integrated with soft, deformable fabric-based memory foam of earmuffs facilitates essential electronic components, such as conductive elastomers, metal strips, signal transducers and a speaker. Such platform incorporates with accessary cables to attain wireless, real-time monitoring of electrical potentials whose information can be displayed on a cell phone during outdoor activities and music appreciation. Careful evaluations on experimental results reveal that the performance of fabricated dry electrodes are comparable to that of commercial wet electrodes, and position-dependent signal behaviors provide a route toward accomplishing maximized signal quality. This research offers a facile approach for a wearable healthcare monitor via integration of soft electronic constituents with personal belongings.

B008.15.43
Flexible PVDF Based Nanocomposite Piezoelectric Nanogenerators for Enhanced Performance

Neeraj Khare and Huidrom Hemojit Singh; Department of Physics, Indian Institute of Technology Delhi, New Delhi, India.

The number of electronic devices used in our daily life has been increasing tremendously since the last decades. Several devices require only few milli-watt power. Piezoelectric nanogenerators based on the flexible piezoelectric polymers mainly Polyvinylidene fluoride (PVDF) is a path-breaking device that can power these small-scale electronic devices directly [1-2]. Although the intrinsic piezoelectric property of PVDF is low, many methods have been employed to enhance the piezoelectric property like thermal treatment, mechanical stretching and electrical poling [3].

In the present work, we will compare the performance of piezoelectric nanogenerator fabricated using various PVDF nanocomposite films. We have achieved enhanced piezoelectric property of PVDF just by adding nanostructures such as ZnO, NaNO3, BaTiO3 without any further heat, electrical or mechanical treatment. XRD, polarization-electric field (P-E) measurement, Fourier transform infrared spectroscopy (FTIR) measurements have been performed, and the reason behind this enhancement in the piezoelectric property has been analyzed and discussed. We have compared the enhancement by adding a different amount of nano fillers of different shapes, and this gives a brief idea of choosing the appropriate nano fillers for enhancing the piezoelectric property of PVDF. Comparison of the performance of these nanogenerators fabricated from PVDF nanocomposites will be presented.

References


B008.15.44
Stiffness Tunable (ST3R) Composite by Mechanical Actuation

Boyce S. Chang, Ravi Tutika, Michael D. Bartlett and Martin Thuo; Materials Science and Engineering, Iowa State University, Ames, Iowa, United States.

Smart responsive composites can be realized using various stimuli including heat, light, swelling, electricity, and magnetic fields to induce a change in material properties. Synthetic challenges, however, impede the fabrication of mechanically responsive materials. We report a thermodynamically driven mechanically responsive composite, exploiting irreversible phase-transformation (relaxation) of metastable undercooled liquid metal core shell particle fillers. As the composite is deformed, the core shell architecture is broken, leading to solidification of the undercooled liquid metal. This results in a 300% increase in Young’s modulus. In contrast to previous phase change materials, this dramatic change in stiffness occurs autonomously under deformation, is insensitive to environmental conditions, and does not require external energy sources such as heat, light, or electricity. We demonstrate the utility of this approach by transforming a flat, flexible composite strip into a rigid, 3D structure that is capable of supporting 50x its own weight. The ability for shape change and reconfiguration are further highlighted, indicating potential for multiple pathways to trigger or tune composite stiffness.

B008.15.45
Flexible Organic/Inorganic Hybrids for High-Performance Wearable Thermoelectrics

Zimeng Zhang and Shiren Wang; Texas A&M University, College Station, Texas, United States.

Flexible organic-inorganic hybrids are promising for high-performance wearable thermoelectric materials. However, current organic/inorganic hybrids suffer from inferior thermoelectric properties due to aggregate nanostructures. In this paper, we fabricate flexible organic-inorganic hybrids by incorporating monodispersed Bi2Te3 nanoparticles into the continuous conductive polymer phase at different loading fraction while no nanoparticle percolation is observed. Monodispersed and non-percolated nanoparticles significantly scatter phonons while continuous polymer phase facilitate the electronic transport, resulting in ultrahigh power factor of ~1350 µW m⁻¹ K⁻² and ultrawide in-plane thermal conductivity of ~0.7 W m⁻¹ K⁻¹. Consequently, figure-of-merit (ZT) of 0.58 is obtained at room temperature, outperforming all reported flexible thermoelectric materials. Thermoelectric properties of as-fabricated hybrids show negligible change for bending 100 cycles, indicating superior mechanical flexibility. These findings provide significant scientific foundation for shaping flexible thermoelectric functionality via synergistic integration of organic and inorganic components.

B008.15.46
3D Printing of Kirigami-Inspired Structures for Flexible Electronics

Derrick Banerjee, Murithi-David Kem, Xochitl C. Hernandez and Konstantinos Sierros; Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States.

Direct ink writing allows for the low-temperature processing of soft 3D functional materials with a wide range of applications from flexible batteries to soft
Design and Synthesis of PS-b-PSS Block Copolymer for Ionic Electroactive Artificial Muscles that avoids the need of mold fabrication. The flexibility of the proposed method also offers a simple method of fabrication of flexible wearables and soft fabrication of different types of microchannels was demonstrated. The proposed method is simple and offers a great potential in fabricating microchannels of fabricated PDMS filaments. PDMS can be easily made functional and writing can be achieved. By extending the concept of the proposed method, in situ diameters, which was driven by the applied pressure. The proposed method has the capability of writing PDMS (addition curing, heat curing as well as UV curing) with a broad range of viscosity. We evaluated the effect of dispensing head velocity (v) and curing time (t) (in case of addition curing) on the diameter of filament extruded through the nozzle. Different types of substrates—including rigid, soft and wearable substrates—were evaluated for adhesion curing) with a broad range of viscosity. We evaluated the effect of dispensing head velocity (v) and curing time (t) (in case of addition curing) on the diameter of filament extruded through the nozzle. Different types of substrates—including rigid, soft and wearable substrates—were evaluated for adhesion procedures were designed according to the application requirements. PS-b-PSS-EMIm has two distinct blocks enabling to handle the antagonistic properties somewhat independently. While conducting block containing full PDMS-EMIm enhances ionic conductivity, structural block with cross-linked PS provides mechanical stability. This polymer was synthesized by RAFT polymerization, and characterized by 1H NMR spectroscopy, gel permeation chromatography, double aberration-corrected transmission electron microscopy, field emission scanning electron microscopy, differential scanning calorimetry, and electrochemical impedance spectroscopy [6].

 herein, we describe an unprecedented block copolymer, polystyrene-b-poly(1-ethyl-3-methylimidazolium 4-styrenesulfonate) (PS-b-PSS-EMIm), which was designed according to the application requirements. PS-b-PSS-EMIm has two distinct blocks enabling to handle the antagonistic properties somewhat independently. While conducting block containing full PDMS-EMIm enhances ionic conductivity, structural block with cross-linked PS provides mechanical stability. This polymer was synthesized by RAFT polymerization, and characterized by 1H NMR spectroscopy, gel permeation chromatography, double aberration-corrected transmission electron microscopy, field emission scanning electron microscopy, differential scanning calorimetry, and electrochemical impedance spectroscopy [6].

The as-produced actuator was investigated over wide-range conditions. At ultra-low voltage of 0.5 V, the actuator exhibited high displacement of 8.2 mm (0.37 % strain), no back relaxation, excellent durability over 14,000 cycles, and fast response of five seconds. Such short rise time is 12 and 120 times smaller than those of PSS-b-PMB and SSPB, respectively [4,5]. These excellent performances demonstrate the proper design and successful synthesis of PS-b-PSS-EMIm, together with the potential of the actuator for applications. We also expect the use of our approach in preparing novel polymers for related fields like fuel cells and solid-state lithium battery.

SESSION BM08.16: Wearable/Flexible Actuators/Sensors
Session Chairs: Kyu-Jin Cho and Wooshul Kim
Friday Morning, November 30, 2018
Hynes, Level 2, Room 209

8:15 AM BM08.16.01
Low Power Flexible Electrostatic Transducers for Haptic Communication Jan Trase1, Zhe Xu1, Xiaomin Han1, Yin Liu1, Frances Lau2, Ali Israr2, Zi Chen1 and John X. Zhang1; 1Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, United States; 2Facebook Inc., Menlo Park, California, United States.

Introduction: Long-range communication has occurred exclusively through visual and auditory means, which disadvantages those for whom these modes of communication are inconvenient or impossible. Current social networking infrastructure does not adequately reproduce normal communication, which
can involve touch when face-to-face. No current integrated wearable technology enables touch-at-a-distance, where the transducer would allow a user's touch to be recorded, digitized, and represented on a remote device. We design a matrix of low-power flexible electrostatic transducers (FETs) with air-gap coupling to the skin for both actuation and sensing functionalities. We then demonstrate the usage of these wearable transducers, which can detect simple sensations from and transmit forces to the skin.

Materials and Methods: We use curved electrodes, flexible substrates, and mechanical buckling to create low-voltage electrostatic actuators that generate large forces over macroscopic distances. The actuators are composed of a pair of Kapton film insulators coated with gold electrodes. One film is buckled and affixed to the other, generating motion when voltage is applied as the films move together and apart. The force sensors are made of porous polyvinylidene fluoride (PVDF), a biocompatible piezoelectric polymer. The device was mounted to a group of subject's forearms to determine comfort and perceptibility.

Results and Discussion: We determined that for optimum perceptibility and comfort, the device should operate at voltages under 500V and frequencies under 100Hz. The electrostatic airgap transducers were found to deliver perceptible forces to the skin when operated with a 500V 1-100Hz signal. The actuator reached its maximum displacement at around 500V, and further increases in voltage did not lead to significant changes in perceptibility. The sensor had a minimum detection threshold of 0.5N, and the voltage output rose linearly with force until 1.5N. We also conducted a pilot user study in which force and comfort were measured at 1, 5, 10, 20, 50, and 100Hz. Users were able to feel the device and qualitatively characterize the frequencies at frequencies above 5Hz. Low frequencies were more comfortable than high frequencies, and maximum comfort was achieved at 5Hz. Conversely, frequencies above 100Hz were found to be less comfortable.

Conclusions: We demonstrated a wearable electrostatic transducer with significant potential to provide a new mode of communication using human touch. The displacement and force results indicated that perceptibility is achievable in low-power situations. The actuator was able to generate displacements of up to 4mm at 500V, and 2mm at 100V. This technology will both allow for communication in situations where auditory or visual communication is difficult, as well as greatly enhance the quality of remote communication for social networking.

8:30 AM *BM08.16.02
Exo-Glove Poly II—Soft Wearable Robot that Enables People with Hand Disabilities to Grasp
Kyu-Jin Cho, Soft Robotics Research Center, Biorobotics Lab. Dept. of Mechanical Engineering, Seoul National University, Seoul, Korea (the Republic of)

Recently, owing to the rapidly increasing number of individuals suffering from spinal cord injury (SCI) and stroke, many wearable devices have been developed to assist with activities of daily living (ADLs) or to help rehabilitation. But there is still a big gap between the users and the technologies that are available, to cope with the wide variety of needs for the people with disability to live an independent life. Seoul National University Biorobotics Lab has been developing soft wearable robots that can meet the unmet needs of the people with disability. Examples include a device that can be used to pressure the belly of people who lost the ability to use their abdominal muscles to help them breathe, speak and even sing, and a simple glove that can be worn by people who cannot move their fingers to enable them to hold various objects. In this presentation, we will present Exo-Glove Poly II, a polymer based soft wearable robot for the hand that enables people who lost their hand function to grasp various objects with their hand. Exo-Glove Poly II is built using polymer for comfort of the user and easy sanitization. Exo-Glove Poly II is composed of wearable body, a glove, and actuation system. Design features to allow adjustment to different hand sizes and to protect users from injury were implemented. To verify the grasping performance of the robot, various experiments were conducted with two SCI patients with lost hand mobility. By restoring the hand function with this assistive technology, we hope that more people with disability will be able to live a better independent life.

9:00 AM BM08.16.03
Mechanics-Guided Design of Active Material—Hard-Magnetic Soft Actuator Ruike Zhao1, 2, Yoonho Kim1, Shawn A. Chester1 and Xuanhe Zhao1, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2The Ohio State University, Columbus, Ohio, United States; 3New Jersey Institute of Technology, Newark, New Jersey, United States.

Composed of polymeric matrices embedded with magnetic responsive particles, magnetoeactive soft materials can rapidly and dramatically deform under magnetic fields. Since existing magnetoeactive soft materials mostly rely on paramagnetic or low-coercivity ferromagnetic particles, they usually give simple deformations such as elongation and compression under applied magnetic fields. Recently, high-coercivity ferromagnetic particles have been embedded in magnetoeactive soft materials, in which complex patterns of hard-magnetic domains can be programmed by three-dimensional printing. As the applied magnetic fields generate stresses and torques on hard-magnetic domains, the hard-magnetic soft materials with patterned domains can give rapid, untethered and complex modes of deformations, leading to new applications in soft robotics, flexible electronics and biomedical devices. This paper will aim to develop a framework of theory, constitutive law and computational model for hard-magnetic soft materials, in order to facilitate rational design of new materials, structures and devices. We adopt a nonlinear field theory that accounts for finite deformation coupled with magnetic fields in soft materials. We propose a new constitutive law named ideal hard-magnetic soft materials and implement it into numerical models with finite-element simulation. The theory, constitutive law and numerical model are validated with a set of experiments on various modes of deformations of hard-magnetic soft materials. In addition, the mechanics-guided complex structures of the 3D-printed hard-magnetic soft materials with programmed magnetic domains are demonstrated.

9:15 AM BM08.16.04
Supramolecular Biomimetic Skins Combining a Wide Spectrum of Mechanical Properties and Multiple Sensory Capabilities Peiwei Wu1, 2; 1Department of Macromolecular Science, Fudan University, Shanghai, China; 2Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China.

Biomimetic skin-like materials, capable of adapting shapes to variable environments and sensing different external stimuli, are of great significance in a wide range of applications including artificial intelligence, soft robots and smart wearable devices. However, such highly sophisticated intelligence has been mainly found in natural creatures while rarely realized in artificial materials. Herein, I will introduce several types of supramolecular polyelectrolytes with different molecular interactions to fabricate biomimetic iontronics and imitate natural skins. Their dynamic viscoelastic networks provide the biomimetic skins with a wide spectrum of mechanical properties, including flexible reconfiguration ability, robust elasticity, extremely large stretchability, autonomous self-healability and recyclability. Meanwhile, polyelectrolytes’ ionic conductivity allows multiple sensory capabilities towards humidity, temperature, strain and stress. Furthermore, in this presentation, I will share insights on the soft material design from the perspective of molecule-level dynamic interactions and hope they are inspiring for facile preparation of artificial neurosensory and neuromuscular systems.

9:30 AM BM08.16.05
Flexible Metasurfaces for Versatile Haptic Interfaces Osama Bilal1, Vincenzo Costanza1, Antonio Palermo1, Paolo Celli1, Ali Israr2, Frances Lau2 and Chiara Daraio1; 1California Institute of Technology, Pasadena, California, United States; 2Facebook, Palo Alto, California, United States.
Haptic feedback is the most significant sensory interface after visual cues. Developing thin, flexible skins that function as haptic interfaces is important for augmenting virtual reality, wearable devices, robotics and prosthetics. For example, adding a haptic feedback interface to prostheses could improve their acceptance among amputees. State of the art haptic technology is still limited by inadequate sensory feedback or complicated actuation mechanisms. Here, we present flexible metasurfaces designed for generic haptic interfaces. When actuated, the metasurfaces can produce complex tactile patterns on the human skin. The metasurfaces are composed of multiple resonant "pixels" that can locally amplify both input displacements and forces. Each of these pixels encodes various deformation patterns capable of producing different sensations on contact. The metasurfaces transform a harmonic signal containing multiple frequencies into a complex preprogrammed tactile pattern.

9:45 AM

Three-Dimensional Microporous Pressure Sensor Fabricated Using Droplet-Based Microfluidic Assisted Emulsion Self-Assembly Jin-Oh Kim and Steve Park; Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of).

Pressure sensors have been a subject of great interest over the past decade, with a wide-variety of exciting applications such as interactive wearable electronics, health monitoring systems, touch screens, and soft robotics with human-like functionalities. Large area processability, flexibility, high sensitivity, ability to sense both low pressure and high pressure range, and high spatial resolution and uniformity are some of the key features necessary for various pressure sensing applications. A variety of methods to detect pressure have been reported such as piezoresistance, capacitance, piezoelectric, optics, and inductance.

Polydimethylsiloxane (PDMS) is often chosen as the dielectric material due to its ease of processability, compliance with human body, and biocompatibility. However, PDMS has a relatively high compressive modulus, yielding devices with low sensitivity. To overcome this issue, PDMS has been microstructured using silicon mold. However, these devices generally lose their sensitivity when pressure exceeds tens of kPa. This restricts their applicability to devices that require large pressure sensing range (e.g. devices that mimic human skin require pressure sensing range of –0.1—100 kPa).

To expand the pressure sensing range, we present a novel droplet-based microfluidic assisted emulsion technique to generate 3-dimensional microporous structure for high performance capacitive pressure sensors. Our technique can generate uniformly sized pores assembled in an orderly close-packed manner over a large area without the use of any sacrificial template. The size of the pores can easily be tuned from 100 μm to 500 μm by adjusting the relative flow rates of the oil and aqueous solutions. The sensitivity of the sensors increased with increasing pore size to as high as 0.85 kPa⁻¹, which can be attributed to the relatively low pressure needed to induce buckling of the columns between the larger pores. Our sensor also exhibited high pressure sensing range up to 100 kPa and high spatial uniformity. Furthermore, we have combined our technique with standard replica molding to generate 3-dimensionally shaped microporous pressure sensors, through which sensitivity was further enhanced to 2.45 kPa⁻¹. Lastly, we have adhered our sensors to human body to detect subtle human motions. These demonstrations of facile and area-processability, high sensitivity, large pressure sensing range, and high spatial uniformity make our device unique and promising for many future pressure sensing applications.

10:00 AM BREAK

10:30 AM BM08.16.07 Highly Flexible Multi-Modal Capacitive Pressure Sensor Responsive to Tactile and Wide Pressure Range Haechang Lee, Hanul Moon, Hyukyun Kwon and Seunghyup Yoo; School of Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Flexible pressure sensors have been attracting great amount of attention as they are key elements in realizing artificial skin, friendly human-machine interface, and wearable healthcare products. To apply pressure sensors to the aforementioned applications, they should not only be highly sensitive in low pressure region to detect tiny stimuli such as tactile or blood pulse, but be operable over a wide pressure range as well to catch up with the performance of human skin. In addition, they need to be thin enough as it can be applied to high flexible products. For this reason, film-type pressure sensors using a variety of materials and structures have been studied. However, it has been challenging to realize a wide pressure sensing range and high flexibility at the same time, because there is a trade-off relation between dynamic range and thickness of the pressure sensors. Furthermore, the problem becomes more difficult considering a multi-modal sensor having high sensitivity in low pressure region as well.

In this study, we propose a flexible capacitive pressure sensor using a structured ionic gel film as a dielectric layer whose capacitance is responsive to applied pressure. The ionic gel film is largely beneficial for high sensitivity attributed to ultra-high capacitance based on electric double layers, and it has suitable mechanical properties as a pressure sensing material because it has low Young’s modulus similar to that of rubber. By structuring the surface of the ionic gel film in several micro-meter scale to utilize confined air between the ionic gel and an electrode, linear response to large pressure range of over 100 kPa was secured. In addition, the complete pressure sensor can be highly flexible because the thickness of the ionic gel film can be reduced near or even below 10 μm. By using an appropriate surface structure of ionic gel film, the sensor shows distinguished response to low and high pressure regions, and it has multimodal sensing capability for tactile and pressure signals by adjusting high sensitivity in low pressure region, 1.1 kPa⁻¹ in the region below 700 Pa.

By using several μm-thick plastic substrates at both bottom and top sides of the ionic gel film, the overall thickness of the pressure sensor can be ca. 20 μm, thus finally the sensor has high flexibility, e.g. foldability or wrinklability. Together with multi-modal sensing capability with high sensitivity and large pressure range, we believe the proposed pressure sensor can be used for the applications requiring both high flexibility and high performance such as wearable or body-attachable devices, and thus will be a key role to realize artificial skin for prosthetic bodies and smart healthcare.

10:45 AM BM08.16.08 Programmable Artificial Muscles with a Feedback Mechanism Mehmet Kanik4, Sirma Orguc2, George Varnavides1, Jinwoo Kim1, Thomas Benavides3, Dani Gonzales4, Timothy Akintilo1, C. Cem Tasan1, Anantha P. Chandrakasan2, Yoel Fink3,4 and Polina Anikeeva1,4; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 5Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 1Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Mammalian muscles exhibit exceptional strength, reliability, ability to self-heal, and responsiveness. Engineering actuators with comparable characteristics for robotics applications require developing materials with properties similar to biological muscles. Current robots use hydraulic and servo actuators; although recent studies have focused on ionic materials or elastomers that can be actuated by heat or electricity, none have yet surpassed the performance of the mechanical systems. Furthermore, fabricating such artificial muscles with high yield and at low cost remains to be demonstrated. Here, we report thermally actuated “artificial muscle” devices produced via a cost-effective iterative thermal fiber drawing technique, which mimics the strength and responsiveness of biological muscle. These fiber-based artificial muscles can be manufactured across size ranges from macro to micro.

To achieve actuation in fibers, we sought out to create bimorph structures by combining two materials with high and low expansion coefficients, respectively: for example, an elastomer and a high-performance engineering polymer. To prototype this approach, we have demonstrated several “muscle”
types using cyclic olefin copolymer elastomer (COCe) and polyethylene (PE). The bimorph fibers were thermally drawn from macroscale preforms and three subjects to elongation stress (cold drawing). Cold drawing created an excessive strain on PE and COCe components, and upon release, the strained fibers assumed a helical shape due to the high resilience of COCe and high plastic deformation in PE. The strained fibers could then be actuated thermally and were outfitted with silver nanowire mesh electrodes to provide feedback akin to the biological muscle. By controlling the fiber dimensions and the built-in strain, the strength and the temporal dynamics of the artificial muscles were engineered.

The observed actuation and feedback of the reported fiber-based artificial muscles indicate their potential utility in robotics, haptics, and prosthetics, at a significantly lower cost and higher throughput than existing actuator technologies.

11:00 AM BM08.16.09
Bioinspired, SWCNT-Coated, Micro-Hexagonal Array Based Electronic Skin for Mechanical Sensing Changwoon Jeong, Seonghwan Lee and Young-Bin Park; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Highly sensitive, flexible electronic skins (e-skins) with multi-modal, vibration sensing ability is of great interest for various applications, such as tactile sensing in robots, earthquake monitoring, human healthcare and wearable electronics. Here, we present an e-skin based on bioinspired, micro-hexagonal pillar arrays coated with single-walled carbon nanotubes (SWCNTs). The interlocking configuration between the meshed arrays allows stable sensing performance under both static and dynamic mechanical stimuli, including pressure, shear, and bending through the piezoresistive principle. Furthermore, the optimized interlocking geometries based on micro-hexagonal pillar arrays show enhanced sensitivity and ability to differentiate various modes of mechanical loading owing to the surface contacts between the microstructures, whose contact-separation behavior depends on the type of loading. We also showed that our e-skin can detect internal and external vibrations for various applications, including earthquake monitoring, smart phone detection and voice recognition, and demonstrated that they can measure different types and intensities of vibration.

11:15 AM BM08.16.10
Flexible Optomechanical Actuators Based on Light-Induced Demagnetization of Low Curie Temperature Composites Meng Li1, Yu Wang1, Aiping Chen1, Bradley Napier1, Wenyi Li1, Scott Crooker1 and Fiorenzo G. Omenetto1; TufTs University, Medford, Massachusetts, United States; 2Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Actuators are components that are used to move a mechanical system or perform shape morphing under certain stimulus. Among various stimuli, light has distinguishing advantages of non-contact control, and being capable of localized actuation with high resolution. Most optomechanical devices can perform simple movement such as bending, twisting, or expansion with simple light modulation. However, it is only with complicated light patterning or structured design that they can achieve complex movement like rotating, folding, walking or waving. There are many situations where complex modulations cannot be enacted, and the versatility is limited by the specific design. In this work, we introduce an approach of wireless actuation based on optically-induced demagnetization which provides multiple opportunities for shape morphing and deformation in response to light to easy-to-use formats. We fabricate light-responsive magnetic composites by incorporating CrO2, in multiple flexible, elastomeric, and mechanically robust, durable materials. Because of their polymorphic nature along with their flexibility and high failure strain, biopolymers (silk fibroin) and elastomers (PDMS) are used as magnetically inert host material matrices for ferromagnetic dopants. When illuminated, the composite is capable of macroscale motion, through the interplay of optically-absorptive elements and low-Curie temperature magnetic materials (CrO2). These composites can be formed into films, sponges, monoliths and hydrogels, and can be actuated with light at desired locations. With no need for specific pattern design and complicated light modulation, we have successfully demonstrated a gripper that is activated by stationary light and is able to grab and release objects. The gripper experiences cyclic tightening and loosening, which has the potential for continuous object gripping and relocation. The combination of magnetic force and localized laser illumination can achieve more complex actuation patterns, other than bending and twisting. A Curie rotary engine powered by light is demonstrated at a rotation speed of 2 rpm. The concepts presented here represent a comprehensive baseline of a composite platform that merges optical and mechanical and magnetic functions. We believe that this approach offers an interesting platform to achieve delicate and desired light-induced motion with easily accessible equipment and facile manufacturing processes, opening opportunities for manufacturing flexible, simple, and cheap actuators at multiple forms from the micro- to the macro-scale.

11:30 AM BM08.16.11
Multifunctional Smart Electronic Glove for Robotic Prosthesis Controls Min Ku Kim1 and Chi Hwan Lee1, 2, 3; 1Biomedical Engineering, Purdue University, West Lafayette, Indiana, United States; 2Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; 3Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States.

The human hand is one of the foremost part of the body in a physical interaction serving as an indispensable instrument to our daily lives. Therefore, any form of disfiguration or loss of the limb can negatively affect quality of life. Current evidence-based interventions demonstrates using robotic prosthetic hands as a supplementary movement aid to restore vital mobility. Recent developments of artificial electronic skin embedded with thin-film based flexible sensors can provide valuable functionality to sense external stimuli, thereby imitating humanlike sensory perception. Despite these technological advances, the devices suffer from difficulties in seamless integration of electronic skin with pre-existing robotic prosthetics, leading to poor physical bonding and degradation of sensor performance. Moreover, the price of these instrumented prosthetics remains consistently high due to the expensive materials used and limited production numbers due to advanced fabrication methods involved, ultimately discouraging its use and adaptation in cost affordable settings. This talk outlines materials, mechanistic design features and rapid prototyping fabrication methods employed for an innovative multifunctional smart electronic glove (or simply e-glove) that can be easily worn onto arbitrary robotic hands to simultaneously replicate the humanlike sensory perception, appearance, skin compliance, and body warmth in a simple, monolithic manner. A demonstrative e-glove system includes mechanically stretchable multimodal sensors that can detect changes in temperature, pressure, and hydration in a wireless fashion. Experimental and theoretical analyses reveal the underlying mechanics of the e-glove during prosthetic fitting and use.

11:45 AM BM08.16.12
Orthogonal Sensor Arrays by Selective Material Design Nicolay J. Pineau, Julia F. Kompalla, Andreas T. Güntner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Wearable devices for continuous monitoring of health parameters could allow personalized health care by guiding therapies, diets, exercise or detect diseases. Human chemical emissions through breath and skin are rich in physiological information, similar to blood assay. Especially the noninvasive monitoring of specific disease- or metabolic-related markers by nanostructured metal oxide gas sensors is promising, as they respond in real-time and feature sizes smaller than the tip of a match. Therefore, they could easily be incorporated into portable or wearable devices. Particularly interesting markers are ammonia, ethanol and acetone, being related to an impaired urea cycle due to kidney or liver disease, gut bacteria and fat metabolism, respectively. Here flame aerosol made nanostructured gas sensors were produced and systematically tailored (e.g. particle size, shape and film morphology) for distinct selectivity to ammonia, acetone and ethanol. An orthogonal array consisting of the individual materials was assembled and tested in 69 different 3-gas
mixtures containing random but realistic concentrations of ammonia (250-2000 ppb), acetone (250-1800 ppb) and ethanol (50-600 ppb), simulating human breath. The here presented array quantified all analytes in the realistic gas mixtures with high accuracy, precision, and high coefficients of determination ($R^2 > 0.88$) needed for real-life applications. As a result, this sensor array shows high potential as compact module for portable or wearable devices for the noninvasive monitoring of metabolic related ammonia, acetone and ethanol in real-time, or could be used to detect entrapped humans after an earthquake.\textsuperscript{a}

\begin{thebibliography}{1}
\bibitem{2} Davies, S., Spanel, P.; Smith, D., \textit{Kidney Int} (1997), 223-228.
\end{thebibliography}

SESSION BM08.17: Energy Conversion/Transfer and Devices

Session Chairs: Svetlana Boriskina and Hong Wang

Friday Afternoon, November 30, 2018

Hynes, Level 2, Room 209
Enhancement and optimization of the receiving input power density is a key to many applications that requires maximizing the energy input, such as energy harvesting, small signal sensing, etc. Normal incidental illumination is the most direct way to maximize the input power density when the input energy is in a form of parallel electromagnetic wave. In nature, many plants have developed phototropism to spontaneously sense and track the light source and maintain their disk to be illuminated normally to the photonic input. By tracking the sun, the sunflowers are able to efficiently raise the temperature of their disk in the morning in time to attract more visits of the pollinators. Tree leaves could also track the sunlight to obtain the highest temperature they can to extract water from the root. Currently there is no synthetic material system can omnidirectionally sense, track and harvest the input emissive energy. In this work, we report a soft material system that can self-adaptively track the energy source whichever the direction of the source goes. We proposed a physically symmetric system based on photo-sensitive polymers. Input photonic energy shines on the geometrically symmetric hydrogel system and induce non-symmetric temperature gradient. The polymer will automatically bend toward the light source. The bending will be terminated when the top of the material points direct to the light source. We studied the tracking system with a simple mechanical model and FEA simulation. The hydrogel system has been optimized to achieve fast and omni-directional real-time tracking in all direction. The light tracking is as fast as 30 degrees per second and the tracking performance covers 360 degrees of azimuthal plane. The error of tracking accuracy is better than 1%. A demonstration of an omni-directional solar vapor generator that maintain > 90% solar energy harvesting even under large incident angles has been achieved. The enhancement of energy harvesting reaches as high as 423% over non-tropistic surfaces, indicating a significant compensation of energy harvesting in the case of the angular incidence attributed to the tracking functionality. We believe that the proposed material system can be applied in many applications that require maximizing their energy input.

2:30 PM BM08.17.04

3D Printed Flexible and Transparent Polymer Piezoelectric Generators for Powering Electronic Devices Nick Adamson1, Alexey Glushenkov1, Mitchell Sessio2, Vanessa Lussini1, Phillip Fox1, Greg Dicinoksl1 and Amanda V. Ellis1; 1Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria, Australia; 2Department of Engineering, La Trobe University, Bundoora, Victoria, Australia; 3Note Issue Department, Reserve Bank of Australia, Craigieburn, Victoria, Australia.

The global need for sustainable and green power generation methods has resulted in renewable energy harvesting technologies such as photovoltaics. This method has low energy conversion efficiencies <15% and only operates at maximum efficiency in direct sunlight. For the purposes of always-on, self-powered sensors and wearable electronics, novel reliable energy scavenging techniques are required. Piezoelectric generators convert mechanical energy from external sources to electricity, with energy conversion efficiencies >35%.

Despite the promising nature of piezoelectric polymers, they are difficult to process into the polar (all- trans) β phase, with high energy methods commonly utilized as an additional step to orient dipoles after deposition as thin films. The β phase of fluoropolymers is desired as it exhibits the highest electromechanical coupling properties. Shear stresses have previously been found to reorient fluoropolymers into the polar β phase. Our computational fluid dynamics models show high shear stresses at the exit of pressure-based 3D printing nozzles, showing the potential for 3D printing techniques to induce the β phase. Increases in aspect ratio of the polymers are linked to an improved electrical output, further enhancing the potential of 3D printing as a deposition method for polymer piezoelectric generators. Recent literature investigating effects of ionic additives to fluoro polymers suggests increased re- orientation from non-polar to polar phase due to ion-dipole interactions, with further enhancement upon doping with low (<1 wt %) concentrations of graphitic carbon nanomaterials (such as carbon nanotubes).

This study presents the prospects of 3D printing of fluoropolymers for their use as piezoelectric generators, removing the requirement of post-processing to align dipoles. The scope for the use of 3D printed piezoelectric polymer microstructures as a method of enhancing voltage output up to 4.5x over that of thin films is discussed. Diffusion kinetics of solvent evaporation-assisted 3D printing is investigated and linked to nucleation into β phase and hence additional increases in voltage of 2x at optimised conditions. Further self-orientation of 3D printed fluoropolymers at room temperature is shown through the utilization of polymer-ionic liquid additive matrices, previously only used in high temperature processing such as melt mixing and extrusion.
Wearable electronics and smart textiles have attractive much attention, because they are expected to monitor biometric information with high precision. One of their major bottlenecks is a power solution to continuously supply electricity to health-monitoring sensors. In particular, it is important to solve this issue when long-term monitoring is required. In this presentation, we will report on recent progresses of ultraflexible organic photovoltaic cells and wireless power transmission for applications to smart apparel and wearables. First, we describe mechanical and environmental stability of ultrathin organic photovoltaic cells. Then, we will explain remaining issues and future prospects of power solutions for wearables.

4:00 PM BM08.17.07
Graphene-Based Nanocellulose Composites for 3D Printed Electrodes
Taylor J. Morrison¹ and Hani E. Naguib², ¹, ²; ¹Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada; ²Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada; ³Institute of Biomaterials & Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada.

Academic interest in additive manufacturing (AM) is rapidly growing as researchers work to find new ways this innovative technology can be applied to revolutionize product prototyping and production in various industries. One of the fields in which there is excellent opportunity for advancement is energy storage. There is a growing demand for specialized energy storage devices due to the increased prevalence of integrated electronics across a wide range of applications. Rising technologies such as wearable electronics, internet-of-things products, and advanced biomedical devices could see significant benefit from mobile power supplies that are more physically versatile and energy dense than what is currently available. The performance and functionality of electrochemical energy storage (EES) devices, namely batteries and supercapacitors, could be significantly improved by the precise control and efficiency offered by AM technologies. AM enables intricately detailed design of both the physical structure and material composition of the final product. Therefore, by employing AM techniques, the components of EES devices could be precisely engineered to maximize performance while fulfilling the specific physical criteria required by the end application.

In this study, graphene-based nanocellulose composites suitable for direct ink writing are developed with the purpose of manufacturing EES electrodes with unique structures on both the macro and nanoscale. Cellulose was selected as the material of focus because of its natural abundance, which would allow cellulose-based inks to be made both sustainably and cost-effectively. Furthermore, when broken down to nanocellulose (NC), this advanced material offers high surface area nanostructures and viscoelastic properties advantageous to this application. In this work, graphene-based materials, including reduced graphene oxide and pristine graphene, are added to NC to create an electrically conductive network. The nanostructures of these inks are examined, and their printability assessed. Additionally, a variety of 3D supercapacitor geometries are printed and tested for electrochemical performance, achieving a maximum specific capacitance of 46 F/g at 5 mV/s.

4:15 PM BM08.17.08
The Role of Responsive Polymers and Hydrogels in ‘Smart’ Material Systems
Raymond Oliver¹ and Lynn Tandler²; ¹Northumbria University, Newcastle upon Tyne, United Kingdom; ²Fashion and Textiles, Royal college of Art, London, United Kingdom.

We are living in an age of technological convergence. Early 21st century materials science and fabrication, when coupled with creative design fundamentals, provide a new and compelling view that can drive innovative applications and manufacturing solutions that also meet human centred needs. This paper demystifies the idea of smart fabrics and discuss current and future developments in woven textiles, their formation and potential use in new product formation scenarios.

Woven textiles are material systems governed by the principles of structural hierarchy. It is this inherent structural complexity that attributes woven textiles with a unique set of properties and, which gives them a performance advantage over other textiles forms. Today, so-called ‘smart’ textiles are beginning to take centre stage due to the majority of accounts still holding to the belief that any piece of textile that presents properties over and above those of conventional textiles is worthy of the description smart. However, the problem here is that smartness in textiles is viewed as a synonym for responsive behaviour: something that is susceptible to changes in the environment such as moisture, temperature, light, electrical current, pH, chemical or pathogen driven external stimuli. This assumption is very misleading since we find from our own work that nearly all textile components are susceptible to changes in the environment to some extent and when we deal with worn apparel, the ‘around body’ stimuli become real and often spasmodic. Therefore, we set out to investigate the claim that a textile as a smart object is to order over claim and presume that the relationship between the inherent properties of materials and the technology on which the material systems are produced are in sync. We will present evidence based data that highlights the responsiveness of different fibres and yarns to support the argument that there are no smart textile materials, only smart textile material systems.

The study indicates revisiting the principles of woven纺织的材料系统是基于结构层次性的。它是由这种内在的结构复杂性所赋予的，赋予了纺织物一种独特的特性，赋予了纺织物性能的独特优势，赋予了纺织物与其他纺织物形式的不同之处。今天，所谓的“智能”纺织物正在崭露头角，因为大多数的账户仍然坚信，任何具有纺织物以外的纺织物自定义的纺织物是值得描述为智能的。然而，这里的问题是，智能性在纺织物中被视为一个同义词，即响应性行为：对环境的敏感性，如湿度、温度、光、电流、pH、化学或病原体驱动的外部刺激。这种假设是非常误导的，因为我们发现我们的工作表明，所有纺织物的组件都对环境的变化敏感，而且在处理穿着的服装时，这种“身体周围”的刺激会变得现实并经常是间歇性的。因此，我们设定的目标是，为了证明纺织物不是一个纺织物材料，只有一种纺织物材料系统。

4:30 PM BM08.17.09
Stretchable Thermoplastic Elastomer Optical Fibers for Sensing of Extreme Deformations in Wearable Devices
Andreas Leber¹, ², Beth Cholst¹, Joseph Sandt¹, Nicolas Vogel¹ and Mathias Kolle¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany.

The design of advanced materials with coupled optical and mechanical properties is an important challenge in materials science. Soft optical systems are particularly versatile for sensing applications in wearable technology, where large and repeated deformations require dynamically responsive materials. To this end, we present stretchable step-index optical fibers, which are capable of reversibly sustaining strains of up to 300% while guiding light. We form these fibers using a continuous and scalable melt-flow process to co-extrude two thermoplastic elastomers. The fibers can be stretched, bent, and indented, which induces detectable, predictable, reversible, and wavelength-dependent changes in light transmission. The fibers utility in sensing scenarios is demonstrated in a knee brace for continuous knee motion tracking, a glove for control of a virtual hand model, and a tennis racket capable of locating ball impacts. Such devices, integrated into wearable textiles could greatly improve quantitative assessment of human motion in rehabilitation, sports, and anywhere else where large deformations need to be monitored reliably.

4:45 PM BM08.17.10
Self-Powered Wireless Optical Transmission of Mechanical Agitation Signals
Wenbo Ding and Zhong Lin Wang; Georgia Institute of Technology, Atlanta, Georgia, United States.

The ubiquitous sensors have accelerated the realization of Internet of Things (IoT) but also raised challenges to the current overcrowding radio frequency
(RF) based communications. The optical wireless communications (OWC) that utilize the wide optic bandwidth can well solve the spectrum crisis and is an appealing complementary solution to the IoT applications. However, the additional direct current (DC) power supply and complicated modulating and power management circuits may limit the large-scale deployment of OWC systems. In this paper, by integrating with triboelectric nanogenerators (TENGs), the light-emitting diode (LED) could be directly transformed into a wireless transmitter that conveys the information associated with mechanical stimuli without additional power supply. With the customized TENG devices and the help of advanced image processing and machine learning techniques, three demonstrations with functions of optical remote control, pressure sensing, and security authentication, were demonstrated. The concept and results in this paper may greatly broaden the application of IoT through the integration of OWC and TENG.

SYMPOSIUM BM09

Bioinspired Macromolecular Assembly and Inorganic Crystallization—From Tissue Scaffolds to Nanostructured Materials
November 26 - November 30, 2018

Symposium Organizers
Chun-Long Chen, Pacific Northwest National Laboratory
Nico Sommerdijk, Eindhoven University of Technology
Tiffany Walsh, Deakin University
Shuguang Zhang, Massachusetts Institute of Technology

Symposium Support
Pacific Northwest National Laboratory

* Invited Paper

SESSION BM09.01: Biomimetic Materials Based on Peptide Self-Assembly
Session Chairs: Chun-Long Chen and Nathaniel Rosi
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Back Bay A

8:00 AM BM09.01.01
Self-Organization of Peptides in Bioinspired Vesicles—Role of Relative Concentration and Helical Separation
Akash Banerjee and Meenakshi Dutt; Chemical and Biochemical Engineering, Rutgers University, Piscataway, New Jersey, United States.

Biological cells can inspire the creation of nanoparticles equipped to store and release hydrophobic drug molecules upon demand. Lipid vesicles impregnated with alpha-helical peptides have demonstrated the clustering of the peptides under equilibrium. The formation of thick, amphiphilic, transmembrane channels via the self-organization of the peptides could be potentially used for the on-demand release of small drug molecules from the hydrophobic core of a vesicle bilayer. We are interested in understanding the driving forces responsible for cluster formations and evaluating their effects using the Molecular Dynamics simulation technique. Coarse grained representations of the molecules are used to resolve the extended spatiotemporal scales relevant to the problem at hand. The bonded and non-bonded interactions between the particles is captured by the Martini force field. We investigate the role of peptide concentration and helical separation on the cluster formation. We find the cluster size to be dependent more on helical separation as compared to peptide concentration. Additionally, we test the role of hydrophobic mismatch to understand the effect of electrostatic interactions between the peptides and lipid molecules. Our results demonstrate negative mismatch to result in larger cluster sizes as compared to a zero hydrophobic mismatch condition due to larger perturbations in the vesicle monolayers.

8:15 AM BM09.01.02
Self-Assembly of Membrane-Active Peptides into Macromolecular-Size Pores
Kalina Hristova1, Sijia Li1, Sarah Kim1, Anna Pittman2, Gavin King2 and William Wimley1; 1Johns Hopkins University, Baltimore, Maryland, United States; 2University of Missouri, Columbia, Missouri, United States; 3Tulane University, New Orleans, Louisiana, United States.

Peptides that self-assemble into pore-like structures in lipid bilayers could have utility in a variety of biotechnological and clinical applications due to their ability to breach the barrier imposed by lipid bilayers. To empower such discoveries, we use rationally designed peptide libraries and high-throughput screens to select peptides based on a particular property, in this case macromolecular-size bilayer poration. Towards this goal, we designed a library based on the bee venom peptide melittin, and we developed a high throughput screen that reports on the passage of macromolecules across lipid bilayers. We identified two peptide families that efficiently assemble into large pore-like structures. One of the families is highly active at pH 7. The other peptide family is pH sensitive, as its self-assembly is triggered by low pH. The pH-triggered peptides could be used for endosomal release of uptaken polar molecules into the cell cytosol, upon endosomal acidification. They also could be used in cancer therapies to selectively permeabilize the plasma membranes of cancer cells, since the vicinity of solid tumors is often acidic. Additional generations can be screened to further fine-tune the properties of these peptides.

8:30 AM BM09.01.03
Exploring the Tubability of the Aggregation and Gelation Process of the Tripeptide Glycyl-Alanyl-Glycine (GAG)
David DiGuiseppi1, Lavenia Thursch2, Nicolas Alvarez2 and Reinhard Schweitzer-Stenner2; 1Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, United States.
Self-assembly of biomolecules is a prominent issue explored in biomedical, biophysical, and bio-material research. Understanding how and why certain peptides/proteins prefer to self-assemble into larger networks can reveal the mechanism of amyloid formation and assist in bottom-up designs of supramolecular structures like gels and nanotubes. Some low molecular weight di- or tripeptides with aromatic residues and terminal groups have been shown to form gels. Contrary to expectations, we recently discovered that cationic glycylalanylglycine (GAG), a tripeptide of low hydrophobicity, forms a gel in 55 mol% ethanol/45 mol% water at room temperature if the concentration exceeds 200 mM. The underlying structure is comprised of unusually long crystalline fibrils (in the 10^3 nm range), which do not exhibit the canonical β-sheet structure. Rheological data and vibrational circular dichroism spectra suggest the existence of two different gel phases, one formed between 15°C and 35°C with left handed twisted fibrils and G’ values at ca. 2*10^4 Pa and another one formed below 15°C with right handed twisted fibrils and G’ values close to 10^5 Pa. Results from DFT calculations indicate that the two phases might be underlie by rather differently structured fibrils. The fluorescence kinetics probing the incorporation of thioflavin T into the hydrophobic interior of fibrils indicate a retarded diffusion of the fluorophore into fibrils that formed rather quickly after incubation above 15°C, while fluorescence increase, and relaxation proceed on a similar time scale for the gel phase formed below this temperature. Upon increasing the temperature, it can preserve this capability until the melting temperature is reached, which suggests that this gel phase has all what it takes to function as a drug delivery system. The potential reformation process of the fibrils probed by UVCD, rheology, and microscopy show that after sitting for 16h above the melting temperature, the fibrils do not have the ability to grow back. Instead, microscopic images suggest the formation of a crystal-type structure that forms in its place. Our results therefore suggest that the gel phases are meta-stable states of the system that form more quickly at or below room temperature. We care currently working on optimizing the gelation/conditioning methods for specific biotechnological applications of the gel as well as characterizing the observed crystal-type structure.

8:45 AM BM09.01.04
Neutral Self-Assembling Multidomain Peptides—Steric Impediment Regulates Nanofiber Formation and Materials Properties Tanja L. Lopez Silva, David G. Leach, I-Che Li, Xinran Wang and Jeffrey Hartgerink; Chemistry Department, Rice University, Houston, Texas, United States.

Peptide-based materials have drawn high interest for their use in biomedical applications such as drug delivery, cell encapsulation, and tissue regeneration. Particularly, self-assembling peptide hydrogels have shown promising properties as biomaterials since their properties and functionality are tunable by their peptide sequence. For example, they are inherently biocompatible and biodegradable, their nanofibrinous structure resembles the extracellular matrix, and they form materials with high-water content. Generally, these peptides utilize ionic amino acids to control self-assembly by changing the pH or ionic strength. Included in these group are the self-assembling Multidomain Peptide nanofibers (MDP), composed of an amphiphilic β-sheet forming core and flanking charged domains, which increase peptide solubility and make the peptide material responsive to pH changes and the presence of ions.

It is known that the biological response and cell behavior is highly dependent on the chemistry of the materials. Positive polymers promote cell adhesion and proliferation while showing concentration-dependent cytotoxicity, whereas neutral polymers, such as PEG, are frequently inert, biocompatible and non-immunogenic. Previously, all MDPs were either positively or negatively charged; therefore, expanding the scope of MDNs to neutral, non-ionic peptides will make distinct biological properties available that are not present in highly charged peptides.

Strategies to control the self-assembly of non-ionic peptides is limited because these peptides tend to have low solubility, aggregate or precipitate in aqueous solutions, making the formation of finite supramolecular structures and self-assembled hydrogels challenging. In this project, we present an alternative mechanism to control the self-assembly of neutral, uncharged multidomain peptides by utilizing steric impediment. Through the study of a series of neutral peptides, we analyzed the effect of the steric interactions on the peptide solubility, aggregation, nanostructure, and hydrogelation. From the series, a novel neutral multidomain peptide hydrogel was developed, which is inert to pH variation and ionic strength. This novel material showed promising properties for biomedical, cell preservation and tissue regeneration applications.

9:00 AM *BM09.01.05
Self-Assembly of 2D Peptide-Based Crystalline Nanomaterials Vincent P. Conticello; Emory University, Atlanta, Georgia, United States.

Structurally defined materials on the nanometer length-scale have been historically the most challenging to rationally construct and the most difficult to structurally analyze. Sequence-specific biomolecules, i.e., proteins and nucleic acids, have advantages as design elements for construction of these types of nanoscale materials in that there can be drawn between sequence and higher order structure, potentially affording ordered assemblies in which functional properties can be controlled through the progression of structural hierarchy encoded at the molecular level. The predictable design of self-assembled structures requires precise structural control of the interfaces between peptide subunits (proteins). However, control of quaternary structure has proven to be challenging to reliably predict, as conservative changes in sequence can result in significant changes in higher order, i.e., supramolecular, structure. We have employed single self-assembling peptides as building blocks for the construction of two-dimensional nano-scale assemblies. In contrast to filamentous assemblies (e.g., fibrils, ribbons, and tubes), protein-based two-dimensional assemblies occur relatively infrequently in native biological systems. We have demonstrated that extended and structurally defined two-dimensional assemblies can be constructed through lateral association of chiral rod-like subunits such as the collagen triple helix. The resultant assemblies can exhibit sequence-dependent control of structure, including growth in the lateral and/or axial dimensions. Moreover, the sheet-like assemblies can be integrated with other self-assembled biological structural motifs, such as DNA origami nano-tiles, to afford self-organized hybrid assemblies. Despite the potential for these two-dimensional assemblies as structurally defined nano-scale scaffolds, it remains challenging to reliably predict and control the structure of the assemblies based on sequence-structure correlations at present.

9:30 AM BREAK

10:00 AM *BM09.01.06

Supramolecular soft matter is a rapidly emerging field that encompasses the rational use of organic molecules to design function in materials. The most promising systems are “supramolecular polymers” since one-dimensional catenation of structural units is a critical feature to create mechanically robust macroscopic systems and directed transport of charge in aligned morphologies. Supramolecular polymers, in contrast to macromolecules in which every monomer is covalently linked through covalent bonds, supramolecular systems are designed using additive noncovalent bonds that are tunable over a very broad range of binding energies encoded in the molecular structure of the “mers”. Furthermore, a major gap in the design of synthetic soft matter is the rational integration of covalent and supramolecular polymers, a concept that is used to craft function in the structures of living organisms. This lecture will describe first entirely supramolecular systems based on peptides and nucleic acids in which dynamics of non-covalently bonded monomers can reversibly form superstructures linked to mechanical and biological functions. Within the domain of hybrid systems in which covalent macromolecules are integrated with supramolecular structures, the lecture will describe materials inspired by muscles that are capable of transferring thermal to mechanical energy, light to mechanical energy, and light to chemical energy in photocatalytic materials.
Macromolecular self-assembly in biological systems takes many forms and enables countless functions across multiple length scales. Often, the structure and function of these assembled structures are dictated by subtle changes in the composition of the molecular building blocks that make up these materials. For example, simple amino acid substitutions can impart significant changes in the structure and function of protein assemblies. Inspired by this theme, we explore here the self-assembly of an ABC triblock peptide-oligoethylene oxide amphiphile with hydrophilic A and C blocks and a hydrophobic B peptide block. By varying the amino acid side chain size and hydrophobicity within the B-block, we observe aqueous self-assembly into polymorphic cellular particles with hierarchical structure and porosity ranging from giant vesicles with foam-like membranes to porous tubular architectures. These structures are characterized microscopically and spectroscopically to determine the relationships between the varied peptide compositions, tunable intermolecular interactions, and the observed morphologies. Additional evaluation of these materials as vehicles for molecular encapsulation and as templates for secondary mineral templating reveal potential new strategies to control hierarchical materials synthesis and assembly through bio-inspired molecular building block design.


10:05 AM BM09.01.08
Modular Peptide-Polymer Conjugates—A Platform Technology for Mucin Analogues

Daniel French, Luis Navarro and Stefan Zauscher; Duke Univ, Durham, North Carolina, United States.

Mucins – the glycoprotein building-blocks of mucus – play diverse and crucial roles in the body. These functions range from lubrication of articular joints and the eye, to the protection of stomach endothelium from the harsh environment of the lumen, to modulation of microflora populations in the digestive and respiratory systems. Despite this diversity, these functions are all attributed to slight modifications in a general structure shared by all mucins: a telechelic triblock polypeptide comprised of terminal association moieties and a heavily glycosylated core which forms a hydrated bottle brush center. In vivo, these versatile functions are achieved by altering glycosylation patterns, crosslinking density, and targeting affinity in a modular fashion. Inspired by this adaptability, we have emulated this general architecture in a modular conjugate analogue mucin platform which engenders general structural features preserved among mucins which we, and others, have identified as key to their function. To recapitulate the mucin backbone, we genetically tether and co-express terminal binding modules with a lysine-rich, elastin-like polypeptide (ELP) central scaffold. Binding modules may include sequences designed to target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct. The regularly-spaced lysines in the ELP scaffold can be harnessed for grafting synthetic polymer bristles. Bristle chemistry may be chosen for a desired property (including non-fouling character and lubricity) independent of the binding and scaffold modules. Our platform is, to our knowledge, the first to adapt the modularity of the mucin architecture into a bio-synthetic platform technology.

To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mCAMP to osteoarthritis and kidney stone disease, two conditions infamous for profound morbidity and high prevalence. In tailoring our analogue mucin to cartilage, we hope to rival the performance of lubricin, a natural mucin which provides lubrication and wear protection to articular joints. Moreover, we seek to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings. In doing so, we have adapted our platform to binding calcium oxalate kidney stones. Association modules are designed to direct assembly on mineral surfaces as well as inhibit further mineralization. Moreover, these modules are designed to form intramolecular associations, facilitating a robust surface coating. The inclusion of non-fouling synthetic polymer bristles provides a means by which to inhibit protein-mediated crystal aggregation. In this platform technology, we have begun to develop a means by which to replicate not only the in vitro function of mucins, but to harness that function to meet additional clinical needs.

11:00 AM BM09.01.09
Design of Bioreponsive Nanogels Inspired by Peptide-Glycan Interactions

Andrew Simonson1, Atip Lawanprasert2, Tyler Goralski3, Kenneth Keiler2 and Scott Medina1; 1Biomedical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; 2Biochemistry and Molecular Biology, The Pennsylvania State University, University Park, Pennsylvania, United States.

Early investigations from The Medina Group identified that binding of cationic membrane-active peptides with negatively charged cell-surface glycans was a critical initiating step to potentiate the peptide’s lytic action. Inspired by this natural system, we have designed a family of biohybrid nanomaterials assembled via electrostatic association of cationic peptides and anionic carbohydrates. Screening a series of peptide-polysaccharide pairs under electrospray synthesis conditions identified that poly-L-lysine (PLL) and hyaluronic acid (HA) rapidly co-assemble to yield nano-scale gel-like particles. Binding modules may include sequences designed to target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct. The regularly-spaced lysines in the ELP scaffold can be harnessed for grafting synthetic polymer bristles. Bristle chemistry may be chosen for a desired property (including non-fouling character and lubricity) independent of the binding and scaffold modules. Our platform is, to our knowledge, the first to adapt the modularity of the mucin architecture into a bio-synthetic platform technology.

To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mCAMP to osteoarthritis and kidney stone disease, two conditions infamous for profound morbidity and high prevalence. In tailoring our analogue mucin to cartilage, we hope to rival the performance of lubricin, a natural mucin which provides lubrication and wear protection to articular joints. Moreover, we seek to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings. In doing so, we have adapted our platform to binding calcium oxalate kidney stones. Association modules are designed to direct assembly on mineral surfaces as well as inhibit further mineralization. Moreover, these modules are designed to form intramolecular associations, facilitating a robust surface coating. The inclusion of non-fouling synthetic polymer bristles provides a means by which to inhibit protein-mediated crystal aggregation. In this platform technology, we have begun to develop a means by which to replicate not only the in vitro function of mucins, but to harness that function to meet additional clinical needs.

11:15 AM BM09.01.10
Template-Driven Peptide Assembly Yields Ultrasound Guided Phase-Changing Nanomaterials

Janna N. Sloan1, Scott A. Zinic2, Joel P. Schneider2, Julianna C. Simon2 and Scott H. Medina1; 1Department of Biomedical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; 2Department of Acoustics, The Pennsylvania State University, University Park, Pennsylvania, United States; 3Chemical Biology Laboratory, National Cancer Institute, National Institutes of Health, Frederick, Maryland, United States.

Phase-changing nanoparticles (PCNs) are a class of materials that undergo solid-liquid-gas transitions in response to various engineered stimuli, leading to their application in fields that include thermal energy storage, bioelectronics and precision medicine. In particular, liquid-shelled perfluorocarbon PCNs
Hierarchical organization across length scales is ubiquitous in the superstructures of living organisms. These highly functional structures form through self-assembly, and have therefore inspired significant research activity on synthetic supramolecular materials over the past decade. We report here on a new family of supramolecular polymers that are formed by peptide amphiphiles and each is labeled with a different small fluorescent dye, and based on earlier work on supramolecular polymers, we find that nano-peptisome size can be precisely controlled by simply modulating the starting peptide and fluorinated solvent concentrations during synthesis, leading to programmable acoustic properties of the final carrier. Further, biomolecular cargo, including peptides and proteins, can be encapsulated within the particle core and directly delivered to the cytoplasm of cells upon US-mediated rupture of the carrier. Bio-imaging studies demonstrate that nano-peptisomes can be tracked and guided using diagnostic B-mode US, while Doppler imaging allows for real-time monitoring of particle activation and rupture in tissue mimetic gels. These results establish nano-peptisomes as a novel theranostic platform capable of image-guided delivery of bioactive macromolecules into cells with spatial and temporal precision.

11:30 AM *BM09.01.11
Guiding Principles for Peptide-Based, Life-Like Nanotechnology  
Rein Ulijn; Advanced Science Research Center (ASRC) at the Graduate Center, Hunter College, Glasgow, New York, United States.

Life’s diverse molecular functions are largely based on only a small number of highly conserved building blocks- the twenty canonical amino acids. These building blocks are chemically simple, but when they are organized in three-dimensional structures of tremendous complexity, new properties emerge, giving rise to the extraordinary machinery of life. So, if just twenty simple building blocks- when appropriately assembled – give rise to the complexity and functionality that can sustain life- then this is clearly a very versatile construction set. Our overall goal is conceptually simple: to figure out how to make nanoscale systems and materials from biology’s building blocks, and to apply these materials to diverse problems, that require them to be interfaced, ideally seamlessly, with living systems, or the natural environment. Different from other research groups, we have an unbiased approach, that is not guided by copying biological systems, and we keep these systems as simple as possible, which lowers barriers to application. The talk will focus on our latest results in three areas: (i) directed discovery of peptide nanostructures with new functions, by searching the sequence space; (ii) application of peptide nanostructures as functional materials (including customizable melanin pigments); (iii) actively assembling systems, that continuously turn over chemical reactions, and the characterization of nanostructure as well as inherent material properties (e.g. extreme stiffness, responsiveness to temperature and pH, stability in aqueous and organic solvents).

1:30 PM *BM09.02.01
Large-Scale Self-Sorting in Supramolecular Assemblies  

Hierarchical organization across length scales is ubiquitous in the superstructures of living organisms. These highly functional structures form through self-assembly, and have therefore inspired significant research activity on synthetic supramolecular materials over the past decade. We report here on a novel bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. A new solution assembled system comprised of theoretically designed coiled coil bundle motifs will be introduced. The molecules and nanostructures are not natural sequences and provide opportunity for arbitrary nanostructure creation with peptides. With control of the display of all amino acid side chains (both natural and non-natural) throughout the peptide bundles, desired physical and covalent (through appropriate “click” chemistry) interactions have been designed to produce one and two-dimensional nanostructures. One-dimensional nanostructures span exotically rigid rod molecules that produce a wide variety of liquid crystal phases to semi-flexible chains, the flexibility of which are controlled by the interbundle linking chemistry. The two dimensional nanostructure is formed by physical interactions and are nanostructures not observed in nature. All of the assemblies are responsive to temperature since the individual bundle building blocks are physically stabilized coiled coil bundles that can be melted and reformed with temperature. Additional, novel nanostructures to be discussed include uniform nanotubes as well as the templated growth of metallic nanoparticles on and in peptide nanostructures. Included in the discussion will be molecule design, hierarchical assembly pathway design and control, click chemistry reactions, and the characterization of nanostructure as well as inherent material properties (e.g. extreme stiffness, responsiveness to temperature and pH, stability in aqueous and organic solvents).
artificial transmembrane pores with molecularly defined structures is instrumental for future bionanotechnology applications. In this work, thermoresponsive synthetic channels based on supramolecular metal-organic complexes (MOCs) have been constructed to transport cell impermeable cargo across the membrane. The channels can be reversibly controlled as they collapse when the temperature is increased and are simultaneously regenerated when the system is cooled down to room temperature. These ON/OFF molecular valves could be used to overcome multidrug resistance (MDR) in cancer cells and as building blocks for artificial cells.

2:30 PM BM09.02.04
Incorporating Hierarchical Structure within Hydrogel Biomaterials Using Multifunctional Collagen Mimetic Peptides Toward Directing Stem Cell Fate 

Eden Ford1, Amber Hilderbrand1, Chen Guo1 and April Kloxin1,2; 1Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware, United States; 2Material Science & Engineering, University of Delaware, Newark, Delaware, United States.

Extracellular matrix (ECM) properties are important regulators of cell function, particularly at early timepoints during bone healing. For example, physical and chemical properties of the ECM regulate cytoskeletal organization, proliferation, and migration of stem cells to the site of bone injuries for commencing repair. Controlling the presentation of such extracellular cues with molecularly engineered materials provides opportunities to direct bone regeneration. We hypothesize that engineering synthetic hydrogels to recapitulate aspects of the early stages of healing in healthy bone will promote stem cell invasion and remodeling processes toward improving bone regeneration of traumatic fractures or critical-sized defects. To test this, we have created well-defined materials to mimic the mechanical properties, biochemical content, and multiscale structure of native tissues, particularly the collagen-rich environment of the clot-like hematoma formed early in the wound healing process.

We have designed multifunctional collagen mimetic peptides (mfCMPs) that are variants of the Proline-Hydroxyproline-Glycine repeat unit of native collagen. Two variants of this peptide were synthesized: one promoting fibrillar assembly through ionic interactions using charged groups (CMP1a) and the other using hydrophobic interactions of aromatic groups on the C- and N-termini to promote end-to-end assembly (CMP2a). Circular dichroism was used to examine triple helical assembly of the peptides and measure associated melting temperatures, where melting temperatures of CMP1a and CMP2a were determined to be 45.0°C and 60.2°C, respectively. Further peptide assembly and fibril formation was investigated with transmission electron microscopy, where fibrils were observed that mimicked aspects of the hierarchical nanostructure of native collagen. For CMP1a, fibrils approximately 35 nm in width and on the order of 1 μm in length were observed, whereas for CMP2a, fibrils approximately 60 nm in width and on the order of 100 nm in length were observed. Toward studying cell response in vitro, these mfCMPs were covalently crosslinked within cell-degradable poly(ethylene glycol) hydrogels, and rheometry was used to characterize the resulting mechanical properties. Hydrogels with storage moduli in the range of 3500-4500 Pa were generated; further, good cell viability was observed within these unique matrices, with approximately 80% viable cells across conditions.

These studies support our hypothesis that incorporation of mfCMPs within a covalent hydrogel network captures aspects of the fibrillar structure of collagen on both the nano- and microscale toward providing a biomimetic matrix that recapitulates key cues found in ‘soft’ collagenous tissues. Ongoing studies of human mesenchymal stem cells within these materials support their relevance for multidimensional cell culture and suggest that the presence of mfCMPs influences cell-matrix interactions and observed cell response.

2:45 PM BM09.02.05
Tuning Bioinspired Macromolecular Assembly with Cation-π Interactions 

Matthew A. Gebbie1, Jacob N. Israelachvili2 and J. Herbert Waite2; 1Stanford University, Stanford, California, United States; 2University of California, Santa Barbara, California, United States.

Cation-π interactions govern the assembly of many bio-macromolecules, including the adhesion proteins of marine organisms. Increasingly, cation-π interactions are also implicated in pathological processes, like the formation of neurodegenerative protein aggregates. Thus, developing molecular level approaches for engineering cation-π interactions is of both fundamental and technological importance. Although cation-π bonding has been extensively studied for gas phase ion-aromatic pairs, the energetics of cation-π adhesion in biological and biomimernal interfaces, where many binding pairs are in close proximity, remains uncharted. In this seminar, I will discuss using molecular force spectroscopy, supplemented by solid-state NMR measurements, to show that the adhesive properties of simple aromatic- and lysine-rich peptides rival those of the adhesion proteins of the marine mussel. Surprisingly, we find that peptides with the aromatic amino acid phenylalanine, a functional group that is conspicuously rare in mussel proteins, exhibit adhesion that significantly exceeds that of analogous mussel-mimetic peptides. More broadly, we find that interfacial confinement fundamentally alters the energetics of cation-π mediated assembly, an insight that is relevant for diverse areas, from influencing bio-controlled crystal formation to engineering novel bioinspired medical adhesives.

3:00 PM BREAK

3:30 PM BM09.02.06
Nanomaterials for Nervous Regeneration 

Fabrizio Gelain; JSBREMIT, IRCSS Casa Solliello della Sofferenza, San Giovanni Rotondo, Italy.

Peptidic biomaterials have been receiving great interest because of their easiness of scale-up production, absence of pathogen-transfer risk, biomimetic properties, nanostructured morphology and customization potential for the specific tissue engineering application. However, their proper usage requires the understanding of the multiple-phenomena taking place at different scale levels during self-assembling. In this presentation, focused on the nanotech advancements in the field of nervous regeneration, we will see some multi-disciplinary researches and advances toward the regeneration of spinal cord injuries. This will bring us from coarse-grained molecular dynamics to electro-spinning of self-assembling peptides (SAPs), from cross-linking of SAPs to 3D high-density neural stem cells cultures. Lastly, in vivo tests of SAP prosthese in animal models of sub-acute and chronic SCI will be discussed.

4:00 PM BM09.02.07
Learning from Nature to Form New Organic Materials for Tissue Regeneration 

Lihi Abramovich; Oral Biology, Faculty of Medicine, Tel Aviv University, Tel Aviv, Israel.

Molecular self-assembly is a key direction in current nanotechnology based material science fields. In this approach, the physical properties of the formed assemblies are directed by the inherent characteristics of the specific building blocks used. Molecular co-assembly at varied stoichiometry substantially increases the structural and functional diversity of the formed assemblies, thus allowing tuning of both their architecture as well as their physical properties. In particular, building blocks of short peptides and amino acids can form ordered assemblies such as nanotubes, nanospheres and 3D-hydrogels. These assemblies were shown to have unique mechanical, optical, piezoelectric and semiconductive properties. Yet, the control over the physical properties of the structure has remained challenging. For example, controlling nanotube length in solution is difficult, due to the inherent sequential self-assembly mechanism. Another example is the control of 3D-hydrogel scaffold’s physical properties, including mechanical strength, degradation profile and injectability, which are important for tissue engineering applications.
Pathogens can thrive in an abundance of environments, and pose a significant threat to human health when irrigation or drinking sources become contaminated. The ability to detect the presence of pathogens or biomarkers, such as proteases, using a biosensing platform that is passive and requires no power can help monitor and prevent outbreaks of infectious diseases. We have developed a tunable protease-responsive platform that demonstrated a red-to-blue color shift for all target molecule concentrations between 20 nM and 4000 nM. Structurally colored particle hydrogels were fabricated by centrifuging monodisperse silica particles along with a 4-arm polyethylene glycol (PEG) and a protease-specific peptide linker into a close-packed microstructure, followed by UV irradiation to polymerize the composite. These films swelled in aqueous solutions, and color shift towards the red region of reflected visible light in response to the degree of swelling. Upon degradation of the peptide crosslink, the particles reassembled into a close-packed structure with interparticle spacing less than the initially centrifuged material. This reduction in particle spacing produced a 240 nm color change from the swollen state to the reassembled state of the material for 205 nm particle composites.

To elucidate the mechanism responsible for the color change, we investigated the role of particle size and charge, and polymer concentration in reassembly after degradation. Both particle size and surface functionalization were varied to produce composites with a range of observable structural colors. The reassembled materials reflected shorter wavelengths than their initially fabricated counterparts, indicating that the interparticle spacing had decreased as much as 45 nm for hydrogels with 230 nm particles. In addition, the reassembled composites reflected nearly identical wavelengths independent of the starting polymer weight fraction in the hydrogel. Ultra-small angle x-ray scattering confirmed that the interparticle spacing decreased and the spacing was the same for the reassembled composites. While the particle size or polymer content did not inhibit the reassembly process, particle surface charge was crucial to the reassembly mechanism. Only highly negative (-60mV) particles reassembled to produce structurally colored composites. PEGylated particle hydrogels did not reassemble, and the corresponding composites degraded into the protease solution. Composites with positively charged (+30mV) particle surfaces aggregated irreversibly into a material that appeared white due to incoherent scattering of visible light. Interaction potential models demonstrated that depletion forces provide necessary attraction for reassembly, with a range of up to 120 nm. These findings offer insight into the parameters that will enable passive monitoring of proteases with precise control of structurally colored particle hydrogel responses.

4:30 PM BM09.02.09
Anti-Biofilm Activity of Graphene Quantum Dots via Self-Assembly with Bacterial Amyloid Proteins Yichun Wang, Usha Kadiyala, Zhi-Bei Qu, Paolo Elvati, Angela Violi, Scott VanEpps and Nicholas A. Kotov; Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Bacterial communities, known as biofilms, cause multiple technological and health problems and represent an essential part of Earth’s ecosystem. The environmental resilience and sophistication of the effects of biofilms acting as a multiscale organism is enabled by extracellular matrix (ECM) that creates a protective network of biomolecules around the bacterial communities. The current antibiofilm agents can interfere with ECM production but, being based on small molecules, they can be degraded by bacteria and diffuse away from biofilms, which reduce their efficacy. Here we show that graphene quantum dots (GQDs) can effectively suppress the growth of Staphylococcus aureus biofilms by preventing the self-assembly of amyloid fibers - the essential component of ECM. Mimicking peptide-binding biomolecules, GQDs form supramolecular complexes with phenol soluble modulins (PSMs), the peptide monomers of amyloid fibers. Experimental and computational results show that GQDs dock at the N-terminal of the peptide and change the second structure of PSM, which disrupts their fibrillation. Commitantly, the resulting free PSM monomers turn on biofilm dispersion signaling pathways that enhance the inhibitory effect. The two-prong anti-biofilm activity of GQDs offer a new strategy for manipulation of ECms of bacterial communities.

4:45 PM BM09.02.10
Soft to Hard Biomimetic Constructs Using Recombinant Proteins Undergoing Conformational Transition Hortense Le Ferrand, Bartosz Gabryeleczyk, Cai Hao and Ali Miserez; Nanyang Technological University, Singapore, Singapore.

Synthetic mechanical gradients based on synthetic and biocompatible hydrogels currently do not achieve the soft to hard transition found in many biological materials like squid beaks or osteochondral cartilage [1]. Indeed, it is difficult to obtain tight molecular packing and high crosslinking density using conventional polymeric building blocks. Here, we employ the recombinantly expressed protein HBP-1 found in the beak of squids, and make use of its folding in presence of polyelectrolytes to expel water and attain high packing density [2,3]. Under acidic pH and in the presence of chitosan, HBP-1 undergoes a conformational transition from predominantly random coil into β-sheet-rich. At increased ionic strength, this conformation change leads to a phase separation from soluble to liquid droplets and a hydrogel-like phase. At a constant volume fraction of chitosan, the elastic modulus of the HBP-1/chitosan composite increases with the protein content. After drying and cross-linking using catechol chemistry, the resulting organic material shows...
similar trend under fully hydrated conditions. This observation is reminiscent to what is observed in the native squid beak. Furthermore, concentration gradients can be controlled based on molecular diffusion and phase separation. With this knowledge, gradients of controlled stiffness can be obtained. The crosslinked gradient results in an increase of elastic modulus from 0.08 up to 1 GPa despite containing 60 vol% of water. The approach explored here may open new avenues for the fabrication of graded materials based solely on organic biomaterials with potential applications for orthopaedic devices and soft-to-hard attachment in hydrated environments.


8:00 AM *BM09.03.01
CrystEM Reveals the Molecular Mechanism of Polymorph Selection in Protein Crystallization Mike Skeate¹, Alexander E. Van Driessche² and Nico Sommerdijk³; ¹ Vrije Universiteit Brussel, Elsene, Belgium; ² Univ. Grenoble Alpes, CNRS, ISTerre, Grenoble, France; ³ Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands.

Macromolecular condensed phases such as protein crystals and gels bear great medical, scientific and industrial relevance, yet a molecular understanding of their initial stages of formation is still missing. Insights on the mechanism of nucleation have the potential to resolve one of the longest-standing questions of crystallization, i.e. polymorph selection. To gain control over the emerging polymorph one needs to have a molecular-level understanding of the pathways leading to the various macroscopic states and the underlying selection mechanisms that govern the process. Here we address the issue by capturing protein crystals at birth using time-resolved cryo-transmission electron microscopy and uncover at molecular resolution the nucleation pathways of the protein glucose isomerase into two crystalline and one gelled state. We show that polymorph selection takes place at the earliest stages of transformation and is based on the specific building blocks (monomers and nanorods) for each space group. Moreover, we demonstrate control over the system by selectively forming desired polymorphs through tuning of the directionality and specificity of inter-molecular bonding. These new insights on the mechanisms of nucleation and polymorph selection open new avenues towards the control of macromolecular phase transitions, which is crucial in the further development of protein-based drug delivery systems and macromolecular crystallography.

8:30 AM BM09.03.02
Building Hierarchically-Ordered 3D Nanomaterials Using 2D Self-Assembling Protein Arrays Francesca Manea and Caroline Ajo-Franklin; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Leveraging self-assembly to pattern proteinaceous crystalline arrays in 2D and 3D offers a highly scalable, bottom up approach to develop nanomaterials with new catalytic, optical or structural applications. However, introducing multiple sites of embellishment into existing 2D protein arrays currently utilizes weak interactions that are either sensitive to external conditions or challenging to re-engineer, limiting the ability to program in bifunctionality and new 3D configurations. Here we address these challenges by developing a means to introduce two orthogonal crosslinking linkages at multiple sites in a highly robust, thermostable 2D crystalline-forming protein. We first engineered the surface-layer (S-layer) protein SbsB from Geobacillus stearothermophilus to display SpyTag or SnoopTag at the C-terminal and two newly-identified locations within SbsB monomer. These regions were able to accommodate SpyTag or SnoopTag peptide tags without affecting the 2D lattice structure. The introduction of tags at distinct locations enabled orthogonal and covalent binding with high precision of SpyCatcher- or SnoopCatcher-protein fusions to micron-sized 2D sheets. By introducing different types of bifunctional crosslinkers, the dual functionalized nanosheets could be programmed to self-assemble into different 3D lamellae, all of which retain their nanoscale order. Additionally, these nanosheets can be functionalized to display two distinct nanomaterial, yielding nanomaterials with emergent optoelectronic properties. Thus, our work creates a modular protein platform that can be facilely programmed to create dual-functionalized 2D and lamellar 3D nanomaterials with novel catalytic, optoelectronic and mechanical properties.

8:45 AM BM09.03.03
Intracellular Phase-Separated Assemblies of Engineered Disordered Proteins Ming-Tzo Wei and Cliff Brangwynne; Princeton University, Princeton, New Jersey, United States.

There is currently a growing interest in biopolymer phase transitions, particularly those involving intrinsically disordered proteins/regions (IDPs/IDRs). It has been found that intracellular liquid-liquid phase separations underlie the assembly of many non-membranous organelles such as P granules, nucleoli, and stress granules. However, little is known about the physics of these organelles, including their internal molecular organization and feedback between their molecular and mesoscale properties. Progress on these questions has been hampered by the lack of detailed phase diagrams, which would elucidate how molecular interactions give rise to emergent droplet properties, particularly condensed-protein concentrations and their physical characteristics.

To answer these questions, we investigate the inter-molecular interaction strengths and the full binodal of a phase-separating disordered protein that induces in-vivo phase transitions, utilizing a novel technique, ultrafast-scanning fluorescence correlation spectroscopy. These measurements led to the recent discovery that phase-separated protein droplets have unusually low densities with large void volumes. The data demonstrate how sequence-encoded conformational fluctuations of IDRs give rise to low overlap volume fractions for driving phase separations. Using inter-molecular interactions of native non-membranous organelles, we develop an optogenetic platform that permits light activation of IDR-mediated phase transitions in living cells. Inter-molecular interaction strengths are quantified and demonstrated how IDR sequences determine intracellular phase separation. These studies can elucidate not only physiological phase transitions but also their links to pathological aggregates.
Our results provide a holistic picture of the dynamics and internal organization of phase separated organelles. By uncovering the relationship between molecular level interactions and emergent mesoscale material properties, this work is foundational for understanding the form, function and potential dysfunction of intracellular phase separated assemblies. Our study has significant impact for an extensive community of researchers, with interests spanning biomaterials, bio-inspired materials, macromolecular assembly, self-assembly, intracellular phase separation, disordered proteins dynamics, polymer chemistry, and bioengineering applications of synthesized intracellular biomimetic materials.

9:00 AM BM09.03.04
Altered Energy-Landscape and Self-Assembly of Protein Crystalline 2D Array at Solid-Liquid Interface Shuai Zhang1, Robert Alberstein2, E. Akif Tezcan3 and James J. De Yoreo4; 1Pacific Northwest National Laboratory, Richland, Washington, United States; 2Department of Chemistry and Biochemistry, University of California, San Diego, California, United States.

Protein 2D materials possess diverse sophisticated and synergistic structures, and inherent chemical and biological functions. Harnessing this paradigm of protein 2D materials for bottom-up biomaterial design, synthesis and application is an attractive task with promising perspectives in biomimetic and material science. Inspired by nature cases, various strategies have been developed to construct protein 2D crystals in bulk solution. Recently, computational protein design methodology has considerably improved the structural and functional complexities of protein 2D/3D supramolecular structures from scratch.1,2 Besides growth in solution, solid-liquid interface has also been used to template few-layer protein 2D materials. However, the solid-liquid interface that is used to artificially grow protein 2D supramolecular structures is generally limited to supported liquid bilayer. It is still not quite clear how solvent mediated protein-surface interactions to define protein thermodynamics, structure and function at solid-liquid interface. That is the obstacle for artificial design and functional applications of protein 2D crystalline arrays in future.

To address these issues, we assembled the variant of L-rhamnulose-1-phosphate aldolase (RhuA), C98RhuA[3], with incorporated Cys mutants, into crystalline 2D arrays on solid-liquid interface of mica. By carefully selecting cations and controlling their concentration, we create isotropic protein monolayer 2D crystals with controlled packing patterns. It is surprising that the crystallizations of the first and second layers is bimodal that follows non-classical and classical pathways, respectively. We also proved that solvent mediated protein-surface interactions can alternate the energy-landscape of protein self-assembly from that in bulk to stabilize the original intermediate and quasi stable phase. C98RhuA can epitaxially grow on top of the surface that has different symmetry. All the findings inspire the novel strategy to synthesize protein crystalline 2D arrays at solid-liquid interface artificially. They also help to elucidate the growth model of protein 2D architectures at solid-liquid interface. They remind us the importance of solvent mediated surface templating in the self-assembly of protein 2D structures both in nature and in human manner.


9:15 AM BM09.03.05
Microbial Factories for Programmed Production of Functional Biomaterials Avinash Manjula Basavanna1,2, Anna Duraj-Thatte1,2 and Neel Joshi1,2; 1Wyss Institute for Biologically Inspired Engineering, Boston, Massachusetts, United States; 2Harvard University, Boston, Massachusetts, United States.

Biological systems are highly complex and sophisticated with unparalleled structure-function correlations. Remarkably, biological systems produce materials with extraordinary properties and functions under ambient conditions, which is in total contrast to humans’ heat-beat-treat strategies. Thus, the capabilities of a technology by which biological networks of a cell can be programmed, offers tremendous potential as cellular factories and to produce biomaterials for various functional applications.

In this regard, we employ a novel technology entitled Biofilm-Integrated Nanofiber Display (BIND) that focuses on the curli system—the primary proteinaceous structural component of E. coli biofilms. Curli are highly robust functional amyloid nanofibers (diameter 4-7 nm) formed by the extracellular self-assembly of a small (13 kDa) secreted protein, CsgA. By genetic engineering, artificial peptide domains were grafted to the amyloid protein CsgA and the resulting CsgA fusion proteins were successfully secreted from the E. coli cells. Remarkably, these engineered fusion proteins were found to extracellularly self-assemble into amyloid nanofiber networks and also exhibited the characteristic functions of the grafted artificial peptide domains. By using BIND technology, E. coli biofilm matrix is conferred with several artificial functions for nanomedicinal, nanomechanical and nanoelectronics applications.

10:00 AM *BM09.03.06
S-Layers—Principles and Applications Uwe Sleytr and Dietmar Pum; Nanobiotechnology, Univ Bodenkultur, Vienna, Austria.

One of the key challenges in nanobiotechnology is the utilization of self-assembly systems wherein molecules spontaneously associate into reproducible aggregates and supramolecular structures. In this contribution, the basic principles of crystalline bacterial surface layers (S-layers) and their use as patterning elements will be described. The broad application potential of S-layers in nanobiotechnology is based on the specific intrinsic features of these monomolecular arrays which are composed of identical protein or glycoprotein subunits. Most important, physicochemical properties and functional groups on the protein lattice are arranged in well-defined positions. Many applications of S-layers depend on the capability of the isolated subunits to recrystallize into monomolecular arrays in suspension or on suitable surfaces (e.g. polymers, metals, silicon wafers) or interfaces (e.g. lipid films, liposomes, emulsomes). S-layers also represent a unique structural basis and patterning element for generating more complex supramolecular structures involving all major classes of biological molecules. Thus, S-layers fulfill key requirements as building blocks for the production of new supramolecular materials and nanoscale devices as required in nanobiotechnology and synthetic biology.


We acknowledge the financial support by the Air Force Office of Scientific Research (AFOSR) (Grant FA9550-15-1-0459).

10:30 AM BM09.03.07
Controlled Formation of Enzyme-Scaffold Complex for Biocatalysis Using a Self-Assembling Protein Template Samuel Ling1, Florence Barraud1, Sophia Prem1, Dominic J. Glover2 and Douglas S. Clark1; 1Department of Chemical and Biomolecular Engineering, University of California, Berkeley,
In nature, enzymes that catalyze multi-step reactions are often organized in close proximity to allow the efficient channeling of intermediates from one active site to another. Diverse synthetic scaffolds based on DNA and proteins have been designed to mimic such spatial control of enzymes, and have proven successful in facilitating cascade reactions. Recent studies revealed that such enhanced catalysis can also result from formation of enzyme agglomerates rather than direct channeling of intermediates between adjacent enzymes, highlighting the need to engineer the interactions that define metabolic clusters. Thus, there is a demand for scaffolds that can effectively crosslink with each other to form higher-order structures in a programmable manner, in addition to simply templating the enzymes.

The g-prefoldin (gPFD) is a filamentous protein isolated from the hyperthermophilic archaeon Methanococcus jannaschii; its remarkable stability, unique modularity, and self-assembly into filaments with chaperone activity render it an ideal building block for the bottom-up construction of functionalized protein nanostructures. Here we propose a strategy to utilize the gPFD to build enzyme agglomerates in tunable fashion. Using the combinations of orthogonal protein-peptide bioconjugation pairs, the gPFD filaments displaying the peptide tags are first conjugated with the enzymes, and then crosslinked using the linker proteins. Thus, the extent of crosslinking is tunable through simply varying the stoichiometry between the scaffold and linker proteins.

We verified the gPFD scaffold’s ability to cluster enzymes in proximity using FRET analysis of the filaments containing fluorescent protein pairs. Subsequently, we investigated the effect of agglomerate formation on the catalytic activities of multi-step reactions using two different model system pairings: glucose oxidase (GOX)-horseradish peroxidase (HRP) and alcohol dehydrogenase (ADH)-aldehyde dehydrogenase (ALDH). Ultimately, the ability to fabricate enzyme-scaffold complexes with programmable stoichiometry and dimensions will enable better control over single- and multi-step enzymatic catalysis.

Mimicking Dividing Cells by Assembly of Protein Structures Inside Aqueous Two-Phase Droplets

In this work, we demonstrate that assembly of macromolecules, such as proteins, can cause aqueous droplets to exhibit division, even in the absence of a cell membrane. The all-aqueous nature of the systems results in tunable interfacial tension, affinity partitioning and osmotic responses. The solubility of different types of macromolecules across the interfaces enables new strategies to assemble structures at the droplet interfaces. While the significantly lower interfacial tension can make stabilization of the interface difficult due to the slow adsorption dynamics by surfactants and particles, structures that have been assembled at the interfaces can be easily expelled. This contributes to the more sophisticated dynamics of the hierarchically structured all-aqueous droplets. These droplets have great potential to be utilized as templates for fabricating materials with novel properties.

Self-Assembly of Elastin-b-Collagen-Like Conjugates Mediated by Triple Helical Parameters

Physicochemical irregularities within extracellular matrix (ECM) proteins such as collagen can lead to a wide range of connective tissue disorders including osteogenesis imperfecta and osteoarthritis. Current pharmaceutical regimens to treat such diseases suffer from off-target effects, suggesting that new approaches for targeted delivery are necessary. In the last decade, ECM-inspired polypeptide materials have garnered significant interest for their ability to selectively mimic specific matrix components such as collagen and elastins, offering new opportunities to control drug delivery within specific tissues. For example, triple helix forming collagen-like peptides (CLPs) comprising (Gly-Pro-Hyp)ₙ amino acid repeats can hybridize with high efficiency to denatured collagen proteins in the body via thermal annealing of peptide and protein single strands into a stable triple helix. Additionally, elastin-like peptides (ELPs) that consist of (Val-Pro-Gly-Xₐₐₐₐ₋₁-Gly₁ₐ₁ₐ₁)ₙ (where Xₐₐₐₐ is any amino acid with the exception of proline) amino acid repeats possess a lower critical solution temperature in which aggregation occurs upon heating above this temperature, making ELPs ideal candidates for on demand drug delivery behavior.

Recently, our group has reported on the design of hybrid peptides with linked CLPs and ELPs, and the assembly of thermoresponsive, elastin-b-collagen-like peptide nanovesicles that are capable of dissociating at high temperature (70°C). These nanovesicles offer intriguing potential in drug delivery applications due to their dual thermoresponsivity and inherent ability to bind to degraded collagen protein. However, in order to make an ELP-CLP nanoparticle with optimal drug delivery properties such as physiologically relevant hybridization to degraded collagen protein, the critical parameters of their self-assembly must first be understood, specifically with respect to the CLP domain. To test the effects of the triple helical (CLP) melting temperature on temperature-dependent nanovesicle assembly and dissociation behavior a small library of ELP-CLP conjugates was made with varying numbers of CLP (G-X-Y) repeats and varied CLP sequences. These conjugates were characterized for their thermoresponsivity and their ability to form self-assembled structures. The melting temperature, repeat length, and overall hydrophilicity of the CLP domain were found to be of critical importance to nanoparticle function.
SESSION BM09:4: Bio-Inspired Materials Based on DNA or Peptide Building Blocks
Session Chairs: Xiang Yang Liu and Tiffany Walsh
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Back Bay A

1:30 PM *BM09.04.01
Colloidal Crystal Engineering with DNA—Creating a Genetic Code for Materials Design Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

The materials-by-design approach to the development of functional materials requires new synthetic strategies that allow for material composition and structure to be independently controlled and tuned on demand. Although it is exceedingly difficult to control the complex interactions between atomic and molecular species in such a manner, interactions between nanoscale components can be encoded, independent of the nanoparticle structure and composition, through the ligands attached to their surface. DNA represents a powerful, programmable tool for bottom-up material design. The Mirkin Group has shown that DNA and other nucleic acids can be used as highly programmable surface ligands (“bonds”) to control the spacing and symmetry of nanoparticle building blocks (“atoms”) in structurally sophisticated materials, analogous to a nanoscale genetic code for material assembly. The sequence and length tunability of nucleic acid bonds has allowed us to define a powerful set of design rules for the construction of nanoparticle superlattices with more than 30 unique lattice symmetries, spanning over one order of magnitude of interparticle distances, with several well-defined crystal habits. Further, this control has enabled exploration of sophisticated symmetry breaking processes, including the body-centered tetragonal lattice as well as the clathrate lattice, the most structurally complex nanoparticle-based material to date (~20 particles per unit cell). The nucleic acid bond can also be programmed to respond to external biomolecular and chemical stimuli, allowing structure and properties to be dynamically tailored. Notably, this unique genetic approach to materials design affords functional nanoparticle architectures that can be used to catalyze chemical reactions, manipulate light-matter interactions, and improve our fundamental understanding of crystallization processes.

2:00 PM BM09.04.02
DNA-Programmed Assembly of Single Crystalline Nanoparticle Superlattices at Interfaces Robert J. Macfarlane; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices with unique structure-dependent physical phenomena. While DNA base pairing has enabled the development of materials with nanometer-scale precision in nanoparticle placement and independent control over particle size, lattice parameters, and crystal symmetry, manipulating the macroscopic shape of the lattices remains challenging. By pairing this “bottom-up” assembly method with “top-down” lithographic techniques and assembling nanoparticle superlattices on a patterned substrate, complete control over crystal size, shape, orientation and unit cell structure can be realized. The key challenges in developing this technique are to first understand how different design factors affect the assembly process in this broken-symmetry system that is assembled at an interface, and subsequently develop structure-property relationships that correlate the above mentioned design parameters with the resulting overall material structure. Here, we examine both at-equilibrium deposition processes capable of generating single crystals with well-defined shapes, as well as post-deposition annealing to transform disordered particle arrangements into crystalline arrays. Using a combination of X-ray diffraction and electron microscopy techniques, both surface morphology and internal thin film structure are examined to provide an understanding of the mechanisms of particle crystallization under conditions where crystal growth is anisotropic due to a boundary condition. This novel method for controlling particle assembly draws several strong analogies to traditionally atomic epitaxy/heteroepitaxy, providing a useful tool for understanding thin film growth processes. As a result, we are able to realize 3D architectures of arbitrary domain geometry and size, thereby making materials with unprecedented precision across multiple length scales.

2:15 PM BM09.04.03
Programmable DNA-Semiconductor Nanostructures for Molecular Delivery Libing Zhang; Leslie Dan Faculty of Pharmacy, University of Toronto, Toronto, Ontario, Canada.

Biotemplated nanomaterials offer great promise in multimodal imaging, biosensing, and molecular delivery. There remains an unmet need for traceable and biocompatible nanomaterials that can be synthesized in a precisely controllable manner. Here, we demonstrate a single-step fabrication method for Quantum Dot-DNA Hydrogels and their successful application in enzyme-responsive drug/siRNA delivery and cell-specific targeting, and the use of a new family of materials – programmable metal/semiconductor nanostructures – for drug delivery and mRNA sensing in drug-resistant cells.

2:30 PM BM09.04.04
Magnesium Stabilized Multifunctional DNA Nanoparticles for Tumor-Targeted and pH-Responsive Chemotherapy Leilei Tian; South University of S&T of China, Shenzhen, China.
Functional nucleic acids, that can target cancer cells and realize stimuli-responsive drug-delivery in tumor microenvironment, have been widely applied for anti-cancer chemotherapy. The high cost, unsatisfactory biostability, and complicated fabrication process are the main limits for the development of DNA-based drug-delivery nanocarriers. Recently, a kind of DNA-Mg2PPI (magnesium pyrophosphate) composite nanoparticles has been produced from rolling circle amplification (RCA), which combine advantages of the designate and high-throughput isothermal amplification technique and the high stability of DNA condensation structures, quickly becoming an attractive biomedical material with great potentials. Herein, instead of using MgPPI, we found that only Mg2+ is sufficiently enough to stabilize the functional DNAs for chemotherapeutic applications. The very long single-stranded RCA product with a high charge density is more prone to form a stable condensation structures compared with a short oligonucleotide. Moreover, the dynamic electrostatic interactions between Mg2+ and DNA can better preserve the functions of DNA, which is more suitable for the design of drug-delivery system. A tumor-targeting Dox-delivery nanoparticle (~ 100 nm) was synthesized by the condensation of RCA products in the presence of an excessive amount of Mg2+, which showed good bio-stability in serum, considerable Dox loading capability, specific cancer-targeting ability, and pH-responsive sustained Dox release. The DNA nanoparticle not only has a simple composition, but also it will keep intact after the excessive exterior Mg2+ is removed, making it safe and ideal for in vivo application. Through cellular and in vivo experiments, we thoroughly demonstrated that this kind of Mg2+ stabilized multi-functional DNA nanoparticles can successfully realize tumor-targeted Dox delivery.

2:45 PM BM09.04.05
DNA-Programmable Nanoparticle Lattices Assembled on Polymer-Patterned Surfaces
Shu Sun1, 2, Dmytro Nykypanchuk2, Gregory Doerk2, Charles Black2, Oleg Gang2, 3 and Diana Lopez2; 1Xi'an Jiaotong University, Xi'an, China; 2Center of Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 3Department of Chemical Engineering, Columbia University, New York, New York, United States.

Photonic and electronic devices require precise control of functional components at the nanoscale. The development of DNA nanotechnology offers a fascinating platform to direct the assembly of nanoparticles into well-organized architectures with prescribed distances and spatial arrangements. Here, we combine DNA-based assembly and diblock copolymer self-assembly to realize the multi-layer assembly of gold nanoparticles into large-area, three-dimensional arrays. Specifically, the assembly of gold nanoparticles is directed through binding with DNA origami that forms arrays, and the array growth is controlled by patterns formed via diblock copolymer on the surface. In our approach, DNA-programmable nanoparticle lattices are sequentially assembled with registry of polymer pattern. We show the potential to assemble functional nanoparticles in layer-by-layer manner with controllable interlayer distance and in-plane arrangements through a combination of surface patterns and DNA nanostructures.

3:00 PM BREAK

3:30 PM BM09.04.06
Engineering Molecular Assembly for 3D Electronics
Thom LaBean, Nikolay Frick and Ming Gao; North Carolina State University, Raleigh, North Carolina, United States.

The ability to design and program complex molecular interactions between synthetic biomolecules (especially polynucleotides and polypeptides) has led to a revolution in artificial nanomaterials capable of self-assembly. For example, DNA-based nanotech entails the design of artificial nucleotide sequences capable of self-assembling into desired geometric shapes and patterns with nanometer-scale precision. These synthetic DNA nanostructures have been shown useful for organizing other materials including inorganic nanoparticles (metals and semiconductors), nucleic acid aptamers, and carbon nanostructures. We are working with DNA self- and directed-assembly to develop a general purpose molecular assembly toolbox useful for a wide variety of applications, especially in nanoelectronics and medicine. One promising future direction is the bottom-up fabrication of electronics components and devices including molecular assembly of wires and metal nanoparticles toward the construction of single-electron transistors, multicomponent devices, and artificial neural networks.

4:00 PM BM09.04.07
Self-Assembled Peptide Nano-Materials for Optics and Electronic Applications
Sharon Gilead and Ehud Gazit; Tel Aviv University, Department of Molecular Microbiology and Biotechnology, Tel Aviv, Israel.

In recent years, a key direction in the field of electronics and opto-electics involves the transition from inorganic to organic components, including organic light emitting diodes (OLED), thus paving the way towards flexible and wearable electronic and light emitting devices. Bio-inspired organic materials may be the next-generation of organic optoelectronic devices based on self-organization principles, which allow facile synthesis, eco-friendliness, resistance to oxidation and no need for heavy metal doping. Recent advances in bioorganic nanotechnology have established the notion that very simple building blocks, such as dipeptides, can form regular nanostructures with distinct mechanical, optical, piezoelectric and electronic properties. In particular, members of the diphenylalanine (FF) peptide archetypal family have been shown to form various morphologies and ordered nanostructures such as tubes, rods, fibrils, spheres, plates and macroscopic hydrogels with nano-scale order. Several studies have explored the piezoelectric properties of the diphenylalanine (FF) peptide. In the presence of an external electric field, vertically aligned FF microrod arrays can be organized on a substrate, resulting in enhanced piezoelectric response. Here we show the ability of FF and other similar peptide assemblies to be used in various electronics and optics application as new bioorganic materials. FF assemblies can act as an active optical waveguiding material, allowing locally excited states to propagate along the axis of the assemblies. In addition, Fmoc capped building blocks exhibit remarkable optical properties, such as quantum confinement and fluorescence. Other rod-like assemblies and toroid-like assemblies exhibit remarkable physicochemical features, including high thermal stability, metallic-like mechanical rigidity, luminescence, piezoelectricity and semi-conductivity. The ability of FF to self-assemble into ordered structures was discovered by a systematic reductionist exploration of biological recognition modules in an amyloidogenic polypeptide. We are applying a similar reductionist approach to expand our search for minimal building blocks towards single amino acids as well as other metabolites such as nucleobases, demonstrating their self-assembly into various ordered structures. Doing this we are enlarging our library of biological building blocks which bear the potential to be novel bio-inspired supramolecular materials for Optics And Electronic applications.

4:15 PM BM09.04.08
Amino Acid-Encoded Biocatalytic Self-Assembly for Transient Functional Nanostructures
Mohit Kumar and Rein Ulijn; Nanoscience, ASRC, City University of New York at the Graduate Center, New York, New York, United States.

One key feature of biological systems is the existence of chemically fueled, transient structure and function, like the on-demand formation/degradation of tubulin, actin fibers etc. Supramolecular polymers as synthetic mimic of such biomaterials has shown great promise in a number of areas, including...
biomedicine, sensing and energy harvesting. However, the main challenge is to actively regulate the shape, function and performance of these materials, while maintaining their physiological conditions. This has spurred recent research towards temporal control of nanostructures, which is achieved by using (bio-)catalysis to activate building blocks and thereby drive assembly. In this regard, potential for design of active supramolecular nanostructures based on peptide nanotechnology is increasingly appreciated. The objective of this work is demonstration of active encoding of nanostructures by using simple amino acids, resulting in transient conducting nanowires and in situ visualize time dependent dynamics of such structure.

We designed a self-assembling core molecule with two in-built competing reactive sites, consisting of the organic semiconductor naphthalenediimide (NDI), conjugated with D and L enantiomer of tyrosine methyl esters. The stereoselective fast enzymatic reaction at the L enantiomer compared to the D enantiomer provides the necessary kinetic competition to achieve temporal control over assembly. By simply adding one of a range of encoding amino acids in the presence of enzyme α-chymotrypsin, we achieve pathway selection between hydrolysis and acylation at both chiral ends. This results in an in situ modification of the amphiphilic structures, giving rise to unique self-assembly trajectories that are time programmed by the nature of encoding amino acid. Taking advantage of the semiconducting nature of the NDI core, electronic wires could be formed and subsequently degraded, resulting in temporally regulated electro-conductivity. Such a system holds great promise towards interfacing biology with electronics. Moreover, by appropriately functionalizing molecules with a fluorophore, the dynamic formation and degradation of nanofibers could be visualized with STED (Stimulated Emission Depletion microscopy) based super resolution microscopy. Such imaging significantly improved the resolution (39%) compared to traditional confocal. Interestingly, the lifetime of transient nanostructures can be completely controlled by simply choosing different amino acids. Overall, the biocatalytic incorporation of encoding amino acids around a functional core offers a general approach to modulate, switch or fine-tune supramolecular structures over time which can now be visualized in situ with superresolution microscopy.


4:30 PM BM09.04.09
DNA Origami-Assembled Light-Emitting Nanoclusters with Controllable Optical Output Honghu Zhang1, Mingxing Li1, Kaiwei Wang1,2, Ye Tian1, Jia-Shiang Chen1, Mingzhuo Liu1, Katherine T. Fountaine3, Donald DiMarzio1, Mircea Cotlet1 and Oleg Gang1, 4; 1Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 2School of Science, Xi'an Jiaotong University, Xi'an, China; 3Department of Chemical Engineering and Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States.

Structural DNA nanotechnology has emerged as a powerful method to fabricate targeted nanoscale architectures. Using rationally designed DNA origami frames, nanoparticles can be coordinated in a prescribed manner in 3D. Here, we have designed DNA origami frames for assembling various nanoparticles in pre-determined locations. The DNA frames have enabled well-defined nanocluster assembly with nanometer-precision positioning, and controllable high-purity stoichiometry with tunable functionality. We have fabricated DNA origami-constructed nanoparticle clusters, consisting of spherical quantum dots (QDs) and gold nanoparticles (AuNPs) that exhibit controllable photoluminescence (PL) when the excitation wavelength is close to surface plasmon resonance of the AuNPs. Furthermore, these DNA-constructed nanoclusters emit highly polarized light. By varying the size and number of AuNPs in the nanoclusters, we have explored correlations between the assembled structures and the PL polarization magnitude and the overall PL enhancement. Our DNA origami based nanoclusters with precisely built 3D architectures provide an efficient route to control single emitter optical output.

4:45 PM BM09.04.10

Stimuli-responsive nanomaterials with reconfigurable structures and properties have garnered significant interest in the fields of optics, electronics, magnetics, and therapeutics. DNA is a powerful and versatile building material that provides programmable structural and dynamic properties, and indeed, sequence-dependent changes in DNA have already been exploited in creating switchable DNA-based architectures. However, rather than designing a new DNA input sequence for each intended dynamic change, it would be useful to have one simple, generalized stimulus design that could provide multiple different structural outputs. In pursuit of this goal, we have designed, synthesized, and characterized pH-dependent, switchable nanoparticle superlattices by utilizing i-motif DNA structures as pH-sensitive DNA bonds. When the pH of the solution containing such superlattices is changed, the superlattices reversibly undergo: (i) a lattice expansion or contraction, a consequence of the pH-induced DNA “bond breaking” and “bond forming” processes. The introduction of i-motifs in DNA colloidal crystal engineering marks a significant step toward being able to dynamically modulate crystalline architectures and propagate local molecular motion into global structural change via exogenous stimuli.

SESSION BM09.05: Poster Session I: Bioinspired Materials
Session Chairs: Chun-Long Chen and Tiffany Walsh
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

BM09.05.01
Tandem Molecular Self-Assembly in Liver Cancer Cells Jie Zhang1, Yanbin Cai1, Ling Wang2 and Zhimou Yang1; 1College of Life Sciences, Nankai University, Tianjin, China; 2College of Pharmacy, Nankai University, Tianjin, China.

Inspired by nature, stimuli-responsive self-assembly has been widely explored for spatiotemporally regulating diverse cellular functions. In situ formation (both pericellular and intracellular) of assemblies of man-made small molecular in cell milieu has been successfully applied for controlling the cell behavior and fate. The differences of the expression levels of bio-signals (i.e., enzyme or small molecule) between cells are favorable natural-source of inspiration for designing precursors to form sophisticated assemblies with enhancing selectivity to target and inhibit diseased cells. We herein describe the tandem molecular self-assembly of a peptide derivative NBD-GFFpYss-ERGD (Tandem Molecular Self-assembly Precursor, TMSP) that is controlled by a combination of enzymatic and chemical reactions. In phosphate-buffered saline (PBS), TMSP self-assembles first into nanoparticles by phosphatase and then into nanofibers by glutathione. Liver cancer cells exhibit higher concentrations of both phosphatase and GSH than normal cells. Therefore, the tandem self-assembly of TMSP also occurs in the liver cancer cell lines HepG2 and QGY7703; TMSP first forms nanoparticles around the cells and then forms nanofibers inside the cells. Owing to this self-assembly mechanism, TMSP exhibits large ratios for cellular uptake and inhibition of cell viability between
A tantalum oxide (Ta₂O₅) film was deposited on the lower electrode deposited by electron beam deposition (EB depo.), and the upper electrode was biomolecule-hostings gels and the chemical interactions between biomolecules and silica host have been investigated. Ethidium bromide (EtBr) high resistance state with low bias voltage and time. It is short-term plasticity well-known as synaptic movement. Also, manganese oxide is similarly deposited to fabricate a usual ReRAM. A structure in which manganese oxide (MnO₂) was sandwiched between the Ta₂O₅ film and the lower intervals of 40 to 50 nm by modifying PEG on the surface of ferritin.

A conceptually new fabrication technique has been developed for the fabrication of composite gel coatings containing commercially available drugs that of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. ZnO, a high mobility -type semiconductor, is a highly attractive transparent material for applications in optoelectronic devices. However, the manufacture of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. In this work we will demonstrate a biomimetic approach for the synthesis and deposition of ZnO films on Si substrates under mild ambient conditions. Simultaneous synthesis and deposition of ZnO nanoparticles (NPs) is achieved in this work by the use of dual affinity peptides (DAPs) as linkers. One segment of the DAP has a strong affinity to the substrate and the other promotes the synthesis of the NPs. The formation of 10-20 nm crystalline NPs in solution was confirmed by transmission electron microscope (TEM) electron diffraction analysis. Further X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) characterization revealed 1[Zn]:1[O] stoichiometry. Initial results demonstrating the in-situ deposition of ZnO NPs on Si using the DAP linkers will also be presented. We will further show that the DAP monolayers reduce the work function of ZnO by ~260 meV. This work demonstrates the great potential of using low-cost and green biomimetic approaches for the fabrication of thin nanocrystalline inorganic films towards implementation in optoelectronic devices.

A tantalum oxide (Ta₂O₅) film was deposited on the lower electrode deposited by electron beam deposition (EB depo.), and the upper electrode was biomolecule-hostings gels and the chemical interactions between biomolecules and silica host have been investigated. Ethidium bromide (EtBr) high resistance state with low bias voltage and time. It is short-term plasticity well-known as synaptic movement. Also, manganese oxide is similarly deposited to fabricate a usual ReRAM. A structure in which manganese oxide (MnO₂) was sandwiched between the Ta₂O₅ film and the lower intervals of 40 to 50 nm by modifying PEG on the surface of ferritin.

A conceptually new fabrication technique has been developed for the fabrication of composite gel coatings containing commercially available drugs that of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. ZnO, a high mobility -type semiconductor, is a highly attractive transparent material for applications in optoelectronic devices. However, the manufacture of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. In this work we will demonstrate a biomimetic approach for the synthesis and deposition of ZnO films on Si substrates under mild ambient conditions. Simultaneous synthesis and deposition of ZnO nanoparticles (NPs) is achieved in this work by the use of dual affinity peptides (DAPs) as linkers. One segment of the DAP has a strong affinity to the substrate and the other promotes the synthesis of the NPs. The formation of 10-20 nm crystalline NPs in solution was confirmed by transmission electron microscope (TEM) electron diffraction analysis. Further X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) characterization revealed 1[Zn]:1[O] stoichiometry. Initial results demonstrating the in-situ deposition of ZnO NPs on Si using the DAP linkers will also be presented. We will further show that the DAP monolayers reduce the work function of ZnO by ~260 meV. This work demonstrates the great potential of using low-cost and green biomimetic approaches for the fabrication of thin nanocrystalline inorganic films towards implementation in optoelectronic devices.

A tantalum oxide (Ta₂O₅) film was deposited on the lower electrode deposited by electron beam deposition (EB depo.), and the upper electrode was biomolecule-hostings gels and the chemical interactions between biomolecules and silica host have been investigated. Ethidium bromide (EtBr) high resistance state with low bias voltage and time. It is short-term plasticity well-known as synaptic movement. Also, manganese oxide is similarly deposited to fabricate a usual ReRAM. A structure in which manganese oxide (MnO₂) was sandwiched between the Ta₂O₅ film and the lower intervals of 40 to 50 nm by modifying PEG on the surface of ferritin.

A conceptually new fabrication technique has been developed for the fabrication of composite gel coatings containing commercially available drugs that of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. ZnO, a high mobility -type semiconductor, is a highly attractive transparent material for applications in optoelectronic devices. However, the manufacture of high quality ZnO thin films requires high temperatures and/or pressure, making the processes expensive. In this work we will demonstrate a biomimetic approach for the synthesis and deposition of ZnO films on Si substrates under mild ambient conditions. Simultaneous synthesis and deposition of ZnO nanoparticles (NPs) is achieved in this work by the use of dual affinity peptides (DAPs) as linkers. One segment of the DAP has a strong affinity to the substrate and the other promotes the synthesis of the NPs. The formation of 10-20 nm crystalline NPs in solution was confirmed by transmission electron microscope (TEM) electron diffraction analysis. Further X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) characterization revealed 1[Zn]:1[O] stoichiometry. Initial results demonstrating the in-situ deposition of ZnO NPs on Si using the DAP linkers will also be presented. We will further show that the DAP monolayers reduce the work function of ZnO by ~260 meV. This work demonstrates the great potential of using low-cost and green biomimetic approaches for the fabrication of thin nanocrystalline inorganic films towards implementation in optoelectronic devices.
Self-assembly is widespread in nature. Supramolecular hydrogels formed by small molecular peptides that self-assemble in water through the noncovalent interactions have the advantages of simple chemical synthesis, easy modification of component units, good biocompatibility and low toxicity, and fluorescence probes have been applied for the detection of important analytes with high sensitivity and specificity. However, they cannot be directly applied for the detection in samples with auto-fluorescence such as blood.

Herein, we demonstrated a simple but effective method of surface-induced self-assembly/hydrogelation for fluorescence detection of an enzyme. First, the peptide precursor NBD-FFPY with fluorescent group NBD was synthesized by solid-phase synthesis method. Then NBD-FFPY could be dephosphorylated to form gelators NBD-FFY by alkaline phosphatase. After the peptide precursor NBD-FFPY was cleaved by the alkaline phosphatase, NBD-FFY can be embedded into the surface of positively charged glass plate. Therefore, the fluorescence intensity of NBD-FFY on the glass surface can be calculated through detecting the fluorescence intensity of NBD-FFY deposited on the surface of the glass was linearly related to the incubation time and the concentration of the enzyme. Even in the complex environments such as blood and cell lysate, our method can still quickly detect the activity of the enzyme.

As a result, surface-induced self-assembly for fluorescence not only expands the application of molecular selfassembly but also provides a useful method that can be applied for direct detection of enzyme activity in complex biological samples such as blood and cell lysates.

Studies on Synthesis and Fluorescence Spectroscopy of Hybrid Magnetic Nanoparticles (Fe3O4-Au) Linked with Fluorescent Molecule

Magnetic and fluorescent nanoparticles are widely studied in biomedical research for their use in drug delivery, cell separation, magnetic resonance imaging (MRI), hyperthermia, various multimodal techniques, etc. In this study, we report a recent work on nanoparticles incorporating with a fluorescent molecule and a superparamagnetic core via nanoscale engineering. Fe3O4-Au hybrid nanoparticles are synthesized via a solution phase chemical reaction in an inert N2 atmosphere. These synthesized hybrid nanoparticles are characterized by UV-Vis-NIR spectroscopy, fluorescence spectroscopy, XRD, TEM, etc. Optimal synthesis conditions are also highly relevant in producing stable and uniform hybrid nanoparticles without impurities. Fluorescence spectroscopy show the correlations between the lifetime and intensity of fluorescence and sizes, compositions, shapes of hybrid nanoparticles as well as the conjugation process to link the nanoparticles to fluorescent molecules. By carefully engineering the growth conditions, such as altering growth temperatures and precursor reagent ratios, functional hybrid magnetic nanoparticles can be optimized for hyperthermia, MRI and other multimodal biomedical applications.

Self-Assembly of Peptide with Polyoxometalates into Nanostructured Materials

Polyoxometalates (POMs) are one of the structurally-characterized anionic oxide nanoclusters that have been frequently used as building blocks to self-assemble organic-inorganic hybrid materials. POMs-based hybrid materials have received attractive attention owing to their applications in catalysts, photovoltaics, molecular magnetism, and biochemistry. Peptoids, a type of sequence-defined synthetic molecules, are composed of repeating N-substituted glycine monomer units and developed as attractive protein-mimetics to combine the advantages of both synthetic polymers and biopolymers. Moreover, peptoids are more thermally and chemically stable in comparison with peptides and proteins. The lack of both intra- and intermolecular backbone hydrogen bonds make peptoids as unique building blocks for controlled self-assembly1-4 and tuning the function of peptoid-based materials. In this presentation, we will report the two alternative approaches to self-assemble organic-inorganic hybrid materials from POMs and peptoids. For the first approach, peptoids containing cationic residues are co-assembled with anionic POMs via electrostatic interaction. Peptoid sequences and the ratio of POMs and peptoids are varied to tune the morphology of the self-assembled hybrid materials. The second approach is based on building POM-containing peptoids by having POMs as peptoid side chains, then these hybrid sequences are self-assembled into hierarchically-structured organic-inorganic hybrid nanomaterials. Comparing to the first approach, the second approach offers the precise control the location and stereochemistry of POMs within peptoid assemblies.

As a result, surface-induced self-assembly for fluorescence not only expands the application of molecular selfassembly but also provides a useful method that can be applied for direct detection of enzyme activity in complex biological samples such as blood and cell lysates.

Magnetic and fluorescent nanoparticles are widely studied in biomedical research for their use in drug delivery, cell separation, magnetic resonance imaging (MRI), hyperthermia, various multimodal techniques, etc. In this study, we report a recent work on nanoparticles incorporating with a fluorescent molecule and a superparamagnetic core via nanoscale engineering. Fe3O4-Au hybrid nanoparticles are synthesized via a solution phase chemical reaction in an inert N2 atmosphere. These synthesized hybrid nanoparticles are characterized by UV-Vis-NIR spectroscopy, fluorescence spectroscopy, XRD, TEM, etc. Optimal synthesis conditions are also highly relevant in producing stable and uniform hybrid nanoparticles without impurities. Fluorescence spectroscopy show the correlations between the lifetime and intensity of fluorescence and sizes, compositions, shapes of hybrid nanoparticles as well as the conjugation process to link the nanoparticles to fluorescent molecules. By carefully engineering the growth conditions, such as altering growth temperatures and precursor reagent ratios, functional hybrid magnetic nanoparticles can be optimized for hyperthermia, MRI and other multimodal biomedical applications.
involving van der Waals force, must be working at the basic level. The thickness of the film implies an alignment of a few poly-Glycine helices in the vertex as attraction and many of them into an ordered side-side arrangement. Such a uniformly flat structure suggests its possible role as a reliable and well-defined platform for further assembly with other molecules as a composite film.

We also found that some short peptides and alpha-hydroxy acids self-assembled into long strings as well as a hydrogel structure under an aqueous condition at specific pHs. The hydrogel has a nano-mesh like structure that can be reconstructed on mineral surfaces and visualized with AFM. We are particularly interested in possible roles of these structures as potential functional biomaterial in the origin of life on the Earth.

**BM09.05.10 Catalytic Self-Assembly of Peptidic Bolaamphiphiles Coordinated with Transition Metal Cofactors** Sang-Yun Lee, Min-Chul Kim and Changjoon Keun; Yonsei Univ, Seoul, Korea (the Republic of).

Peptidic bolaamphiphile is an biomimetic amphiphilic molecule whose biochemical activity can be tuned by the designer peptides. The peptidic bolaamphiphiles have peptide or amino acid segments as hydrophobic moieties that are associated with the central alkyl chain to display amphiphilic property. Similar to other amphiphilic molecules, these peptidic bolaamphiphiles self-assemble to form complex structures while exposing the biological component to the surface in an aqueous medium. Here, assembled structure of histidyl bolaamphiphiles was exploited as a biomimetic host matrix whose histidine imidazoles are exploited as ligands to coordinate with transition metal ions. By coordinating with transition metal ions, metalloenzyme-mimetic catalysts could be built. In particular, catalytic activity for CO2 hydration and oxidation of organic compounds could be realized by coordinating various transition metal ions to the histidyl bolaamphiphile assembly. Furthermore, the catalytic water evolution was achieved by introducing iridium to the histidyl bolaamphiphile assembly. The prepared metal-bolaamphiphile catalyst was surveyed with spectroscopic studies to verify the origin of the catalytic activity. This assembly of peptidic bolaamphiphiles will be beneficial for the building of catalyst mimicking various metalloenzymes.

**BM09.05.11 Thermodynamic Properties of Pluronic F127 Micelles with Added Cefepime Determined by Differential Scanning Calorimetry** Lydia M. Menah1 and Brian J. Love1, 2; 1Material Science and Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Biomedical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Aqueous amphiphilic copolymer solution have been made with varying amounts of a third constituent with the notion of forming drug loaded gels. Our research group is interested in how additive molecules perturb the structure of amphiphilic copolymers that are known to form colloidal crystals. We are investigating whether likely correlations exist between how strongly the drug interacts within the hydrophobic and hydrophilic regions of micelles and colloidal crystals and how bioavailable the drug is as it elutes from within the gel. We have made 25% aqueous solutions of PEO-PPO-PEO copolymers (F-127, BASF) formulated and tested between -5°C and 50°C. Rheology, and DSC have been the primary tools of measurement and we have focused our initial efforts on cefepime to observe how its presence affects micelle formation and colloidal crystallization. Drug-loaded polymers are of interest as schemes within the drug delivery community for controlled release and other studies have been done using dendrimers, and responsive polymers contained within other polymers. We have found that when Cefepime has been added in concentrations ranging from 2-8% of the mass of a 25% PEO-PPO-PPO copolymer solution, the onset temperature for micelle formation systematically drops with increasing cefepime concentration. The change is not dramatic, 9.1°C ±5.1 for neat, while 4.5°C ±5.1 for 8%, the trend is apparent. The size of the endotherm does not show the same systematic trend and within the realm of statistical analysis, the size of the endotherm is invariant to cefepime concentration. At 2°C/min, the energy of the gel formation is masked by the rest of the endotherm linked with micelle formation. We are testing a lower ramp rates in order to observe the transition linked with the gel. Separately we have resolved that the gel is clearly forming and requires a cold re-equilibration to break up the gel structure. It can be inferred that cefepime is acting as a chaperone to allows micelles to nucleate more easily at lower temperature. We will present on the gel formation temperatures, enthalpies, and transitions to show the structural formation and development of the other polymers-drug complexes beyond cefepime/F-127.

**BM09.05.13 β-Sheet Crystallization-Driven Supramolecular Peptide Nanoagents with Structure-Dependent Theranostic Functions** Inhye Kim1, 2 and Eunji Lee1; 1School of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); 2Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon, Korea (the Republic of).

Versatile, one-dimensional (1D) supramolecular theranostic nanoagents were developed by β-sheet crystallization-driven-assembly of peptide amphiphiles (PAs) attached with paramagnetic metal ion (gadolinium, Gd3+)-chelating moiety and tumor cell-targeting segment, respectively. Paramagnetic metal-attached scaffolds have attracted much attention as magnetic resonance imaging (MRI) contrast agents (CAs). Many efforts have been devoted to enhance MRI efficacy of commercial CAs by adopting supramolecular scaffolds to overcome the disadvantages with low sensitivity and specificity. Here, fibrils, driven by the assembly of PA with hydrophobic β-sheet-forming peptide block, were utilized as a theranostic nanoscaffold with drug-loading within their robust core. The resulting 1D nano-aggregates allowed successful intracellular delivery of doxorubicin (DOX) to target cancer cells and contrast-enhanced MR imaging by high longitudinal (T1) relaxivity of water protons. Correlation between the structural nature of fibrils formed by PA-assembly and its diagnostic efficacy was elucidated. The nanostructured theranostics with desirable functions may thus be a useful strategy for the generation of tailor-made biocompatible nanomaterials.

**BM09.05.14 Graphitization and Strength of Annealed Silks and Synthetic Polymer Fibers** Thomas Dugger1, Sourangsu Sarkar2, Sandra Correa-Garhwal1, Mikhail Zhernenkov1, Hourng Kim Chea1, Cheryl Hayashi4 and David Kisailus1; 1University of California, Riverside, Riverside, California, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States; 3Brookhaven National Laboratory, Upton, New York, United States; 4American Museum of Natural History, New York, New York, United States.

Silks have been proposed as superior carbon fiber precursors to synthetic polymers. β-sheet nanocrystals, the main contributor to silk's strength, have a favorable structure to graphitize upon annealing. Due to their uniform dispersion throughout the fiber and preferential alignment along the long axis of the fiber, silk-precursor carbon fiber could be stronger than traditional carbon fiber made from polycrylonitrile (PAN). To investigate this theory, we compare the degree of graphitization, graphite crystal orientation, and tensile strength between spider silks, silkworm silk, PAN, and poly(vinyl alcohol).

**BM09.05.15 Fabrication of 2D Protein Films and 3D Protein Hollow Spheres via Alternative Self-Assembly of α-Synuclein and Their Applications** Sookkoo Lee1, Ghibom Bhak2 and Seung R. Paik1; 1Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of); 2Organic Chemistry University of Santiago de Compostela (USC), Center for Research in Biological Chemistry and Molecular Materials (CIQUS), Santiago de Compostela, Spain.
Understanding the self-assembly process of amyloidogenic proteins is valuable not only to find their pathological implications but also to prepare protein-based biomaterials. α-Synuclein (αS), a pathological component of Parkinson’s disease, producing one-dimensional (1D) amyloid fibrils, has been employed to generate two-dimensional (2D) protein films and three-dimensional (3D) protein hollow spheres (PHS) via its alternative self-assembly at either high temperature or rapid-freezing condition, respectively. At a high temperature of 50°C, αS molecules self-assembled into the 2D film whereas 1D amyloid fibrils were produced at 37°C. This alternative self-assembly phenomenon could be attributed to structural plasticity of the intrinsically disordered protein of αS which turns into a surface active agent at the air-water interface at the high temperature. The αS 2D film was also routinely prepared at the oil-water interface and used as a framework of molecular assembly to give rise to a polydiacetylene-based sensing material. 10,12-Pentacosadiynoic acids (PCDA) were aligned on the film in a spatially organized way and then photo-polymerized to induce the n-conjugated molecular assembly yielding blue color. Its colorimetric transition to red was induced by increasing temperature. This functionalized protein film increased its height to 60 nm from 40 nm upon the PCDA immobilization and exhibited enhanced physical and chemical stability. In addition, the modified film showed remarkable high electrical conductivity only in the red state. Under frozen condition, on the other hand, PHS were produced from αS oligomers via rapid freezing, frozen incubation, and freeze-drying process. PHS prepared with αS-eosin conjugates and focused ion-beam severance of PHS confirmed their empty core structure. While PHS were stable at room temperature, they were immediately converted into amyloid burs comprised of protein nanofibrils upon heating. Therefore, PHS could be considered a constrained spherical structure transformable into biocompatible matrix material in nanoscale which could be used as a fill-in agent to improve mechanical strength of living tissues like skin as well as hydrogels in general. In this study, we have demonstrated selective fabrication of the amyloidogenic protein of αS into either 2D or 3D structures and their use as potential protein-based biomaterials.

BM09.05.16

Chain-Like Superstructures of Macromolecular Micelles for Linear Assembly of Plasmonic Nanoparticles and Fluorophores

Kyungtai Kim, Sukwoo Jang, Jonghyuk Jeon, Donghwi Kang and Byeong-Hyeok Sohn; Seoul National Univ, Seoul, Korea (the Republic of).

In living organisms, we can find various chain-like structures in microscale, which are usually self-assemblies of biomacromolecules. For example, fibrils in a tissue consist of collagen as a biomacromolecular building block. Assemblies of collagens by controlled hydrogen bonding produce elongated supramolecular chains of fibrils. Similarly, colloidal nanoparticles having patches can be employed as effective building blocks for chain-like superstructures. Well-defined patches on nanoparticles can serve bonding parts for assembling process of linear chains. Especially, macromolecular micelles can have distinct patches on their surface so that they can be assembled into linear superstructures. In this presentation, we polymerized chain-like superstructures with patchy micelles of diblock copolymers and then utilized them for linear assembly of plasmonic nanoparticles and fluorophores. The growth of nanoparticles was controlled within the cores of macromolecular micelles in chain-like superstructures. In addition, fluorescent dyes were selectively attached to the core-forming blocks of macromolecular micelles to organize them into linear assemblies. We also produced red-, green-, and blue-emitting linear superstructures by varying the dyes attached to the core-forming block. We characterized optical properties of chain-like superstructures functionalized with plasmonic nanoparticles and fluorophores.

8:00 AM *BM09.06.01 Biominalization-Inspired Self-Organized Organic/Inorganic Composites—Stimuli-Responsive Ordered Nanorod Materials and Aligned Thin Films Formed with Macromolecular Templates

Takashi Kato; The University of Tokyo, Tokyo, Japan.

Biomimeralization-inspired synthesis of organic/inorganic composites has attracted attention. We have been developing a variety of composite materials based on macromolecular templates.[1] Here we report hydroxyapatite and calcium carbonate nanorods composites that exhibit liquid-crystalline properties and zine oxide thin-films with controlled aligned structures. The TEM observations of the nanorod composites show that they have crystalline structures covered with acidic macromolecules.[2] These nanorods exhibit colloidal liquid-crystalline states. Hydroxyapatite nanorod materials are aligned under application of an external magnetic field.[2] Magneto-optical response has been achieved for the liquid-crystalline states under crossed polarizers. Liquid crystalline materials are also obtained for calcite nanorods.[3] We have also applied bioinspired synthesis to the development of functional ZnO thin-film materials with oriented structures.[4] We have succeeded in the biomeralization-inspired synthesis of composite thin films comprising of zine hydroxide carbonates that are not found in biominalers. The composite thin films are converted to ZnO thin films with ordered structures through thermal treatment. Bioinspired syntheses are useful approaches to the development of new functional materials by low-energy consumption and environmentally friendly processes.


8:30 AM BM09.06.02

Utilizing GLC-TEM to Elucidate Magnetosome Biominalization in Magnetotactic Bacteria

Emre Firlar1,2, Meagan Ouy1, Agata Bogdanowicz2, Leigha Covnot1, Boao Song2, Yash Nadkarni2, Reza Shahbaziyan-Yassar2 and Tolou Shokuhfar1; 1Bioengineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois, United States.

Biomimicking of Fe3O4 magnetosome synthesis ex situ is of interest due to the potential uses in the physical and medical field, and is thus important to understand the biominalization pathway for the magnetosomes in magnetotactic bacteria. Conventional TEM approaches use fixation of bacteria preventing monitoring the dynamics or using fluid cell TEM holder which does not have enough spatial resolution. Therefore, in this work, graphene liquid cells (GLC) were used to encapsulate magnetotactic bacteria after mixing them with iron rich growth medium, thus maintaining the native environment. For the first time, the formation of these nanoparticle and increased nanoparticle contrast due to advancing biominalization using GLC-TEM was monitored.
Through electron energy loss spectroscopy (EELS) analysis, the presence of graphene optical gap, water exciton peak and graphene σ+π bond were monitored at 6 eV, 8.5 eV and at 14 eV, respectively. Formation of radiation induced H2 bubbles and magnetosomes were observed as well, indicating the presence of liquid during electron imaging. Fe2o (octahedral), Fe3o (tetrahedral), Fe(III) (octahedral) and FeOOH reference spectra were used to fit the experimental data. Relative ratio of Fe2+ to Fe3+ was calculated to be 0.35. Magnetite was known to be able to be converted to first maghemite and then to hematite via the electron beam exposure. Considering this ratio will be 0.5 for a perfect Fe3O4 (1x Fe2+, 2x Fe3+), hematite is the strongest candidate to be present in addition to magnetite in magnetosomes contributing to higher Fe3+ content. At different time scales after iron induction, (i) an increase of the magnetosome image contrast was reported by the line profile drawn across the magnetosome and increased TEM contrast showed increased mass-thickness in the image, which indicates progression in biomineralization and incorporation of more Fe3O4 molecules to this particle; and (ii) an increase in the number of magnetosomes were observed.

8:45 AM BM09.06.03

In nature we can find many examples of organic-inorganic nanocomposites with exceptional properties. For example, diatoms are unicellular algae whose cell walls are formed form hierarchical nanostructured silica. Euplectella sp. is a siliceous sponge that can assemble a mechanically resistant glass cage with nano- to macro- hierarchical organization. In both cases the formation process occurs by the intricate interactions between macromolecules and the silica precursors. These beautiful examples provide inspiration for the controlled formation of structurally complex silica based materials under ambient conditions.

In this paper we present a detailed study on the use of synthetic macromolecules to control silica morphology using two strategies: 1) mineralization of silica in pre-assembly macromolecular templates with defined pores and 2) the co-assembly of silica precursors and nanoparticles with macromolecules. Using (cryo)-electron microscopy, (cryo)-electron tomography and liquid phase electron microscopy we investigate the formation processes and characterize the hierarchically porous silica structures.

We discuss the underlying principles of silica mineralization in confinement and design strategies for making hierarchically porous silica based materials. Such porous materials have many potential applications including insulators, sensors, catalysts and drug delivery vehicles. We hope the insights provided by our detailed investigation will help towards the rational design and understanding of mechanisms formation of porous silica based materials.

9:00 AM BM09.06.04
Mineralization in Bio-Inspired Metal-Coordinate Polymer Hydrogels Niels Holten-Andersen, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Biominerals have been widely studied in part due to their unique mechanical properties, afforded by their inorganic-organic composite structure and well-controlled growth in macromolecular environments. More recently, growing concerns over climate change and environmental sustainability and the emerging relevance of green chemistry make biomineralization an even more attractive process to study. Here, we focus on the earlier stages of mineral nucleation and growth in macromolecular environments, where an organic, hydrogel matrix dominates the bulk properties of the material and the mineral is distributed throughout the matrix as nano- and/or microparticles. The phase, morphology, and size of the particles can be controlled using the choice of the hydrogel, functional moieties on the gel polymer backbone and soluble additives. Depending on the choice of organic matrix and inorganic mineral, the matrix can be dissolved to leave highly uniform particles, or the matrix can be left intact, creating a hydrogel-mineral composite with improved mechanical properties through organic-inorganic interfacial interactions or additional functionality, such as magnetic properties.

9:15 AM BM09.06.05
Towards Templating 2D Magnetite Platelets via Bio-Inspired Approaches Bernette Oosterlaken1, 2, Giulia Mirabello1, 2, Yifei Xu1, 2, Joseph P. Patterson1, 2, Heiner Friedrich1, 2 and Nico Sommerdijk1, 2; 1) Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; 2) Institute for Complex Molecular Systems, Eindhoven, Netherlands.

Magnetite, Fe3O4, is a naturally occurring iron oxide. Magnetite has excellent mechanical properties, as well as magnetic properties. Its magnetic properties depend on crystal size and shape. In nature, the formation of magnetite is precisely regulated, as controlled size and shape crystals are specifically tuned depending on the biological function, even at ambient and aqueous conditions.

Inspiration for this work was found in nature, where specialized vesicles with associated transmembrane proteins are directing nucleation and growth of the magnetite crystals. Achieving a similar level of control over crystal shape and size thus far has been challenging in synthetic procedures and the processes behind templated magnetite mineralization are still poorly understood.

Little work has been done on templated magnetite formation so far. In a bio-inspired approach, we are investigating templated magnetite growth, to precisely tune the size and shape of the magnetite crystal into a certain shape. The targeted crystal shape in this project is 2D platelets. 2D platelets of magnetite might have appealing magnetic properties, such as magnetic vortices, which result in in-plane magnetization.

A suitable template to direct magnetite growth into 2D crystals is collagen. Collagen is known to template the formation of calcium phosphate into 2D platelets, but also lepidocrocite (γ-FeOOH) (Xu et al., in preparation, 2018). By growing magnetite into a collagen template, we are creating a novel collagen-based hybrid material with excellent mechanical and magnetic properties. To the best of our knowledge, we are the first to explore the possibilities of growing magnetite in a collagen template.

To template magnetite inside a collagen matrix, magnetite formation outside the collagen template should be inhibited. Acidic (bio-)molecules, like polypeptides, are shown to influence magnetite crystal growth. As such, those polypeptides are used to assist in mineral formation inside the template, similar to what has been exploited for calcium phosphate mineralization in a collagen matrix before.

Combining spectroscopic techniques such as Raman spectroscopy with advanced electron microscopy techniques might provide us with new insights in the mechanisms behind magnetite formation inside the template. CryoTEM already has been shown to be of great value when addressing mineral formation mechanisms. Liquid phase electron microscopy (LP-EM) allows to visualize the processes in-situ and therefore is an appealing complementary technique to CryoTEM. Preliminary experiments in the confined space of the liquid cell that is used for LP-EM measurements show that magnetite indeed has formed inside the liquid cell. After optimization of the experimental conditions, LP-EM allows for in-situ visualization of templated magnetite formation.

9:30 AM BREAK
of incubation in phosphate buffered solutions (PBS), BSA immobilized and aligned exclusively along the biosilica micropatterns, while the FITC-BSA was noted, while the response on the unpatterned controls was randomized. Additionally, FTIC-labeled BSA and R5 were printed together and after 6 days biomineralization was demonstrated. This cost-effective micropattern design scheme can meet a wide range of needs in the biomedical field with labeled R5 and observed by fluorescence microscopy. hMSCs were cultured on the micropatterned hydrogels and specific alignment along the printed lines showed limited guidance of cell orientation in relatively short culture periods. Silica-based micropatterns are popular in many biomedical fields.

The organisation and function of biological systems is based on compartmentalisation. Biomimeralisation processes, which lead to the generation of mineral-based structures such as bones, teeth and seashells are no exception to this. Biominerals form within the confines of “privileged environments” delineated from the organism, where spatial constraints and chemical conditions can be precisely controlled. Despite this, the influence of confinement on crystallisation processes is poorly understood. This talk describes a series of systematic investigations into the effects of confinement on the formation of a range of important crystal systems including calcium carbonate, calcium sulfate and calcium phosphate. Rods of controlled glassy gels (CGs) with sponge-like structures were used to access thin nanoscale confinement. X-ray absorption and diffraction tomography were used to study the precipitation of a population of calcium sulfate particles within these environments and we show that bassanite (CaSO4·0.5H2O) whose existence as a precursor to gypsum (CaSO4·2H2O) has been disputed – is stable in the CGs for periods of at least three weeks. We can also monitor the transformation from bassanite to gypsum and investigate how this leads to fracture of these porous media. At larger length scales, microfluidic devices including a novel “crystal hotel” that comprises a series of “rooms”, are used to grow larger crystals. These offer many features including flow, confinement and the possibility of changing reaction conditions with time that are common to biological systems. These devices were used to image the development of crystals within confined volumes and to study the effects of soluble additives on calcium carbonate precipitation at early times. Our results show that the additives have no effect on crystal morphologies until the crystals reach at least 100 nm in size. Finally, the cylindrical pores of track-etched membranes were used to study the effects of confinement on calcium carbonate and calcium phosphate precipitation. We show that the polymorph of CaCO3 changes from calcite to aragonite as the pore diameter decreases, and that aragonite is the major polymorph in 200 nm pores when low concentrations of magnesium and sulfate ions are also present. Finally, calcium phosphate precipitation in this system generates highly orientated single crystal of hydroxyapatite in small pores, where the degree of orientation is comparable to that seen in bone. Confinement therefore enables effective control over crystallisation processes, and as such promises the ability to optimise the synthesis of crystalline materials.

In the development of the invertebrate calcium carbonate skeletal elements, protein families are involved in the coordination of mineralization events. In many instances this process begins with the formation of amorphous calcium carbonate mineral nanoparticles which are assembled into mesoscale crystals (calcite, aragonite, vaterite) and this assembly process creates many mechanistic features of these crystals that are important for material integrity. We have observed that in the mollussk shell and sea urchn spicules that this mineralization process is guided by the formation of matrix protein hydrogel phases that stabilize, assemble, and organize mineral nanoparticles, create nanotextured crystal surfaces, and form intracrystalline nanoainclusions within the mineral phase that introduce elastic deformability to the mineral phase. These protein hydrogels form in response to protein-protein interactions that are entropically driven by intrinsically disordered and modified globular protein domain sequences, as well as protein-carbohydrate interactions involving glycoproteins. We hope that materials science will develop similar principles to create the next generation of composite materials under ambient conditions.

Well-designed micropatterns present in native tissues and organs involve changes in extracellular matrix compositions, cell types and mechanical properties to reflect complex biological functions. However, mimicking these micropatterns in vitro remains a challenge and the patterning strategies often showed limited guidance of cell orientation in relatively short culture periods. Silica-based micropatterns are popular in many biomedical fields including in vitro tissue models, due to the biocompatibility and high versatility of silica. Yet, harsh conditions (e.g. extremely high temperature and/or pressure) are often required to create silica patterns, and bonding between substrates is not strong enough. In this work, a de novo design strategy to code functional micropatterns to engineer cell alignment through the integration of aqueous-peptide inkjet printing and site-specific biomimeralisation is presented. Inkjet printing provides direct writing of macroscopic biosilica selective peptide-R5 patterns, which allow site-specific growth of silica nanoparticles through in situ biomineralisation, with micrometer-scale resolution on the surface of a biopolymer (silk) hydrogel to achieve the alignment of human mesenchymal stem cell (hMSCs) and enhanced immobilization of bovine serum albumin (BSA). To create the micropatterns, peptide-R5 was inkjet printed on the surface of enzymatically crosslinked silk hydrogels, followed by subsequent silicification to induce biosilica deposition. Linewidth and gap distance between each printed line were manipulated by adjusting drop spacing and drop volume during printing. Biomimeralisation was confirmed by examining silica nanoparticles covering the printed lines but not elsewhere. A 20 µm pattern gap distance and 1 µm linewidth were achieved. Well-defined peptide patterns on the substrate were also evidenced by printing fluorescein isothiocyanate (FITC)-labeled R5 and observed by fluorescence microscopy. hMSCs were cultured on the micropatterned hydrogels and specific alignment along the printed lines was noted, while the response on the unpatterned controls was randomized. Additionally, FITC-labeled BSA and R5 were printed together and after 6 days of incubation in phosphate buffered solutions (PBS), BSA immobilized and aligned exclusively along the biosilica micropatterns, while the FITC-BSA alone extended over the surface, which suggests improved protein stability and alignment on micropatterns. A de novo strategy to design functional micropatterns to engineer cell alignment and protein immobilization through inkjet printing and site-specific biomimeralisation was demonstrated. This cost-effective micropattern design scheme can meet a wide range of needs in the biomedical field with implications for broader material designs.

The production of crystalline materials with structures and properties resembling those of biominerals is a challenging synthetic goal. Biominerals are invariably composite materials in which organic matrices are associated with the inorganic phase, even single crystal biominerals contain proteins embedded within the crystal lattice. Biominerals therefore provide a unique inspiration for the design and synthesis of new materials.

This talk explores how this biogenic strategy can be used to generate synthetic crystals with novel composite structures and properties and to determine the “design rules” which govern the occlusion of additives within crystals. Using polymer particles rather than proteins as simple crystal growth additives, High levels of particle occlusion is achieved by tuning the particle surface chemistry and the crystal growth conditions within calcite single crystals.
Our strategy is extended to generate nanocomposites in which inorganic nanoparticles are distributed throughout a crystal matrix with true nano-scale mixing. Highly effective incorporation of gold and magnetic nanoparticles was achieved within host carbonate- and sulfate-minerals by controlling the nanoparticle surface chemistry using a physically-adsorbed double hydrophilic diblock copolymers. This methodology can potentially be applied to a huge number of nanoparticle/ host crystal systems, where its experimental simplicity makes it an attractive and general method for generating composite materials.

11:30 AM *BM09.06.10
Exploring the Abiotic-Biotic Interface—From Fundamentals to Biomimetic Composites Carole C. Perry; Nottingham Trent Univ, Nottingham, United Kingdom.

Events occurring at the solid/aqueous interface (i.e. molecular recognition, adsorption, desorption etc.) underpin a variety of technologies used in the biomedical and biotechnological fields. The use of nanoparticles and multifunctional nanoparticles that combine recognition and targeting with specific properties is widespread for the development of clinical diagnostic tools or therapeutic platforms. Although we are developing understanding of how materials are made in nature there is a long way to go in applying that knowledge in a systematic and predictive fashion to develop new composite materials.

This presentation will highlight (a) aspects of our recent exploration of the effect of surface chemistry on peptide material interactions using both simulation (DFT) and experiment, and (b) show how we can apply this understanding to the development of novel biomimetic composites based on Pt/Au and MOFs.

In all our studies we use a wide range of experimental techniques to characterise our (bio) materials and measure their behaviour at interfaces. The research presented will include new methods being developed specifically to probe such interactions.

SESSION BM09.07: Biomimetic Crystallization
Session Chairs: Chun-Long Chen and Nico Sommersdijk
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Back Bay A

1:30 PM *BM09.07.01
Creation of Hierarchical Material Structures Using Molecular Specificity Yu Huang; University of California, Los Angeles, Los Angeles, California, United States.

Material formation in nature is precisely controlled in all aspects from crystal nucleation, growth to assembly to deliver superior functions. Specific biomolecule-material interactions have been hypothesized to play important roles in these processes. Proteins, polymers and small molecules have been extensively explored to replicate the degree of control in material formation in vitro and for nonbiogenic materials. However the organic-inorganic interfacial interaction is still far from being understood which hinders the further advancement of biomimetic material formation. In this talk I will share our efforts on decoding the myth of biomolecular specificity to material surface and their roles in controlling crystal nucleation and growth. The selection of facet specific short peptides and their abilities in guiding predictable morphology control of Pt nanocrystals will be first demonstrated. Then detailed experimental and theoretical studies on binding mechanism will be discussed. These studies open up opportunities in understanding the molecular details of inorganic-organic interface interaction, which can one day lead to the development of a library of molecular functions for biomimetic materials design and engineering.

2:00 PM *BM09.07.02
Leveraging Molecular-Level Control of Peptide Constructs to Direct the Synthesis, Structure and Properties of Chiral Nanoparticle Superstructures Nathaniel Rosi; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Replacing one atom or linkage in an organic molecule or polymer can dramatically affect its structure and properties. Chemists have leveraged the power of synthesis to adjust and fine tune the properties of molecules. Nanoparticles are a class of fundamental structural and functional building blocks for the construction of new materials. The properties of these materials depend intrinsically on the size, shape, and composition of the constituent nanoparticles as well as the precise organization of the nanoparticles within the material. In order to fine tune the properties of the material, we must be able to carefully adjust the organization of its component nanoparticles. Can we use the power of synthetic chemistry to program and carefully adjust the structure and properties of hierarchical nanoparticle-based materials? This talk deals with peptide-based methods for controlling the synthesis and assembly of nanoparticles into well-defined chiral helical architectures. Rigorous molecular models of peptide assemblies will be detailed. It will be demonstrated that the atomic make-up of the peptide constructs can be carefully adjusted and that these subtle yet purposeful modifications lead to non-trivial structural changes to the chiral nanoparticle superstructure assembly and properties.

2:30 PM BREAK

3:30 PM *BM09.07.03
Engineering Biology for Design and Assembly of Functional Materials Rajesh Nair; Joseph Slocik, Kristi Singh, Maneesh K. Gupta, Kuang Zhifeng and Patrick B. Dennis; Air Force Research Laboratory, Dayton, Ohio, United States.

Biological systems offer inspiration and exciting opportunities for creating biomimetic materials, structures and devices. The assembly of individual biomolecular units into well-defined, higher-order functional structures is a hallmark of biological systems, and is exemplified in the self-organization of biological building blocks into supramolecular structures (e.g. peptides, proteins, nucleic acids, viruses). Such biological materials/systems offer inspiration and exciting opportunities for creating biomimetic materials, emulating processes and inspiring the design of devices. Furthermore, the ability to use synthetic biology tools to manipulate the genetic information encoding for biomolecules of interest allows one to design materials with tailored functionalities and properties. I will describe in my talk our research on engineering biology to create designer biomolecules or enabling the assembly of functional materials for various applications.

4:00 PM BM09.07.04
Investigations into the Mechanism of Biosilicification Under In Vitro Conditions Sai Maddala1, Ernst van Eck2, Paul H. Bonans1, Heiner Friedrich1 and Nico Sommersdijk1; 1TU Eindhoven, Eindhoven, Netherlands; 2Radboud University, Nijmegen, Netherlands.
Diatom biosilicas possess intricate organization, whilst requiring only ambient synthesis conditions. Their remarkable morphological properties have been a source of intense interest for chemists and biologists. Understanding the mechanisms involved in the morphological control of biosilica could inspire the production of new functional materials.

Here, we present results from our in vitro investigations into biomineralization of silica. Our investigations focus on mimicking the conditions present in the silica deposition vesicle of the diatoms; high silicic acid concentration (0.10 to 0.34 M), salinity, the presence of polyamines and mildly acidic pH (pH 5.5). Understanding the silica formation in these conditions is key to unravelling the mechanism of silica biomineralization. Tetramethy orthosilicate (TMOS) was used as silica precursor, as it readily hydrolyses to give metastable silicic acid solutions. pH was maintained at 5.5 using an autotitrator. Silicic acid consumption was monitored using ammonium molybdate assay. In the absence of polyamine additives, and under high salt conditions (NaCl concentration 0.45 M) free silicic acid was consumed in two stages, first a portion of it undergoes rapid condensation within 5 minutes, and the remainder stays unreacted for the next 27 minutes, followed by complete reduction in concentration by 43 minutes. Previous investigations into silica formation were generally performed in pure water, and this two-stage silicic acid consumption process was not observed. The role of polyamines on silica particle formation was monitored under real-time conditions using Dynamic Light Scattering (DLS). We used polyallylamine hydrochloride (PAH, Mw 15000 g/mol) as polyamine mimic. In the absence of PAH, silica particles were observed as soon as TMOS completely hydrolysed in water. In the presence of PAH, the particle formation wasn’t observed for the first 76 minutes, suggesting that the polyamines could potentially inhibit silica formation. Argon sorption porosimetry of silica gels obtained in the absence of PAH had a surface area of 170 m²/g and a pore size of 7.05 nm. Whereas in the presence of PAH, the surface area was 230 m²/g and pore size of 3.36 nm. Further analysis was performed using Cryo-TEM and solid state ²⁹Si NMR.

Our results indicate that under the conditions found in silica deposition vesicle of diatoms, silicic acid undergoes rapid condensation and that the presence of polyamines retard this process. This suggests that the polyamines could crucially help stabilize and store silicic acid. While the exact mechanism will be the subject of future research, our results help explain an important intermediate step in silica biomineralization.

4:15 PM BM09.07.05
Building Biomimetic Bone at Higher Level of Organization Eléa Besson¹,², Clement Sanchez³, Marco Faustiní¹,² and Nadine Nassif³,⁴; UMR 7574 - Laboratoire de Chimie de la Matière Condensée de Paris, Paris, France; ²Sorbonne Université, Paris, France; ³CNRS, Paris, France; ⁴ESPCI, Paris, France; ⁵Collège de France, Paris, France.

Bone is a composite material which closely associates a dense and organized collagen organic matrix (mainly type I collagen fibrils) with an apatite mineral network. From nanometers to millimeters and beyond, bone is hierarchically structured to provide maximum strength with a minimum of material. The structure/function relationship being crucial in bone, attention needs to be paid to the long-range collagen/hydroxyapatite (HA) structure in models set in vitro. Recently, the cholesteric geometry was reproduced in the laboratory (Wang and al., Nat Mater 2012).

The aim of this work is to reach higher levels of bone hierarchical organizations enlarging the relevance and applications of bone models. We are working on two different organizations: the trabecular and the cylindrical motif (osteons) of the cortical bone. Both imply the texturization of the liquid-crystalline collagen liquid-crystal phases to control the spatial arrangement of the oriented domains. Thanks to the geometry, the direction of the flow or and the confinement, the shear forces involved may have an effect on the resulting organization.

The resulting hybrid biomimetic materials and their hierarchical organization require various characterization techniques (e.g. in-situ observations by polarized optical microscopy (birefringence) and investigation by SAXS/WAXS of the directed co-assembly of the organic/inorganic phases, electronic microscopies, mechanical tests etc).

By using an original strategy, we aim to improve our knowledge on processes involved in the bone tissue (morphogenesis) as well as build new biomimetic hierarchically-structured materials that offers remarkable scaffolds to repair larger defects for bone tissue engineering.

4:30 PM *BM09.07.06
Harnessing the Precision of Biorecognition for the Development and Assembly of Responsive, Functional Inorganic Nanomaterials Marc R. Knecht, Univ of Miami, Coral Gables, Florida, United States.

Nature has exploited the precision of biorecognition events for the development inorganic materials for critical applications ranging from protection against predation to structural support. These materials are generated under sustainable conditions where the translation of such approaches to material compositions of technological importance could provide pathways to address current needs in applications ranging from energy harvesting and storage to biological sensors and theranostic systems. At present, only minimal understanding is known concerning the direct interaction between biological and bio-inspired molecules (e.g. peptides, DNA, peptoids etc.) with inorganic materials, where the ability to predictably design these biomolecules with affinity for the target system remains unachieved. By having such capabilities, the ability to fabricate functional materials with desired properties on demand could be accessed for immediate use in targeted applications. In addition, due to the great complexity achievable from biosystems, the biomolecules could be designed with secondary functionalities beyond inorganic material affinity, thus generating final structures with multifunctional capabilities. Our research has focused on the design of new bio-inspired systems with the ability to fabricate functional inorganic materials and drive their assembly in three dimensions. This assembly process is accessed based upon the multifunctional capability of the peptides to recognize and bind the inorganic surface, while simultaneously self-organizing in three dimensional space. In one instance, the self-assembly process is driven through biomolecule-biomolecule interactions, while in a second case, the assembly process is achieved through crosslinking of multiple inorganic materials from a single biomolecule. This research demonstrates multiple, disparate pathways from which biorecognition events can be exploited to drive inorganic material assembly, which could be tailored to different systems based upon biomolecular affinity.
Dehydration Stability Analysis of DNA-Guided Nanoparticle Superlattices

Yakuto Sumi, Takumi Isozai, Shoko Kojima, Shunta Harada, Toru Ujihara, and Miho Tagawa
Graduate School of Engineering, Nagoya University, Nagoya-shi, Japan; Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya-shi, Japan.

Supramolecular hydrogels hold great promise for controlled drug delivery. We reported on a supramolecular hydrogel based on an aldehyde-terminal peptide. The hydrogelator could form Schiff base with amine drugs. The resulting hydrogels showed an ultra-stable property in highly acidic or basic aqueous solutions. Due to the pH-responsive property of Schiff base, the hydrogels could be applied for controlled release of encapsulated amine drugs (doxorubicin).

As a result, doxorubicin released faster at acidic pH values (5.5, 6.5) than neutral pH value (7.4) in the hydrogels (The 24 hours accumulative released percentage of Dox at pH 5.5, 6.5 and 7.4 was 15.38, 13.45 and 10.98%, respectively.). Tumor microenvironment was reported having acidic pH values from pH 5.8 to pH 7.6. We think our strategy provides a novel peptide-based hydrogel that may be applied in controlling delivery of amine containing therapeutics.

Catalyzed Organic Reactions in Aqueous Media Using Hierarchically-Structured Nanomaterials Assembled from Sequence-Defined Peptoids

Tengyue Jian and Chun-Long Chen; Pacific Northwest National Laboratory, Richland, Washington, United States.

Natural enzymes are highly efficient and selective catalysts that present unique catalytic microenvironments. Development of highly stable enzyme- mimic catalysts using sequence-defined synthetic molecules is of great benefit to the area of biomimetic catalysis and facilitate our understanding of the structure-dependent catalytic performance. Here we report the design and synthesis of peptoid-based biomimetic materials with hierarchical structures for catalyzing the direct asymmetric aldol reaction and hydrolysis reaction in aqueous media. First we synthesized and assembled 20 proline-containing membrane catalysts, and demonstrated their catalysis of asymmetric aldol reaction with high conversion yields and good enantio- and diastereoselectivities. We further showed that both the enantio- and diastereo-selectivities of this aldol reaction are highly dependent on the hydrophobic microenvironment built around catalytic sites. For the hydrolysis reaction, we found that imidazole and pyridine-containing 2D membranes catalyzed this reaction in aqueous media with high efficiency. We demonstrated the use of peptoid nanomembranes for degradation of nerve agent simulants: 4-nitrophenyl phosphate and acyl ester (nitrophenylacetate and pyrene ester). In this catalyzed hydrolysis reaction, we found that the addition of Zn²⁺ and Cu²⁺ significantly accelerated the hydrolysis rate. We further demonstrated that these catalyzed organic reactions are highly dependent on the morphology and crystallinity of peptoid assemblies.

Ultrastable Supramolecular Hydrogel of Hydrophobic Peptides Prepared by a Hydrolysis Process

Guojuan Pu; State Key Laboratory of Medicinal Chemical Biology, Nankai University, Tianjin, China.

Supramolecular hydrogel based on peptides self-assembly have attracted extensive research interests in recent years, but its application in the field of nanomedicine is still limited by its poor stability in extreme environments. The number of hydrophobic amino acids directly affects the solubility of the peptides and the properties of the hydrogel. Peptides FF (F: Phenylalanine) has strong assembly capability, those hydrogels based on dipeptide of FF are the most widely investigated. Organic solvent is always required to dissolve peptides because of its strong hydrophobic properties. However, there is no hydrogel containing more than three Phenylalanine currently in aqueous solution.

Therefore, we describe a method for the preparation of hydrogels containing hydrophobic FFFF and FFFFF sequences by ester bond hydrolysis, which resulted in two highly potent peptide hydrogels formed by Nap-GFFFF-GP-EE and Nap-GFFFF-GP-EE (GP: Glycolic Acid). Then the transparent hydrogel containing more than three Phenylalanine currently in aqueous solution.

In conclusion, a novel method was constructed to promote hydrophobic peptides to dissolve in water and form a supramolecular hydrogel by the ester and the bond hydrolysis method, even if the molecule itself is unable to form a hydrogel and there is low solubility with ultrasound or heat means. This approach should be applicable for exploring supramolecular assemblies formed by other hydrophobic peptides. From the above, useful information for
BM09.08.05
Organic-Inorganic Bio-Hybrid Nanoparticle for Systemic Cellular Delivery of Superoxide Dismutase to Prevent Acetaminophen-Induced Hepatotoxicity and Liver Injury
Min Sang Lee and Ji Hoon Jeong; Sungkyunkwan University, Suwon-si, Korea (the Republic of).
Direct delivery of proteins into cells has been considered an effective approach for treating the protein-related diseases. However, clinical use of proteins has still been limited due to their instability in the blood and poor membrane permeability. To achieve an efficient cellular delivery of the protein to target cells via a systemic administration, a multifunctional carrier system having desirable stability both in the blood stream and the cells, specific cell-targeting property and endosomal escape functions may be required.
In this study, we designed organic-inorganic bio-hybrid nanoparticle containing an active enzyme by cross-tethering multiple superoxide dismutase (SOD) molecules with 3,4-dihydroxystyrenylamine (L-dopa)-derivatized hyaluronic acid (d-HA). SOD was conjugated with d-HA by reacting surface amines of SOD with catechol moiety of d-HA through Michael-type addition and Schiff base formation, which forms a hydrophilic network mesh pouch containing multiple SOD molecules tethered with HA chain networks. The free catechol groups that were not involved in the conjugation chelated calcium ions, resulting in formation of ultra-small calcium phosphate nanoparticles (USCaP, 2-5 nm) decorated on the surface of the nanoparticle. The permeable shell of hydrophilic HA chains effectively protects the enzyme from degradation in the blood after intravenous administration and provides an additional function for targeting hepatocytes expressing HA receptor (CD44). The structure and catalytic activity of the enzyme molecules in the nanoparticle were not significantly compromised in the nanoparticle. In addition, dissolution of USCaP in acidic environment efficiently improved the endosomal escape after cellular uptake, resulting in the rapid release of d-HA/SOD into the cytoplasm. The SOD-containing nanoparticle fortified with USCaP was used for the treatment of acetaminophen (APAP)-induced fulminant hepatotoxicity and liver injury. The systemically administrated nanoparticle achieved the efficient hepatic cellular delivery of SOD and resulted in efficient removal of reactive oxygen species (ROS) in the liver and remarkable improvement of APAP-induced hepatotoxicity and liver injury in animals.
BM09.08.06
Fine-Tuning Core-Shell Nanoparticle Growth by Exploiting Ions Doping
Jianxiong Zhao, Xian Chen, Bing Chen and Feng Wang; Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.
Predicting and tailoring the morphology of core shell nanoparticle is indispensable in obtaining desirable properties for optical and biological applications. However, the incomplete and discontinuous shell growth induced by heterogeneity in structure and chemical bonding may reduce the luminescence intensity and detriment to particle uniformity. Here, we demonstrate a strategy of ions doping for forming continuum NaREF4 (RE= rare earth) shell growth on heterogeneous core.
Compared to those un-doped shell which formed homogeneous nucleation surround the core. We show that doping can greatly reduce the energy barrier of heteronucleation, making shell successfully deposit on core. The core shell structure are distinguished by using high-angle annular dark-field scanning transmission electron microscopy. The shell growth process at different reaction stages are revealed by transmission electron microscopy observation on nanoparticle extracted during the reaction. We show that nascent shell layer formed at low energy crystallographic facets, afterward, shell extended and merged together over entire core surface.
We applied the strategy on core particle with different size and dimensions. All shell growth is stabilized but with some morphology variation for different core shape. The TEM analysis show that shell growth is not only strongly dependent on the nature of the different facet, but also reliant on mechanical flexibility of core. Moreover, the strategy improves both upconversion emission and lifetime of core shell nanoparticle and simultaneously provide novel platforms for building multifunctional self assembled composites.
BM09.08.07
Liquid Crystalline Disubstituted Polyacetylene-Preparation, Properties and Possible Applications for Biomimetic Materials
Kyoka Komaba2, Masashi Otaki1 and Hiromasa Goto1; 1University of Tsukuba, Tsukuba, Japan.
Many polymers mimicking ecosystem such as DNA have been synthesized. Synthesis of helical macromolecules has been inspired by such natural polymers. In this report, we synthesized disubstituted polyacetylenes using tantalum based catalyst. Chemical structure and optical properties of the polymer thus synthesized in this study are characterized with infrared absorption spectroscopy (IR), gel permeation chromatography(GPC), UV-vis absorption (UV) spectroscopy, circular dichroism (CD), fluorescence spectroscopy, and polarized optical microscopy analyses. Polyacetylene as a conductive polymer has some drawbacks such as poor stability in the air, no solubility, low processability. Introduction of substituent to the polyene backbone allows improvement of its disadvantages. Introduction of liquid crystal group can improve such drawbacks. We synthesized liquid crystal polyacetylenes for potential applications in biological field.
We succeeded in synthesis of disubstituted polyacetylene using tantalum chloride catalyst (Y = 41%). GPC result indicated that number average molecular weight (Mn) of the polymer is to be > 1,000,000 and degree of dispersion (Mw/Mn) ca.1.4.
The IR spectroscopy measurements confirmed that polyene was successfully produced by opening of the C≡C bond of the monomer in the polymerization. Polymer shows two absorption maxima at around 370 nm and 430 nm in the UV-vis. These absorption bands are derived from p-p* transition of the main chain. The polymer shows no CD signals. This result indicates that the polyacetylene derivative synthesized in this report contains equimolar amount of right-handed and left-handed helical structures, resulting in racemic state. This polymer shows fluorescence signal at around wavelength 500 nm. Polarizing optical microscopy observations for the drop cast film from toluene solution deposited on a glass substrate was carried out. This polymer shows fan-shaped texture of smectic liquid crystal with lyotropic liquid crystallinity. The layer structure has similarity to biological membrane. This unique structure may be artificial lipid bilayer membrane.
In this work, we achieved synthesis of disubstituted polyacetylenes with large molecular weights, showing lyotropic liquid crystallinity with layer structure. We evaluated that the simple synthesis of liquid crystal polyacetylene derivatives having no mesogenic group from readily available monomers affords to producing of the biomimetic lipid bilayer membrane.
BM09.08.08
Selenium- and Tellurium-Containing Block Copolymer with Multi-Hierarchical Oxidation Response
Lu Wang and Huaping Xu; Department of Chemistry, Tsinghua University, Beijing, China.

Many polymers mimicking ecosystem such as DNA have been synthesized. Synthesis of helical macromolecules has been inspired by such natural polymers. In this report, we synthesized disubstituted polyacetylenes using tantalum based catalyst. Chemical structure and optical properties of the polymer thus synthesized in this study are characterized with infrared absorption spectroscopy (IR), gel permeation chromatography(GPC), UV-vis absorption (UV) spectroscopy, circular dichroism (CD), fluorescence spectroscopy, and polarized optical microscopy analyses. Polyacetylene as a conductive polymer has some drawbacks such as poor stability in the air, no solubility, low processability. Introduction of substituent to the polyene backbone allows improvement of its disadvantages. Introduction of liquid crystal group can improve such drawbacks. We synthesized liquid crystal polyacetylenes for potential applications in biological field.
We succeeded in synthesis of disubstituted polyacetylene using tantalum chloride catalyst (Y = 41%). GPC result indicated that number average molecular weight (Mn) of the polymer is to be > 1,000,000 and degree of dispersion (Mw/Mn) ca.1.4.
The IR spectroscopy measurements confirmed that polyene was successfully produced by opening of the C≡C bond of the monomer in the polymerization. Polymer shows two absorption maxima at around 370 nm and 430 nm in the UV-vis. These absorption bands are derived from p-p* transition of the main chain. The polymer shows no CD signals. This result indicates that the polyacetylene derivative synthesized in this report contains equimolar amount of right-handed and left-handed helical structures, resulting in racemic state. This polymer shows fluorescence signal at around wavelength 500 nm. Polarizing optical microscopy observations for the drop cast film from toluene solution deposited on a glass substrate was carried out. This polymer shows fan-shaped texture of smectic liquid crystal with lyotropic liquid crystallinity. The layer structure has similarity to biological membrane. This unique structure may be artificial lipid bilayer membrane.
In this work, we achieved synthesis of disubstituted polyacetylenes with large molecular weights, showing lyotropic liquid crystallinity with layer structure. We evaluated that the simple synthesis of liquid crystal polyacetylene derivatives having no mesogenic group from readily available monomers affords to producing of the biomimetic lipid bilayer membrane.

Nanomaterials with hierarchical responsiveness are of great significance for not only fundamental science but also future biomedical applications due to sophisticated and hierarchical physiological environments. Here, we report a selenium- and tellurium-containing block copolymer that can be stepwise oxidized by both chemical methods and electrochemical methods. Differences in sensitivity to the oxidation of selenium and tellurium were employed. By tuning the concentration of the oxidant and oxidation periods, self-assembly behaviors of the copolymer were tuned by stepwise chemical oxidation. After
Stimuli-responsive DNA hydrogels, albeit the potential advantages like biocompatibility and ease to functionalize, problems remain in the reconciliation between facile fabrication and stimuli-responsiveness. In this study, by rationally designing the sequence of DNA chains, pH-responsive sites-namely, i-motif forming sequences (IFSs)—were introduced during rolling circle amplification. At pH 5.0, the resultant gelation occurs driven by the formation of intermolecular i-motifs as crosslinkers.

To better evaluate the sequence influence on the responsiveness, three IFSs were designed and named as I1, I2, and I3 whose sequences are CCCCTCCCCC, CCCTCCCTCCCT, and CCAATCCCAATCCCAATCCCC. Three IFSs form primarily inter-molecule, both inter-and intra-molecule and primarily intra-molecule i-motif structure respectively. The difference in sequence reflects on the pH-responsiveness during sol-gel transition. When adjusting the pH from 5.0 to 8.0, I1 quickly dissolved while I2 became softer but remain intact and I3 became more dispersed in the buffer. We draw a conclusion that the gelation process can be tuned via sequence design. An IFS favoring intramolecular i-motif leads to mechanically weak, thermally unstable yet pH-sensitive hydrogel while for IFS favoring intermolecular i-motif structure, gelation may occur along with quick condensation which promotes non-specific interactions within the gel.

The microstructure of the hydrogel was investigated to dig some evidence of the gelation mechanisms. RCA products at neutral (pH 7.5) and acidic condition (pH 5.0) were observed under scanning electron microscope. Of all three samples, flower-like microstructures (FMs) with diameter of 2-3 μm was observed in a large amount. FMs were believed to be a in situ formed by-product of DNA polymerization and performs a crucial role in gelation process. Form the SEM images, the hydrogel morphology featured with thick DNA matrix embedded with FMs. For sol, the FMs is more visible due to the lack of matrix surrounding. Also, the different properties of specimen can be explained. For I1, dense matrix already formed in neutral pH indicating many crosslinking sites that are not i-motif structures. For I3, the matrix is in acidic buffer is relatively looser which is consistent with the weak stability. Worth noting that there is no RCA matrix in I2 after redissolved in pH 8.0 buffer yet the FMs remain unchanged. This proves that FM, as a condensed complex of DNA and magnesium pyrophosphate (MgPPi), has no pH-responsiveness and that the pH-adjusting gelation exclusively relies on introduced i-motif sequences.

To summarize, this work proposed a facile method to produce pH-responsive DNA hydrogel. Also, the influence of three different IFS sequences on gelation mechanism as well as their interaction with flower-like microstructures were investigated.

BM09.08.10

Hybrid Thin-Film Formation of Zinc Layered Hydroxides with Intercalated Organic Molecules Through a Biominalization-Inspired Approach

Satoshi Kajiyama, Takashi Kato and Fumiya Katase; Univ of Tokyo, Tokyo, Japan.

Biominalization-inspired crystallization is one of effective approaches for the development of hierarchical structures from nano- to macro- scales under ambient conditions [1-3]. In biominalization, acidic polymers induce amorphous states of inorganic crystals with the interaction between acidic groups and metal ions. The amorphous states are useful as precursors for inorganic crystals with ordered structures [4,5]. We have achieved the formation of hybrid thin films based on zinc hydroxide carbonate (ZHC) with ordered nanostructures through biominalization-inspired approach utilizing amorphous precursors. ZnO thin films have been obtained with ordered structures from ZHC ordered hybrid thin films through thermal treatment [6]. In the present study, we demonstrate that hybrid thin-film formation composed of zinc layered hydroxides with intercalated organic molecules through the biominalization-inspired approach utilizing amorphous states as precursors. The amorphous precursors for zinc layered hydroxides with intercalated organic molecules were prepared in the presence of poly(acrylic acid). Polymer thin-film matrices were immersed in aqueous solution containing the amorphous precursors in order to develop hybrid thin films. The structures of resultant hybrid thin films composed of layered zinc hydroxides have been examined with polarizing optical microscopy, scanning electron microscopy and X-ray diffraction. These characteristics revealed that the hybrid thin films of layered zinc hydroxides exhibit macroscopically ordered structures. Hybrid thin films comprising of the layered zinc hydroxides are converted to ZnO thin films through thermal treatment. The resultant ZnO thin films exhibit macroscopically ordered structures. It is elucidated that ordered structures of ZnO thin films depend on the molecular structure of intercalated guest molecules as well as the original structures of hybrid thin films of layered zinc hydroxides. These results suggest that the biominalizationapproach is useful for the development of functional ZnO materials with ordered structures.

References

BM09.08.12

Macromolecular Assembly of DNA into Complex Nanostructures via Hybridization Chain Reaction

Laura A. Lanier and Harry Bermudez; Univ of Massachusetts-Amherst, Amherst, Massachusetts, United States.

Through the use of a macromolecular self-assembly technique called hybridization chain reaction (HCR), we have created complex, well-defined nanostructures. HCR is a supramolecular polymerization of DNA that proceeds as an isothermal cascade of strand displacement reactions. Two DNA monomers are kinetically trapped in hairpins until the addition of an initiator strand opens the hairpin of one monomer through a strand displacement reaction. The unhybridized end then opens the hairpin of the other monomer through a strand displacement reaction. This cascade of strand displacement reactions continues, producing a supramolecular DNA polymer. This project aims to demonstrate the living mechanism of HCR. Further, the living nature of HCR is used to create well-defined nanostructures of DNA by HCR in order to expand the design toolbox of DNA for potential applications in such fields as nanomedicine, sensing, synthetic biology.

References
We have demonstrated that HCR produces supramolecular polymers of DNA in a controlled manner through a living polymerization mechanism. Through molecular assembly by HCR, DNA polymers of narrow dispersity are produced whose molecular weight is controlled by the stoichiometric ratio, consistent with a living polymerization mechanism. Additionally, HCR polymerization can be continued by the addition of further monomer, demonstrating its living nature by the absence of termination and chain transfer reactions. Identification of the living character of HCR presents new opportunities in macromolecular assembly of structural DNA nanotechnology and molecular biology.

Utilizing the demonstrated living nature, complex, well-defined nanostructures are created via HCR. Bottlebrush structures are created by modifying the monomer to include an additional overhang that initiates a secondary HCR polymerization with aspect ratio controlled by the stoichiometric ratios of the initiator and monomer strands of each HCR sequence. Supramolecular star polymers are created by modifying a four-arm star to initiate HCR from each arm. The growth of each arm is independently controlled, allowing for the creation of asymmetric DNA star polymers. The creation of these complex nanostructures is demonstrated by gel electrophoresis and atomic force microscopy.

**BM09.08.13**

**Enzymatically Activated Aggregation and Cell-Adhesion of Peptide-Nanoparticle Conjugates for Surface-Enhanced Raman Spectroscopy (SERS) Based Diagnostics and Imaging**

Hailing Huang1, 2, 3, Stephen O’Brien1, 2, 3, Duncan Graham4 and Rein Ulijn5, 2, 3, 4

1 The City College of New York, New York, New York, United States; 2 CUNY Advance Science Research Center, New York, New York, United States; 3 The Graduate Center, City University of New York, New York, New York, United States; 4 Applied and Pure Chemistry, University of Strathclyde, Glasgow, United Kingdom; 5 Chemistry, Hunter College, New York, New York, United States.

In cancer research, multi-functionalized gold nanoparticles (GNPs) have advanced to realize simultaneous diagnosis and therapy (i.e. theranostics) due to their excellent optical properties and accessibility of surface modification. An example of GNPs used for cancer theranostics is to functionalize the surface using Raman reporter molecules for surface enhanced Raman spectroscopy (SERS) and incorporate anti-cancer drug molecules on the surface. One critical aspect of using nanomedicines for cancer treatment is to ensure that the administered drugs reach and accumulate at the tumor site, rather than retaining at healthy parts of the body or being eliminated by the reticuloendothelial system. Unfortunately, during the past 10 years, the delivery efficiency of nanoparticles has not been improved significantly, and only a median of 0.7% of injected dose of nanoparticles reached the tumor. Increasing the delivery efficiency is therefore one of the greatest challenges for the development of cancer nanomedicines.

In this study, an enzyme responsive peptide functionalized GNP is designed to target metastatic tumor cells with a new dual-action targeting mechanism. Immobilized peptides with which contain an enzyme- cleavable linker which incorporates a cysteic acid adhesive ligand are immobilized onto GNP and recognized and cleaved by collagenase MMP-9. MMP-9 is overexpressed by malignant tumor cells and plays a central role in metastatic cancer progression by degrading proteins in the extracellular matrix (ECM). The enzymatic product fragments retained on the surface of GNP, LRGIDC, trigger nanoparticle self-assembly and enhances SERS signals. Moreover, the RGD motif binds preferentially to αvβ3 integrins which are protein receptors overexpressed on tumoral endothelial cells primarily during angiogenesis. The advantage of this design is that the surface functionalized GNPs remain an inactive state through the blood circulation and become active once they reach the tumor ECM, not only exposing the RGD surface for cell binding, but also enabling tumor diagnosis by SERS. This active targeting mechanism can potentially reduce the binding of RGD to non-tumoral integrins and increase the delivery efficiency of the nanoparticles.

**References:**

**BM09.08.14**

**Octopus-Inspired Adhesive and Conductive Patch Sensor for Biosignal Monitoring**

SeungHoon Choi1, HeonJoong Lee2 and Changhyun Pang2, 3

1 Sungkyunkwan University Advanced Institute of NanoTechnology, Suwon, Korea (the Republic of); 2 School of Chemical Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of); 3 Samsung Advanced Institute for Health Science and Technology, Suwon, Korea (the Republic of).

The attachment phenomena of various hierarchical architectures found in nature have extensively drawn attention for developing highly biomimetic adhesives for skin or wet inner organs. Scientists have reported biospired skin adhesives with various multiscale architectures including patches with mushroom-shaped tips with or without conductive materials, microneedles, and miniaturized octopus-like suction cups. Adhesives with mushroom-shaped tips have demonstrated enhanced attachment by van der Waals interactions on dry skin, and stabilized contact to active skin surface underwater by embedding the patch underneath swimwear. These adhesives, however, cannot maintain adequate adhesion on wet skin or skin under flowing water. Microneedle patches have indicated striking adhesion performances through mechanical interlocking, but they are more appropriate for wound closure or invasive therapies rather than reversible and residue-free dermal attachment. In recent years, hierarchical structures of octopus suckers have been investigated for their unique reversible adhesion in both dry and wet conditions. The octopus sucker can be divided into two parts: 1) the protruded cup-like upper portion (infundibulum) and 2) the lower portion with a dome-like protuberance (acetabulum). For such adhesive capabilities, suction cups of octopi have been mimicked to develop reusable and residual-free skin patches for versatile medical applications. Here, we present an octopus-inspired skin-adhesive with meniscus-controlled unfoldable 3D microsuckers in micropillars, as well as its application to a stretchable patch sensor composed of carbon-based conducting polymer composite (CPC) films. Mimicking the rim and infundibulum of octopus suction cups, the microsuckers are fabricated by controlling the wetting properties of a liquid precursor during simple molding. Moreover, the adhesive shows strong dry/wet adhesion performances in both pull-off and peeling-off directions against a wafer and rough, hairy skin. Finally, the patch sensor incorporated with 3D microsuckers displays sensitive and reliable piezoresistive responses to lateral strain and vertical pressure. With high conformity on human skin and water-resistant nature, our patch sensor demonstrates efficient detection of not only electrocardiogram (ECG), but also the motion of a human finger even in an underwater environment. We believe that this work represents a timely, methodological advance in nature and breakthrough in the fields of wearable and skin-attachable sensor devices for future healthcare applications.

**BM09.08.15**

**Antimicrobial Modification of K-Wires via Novel Polymer Grafting Technology**

Mikhail A. Bredikhin1, Dmitry Gil2, Christopher Gross3, Igor Luzinov4 and Alexey Vertegel1; 1 Bioengineering, Clemson University, Clemson, South Carolina, United States; 2 Medical School, Harvard University, Boston, Massachusetts, United States; 3 Department of Orthopedics, Medical University of South Carolina, Charleston, South Carolina, United States; 4 Materials Science & Engineering, Clemson University, Clemson, South Carolina, United States.
**Introduction:** Kirschner wires are the external smooth stainless-steel pins that are used today in bone fracture fixation. These wires provide the surface for bacteria to adhere onto and form a biofilm, which makes them considerably less-susceptible to antibiotics. The solution to this problem has been an active area of research.

Surface coatings of implants with bioactive molecules is a modern approach to modify implant’s function. However, in the case of K-wires, coating the pin with an antibiotic would not have much effect in vivo since this coating is poorly adherent and would be easily removed when the wire is drilled by a surgeon. In this work, we propose a novel method of grafting the K-wires with highly adherent polymer. Specifically, this study utilizes cross-linkable random “brush” copolymer of OEGMA, GMA, and LMA, which can be covalently attached to solid surfaces. Such polymeric coating can be loaded with an antibiotic, allowing both the protection of the antimicrobial coating during insertion into the bone and optimal release over time.

**Materials & Methods:** Gentamicin sulfate (GS), butanone-2 (MEK) and other materials were purchased from Sigma-Aldrich. The polymeric “brush” is synthesized via solution polymerization. grafting of the polymer onto the surface was performed by dip-coating. The wires were dipped in the MEK solution of the polymer. Following thermal cross-linking of the polymer, the polymer-coated wires were submerged and kept in aqueous GS solution for 24 hours. Finally, the wires were washed with DI water to remove weakly-bound drug, and then air-dried. For the negative controls, the wires were dipped in the plain MEK solution and the MEK-Chloroform solution of polyactic acid (PLA). The next steps were the same as for the polymer-coated wires. Surface of the wires was then characterized using AFM, SEM, and FT-IR.

Antimicrobial in vitro studies were carried out with *S. aureus*. We have tested the ability of the prepared wires to kill planktonic bacteria exposed to them and to prevent biofilm formation on the wire surface by colony forming unit (CFU) plate count method using standard FDA protocols.

Finally, coated wires were drilled into human femur model. Their antimicrobial efficacy was assessed again after this procedure.

**Results and Discussion:** While the uncoated wires showed no anti-bacterial activity, the polymer-coated wires were highly antimicrobial showing maximum inhibiting concentration of 10⁻⁵ CFUs/ml/cm of wire. The PLA-coated wires exhibited similar antimicrobial effect. However, only the polymer-coated wires retained bactericidal properties after drilling into human femur bone model. PLA layer was almost completely removed after the mechanical shear stressing by drilling, which was confirmed by FT-IR analysis of the surface. Thus, the polymer coating of K-wires provides an appropriate drug-carrying and drug-protecting system for the bone implant, where the shear stress during implantation plays a significant role.

BM09.08.16

**Ultra Long-Scale Silver Nanowire with Self-Templating M13 Bacteriophage**

Kyoung Lim¹, JongMin Lee¹, Vasanthan Devaraj¹, Yeong Ju Lee¹ and Jin-Woo Oh¹, ², ³, ⁴

¹Research Center for Energy Convergence and Technology Division, Pusan National University, Busan, Korea (the Republic of); ²Department of Nanoenergy Engineering, Pusan National University, Busan, Korea (the Republic of); ³Institute of Physics, Pontificia Universidad Catolica de Chile, Santiago, Chile; ⁴Departamento de Física, Universidad Tecnica Federico Santa Maria, Valparaiso, Chile.

These days, electron devices demand high performance electrode. Ag nanowire is the most promising candidate because it has excellent electrical property, however, the process of Ag nanowire synthesis is complicated and it is difficult to obtain long-scale Ag nanowires in traditional methods. M13 bacteriophage is a helical structured biomaterial with 6.6 nm of the diameter and 880 nm of the length. M13 bacteriophage can be reproduced through self-cloning and modified the chemical properties by genetic engineering. According to these properties, M13 bacteriophage is very useful as a template. In this work, we fabricated ultra long-scale Ag nanowire using genetically engineered M13 bacteriophage. We observed that the crystallinity of Ag nanowire (length or diameter) was affected as changing the engineered chemical structure on major coat protein of M13-bacteriophage. The range of Ag nanowire was around 50 nm to 200 nm and the average length and diameter were around 100 um and 1 um, respectively. The maximum length of Ag nanowires that was observed was 300 um. The existence and morphology of Ag nanoparticles and nanowires were confirmed by FE-SEM (field emission scanning electron microscope) and high resolution TEM (transmission electron microscope). To examine the components of Ag nanoparticles and nanowires, map profiling was conducted by EDS (energy dispersive spectroscopy).

BM09.08.17

**High-Density Enzyme Array on Self-Assembling Protein Template for ELISA-Type Detection of Biomarkers**

Gi Ahn Jung, Samuel Lim and Douglas S. Clark; University of California, Berkeley, Berkeley, California, United States.

Enzyme-linked immunosorbent assay (ELISA) provides a simple and convenient way to detect biomarkers, and is widely used as a diagnostic tool. The components of ELISA consists of a primary antibody specific to the target antigen, and a secondary antibody that binds the primary antibody to render it detectable; commonly, the secondary antibody is coupled to an enzyme that allows for a colorimetric assay. Although conventional ELISA has proven very useful in both research and clinical applications, it can suffer from poor sensitivity when the biomarker concentration is too low.

We propose a strategy to enhance the sensitivity of ELISA based on the self-assembling filamentous protein g-prefoldin (gPFD), which was isolated from the hyperthermophilic archaean *Methanocaldococcus jannaschii*. Using the streptavidin-biotin interaction, gPFD was engineered to template horseradish peroxidase (HRP) enzymes in high density and close proximity along its filamentous backbone; subsequently, the HRP-gPFD complex was fused to the secondary antibody. Each secondary antibody is coupled to the array of HRP enzymes, with the aim of increasing the antigen sensitivity compared to conventional ELISA. The strategy demonstrated here may further improve currently used ELISA techniques, allowing for the efficient detection of biomarkers in both research and clinical settings.

BM09.08.18

**Study of the Behavior of an Artificial Membrane Immersed in Aqueous Medium**

Marcelo A. Cisternas¹, ², ³, Sebastian A. Molina¹, ², ³, María J. Retamal², ³, ⁴, Nicolás H. Moraga¹, ², ³, Hugo I. Zelada¹, ², ³, Tomas P. Corrales¹, ², Diego I. Diaz¹, ², Rodrigo E. Catalan¹, ², ³ and Ulrich G. Volkmann¹, ², ³

¹Instituto de Física, Pontificia Universidad Catolica de Chile, Santiago, Chile; ²Facultad de Quimica, Pontificia Universidad Catolica de Chile, Santiago, Chile; ³CIEN-UC, Pontificia Universidad Catolica de Chile, Santiago, Chile; ⁴Departamento de Fisica, Universidad Tecnica Federico Santa Maria, Valparaiso, Chile.

Self-assembly of artificial membranes on solid substrates has gained importance due to the potential applications in the field of BioNanotechnology. Artificial membranes represent models for study of the behavior of biological membranes, which are the base of the cell membrane structure. The cell membrane is composed by different kind of lipids and proteins that change their behavior when they are stimulated physically and/or chemically.

Samples were made using a silicon substrate to support the lipids that compose the membrane. First, the substrate were cleaned using the Tidswell method to remove all organic material from the surface. Second, we evaporated the DPPC phospholipid that self-assembled in bilayers when hydrated. The growth of the DPPC layer on the substrate was controlled in situ using Very High Resolution Ellipsometry (VHRE) to obtain the specific thickness of the film.

In our previous work, we measured the capacitive response of the system composed by a phospholipid bilayer on a thin chitosan (CH) layer, both deposited onto silicon substrate and immersed into a protein solution of gramicidin. The change of the capacitive response permit us to confirm the gramicidin ion channel formation across the membrane, to transform our phospholipid bilayer into an artificial membrane. Our results showed a change in the system response due to the protein insertion across the membrane, but it was necessary to perform a detailed study of the membrane immersed into an aqueous medium.
In this work, the behavior of the artificial membranes immersed into an aqueous medium was studied. This medium simulates the natural environment of the biological membrane in laboratory conditions. For this purpose, was designed and constructed an aqueous cell as an accessory of our VHRE. In this cell we immersed the substrate and applied temperature ramps to measure the phase transitions of the phospholipid bilayer.

Acknowledgments

UGV: Fondecyt Project 1180939 and Conicyt-PIA ACT1409. TPC: Fondecyt PAl 7912010015, Initiative Fondecyt 11160664, Projects Research Line USM 116.11.4. MJR: Post Doctorate Project Fondecyt 3160803. MAC: PhD Scholarship CONICYT. RSC: MSc Scholarship CONICYT.

References.


**BM09.08.19**

The Differences Between Colloidal and Crystalline Evaporative Deposits

Samantha McBride, Kripa K. Varanasi and Rachael S. Skye; 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Michigan, United States; 2Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Michigan, United States.

Evaporative deposits (for example, the well-known coffee-ring) are widely studied to improve technologies such as inkjet printing or to understand crystal fouling of infrastructure. Evaporative deposition can also be used as a tool for micro-scale assembly, as precipitates self-assemble into structures on extremely small length scales. Altering the conditions of evaporation allows for a large amount of control over the properties and structure of the resultant deposit. The morphology of inorganic crystalline patterns deposited from evaporating drops of saline solution are largely dependent on the wetting properties of the solid substrates they are placed on, with hydrophobic surfaces yielding localized deposits and hydrophilic surfaces causing larger, ring-shaped deposits. However, to date, little attention has been given to the role of surface energy on the crystal formation itself, with the crystal being treated as a simple product of the fluid flow rather than a separate entity that also interacts with the substrate chemistry. Here, we test the hypothesis that the surface energy of the burgeoning crystal faces will also contribute to the morphology of the crystalline deposits left from evaporating drops. To this end, experiments were performed on six different substrate chemistries. Substrate surface energy was analyzed by polar and non-polar components. We will show how the interactions between the growing crystals and the substrate affect the morphology of the resultant deposit. For drops containing colloidal nanoparticles, the deposit shows two modes, precipitating either in a ring or in a condensed disk, while drops containing crystals can also show intermediate modes of small or partial rings. These results have important implications for evaporative self-assembly as they present a method for tuning deposit morphology based on both substrate chemistry and the crystal chosen.

**BM09.08.20**

Influence of the Formation Time of Amorphous CaCO3 on Its Degree of Hydration and Stability

Huchuan Du, Mathias Steinacher, Camelia Borca, Thomas Huthwelker, Anna Murello, Francesco Stellacci and Esther Amstad; 1Paul Scherrer Institut, Villigen, Switzerland; 2Institute of Materials Science, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Calcium carbonate (CaCO3) is an abundant biomineral that nature often uses as a structural material because of its excellent mechanical properties. Inspired by the excellent mechanical properties, a lot of work has been devoted to producing CaCO3-based functional materials. However, the structures and properties of these biomimetic CaCO3-based materials significantly differ from those of natural counterparts. To gain a closer control over the mechanical properties, a better understanding of the influence of processing conditions on the formation and stability of amorphous CaCO3 (ACC) particles, that serve as transient precursors for CaCO3 crystals, is crucial. Here, we will present a new method to study the early stages of ACC particles formation using a microfluidic spray-drier. The microfluidic spray-drier forms Ca(OH)2 containing aqueous drops that react with CO2 and rapidly dry, thereby quenching the formation of ACC particles at early stages without the need of any organic solvent. We show that the amount of mobile water contained in ACC particles increases with increasing formation time and hence with increasing particle size. As a result, larger particles are less stable against temperature-induced solid-state crystallization and electron beam-induced decomposition than smaller counterparts. The amount of mobile water contained in ACC can be strongly reduced if certain organic additives, such as poly(acrylic acid) (PAA), is incorporated into ACC particles. As a result of the reduced mobility of water, these additive-stabilized particles are much more stable against crystallization and electron beam-induced decomposition. These insights might open up new opportunities to fabricate biomimetic CaCO3-based materials with tunable structures and hence with properties that can be adapted to the specific needs of the different applications.

**BM09.08.21**

Synthesis of Ion Substituted Ceramic Core-Shell Particles for Dental Applications

Camilla Berg, Wei Xia and Håkan Engqvist; Engineering Sciences, Uppsala University, Uppsala, Sweden.

Calcium phosphate spheres are interesting alternatives for dental applications due to their chemical similarity to teeth and biocompatibility.1 A spherical shape with a hollow core allows for loading of therapeutic agents for drug delivery which potentially could be combined with other applications such as tooth remineralization and treatment of hypersensitivity.1 Precipitation reactions are one of the techniques used for synthesizing spherical particles, but little shape with a hollow cores allows for loading of therapeutic agents for drug delivery which potentially could be combined with other applications such as tooth remineralization and treatment of hypersensitivity.1 Precipitation reactions are one of the techniques used for synthesizing spherical particles, but little

Acknowledgments

UGV: Fondecyt Project 1180939 and Conicyt-PIA ACT1409. TPC: Fondecyt PAl 7912010015, Initiative Fondecyt 11160664, Projects Research Line USM 116.11.4. MJR: Post Doctorate Project Fondecyt 3160803. MAC: PhD Scholarship CONICYT. RSC: MSc Scholarship CONICYT.

References.


**BM09.08.19**

The Differences Between Colloidal and Crystalline Evaporative Deposits

Samantha McBride, Kripa K. Varanasi and Rachael S. Skye; 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Michigan, United States; 2Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Michigan, United States.

Evaporative deposits (for example, the well-known coffee-ring) are widely studied to improve technologies such as inkjet printing or to understand crystal fouling of infrastructure. Evaporative deposition can also be used as a tool for micro-scale assembly, as precipitates self-assemble into structures on extremely small length scales. Altering the conditions of evaporation allows for a large amount of control over the properties and structure of the resultant deposit. The morphology of inorganic crystalline patterns deposited from evaporating drops of saline solution are largely dependent on the wetting properties of the solid substrates they are placed on, with hydrophobic surfaces yielding localized deposits and hydrophilic surfaces causing larger, ring-shaped deposits. However, to date, little attention has been given to the role of surface energy on the crystal formation itself, with the crystal being treated as a simple product of the fluid flow rather than a separate entity that also interacts with the substrate chemistry. Here, we test the hypothesis that the surface energy of the burgeoning crystal faces will also contribute to the morphology of the crystalline deposits left from evaporating drops. To this end, experiments were performed on six different substrate chemistries. Substrate surface energy was analyzed by polar and non-polar components. We will show how the interactions between the growing crystals and the substrate affect the morphology of the resultant deposit. For drops containing colloidal nanoparticles, the deposit shows two modes, precipitating either in a ring or in a condensed disk, while drops containing crystals can also show intermediate modes of small or partial rings. These results have important implications for evaporative self-assembly as they present a method for tuning deposit morphology based on both substrate chemistry and the crystal chosen.

**BM09.08.20**

Influence of the Formation Time of Amorphous CaCO3 on Its Degree of Hydration and Stability

Huchuan Du, Mathias Steinacher, Camelia Borca, Thomas Huthwelker, Anna Murello, Francesco Stellacci and Esther Amstad; 1Paul Scherrer Institut, Villigen, Switzerland; 2Institute of Materials Science, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Calcium carbonate (CaCO3) is an abundant biomineral that nature often uses as a structural material because of its excellent mechanical properties. Inspired by the excellent mechanical properties, a lot of work has been devoted to producing CaCO3-based functional materials. However, the structures and properties of these biomimetic CaCO3-based materials significantly differ from those of natural counterparts. To gain a closer control over the mechanical properties, a better understanding of the influence of processing conditions on the formation and stability of amorphous CaCO3 (ACC) particles, that serve as transient precursors for CaCO3 crystals, is crucial. Here, we will present a new method to study the early stages of ACC particles formation using a microfluidic spray-drier. The microfluidic spray-drier forms Ca(OH)2 containing aqueous drops that react with CO2 and rapidly dry, thereby quenching the formation of ACC particles at early stages without the need of any organic solvent. We show that the amount of mobile water contained in ACC particles increases with increasing formation time and hence with increasing particle size. As a result, larger particles are less stable against temperature-induced solid-state crystallization and electron beam-induced decomposition than smaller counterparts. The amount of mobile water contained in ACC can be strongly reduced if certain organic additives, such as poly(acrylic acid) (PAA), is incorporated into ACC particles. As a result of the reduced mobility of water, these additive-stabilized particles are much more stable against crystallization and electron beam-induced decomposition. These insights might open up new opportunities to fabricate biomimetic CaCO3-based materials with tunable structures and hence with properties that can be adapted to the specific needs of the different applications.

**BM09.08.21**

Synthesis of Ion Substituted Ceramic Core-Shell Particles for Dental Applications

Camilla Berg, Wei Xia and Håkan Engqvist; Engineering Sciences, Uppsala University, Uppsala, Sweden.

Calcium phosphate spheres are interesting alternatives for dental applications due to their chemical similarity to teeth and biocompatibility.1 A spherical shape with a hollow core allows for loading of therapeutic agents for drug delivery which potentially could be combined with other applications such as tooth remineralization and treatment of hypersensitivity.1 Precipitation reactions are one of the techniques used for synthesizing spherical particles, but little is known about the mechanism behind the sphere formation, which makes tuning of the material properties challenging. Previously, it has been shown that substituting ions can influence the crystallization process, which can enable greater control during the synthesis.4 In this study, several different substituting ions has been used in the synthesis of alkaline earth phosphates, to further investigate their role in sphere formation and to develop a robust synthesis technique.

Particles of alkaline earth phosphates (Ca, Sr and Ba) were synthesized with a precipitation reaction. Solutions with constituent anions and cations were mixed at room temperature, and substituting ions (Mg, Ca or Sr) were added before heating at 60-100 °C. Reaction times varied between 10 minutes to 24 hours. Characterization of precipitates was performed with SEM, DLS and FIB to analyze morphology, size and cross-sections of the spheres. Crystal structure and atomic composition was analyzed with XRD and ICP-OES.

Without substituting ions, precipitates had no specific shape and crystallized in an apatitic structure or as a hydrogenated phosphate. Substituting ions stabilized the initial amorphous phase during the reaction, hindering rapid crystal growth which allowed for self-assembly into hollow, spherical particles with a diameter between 300-700 nm. The phase composition and degree of ion substitution in the precipitates depended on the size and concentration of the substituting ions. The amount of substitution was determined in the range between 5-30 %, where precipitates with a low degree of substitution crystallized in a structure similar to β-tricalcium phosphate, whereas materials with a higher degree of substitution had an amorphous structure.
In this study it was shown that it was possible to obtain hollow, spherical particles of calcium-, strontium- and barium phosphate, by using substituting ions during a precipitation reaction. This indicates that the approach can be used to tailor the properties of spherical particles intended for dental applications.


BM09.08.22
Self-Assembly of Nematic Liquid Crystals in Drops of Dried Lysozyme

Amusya Pal and Germano S. Iannacchione; Physics, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

In the recent years, an active area of research involves using liquid crystals (LCs), e.g. 5CB (4-Cyano-4’-pentylbiphenyl), for sensing biological and chemical analytes. Another active area of research studies drying drops of liquid revealing a rich interplay of fundamental mechanisms resulting in emergent patterns at the final dried state. In this presentation, these two areas are bridged by asking a basic question of the influence and the self-assembly, in the final dried state, of adding the liquid crystal, 5CB, with the initial protein solution of lysozyme and de-ionized water. The investigation is done using bright-field and cross-polarizing microscopy and quantified using image processing software- ImageJ and Fiji. It is observed that the crack patterns in the final dried state of the protein is influenced by the presence of small amounts of 5CB. Since the protein lysozyme is not birefringent, cross-polarizing microscopy closely monitors the distribution of the LC, while the bright-field microscopy probes the crack patterns that emerge. To understand the final deposits, the time evolution of the drying dynamics of the drops with and without 5CB are monitored. It is found in both drops that all the particles move to the drop edge due to convective flow, but with the LC, partial phase separation into droplets occurs while some LC remains mixed and dispersed into the channels formed by the protein particles. This work demonstrates the utility of using a bulk thermotropic LC as a probe material in a protein solution, revealing new information on the protein self-assembly during the drying process.

BM09.08.23
Scalable Colloidal Self-Assembly by Deionization, Coacervation and Epitaxy

Rodrigo Guerra and Paul M. Chaikin; New York University, New York, New York, United States.

Charging and ionic conductance are ubiquitous properties of biomolecular and colloidal dispersions that also profoundly affect their stability and phase behavior. Rigorous deionization of macromers induces long-range electrostatic forces that can drive colloidal crystallization, and small changes in salinity can drive large changes in the assembly of oppositely charged particles, polyelectrolytes, and polyelectrolyte complexes. Here we demonstrate a new technique to control the salinity of colloids and solutions in-situ, and show how it may be combined with polyelectrolyte coacervation and epitaxial templating to produce self-assembled crystals of oppositely charged colloidal particles using materials techniques that are inexpensive and scalable.

BM09.08.24
Active Control of Calcium Carbonate Heterogenous Nucleation Using Mechanically Tunable Elastic Surfaces

Jay M. Taylor, Abhiteja Konda and Stephen A. Morin; University of Nebraska-Lincoln, Lincoln, Nebraska, United States.

Biological systems are capable of sophisticated and active control over the nucleation and growth of crystalline material. Their ability to control and direct the mineralization process enables the formation of intricate biological minerals with complicated micro-/nanoscale architectures with inanimate physical properties. Synthetic systems capable of such active control over crystal nucleation remain limited. Herein, a simple synthetic system that uses macroscopic physical strain in soft, elastic, silicone surfaces is used to control the rate of heterogeneous calcium carbonate nucleation in mild aqueous solutions. As the rate of heterogeneous nucleation is governed by the specific interfacial energies of system (i.e., calcite, water, and silicone surface), the application of mechanical stress to the chemically modified silicones alters the surface chemical composition and by relation the interfacial energies, thus altering the rate of heterogeneous nucleation. In this system the rate more than doubles between the lowest and highest strain state on the silicone surface. The ability to tie nucleation rate to physical mechanical strain can enable temporal and spatial control over the nucleation process. The results presented herein provides a level of control over nucleation that has not yet been demonstrated, and will be of interest to those studying nucleation, biomineralization, and crystal engineering, and will have applications in adaptive materials, anti-fouling surfaces, and ice prevention.

BM09.08.25
Amoeba-Like Self-Oscillating Polymeric Fluids with Autonomous Sol-Gel Transition

Michika Onoda1, Takeshi Ueki4, Ryota Tamate2, Mitsuhiro Shibayama2 and Ryo Yoshida; 1 The University of Tokyo, Tokyo, Japan; 2Yokohama National University, Kanagawa, Japan; 3Institute for Solid State Physics of the University of Tokyo, Chiba, Japan; 4National Institute for Materials Science, Ibaraki, Japan.

One of the important feature of living organisms is the dynamic behavior based on the hierarchical spatio-temporal structuration of building blocks driven by chemical signals. For example, spontaneous assembly and disassembly of actin networks play a central role in muscle contraction, cell division, and motility of protists. Despite these concepts are widely accepted as key components of biological systems, there are few reports that reproduce the dynamic behaviors based on the hierarchical spatio-temporal structuration by using only synthetic materials.

In contrast, we have reported structural oscillations of micelles and vesicles by totally synthetic AB diblock copolymer (di-BCP) incorporated a catalyst site of the Belousov-Zhabotinsky (BZ) reaction, without applying any on-off switching. In addition, we recently succeeded in realizing autonomous viscosity oscillation induced by microscopic self-oscillation between formation and break-up of the micellar network structure by preparing ABA tri-BCP. However, the viscosity amplitude was still limited (~2 mPa s).

Herein, we describe the self-oscillating ABC tri-BCP exhibiting autonomous sol-gel transitions assisted by dynamic structural oscillations between association and dissociation of the percolated network structure similar to a living amoeba. The target multiblock copolymer is synthesized by sequential reversible addition-fragmentation transfer (RAFT) polymerization incorporating a thermoresponsive A segment, a hydrophobic B segment, and a self-oscillating C segment. Unique oscillation behaviors of the multiblock copolymer are investigated in terms of time-resolved dynamic light scattering techniques for a dilute polymer solution and dynamic viscoelastic measurements for a concentrated polymer solution. As a result, novel oscillation behaviors among large viscosity oscillation, sol-gel oscillation, and viscoelastic oscillation are successfully demonstrated. The maximum amplitude of the viscosity is about 2,000 mPa s, which is 1,000 times larger than previous report and equal to the oscillation amplitude in a living amoeba. We also demonstrate an intermittent forward motion of a droplet of the polymer solution synchronized with the autonomous sol-gel transition. This marvelous polymer solution bears the potential to become the base for a type of slime-like soft robots that can transform their shape kaleidoscopically and move autonomously, which is associated with the living amoeba that move forward by a repeated sol-gel transition.
8:00 AM *BM09.09.01


In the idealized laboratory environment crystallization from pure solutions can follow either a single or a multistep nucleation pathway. The latter case involves the formation, aggregation and transformation of precursor particles to the final crystals [e.g. 1-3]. But, in most natural and industrial crystallization environments additives play a key role and are a central part of biomineralization, of functional material synthesis or of anti-scaling strategies, to name just a few. To gain full understanding and therefore control over crystallization, the possible interactions between additives and the precursor particles, intermediate and final phases need to be precisely unraveled.

In order to elucidate how additives get the job done we studied in situ and at the nanoscale the early stages of mineral formation in the presence of additives and compared them to the pathway observed for the additive free system [e.g. 4,5]. In this presentation, an overview of nucleation in the presence of additives will be given. Special emphasis will be placed on the interaction of organic molecules with precursor particles and how this affects the dynamics of the nucleation pathway.


8:30 AM BM09.09.02


Liquid coacervate is a metastable state where biopolymers assemble into densely packed droplets of low interfacial energy. In biology, coacervates may form inside the cells under variation of physiological conditions, for example under chemical stress [1]. Liquid coacervates form through spinodal decomposition but yet little is known about the path by which coacervate micro-droplets are formed: nucleation and growth, coalescence of smaller droplets, or formation of intermediate states? Here, we use as a model system a protein from the squid beak (HBP-2), whose recombinant version was recently shown to exhibit coacervation triggered by variations of pH and ionic strength [2]. Optical observations indicate that far from the spinodal conditions, coacervation occurs after a lag time and exhibits a linear increase in droplet density. Furthermore, time-dependent circular dichroism reveals that droplet formation coincides with the folding of HBP-2 into β-rich structures. Finally, direct observations under liquid transmission electron microscopy (liq-TEM), shows the nucleation of droplets of 1.5 to 2 nm in diameter, 20 nm entities and a network-like structure. At high ionic strength, the hydrogel-type of network shrinks, leading to the formation of dense discrete droplets. To the best of our knowledge, our study is the first example of in-situ observation of liquid-liquid phase separation under TEM. Understanding the precise assembly pathway of proteins into coacervates may help developing tools to prevent its occurrence when coacervates are the precursors of phases (such as amyloids) associated with pathological diseases [1].


8:45 AM BM09.09.03

Interfacially-Driven Nanoparticle Nucleation—A New Pathway to Mesocrystal Formation Guomin Zhu1, 2, Maria Sushko2, Jinhui Tao2, John Loring2, Benjamin Legg1, Jennifer Solits2, Chongmin N. Wang2 and James J. De Yoreo1, 2; 1University of Washington, Seattle, Washington, United States; 2Pacific Northwest National Laboratory, Richland, United States.

A diverse class of materials, including many biominerals, exhibit characteristics of mesocrystals: single crystals composed of distinct nano-sized domains that are atomically aligned. The formation of such structures is often attributed to crystallization through oriented attachment (OA). However, many unanswered questions about the fundamental drivers and dynamic progression of this process remain. Here we focus on the crystallization of hematite (hem, Fe2O3) from ferrihydrite (fh) as an example. In pure solution the resulting hem crystals are well faceted cuboctahedra, but in the presence of oxalate hem particles, the ligands bias the growth process towards oriented attachment. The common observation of crystals that appear to have formed via OA in solutions that are largely devoid of individual particles, suggesting this growth scenario may be widespread.

9:00 AM BM09.09.04

Negative Poisson’s Ratio of a Natural Nanocomposite Studied by In Situ TEM Mechanical Testing Jinkyung Kim, Jinsol Seo, Jiwon Jeong, Jeehun
The teeth of limpets are reported to be the strongest natural material, with tensile strength values ranging from 3 to 6.5 GPa. However, the origin of ultrahigh strength of limpet teeth is still unknown. Lipmets use conveyor belt-like radula to scrape rocks and extract algae during feeding. These processes require extremely strong teeth. Limpet teeth show characteristic composite nanostructures consisting of high volume fraction of reinforcing goethite crystals and softer amorphous hydrated silica matrix. The volume fraction and morphology of goethite crystals are heterogeneous at different locations of the tooth, which leads to site-specifically heterogeneous mechanical properties. The present work reports on the relationship between microstructures and deformation mechanisms of limpet teeth, using transmission electron microscopy (TEM) and in-situ TEM deformation. At the leading part of a limpet tooth, goethite crystals are mainly aligned along the principal direction of a tooth. The goethite crystals are rod-shaped, with approximately 30 nm in diameter and 300 nm in length. The volume fraction of the goethite crystals is approximately 50 %. TEM characterization of a longitudinal section at the tip of a limpet tooth shows both normally and laterally aligned goethite crystals, with some clusters of the normally aligned crystals. In addition, transition areas at the interfaces between goethite crystals and amorphous matrix are frequently observed. Atomic scale scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analyses show that the transition areas have different atomic structures and chemical composition from the original goethite crystals. The trailing part of a limpet tooth shows larger goethite crystals, with lower volume fraction than the leading part. To understand deformation behavior of limpet teeth, in-situ TEM deformation experiments were conducted using the samples taken from the tip of a limpet tooth. Upon tension, the samples show both positive tensile and transverse strain, which indicates negative Poisson’s ratio. The rotation of laterally-aligned goethite crystals appears to result in observed negative Poisson’s ratio. When the sample fractures, a crack propagates very fast right after its initiation. The ultrahigh strength of limpet teeth is expected to delay initiation of cracks. The present work will discuss the relationship among microstructures, deformation/fracture behavior and mechanical properties of limpet teeth. This could provide an insight into design of bioinspired engineering composite materials with superior strength and toughness.

9:15 AM BM09.09.05
Barrier-Free Nucleation of 2D Phage-Selected Peptide Films on MoS2 Surfaces Jiajun Chen1,2, Enbo Zhu1, Juan Liu4, Hendrik Heinz4, Yu Huang2 and James J. De Yoreo1-2, University of Washington, Richland, Washington, United States; 3Pacific Northwest National Laboratory, Richland, Washington, United States; 4University of California, Los Angeles, Los Angeles, California, United States; 5University of Colorado Boulder, Boulder, Colorado, United States.

Directed assembly of two-dimensional molecular arrays on crystal surfaces has been widely investigated to reveal the structural and energetic relationships between the substrate and overlying architecture. Progress has been achieved in understanding and controlling their assembly, yet little is known about the mechanism by which they nucleate. Understanding the dominant pathways and formation kinetics would enable precise control over phase and morphology during synthesis of 2D materials. In our study, short peptides were selected for their ability to bind to MoS2(0001). We studied nucleation and growth of 2D films of these peptides directly with in situ atomic force microscopy and compared our results to molecular dynamics simulations. We find the peptide arrays exhibit an epitaxial relationship to the underlying hexagonal lattice, but assemble one row at a time from dimeric units, and grow along three equivalent directions. The nuclei are ordered from the earliest stages without evidence for a transient precursor phase. Although the final crystals are 2D, due to the 1D nature of the constituent rows, there is no critical size, and the nucleation rate varies linearly with concentration and is finite for all concentrations above the solubility limit. Our results verify long-standing but unproven predictions of classical nucleation theory while revealing the key interactions responsible for ordered assembly.

9:30 AM BREAK

10:00 AM *BM09.09.06

Self-assembled macromolecular architectures exhibit a range of structural motifs such as particles, fibers, ribbons and sheets with functions that include selective transport, structural scaffolding and mineral templating. Although the sequence of the molecules dictates their governing interactions, function emerges from the mesoscale organization that arises from assembly. In the classical picture of assembly, order develops concomitantly with condensation as part of the microscopic density fluctuations inherent to all systems. However, establishment of long-range order in macromolecular structures almost always requires significant changes in conformation away from that seen in the monomeric state. Moreover, the presence of hydrophobic regions drives aggregation events that compete with ordered assembly. The impact of such structural transformations and transient states on the assembly process are a current subject of intense research. Using in situ techniques including AFM and optical and dynamic force spectroscopy, we have investigated the dynamics of assembly and intermolecular interactions for a number of natural protein and synthetic sequence-defined polymer systems assembling from solution on surfaces. In non-rigid systems, the results show that conformational transformations impose kinetic limitations on the nucleation of order. Transient fluctuations no longer provide a pathway to order; instead, the system must be driven to stabilize amorphous or liquid-like precursors. Moreover, once ordered structures nucleate within these precursors, conformational changes of the remaining solution-phase monomers are catalyzed by the presence of the ordered nucleus. However, the final architecture depends strongly on the interplay between protein-protein, protein-surface, and protein-solvent interactions. In particular, the introduction of high salt concentration, which screens electrostatic repulsion and introduces large entropic effects, leads to ordering processes reminiscent of colloidal systems. Small changes in sequence that alter the balance of hydrophobic and electrostatic interactions can induce a switch in assembly pathway between the multi-stage process described above and direct formation of the ordered structure. Finally, building 2D structures at interfaces out of molecules that assemble one row at a time, eliminates the barrier to nucleation and creates an asymmetry in nucleation kinetics for the first row and all subsequent rows, creating a simple means to tune the aspect ratio of the resulting 2D materials. The results of these studies suggest that the requirement of conformational transformation introduces a timescale for structural relaxation that differs from that of the density fluctuations and thus alters the pathway and kinetics of assembly, but that the details of macromolecular sequence, solvent interactions, and the architecture of the ordered phase can be used to influence barriers, pathways and outcomes.

10:30 AM BM09.09.07
In Situ Atomic Force Microscopy of DNA-Mediated Nanoparticle Assemblies in Solution Mikhail Shekhirev, Eli Sutter and Peter Sutter, Univ of Nebraska-Lincoln, Lincoln, Nebraska, United States.

Self-assembled nanoparticles into crystalline superlattices is an attractive approach toward fabricating metamaterials with tunable properties. Synthetic DNA as a “bonding agent” provides programmable crystallization of nanoparticle superlattices according to well-defined rules [1]. Remarkable progress has been made in fabricating 3D architectures with different crystal symmetries and consisting of different building blocks. Recently, research interest has shifted towards tuning structural parameters of the superlattices in response to external stimuli to creative adaptive materials architectures. Techniques for following such complex processes in the native solution environment have so far been limited mostly to X-ray scattering methods, with real space imaging (e.g., by liquid cell electron microscopy [2,3]) still in its infancy.

Jeong, Zhen Wang and Sang Ho Oh; Sungkyunkwan University, Suwon, Korea (the Republic of).
Here we present results of an investigation of DNA-mediated nanoparticle superlattices using in-situ atomic force microscopy (AFM). AFM is a powerful technique for direct imaging of soft samples, including DNA, in solution. However, AFM on DNA-bonded nanoparticle superlattices is challenging due to the weak base-pairing interaction between oligonucleotides and possible damage by the scanning probe. We demonstrate that by using peak-force tapping with precise control over the imaging forces, we can achieve continuous imaging without any significant perturbation of the nanostructures. Such non-invasive imaging in solution revealed a close-packed hexagonal arrangement of nanoparticles in surface-bound single- and few-layer superlattices. In contrast to direct imaging, indirect imaging of the assemblies allows the identification of particle arrangements within individual ordered and disordered domains, thus providing local information not accessible in reciprocal space. This approach shows systematic differences in the equilibrium distance of the DNA-coupled nanoparticles, for example in different layers of multilayer crystals or between central and edge regions in single-crystalline monolayer domains. Finally, we discuss in-situ AFM experiments toward understanding the reconfiguration of DNA-mediated nanoparticle superlattices in response to external stimuli, e.g., changes in solvent polarity and addition of DNA intercalants. Our in-situ real-space observations provide unprecedented insight into the behavior of DNA-nanoparticle conjugates as “programmable atom equivalents”.


**10:45 AM BM09.09.08**

**Towards Colloquen—Zinc Oxide Hybrid Materials**

Mark M. van Rijt1, 2, 3, Heiner Friedrich1, 2, 3 and Nico Sommerdijk1, 2, 3; 1Laboratory of Materials and Interface Chemistry and Centre for Multiscale Electron Microscopy, Eindhoven University of Technology, Eindhoven, Netherlands; 2Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; 3Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands.

In biology hierarchical organic-inorganic composites show highly tailored properties due to their precise control over shape and structure. One example is the mineralization of collagen with calcium phosphate in bone which results in remarkable mechanical properties. Its highly-defined pores make collagen a template of interest for more inorganic phases than only calcium phosphate.

One of these inorganic phases is Zinc oxide (ZnO). ZnO is a metal oxide with a range of electro and opto-electronic properties, among them piezo-electric behavior. By mineralizing ZnO in the confinement of collagen enhanced and selective control of its piezo-electric behavior should be achievable. ZnO has previously been synthesized under mild “bio-friendly” conditions using hydrothermal synthetic strategies; aqueous environment, low temperatures (50–80 °C) and ambient pressure. However, the initial stages and the mechanism of ZnO formation are rather poorly understood, making the incorporation of ZnO into collagen at this stage rather challenging.

The current steps in this work therefore focus on understanding the initial stages of ZnO formation. Preliminary results using conventional transmission electron microscopy (TEM), cryogenic TEM (cryoTEM) and selected area electron diffraction (SAED) studies suggest a multi-step precursor assisted mechanism. The formation of a nano-platelet precursor phase is observed by cryoTEM within the first minutes, showing no crystallinity with SAED. These platelets evolve into irregular sheets. At this stage nucleation of ZnO particles ~2-3 nm in diameter on the surface of the precursor sheets is observed, with SAED confirming the presence of ZnO. These primary particles subsequently grow into ZnO pillars via particle attachment. By elucidating this mechanism of formation using advanced cryoTEM and liquid phase TEM studies and by further studying the use of charged polymers and polypeptides as crystallization directing agents, we aim at obtaining new insights for the design and formation of collagen–ZnO hybrid materials.

**11:00 AM BM09.09.09**

**Iron Sulfide Supraparticles as Artificial Viruses for Gene and Gene Editing Therapies**

Emine Turali-Emre, Ahmet Emre and Nicholas A. Kotov; University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Gene and gene editing therapies have been widely investigated for treatment of inherited or acquired genetic diseases. Efficient delivery of therapeutic agents has become a significant barrier in clinical applications due to the toxicity and instability of the vectors in the complex intracellular environment. Among non-viral vectors, individual inorganic nanoparticles (NPs) have become a popular strategy for nucleic acid delivery. However, the nanoshell geometry of viruses is advantageous for the geneCRISPR cargo protection. Therefore, we synthesized L-cysteine stabilized iron-based inorganic nanoparticles which self-assemble into supraparticles with nanoshell geometry. Transmission electron microscopy (TEM), TEM tomography and dynamic light scattering (DLS) were used to characterize the virus-like supraparticles’ size, shape, and charge. Our results indicate that virus-like supraparticles contain continuous compartments, are positively charged (25±7.2 mV) and 74±21 nm in diameter. We loaded the DNA in the compartments during the formation of supraparticles. We tested these complexes in circular dichroism, UV-Vis spectroscopy, electrophoretic mobility shift and protection assays. Since iron sulfide is a natural material, it presumably has low cytotoxicity and high biocompatibility. Supraparticles can condense DNA, protect it against degradation, penetrate through cellular membranes and facilitate endolysosomal escape in gene therapy. Therefore, development of these particles can be used as an effective cargo delivery tool for gene and gene editing therapies.

**11:15 AM BM09.09.10**

**Biomimetic Molecularly Imprinted Photonic Crystal for Small Molecule Detection**

Prathyushakrishna Macha1, Abigail Juhi1 and Milana C. Vasilyev1; 1University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States; 2Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, United States.

In recent times, an increase in opioid related deaths have occurred due to the addition of synthetic opioids such as Fentanyl and carfentanil. Though there are conventional techniques, they are not designed for on-site detection of these molecules and are tedious. Photonic crystal structures have garnered significant interest in the fields of antireflective coatings, gas sensors, omnidirectional mirrors and label-free biological sensing. These have advantage over the conventional techniques as the structural enhancement and local changes in the refractive index (RI) allows for highly sensitive label-free onsite small molecule detection. The species *Bosere Cucumis* and *Ameniopsis Leidyi* of phylum Ctenophora have two-dimensional (2D) photonic crystals in their combs, which occur relatively less frequently in nature. The structures which occur in the eutomorphs were studied by embedding and morphology studies using cross-sections created using an ultratome and studied them to understand the nanoscale arrangements with the help of a transmission electron microscope.

Two-photon lithography, ebeam lithography, and nainoimprint lithography, were used to replicate these arrangements. The photonic crystal templates formed were observed using scanning electron microscopy and their reflectivity, Raman scattering, refractive indices were analyzed and further used for designing a molecularly imprinted photonic crystal (MIPC) to detect the target molecules as a colorimetric sensor.

**11:30 AM BM09.09.11**

**3D Self-Assembly of Nanocrystals via Co-Crystallization with Proteins**

Hyewon Kim, Xiaoting Guo, Yasutaka Nagaoka, Ou Chen and Vicki L. Colvin;
It has been a challenge to develop a facile and versatile method to achieve the 3D arrangement of nanocrystals. On the other hand, nature utilizes self-assembly process to produce the complex structured functional materials. Here, we present how the process of protein crystallization can provide a means for achieving the 3D arrangement of nanocrystals. By controlling the interaction between nanocrystals and protein, we achieved incorporation and the 3D arrangement of nanocrystals within protein crystals.

We chose hen egg white lysozyme (HEWL) and gold nanocrystals as a model system. For co-crystallization, weak attraction between nanocrystals and HEWL is required. We controlled interaction between gold nanorods (AuNRs) and hen egg white lysozyme (HEWL) by functionalizing AuNRs with poly (ethylene glycol) (PEG). When gold nanorods are functionalized with large molecular weight PEG, weak attractive interaction between AuNRs and HEWL arises. This weak interaction leads to facilitate nucleation of HEWL crystals and incorporation of AuNRs into HEWL crystals. Controlling directed self-assembly of nanoparticles requires understanding interactions between nanoscale building blocks. We used HPIC to understand the interaction between the gold nanocrystals and HEWL. Single crystal x-ray scattering confirms that the lattice parameter of HEWL is preserved when AuNRs are incorporated. We used SAXS, TEM, and the polarized optical microscopy to show that AuNRs are incorporated into lysozyme crystals and AuNRs inside the crystals have some ordered arrangement within HEWL crystal structure.

The phenomenon was independent of nanoparticle shape and type. We found other nanoparticles, such as iron oxide, quantum dots, and spherical gold nanoparticles also proceed co-crystallization with HEWL when the surface grafting density of PEG was low. This confirms that the surface properties of NP-PEG conjugates, rather than the nanoparticle itself, dictates the protein-nanoparticle solution interactions and the subsequence incorporation of nanoparticles into biomolecular crystals. In addition, proteins other than HEWL shows co-crystalization with these NP-PEG conjugates, which indicates this process can be applied to various 3D arrangement of nanocrystals.

11:45 AM BM09.09.12 Bioinspired Templating and Assembly of Heme Crystals for High-Performance Energetic Materials Chia Hung1, Andrea R. Poole1,2, Joseph Slocik1,2, Rajesh Naik1, Patrick B. Dennis1, Wendy J. Crookes-Goodson1 and Maneesh K. Gupta2, 1Air Force Research Laboratory, Wpafb, Ohio, United States; 2UES, Inc., Dayton, Ohio, United States.

Thermite reactions with nano-scale particles have attracted much study due to their high flame temperatures and combustion velocities. Mixing chemically synthesized heme crystals (hemoozoin) with aluminum nanoparticles (nAl), Slocik and co-workers (Slocik, 2015) demonstrated nanocomposites with increased energy output and combustion rates. Hemozoin are naturally produced by malaria parasites Plasmodium falciparum through bio-templated crystallization of heme B by Histidine-Rich Protein II (HRPII). Proteins with high histidine content with metal-coordinating functions are present in many organisms, including the Nereis virens jaw protein 1 (Nvjp1). Although rich in histidine and natively found to coordinate Zn(II), Nvjp1 does not share similar histidine-repeat motifs as HRPII. Here, we demonstrate the ability of Nvjp1 proteins to template hemozoin formation. Recombiantly produced Nvjp1 was incubated with iron-containing heme and efficiently formed hemozoin crystals. X-ray diffraction confirmed the crystal structure of the templated hemozoin crystals. Additionally, Nvjp1 was utilized to assemble hemozoin crystals directly on the surface of nAl yielding thermite nanocomposites. Results demonstrated that hemozoin formation is feasible with orthogonal proteins, therefore expanding the repertoire of candidates for bio-templated heme crystal formation. Through engineering of these proteins, the ability to control the size and shape of hemozoin crystals and hence the energy output of thermite nanocomposites could be realized.

Reference:
Elastin is the dominant building block of elastic fibers that impart structural integrity and elasticity to a range of important tissues, including the lungs, blood vessels and the skin. The elastin polymer is assembled from its molecular precursor tropoelastin. Historically, elastin’s dynamic nature has precluded traditional approaches such as X-ray crystallography to understand its detailed features. Here, I describe recent work using atomistic and coarse-grained models for predicting elastin’s multiscale structure and mechanical properties. We use the models to probe the function of key molecular regions, investigate disease etiology and explore implications for hierarchical assembly. The elastic fiber assembly process begins with a coacervation stage where monomers reversibly self-assemble into n-mer structures. Starting with the monomer as the basis for coarse-graining, we map the atomistic model to a MARTINI-based coarse-grained framework fortified with an elastic network. We show that directed assembly takes place through nucleation events and resulting aggregates display preferential domain positioning for enhanced cross-linking. Our results suggest that the irreversible coalescence of n-mer assemblies into higher-order fibrillar structures may be reinforced in the initial stages of coacervation by directed assembly.

2:15 PM BM09.10.03
Designing Hybrid Biological Materials—Controlling Morphology via Molecular Composition
Srinivas Mushnoori1, Cassandra Schmidt1, Vikas Nanda2 and Meenakshi Dutt1; 1Biomedical Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Center for Advanced Biotechnology and Medicine, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Peptide self-assembly is a field that shows great promise in the domain of controllable and shape tunable biomaterials. Their unique properties allow for a building blocks approach to materials design. In this study, mixed systems of two carefully selected peptides (i.e. diphenylalanine and phenylalanine-asparagine-phenylalanine) are explored for their self-assembly properties. We report a rich polymorphism in the assemblies of these peptides and explain the relationship between peptide molecular structure and the morphology of supramolecular assembly.

2:30 PM BM09.10.04
Simulating the Effect of Organic Molecules on Clustering in Calcium Carbonate and Phosphate—A Key Stage in Bioimineralisation
Aaron Finney1, Riccardo Innocenti Malini2, Colin L. Freeman1 and John H. Harding1; 1University of Sheffield, Sheffield, United Kingdom; 2Empa, Swiss Federal Laboratories for Materials Science and Technology, St. Gallen 9014, Switzerland.

Calcium carbonate and calcium phosphate are the most important biominerals in nature but there is still no consensus on how they form. Many nucleation and growth mechanisms have been and continue to be proposed. An amorphous phase is known to preceed both calcite and phosphate phases. It is also known that both inorganic and organic additives can affect the crystallisation process, the polymorphs formed, and the physical properties of the resulting materials. Simulations have frequently been used to try to unravel the complex mechanisms involved but require considerable computer resources to reach the long timescales required.

Recent work on calcium carbonate solutions at low concentration in the presence of amino acids has shown that they exhibit behaviour typical of that expected by classical nucleation theory with free ions, ion pairs and other small clusters present. At high concentration the amino acids self-assemble into aggregates, facilitated by ‘spectator’ ions and usually by bicarbonate ions. Liquid-like clusters form from the remaining calcium carbonate. These are also seen at the surface of the amino acid aggregates. When simulations are performed in the presence of oligopeptides (amino acid hexamers) liquid-like networks are formed, seeming to stabilise a dense liquid phase. Calcium phosphate also forms liquid-like clusters in the presence of amines, in this case the buffer tris(hydroxymethyl)aminomethane (TRIS). The simulations suggest that TRIS favours the formation of negatively charged complexes, and we believe that these are responsible for the inhibitory effect of TRIS. More generally, the formation of charged large aggregates could explain the formation of dense liquid phases in phosphate solutions.

We discuss the implications of these results for the role of a dense liquid phase in the nucleation mechanism for calcium carbonates and phosphates, connecting with the long-established proposal by Gower of the importance of a polymer-induced liquid phase (PILP) in the nucleation of biominerals.

2:45 PM BM09.10.05
Understanding Polymorph Selection in Calcium Carbonate
Colin Freeman1, Aaron Finney1, Riccardo Innocenti Malini2 and John H. Harding1; 1University of Sheffield, Sheffield, United Kingdom; 2Empa, Swiss Federal Laboratories for Materials Science and Technology, St Galen, Switzerland.

Within biomineralisation we frequently see the expression of both calcite and aragonite with the later being common in many marine organisms probably due to its enhanced material properties. These two polymorphs are very similar and differ only marginally in thermodynamic stability to favour calcite [1]. Despite its abundance in the natural world, aragonite is difficult to synthesise in the lab, requiring Mg or other additives. An alternative method is to raise the solution temperature above 70°C [2] despite the fact that the actual thermodynamic stability is unchanged at this these temperatures. The lack of aragonite and even its general absence from a solution during crystallisation implies that the nucleus must be unstable and quickly dissolve. This is at odds with recent simulation work that demonstrates that the surfaces of aragonite may be more stable in water than their calcite counterparts [3].

Computational molecular dynamics provides an ideal tool to study this unusual phenomena. We have studied the interfacial energies of a range of calcium carbonate polymorphs in contact with water and amorphous calcium carbonate with varying water concentrations. We use this data to demonstrate the stability of the different calcium carbonate nuclei. Using a statistical analysis of the structure we are able to identify the first stages of nuclei formation and discuss the potential structural features of these. This investigation reveals that kinetics rather than thermodynamics may be dictating the phase selection.


3:00 PM BREAK

3:30 PM BM09.10.06
Hierarchical Assembly of Computationally Designed Coiled Coils into Tunable 1D Architectures
Nairiti J. Sinha1, Dongdong Wu1, Chris Kloxin1, Jeff Saven2 and Darrin J. Pochan1; 1University of Delaware, Newark, Delaware, United States; 2University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Computational design guided self-assembly of biomolecules such as peptides has emerged as a new paradigm for engineering novel biomaterials in a bottom-up fashion. We exploit lithographic computationally designed homotetrameric antiparallel coiled coils as modular cylindrical Legos for assembling hierarchical 1D architectures using a hybrid physical-covalent assembly pathway. Specifically, the coiled coils are functionalized at the N-termini with either thiol-containing cysteine or maleimide functional groups and subsequently linked together via the Thiol-Michael ‘click’ reaction to form novel 1D...
chains of coiled coils. While the aspect ratio of these chains can be easily manipulated by changing the stoichiometric ratio of cysteine to maleimide functionalized coiled coils, the flexibility of the chains can also be tuned by the linker type between the coiled coils. Thus, a short linker results in stiff rods with large persistence lengths while a longer flexible linker yields flexible fibers, both of which are clearly visible in Transmission Electron Microscopy (TEM) analyses. Small Angle Neutron Scattering (SANS) has confirmed that these 1D chains of coiled coils are ca. 2 nm in diameter that is comparable with the designed cross-section of a coiled coil. Furthermore, stiff rods that are ca. 100 nm in length form liquid crystal domains at high concentrations that have a smectic like birefringence texture. The addition of sodium chloride salt changes the liquid crystal phase to one having a mosaic like birefringence texture. We propose that this is because the rods are net negatively charged in pure water and addition of salt screens the charge on the rod exterior which results in the observed change in the liquid crystal phase. This is supported by SANS of rods which exhibits a correlation hole in the intensity curve due to repulsion between rods in low ionic strength solution which disappears when salt is added.

3:45 PM BM09.10.07
Computational Design of Hierarchically-Assembled Multi-Component 2D Protein Materials Ariel J. Ben-Sasson1, William Sheffler1, 2, David Baker1, Fang Jiao2 and James J. De Yoreo2; 1Biochemistry, University of Washington, Seattle, Washington, United States; 2Physical Sciences, Pacific Northwest National Laboratory, Richland, Washington, United States.

The major advances in computational engineering of symmetric protein assemblies and characterization methods forms the basis for the design of novel materials, systems, and devices. A grand challenge that remains is the ability to generate multi-component assemblies with unbound symmetry that could theoretically grow infinitely either in vivo or in vitro. In other words, the challenge is to design protein components that would never self-assemble but co-assemble under a variety of conditions: in living cells, Eppendorf tube, or an advanced 3D printer.

In this work, we developed a computational method for the design of multi-component 2D protein assemblies by combining a number of design principles: Introducing plane symmetry constraints into the Rosetta software suite to engineer assembly pathways for hierarchical assembly of protein arrays. Computational interface design of multi-component non-covalent, weak, interactions to create a highly geometrical specific interaction. Use of dihedral building blocks whose internal symmetry favors planar assemblies. As a first milestone, we show in vivo assembly of ordered arrays that are obtained by introducing a multistronic vector carrying the genes of both proteins. Post lysis TEM characterization resolves the structure to 14 Angstrom, and pre-lysis optical characterization confirms the assembly takes place while proteins are expressed within the cells. As a second milestone we show in vitro assembly, which offers a controlled assembly environment that can be tuned, optimized, and applied to different practical purposes. We show that ordered micrometer scale arrays are robustly formed when the components are mixed in concentrations that are two orders of magnitude below those in which they are stably stored. Finally we show that multiple functional components can be either genetically fused or attached post-expression to the arrays, offering a direct route to introduce emerging, assembly-related, functionalities.

These recent achievements in the design, control, and optimization of the assembly process of complex protein 2D arrays, offers a new platform to generate biologically synthesized, synthetic materials, with custom designed functions beyond those found in nature.

4:00 PM BM09.10.08
Kinetically Dependent M13 Bacteriophage-Based Self-Assembled Nanostructures for Dynamic Gap Plasmonics Vasanthan Devaran1, JongMin Lee1, Jiye Han1, Kyoungh Lim1, Yeong Ju Lee1 and Jin-Woo Oh1, 2; 1Research Center for Energy Convergence and Technology Division, Pusan National University, Busan, Korea (the Republic of), 2Department of Nano Fusion Technology, Pusan National University, Busan, Korea (the Republic of).

Significant progress on the fabrication of highly ordered and hierarchically organized nanostructures through self-assembly methods had received greater attention in recent years. One of the critical highlights of processing a fabrication using self-assembly was its ability to surpass the critical structural and functional complexity issues occurring with current bottom-up and top-down approaches. In this work, a bacterial virus – M13 bacteriophage (phage) is used to fabricate self-assembled nanostructures based on drop-cast fabrication technique. The employed drop-cast fabrication method is simple, straightforward and cost-effective and doesn’t require any post-processing methods like etching or lithography to demonstrate (gap – tunable) plasmonic nanostructures. Upon drop-casting M13 phage solution on the substrate, by exploiting natural evaporation kinetics at the meniscus, different distance-dependent nanostructures were formed in a single fabrication attempt: networking-like structure close to the center, bundled or single nanowire in the middle, and an island (or dot) close to sides. Reproducibility of these nanostructures was possible even when changing few fabrication parameters such as follows: when using different types of phages like wild-type, WHW-type, and metalized (silver- or gold- coated) M13 phages; depositing on different substrates like glass slide, silicon, and gold coated silicon. Size control of networking nanowires (diameter range – 10 nm – 150 nm) and islands (diameter range – 200 nm – 1000 nm) was possible by varying the concentration of M13 phages or with changes in humidity. Experimental plasmonic studies like scattering, absorption, electric field enhancement were carried out and verified by three-dimensional finite difference time domain simulations (3D FDTD). M13 phage-based nanostructures exhibited an excellent dynamic plasmonic properties using above-mentioned size control conditions. In that, mainly, it was possible to demonstrate a clear tunable gap based plasmonic scattering using humidity control. By varying the humidity, the gap between two nanowire structures or islands were either increased or decreased leading to dynamic changes in scattering resonances or in near-field enhancement. We hope our kinetically controlled self-assembled fabrication approach utilizing M13 phage will open exciting applications in the field of sensors, plasmonics, photonics, lithography-free fabrication of highly ordered nanostructures, and so on.

4:15 PM BM09.10.09
Liquid Crystalline Behaviour of Surface Modified Laponite Clay Suspensions Peicheng Xu; University of Cambridge, Cambridge, United Kingdom.

We present two new routes to surface modify either the negatively charged flat surfaces of Laponite discs with the comb-polymer, PLL-PEG (polylsine-polyethylen glycole) or the positively charged rims of these particles with the cucurbit[7]uril, CB[7], a barrel shaped molecule. We demonstrate that the PLL-PEG coating can completely suppress the ageing typically observed in aqueous Laponite solutions, thus allowing for the first time to access the dichotic liquid crystalline phases of these clays. We distinguish between three scenarios, insufficient coatings, perfect and excess coatings leading to different liquid crystalline textures. In the case of the functionalization with CB[7] we observe a very different evolution into the formation of lamellar sheets of laponite particles leading to a smectic like texture, with a large spacing between the lamellas caused by the long-ranged Coulomb repulsion between the negatively charged particles.

4:30 PM BM09.10.10
Insights into the Interaction of Select Amino Acids with Anatase TiO2 via DFT Calculations Sai Phani Kumar Vangala and Parag A. Deshpande; Department of Chemical Engineering, Indian Institute of Technology Kharagpur, Kharagpur, India.

Design of biocompatible materials with improved properties have found increasing attention due to the effective interaction of biomolecules with inorganic surfaces in their applications in implantology, biosensors and bioelectronics. TiO2 has been widely studied for this purpose as an inorganic support to
Flow Imaging Technology for Evaluation of Polymer Microparticles—Analyzing Millions of Elastin-Like Polymer Coacervates One at a Time
Laura Marvin, James Vesenka, Wynter Paiva and Eva Rose M. Balog; Chemistry and Physics, University of New England, Biddeford, Maine, United States.

Biological and bioinspired polymer microparticles have broad biomedical and industrial applications, including drug delivery, tissue engineering, surface modification, environmental remediation, imaging, and sensing. Full realization of the potential of biopolymer microparticles will require methods for rigorous characterization of particle sizes, morphologies, and dynamics, so that researchers may correlate particle characteristics with synthesis methods and desired functions.

Toward this end, we evaluated biopolymer microparticles using dynamic imaging particle analysis, also known as flow imaging. This technology is becoming more widely used in the biopharmaceutical industry but is not yet well-known among the materials community. Our polymer, a genetically engineered elastin-like polypeptide (ELP), self-assembles into micron-scale coacervates.

We performed flow imaging of ELP coacervates using two different instruments, one with a lower size limit of approximately 2 microns, the other with a lower size limit of approximately 300 nanometers. We validated flow imaging results by comparison with dynamic light scattering and atomic force microscopy analyses. We explored the effects of various solvent conditions on ELP coacervate size, morphology, and behavior, such as the dispersion of single particles versus aggregates. We found that flow imaging is a superior tool for thorough and statistically powerful particle analysis of ELP coacervates in solution. We anticipate that researchers studying many types of microscale protein or polymer assemblies will be interested in flow imaging as a tool for rapid, quantitative, solution-based particle characterization.

Bioinspired Assembly of Small Molecules in Cell Milieu
Zhaoqiazi Feng, Hninmin Wang and Bing Xu; Brandeis University, Waltham, Massachusetts, United States.

Self-assembly, the autonomous organization of components to form patterns or structures, is a prevalent process in nature at all scales. Particularly, biological systems offer remarkable examples of diverse structures (as well as building blocks) and processes resulting from self-assembly. The exploration of bioinspired assemblies not only allows for mimicking the structures of living systems, but it also leads to functions for applications in different fields that benefit humans. In the last several decades, efforts on understanding and controlling self-assembly of small molecules have produced a large library of
candidates for developing the biomedical applications of assemblies of small molecules. Moreover, recent findings in biology have provided new insights on the assemblies of small molecules to modulate essential cellular processes (such as apoptosis). These observations indicate that the self-assembly of small molecules, as multifaceted entities and processes to interact with multiple proteins, can have profound biological impacts on cells. Here we illustrate that the generation of assemblies of small molecules in cell milieu with their interactions with multiple cellular proteins for regulating cellular processes can result in primary phenotypes, thus providing a fundamentally new molecular approach for controlling cell behavior.

BM09.11.05
Enamel Proteins for Guided Mineral Growth Karina M. Carneiro; Dentistry, University of Toronto, Toronto, Ontario, Canada.

Dental enamel is the outermost layer of teeth and is the hardest, most mineralized tissue in the human body. Its high crystallinity and hierarchical organization provide function and form the critical protective interface against external factors. Enamel formation involves a multi-step process guided by a complex mixture of proteins secreted by specialized cells. Key features of the underlying biomineralization mechanism remain unknown, primarily because the matrix is completely degraded during tissue formation. Amelogenin (AMEL) is the main protein present during enamel formation, with a suggested role in acting as a scaffold for mineralization to occur. Amelotin (AMTN) is a recently discovered enamel matrix protein that is secreted in small amounts during tissue maturation. Previous studies have shown its role in enhancing mineralization in vitro. In this presentation, I will describe the hierarchical self-assembly of AMEL and AMTN, their functional relationship, and their individual and combined effects on calcium phosphate mineralization. Specifically, I will show evidence that AMTN promotes directional crystal growth on AMEL supramolecular structures under biomimetic conditions, suggesting a similar guided mineralization mechanism may occur in vivo during enamel formation.

BM09.11.06
Chiral Tartaric Acid Can Selectively Regulate Brushite Bioceramic Crystallization Hanan M. Moussa1,2; Wenge Jiang1; Alaa Mansour1; Amir El Hadad1; Hailua Pan1; Jun Song1; Marc McKee1 and Faleh Tamimi3

In natural biomineralized structures such as bone, teeth and nacre, remarkable mechanical properties result from the control of growth and organization of inorganic brittle crystals by specialized biomolecules (i.e. proteins); this interplay provides high-performance material strength and toughness. These biomolecules found in biominerals are homochiral, one of the most distinctive biochemical signatures of life, where they are composed exclusively of L-enantiomers of amino acids enriched in acidic carboxyl groups. Brushite bioceramics have been attracting great attention as a bone substitute material because they are biocompatible and resorbable under physiological conditions. However, brushite bioceramics alone are brittle, and their mechanical properties are far inferior to bone.

We have discovered that brushite crystals have a chiral dynamic growth step susceptible for interaction with matching chiral molecules. Indeed, the growth of the chiral brushite step can be inhibited by stereochemical matching with the L-enantiomer of tartaric acid (L-(+)-Tar), hence inhibiting crystal precipitation and growth. Following on this discovery, here we also show that the simple addition of L-(+)-Tar can decrease the subunit crystal size of brushite bioceramics, and endow the bioceramic with high compressive strength and fracture toughness. In contrast, addition of the D-(−)-Tar enantiomer had an inverse negative affect on the mechanical properties, resulting in lower compressive strength and fracture toughness due to increased porosity. These observations are predicted by mathematical models that precisely described the inverse relationship of the mechanical properties with both subunit crystal size and total porosity content. These findings provide insight into the role of chiral L-biomolecules in biomineralization, and they inform the rational for fabrication of bioceramics having controlled crystallographic structure and enhanced mechanical properties.

BM09.11.07
Large Surface Plasmon Enhanced Fluorescence of Organic Dye Using M13 Virus-Based Framework and Its Application for In Vitro E.coli Detection Shengnan Huang1,2; Jifa Qi3,2; Dane W. deQuilettes3,4; Xiangnan Dang3; Neelkanth M. Bardhan3,2 and Angela Belcher1,3,2

Fluorescence spectroscopy is a powerful tool for studying biological processes, but its applicability is often limited by the fluorophores, which should have high specific binding and emission efficiency. In this regard, M13 virus, a versatile biotemplate, has been used to assemble fluorophores on its viral capsid with molecular precision and to target various cells. Although the M13-fluorophore ensembles have high targeting specificity, these systems suffer from poor detection sensitivity due to low quantum yield of the fluorophores. To address such limitations, we demonstrate a new, simple method to fabricate arbitrary arrangements of flexible high-aspect-ratio nanopillars using a combination of two-photon lithography and oxygen plasma etching. We show that the method can create millimeter-size arrays of nanopillars with tunable dimensions, cross-sections, bending stiffnesses, tilt angles and aspect ratios. In particular, we demonstrate aspect ratios up to 500, more than 15 times larger than has been shown in other fabrication methods such as replica molding, photolithography and e-beam lithography. We also show that high-aspect-ratio nanopillars assemble into chiral twists through kinetically controlled evaporation.

BM09.11.08
Fabrication and Self-Assembly of Hierarchical Nanostructures Moha M. Shahjamali and Vinothan N. Manoharan; School of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts, United States.

In nature, hierarchical structures such as arrays of pillars are source of various functionalities and have inspired broad applications in surface engineering, heat/electron transfer and sensing. However, traditional top-down fabrication approaches suffers from low control over their aspect ratio, tilt angle, lattice arrangement and flexibility.

To address such limitations, we demonstrate a new, simple method to fabricate arbitrary arrangements of flexible high-aspect-ratio nanopillars using a combination of two-photon lithography and oxygen plasma etching. We show that the method can create millimeter-size arrays of nanopillars with tunable dimensions, cross-sections, bending stiffnesses, tilt angles and aspect ratios. In particular, we demonstrate aspect ratios up to 500, more than 15 times larger than has been shown in other fabrication methods such as replica molding, photolithography and e-beam lithography. We also show that high-aspect-ratio nanopillars assemble into chiral twists through kinetically controlled evaporation.
How do polymer crystals differ from small molecule crystals? With the recent advent of sequence-defined peptoid polymer chemistry, we can now readily synthesize molecularly pure, peptoid polymers, with precision, atomic control of their molecular structure. This allows us to systematically explore how the chemical structure of a polymer chain effects its ability to crystallize and pack into well-defined assemblies. It allows us to explore the impact of main chain length and side chain shape on molecular crystallization. Here we used X-ray scattering and cryo-TEM to examine a series of crystalline, sequence-defined peptoid diblock copolymers, where we varied the main chain length, side chain chemistry and size, terminal groups and monomer composition. The peptoids assemble into both 2D and 3D lattices, depending on solvent conditions, allowing a variety of characterization tools to be used to elucidate the molecular structure and packing configuration. Interestingly we found that in over 22 crystalline peptoid polymers reported in the literature, all of them likely share a similar packing motif, where the chains are extended, and the backbones are in an all-cis conformation. This common structural motif over a wide variety of structures, suggests favorable backbone-backbone interactions resulting in chain alignment, and provides great opportunities to engineer these crystals by using synthesis to introduce point mutations to introduce specific function.

8:30 AM **BM09.12.01
Universal Backbone Conformation in Peptoid Polymer Assemblies**

Sunting Xuan, Doug Greer, Nitash Balsara and Ronald N. Zuckermann; Lawrence Berkeley National Lab, Berkeley, California, United States.

In recent years, block copolymers have attracted much attention for they can be used as building blocks to fabricate 1/2D nano-/micro- architecture driven by crystallization, electrostatic interaction and crosslinking. We combine conjugated fluorescent block poly (phenylene vinylene) (PPV) and poly (2-vinyl pyridine) (P2VP) to build rod-coil type diblock copolymer PPV-P2VP with strong fluorescence and self-assembly property. Nano-/micro-supramolecular fluorocent architectures of the copolymers were obtained by dissolving-cooling-aging process. The obtained structures could be transformed from one-dimensional (ribbons) to two-dimensional (square micelles) by changing the alkyl side chains of PPV blocks, and the scale of the structures could be controlled by changing the block length ratio of PPV and P2VP in the copolymer. The self-assembled morphology of the low block ratio exhibits a significant concentration dependence, and the concentration dependence disappears as the block ratio increases. The morphological characterization and kinetic studies of the formed nano-/micro-architectures show that the conjugated forces play an important role in self assembling process.

9:00 AM **BM09.12.02
The Controlled Self-Assembly of Fluorescent Block Copolymers Driven by π-π Interaction**

Feng He; Department of Chemistry, Southern University of Science and Technology, Shenzhen, China.

Many applications in tissue engineering, flexible electronics, and soft robotics call for approaches that are capable of producing complex three-dimensional (3D) architectures in soft materials. Uncovering the principles that biological systems utilize to develop complex 3D shapes and patterns (i.e. morphogenesis) is a promising route. Although the general principles dictating how differential cell growth leads to the formation of 3D shapes in plant tissue morphogenesis have been identified, an in vitro system that can closely mimic the process of tissue growth and morphogenesis is still missing. In this work, we use polyacrylamide hydrogel as a model system to mimic plant tissue growth. Our strategy takes advantage of the detrimental effect of polymerization inhibitors (i.e. oxygen) by turning it into an effective way to manipulate hydrogel formation. We demonstrate that the polymerization of polyacrylamide hydrogel is able to faithfully resemble all the essential features of plant tissue growth and morphogenesis. During polymerization, the oxygen plays a role mechanistically similar to the role of growth factors in tissue growth, and the continuous growth of hydrogel enabled by diffusion of monomers/cross-linkers into the porous hydrogel is similar to the mechanisms of tissue growth enabled by nutrient transport through vascular networks. The cross-linked hydrogel structure enabled by covalent bonds resembles the concept of interconnected cell walls in plant tissues. Similar to the differential growth in plant tissues facilitated by non-uniformly distributed growth factors and/or different growth rates among different constituent parts, accumulated residual stress as a result of differential polymerization of hydrogel leads to the formation of 3D structures. Our technique opens up new avenues to studying many growth phenomena found in nature and generating complex 3D structures to benefit diverse applications.

9:15 AM **BM09.12.03
Universal Backbone Conformation in Peptoid Polymer Assemblies**

Changjin Huang1, David Quinn1, Subra Suresh2 and K. Jimmy Hsia1; 1Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Nanyang Technological University, Singapore, Singapore.

Many applications in tissue engineering, flexible electronics, and soft robotics call for approaches that are capable of producing complex three-dimensional (3D) architectures in soft materials. Uncovering the principles that biological systems utilize to develop complex 3D shapes and patterns (i.e. morphogenesis) is a promising route. Although the general principles dictating how differential cell growth leads to the formation of 3D shapes in plant tissue morphogenesis have been identified, an in vitro system that can closely mimic the process of tissue growth and morphogenesis is still missing. In this work, we use polyacrylamide hydrogel as a model system to mimic plant tissue growth. Our strategy takes advantage of the detrimental effect of polymerization inhibitors (i.e. oxygen) by turning it into an effective way to manipulate hydrogel formation. We demonstrate that the polymerization of polyacrylamide hydrogel is able to faithfully resemble all the essential features of plant tissue growth and morphogenesis. During polymerization, the oxygen plays a role mechanistically similar to the role of growth factors in tissue growth, and the continuous growth of hydrogel enabled by diffusion of monomers/cross-linkers into the porous hydrogel is similar to the mechanisms of tissue growth enabled by nutrient transport through vascular networks. The cross-linked hydrogel structure enabled by covalent bonds resembles the concept of interconnected cell walls in plant tissues. Similar to the differential growth in plant tissues facilitated by non-uniformly distributed growth factors and/or different growth rates among different constituent parts, accumulated residual stress as a result of differential polymerization of hydrogel leads to the formation of 3D structures. Our technique opens up new avenues to studying many growth phenomena found in nature and generating complex 3D structures to benefit diverse applications.

9:30 AM BREAK

10:00 AM **BM09.12.04
Universal Backbone Conformation in Peptoid Polymer Assemblies**

Sunting Xuan, Doug Greer, Nitash Balsara and Ronald N. Zuckermann; Lawrence Berkeley National Lab, Berkeley, California, United States.

Two-dimensional (2D) nanostructures, typified by graphene or metal dichalcogenide nanosheets, are of interest in a broad range of applications including optoelectronics and photovoltaics. Solution-phase block copolymer (BCP) self-assembly is a widely-studied method to produce nanostructures using soft materials, although examples of dimension control using such methods are rare. Crystalline-coil BCPs can undergo living crystallization-driven self-assembly (CDSA), resulting in BCP micelles of controlled size and low polydispersity. Furthermore, length control over amphiphilic 1D BCP micelles have allowed access to complex superstructures, such as “windmill” supermicelles and large micelle superlattices. Recently we have extended living CDSA to the formation of 2D structures, through seeded-growth of BCP/homopolymer blends and charge-terminated crystallizable homopolymers. Various 2D platelet morphologies of controllable area and aspect ratio are now accessible. These methods can be applied to bio-compatible or optoelectronic crystalline polymers, providing materials with potential application in nanomedicine or nanoelectronics.
References
domains, our group recently reported their self-assembly into highly crystalline membrane-mimetic 2D nanomaterials and 1D nanotubes. We demonstrated that the peptoid-based nanomaterials are highly stable and a wide range of functional groups can be precisely placed within these materials as peptoid side chains. Furthermore, our mechanistic studies indicate that the packing of hydrophobic side chains is the key for the stabilization of these biomimetic nanomaterials. To gain the atomic level of understanding the self-assembly of these 2D and 1D nanomaterials, herein, we report the design and synthesis of short peptoid oligomers for self-assembly of biomimetic nanomaterials with similar structures. X-ray diffraction data indicate that nanomaterials assembled from these short sequences are highly crystalline and the change of one side-chain group at the N-terminal can significantly influence the materials formation process. By analyzing the XRD data of a number of biomimetic materials assembled from peptoids with similar chemistries, and the assistance of CryoEM and AFM characterizations, we gained a better understanding of peptoid assembly process and the structures of 2D and 1D peptoid-based nanomaterials.

11:15 AM BM09.12.10
Self-Assembly and Supramolecular Chirality Reversal of a Sophorolipid-Functionalized Chromophore Kyle C. Peters1, Shekar Mekala2, George Heidbreder1, Richard A. Gross3 and Kenneth Singer1; 1Physics, Case Western Reserve University, Cleveland, Ohio, United States; 2Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, New York, United States.

Bio-based, self-organizing molecules are of considerable interest as functional materials due to their structural versatility, mildly-sustainable bio-synthesis, and sophisticated nano-architectures that introduce chirality. This work is focused on molecules designed to exploit the light-absorbing and macromolecular self-assembly abilities of Nature for potential organic materials. Among these potential candidates, photoactive chromophores show promise for providing (opto)electronic and highly tunable structure and morphology. Additionally, a distinct class of microbially produced glycolipid biosurfactants, known as sophorolipids, show promise for providing the driving mechanism for self-assembly through carbohydrate hydrogen bonding. Herein, we explore the self-assembly and optical properties of a novel series of sophorolipid-functionalized zinc porphyrin molecular geometries that provide an intricate interplay among steric, π-π and hydrogen bonding interactions. We have investigated the delicate interplay of these non-covalent self-organizing interactions and their influence on multi-chromophoric aggregation by precise structural modification of the sophorolipid’s hydrogen bonding moiety and steric interactions through hydrocarbon chain modulation. Spectroscopic studies reveal solvent-promoted self-assembly in dilute methanol/water solution. It was found that helical supramolecular structures form by strong carbohydrate hydrogen bonding interactions, in contrast to nanosphere formation with acetyl-group substitution that eliminates hydrogen bonding interactions. Temperature-dependent UV/vis absorption and circular dichroism show that helical supramolecular polymerization proceeds through a cooperative mechanism of self-assembly for compounds that contain free hydroxyl groups capable of hydrogen bonding interactions. Further, it was discovered that shortening of the sophorolipid hydrocarbon chain promotes helical reversal accompanied with a large increase in the cooperative nature of assembled structures.

11:30 AM BM09.12.11
Anti Fatigue-Fracture Hydrogels by Forming Percolated Crystal Domains Shaoting Lin, Hyunwoo Yuk, Ji Liu, Xinyue Liu, Hyun C. Loh, Admir Masic and Xuanhe Zhao; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Natural materials in human body (e.g. heart valves, cartilages and muscles) can undergo millions of cycles without losing their functionality. However, synthetic hydrogels including recent developed tough hydrogels are susceptible to fatigue-failure even under a few thousands of cycles. To date, there are no unraveled mechanisms proposed yet to design anti fatigue-fracture hydrogels, which limits synthetic hydrogels’ applications that require long-term robust performance. Here, we report a biomimetic strategy to design anti fatigue-fracture hydrogels via controlled crystal domains. The strategy is to form percolated crystal networks in semi-crystalline hydrogels, retarding crack initiation under cyclic loading owing to high-strength crystal. To validate the proposed strategy, we use the poly(vinyl alcohol) (PVA) hydrogel as an exemplar material system and adopt a new experimental method to measure the fatigue threshold of the semi-crystalline networks with controlled crystal morphology. We show that the critical fracture energy for fatigue-fracture (i.e. fatigue threshold) can increase up to 1000 J/m² as the crystallinity in semi-crystalline network reaches the percolation threshold, higher than that of existing reported hydrogels in the order of 1-100 J/m². Following the design strategy, we further demonstrate two approaches to improve long-term mechanical performance: enhancing fatigue threshold via inducing local crystal domains around crack tip and achieving long-term high strength with crystal reinforcement.

11:45 AM BM09.12.12
Small Angle Neutron Scattering Analysis of Gold Induced Gel Formation of Chitosan Radha Perumal Ramasamy1 and Vinod K. Aswal2; 1Department of Applied Science and Technology, ACT Campus, Anna University, Chennai, India; 2Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, India.

Biopolymers are studied extensively due to its wide applications in the field of bio-technology, micro fluids and lab on chip devices. Chitosan is natural biopolymer derived from chitin. It has wide applications in bio-medical engineering because of its biocompatibility and biodegradability. Also, chitosan act as reducing and stabilizing agent for the metal ions. Chitosan is also a good candidate in batteries as membranes. It is therefore important to study the conformational changes of chitosan. Understanding the conformational changes in chitosan will help us better understand the microstructural modifications taking place inside membrane made using chitosan. In this research work, SANS was used to understand the modifications in the radius of gyration (Rg) values of chitosan in (i) solution, (ii) in presence of HAuCl₄ and (iii) in presence of LiClO₄. Small Angle Neutron Scattering is a useful technique for the characterization of biological materials. SANS experiments involve scattering of a monochromatic neutron beam from the sample and measures the scattered neutron intensity as a function of scattering vector. The wavelength of the neutron beam used was 5.2 Å with a resolution (Δλ/λ) of about 15%. All of the data were collected in the accessible Q range of 0.017−0.35 Å⁻¹. All of the SANS data were corrected for the background, the empty cell contribution, and solvent contribution, and were normalized using standard procedure. Chitosan solution was prepared by adding 1% (w/v) of chitosan powder, 1.5% (w/v) of acetic acid to D₂O. When HAuCl₄ was added to chitosan solution, higher concentrations of HAuCl₄ (more than 3mM) gave rise to gels. When chitosan solution was dried in a dish it gave rise to films. SANS shows that the chitosan solution (liquid) had greater Rg value than the chitosan film. For chitosan-gold gels the Rg value did not change in gels from that of solution. There was no correlation length for the fitting for chitosan in solution, however there was correlation length observed in the gels. This indicates that in gels the chitosan units are more localized than in solution phase. To chitosan solutions and chitosan-gold gels LiClO₄ was also added. The films formed by solution casting chitosan-LiClO₄ solution and gels formed using Chitosan-3mM HAuCl₄-LiClO₄ were also analyzed using SANS. The Interestingly, chitosan-Au-Li film shows the formation of star like structures which are not observed in case of gels. The correlation length for Chitosan-3mM HAuCl₄-LiClO₄ was less than that of Chitosan-3mM HAuCl₄ gels while the Rg in gels is nearly same for both Chitosan-3mM HAuCl₄-LiClO₄ and Chitosan-3mM HAuCl₄ gels. Hence we conclude that HAuCl₄ can localize chitosan units in solution leading to formation of gels and the incorporation of LiClO₄ in chitosan-gold gels can make the correlation length smaller and thereby affect the gels mechanical properties.
Changing the chemical and physical properties of a surface is important for many fields. This includes the design of new medical devices, antifouling materials and smart surfaces. Surface chemistry and topography determine the interactions of biomolecules with an implant and therefore govern its fate in the body. It also controls the interactions of surfaces with other biological entities such as bacteria and cells that lead to the undesirable process of biofouling.

This lecture will present a new platform for the formation of functional coatings. The coating is based on simple peptides that self-assemble into a layer on various surfaces. The functionality of the coating is controlled by the sequence of amino acids of the peptide. This peptide-based coating can resist biofilm formation and direct cell attachment. It could be useful in hospitals to prevent health-associated infections, in water desalination facilities to arrest membrane blockage by biofouling and in the design of implants.

2:00 PM BM09.13.02
Aerosol-Assembled Re-Entrant Textures for Superamphiphobic Coatings and Devices William S. Wong¹, Zuankai Wang², Antonio Tricoli³ and Vincent Craig⁴; ¹Physics at Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany; ²Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Hong Kong, China; ³Research School of Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia; ⁴Applied Mathematics, The Australian National University, Canberra, Australian Capital Territory, Australia.

Top-down fabricated re-entrant profiles are ubiquitous in the field of superamphiphobicity. However, their complex geometrical design and poor scalability presents significant challenges. Alternatively, bottom-up assembled superamphiphobic surfaces do exist, but true evidence of re-entrancy is, to our knowledge, never demonstrated. Inspired by these limitations, we propose the use of aerosol-assemble for achieving stochastic agglomerate textures with distinct and potentially tunable re-entrant profiles. Modifications to deposition parameters enabled a transitional-shift from quasi-pillar shaped geometries to quasi-inverted trapezoidal configurations. For the first time, re-entrancy and stochastically developed superamphiphobicity were correlated, validated using experimental wetting and computationally simulated particle assembly. Coatings developed were superamphiphobic-functional, preserving the Cassie-Baxter state (CA > 150°, SA < 10°) with fluids down to surface tensions of ca. 25 mN/m. Owing to the dimensional- and geometry-independent self-assembly, this technique is capable of producing functional coatings on highly complicated substrate profiles, even within fine needle capillaries. To this end, a series of contamination-proof, contact-free micro(fluid)mechanical devices were fabricated. They culminated in the unprecedented demonstration of producing and manipulating nano-liter droplets from ultra-low surface tension fluids. We hope that our findings could take root within and beyond the field of functional superdewettability, advancing progress in emerging fields such as high-resolution 3D printing, tissue- and biomedical engineering.

References

2:15 PM BM09.13.03
Understanding the Impact of Ligand Composition on Protein Corona Formation around Au Nanoparticles Sam Hoff¹, Desiré Di Silvio², Sergio Moya², Ronald Ziolo³ and Hendrik Heinz³; ¹University of Colorado Boulder, Boulder, Colorado, United States; ²Soft Matter Nanotechnology Group, CIC biomaGUNE, San Sebastian, Spain; ³Centro de Investigación en Química Aplicada, Saltillo, Mexico.

The makeup of coatings on nanoparticles in biological systems has an important impact on the fate and stability in cells and tissues. Ligands attached to nanoparticles, as well as protein coronas which form around nanoparticles in physiological environments, can be altered to change the destination of the nanoparticles, the time in the blood stream, and potential therapeutic functions. In this study, molecular dynamics is employed to study how the chemistry of end groups and length of ligands attached to gold nanoparticles affects the accessible surface structure. The structure and end groups have a marked change on the binding ability and binding conformation of Bovine Serum Albumin and Concanavalin A. PEGylated chains ending in a butanamide present a much smoother surface structure on the nanoparticle compared to that of PEGylated ligands ending in glucosamine which forms a rough surface capable of forming many weak unspecific non-covalent bonds. We use the CHARMM27 Interface force field which yields interfacial properties directly comparable to measurements. The study is being driven by experimental results and is expected to give insight into how protein - ligand interactions work, as well as an advanced understanding of ligand conformations, opening doors to designing ligands with the purpose of forming specific protein coronas to control the destination of nanoparticles for therapeutic activity.
Plasmmonic nanoparticle/semiconductor composites hold promise for optoelectronic applications ranging from solar cells to photocatalysts. There are two typical morphologies for such heterostructures, core-shell nanoparticles and pre-formed semiconductor nanostructures that are decorated with nanoparticles, but both have significant limitations on the degree to which the absorption and charge transfer can be enhanced. A composite architecture in which multiple nanoparticles can be incorporated into a crystalline rod without the insulating barriers associated with ligands could allow us to further enhance optoelectronic performance. BiomimORIZATION routinely creates composite crystals, where second phases are incorporated within single crystalline domains, thereby imparting improved functionality to the composite compared to a pure single crystal. Organisms use a combination of strategies (chemical and physical) to form these composites. Here, we focus on the bio-inspired growth strategy of crystallization in physical confinement as a means to create composite plasmimonic nanoparticle/semiconductor nanostructures. Our group previously showed that track-etched membranes could be used as a template for the formation of composite CuO/Au nanoparticle rods, where a large number of Au nanoparticles are encapsulated within crystalline cuprite nanorods (Chem. Mater. 2017). In this work, we show the generalizability of this physical confinement-based approach to create other semiconductor/nanoparticle composites, such as Cu2O/Ag and ZnO/Au. First, we load the track etched membrane with nanoparticles of an appropriate diameter with respect to the diameter of the pores such that the nanoparticles jam within the pores of the membrane. Then, using low-temperature, aqueous growth methods, we grow metal oxide semiconductors, which grow into the membrane pores and encapsulate the nanoparticles. By incorporating collections of nanoparticles into crystalline rods, we access a relatively unexplored morphology of plasmimonic nanoparticle/semiconductor heterostructure that we predict may have enhanced light collection and charge separation compared to the current typical morphologies.

Precisely programmed block copolymers self-assemble nano-structures such as micelles, vesicles and nanotubes in aqueous solution, have attracted increasing interests from all over the world as the biomaterial which has potential mainly for medical applications. Most typical example is the polymeric micelles with distinctive core-shell architecture, have great potential as drug delivery systems (DDS) to cancer and other intractable diseases. Hydrophilic shell provides polymeric micelles with stealth effect against foreign body recognition system in the body, while inner core works as a nano-reservoir of various cargo compounds. The polymeric micelle provides a promising system for delivery of therapeutic or diagnostic agents to diseased parts of the body, particularly solid cancers which have blood vessels with enhanced permeability, and some clinical trials are currently in progress. Meanwhile, designing a polymeric micelle that transports nucleic acid-based drugs such as siRNA, mRNA and pDNA have great potential for the therapy of central nervous system (CNS) disorders, through the barrier of a normal blood vessel with unenhanced permeability remains a challenging task. For the development of DDS to the CNS, blood brain barrier (BBB) is the obstacle, which excludes most drugs with the tight junction between brain capillary endothelial cells (BCECs). Recently our group developed glucose decorated polymeric micelles (Gluc/m) targeting glucose transporter 1 (GLUT1). GLUT1 is highly expressed on the BCECs and its localization can be manipulated by controlling the blood glucose level. Optimizing glucose ligand density on the surface of Gluc/m and glycemic control, Gluc/m achieved 6 % dose/g accumulation in the brain and attained its BBB penetrating ability. Although glucose-decorated micelles with short length PEG chains (2 kDa) can be recognized by GLUT1 and observed accumulating in brain, micelles with long length PEG chains (12 kDa) cannot recognize GLUT1. For increasing stability of micelles and loading various drugs, the development of ligand-loaded micelles with high molecular weight PEGs which maintains the ligand accessibility is needed. Previous research hypothesized that the ligand mobility is restrained by the neighboring PEG chains and the accessibility of ligands to the receptor is reduced when longer ligand-installed PEG chains attached to nanoparticles. In this research, for the purpose of overcoming PEG dilemma, the novel polymeric micelle consisting of long PEG conjugated to the glucose ligand and short PEG was developed. This technique is called cocktail PEGylation, and mixing short PEG is expected to increase the mobility of ligand molecules. The interaction between Target Membrane Proteins and Ligand-Decorated Polymeric Micelles Penetrating Blood-Brain Barrier Noriko Nakamura1,2, Yasutaka Anraku1,2, Shigeto Fukushima2, Kazuko Tou1, Horacio Cabrall1,2 and Kazunori Kataoka1,2; 1The University of Tokyo, Tokyo, Japan; 2Innovation Center of NanoMedicine, Kanagawa, Japan.

Nitrile oxide (NO) is a physiological molecule that plays a key role in our body such as, vasodilation and inflammation. In respect of inflammation, NO is known to be related with RA which is a chronic inflammatory autoimmune disease that involves the joints. NO from abnormal macrophage upregulates osteoclasts to destroy a cartilage and recruits other immune cells inducing inflammation. In our group, we already reported NO-responsive macro-sized hydrogel by synthesizing NO-cleavable crosslinker. Herein, we further investigate NO-responsive nanogel for treating RA. The abnormal macrophage in the RA lesion secretes much higher concentration of NO compared with normal one. Thus, we designed NO-responsive nanogel that removes NO in abnormal joint and then alleviates a progress of RA. We represented the formation of the nanogel using acrylamide and NO-cleavable linker and showed its swelling behavior responding to NO through transmission electron microscopy (TEM) and dynamic light scattering (DLS). We also confirmed higher NO capturing efficiency of NO-cleavable crosslinker than N, N'-methylene bis-acrylamide via gries assay. For in vivo study, we prepared a collagen-induced arthritis mouse model in DBA/1 mice. The therapeutic effect of the nanogel in suppression of the onset of arthritis in each paw of mice was as effective as dexamethasone, a commercial anti-rheumatoid arthritis drug. Therefore, our findings may suggest a potential biomedical application for clinical translation.
nanostructured carrier is not orthogonal, which affects not only the structure of carrier but also the loaded amount of each cargo molecule. Therefore, development of a nanostructured carrier which facilitate orthogonal loading of the cargo molecules has been highly demanded. Herein, we report an ingeniously designed Pt(IV)-mediated polymeric architecture (Pt-PA) for combinatorial gene and chemotherapy to address the issue. The Pt(IV) prodrug, which has two reaction site, enabled the crosslinking of low-molecular-weight (MW) polyethyleneimine (PEI) to form high-MW PEI. Accordingly, the Pt-PA exhibited successful self-assembly into nano-sized complex with therapeutic gene (i.e. siRNA) without any influence on the loading of Pt(IV), because Pt(IV) has been already incorporated in a polymer architecture by chemical conjugation. The self-assembled complex could be dissociated specifically under redox environment due to an inherent characteristic of the Pt(IV) crosslinker. Therefore, simultaneous release of both active Pt(II) drug and gene was monitored at intracellular reducing environment, resulting in enhanced gene silencing effect and anticancer effect. In animal study, an improved therapeutic effect of the nano-sized complex was observed, which can be explained by tumor targeting via EPR effect of nano-sized complex as well as enhanced intracellular release of drug and siRNA at reducing environment. Taken together, overall results from in vitro and in vivo studies strongly manifest the therapeutic potential of our nanostructured Pt(IV)-mediated polymer architecture.

4:15 PM BM09.13.09
Facile Formulation of poly(phenylboronate) Nanoconstruct by Simple Mixing with Diol-Containing Hydrophobic Chemotherapeutics and Its Biomedical Application
Junseok Lee, Jinhwan Kim, Yeong Mi Lee and Won Jong Kim; POSTECH, Pohang, Korea (the Republic of).

To date, self-assembled nanostructures have drawn enormous attention for biomedical application. Since nano-scaled particulates are known to be accumulated into the tumors easily via an enhanced permeation and retention (EPR) effect, such nanostructures have been exploited as delivery system for therapeutic small molecules. However, convoluted synthetic process of conventional nanostructures has impeded to achieve feasible and reproducible clinical applications. Herein we report a facile formulation of self-assembled nanostructure for systemic delivery of diol-containing hydrophobic chemotherapeutics, andrographolide (AND) and doxorubicin (DOX). In these studies, formation of a stable nanoconstruct enabled to enhance the water solubility of AND or efficiency of DOX. Phenylboronic acid (PBA) was grafted on the hydrophilic polymer to form poly(phenylboronate) (pPBA) and nanoconstruct was easily formulated by simple mixing with drug through the formation of phenylboronic ester with 1,3-diol of drugs. The release profile of drug was pH-responsive owing to the intrinsic property of phenylboronic ester. Moreover, tumor targeting ability of nanoconstruct was demonstrated in vitro and in vivo driven by an inherent property of residual PBA. Finally, antitumor effect of nanoconstruct was highly effective in vivo even in comparison with free drug. Taken together, our judiciously designed pPBA/drug nanoconstruct suggests a new paradigm of self-assembled nanostructure with variant potential in biomedical application.

SYMPOSIUM CM01

Solid-State Chemistry of Inorganic Materials
November 26 - November 30, 2018

Symposium Organizers
Ashfia Huq, Oak Ridge National Laboratory
Kirill Kovnir, Iowa State University of Science and Technology / Ames Laboratory
Antoine Maignan, Centre National de la Recherche Scientifique, CRISMAT Laboratory
Corey Thompson, Purdue University

Symposium Support
ACS Division of Inorganic Chemistry
Chemistry of Materials | ACS Publications
Crystal Growth & Design | ACS Publications
Inorganic Chemistry | ACS Publications
International Centre for Diffraction Data (ICDD)
Journal of Physics and Chemistry of Solids | Elsevier
Journal of Solid State Chemistry | Elsevier
LC Technology Solutions Inc.
Malvern Panalytical
National Science Foundation, Division of Materials Research
NETZSCH Instruments North America, LLC
Physical Review Materials | American Physical Society
Science and Technology of Advanced Materials| National Institute for Materials Science

* Invited Paper

SESSION CM01.01: Perovskites and Beyond
Session Chairs: Kirill Kovnir and Corey Thompson
Monday Morning, November 26, 2018
Hynes, Level 2, Room 203
8:00 AM #CM01.01.01
Lone Pairs in the Halide Perovskites, Hidden and Otherwise
Douglas Fabini¹, Geneva Lauria², Constantinos Stoumpos², Mercouri G. Kanatzidis³ and Ram Seshadri¹; ¹Materials, University of California, Santa Barbara, Santa Barbara, California, United States; ²Chemistry, Bates College, Lewiston, Maine, United States; ³Department of Chemistry, Northwestern University, Evanston, Illinois, United States.

The ABX₃ halide perovskites that have attracted so much renewed attention mostly possess B = Sn²⁺ or Pb²⁺, with m² lone pairs of electrons. These lone pairs are frequently hidden, in the sense that the crystal structures are not consistent with the presence of a stereochemically active lone pair that would result in certain characteristic distortions of MX₆ polyhedra in the structure. The influence of such hidden lone pairs can be found in numerous perovskites including the hybrids with methylammonium [4 = CH₃NH₃⁺] and formamidinium [4 = CH(NH₂)₂⁺], where the lone pairs are associated with proximal instabilities that can profoundly influence materials properties. We will discuss the understanding that we have developed from extensive real and k-space studies of local and average structure in these materials using synchrotron and neutron scattering, DFT calculations and NMR studies complement the structural studies to obtain a coherent picture of what is happening, and where all the red herrings are. This work was supported by U.S. DOE, Office of Science, through DE-SC-0012541.

8:30 AM CM01.01.02
A Study of Dynamic Tilt in Perovskites—Bridging the Gap Between Simulation and Experiment
Christopher M. Handley, Robyn Ward, Colin L. Freeman, John H. Harding and Ian M. Reaney; University of Sheffield, Sheffield, United Kingdom.

Tilting in perovskites is a well-documented structural phenomenon, which occurs due to the mismatch in the A and B site ion sizes. We can observe the influence of these tilts through selected area diffraction patterns (SADP), and classify them using Glazer notation. However, Glazer notation is limited as it only classifies tilt for the time-averaged system structure, and assumes that the octahedra are regular in shape. Attempts have been made to simulate transmission electron microscope (TEM) patterns for SADP for each perovskite titling motif, but it has been limited to static simulations and assumes ideal SADPs.

We have developed a new methodology that uses a combination of commercial (CrystalMaker) and in-house (PALAMEDES) programs, to analyse the dynamics of perovskite tilts from molecular dynamics simulations, and in turn use these simulations to simulate time averaged TEM and X-ray diffractions (XRD).

Simulations of CaTiO₃, BaTiO₃, and solid solutions of BCT and BST have been performed using DL_POLY 4. The calculated diffraction patterns and spectra for these materials compare well to experiment. In addition, we are able to use PALAMEDES, to extract dynamic measures of structural features, such as the magnitudes and oscillations of the tilt angles, volumetric distortions, local dipoles, and the phase of the tilts - both locally and at longer ranges.

Through our methodology we are able to demonstrate the influence that temperature and dopants have on perovskite structure, in particular their dynamical traits, and how these dynamics are detected or masked by experimental TEM and XRD, and ultimately have a basis for how it is the dynamics of structural features that underpins the material properties.

6. 8:45 AM CM01.01.03
Tunable Emission in Multinary Halides
Bayrammurad Saparov¹, Mao-hua Du² and Rachel Roccanova¹; ¹University of Oklahoma, Norman, Oklahoma, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

One of the projects in our group targets the synthesis, modeling, single crystal growth, and characterization of low cost multinary halides for light emission applications (e.g., solid-state lighting, scintillators etc.). Taking advantage of the simple processing and rich chemistry of multinary halides including hybrid organic-inorganic halides, we controllable prepared a series of 2D, 1D and 0D crystal structures featuring perovskite-derived and non-perovskite crystal structures. Tunable light emission properties of the obtained materials were characterized using UV-vis absorption, photoluminescence (emission, excitation, time-resolved, temperature-dependent, quantum yield etc.) and density functional theory calculations.

In luminescent hybrid Sn- and Pb-based halides, the inorganic Sn/Pb-halide networks (or clusters) are usually responsible for the observed luminescence due to their relatively small energy gaps of the inorganic substructures compared to those of organic molecules. The low energy gaps of the inorganic substructures in such cases are ensured by the relatively small electronegativity difference between Sn/Pb and halogen elements, which results in valence bands dominated by halogen orbitals and conduction bands primarily made of metal orbitals. In principle, the band alignment in hybrid halides can be altered by (1) combining pairs of metal and halogen elements with large electronegativity difference to accommodate organic molecules’ frontier orbitals, or (2) by utilizing low-gap aromatic molecular cations. The hybrid metal halides studied in our group feature electropositive metals such as Zn and Cd, among others, and aromatic organic cations, yielding unusual band alignments at the organic-inorganic interface. Thus, we were able to obtain compounds showing type-I band alignment with bands near the band gap originating from the inorganic component, type-I band alignment based on organic molecules, and also type-II band alignment featuring both organic and inorganic states. Therefore, depending on the specifics of their band structures, highly tunable light emission of our compounds are attributed to inorganic or organic substructures, or a combination of both.

In this talk, I will provide fresh examples of highly luminescent multinary halides prepared in our group including several examples of broadband white-light emitters, and efficient deep blue emitters, both of which are sought for solid-state lighting applications. The highest room temperature photoluminescence quantum yield (PLQY) values measured in our lab include 3% for a white-light emitting hybrid zinc bromide compound, and 26% for blue-emitting all inorganic Cu halides. Importantly, this work paves the way to band alignment engineering of organic and inorganic components in hybrid organic-inorganic halides to controllably create type I and type II band alignments, and to fabricate materials where the emission originates from organic, inorganic or both components.

9:00 AM CM01.01.04
Tuning the Magnetic Anisotropy in the Layered Chromium Mixed Halides
Fazel Fallah Tafti, Mykola Abramchuk, Samantha Jaszewski, Kenenth
Magnetic anisotropy is the tendency of spins to align in a certain crystallographic direction - the easy-axis. Without anisotropy, thermal fluctuations prevent magnetic ordering in two dimensions according to the Mermin-Wagner theorem. In layered materials, the two limits of the easy-axis are in-plane (XY) and out-of-plane (Ising). Recent advances in exfoliation and device fabrication have led to the discovery of ferromagnetic ordering with Ising anisotropy in CrI₃ monolayers. It is theoretically conjectured that spin-orbit coupling (SOC) provided by halide atoms on the super-exchange path yields the magnetic anisotropy. Here, we design a unique experiment to probe this idea by growing a series of CrIₓBr₃ and CrIₓBr₄ crystals where SOC is tuned between CrI₃ with XY and CrI₄ with Ising anisotropy. We discover a continuous rotation of the easy-axis from XY to Ising with increasing x. Remarkably, the magnetic ordering temperature, optical gap, and inter-layer spacing are also tuned linearly with x. This is the first observation of a continuous rotation of the easy-axis and the effect of SOC on the super-exchange path. Methods presented here can be extended to produce other metal mixed halides to fabricate tunable heterostructures and spintronic devices.

References:

9:30 AM BREAK

10:00 AM CM01.01.06

Colloidal nanocrystals of APbX₃ perovskites \( A=\text{Cs}^+, \text{CH(NH}_2\text{)}_2^+, \text{Br}^-, \text{I}^- \): structural aspects, self-assembly and potential applications Maksym Kovalenko M. V. Kovalenko et al. *Chemistry and Applied Biosciences, ETH Zurich, CH-8093, Switzerland; Empa—Swiss Federal Laboratories for Materials Science and Technology, CH-8600, Dübendorf, Switzerland*.

We survey the synthesis methods for colloidal lead halide perovskite nanocrystals (APbX₃, NCs, A=Cs⁺, FA⁺, FA= formamidinium; X=Cl, Br, I), structural chemistry and structural dynamics, and prospects of these NCs for optoelectronic applications such as in television displays, light-emitting devices, and solar cells, emphasizing the practical hurdles that remain to be overcome. The spontaneous and stimulated emission spectra of these NCs are readily tunable over the entire visible spectral region of 410-700 nm [1-2]. The photoluminescence of these NCs is characterized by narrow emission line-widths of 12-42 nm, wide color gamut covering up to 140\% of the NTSC color standard, high quantum yields of up to 100\%. Cs\(_2\)FA\(_x\)Pb\(_{1-x}\)I₃ and Cs\(_x\)FA\(_{1-x}\)Pb\(_2\)I₅ reach the near-infrared wavelengths of 800 nm [3]. Their processing and optoelectronic applications are, however, hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface capping molecules during isolation and purification. A new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules such as 3-(N,N-dimethyldecylammonio) propanesulfonate, resulting in much improved chemical durability had been developed [4]. Perovskite NCs also readily form long-range ordered assemblies, known as superlattices. These assemblies exhibit accelerated coherent emission (superfluorescence), not observed before in semiconductor nanocrystal superlattices [5].

L. Protesescu et al. *Nano Letters* 15, 2015, 3692-3696
M. V. Kovalenko et al. *Science* 2017, 358, 745-750
G. Raine, M. Becker, M. Bodnarchuk et al. 2018, submitted

10:30 AM CM01.01.07
First Principles Investigation of Metal-Insulator Transitions in Rare-Earth Nickelates Induced by Chemical Doping Pilsun Yoo and Peilin Liao, Purdue University, West Lafayette, Indiana, United States.
Chemical doping driven metal-insulator transitions (MIT) can be adopted for solid-state field effect devices, solid electrolytes for solid oxide fuel cells, and active terahertz spectrum photonic devices. The electrical conductivity of SmNiO$_3$ decreases by ~8 orders of magnitude when it is chemically modified by hydrogen atoms. We applied first principles calculations to study geometric, electronic and optical properties of perovskites during chemical doping induced MIT. We showed that the DFT+U method with the PBEsol functional and $U_{\text{eff}} = 2$ eV produced results in good agreement with experiments for both insulating and metallic phases of SmNiO$_3$. We further examined changes in geometry and electronic structures for hydrogen doping in a series of rare earth nickelates. These current findings provide physical insights for future experimental investigation to develop efficient metal-insulator switching devices.

10:45 AM CM01.01.08
Exploring Tunable Persistent Luminescence in Chromium-Substituted Spinel Phosphors Erin Finley; University of Houston, Houston, Texas, United States.

Developing new persistent luminescent phosphors, which have applications ranging from emergency signage to children’s toys, requires an improved understanding of the mechanism that drives their distinctive optical properties. The current consensus is that the long luminescence lifetime stems from a relationship between the inorganic host crystal structure’s band gap and the position of defects that form electron trap states. Fortunately, investigating the crystal chemistry and electronic structures of well-known persistent luminescent phosphors based on the chromium substituted spinel ZnGa$_2$O$_4$ offers a platform to study this mechanism. Substituting Cr$^{3+}$ into this host crystal structure produces a long lifetime red emission as a result of the spin forbidden $^2E \rightarrow ^4A_2$ transition of the $5d$-orbitals. This electronic transition results in a phosphorescence emission decay that is further extended by anti-site defects that act as electron traps. Research has shown that substituting aluminum onto the gallium site can change the luminescence lifetimes by varying the size of the band gap and presence of structural defects. Therefore, this work presents the preparation and investigation of persistent luminescence in the solid solution Zn(Cr$_{6-x}$Al$_x$)$_2$O$_4$Cr$^{3+}$ ($x = 0-1$). Employing a combination of luminescence spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and density functional theory this work provides valuable insight into the relationship between the inorganic host crystal structure and the persistent luminescence mechanism. These results provide a pathway to aid in the discovery of new persistent luminescent phosphors with a range of both emission wavelengths and luminescence lifetimes.

11:00 AM CM01.01.09
The Magnetic Properties of Triple Perovskites—Spin Glasses, Ferrimagnets and Relaxors Peter D. Batlle1, Emily C. Hunter1, Chun-Mann Chin1, Yuwei Tang2, Mylene Hendrickx2, Joke Hadermann2 and Maxim Avdeev3, 4; 1Oxford Univ, Oxford, United Kingdom; 2Physics, University of Antwerp, Antwerp, Belgium; 3ANSTO, Lucas Heights, New South Wales, Australia; 4The University of Sydney, Sydney, New South Wales, Australia.

This contribution is centred on the magnetic properties of so-called triple perovskites having the general formula La$_{3-a}$A$_a$B$_2$O$_9$ where $A$ is Ca, Sr or Ba, $B$ is Fe or Ni; $B'$ is Nb, Ta, Sb or Te and $0 \leq x \leq 3$. Many of these compounds adopt a cation-ordered, monoclinic perovskite-like structure in which there are two crystallographically-distinct six-coordinate sites with equal multiplicities. The cation ordering over the octahedral sites thus involves arranging two cation species that are present in a 2:1 ratio over two sites that are present in a 1:1 ratio. We have shown, by a combination of neutron diffraction and electron microscopy, that one of the two sites is usually occupied entirely by the more abundant cation, $B$, while the other is occupied in a ratio of 0.333:0.666 by $B$ and $B'$, respectively. If $B$ is magnetic and $B'$ is diamagnetic and the nearly-linear nearest-neighbour $B - O - B$ interaction is dominant and antiferromagnetic, then the imbalance in the concentration of magnetic $B$ cations on the two sites would be expected to lead to ferrimagnetism and a net magnetisation below the Curie temperature. This idealised behaviour is rarely observed in practice. Magnetometry data collected on La$_3$Ni$_2$SbO$_9$ were consistent with the model but no magnetic Bragg scattering was observed in a neutron diffraction experiment carried out below the magnetic transition temperature until a magnetic field was applied; we therefore described this compound as a relaxor ferrimagnet. La$_3$Ni$_2$TaO$_9$ behaves in a similar manner but La$_3$Ni$_2$NbO$_9$ is a spin glass. However, the magnetisation of the latter composition increases markedly when 12.5 % of the Ni$^{2+}$ cations are replaced by Cu$^{2+}$. In the case of SrFe$_2$TeO$_6$ the six-coordinate cations order in a different, trigonal pattern, although domains of a 1:1 tetragonal phase were revealed by electron microscopy. The monoclinic structure is adopted by the Co-doped composition Sr$_2$LaFeCoSbO$_9$, which shows a novel cation ordering pattern: all the Sb$^{5+}$ cations are on the same six-coordinate site and all the Co$^{3+}$ cations are on the other; the Fe$^{3+}$ cations are distributed evenly across both sites. This results in the observation of long-range magnetic order by neutron diffraction, with a Curie temperature of ~215 K and a saturation magnetisation of ~1 Bohr magneton per formula unit. Attempts to synthesize the calcium and barium analogues of this composition, or to replace cobalt by nickel, resulted in samples that were shown to be amorphous.

11:15 AM CM01.01.10
Reassessing Pauling’s Rules Janine George, David Waroquiers, Davide Di Stefano, Gian-Mario Rignanese and Geoffroy Hautier; Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium.

Pauling’s rules are essential for solid state chemistry [1,2]. In the first publication of the rules, Pauling has already stated several of their drawbacks [2]. For instance, they are presumed to only work for very ionic compounds such as oxides and fluorides [2]. Surprisingly, there is no statistical sound answer on how well all Pauling’s rules perform for oxides up to today in literature. In this contribution, we will provide such an answer. To do so, all five Pauling rules are checked on thousands of oxides from the Materials Project [3] that originally stem from the experimental database ICSD. We will start from a very recent analysis of the statistics of the coordination environments of oxides [4]. A special focus will be on the rules describing the connections of the coordination polyhedra because the knowledge on the performance of these rules is especially sparse. Deviations from Pauling’s rules and their origins will also be discussed.

Acknowledgements: Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI).

References:

11:30 AM CM01.01.11
Materials Discovery and Reaction Design Tyrel McQueen; Johns Hopkins Univ, Baltimore, Maryland, United States.
A grand challenge in solid state materials chemistry is to achieve the same level of control over bond-making and bond-breaking as afforded by well-known organic reaction paradigms. In this talk, I will present recent work on the discovery of new organo-halide electronic materials and mineral-derived quantum spin liquids. Despite disparate synthetic approaches, these subjects are unified by having progress made through an enhanced understanding of reaction pathways, and demonstrate systematic approaches to solid state materials synthesis. The importance of tightly coupling experimental characterization with theoretical modeling will be highlighted.

1:30 PM CM01.02.01
Synthesis and Thermoelectric and Magnetic Properties of Novel Borides Takao Mori1, 2; 1WPI-MANA, National Institute for Materials Science (NIMS), Tsukuba, Japan; 2Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

Boron atoms in boron-rich materials have the tendency to form clusters or 2D sheets. As a synthesis method we have discovered that small amounts of third elements like C, N, and Si in borides can function as bridging sites, and result in the formation of novel and varied boron cluster structures. In addition to thermal stability and high hardness derived from the strong covalent bonding of boron, these structured borides possess strong structure-property relationships, leading to interesting properties in thermoelectrics (TE) and magnetism. Borides are promising for high temperature TE applications in thermal power plants, steelworks, incinerators, focused solar power, etc. [3]. Recent topics will be presented. Discovery of TE enhancement in Sm [4] and Yb phases in RB66 is indicated to be due to mixed valency, while carrier delocalization is indicated as the enhancer for metal-rich YB48. Conventionally difficult p, n control has been achieved for elemental boron [5], and also AIB-type analogous 2D layered borides. Borides have exhibited several novel structure-based mechanisms for intrinsic low thermal conductivity, and I will also present very strong phonon blocking behavior discovered in a 2D layered boride [6]. In regard to magnetism, unexpectedly strong magnetic coupling was previously discovered in dilute f-electron insulating borides, leading to interesting 1D dimer-like, 2D spin glass, 3D behavior [7]. The boron icosaahedron cluster has been indicated to function to dramatically strengthen the magnetic interaction, and will be presented, in addition to recent developments in 2D layered borides.


2:00 PM CM01.02.02
Disorder in Semiconducting Ternary Nitrides Stephanie Lany1, Jie Pan1, Jacob Cordell2, Wenhao Sun3, Aaron Holder1, Sage Bauers1, Angela N. Fioretti1, Elissabeta Arca1, Gerbrand Ceder1, Adele Tamboli1 and Andriy Zakutayev1; 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Oxides comprise a large number of insulators or semiconductors, often with rather poor electronic properties. In contrast, nitrides have often better electronic properties, but have much smaller number of known phases, in particular regarding ternary or multinary compounds. Due to the inherent relative instability of nitrides relative to N2, such ternary nitrides are often grown as thin films at relatively low temperatures, leading to crystal structures with atomic disorder. Using first principles and Monte-Carlo calculations, we investigate the effects of disorder on the electronic structure. Case studies include ZnSnN2, which has attracted interest as photovoltaic material, and which tolerates large off-stoichiometry without adverse effects on the electronic properties. We discuss the possibility to remove undesirable electronic localization effects by controlling short range order, even when the material remains long-range disordered. A second example are the Mg-TM-N (TM = Ti, Zr, Hf, Nb) nitrides, which have recently been identified as a particularly stable region in the map of ternary nitrides. First principles structure search and electronic structure calculations predict rocksalt structure semiconductors with low effective masses and large dielectric constants. Disorder not only affects the electronic properties directly, but it also can tip the balance between competing structure types, thereby playing a crucial role in the phase formation and the ensuing materials properties.

2:15 PM CM01.02.03
Lithium Alkaline-Earth Metalide-Nitrides—From Simple to Complex Peter Hoehn, Matej Bobnar, Manisha Pathak, Yuri Prots and Yuri Grin; MPI-CFPS, Dresden, Germany.

Depending on preparation conditions and composition, phases obtained in the quaternary systems Li–AE–M–N (AE = Ca, Sr, Ba; M = Ga, In, TI, Ge, Sn, Pb) range from nitridometalates (e.g. (Ca,N3)[GaN4] 24, Ca[Ge,N2] 23) via nitride-metalides (e.g. (Ca,N4)[M2] 13, to intermetallic species without nitrogen (e.g. LiBa[Sn] 4). They may contain nitrogen as isolated N3– anions or complex anions [M,N3–] of different dimensionality with coordination numbers M by N typically between two and four, respectively. Whereas the bonding within these complex anions and frameworks is essentially covalent, nitridometalates are stabilized by predominantly ionic bonding through counterions like alkali (A) or alkaline-earth (AE) cations. In contrast, bonding in metalide-nitrides is dominated by metallic and ionic interactions. Structural data for the majority of phases reported up to now had been derived from X-ray single crystal data, whereas single-phase powder samples had to be employed for investigation of physical properties, since no sufficiently large single crystals were available.

Here we report on crystal growth experiments in lithium melts by modified high-temperature centrifugation aided filtration (HTCAF) 3, which resulted in specimens of up to 5 mm in length and 50 mm2 in volume. Generally, due to the mode of preparation the thermodynamically most stable phases are precipitated from the reaction mixtures of Li, Li3N, AE, N2 or AE3N, and M, which leads to significantly different results concerning composition of products with respect to reaction temperatures and the alloying ratio, which is illustrated by the following set of examples: (Sr,N0.5)[Pb] 6 crystallizes in the perovskite type with a 2×2×2 superstructure, Li4(Li3Sr)[NiPb] 7 features an ordered variant of the ScAl12 type structure, whereas Li4+(Sr,N)[Ga4]+[Ga] crystallizes in a new structure type. Li2[Sn,N]{Ga2} (8) is isotypic to the σ-carbide Fe3W3C. Most phases show diamagnetic behaviour and electrical resistivities of about 1×103 Ωm.
mechanism that is not present in a typical hard material. The understanding gained by studying the electronic structure as a function of strain explains the unique coexistence of high hardness and ductility in Mo$_2$BC. These results provide a new perspective on the design of future mechanical materials by crystal structure reveals an unusual strain-stiffening due to the formation of pseudo-gaps with a remarkable bond-breaking and concurrent bond-formation.

### 3:00 PM *CM01.02.04*

**Boron—Enabling Metal-Rich Structures and Magnetic Materials**  
Boniface Fokwa; University of California, Riverside, Riverside, California, United States.

Boron tends, like carbon and silicon, to form covalent molecular as well as extended compounds, but boron’s ‘electron deficiency’ enables the formation of multicenter B-B bonds, and therefore unexpected compounds. Boron reacts with most metals to form the large class of metal borides, ranging from the boron-richest YB$_6$ monochromator up to the metal-richest Nd$_8$Fe$_2$B permanent magnet. This huge composition range, coupled with the unusual chemical bonding, makes this class of materials an ideal playground for unexpected discoveries. In this seminar, I will present our recent works on “designing” new materials, all of which contain boron. I will show that boron does not help build new crystal structures but it also plays a prominent role on the studied properties. Furthermore, I will present a new reaction developed recently that enables the synthesis of these materials at the nanoscale, a major step toward fulfilling their huge potential.

### 3:30 PM *CM01.02.05*

**Stoichiometric B$_{13}$C$_2$—Structural Stability and Mechanism of Compression up to 68 GPa**  
Irina Chuvashova$^{1,2}$, Elena Bykova$^3$, Maxim Bykov$^2$, Volodymyr Svitlyk$^4$, Leonid Dubrovinsky$^5$ and Natalia Dubrovinskaiia$^1$; 1Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany; 2BGI, University of Bayreuth, Bayreuth, Germany; 3Photon Science, Deutsches Elektronen-Synchrotron, Hamburg, Germany; 4European Synchrotron Radiation Facility, Grenoble, France.

Boron carbide is a ceramic material with unique properties widely used in numerous, including armor, applications. Its mechanical properties, mechanism of compression, and limits of stability are of both scientific and practical value. The structure of boron carbide consists of icosahedra (B$_2$: or B$_3$:C), located in the corners of the rhombohedral unit cell, and linear chains (C-B-B or C-C-B or C-C-C) oriented along its body diagonal. According to numerous early studies, boron carbide exists as a single-phase material within a wide homogeneity range, from ~7 at. % (B$_3$:C) to ~20 at. % (B$_3$:C) of carbon. Synthesis and investigations of single crystals of boron carbide have been reported for “nearly stoichiometric B$_3$:C”, B$_2$:C, B$_3$:C, and B$_3$:C$_2$. On the basis of studies of single crystals, there is a dispute in the literature data whether there is or is not a phase transition in this material. Bulk compressibility of boron carbide compared to compressibility of icosahedra has been a matter of debate. Nelmes et al. reported the crystal structure to be more rigid than the icosahedron cluster, whereas Dera et al. observed an opposite relation. In the present work we have studied the compressional behavior of the stoichiometric boron carbide B$_3$:C$_2$ in the pressure interval up to 68 GPa. Unlike the previous experimental observations, our single-crystal synchrotron X-ray diffraction investigations revealed structural stability of the boron carbide in the studied pressure range. A comparison of the compressional behavior of B$_3$:C$_2$ with that of α-B, γ-B, and B$_3$:C showed that it is determined by the types of bonding involved in the course of compression. Neither ‘molecular-like’ nor ‘inverted molecular-like’ solid behavior upon compression was detected that closes a long-standing scientific dispute.

### 3:45 PM *CM01.02.06*

**Unexpected Origin of Strength in Mo$_2$BC**  
Aria Mansouri Tehrani, Amber Lim and Jakob Brsgoch; University of Houston, Houston, Texas, United States.

In the search for new superhard materials using machine learning, we recently prepared the high hardness, ultraincompressible compound, Mo$_2$BC. This compound is not only extremely hard but according to the calculated bulk and shear moduli ratio (G/B) it is also ductile, which is contrary to most superhard materials like diamond or ReB$_6$. Mo$_2$BC crystallizes in a highly anisotropic, pseudo-layered orthorhombic crystal structure containing alternating layers of boron and carbon rich planes. The complexity of this compound and its exceptional mechanical properties motivated an in-depth examination of the structure-property relationship using density functional theory. Calculating the tensile and shear stress-strain behavior to probe the ideal strength of the crystal structure reveals an unusual strain-stiffening due to the formation of pseudo-gaps with a remarkable bond-breaking and concurrent bond-formation mechanism that is not present in a typical hard material. The understanding gained by studying the electronic structure as a function of strain explains the unique coexistence of high hardness and ductility in Mo$_2$BC. These results provide a new perspective on the design of future mechanical materials by contrasting the notion of avoiding materials with pseudo-layered structures.

### 4:00 PM *CM01.02.07*

**Understanding the Crystal Structures of In$_2$Se$_3$**  
Philipp M. Konze$^1$, Michael Küppers$^1$ and Richard Dronskowski$^{1,2}$; 1Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany; 2Juelich-Aachen Research Alliance (JARA-HPC), RWTH Aachen University, Aachen, Germany.

Phase-change memories (PCMs) are promising candidates for storage class memories, bridging the gap between traditional DRAM and Flash storage. Their targeted synthesis and characterization therefore become an interesting field for chemists, physicists, and material scientists alike. Traditional PCMs, such as GeSbTe, use the differences in reflectivity or resistivity between an amorphous and a crystalline phase, where switching is performed using heat, either through radiation or Joule heating. This local melting and quenching has become a limiting factor for the energy efficiency of these materials. Switching, instead, between two closely related crystalline structures, as proposed for chalcogenide superlattices (CSLs), promises to increase their energy efficiency and reduce mechanical stress within a device. One possible candidate as a CSL is In$_2$Se$_3$. In$_2$Se$_3$ was first characterized over 100 years ago, but only recently attracted interest as a promising candidate for applications such as solar cells, photodiodes, and phase-change memories. Despite the growing interest for possible uses, its polymorphism and structures remain poorly understood. Combining X-ray diffraction and transmission electron microscopy, we will present the crystal structures of In$_2$Se$_3$ and rationalize their local environments using chemical bonding analysis. We aim to understand different coordination environments through covalent, as well as ionic contributions, comparing them to prototypical structure types such as B$_2$:Se$_2$. In doing so, we will highlight some new features of our chemical bonding analysis tool LOBSTER.

### 4:15 PM *CM01.02.08*

---

Cation-Ordering in Tri-Rutile Ternary Antimony Oxide Systems

Winnie Leung1, Elizabeth Martin1, Robert Palgrave1 and David O. Scanlon1, 2, * 1Department of Chemistry, University College London, London, United Kingdom; 2Harwell Science and Innovation Campus, Diamond Light Source Ltd., Didcot, United Kingdom; 3University College London, Thomas Young Centre, London, United Kingdom.

The search for novel, earth abundant materials to be used as transparent conductors and/or in thermoelectric devices has resulted in recent interest in the ternary Sb(V)-oxides. A key example is ZnSb2O6, known to have an ordered tri-rutile structure which consists of Mo6 octahedra (where M is Zn or Sb) and edge-sharing atoms in the order of Zn-Sb-Sb-Zn. Early reports demonstrated the potential of ZnSb2O6 as a new transparent-conducting oxide (TCO) due to its high carrier concentration in the near-IR region and wide band gap of 3.5 eV. While recent calculations by our group indicate a large thermopower and low thermal conductivity at elevated temperatures, once sufficient carrier concentrations are present, making the system of interest for thermoelectricity (TE). Pure ZnSb2O6, however, is non-conductive; hence to enhance the electrical conductivity one needs to dope it with metal ions such as Co, Ni, Cu, Al and In. Indeed, these doped systems have been shown to possess higher electrical conductivity than the nominally pure material. Nevertheless, the mechanism of doping and associated cation ordering in ZnSb2O6, upon which the structural and chemical properties are strongly dependent, remain unknown.

In this study, we have successfully doped ZnSb2O6 with various metal ions such as Ni(II), Ga(III), Cr(III), Al(III), In(III) and Nb(V), and have investigated the structural properties of these doped samples via powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), ultraviolet and visible spectroscopy (UV-vis) and energy-dispersive x-ray spectroscopy (EDXS). Where applicable, we make comparisons with computational work done within our group. Our results help elucidate the cation ordering and doping mechanisms in each case, allowing us to determine the optimum doping strategies to facilitate TCO and TE applications.

References

4:30 PM *CM01.02.09
Borates as Cathodes for Li- and Mg-Ion Batteries

Sian E. Dutton; University of Cambridge, Cambridge, United Kingdom.

Polyanion materials are attractive for use as electrodes in Li-ion batteries due to their chemical stability and high operating voltages. Studies of polyanion compounds doped with Mg, typically assume that there is no Mg-ion transport and that the dopant Mg-ions are electrochemically inactive. In this talk I will present our results on the structure and electrochemical properties of magnesium, transition-metal borates. Despite their being cation disorder between the magnesium and transition-metal sites I will show that it is possible to remove electrochemically remove Mg and subsequently intercalate Li ions. The role of the crystal structure on the ion transport will be discussed and the results of testing MgMnB2O6 vs. a Mg metal anode will be presented.

SESSION CM01.03: Poster Session I: Solid-State Chemistry of Inorganic Materials

Session Chairs: Ashfia Huq and Antoine Maingnan

Monday Afternoon, November 26, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

CM01.03.01
Solvothermal Intercalation of Iron-Amine Complexes into Iron Sulfide Layered Materials

Colin Harmer and Kirill Kovnir; Iowa State University, Ames, Iowa, United States.

Recent interest in the intercalation chemistry of layered iron chalcogenides has led to the discovery of many new compounds with magnetic properties ranging from simple paramagnetism to antiferromagnetism and superconductivity. The parent superconducting compounds, mackinawite-FeS and β-FeSe, are composed of iron-chalcogen layers stacked via van der Waals forces. These relatively weak interlayer forces make iron chalcogenides suitable candidates for intercalation studies. Numerous reports have shown that drastic changes to magnetic behavior can arise from intercalation by a variety of species, such as, simple cations, metal hydroxides, metal-amine complexes, and neutral organic molecules. Although a wide variety of intercalates are possible, their diversity can pose a challenge when trying to assess direct relationships between the intercalated species and bulk properties. One approach towards a more systematic study is to intercalate iron-chalcogenides with a coordination complex and subsequently tune the complex while assessing structural and property variations. Our study focuses systematically modifying the ligand of the previously reported [FeS3]2–[Fe(en)]●en compound, while observing changes to the structure, stability and bulk thermodynamic properties. [FeS3]2–[Fe(en)]●en consists of [FeS3]2– layers intercalated by tris(ethylenediamine)iron(II) and a free ethylenediamine. Through solvothermal synthesis, we have made two new compounds intercalated with bidentate amines, 1,2-diaminopropane and 2,2’-bipyridine. We show that the interlayer spacing increases with the size of the coordination Fe-amine complex. This work will focus on the solvothermal synthesis, structure, and properties of the ethylenediamine, 1,2-diaminopropane and 2,2’-bipyridine-containing compounds.

CM01.03.02
Need for a SCAN+U Framework to Describe the Oxidation Energetics of Transition Metal Oxides

Sai Gautam Gopalakrishnan and Emily A. Carter; Princeton University, Princeton, New Jersey, United States.

Transition metal oxides that can tolerate a large number of oxygen vacancies, specifically systems containing the redox-active Ce, Mn, and Fe atoms, are crucial ingredients for generating renewable fuels via two-step, oxide-based solar thermochemical reactors. However, any predictive modeling such as using density functional theory (DFT) calculations, needs to accurately describe the energetics of redox reactions (and, subsequently, defect formation) involving transition metals, if new candidate materials are to be found. Recently, the strongly constrained and appropriately normed (SCAN) exchange-correlation (XC) functional was developed, which impressively satisfies all the 17 known constraints for the behavior of any XC functional. However, the ability of SCAN to describe redox energies involving transition metal atoms thus far has remained unexplored. Based on calculated enthalpies for oxidation reactions involving binary Co-, Mn-, and Fe-oxides, we find that SCAN systematically overestimates measured oxidation enthalpies, due to remaining self-interaction errors in the description of their ground-state electronic structure. Adding a Hubbard U term to the transition metal centers, where the U is...
derived from oxidation enthalpies, significantly improves the qualitative agreement of the calculated electronic structure with experiments. Also, the SCAN+U-calculated lattice parameters exhibit marginally better quantitative agreement with experimental values. Importantly, SCAN+U predicts the right ground state polymorph for all transition metal oxides considered in this work, unlike SCAN, which yields erroneous predictions for CeO₂, MnO₂ and Fe₂O₃. Hence, we conclude that the DFT-SCAN+U framework with an appropriately determined U, is required to describe accurate ground-state energies and qualitatively consistent electronic structures for most transition metal oxides and sulfides.

CM01.03.03 Magnetic and Dielectric Properties of Single Crystal GaFeO₃ Mitsuhiro Itoh¹, Shintaro Yasui¹, Tsukasa Katayama², Hiroki Moriwake³, Ayako Konishi³, Jianding Yu¹ and Yosuke Hamasaki⁴; ¹Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama, Japan; ²Department of Chemistry, The University of Tokyo, Bunkyo-ku, Japan; ³Nanomaterials Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan; ⁴Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan; ⁵Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; ⁶Department of Applied Physics, National Defence Academy, Yokosuka, Japan.

κ-Al₂O₃-type GaFeO₃ is a promising multiferroic material due to the coexistence of a large spontaneous magnetization and polarization near room temperature. Currently, the physical properties of GaFeO₃ are not clearly verified, making it an interesting study. Quite recently, a study on ε-Fe₂O₃ which is isostructural to GaFeO₃, Garcia-Munoz et al. (Chem. Mater. 2017, 29, 9705) unveiled a new magnetic ordering at 850 K, higher than the conventional T_N at 480 K. In order to design κ-Al₂O₃-type GaFeO₃ multiferroics, it is essential to know the similarities in the properties between κ-Al₂O₃-type ε-Fe₂O₃ and ε-Fe₂O₃. In the current study, we present the magnetic, electric, and thermal properties of single crystalline GaFeO₃ (space group Pnã2₁) and compare it with that of ε-Fe₂O₃. The as-grown GaFeO₃ crystal was found to have modest, anisotropic electrical resistivities of 5.7×10³, 3.6×10³, and 5.7×10³ Ω m at room temperature along the crystallographic axes of a, b, and c, respectively. Dielectric measurements revealed that the dielectric constant is largest for the a-axis, around 31 when below 50 K, and the dielectric loss abruptly increases above 50 K. Polarization switching could not be observed even at extremely large electric field of 350 kV/cm at 77 K, due to the high coercivity, although the value of polarization by ab initio calculation is ~21 μC/cm² and polarization switching energy is ~100 meV/f.u.. Magnetic measurements revealed that spontaneous magnetization appears below 540 K in two steps, similar to that reported for ε-Fe₂O₃. Partial magnetic ordering takes place at 540 K (T_N1), with Fe³⁺ ions in regular distorted octahedral Fe₁d and Fe₂d positions ordering antiparallel to one another. Upon further cooling at 200 K (T_N2), the remaining Fe³⁺ ions in regular octahedral Fe₁d and tetrahedral Fe₄d order antiparallel to one another. Heat capacity measurement by the relaxation method and differential scanning calorimetry revealed that there are faint heat anomalies around T_N1 and T_N2, corroborating that spin alignment at these temperatures is fairly diffuse. These results are consistent with the data of XMC. Substitution of Ga for Fe in ε-Fe₂O₃ leads to a decrease in T_N1 and T_N2 from 850 to 540 K and from 480 to 200 K, respectively, caused by a dilution of magnetic Fe by nonmagnetic Ga and preferential site occupation of Ga in Fe₁d and Fe₄d sites. All the data will be compared with those for κ-Al₂O₃-type ε-Fe₂O₃ (A=Al, Cr, Ga, Fe, Rh, Sc, and In) thin films.

CM01.04 Hydrothermal Synthesis of New Pentavalent Bismuthates Md Saiduzzaman, Nobuhiko Kumada, Takahiro Takei and Sayaka Yanagida; Centre for Crystal Science and Technology, University of Yamanashi, Kofu, Japan.

The hydrothermal method is a useful synthetic route for the preparation of new bismuthates with a variety of crystal structures like ilmenite, perovskite and pyrochlore-type structures. Some of these exhibit unique properties such as photocatalysis and superconductivity. In our research, we synthesis highly crystalline BaBi₂O₆ and two new pyrochlore-type metallic bismuthates (Ca₂Bi₂O₇ and Sr₂Bi₂O₇) by hydrothermal reaction using Na₂BiO₃·nH₂O. The crystal structure of these compounds were refined by using synchrotron X-ray powder diffraction (SXRPD) data. We investigated their photocatalytic property.

All hydrothermal reactions were performed in Teflon-lined autoclaves. Na₂BiO₃·nH₂O with Ba(OH)₂·8H₂O, Ca(OH)₂, Sr(OH)₂·8H₂O with 1:1, 1:1, 1:1.8 molar ratios were placed in Teflon-lined autoclaves and heated at 80 °C, 90 °C and 120 °C respectively for 2 days. Samples were filtered, washed and dried. Crystal structure was determined by XRD using monochromated CuKα radiation (RINT-2000, Rigaku). SXRPD measurements were performed using beam line BL02B2 at the SPring-8 facility. RIETAN-FP and VESTA were used for crystal structure refinement and drawing respectively. The thermal stability was investigated by TG-DTA (RIGAKU Thermo Plus). Band gap were measured by diffuse reflectance spectroscopy (JASCO V-550 spectrometer). DFT were performed using Vienna ab initio Simulation Package (VASP). The temperature dependent electrical resistivity was measured between 300.0 K and 1.8 K using a standard four-probe method (PPMS, Quantum Design). The photocatalytic activities were examined for the decomposition of phenol (20 ppm) under visible light from a 300 W Xe lamp (UXR-300DU, Ushio Inc.).

The XRD patterns of Ca and Sr bismuthates could be indexed with the cubic system (pyrochlore-type, Pd-3m) and that of Ba bismuthate with the trigonal system (P3bSbO₃-type, P-31m). From the chemical analysis (ICP) Ca:Bi, Sr:Bi and Ba:Bi molar ratios were 1:1, 1:1 and 1:2 respectively. The Rietveld refinements of BaBi₂O₆, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ from SXRPD data led to the final reliability (R) factors were (R_p=5.53%, R_w=4.28%) and (R_p=6.40%, R_w=4.83%) respectively. The lattice parameters of BaBi₂O₆, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ were a=5.57534(6) Å, c=5.7381(1) Å, a₀=10.7642(6) and a₀=10.9413(6) respectively. Above 200 °C all the bismuthates decomposed consequently mass loss being due to the reduction of Bi³⁺ to Bi²⁺. BaBi₂O₆ exhibited photocatalytic activity for phenol degradation under visible light. However, Ca₂Bi₂O₇ and Sr₂Bi₂O₇ showed strong oxidation property for the degradation of phenol under dark condition. This is due to the metallic behavior evidence by DOS calculation and supported by temperature dependent resistivity data indicated that these compounds possessed very low resistivity at room temperature. While BaBi₂O₆ is a semiconductor exhibited by band gap energy estimation and supported by DOS calculation.

CM01.03.05 Cluster Analysis of a Cast Aluminum Alloy Utilizing an Atom- Probe Tomography Won Sang Shin, Kyo Jin Hwang, Dong Hyuck Jung and Yoon Jun Kim; Material Science Engineering, Inha University, Nam-gu, Korea (the Republic of).

Cast Aluminum alloys are widely used in the automotive and aerospace industries, due to their high strength to weight ratio, good corrosion resistance and recyclability. An A356 cast aluminum alloy (Al – 7 wt.%Si – 0.3 wt.%Mg), contains approximately 50% eutectic microstructure. Such a high content of Si with various casting conditions plays a significant role in strengthening of A356 alloy by controlling eutectic morphology and precipitate other intermetallic compounds. Understanding the way to form Si nanoclusters soluble in the α-matrix is necessary in order to provide high strength and fatigue properties to the A356 alloys. Quantification of nanoclusters' size, distribution, and composition gives insight into how type of atoms in the aluminum matrix migrate and attract or repel other types of alloying elements. The morphology of Si nanoclusters in A356 alloy is analyzed using an Atom Probe Tomography (APT). Samples were differently aged at the temperatures of 110°C, 130°C, and 150°C for 2 hours. Although typical size of nanoclusters is a few nanometers or even less than nanometers which makes characterization difficult, APT can provide not only a nano- or sub-nano scale clusters’ information such as size, distribution, and composition but also three-dimensional (3-D) chemical and spatial information.

APT raw data can be further analyzed using the well-known maximum separation algorithm in order to define and characterize the nanoclusters. The input
parameters required for this algorithm, for example dmax and Nmin, were carefully selected for agglomerated Mg and Si ions in an α-aluminum matrix. Applying those cluster parameters along with additional correction variables, such as envelopment and erosion distances for Al, Si, and Mg ions, Mg-Si nanoclusters in an α-aluminum matrix were quantitatively analyzed determining their size distributions and average sizes, etc. Obtained clusters’ information can be correlated the age-hardening process of the A356 alloy comprising types of solid solution aluminum prior to decomposition sequence commenced.

CM01.03.06 Atomic Diffusion in the Low Temperature Synthesis of Perovskite-Type (A$^+$B$^-$)O3 (A, B = Sr, Ba; B$^+$ = Ti, Zr) Using Hydroxides and Hydroxal Gels at 50 °C

Y. Yamaguchi

Synthesis of perovskite-type oxides in a solid state reaction requires high-temperature heat-treatment at around 1000 °C to cause sufficient diffusion of metal ions. Therefore, various synthesis methods such as sol-gel method have been studied to reduce a reaction temperature and obtain fine-particles. Until now, we have successfully synthesized perovskite-type ABO3 (A: alkaline earth; B = Ti, Zr) by only leaving the mixture of A(OH)x-nH2O and BO2 hydroxal gel at around 50 °C for several days. The SrTiO3 synthesized by this method at room temperature had a highly crystallized fine particles and exhibited higher photocatalytic activities than that synthesized by sintering at 1000 °C[1]. The reaction mechanism was considered that BO2 hydroxal gel worked as an acid to react with A(OH)x which worked as a base. In addition, SrTiO3 synthesized at room temperature by this method in this study, (A$^+$B$^-$)BO3 (A, B = Sr, Ba; B$^+$ = Ti, Zr) were synthesized to investigate further detailed reaction mechanism, especially cation diffusion in A- and B-sites.

Starting materials for (A$^+$B$^-$)BO3, A(OH)x-8H2O and BO2 hydroxal gel prepared by precipitation method. The water content of hydroxal gel was determined by TG-DTA. Mixed A(OH)x-4H2O and BO2 hydroxal gels were sealed in a vial bottle. The vial was kept at 50 °C for several days. In order to investigate the diffusion of A-site cations, we attempted to synthesize (Ba,Sn)3 TiO5 using Sr(OH)2, Ba(OH)2, and TiO2 hydroxal gel. A-site substituted perovskite phase was obtained, this is the first time to synthesize perovskite solid solution by this low temperature synthesis method. Though Sr and Ba were present in separate particles as starting materials, both the elements were mixed at the atomic level in reacted compound to form A-site disordered perovskite phase. This result indicated that alkaline earth cations diffused long range even at low temperature of 50 °C. We also attempted to synthesize Ba(Zr0.5Ti0.5)O3. When Ba(OH)2, ZrO2 hydroxal gel, and TiO2 hydroxal gel were used as starting materials, mixture of perovskite-type BaZrO3 and BaTiO3 were obtained. On the other hand, when Ba(OH)2 and (Zr0.5Ti0.5)O2 solid solution hydroxal gel were used as starting materials, perovskite solid solution Ba(Zr0.5Ti0.5)O3 were obtained. The obtained phases depended on the starting materials. If all the ions diffuse long range, thermodynamically stable phase must be obtained. Therefore, B-site cations diffuse only short range in contrast to A-site cations. It is concluded that the A cations diffuse into the B cation network to form a perovskite phase at low temperature of 50 °C.


CM01.03.07 Investigating the Effects of Surface Ligand Concentration on the Magnetic Properties of Semiconductor Nanocrystals

Alex Khammang1, Robert W. Meulenberg2

Semiconducting nanocrystals (NCs) have been utilized in optoelectronic devices like solar cells and laser emitting diodes and semiconductor materials have biomedical applications such as biological markers. These types of materials typically consist of an inorganic core, which dictates most of the physical properties, and an organic layer on the surface, which helps dictate chemical stability. While much work has been performed towards understanding the fundamental physics of the core NC, the surface science of these materials remains relatively unexplored. Although we stated that the surface of NCs help drive chemical stability, recent reports have suggested that the surface layer does much more, including effecting photoluminescence (PL) quantum yields, PL lifetimes, and electrical properties. Quite remarkably, the surface layer even has shown to convert nominally non-magnetic materials, such as CdSe and ZnO, into “magnetic NCs”. This result is curious, as the bulk state of these materials exhibit diamagnetic properties. These exciting results suggest that it may be possible to pair these induced magnetic properties with the inherent PL properties of these materials. This multi-functionalization of CdSe and ZnO, into “magnetic NCs”. This result is curious, as the bulk state of these materials exhibit diamagnetic properties. These exciting results suggest that it is possible to pair these induced magnetic properties with the inherent PL properties of these materials. This multi-functionalization of CdSe and ZnO, into “magnetic NCs”.

To gain further insight on how the surface layer affects the magnetic properties, this work alters the surface chemistry by controllably varying the surface ligand concentrations and by systematically varying the types of ligands (i.e. headgroup) on the surface of spherical NCs. In addition, we will study how the NC shape and interface can affect the magnetic properties by examining materials like nanowires and core/shell materials. This study will provide detailed information on how the surface ligands and interfacial layers in a NC can lead to unique magnetic properties.

CM01.03.08 Citrate-Controlled Optical Properties of Solution Deposited PbSe Thin Films

Michael Shandalov1, Maayan Perez2, Eyal Yahel1 and Yuval Golan2

Chemical bath deposition is an efficient method to reproduce high quality thin films. Extensive work has been done on deposition of lead chalcogenides due to their technological importance as infrared detectors and emitters [1]. Our group has previously reported on the ability to obtain desirable optical and microstructure of lead selenide at high pH (>13) by optimizing reactants concentration, temperature and growth duration [2,3]. There is an important advantage in understanding the kinetics influencing the deposition of PbSe at relative low pH (<13) and gaining further control on film's morphology related to optical properties. Trisodium citrate (TSC) is a commonly used co-complexing agent during chemical deposition of the lead selenide, which allowed us to deposit films at lower pH, yet its exact role has not been systematically studied [3]. This work focuses on the effect of citrate and pH on the kinetics involved in the deposition of PbSe and on microstructure related optical properties of the films.


CM01.03.09 High Pressure H2 and D2 Annealing Effects on the Interface Characteristics Between H2O2 and SiGe:

Soongheum Choi1, Jinyong Kim1, Jinbum Kim1, and Hyungsup Kim1

As a next-generation channel material for high performance transistors, such as fin and gate-all-around field-effect transistors, Si1–xGe, has been considered
to be the most promising due to its high carrier mobility and excellent compatibility with the current Si-based integration processes [1]. However, for successful implementation of Si$_x$Ge$_{1-x}$, it is imperative to improve the interface properties with the adjacent high-k gate dielectrics. For the high-k dielectrics on both Si and III-V compounds, post-metalization annealing (PMA) in high pressure H$_2$ and D$_2$ ambient was demonstrated to be effective in lowering the interface state density [2, 3]. However, its application to the high-k/Si$_x$Ge$_{1-x}$ structure has been rarely studied.

In this presentation, we compared the electrical and interface characteristics of the HfO$_2$ films grown on Si$_{0.7}$Ge$_{0.3}$ after different PMA: conventional forming gas annealing (4% H$_2/96%$ N$_2$ at 1 atm), and high pressure H$_2$ and D$_2$ annealing (20 bar). Immediately after native oxide cleaning of epitaxially-grown of Si$_{0.7}$Ge$_{0.3}$, films on Si, the HfO$_2$ (nominally 5 nm) films were grown using atomic target deposition at 250 °C. Following the metal electrode formation, PMA was conducted at 300 °C for 30 min, and then various electrical measurements were conducted. The detailed electrical properties of the capacitors after different PMA, including the interface state density, will be discussed. In addition, the chemical analysis results of the high-k/Si$_x$Ge$_{1-x}$ interface will be presented.


CM01.03.10
Sterically Controlled Solid-State Mechanocatalysis Under Hydrostatic Pressure Hao Yan1, 2, Fan Yang1, 2, Jing Pan1, 2, Wendy L. Mao1, 2, Giulia Galli1, 2, Peter R. Schreiner1, Zhi-Xan Shen1, 2 and Nicholas A. Melosh1, 2, Materials Science and Engineering, Stanford University, Stanford, California, United States; 1SLAC National Accelerator Laboratory, Menlo Park, California, United States; 2Geophysical Sciences, Stanford University, Stanford, California, United States; Chemistry, Hong Kong University of Science and Technology, Hong Kong, Hong Kong; 1Institute of Molecular Engineering, The University of Chicago, Chicago, Illinois, United States; 4Physics, Stanford University, Stanford, California, United States; 1Institute of Organic Chemistry, Justus-Liebig University, Giessen, Germany.

Mechanical stimuli can modify the energy landscape of chemical reactions and enable new reaction pathways, offering a complementary synthetic strategy to conventional chemistry. Mechanocatalytic mechanisms under tensile stress have been extensively studied in one-dimensional polymers. In these systems, the pulling force stretches chemical bonds, initiating the reaction. Recently, it has also been shown that forces orthogonal to the chemical bonds can alter the rate of bond dissociation. However, these bond activation mechanisms have not been possible with isotropic, compressive stress (i.e., hydrostatic pressure) in three-dimensional solids. Here we show that mechanochemistry through isotropic compression is possible by molecularly engineering structures that can translate macroscopic isotropic stress into molecular-level anisotropic strain. We engineer molecules with mechanically heterogeneous components consisting of a compressible (‘soft’) mechanophore and an incompressible (‘hard’) ligands. In these ‘molecular anvils’, isotropic stress leads to relative motions of the rigid ligands, anisotropically deforming the compressible mechanophore and activating bonds. Conversely, rigid ligands in steric contact impede relative motion, blocking reactivity. We combine experiments and computations to demonstrate hydrostatic-pressure-driven redox reactions in metal-organic chalcogenides incorporating molecular elements with heterogeneous compressibility, where bending of bond angles or shearing of adjacent chains activates the metal-chalcogen bonds leading to formation of elemental metal. These results reveal an unexplored mechanism and enable new possibilities for high-specificity mechanosynthesis. Recent results applying the molecular anvil strategy to the activation/reduction of carbon dioxide will also be discussed.

CM01.03.11
High-Mobility N- and P-Type Cu$_3$N Thin Films Realized by Novel Direct Nitriding Synthesis and Computational Doping Design Kosuke Matsuoka1, Kou Harada1, Yu Kumagai1, Shogo Koshiya2, Koji Kimoto2, Shigenori Ueda2, Masato Sasa1, Akhiro Maeda1, Tomofumi Susaki1, Masaki Kitano1, Fumiyasu Oba1, 2 and Hideo Hosono1, 2, Tokyo Institute of Technology, Yokohama, Japan; 1National Institute for Materials Science, Tsukuba, Japan.

Copper nitride (Cu$_3$N) has an indirect bandgap of ~1.0 eV and a high absorption coefficient of ~10$^5$ cm$^{-1}$ above ~2.0 eV, and therefore is considered as an earth-abundant and environmentally-benign absorber candidate in thin-film photovoltaics. Its self-doping mechanism has been discussed theoretically, but a comprehensive understanding of the doping mechanism and intrinsic behavior of pure Cu$_3$N is still lacking owing to the low crystalline quality. We show that bipolar doping with high electron and hole mobilities in high-quality Cu$_3$N is realized by our novel gaseous direct nitriding reaction utilizing a catalytic ammonia oxidation to form Cu$_3$N from Cu metal. This reaction overcomes the thermodynamic constraint associated with its high positive formation enthalpy (~83.7 kJ mol$^{-1}$) and provides high-quality Cu$_3$N films showing resistive n-type behavior. P-type conduction is realized by flowing doping into the interstitial site as predicted by density functional theory calculations and directly proven by electron energy loss spectroscopy combined with scanning transmission electron microscopy. The electron and hole mobilities of undoped n-type and F-doped p-type films are as high as 200 and 80 cm$^2$(Vs)$^{-1}$, respectively. Our synthetic methodology for high-quality n- and p-type films applicable to uniform and large-area deposition would open up the possibility for Cu$_3$N as an alternative photosorbber in thin-film photovoltaic cells.


CM01.03.12
Defects Behavior in Disordered Iron Oxide Synthesized from Grain-Oriented Iron Foils Karen A. Neji1, José Alfredo Andrade Adame2, Ramón Pelá1, 2, Roberto Baca1, 2, Dr. of Nanoscience and Micro-Nanotechnology, ENCB, Instituto Politecnico Nacional, Mexico City, Mexico; 1IPHII, Instituto Politecnico Nacional, Mexico City, Mexico; 2Department of Electrical Engineering, Solid State Electronics Section, Centro de Investigacion y de Estudios Avanzados del Instituto Politecnico Nacional, Mexico City, Mexico; 3Department of Electronics, ESIME, Instituto Politecnico Nacional, Mexico City, Mexico.

Disordered iron oxide thin-films synthesized from grain-oriented iron foils were grown on both glass and Si (100) n-type substrates by vacuum evaporation followed by thermal oxidation at low temperatures. Defects such as vacancies formation has been studied using Atomic Force Microscopy (AFM) and Raman Spectroscopy. The kinetic of oxidation as a function of surface parameters was investigated by AFM studies. The vibrational modes (bands) connected with the vacancies formation and magnetic ordering into the iron oxide structure were validated by Raman spectroscopy. Space-charge effects can be influenced by discontinuous growth of iron oxide and correlated with their structure parameters. Finally, the disordered iron oxide will be useful for the next generation of adaptive oxide devices.

CM01.03.13
Chemical, Structural and Photovoltaic Properties of Graded CdS$_x$Se$_{1-x}$ Thin Films Grown by Chemical Bath Deposition on GaAs(100) Ofrs Friedman, Omri Moscovitch and Yuval Golan; Department of Materials Engineering and the Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel.
CdS$_x$Se$_{1-x}$ films are direct band gap ternary semiconductors that can harvest photon energy in an energy range from 2.42 eV (CdS) to 1.74 eV (CdSe) by compositional tuning or chemical gradation. Growth of such films using chemical bath deposition (CBD) is advantageous due to low production costs and the ability to easily control initial bath composition. We have recently demonstrated monocrystalline CdS and CdSe deposited on GaAs substrates by CBD. In this work we present the chemical, structural and photovoltaic properties of Cd(S,Se) solid solution thin films deposited on GaAs(100) substrates by CBD. The structural and chemical properties of the films were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), analytical transmission electron microscope (A-TEM) and energy dispersive spectroscopy (EDS) mapping. We present evidence of chemically graded films that were formed by controlling the initial anion concentrations in the bath, which affect nucleation and growth of the films. The films are polycrystalline in nature, with a thin zinc blende layer formed directly onto the GaAs substrate, on top of which a highly oriented nano-columnar layer of wurtzite Cd(S,Se) is obtained. Finally, current-voltage measurements of GaIn-eutectic/GaAs/Cd(S,Se)/In device were conducted at room temperature under 1 sun. We demonstrate the photo-response dependence on the S/Se ratio in CdS$_x$Se$_{1-x}$ based photovoltaic cells.


CM01.03.14

Revealing the Atomic Arrangement of Dopants in the Layered Oxide Cathode Structure

Soroosh Sharifi-Asl,1 Jason Croy,2 Mahalingam Balasubramanian3 and Reza Shabbazian-Yassar1; 1Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Chemical Science and Engineering, Argonne National Laboratory, Argonne, Illinois, United States; 3Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States.

The positive electrode of rechargeable-ion battery, which is normally a layered oxide ceramic material, is known as the bottleneck of this technology. Based on the numerous studies focused on the degradation mechanisms of cathode materials, it has been proposed that cationic doping with electrochemically-inactive metals such as Al, Ti and Mo improves the cycling stability and electrochemical performance of cathode materials. LiCoO$_2$ is one of the most widely used cathode materials in Li-ion batteries. It has a layered hexagonal (R3m) structure, which allows for free Li-ion mobility during the electrochemical cycling. LiCoO$_2$ has a very high theoretical capacity of 270 mAhg$^{-1}$, only half of which can be reversibly utilized to maintain a stable cycling condition. The reason is, Li deintercalation higher than a certain extent results in migration of Co ions into the Li sites that leads to the layered to spinel/rock-salt phase transition, an irreversible reaction that results in rapid capacity fading. To combat this issue metal doping has been pursued as a promising direction in the literature. The electrochemically inactive cations act as stabilizing skeleton in the cathode structure and resist against the structural collapse upon high extent of Li-deintercalation. However, the dispersion of such dopant cations in the cathode structure is not truly investigated and it is normally assumed that dopants will disperse uniformly into the cathode structure.

In this study, we utilized aberration-corrected scanning transmission electron microscopy (AC-STEM) together with analytical electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) to study the atomic structural arrangement of W-doped LiCoO$_2$. High angle annular dark field imaging (z-contrast imaging technique) that can distinguish between Co and W atoms is utilized in our investigation. Interestingly, our results indicate that in the W-doped LiCoO$_2$ sample, W atoms prefer to occupy a distinct Co layer and form separate LiWO$_2$ layers inside the LiCoO$_2$ matrix. The mechanism of such abnormal atomic arrangement is being investigated by computational calculations. Furthermore, structural analysis at various state of charge and cycling conditions is studied to reveal the role of W layers on the structural stability of W-doped LiCoO$_2$. In addition, to test the structural stability of such local W rich layers, controlled beam damage experiments have been carried out that demonstrate higher stability of W layers against beam knock-on damage. Overall, presenting the first atomic demonstration of dopant arrangement inside the layered-oxide cathode structures can explain many questions regarding the role of dopant on the electrochemical performance of the cathodes and can have a great contribution in designing superior cathode materials for next generation of Li-ion batteries.

CM01.03.15

Towards the Application of Large Zeolite Particles as PEPT Tracers

Dan Parsons2, Joe Hriljac3 and Andy Ingram1; 1School of Chemical Engineering, University of Birmingham, Birmingham, United Kingdom; 2School of Chemistry, University of Birmingham, Birmingham, United Kingdom.

PEPT (Positron Emission Particle Tracking) is a powerful technique used to elucidate dynamics in chemical engineering processes[1]. Visualizing dynamics with PEPT relies on incorporating tracer particles, radioactively labelled with a $\beta^+$-emitting isotope, into the system under study. The most commonly applied tracer particles are resin or glass beads with diameters in the range 0.1 – 4 mm. Large glass beads (> 1 mm) may be activated directly in a cyclotron, converting some oxygen in the glass to F$^{-}$; however, this is not possible for smaller glass beads and resin particles (< 1 mm), instead these are labelled by surface adsorption or ion-exchange, respectively, from aqueous solutions containing F$^{-}$[2]. Low affinities for F$^{-}$ in existing tracers limits the ability to label particles smaller than 100 μm, hence tracer particles are often much larger than the granular material they represent, and the properties of the tracer material are also often atypical of the granular material in true systems, ultimately limiting the applications of PEPT studies and potentially the accuracy of results obtained[3]. The aim of the current work is to develop syntheses that provide control of particle size and morphology for materials with high affinities for the $\beta^+$-emitting isotopes of interest.

Our work has applied established methods to successfully synthesize large crystals, or particles, of zeolites with the faujasite, LTA and mordenite structures in the size range of interest, 10 - 100 μm. Methods employed have included the addition of tetraethanolamine to gels, retarding the crystal growth thus producing larger crystals over extended periods of time, synthesizing large zeolite crystals with faujasite and LTA topologies. Moreover, the use of tetraethylammonium ions as structure directing agents in siliceous gels has produced large particles of zeolites including mordenite. The most commonly used $\beta^+$-emitting isotopes for labelling tracers in PEPT are F$^{-}$ and Ga-68, owing to ease of production and suitable half-lives. We have demonstrated the affinity of large zeolite particles for uptake of both cationic and anionic species, viz. Ga$^{3+}$ and F$^{-}$, from aqueous solution by ion-exchange and adsorption, respectively.

Ultimately, we have produced crystalline tracers in the size range of interest which may be labelled by exploiting the innate affinity of the material for the species of interest. The application of crystalline tracers that are smaller than any previously used in PEPT studies have the potential to provide more accurate information on dynamics in many industrially important processes including mixing and fluidization phenomena.


CM01.03.16
Solid Electrolytes Particle Size Effect in All-Solid-State Batteries

Qingsong Tu, Gerbrand Ceder and Tan Shi; University of California, Berkeley, California, United States.

All-solid-state battery (SSB) is a promising candidate to replace the conventional lithium ion batteries. It not only has improved safety, but also could have larger energy density by utilizing Li metal anode. However, two factors limit the cathode loading in current SSBs and lead to low energy density. 1) Large amount (30 wt% - 50 wt%) of solid electrolyte (SE) in the cathode composite is required to provide sufficient ionic diffusion pathways. 2) Cathode composite thickness is limited by the poor ionic diffusion in the cathode composite.

We address these two issues by improving the Li ion conduction network through cathode morphology optimization. Our theoretical calculation and experimental data both show the relative particle size of cathode and SE greatly modifies the ionic percolation in the cold pressed cathode composite. Through simple SE particle size optimization, we were able to reduce the SE needed in the cathode composite and increase the cathode composite thickness without sacrificing specific capacity, resulting in an increased full cell energy density.

CM01.03.17

Field-Induced Magnetic Order Switching of A'-site Iron Spins in CaFeTiO₄

Midori Amano Patino¹, Fabio Denis Romero², Masato Goto¹, Takashi Saito³ and Yuichi Shimakawa⁴; ¹Institute for Chemical Research, Kyoto University, Kyoto City, Japan; ²Hakubi Center for Advanced Research, Kyoto University, Kyoto City, Japan.

Materials which adopt the ABO₃ perovskite lead to a significant tilting of the corner sharing BO₆ octahedra and give way to square-coordinated units or “A” sites. In this work we got particularly interested in the quadruple perovskite phase CaFe₂TiO₄ in which the B-site Ti³⁺ ions are nonmagnetic therefore allowing the investigation of the unusual magnetic behaviour of the Fe²⁺ spins forming the A’-site sublattice. We synthesized this compound using high-temperature high-pressure techniques, and characterized its magnetic properties for the first time. This phase had been previously observed, but not fully characterized. [3] Here we confirm the presence of Fe²⁺ S = 2 centers at the square planar A’ sites in CaFe₂TiO₄ from Curie-Weiss magnetic susceptibility and Mössbauer data. Magnetic susceptibility data show a maximum at 2.8 K suggesting AFM (antiferromagnetic)-like behaviour of the Fe²⁺ spins. Interestingly, such state switches to a ferromagnetic-like behaviour under the application of magnetic fields H ≥ 1 T. Therefore, the applied magnetic field is capable of inducing a FM-like structure on the A’-site Fe²⁺ S = 2 spin sublattice. DFT calculations for the AFM and FM spin arrangements for the Fe²⁺ spin sublattice in CaFe₂TiO₄ reveal that the two states are very close in energy. We propose that the comparable energies of the AFM and FM states lead to competition between the two spin configurations.


CM01.03.18

Synthesis of Alumina-Doped Zirconia Microparticles for High-Temperature Applications

Gregor T. Dahl¹, Sebastian Döring¹, Tobias Krekeler², Martin Ritter², Horst Weller¹ and Tobias Vossmeyer¹; ¹Physical Chemistry, University of Hamburg, Hamburg, Germany; ²Electron Microscopy Unit, Hamburg University of Technology, Hamburg, Germany.

Zirconia and similar ceramics are widely used in high-temperature applications. In the past decades, significant efforts have been focused onto the synthesis and characterization of well-defined ceramic particles in terms of size, shape and composition in order to control their properties precisely. Current research aims at the application of ceramic microparticles in advanced thermal barrier coatings, structure-based colorants for ceramics and thermophotovoltaics.[1-4] Most of these application environments require materials with a high resistance against thermal degradation, which is usually achieved to some degree by doping of the bare ceramic material. Hence, our research addresses the development of synthetic routes for doped zirconia microparticles with accurate tunability of the product’s size and morphology, as well as the examination of the mechanisms underlying the structural degradation under thermal stress.

Recently, we focused on the sol-gel fabrication of well-defined spherical alumina-doped zirconia microparticles and their high-temperature behavior. This material system is to date far less understood than related materials, e.g. yttria-stabilized zirconia, regarding their synthesis and thermally induced structural changes. However, rare and contradictory results in the literature provide a profound understanding of the involved fundamental physical processes highly desirable. Here, we examine the role of the reaction conditions during particle fabrication and the dopant concentration using ex situ characterization of particle samples before and after annealing at different temperatures.

TEM/EDX analyses suggest that homogenous alumina-doping of zirconia microparticles fabricated via a stabilizer-assisted sol-gel protocol at Al/(Al+Zr) molar concentrations between 2 % and 50 % can easily be achieved by using mixed Zr- and Al-alkoxide precursors. The degree of doping can be precisely adjusted by the precursor ratio. Evident effects of the latter on the resulting particle size can be compensated in a controlled way by a variation of the amount or composition of involved stabilizing agents. TEM images of particle samples annealed at temperatures between 800 °C to 1200 °C imply that their structural integrity is progressively maintained with increasing amount of Al. Qualitative XRD analysis using Rietveld refinement reveals a correlation between the Al amount and the stabilization of the tetragonal polymorph against the destructive martensitic transition to the monoclinic phase and inhibited grain growth. Evident dopant segregation after annealing revealed by EDX mappings suggests a reduction of the propagation of grain boundaries during sintering (solute drag effect).


CM01.03.19

Structural and Functional Investigations of Substitutions in the Ionic Conducting Li-Argyrodite Family

Nicolò Minafra and Wolfgang G. Zeier; Justus-Liebig-Universität Gießen, Giessen, Germany.

Inorganic solid electrolytes have garnered considerable attention as separators in lithium-ion battery applications as they may solve the safety problems and improve energy and power density of the conventional devices using liquid electrolytes.¹ Inspired by such technological interest, in this work we studied an inorganic crystalline solid that belongs to the Li-argyrodite family,² with the general formula Li₆PS₄Br. While this compound is known for its high ionic conductivity of Li⁺ ions, the influence of aliovalent and isoelectronic substitutions on the structure and transport properties are unknown.

In this work, we will present the influence of aliovalent substitution of P⁵⁺ with Si⁴⁺ and isoelectronic substitution of Se²⁻ for S²⁻ on the structure-transport
correlation in lithium conducting argyrodites. Structural changes arising from the substitution were monitored through Rietveld refinements of the experimental X-ray powder and neutron diffraction data, and severe changes in the lithium substructure and site ordering can be found. The found changes in the lithium substructure and site ordering can be used to explain the changes in the Li+ ionic conductivities as measured by impedance spectroscopy. This work provides an approach to a better understand structure-property relationships in solid electrolytes. The herein found correlations between composition, structure and functional properties contributes towards a general framework and universal strategy to design solid materials with fast ionic diffusion.

References:
4. Manuscript submitted

CM01.03.20
Synthesis and Characterization of ZrO2@SiO2/Al2O3 Core-Shell Particles for Application as Structural Colors and Thermal Barrier Coatings
Maik Finsel1, Jil Rüter1, Maria Hemme1, Kaline F. Furlan1, Guoliang Shang4, Robert Blick3, Robert Zierold3, Alexander Petrov4, Manfred Eich4, Hoest Weller1 and Tobias Vossmeier1; 1Physical Chemistry, University of Hamburg, Hamburg, Germany; 2Advanced Ceramics, Hamburg University of Technology (TUHH), Hamburg, Germany; 3Center for Hybrid Nanostructures, University of Hamburg, Hamburg, Germany; 4Optical and Electronic Materials, Hamburg University of Technology (TUHH), Hamburg, Germany; 5ITMO University, St. Petersburg, Russian Federation; 6Materials Research, Helmholtz-Zentrum Geesthacht Center for Materials and Coastal Research, Geesthacht, Germany.

In recent years, zirconia (ZrO2) micro- and sub-microparticles gained considerable attention due to their outstanding properties, including chemical inertness, thermal stability and high refractive index. These excellent features of zirconia-based materials enable a broad variety of applications ranging from fuel cells, catalysis, sensors to electro- and bioceramics. Furthermore, zirconia (sub-)microparticles are interesting for applications as building blocks of photonic glasses for high-temperature applications, including structural colors (SC) and thermal barrier coatings (TBC).

For structural colors, well-defined monodisperse core-shell particles with smooth surface and strong refractive index contrast are needed. These requirements can be achieved by encapsulation of spherical zirconia submicroparticles with a suitable shell material. For example, to achieve the desired properties for structural colors Al2O3, SiO2, and polymers are attractive materials to form the shell. Most synthesis methods for such core-shell particles use organic ligands (e.g. polymer, citric acid) as adhesive layer between the core and the shell. One of the main obstacles of this approach is that it precludes high-temperature applications. Here, we developed a straightforward approach to prepare ZrO2@SiO2 core-shell composites without using additional organic coupling agents. First results show that changing the silica shell thickness varies the optical properties in the visible region. Furthermore, we demonstrate that the ZrO2@SiO2 core-shell particles withstand temperatures up to 1000 °C whereas size-comparable zirconia particles and core-shell particles using polyvinylpyrrolidone (PVP) as interfacial layer disintegrate when heated up to 800 °C as shown by XRD, SEM and cross-sectional TEM characterization.

For thermal barrier coatings, low-thermal conductivity ceramics such as Y-stabilized zirconia (YSZ) are used to provide thermal insulation of the underlying superalloy in gas-turbine engines operated in aircrafts. One of the main obstacles of this system is the oxygen diffusion through the ceramic TBC due to oxygen vacancies, which leads to corrosion and failure of the turbine blade. We show that YSZ microparticles are interesting for TBC application with broadband thermal radiation reflection and decreased thermal conductivity at temperatures up to 1500 °C. Furthermore, we used a sol-gel synthesis and atomic layer deposition (ALD) for Al2O3 deposition on YSZ and ZrO2 microparticles to decrease oxygen diffusion and thus to improve high-temperature stability. These core-shell microparticles were characterized by XRD, SEM and IR-reflection measurements.


CM01.03.21
Mechanical and Microstructural Characterization of a 3003 Aluminum Alloy Processed by Repetitive Corrugated-Straightening (RCS)
Carlos A. Reyes Ruiz1, Carlos G. Figueroa Alcantara2, Jose G. Gonzalez Reyes1 and Armando Ortiz Prado1; 1Departamento de Diseño y Manufactura, Facultad de Ingeniería, Universidad Nacional Autónoma de México, Mexico, Mexico; 2Centro Tecnológico Aragón, Facultad de Estudios Superiores Aragón, Universidad Nacional Autónoma de México, Mexico, Mexico; 3Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, Mexico.

Repetitive corrugated-straightening (RCS) is a severe plastic deformation technique that has been applied to an extensive amount of materials due to its capability to generate ultra-fine grain microstructures. Through remarkable grain size reduction, this process led to improved mechanical properties such as strength, hardness, endurance, etc. The aim of the present work was to study the mechanical and microstructural effects of a repetitive corrugated-straightening process using a novel die geometry. A 3003-O aluminum alloy sheet was processed at room temperature up to 6 RCS passes. Deformed samples showed improvements in yield strength. Nonhomogeneous deformation zones were determinate by means of microhardness tests and were correlated to low (LAGB) and high (HAGB) grain boundary and regions measured by means of electron backscattered diffraction (EBSD) mapping. Samples did not change at increasing the number of passes. However, surface quality showed that root mean square roughness (Rrms) increased after the first RCS pass. Initial texture components were not modified at early stages of the processing, but showed an orientation spread at latest stages. Grain lattice distortion, obtained by Williamson–Hall plots, exhibited a maximum after one RCS pass, decreasing as passes number increased. Crystallite size decreases as function of RCS passes.

Acknowledgements: Reyes-Ruiz gratefully acknowledges to DGAPA for his postdoctoral fellowship. G. Gonzalez acknowledges the funding support by PAPIIT IN107917. A. Tejeda, O. Novelo, and E. Hernández-Mecinas, are also acknowledged for their technical support.

CM01.03.22
Fast Interfacial Li+ Diffusion in Nanostructured LiF and LiF-Al2O3 Composites as Seen by NMR Spectroscopy
Stefan Breuer, Veronika Pregartner and Martin Wilkening; Institute for Chemistry and Technology of Materials, Graz University of Technology, CD-Laboratory for Lithium Batteries, Graz, Austria.

Understanding ionic diffusion in solids is a very vital topic in material science. Currently we put much effort into finding suitable materials that meet the
needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport.\textsuperscript{2-3} LiF attracted our attention as it has a versatile range of application. It can be used as a component for electrode materials with high capacity;\textsuperscript{2} moreover, it is a fundamental component of the solid electrolyte interface (SEI).\textsuperscript{4} Understanding ionic transport in and across the SEI is a topic of utmost importance.\textsuperscript{5}

Here we studied ionic transport in nanocrystalline LiF and nanocrystalline LiF:Al\textsubscript{2}O\textsubscript{3} composites to study interfacial ion transport properties. It is well known that the properties of materials with nm-sized structures, particularly if we consider ionics transport, can be significantly different from those of their coarse-grained counterparts.\textsuperscript{6} To investigate the relationship between macroscopic and microscopic ion dynamics, we used conductivity spectroscopy and \textsuperscript{7}Li, \textsuperscript{9}F nuclear magnetic resonance (NMR) spectroscopy. The former method, which is sensitive to long-range ion transport, reveals significant higher conductivity values for the nanocrystalline LiF compared to the microcrystalline sample. Joint milling the ionic conductor with an insulator successfully enhances the conductivity even more. We observed an increase in ion transport by up to three orders of magnitude for LiF:Al\textsubscript{2}O\textsubscript{3} (70:30 vol %). Variable-temperature NMR line shapes recorded under static conditions reveal a fast and a slow Li spin reservoir at elevated temperatures. Obviously, the interfacial regions at the LiF:Al\textsubscript{2}O\textsubscript{3} contacts provide fast diffusion pathways for the Li ions. These atomistic insights available by NMR support earlier concepts that interfacial disorder and strain as well as space charge zones considerably influence overall ion transport in (nanocrystalline) conductor:insulator composites.\textsuperscript{8-11}

References:

CM01.03.23

Microwave Synthesis of Transition Metal Oxide Nanoparticles Adsorbed on Silica Nanosprings for Energy Applications

Pierre Magri\textsuperscript{1}, Noura Zahir\textsuperscript{1}, Sara Soltni\textsuperscript{1}, Jean J. Gaumet\textsuperscript{1}, S\ébastien Dilliberto\textsuperscript{2}, David N. McIlroy\textsuperscript{1}, Wen Luo\textsuperscript{3} and Liqiang Ma\textsuperscript{4}; 1Jean Barriot Institute, University of Lorraine, Metz, France; 2Jean Lamour Institute, University of Lorraine, Nancy, France; 3Physics, Oklahoma State University, Stillwater, Oklahoma, United States; 4Wuhan University of Technology, Wuhan, China.

SiO\textsubscript{2} nanosprings (NS) are used not only for support and substrates in various chemical, biological and medical applications, but also for photovoltaic development and hydrogen storage depending on the choice of the coating on the NS\textsuperscript{[1,2]}. SiO\textsubscript{2} NS are now readily coated with metal oxides, which make them interesting devices for sensors based on redox processes, particularly with semiconducting elements\textsuperscript{[3]}. The use of microwave (MW) chemistry has become more and more common as a means to synthesize nanoparticles on the silica NS using two joint mechanisms for heating, dipolar polarization and ion conduction. However, to ensure the stability of the SiO\textsubscript{2} NS, it is better to first synthesize the nanoparticles by MW reaction before adding them to the NS. In this context, we present herein some MW synthesis of transition metal oxide (TMO) and mixed metal oxide (MMO) nanoparticles (Zn, Co, V) followed by direct absorption on SiO\textsubscript{2} NS. Defect-rich TMO and MMO nanoparticles are synthesized by preparing various metal acetylacetonate solutions in different H\textsubscript{2}O/EtOH volume ratios. After MW irradiation up to 1 h, the resulting precipitates were filtered, washed with EtOH, and dried at 80°C \textsuperscript{[4]}. Finally, the nanoparticles were added to various NS in EtOH. SEM, TEM and X-Ray diffraction confirmed the presence of metal-oxide nanoparticles in a different size range and shapes depending on the solvent ratio and the MW irradiation time. The quantification of ligands originating from the precursors was determined by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). After SEM and TEM characterizations, the optical properties of the different TMO and MMO nanoparticles were carefully measured by UV-Visible photoluminescence and absorption spectroscopy. The same analytical protocol was performed after adsorption on SiO\textsubscript{2} NS. It shows that integrity of defect-rich TMO or MMO nanoparticles (constant visible light emission for ZnO at 570 nm for example) is preserved when deposited onto the NS. Such results on this stability show the potential of using a metal-oxide shell with a silica NS core as an absorber/emitter when connected to a metal contact.

References:
\[3\] P.V. Bakharev, D.N. McIlroy Nanotechnology, 25, 475501 (9pp) (2014).

CM01.03.24

Impact of the Isovalent Alloying on the Thermoelectric Properties of Yb\textsubscript{1-x}MnSb\textsubscript{x}

Giacomo Cerretti, Sabah K. Bux and Jean-Pierre Fleurial; Jet Propulsion Laboratory, Pasadena, California, United States.

Yb\textsubscript{1-x}MnSb\textsubscript{x}, with a zT of about 1.2 at 1200 K, is the highest performing p-type materials for high temperature thermoelectric applications. Structurally it belongs to the Zintl phase family A\textsubscript{4}MnP\textsubscript{4}, (where A = Ca, Sr, Ba, Eu, and Yb; M = Al, Mn, Zn, Ga, Nb, In, and Cd, Pn = P, As, Sb, Bi), which is formed by 14 A\textsuperscript{2-}\textsuperscript{2} cations, a MPn\textsubscript{4} tetrahedron, a linear Pn\textsubscript{3} trimer, and 4 Pn\textsubscript{3} anions. This chemical configuration gives the possibility to independently manipulate the electronic and thermal transport properties of the compound by using different alloying species and adjusting their concentrations. In this contribution, we want to show how different alloying approaches affect the chemical and structural properties of the Yb\textsubscript{1-x}MnSb\textsubscript{x}, and how this translates into the manipulation of the thermoelectric properties. Specifically, we studied the impact of the isovalent partial substitution on the Yb and Mn sites with Sr and Co/Pd respectively. The lack of filled f-orbitals in Sr could result in large changes in the DOS due to the different nature of the chemical bonding. Additionally, the bigger cationic radius of Sr compared to Yb will decrease the bond length generating a higher chemical pressure, and in turn altering the thermal transport properties of the material. Partial substitution of the Mn\textsuperscript{2+} ions by isovalent elements could increase the covalent nature of the bonding to reduce the effective mass and hence to increase the carrier mobility. The results of the isovalent substitution study will be presented and discussed.

CM01.03.25

Negative Magnetisation in A\textsubscript{4}T\textsubscript{2}Cr\textsubscript{2}B\textsubscript{2}O\textsubscript{6}, Perovskites

Emily C. Hunter\textsuperscript{1}, Peter D. Battle\textsuperscript{2}, Maxim Avdeev\textsuperscript{3, 4}, Mylene Hendrickx\textsuperscript{5} and Joke Hadermann\textsuperscript{6}; 1The University of Oxford, Oxford, United Kingdom; 2ANSTO, Lucas Heights, New South Wales, Australia; 3The University of Sydney, Sydney, New South Wales, Australia; 4Physics, University of Antwerp, Antwerp, Belgium.
This research explores the compositional sensitivity of the magnetic properties of $A^2'\text{Sr}_2\text{Cr}_2\text{SbO}_9$ perovskites where $A^2'$ is La or Pr; $A^2'$ is Sr or Ca and $B$ is Nb, Nb or Ta. In monophasic compounds of this type the cations occupying the B sites can be partially ordered or fully disordered. Alternatively the material can phase-separate to give regions in which the cations are ordered and others in which they are disordered. Neutron diffraction and electron microscopy have shown that in compositions where there is cation order two crystallographically distinct B sites are present in a 1:1 ratio, despite the two cation species being present in a 2:1 ratio.

The extent of the cation ordering affects the magnetic properties of the perovskite. For example, $\text{LaSr}_2\text{Cr}_2\text{SbO}_9$, which has a high degree of cation order, is a ferrimagnet while $\text{PrSr}_2\text{Cr}_2\text{NbO}_9$ and $\text{PrSr}_2\text{Cr}_2\text{TaO}_9$, which contain both cation-ordered and disordered regions, are spin glasses. $\text{PrSr}_2\text{Cr}_2\text{SbO}_9$ still behaves as a ferrimagnet, despite containing disordered regions. We shall focus on $\text{PrCa}_2\text{Cr}_2\text{NbO}_9$ and $\text{PrCa}_2\text{Cr}_2\text{TaO}_9$ which are both fully disordered, adopting the space group $\text{Pmnr}$. In these compounds the Ct cations order antiferromagnetically below ~120 K, however, magnetometry studies show that the field-cooled magnetisation becomes negative below 50 K for $\text{PrCa}_2\text{Cr}_2\text{NbO}_9$ and below 80 K for $\text{PrCa}_2\text{Cr}_2\text{TaO}_9$. The direction of the net magnetisation can be flipped by applying magnetic fields of 1000 Oe to $\text{PrCa}_2\text{Cr}_2\text{NbO}_9$ and 3000 Oe to $\text{PrCa}_2\text{Cr}_2\text{TaO}_9$ and both compounds show a large degree of hysteresis in $M(H)$.

In these compounds the Cr cations order antiferromagnetically below ~120 K, however, magnetometry studies show that the field-cooled magnetisation becomes negative below 50 K for $\text{PrCa}_2\text{Cr}_2\text{NbO}_9$ and below 80 K for $\text{PrCa}_2\text{Cr}_2\text{TaO}_9$. The direction of the net magnetisation can be flipped by applying magnetic fields of 1000 Oe to $\text{PrCa}_2\text{Cr}_2\text{NbO}_9$ and 3000 Oe to $\text{PrCa}_2\text{Cr}_2\text{TaO}_9$ and both compounds show a large degree of hysteresis in $M(H)$.

In metallic fuels, fission products generated during operation react with the cladding materials leading to fuel-cladding-chemical interactions (FCCI). The FCCI results in degradation of the cladding wall and eventual rupture of the cladding if the fuel is operated for higher burnup. Use of a dopant in the fuel matrix, which can form intermetallic compounds with lanthanide fission products (e.g., Nd, Ce, Pr, and La), is proposed to be one of the effective ways of mitigating FCCI. Here we used ab-initio calculations based on density functional theory (DFT) to study the interactions between different possible dopants (such as Se, As, Pd, In) and the lanthanide fission products. Based on the calculations, arsenic and selenium were identified as potential dopants to arrest the major lanthanides within the uranium matrix effectively. The relative preference of identified novel dopants in binding with another fuel component, Zr, is also evaluated. Finally, we present an approach that can be used in selecting a dopant to bind a particular lanthanide inside the fuel matrix based on their intrinsic properties such as electronegativity and atomic size. The approach used in this study is generic; so it has implication in other areas of research related to alloy design. This research is being funded by DOE-NEUP, grant # DE-NE0008557.

**CM01.03.26**

**A Novel Approach of Dopant Selection to Immobilize Lanthanides in Uranium-Based Metallic Fuels**

Rahi Khanal1, Nathan Jerred1-2, Indrajit Chari1, Michael Benson2, Robert Marian1i and Sanrat Choudhury1;

1University of Idaho, Moscow, Idaho, United States; 2Idaho National Laboratory, Idaho Falls, Idaho, United States.

In metallic fuels, fission products generated during operation react with the cladding materials leading to fuel-cladding-chemical interactions (FCCI). The FCCI results in degradation of the cladding wall and eventual rupture of the cladding if the fuel is operated for higher burnup. Use of a dopant in the fuel matrix, which can form intermetallic compounds with lanthanide fission products (e.g., Nd, Ce, Pr, and La), is proposed to be one of the effective ways of mitigating FCCI. Here we used ab-initio calculations based on density functional theory (DFT) to study the interactions between different possible dopants (such as Se, As, Pd, In) and the lanthanide fission products. Based on the calculations, arsenic and selenium were identified as potential dopants to arrest the major lanthanides within the uranium matrix effectively. The relative preference of identified novel dopants in binding with another fuel component, Zr, is also evaluated. Finally, we present an approach that can be used in selecting a dopant to bind a particular lanthanide inside the fuel matrix based on their intrinsic properties such as electronegativity and atomic size. The approach used in this study is generic; so it has implication in other areas of research related to alloy design. This research is being funded by DOE-NEUP, grant # DE-NE0008557.

**CM01.03.27**

**Ozone-Mediated Synthesis of Ceria Nanoparticles**

Anuja Bhalkikar and Chin Li Cheung; Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Numerous methodologies have been developed for the synthesis of cerium oxide or ceria, a commercially important lanthanide oxide. Some of the techniques employ long reaction times, elevated temperatures and/or pressures, expensive metal alkoxides and caustic alkalis. This necessitates the need to develop milder, environment friendly synthetic routes for cerium oxide generation. Herein, we report a rapid, room temperature methodology to synthesize fluoride-structured ceria nanoparticles using cerium (III) salts and ozone in the presence of short chain primary, secondary, and tertiary alcohols. This simple technique produced nanoparticles with higher oxygen vacancy compared to that of bulk ceria. Chemical species in the reaction mixtures were studied to elucidate a possible growth mechanism of these nanoparticles from ozonating alcoholic solutions of cerium salts. The catalytic activity of ceria nanoparticles towards the oxidation of carbon monoxide (CO) was further evaluated and compared with that of commercial bulk ceria.

**CM01.03.28**

**How to In Situ Follow the Evolution of Dislocation Configurations During Mechanical Testing on Bulk Specimen?**

Ben Haj Slama Meriem1, 2, Hana Kriaa1, 2, Julien Guyon1, 2, Nabilal Maloufi1, 2, Jean-Jacques Fundenberger1, 2 and Antoine Guittion1, 2;

1Université de Lorraine – CNRS – Arts et Métiers ParisTech – LEM3, Metz, France; 2Labeix Damas - Université de Lorraine, Metz, France.

In the aim of following the fast evolution of the industrial demands, developing innovative techniques that allow to understand and to predict the mechanical properties of materials has become a necessity for the Materials Science community. For instance, mechanical tests followed by microstructural investigations provide engineers with the necessary information to computationally predict the mechanical performance of components. In situ mechanical testing combined with microscopy techniques (SEM and TEM) [1,2] is well known for studying the instantaneous evolution of microstructures during exposure to stress. Such experiments allow capturing footprints of the deformation mechanisms responsible for the changing microstructure. For instance, in-situ testing combined with TEM is generally required for studying the instantaneous evolution of defects during exposure to stress. Today various approaches inside a TEM exist: TEM holders with a simple mechanical actuation [3], elaborated testing units that fit inside the pole pieces [4,5] or by playing with various coefficients of thermal expansion [1]. Nevertheless, in-situ TEM mechanical testing is experimentally very tough. In addition to the difficult control of the deformation conditions, the space available is generally less than one centimeter and statistics on physical mechanisms is scientifically very weak. Indeed, TEM needs an electron transparent specimen with a thickness of ~100 nm with a useful field of view of few µm².

Therefore, fundamental questions on the representativeness of observed phenomenon must be raised when extrapolating discussions to a millimeter-size specimen.

In this framework, we have successfully combined mechanical testing of bulk specimen with an in-situ avant-gardist dislocation-scale characterization technique; the accurate Electron Channeling Contrast Imaging (aECCI) [6]. aECCI is a non-destructive groundbreaking procedure that provides, inside a TEM, diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [7,8]. Firstly, technological challenges such as defect contrast comprehension and experiment procedure will be presented. Secondly first in-situ results will be discussed and they clearly show the full potentialities of this groundbreaking and powerful testing set-up.

**References**

**CM01.03.29**

**Fundamental and Experimental Aspects of Diffraction for Characterizing Dislocations on Bulk Materials by Electron Channeling Contrast Imaging in Scanning Electron Microscope**

Hana Kriaa1, 2, Antoine Guitton1, 2 and Nabila Maloufi1, 2; 1CNRS, Arts et Métiers ParisTech, Université de Lorraine, Metz, France; 2Labex Damas, Université de Lorraine, Metz, France.

The SEM is an easier way to use electron microscope compared to TEM essentially because of the possibility to observed centimetric bulk specimen and the larger space available in the chamber. SEM can access diffraction contrast on bulk materials with the phenomenon of electron channeling [1]. The Electron Channeling Contrast Imaging (ECCI) is a non-destructive groundbreaking technique offering the ability to provide, inside a SEM, TEM-like diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [2, 3]. Electron channeling contrast is produced from electrons, that channel down the crystal planes. Strain and defects distort the crystal planes, which produce changes in backscattered electron intensity leading to a contrast on the image. Dislocations for example can be characterized by ECCI using the well-known TEM $g \cdot b = 0$ and $g \cdot b_{x}u = 0$ extinction criteria [4] where $g$ is the diffraction vector and $b$ the Burgers vector. In this study, fundamental and experimental aspects of electron diffraction for characterizing dislocation by ECCI in SEM are reported [5]. The $(g \cdot g - g)$ method is explored on several dislocation configurations in an Intertistitial-Free steel sample. Moreover, the first detailed characterization of a dislocation dipole by ECCI [4, 5] is presented.

**References**


**CM01.03.30**

**Structural, Raman and Electrical Characterization of Nanocrystalline ZnSe Thin Films Deposited by Pulse Laser Deposition**

Pawan Kumar1, 2, Arvind Kumar1, Trilok Pathak1, Sita Dugu1, Rajesh K. Katiyar1, Alvaro Instan1 and Ram Katiyar1; 1Department of Physics, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, Puerto Rico, United States; 2Department of Physics, Gurukul Kangri Viswavidyalaya, Haridwar, India; 3Department of Physics, Kalindi College, Delhi University East Patel Nagar, Delhi, India.

Thin films of group II–VI semiconductor compounds have attracted considerable attention due to their novel physical properties. As a wide band-gap material, ZnSe is a potential candidate showing compatibility for optoelectronic devices based on the thin film technology [1, 2]. Zinc Selenide (ZnSe) thin films were deposited by Pulse Laser Deposition (PLD) technique on Si-p type substrates at different substrate temperatures. The substrate temperatures were fixed at 150°C, 200°C, 250°C, & 300°C respectively during the growth of the samples. The structure of ZnSe was confirmed by using X-ray diffraction pattern. The surface morphology and roughness of thin films were investigated by atomic force microscopy. The atomic bond behavior at room temperature and at lower temperatures (30°C to -190°C) were studied by Raman spectroscopy. The n-ZnSe/p-Si hetero junction thin films were characterized by current-voltage (I-V) and capacitance-voltage (C-V) measurements at different temperatures (273K to 373K). These films are promising candidates for applications in solar cells and sensors.


**CM01.03.31**

**Development of Highly Hydrogen-Sensitive Thermal Desorption Spectroscopy System—For Detection of Extremely Low Concentration Hydrogen in Oxide Semiconductors**

Hidenori Hiramatsu1, Taku Hanna1, Isao Sakaguchi1 and Hideo Hosono1; 1Tokyo Institute of Technology, Yokohama, Japan; 2National Institute for Materials Science, Tsukuba, Japan.

Hydrogen is the most unavoidable and uncontrollable impurity in semiconductor devices because of the ease of contamination during fabrication processes, even under an ultra-high-vacuum (UHV) atmosphere. This impurity results in serious problems such as instability of thin-film transistors and unintentional carrier doping. The detection limit of various techniques strongly depends on the sample volumes because a larger total amount of hydrogen facilitates detection. Thus, many quantitative and sensitive hydrogenic semiconductor device technology is generally based on thin-film deposition and fine-scale processing technologies, for which material purification and refinement of processing techniques have been rapidly advancing. Thus, the development of highly sensitive hydrogen detection techniques for small-volume samples such as thin films with nanometer-scale thicknesses is critical to investigate the effects of hydrogen impurities for practical semiconductor devices.

In this study, we developed a highly hydrogen-sensitive thermal desorption spectroscopy (HHS-TDS) system to detect and quantitatively analyze low hydrogen concentrations in thin films [REF]. The system was connected to an in situ sample-transfer chamber system, manipulators, and an rf magnetron sputtering chamber under an UHV atmosphere of ~10^-8 Pa. The following key requirements were proposed in developing the HHS-TDS: (i) a low hydrogen residual partial pressure, (ii) a low hydrogen exhaust velocity, and (iii) minimization of hydrogen thermal desorption except from the bulk region of the thin films. To satisfy these requirements, appropriate materials and components were selected, and the system was constructed to extract the maximum performance from each component. Consequently, ~2000 times higher sensitivity to hydrogen than that of a commercially available UHV-TDS system was achieved. Quantitative analysis of an amorphous oxide semiconductor InGaZnO4 (IGZO) thin film (hydrogen concentration of 4.5 × 10^17 atoms/cm^2), which is the minimum concentration among previously reported IGZO was demonstrated using the HHS-TDS system. This concentration level cannot be detected using UHV-TDS or secondary ion mass spectroscopy (SIMS) systems. The hydrogen detection limit of the HHS-TDS system was estimated to be ~1 × 10^17 atoms/cm^2, which implies ~2 orders of magnitude higher sensitivity than that of SIMS (~10^19 atoms/cm^2). This detection limit is the most sensitive among various conventional analysis techniques, to our knowledge, in the case of thin-film samples. We will also discuss role of hydrogen in oxide semiconductors such as IGZO, which are practically applied to channel layers of thin-film transistors in electronic display devices such as organic light-emitting diode displays and smartphones.


**CM01.03.32**

**Role of Surface Oxidation in the Dehydrogenation of Complex Metal Hydrides**

James L. White1, Andrew J. Rowberg2, 3, Liwen Wan4, 4, ShinYoung Kang2, Tadashi Ogitsu2, Robert D. Kolansinski3, Josh A. Whaley1, Timothy C. Wang1, A. A. Baker2, Jonathan R. Lee2, Yi-Sheng Liu4, Lena Trotochaud4, Jinghua Guo4, Vitalie Stavila1, David Prendergast4, Hendrik Bluhm4, Mark Allendorf1, Brandon Wood2 and Farid El Gabaly1; 1Sandia National Labs, Livermore, California, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States; 3University of California, Santa Barbara, Santa Barbara, California, United States; 4Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Complex metal hydrides have high hydrogen storage capacities and the potential to be employed in hydrogen fuel cell vehicles. However, many of these
materials remain limited by slow kinetics in their cycling reactions between hydrogenated and dehydrogenated states. In addition, mechanisms for hydrogen formation on the surface have been postulated for several hydrides but not directly investigated during desorption. Using both operando and ex situ measurements, on several length scales, combined with ab initio simulations, we show an unambiguous view of the surface chemistry evolution in dehydrentgenating NaAlH4 and Mg(BH4)2. Shifts in speciation are observed in real time during desorption using ambient pressure X-ray photoelectron spectroscopy and low-energy ion scattering, and detailed computational models provide atomistic descriptions and energetics of the observed surface processes. While adventitious oxidized species on the surface are often assumed to be inert or inhibitory for metal hydrides, we show that, instead, they participate in the release of hydrogen, in some cases with lower computed barriers than pristine, unoxidized surfaces. Hydrogen enrichment near the surface indicates that dehydrenation in NaAlH4 is limited by surface processes, which have the potential to be improved through optimization of the extent surface processes described here.

CM01.03.33
Galvanic Simulation of Photoelectron Spectra Adam J. Jackson1, 2, Alex M. Ganose1, 2, Anna Regoutz4 and David O. Scanlon1, 2, 3; 1 Dept of Chemistry, University College London, London, United Kingdom; 2 Thomas Young Centre, University College London, London, United Kingdom; 3 Diamond Light Source Ltd, Didcot, United Kingdom; 4 Dept of Materials, Imperial College London, London, United Kingdom.

Photoelectron spectroscopy (PES) is a powerful tool for the characterization of materials by probing their electronic structure; indeed, experiments with x-ray sources in the early part of the 20th century contributed to the modern understanding of electronic structure.[1, 2] In the later part of the 20th century, computational methods become available for ab initio predictions and analysis of electronic band structure. With the widespread use of density-functional theory, it is now a routine procedure to compute an accurate density of states (DOS) for a hypothetical structure. The occupied energy levels in the DOS should map directly to the first-order transition energies observed in photoelectron spectroscopy, providing insight into valence band phenomena.[3, 4]

However, additional processing is required to form a realistic simulated spectrum. There are several mechanisms causing broadening, typically modelled with Gaussian and Lorentzian functions.[5, 6] In addition, relative peak intensities generally match the DOS poorly until corrected. The Gelius model assumes that the contributions of bands will be dominated by their behaviour close to atom centers.[7] This allows free-atom photoionization data to be used with a DOS which is decomposed into atomic contributions (e.g.[3]). Although the data for this process is widely available, the analysis is not performed routinely, partly because it is tedious. We have automated this process and present an open-source package to assist the community in the implementation of this analysis.[8] Free-atom data has been parametrised to enable the selection of optimal HAXPES energies and exploration of the system sensitivity before expensive synchrotron measurements are performed.

1. Rutherford, E. (1914) Phil. Mag. S. 6. 28 (165) 305-319

CM01.03.34
Synthesis, Structural and Magnetotransport Properties of Antiferromagnet-Fe3O4: Epitaxial Thin Films Obtained by Polymer Assisted Deposition Myriam H. Aguierre1, 2, Engienio Otal1, Manuela Kim1, Rafael Ramos3 and Francisco Rivasdulla1; 1 Institute of Nanoscience of Aragón-Laboratory of Advanced Microscopy, Zaragoza, Spain; 2 Dept. of Physics Condensed Matter, University of Zaragoza, Zaragoza, Spain; 3 U.T.N.-CONICET, Buenos Aires, Argentina; 4 Ciquus-University of Santiago de Compostela, Santiago de Compostela, Spain; 5 AIMR-Tohoku University, Sendai, Japan.

Bismuth ferrite (BiFeO3, BFO) has been widely studied for its unique magnetoelectric properties at room temperature, such as antiferromagnetism coupled with ferroelectricity. It has also been shown to display various novel phenomena, e.g., an increased conductivity at specific ferroelectric domain walls, photovoltaic properties, and new structural phases in thin films. Understanding microstructure and phase evolution in multiferroic BFO thin films is an important issue, because interesting physical properties with practical applications are related to the microstructure and 2D nanostructures. This manuscript is also related with the synthesis/fabrication of the thin film. In this study, we address the polymer assisted deposition synthesis (PAD), a chemical technique of deposition with high control of thickness, stoichiometry and epitaxial crystallinity. This method allows to produce a high quality epitaxial thin films of BiFeO3 on SrTiO3. We present a detailed investigation on the atomic structure, morphology and microstructure of BFO/STO thin films based on studied by various transmission and scanning transmission electron microscopy techniques (in particular, with a probe Cs -corrector for atomic resolution in the latter case). Correlation with magnetotransport and thermal properties of the epitaxial films are also addressed.

CM01.03.35
Influence of Surface Chemistry on the Electrocatalytic Activity of Oxygen Electrodes for Solid Oxide Fuel Cells Clement Nicollot, Dmitri Kalaev, Chang Sub Kim, Thomas Deffevere and Harry L. Tuller; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Solid oxide fuel cells (SOFCs) offer direct conversion of hydrogen or hydrocarbon fuels to electricity with high energy conversion efficiency (>50%). In reverse electrolysis operation, powered by wind or solar generated electricity, the same devices produce H2 for later consumption, thus serving as a valuable means of energy storage. The electrode polarization related to electrochemical reactions at the gas/solid interface of the cathode is often the dominant flux limiting mechanism. Accumulating surface impurities (e.g. Si, Na, Al, Cr, and Sr) leads to reduction of long term durability. Identifying means for overcoming the detrimental impact of surface impurity accumulation on oxygen surface exchange kinetics can be expected to result in high payoffs in both improved performance and extended operating life. Pr-doped ceria (PCO), a mixed ionic and electronic conductor with a high electrocatalytic activity toward the oxygen reduction reaction, has a strong advantage over state-of-the-art materials such as La0.6Sr0.4CoO3-δ and La0.6Sr0.4Co0.2Fe0.8O3-δ by not containing strontium, known to readily segregate to the solid gas interface, thereby limiting catalytic activity. Silicon contamination, however, remains a problem even with Sr-free materials, given external sources such as glass sealants, or as an impurity in precursor materials used to fabricate the devices. This work focuses on Si contamination of PCO cathodes, observed to reduce electrode kinetics by as much as several orders of magnitude. By controlling the levels of Si contaminant applied to PCO thin films by wet chemical methods, it becomes possible to systematically study its impact on the oxygen reduction reaction by an in-situ optical transmission relaxation method. We also further investigate the feasibility of using lanthanum as an efficient Si getter [1], and extend this strategy to study the effect of various single valence oxides on the oxygen surface exchange rates of PCO.


CM01.03.36
Probing the origin of multicolor emission in La$_2$Zr$_2$O$_7$ nanoparticles (NPs) is crucial for its applications as tunable phosphors and assessing the effects of doping, varying particle size and other factors on its optical properties. In this work, the effect of doping has been explored by making size tunable La$_2$Zr$_2$O$_7$:Eu$^{3+}$ (LZOE) NPs by varying the concentration of precipitating agent in molten salt synthesis. The effect of such changes has been explored on structure, surface area, photoluminescence, radioluminescence, lifetime and quantum yield of LZOE NPs. Furthermore, the effect of changing B site ions by replacing Zr$^{4+}$ with Hf$^{4+}$ on optical properties of undoped NPs and europium ion doped NPs is investigated to find suitable pyrochlore host for phosphor and scintillator applications. Photoluminescence spectroscopy on undoped La$_2$Zr$_2$O$_7$ (LZO) and La$_2$Hf$_2$O$_7$ (LHO) NPs shows violet-blue emission from the LHO NPs whereas the LZO NPs display both violet-blue and red emission upon UV irradiation. Such differences has been explained based on density functional theory (DFT) calculated density of state (DOS), which presented different energetics of ionized oxygen vacancies in LHO and LZO. The differences in luminescence spectroscopy of the La$_4$Zr$_2$O$_7$:Eu$^{3+}$ (LZOE) and La$_4$Hf$_2$O$_7$:Eu$^{3+}$ (LHOE) NPs highlighted higher quantum yield, emission output, radioluminescent intensity and luminescence lifetime from the LHOE NPs which could be highly beneficial in newer pyrochlore materials for red phosphors, scintillators and fluorimmunoassays.

**SESSION CM01.04: Experimental and Theoretical Approaches in Solid-State Chemistry**

**Session Chairs: Boniface Fokwa and Yuri Grin**

**Tuesday Morning, November 27, 2018**

**Hynes, Level 2, Room 203**

8:00 AM *CM01.04.01*

**Lateral Size Control of Multiple Anions in Oxyhydrides and Oxychalcogenides**

Hiroshi Kageyama, Kyoto Univ, Kyoto, Japan.

We show how difference in anion compressibility in mixed-anion compounds gives rise to drastic changes in structures and resultant chemical and physical properties. For example, we recently found from the high-pressure XRD of SrV$_2$H that H$^+$ is extraordinary compressible, as compared with oxide, providing an interesting platform to tune crystal field stabilization energy and thus physical properties [1]. Such flexible nature of hydride is useful to drive a structural phase transition in oxyhydrides [2]. The presence of chalcogenides anions (e.g., Se$_2^-$) with greater compressibility than oxide anions leads to extensive control of metal–oxide distance, leading to unusual spin state [3].


8:30 AM *CM01.04.02*

**Learning Solid State Chemistry from Atomic Fluctuations—A Statistical Physics and Machine Learning Approach**

Rama K. Vasudevan, Lukas Vlcek and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A key aspect of statistical physics is that the fluctuations of a system encode information about the response of the system to changing thermodynamic variables. However in most studies, structural and chemical fluctuations in materials characterization are seen as a hindrance, that complicates analysis. Here, we present a method to take advantage of atomic-scale observations of chemical and structural fluctuations and use them to build a generative model that can be used to predict the phase diagram of the system in a finite temperature and composition space. We show the example for understanding cationic segregation in a manganese thin film (La$_{0.8}$Ca$_{0.2}$MnO$_3$), where a combination of in-situ atomic imaging via scanning tunneling microscopy as well as bulk measurements of composition as a function of layer (via angle-resolved x-ray photoemission spectroscopy) enables constraining the generative model. Through use of a recently developed statistical distance framework, the fluctuations in the system are inherently captured (as opposed to averaged out). The model leads to the prediction of weak segregation forces in bulk (attributable to elastic effects) and weak de-segregation forces in the surface (attributable to electrostatic interactions), which agree with recent quantum-chemical calculations (J. Am. Chem. Soc. 135, 7909 (2013)), but which are derived entirely from experiment. We further extend this approach to mapping atomic dynamics observed with scanning transmission electron microscope, providing insight into solid state chemistry on a single-defect level. This approach can be applied to a large array of systems, wherein the observed fluctuations can be exploited to understand the interactions between the constituent components of the system.

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division (R. K. V., S. V. K., L.V). Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

8:45 AM *CM01.04.03*

**A Structural Characterization Challenge Using Atomic Pair Distribution Function Based on Electron Diffraction**

Iamara C. Nogueira, Edson R. Leite, Jefferson Bettini and Gustavo Azevedo; 1Physics Department, Federal University of Amazonas (UFAM), Manaus, Brazil; 2LNNano-CNPEM, Campinas, Brazil; 3Chemistry Department, Federal University of São Carlos, São Carlos, Brazil; 4LNLS-CNPEM, Campinas, Brazil.

In this work, we intend to investigate the extent of information about the size-dependent structure of nanoparticles from the atomic pair distribution function (PDF) method. However, we intend to use the PDF method in an innovative way. Instead of using x-ray and neutron powder diffraction data, we will use electron diffraction data acquired from a conventional transmission electron microscope (TEM), that we will call PDFe. We will show results regarding the characterization of reference materials (amorphous Carbon and gold nanoparticle) in order to establish a protocol of characterization and to confront the results obtained by electron diffraction with results (from the literature) obtained by other scattering techniques. Another important point of our work is to use the PDFe to characterize nanoparticles, more specifically, we performed the accurate determination of atomic-scale structure and structural defects of Zirconium Oxide (ZrO$_2$) nanoparticles synthesized by different sol-gel routes, considering the tetragonal and monoclinic phases. The advantages and disadvantages of using electron diffraction (using a transmission electron microscope) will also be presented to obtain the PDF.

9:00 AM *CM01.04.04*

**Expanding the Toolset for Colloidal Synthesis and Integration of Functional Inorganic Nanomaterials**

Dmitri V. Talapin; Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois, United States.
The synthesis of inorganic nanomaterials has seen impressive developments, both in the fundamental understanding of nucleation, growth and surface chemistry of inorganic phases, and in the ability to prepare functional materials with precisely engineered optical and electronic properties. However, the lack of atomic precision in nanomaterial synthesis restricts our ability to harness all the power of this broad and diverse class of matter. Heterogeneity introduces broadening of the absorption and emission spectra, reduces charge carrier mobility in nanocrystal solids, and generally restricts our ability to engineer nanomaterials. I will discuss new approach for colloidal synthesis of nanomaterials with minimal, ideally no, size distribution. The concept is inspired by gas-phase atomic layer deposition (ALD) widely used in microelectronics. Our studies show that the ALD concept can be successfully implemented in solution and, when applied to nanomaterials, enables layer-by-layer growth of crystalline lattices with close-to-atomic precision.

I will also discuss recent advances in the surface chemistry of semiconductor nanostructures. Molecular inorganic species can be designed to electronically couple individual nanostructures into nanocomposite materials with high electron mobility. By making surface ligands photochemically active, we introduce a general approach for photosensitiser-free, direct optical lithography of functional inorganic nanomaterials (DOLFIN). Examples of patterned materials include metals, semiconductors, oxides, and magnetic and rare earth compositions. No organic impurities are present in the patterned layers, which helps achieve good electronic and optical properties. The ability to directly pattern all-inorganic layers using a light exposure dose comparable to that of organic photoresists opens up a host of new opportunities for additive nanomanufacturing.

9:30 AM BREAK

10:00 AM - CM01.04.05
Structures, Magnetism and Soft Chemistry of Layered Oxide Chalcogenides and Oxide Pnictides
Simon Clarke; University of Oxford, Oxford, United Kingdom.

Oxide chalcogenides and oxide pnictides have become of increasing interest following the discovery of the iron-based pnictide and chalcogenide superconductors. In this talk, I will present the synthesis (using high-temperature and soft techniques), crystal structures and physical properties of a series of layered oxide arsenides and oxide chalcogenides will be described and the changes in magnetic ordering and other physical properties will be described as functions of temperature and composition, and related to changes in crystal structure. Examples will include the complex magnetic ordering in Sr2Fe3Se2O3, the changes in magnetic structure of A2Cr2O5Sr2xLa(1−x)O3 (A = Sr, Ba) as a function of temperature and the changes in magnetic structure in the series Sr2CoO2Cu2−xSe2, Sr2CoO2Ag2−xSe, Sr2MnO2Cu1.5−xSe and Sr2MnO2Ag1.5−xSe and the homologous series Sr2Mo2O2Cu2m+ySm1−x+y which serves as a function of coinage metal content, and hence transition metal oxidation state, and which will be correlated with composition and structure.

10:30 AM - CM01.04.06
A Soft Chemistry Route to Control the Oxidation States of Dopants in Inorganic Phosphors
Romain Gautier; Centre National de la Recherche Scientifique, Nantes, France.

Photoluminescence properties are important for different applications such as solid-state lighting, sensors, and display devices. Among the materials exhibiting such properties, doped phosphors are of particular interest owing to high thermal stability and potentially high quantum efficiency. Interestingly, the photoemission of such doped materials differs according to the oxidation states of their dopants. The reduction under controlled atmosphere or the co-doping with other cations enable to target dopants in specific oxidation states but this control is usually poor.

In this context, we carry out a soft chemistry route to reduce the dopants of inorganic phosphors by heating the solid-state compounds at low temperature with oxygen getters in glass tubes sealed under vacuum. This soft reduction enables to control the ratio Ni3+/Ni2+ in SrTiO3:Ni and Eu3+/Eu2+ in SrAl2O4:Eu or (CaMg)x(NaSc)1−xSi2O6:Eu [1-3]. The optical properties could also be tuned according to these ratio. The control of the ratio Ni3+/Ni2+ in SrTiO3:Ni allowed the tuning of IR photoluminescence vs. optical absorption which could have potential applications in biomedicine. For SrAl2O4:Eu or (CaMg)x(NaSc)1−xSi2O6:Eu, the photoluminescence corresponding to the 4f-4f transition of Eu3+ dopant vs. the photoemission corresponding to the 4f-5d transition of Eu2+ dopant can be tuned to control the photoluminescence color of these compounds. In the specific case of (CaMg)x(NaSc)1−xSi2O6:Eu, the additional modification of the solid-solution composition enables to design a white phosphor for potential applications in solid-state lighting.

1:00 PM - CM01.04.07
Preparation and Characterization of Graphite Terinary Intercalation Compounds Containing Alkaline Earth Metal Cations and Ethyleneimine
Wei Xu and Michael Lerner; Department of Chemistry, Oregon State University, Corvallis, Oregon, United States.

A series of new ternary graphite intercalation compounds (GICs) containing alkaline earth metal cations (M=Mg, Ca, Sr, Ba) and ethyleneimine (en) are reported. These GICs are deep blue to green in color and can be prepared as phase pure compounds by the direct reaction of graphite powder and the metal in liquid en at mild temperatures (25-100 °C) under an inert atmosphere. X-rays diffraction and thermal analyses were employed to determine the structural and composition. [M(en)2]C60 and [Ba(en)2]C60 can be obtained as stage-1 GICs with gallery expansions of 0.55 and 0.46 nm, respectively, indicating the presence of intercalate monolayers with the en co intercalates oriented perpendicular to the encasing graphene layers. Reactions with Ca and Sr metals form [Ca(en)]3C60 and [Sr(en)]3C60, which are stage-1 GICs with intercalate bilayers and expansion heights of 0.76 nm. The effect of reaction temperature, stoichiometries, and time on product phases will be described. The complexes formed by the cationic intercalates within GICs are highly unusual, with low oxidation states exhibited by some of the cations and M-M bonding to form intercalate clusters.

11:00 AM - CM01.04.08
Understanding and Designing Novel H⁺ Ionic Conductors Based on First Principles Calculations—Toward Facile Anion Conduction in Oxide-Based Materials
Qiang Bai, Xingfeng He, Yizhou Zhu and Yifei Mo; 1University of Maryland, College Park, Maryland, United States; 2Maryland Energy Innovation Institute, College Park, Maryland, United States.

H⁺ ion conductor materials have the great potential to enable high-energy density electrochemical storage based on hydrogen. Fast H⁺ conduction has been recently demonstrated in the (CaMg)1−xSr2xLi2(H2O)x−yO3 (0 ≤ x ≤ 1, 0 ≤ y ≤ 1) oxide materials. However, little is known about the H⁺ diffusion mechanism in this new material and its unique structure. The origin of such exceptional H⁺ conduction in the oxide-based materials is of great interest. Using first-principles calculations, we studied the energetics and diffusion mechanisms of H⁺ ions as a function of structures and compositions in this oxyhydride system. Our study identified that fast H⁺ diffusion is mediated by H⁺ vacancies and that the fast two-dimensional or three-dimensional H⁺ diffusion is activated by different anion sublattices in different compositions. In addition, novel doping was predicted from ab initio computation to increase H⁺ conductivity in these materials. The unique two-anion-site feature in this structural framework enables highly tunable lattice and minimizes the blocking of anion diffusion by oxygen sublattice, allowing high mobile-carrier concentration and good diffusion network. This conclusion offers general guidance
Electrides are compounds in which electrons serve as anions. First electride material was synthesized by James Dye in 1983 (JACS 1983) who obtained the crystal by dissolving alkali metal into an ether solution of crown-ether solution. We reported the first RT stable electride, C12A7:e, in 2003 (Science 2003) using insulating 12CaO7Al2O3(C12A7) with nano-cage structure. Resulting C12A7:e- is metallic conducting and exhibits BCS-type superconductivity (JACS 2007, PRB 2008, Phil.Trans A 2014). A unique property of C12A7:e- has low work function (2.4eV) comparable to alkali metals but chemically and thermally stable (Adv.Mat.2007). Electride materials had been restricted to crystal to 2011. We obtained amorphous C12A7:e- by rapid quenching (Science 2011) molten C12A7:e- or sputtering. Amorphous electride, characterized by anionic electron at interstitial position, is a novel class of amorphous semiconductors (PNAS 2016).

We have examined to apply C12A7:e to electronic devices(Adv.Mat.2004, JPCC 2007), and chemistry such reducing regent (Org Lett 2007) usable in aqueous media. The representative examples are: Ru-loaded C12A7:e- works an effective catalyst for ammonia synthesis at mild conditions(Nat.Chem.2012) and is free from hydrogen poisoning which is known as a common drawback of Ru-catalysts (Nat.Comm.2015). Amorphous C12A7:e- thin film with low work function and high optical transparency is promising as an electron injection layer, an obstacle, in organic light emitting diodes(PNAS 2017).

C12A7:e may be regarded as 0D-electride viewed from dimensionality of anionic electrons. The concept of electride was extended to 1D and 2D materials. Several 1D/2D electride materials such as Y5Si3 (JACS 2016) and LaScSi (Adv.Mat. 2017) were found by extending the system to intermetallics. Sr5P3 is a 1D electride material with low work function (2.4eV) comparable to alkali metals but chemically and thermally stable (Adv.Mat.2007). We obtained amorphous C12A7:e- by rapid quenching (Science 2011) molten C12A7:e- or sputtering. Amorphous electride, characterized by anionic electron at interstitial position, is a novel class of amorphous semiconductors (PNAS 2016).

Electrides are rare ionic compounds in which an electron does not occupy an atomic orbital but rather acts as an anion. This electron is expected to behave differently to those occupying the valence state of standard materials, making electrides desirable as electron emitters,[1] nonlinear optical switches,[2] superconductors,[3] battery anodes,[4] and catalysts for applications ranging from compound synthesis to CO2 splitting.[5]

We use high-throughput screening and advanced calculations to identify undiscovered electrides among all known materials. Our method recovers the compounds Ba3ScN3 and Sr3CaN3 as electrides. These ternary nitrides are the first known case of electrides containing a transition metal element, which is surprising as one would expect a redox active transition metal to accept the anionic electron rather than allowing its existence in the lattice. We confirm these results with self-consistent GW theory, one of the most accurate methods available for charge density prediction. Besides these compounds we find more than 60 previously unknown electrides along with 4 already known, significantly expanding this class of industry-relevant materials.

Harnessing Chemical Frustration Toward the Creation of Modular Intermetallic Phases

Recent years have witnessed growing interest in the research of thermoelectric materials. Intermetallics offer immense opportunities for the creation of new materials, with their crystal structures ranging from simple packings to complex arrangements that lead one to invoke cells containing thousands of atoms or higher-dimensional axes. However, navigating this structural diversity is made challenging by the need for predictive principles relating composition, structure, and properties. In this presentation, we will derive lessons from some of the most complicated intermetallic structures toward the development of one such principle: chemical frustration. A common theme that can be perceived in complex intermetallics structures is microscopic segregation between competing interactions. Using the results of theoretical calculations, we will develop mechanisms that will be derived by which competition between segregation and attraction between incompatible structural motifs can emerge in these phases. For example, in the epitaxial stabilization mechanism, structures with strains of opposite signs in the interactions between the majority elements have to opportunity for the cancellation of these strains at interfaces between them. Similarly, in the electron-hole pairing scheme the potential for electron transfer across interfaces is viewed means of stabilizing multi-domain character. Based on these mechanisms, the chemical pressure schemes and non-optimal electron counts of simple but geometrically distinct compounds are used as measures of their potential reactivity toward intergrowth. New crystal structures that have been encountered in our synthetic attempts to induce frustration in intermetallic systems following these and other approaches will also be presented and analyzed.
properties, including Fermi surface, electron localization and charge transfer, will be discussed, thus enabling an in-depth understanding of the fundamental properties of these new materials.

3:45 PM CM01.05.06
FeSi as New Conductive Layer for Fe-Based Superconductors Sophie Tence1 and Andres Cano1; 1Institut Néel, Grenoble, France; 2Institut de Chimie de la Matière Condensée de Bordeaux, Bordeaux, France.

Since the discovery of unconventional superconductivity in Fe-based materials in 20081, Fe-based superconductors (Fe-SC) have attracted much attention and have been the subject of intense and systematic investigations. To date, in high-Tc Fe-SC, iron is invariably associated to toxic pnictogen or chalcogen elements (P, As and S, Se, Te respectively) in the conductive layer. This circumstance raises the important fundamental question about the link between Fe-based superconductivity and the apparent need of these pnictogens and chalcogens. Besides, Fe-SC are usually obtained by solid state reaction with possibly the use of high pressure.

In this context, we have recently synthesized the new silicide hydride LaFeSiH by solid-gas hydrogenation of the precursor LaFeSi. Preliminary results show that this hydride is stoichiometric to the 111 Fe-SC compounds (e.g. Pr4V(213)). Interestingly, LaFeSiH displays onset of superconductivity at 11 K as evidenced notably on the resistivity measurement on single-crystal2. This hydride also presents other structural, magnetic and electronic similarities with the previously reported Fe-SC compounds, similarities that will be presented in this talk. Therefore, LaFeSiH can be considered as the first Fe-SC obtained by solid-gas hydrogenation and free from toxic pnictogen and chalcogen elements. This is the first member of a new class of materials with which we have surpassed traditional pnictide and chalcogenide compounds and promoted, for the first time, original Fe-based silicides to unconventional high-temperature superconductors.


4:00 PM CM01.05.07
Exploiting Controlled Nanoarchitecture to Study Structure-Property Relationships in [(SnSe)1+δ][TiSe2]. Thin-Film Heterostructures Danielle M. Hamann1, Sage Bauers2 and David C. Johnson1; 1Chemistry, University of Oregon, Eugene, Oregon, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Recent research on monolayers and their heterostructures has led to the discovery of numerous emergent properties. These can be markedly different from those of the respective bulk materials and are not always additive, making the properties of heterostructures difficult to predict. Self-assembly of designed precursors with composition profiles that mimic the desired product allows for the synthesis of superlattice heterostructures with controllable stacking sequences between the layers, or “nanoarchitecture”. Using this unique control, homologous series of compounds are prepared where the layer thickness of a single constituent is changed with unit-cell precision, allowing the study of properties as a function of material thickness or stacking order. One family of compounds with properties dependent on nanoarchitecture is [(SnSe)1+δ][TiSe2], where n and m can be individually varied. These compounds exhibit thickness-dependent structural distortions, degree of interlayer templating, and transport properties. Interestingly, distortions in the SnSe constituent are a result of a surface area to volume competition and are influenced by interfaces with TiSe2. When single layers of TiSe2 and SnSe are interleaved there is an unexpected lattice match between constituents that results in regions of alignment in an otherwise rotationally disorder system. Coupled with the structural distortions are changes in resistivity, Hall, and Seebeck coefficients. Measurements suggest competition between n-type TiSe2 and p-type SnSe, with the specific properties dependent both on the constituent ratios as well as their dimensionality. The ability to study the properties in these heterostructures is a result of precise layer control through synthesis of systematically varied compounds. Using this technique to gain advanced knowledge about the source of emergent properties in heterostructures will facilitate future “materials by design” approaches to target and optimize a desired property for a specific application.

4:15 PM CM01.05.08
From Quasicrystals to Crystals and Superconductors in Ca–Y–Au–Al Joyce Pham1,2; 1Walter Schnelle1, Gudrun Auffhammer1, Claudia Fels1 and Gordon J. Miller1,2; 1Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany; 2Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa, United States; 3U.S. Department of Energy, Ames Laboratory, Ames, Iowa, United States.

In the Au-rich region of the Ca–Au–Al system, an icosahedral quasicrystal (i-QC) CaAu4.5–xAl2.5+x, was discovered and shown to irreversibly transform into the cubic 2/1 crystalline approximant (CA) Ca21Al20(205) (space group (no. 205); Pearson symbol: cP722; a = 23.8918(2) Å) via in-situ X-ray diffraction, thereby providing direct experimental evidence for the relationship between QCs and their associated CAs. The 2/1 CA crystallizes in a Tais-type structure and, following the polar intermetallic depiction, the atoms of different electronegativities, viz., electronegative Au vs. formally electronegative Ca, are arranged in concentric shells. As part of an overarching chemical pressure and valence electron count investigation, the cubic 1/1 CA Y3Au14(0.082)Al4.49(1) (space group (no. 204); Pearson symbol: cP122; a = 14.462(2) Å) was discovered and shown to also crystallize in the Tais-type, and in which preliminary magnetization data show potential surface superconductivity behavior below Tc around 3.7 K. The QC-CA transformation, crystallographic structure, and atomic site preference analysis of Ca–Au–Al, along with the crystal and electronic structures, chemical analysis, and preliminary transport properties, including resistivity and specific heat, of the 1/1 CA Y3Au14(0.082)Al4.49(1) will be presented for discussion.

4:30 PM CM01.05.09
Complex Intermetallic Alloys Anja V. Mudring; Stockholm University, Ames, Iowa, United States.

The design of new materials with desired chemical and physical characteristics requires thorough understanding of the underlying composition–structure–property relationships and the experimental possibility of their modification through the controlled involvement of new components. From this point of view intermetallic phases, a class of compounds formed by two or more metals, present an endless field of combinations that produce several chemical compounds and classes ranging from simple alloys to true ionic compounds. Polar intermetallics (PICs) belong to the class that is electronically situated in the middle, between Hume-Rothery phases and Zintl compounds and possessing an a/b (valence electron per atom) values around two. In contrast to the latter, where logical rules of formation and classification systems have been developed decades ago, polar intermetallics remain a dark horse with a huge diversity of crystal structures, but unclear mechanisms of their formation. Partial incorporation of structural and bonding features from both nonpolar and Zintl compounds is commonly observed here. A recent number of PICs can be described in terms of complex metallic alloys (CMAs) following the Hume-Rothery electron counting schemes, but, exhibit electronic structure changes that cannot be explained by the latter. For that reason, research efforts are aiming at the discovery and synthesis of new polar intermetallic compounds, their structural characterization and properties' investigation in line with the
analysis of the principles connecting all these components. Understanding of the basic structural tendencies is one of the most anticipated outcomes of this analysis and systematization of the available knowledge is the initial and the most important step. The occurrence of different structure types for PICs ranging from commonly encountered AlB2 or BaAl4 types in line with the recently discovered diamond-like homometallic networks, formation of local five-fold symmetry, different types of tunneled structures and more complex intergrown multicomponent structures will be discussed.

CM01.06.01
Novel Heteroleptic Tin Precursors for Atomic Layer Deposition of Tin Oxide Thin Films Applications Seong Ho Han1, 2, Ho Keun Park1, 2, Chang Gyoum Kim1, 2, Seung Uk Son1 and Taek-Mo Chung1, 2; 1Thin Film Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Department of Chemistry, Sungkyunkwan University, Suwon, Korea (the Republic of); 3Advanced Materials and Chemical Engineering, University of Science and Technology, Daejeon, Korea (the Republic of).

Over the past decade, oxide semiconductor materials have attracted significant interest as important materials for various applications, including thin film transistors (TFTs), gas sensors, lithium batteries, and solar cells. Particularly, p-type tin(II) monoxide (SnO) has generated considerable research attention owing to its wide optical band gap energy (2.7-3.0 eV), which can translate into the possibility of completely transparent electronic devices. Moreover SnO based TFT recently showed a record field effect mobility of ~6.75 cm2/Vs and Hall mobility of ~17.6 cm2/Vs. On the other hand, tin(IV) dioxide (SnO2) which is an n-type material, with a wide band gap energy of ~3.6 eV and excellent optical, electrical, and chemical properties is also constantly under investigation to improve upon its properties for various applications. SnO2 is transparent under visible light and has a resistivity that can extend over a wide range depending on the deposition process and the growth conditions. Doped SnO films have also demonstrated good performance as transparent conducting oxides for solar cells.

Generally, chemical vapor deposition (CVD) and atomic layer deposition (ALD) are the preferred growth methods for uniform and conform thin films. Moreover, SnO and SnO2 can be selectively deposited by controlling the oxidation state of the Sn(II) precursor and the oxygen source. In the case of ALD, several attempts have been made to grow SnO or SnO2 films using different Sn precursor/reactant combinations. Unfortunately, most of the attempts have only resulted in n-type SnO films. Only few reports have shown the successful deposition of SnO films including a recent publication from our lab.

Recently, the importance of heteroleptic precursors with improved properties have been highlighted by a number of reports. Most common precursors exist as homoletic type in nature, where identical ligands are bonded to a metal center. In contrast, a heteroleptic precursor is a metal complex with two or more distinct ligands attached to the metal center. Reports have shown that heteroleptic precursor design through suitable ligand selection could result in several improved properties in comparison to the homoletic precursors. Even though the selection of suitable ligands for heteroleptic metal precursors is as challenging as designing a new ligand for homoletic precursors, the heteroleptic precursors are advantageous because of the availability of several ligands and their complexes with well-known properties to choose from.

To develop novel tin(II) precursors for thin film applications, we have synthesized new tin complexes using tin(II) chloride as starting material. The resulted complexes were characterized by various analysis equipments such as nuclear magnetic resonance (NMR), elemental analyses (EA), thermogravimetric analysis (TGA), and single crystal X-ray diffraction. The detailed applications of thin films by ALD will be shown in the presentation.

CM01.06.02

Transparent conducting oxides (TCOs) have been a very hot topic over the past few decades due to their great importance in electronic industries including touch screen display, organic light emitting diodes (OLED) and liquid crystal displays (LCD). However, the majority of TCOs used currently all belong to N-type TCOs. The lack of high performance P-type transparent conducting oxides (TCOs) presents a huge problem in many optoelectronic applications ranging from organic light emitting diodes (OLED) to transparent electronics. Oxychalcogenide based P-type TCOs are very promising due to the recent outstanding results in terms of P-type conductivity and transparency. Oxychalcogenides with the basic form of LnCuOCh have layered structure consisting of alternating [LnO] layers and [CuCh] layers, which allows more degrees of variation. LaCuOSe with the band gap 2.85eV has lower conductivity than LaCuOSe of band gap 2.85eV. In this work, LaCuOSe has been firstly prepared via our novel solid state reaction without using commonly used toxic gas H2S. The LaCuOSe prepared in this shows high conductivity due to the absence of hydrogen atoms in the process. Then LaCuOSe was doped with Se via solid state reaction to prepare LaCuOSe1-xSex without any impurities. The optical properties of the polycrystalline samples were studied by UV-Vis spectroscopy, and the chemical states of the aforementioned five elements in films with varying concentration of Se were examined by using X-ray photoelectron spectroscopy (XPS). The electrical properties were measured by four point probe method. The detailed atomic structures and doping sites of the LaCuOSe1-xSex samples were analyzed by scanning transmission electron microscopy (STEM).

CM01.06.04
Brownmillerite Type SrCoOz (z = 2 for Oxygen Enrichment—Optimization of Absorption Parameters Aswathy M. N and Arun M. Umarji; Materials Research Centre, Indian Institute of Science, Bengaluru, India.

Ternary oxides are known for many applications like solid oxide fuel cells, catalysis and gas sensing. These oxides can be oxygen non-stoichiometric if transition metals with variable oxidation states are present. This can be regarded as a functionality when the extent of oxygen vacancies inside the lattice is very high. They can transport oxygen through the lattice if a partial pressure gradient of oxygen is applied. This is normally exploited in case of oxygen separation membranes and solid oxide fuel cells. Perovskite oxides (general formula ABO3) are promising candidates as they can exist in a variety of oxygen non-stoichiometric forms by varying temperatures and oxygen partial pressures. SrCoO2 (Perovskite, Pm-3m) is one such material which reversibly transforms to SrCoO2 (Brownmillerite, Ima2) phase at 623 K. Here in we report the application of Brownmillerite SrCoO2 for oxygen enrichment. Brownmillerite (BM) SrCoO2 phase has been stabilized to date only by liquid nitrogen quenching. We report a cost-effective method of quenching for the stabilization of the BM SrCoO2. The solution combustion synthesized powder was calcined and sintered at 1223 K in pellet form. This pellet was quenched to 473 K using Al foil pads to stabilize the intact ceramic with Brownmillerite phase. A simple home-built volumetric setup has been fabricated for studying the oxygen storage property of the material. The sample was pre-treated with a higher partial pressure of oxygen at 673 K to form the oxygen-rich perovskite phase and this phase was heated at lower pressure to study the desorption characteristics. The pressure change observed when sample
energy dispersive X-ray spectroscopy (EDX). The chemical environment of the doped Ag atom was studied by Extended X-ray Absorptance Fine Structure synthesized via a hydrothermal reaction. The products were identified using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and K4Nb6O17.nH2O structure, the radial distribution functions (RDF) measurement suggest that the Ag atoms are incorporated in the interlayers. The XANES (EXAFS) measurement. The photocatalytic activity was evaluated by analyzing the kinetics of the decomposition of a 20 ppm phenol solution under UV light irradiation. The development of non-Pt based electrocatalysts for the hydrogen evolution reaction (HER) is a pre-requisite for the generation of hydrogen, a feasible and cost-effective source of hydrogen. Structural transitions and generating metal deficiency are the effective ways of manipulating the d-band centre of a metal surface which enhances the catalytic activity of metal nanoparticles towards the HER. Charge-transfer from in situ generated oxide species to the metal centre also leads to an enhancement in catalytic activity towards the HER. In the present work, we report a facile colloidal synthesis of PdBi nanoparticles using sodium borohydride as the reducing agent. Upon annealing the as-synthesized nanoparticles, a phase transition from the lower symmetry monoclinic phase to the higher symmetry tetragonal phase has been observed, and hence a change in morphology from agglomerated to core–shell nanoparticles. Potential electrochemical cycling of both monoclinic and tetragonal PdBi leads to the formation of a Pd-rich PdBi2 alloy with enhanced catalytic activity (onset potential: ∼11 mV and ∼18 mV vs. the RHE, 20 mA cm−2 current density at an overpotential of ∼140 mV and ∼207 mV for monoclinic and tetragonal phases, respectively). The low co-ordination number of Pd active sites formed by the dissolution of Bi alters the d-band centre of Pd, and hence the optimal energy required for hydrogen adsorption leading to enhanced activity. Although the obtained composition after potential cycling is almost similar for both phases it is seen that the dealloyed monoclinic phase shows higher activity as compared to the dealloyed tetragonal one. Cyclic voltammometry of the monoclinic PdBi2 shows the formation of Bi–O species after potential cycling. Electron transfer from the Bi–O species to the Pd centre enhances the charge-transfer kinetics of the HER on the catalyst surface and hence an increased catalytic activity of the monoclinic phase as compared to the tetragonal one. Thus, in situ generated oxide species facilitate charge-transfer from oxide to the metal surface which in turn enhances catalytic activity towards the HER.

The K2O-Nb2O5-H2O hydrothermal system produces potassium niobates with various crystal structures such as layered-, pyrochlore-, perovskite-, or tunnel-type structures depending on the reaction conditions. This system is a promising candidate for lead-free piezomaterials, optical devices, and hydrogen storage. Structural transitions and generating metal deficiency are the effective ways of manipulating the d-band center of a metal surface which enhances the catalytic activity of metal nanoparticles towards the HER. In the present work, we report a facile colloidal synthesis of Ag-incorporated potassium niobates; a layered K4Nb6O17.nH2O, a pyrochlore-type (K,H)NbO3.nH2O, and a perovskite-type KNbO3, were also observed. Defined and sharp Raman modes as well as characteristic luminescence peaks for all the samples due to f–f transitions. The morphology was confirmed by FE-SEM showing structures in the nanosized range. These results show possible application of these materials to suppress the demand for conventional luminescent biomarkers as well as new optical devices.

The K2O-Nb2O5-H2O hydrothermal system produces potassium niobates with various crystal structures such as layered-, pyrochlore-, perovskite-, or tunnel-type structures depending on the reaction conditions. This system is a promising candidate for lead-free piezomaterials, optical devices, photocatalysts, ion-exchangers etc. So far, there have been several investigations on photocatalysis, including water splitting and degradation of organic contaminants in water. Here we investigate Ag incorporation into the K2O-Nb2O5-H2O system under hydrothermal conditions and the photocatalytic activities of these as synthesized potassium niobates. Three types of Ag-incorporated potassium niobates; a layered KNbO3:nH2O, a pyrochlore-type (K,H)NbO3:nH2O, and a perovskite-type KNbO3, were synthesized via a hydrothermal reaction. The products were identified using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The chemical environment of the doped Ag atom was studied by Extended X-ray Absorbance Fine Structure (EXAFS) measurement. The photocatalytic activity was evaluated by analyzing the kinetics of the decomposition of a 20 ppm phenol solution under UV light irradiation.

Low crystalline layered type, and highly crystalline pyrochlore and perovskite-type compounds were obtained by the hydrothermal reaction. In the layered KNbO3:nH2O structure, the radial distribution functions (RDF) measurement suggest that the Ag atoms are incorporated in the interlayers. The XANES spectra and RDF for pyrochlore-type, (K,H)NbO3:nH2O, Ag, indicate that Ag atoms exist as Ag+ ions, in the tunnels of the pyrochlore-type structure. On the other hand, the XANES spectra and RDF for perovskite-type KNbO3:Ag show an environment similar to Ag metal. The optical band gap energies for layered-, pyrochlore-, and perovskite-type compounds incorporated with Ag are estimated to be 3.1, 3.0, and 3.1 eV respectively. The photocatalytic activity of the layered-type Ag-doped compound is comparable with that of the perovskite-type compound and superior to that of the pyrochlore-type compound without Ag. Nevertheless, the degradation rate of phenol on the layered-type compound is lower than that of the undoped compound. These results can be explained by the difference in local environments of the Ag atoms in these structures. The higher photocatalytic activity of the perovskite-
Novel Copper Precursor Based-Deposition of Cu₂O and CuO Thin Films Using Atomic Layer Deposition

Seungmin Yeo1, 2, Jeong Hwan Han1, Gun Hwan Kim1, Bo Keun Park1, Chang Gyuon Kim1 and Taek-Mo Chang1, 4; 1 Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2 Yonsei University, Seoul, Korea (the Republic of); 3 Seoul National University of Science and Technology, Seoul, Korea (the Republic of); 4 University of California, San Diego, California, United States.

Copper oxide has been attracted considerable attention because of its favorable intrinsic characteristics such as environmental-friendly, low-cost and reconfigurable electronic structure. Among various copper oxides, cuprous oxide (Cu₂O) and cupric oxide (CuO) are well known for many kinds of applications due to their attractive electrical characteristics. For example, Cu₂O and CuO show the n- and p-type characteristic when they have crystalline structure of cubic and monoclinic, respectively, and their combination can be utilized in various applications such as gas sensor, photodiode, anode materials in batteries, thin film transistors (TFTs), solar cells, and photo-catalysts. Until now, however, atomic layer deposition (ALD) based thin film fabrication of Cu₂O and CuO have not been seriously studied yet.

In this research, Cu₂O and CuO thin films were successfully deposited by ALD technique using novel copper precursor, (bis(1-dimethylamino-2-methyl-2-butoxy)copper) (Cudmbnmb) for copper source, and H₂O and O₃ for oxygen source, respectively. To clarify the structural and electrical characteristics of individual thin films, X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF) analyses were performed. All the analyses results demonstrated that Cu₂O and CuO thin films have cubic and monoclinic structure with low C-impurity in it. The XPS measurement also showed consistent result with XRD analysis. The electrical characteristic was investigated using UV-Visible (ultraviolet-visible) spectroscopy, and it revealed that each thin film has favorable optical band-gap. The more detailed experimental procedures and physical/chemical characterization results of thin films will be discussed in presentation.

CM01.06.09
Thermodynamic, Crystal Structural, Electric and Magnetic Studies on (K₂SrₓCu₃₋ₓSeO₇)₄ and (K₂SrₓCu₃₋ₓSeO₇)₄, (Bi, Pb)₀.₀₂₋₀.₂₀ flux the formation was at low temperature. Then it is formed in air at atmospheric pressure, K₂CuSe₂O₇ compound at 400 °C. With N₂ flux the formation was at low temperature. Then it is formed in air at atmospheric pressure, K₂CuSe₂O₇ at 300 °C/12 h and K₂CuSe₂O₇ at 400 °C/12 h, faster and low T process, that the ones reported. TB reaches a maximum at 150 K.

CM01.06.10
Substitutional Solute Atom Effect on Dislocation Motion in FCC Iron Alloys—An Atomistically Informed Kinetic Monte Carlo Study Shuhei Shinzato1, Masato Wakeda1 and Shigenobu Ogata1, 2; 1 Osaka University, Osaka, Japan; 2 National Institute for Materials Science, Tsukuba, Japan; 3 Kyoto University, Kyoto, Japan.

Solute atom changes the mechanical properties of alloys, which is known as solid solution strengthening and softening. This solute atom effect is widely used to control the mechanical strength of alloys. In this work, we analyze the solute effect on screw dislocation motion in FCC iron, which dominates plastic deformation of BCC iron, using an atomistically informed kinetic Monte Carlo (kMC) model. The kMC model represents dislocation motion via kink-pair nucleation and migration, and all of the necessary kMC parameters, such as activation energies of kink-pair nucleation and migration and its stress dependency, are computed using atomistic methods based on developed interatomic potential. We successfully predicted the solute effects on dislocation velocity, temperature dependent yield strength, and activation volume of dislocation motion.

CM01.06.11
A Comparative Study on Ca-Doped and Sr-Doped Gd₂Ti₃O₁₀ for Microwave Absorption Applications Qinlong Wen1, 2, Wancheng Zhou1, Fa Luo1, Dongmei Zhu1 and Yongmin Liu2, 3; 1 State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an, China; 2 Department of Mechanical & Industrial Engineering, Northeastern University, Boston, Massachusetts, United States; 3 Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States.

With the development of communications industry, unexpected and harmful electromagnetic waves have raised concerns about the impact on communication devices, aircraft, and human beings. A wide variety of microwave absorption materials (MAMs) have been investigated based on magnetic, dielectric, semiconducting and conductive materials. Most of the conventional absorbers are 1-5 mm thick, which degrades their practical applications. In order to reduce the thickness of MAMs, we need to judiciously engineer the complex permittivity of the absorber. Towards this goal, we have doped...
Gd$_2$Ti$_5$O$_{15}$ with Ca and Sr, and systematically investigated their dielectric and microwave absorption properties in the frequency range of 8.2-12.4 GHz (X-band). The samples were prepared by hot press method according to the chemical formulas Gd$_2$M$_x$Ti$_2$O$_7$ (M = Ca, Sr; x = 0.03, 0.06, 0.09 and 0.12). The XRD patterns of Gd$_2$M$_x$Ti$_2$O$_7$ show typical pyrochlore-type crystal structure. There exist oxygen vacancies in all the samples according to the thermogravimetric analysis, which have significant effects on the electric conductivity and dielectric properties. When the Ca doping concentration is less than 9wt%, there are no big influences on the dielectric properties. When it reaches 12wt%, the real part of permittivity increase from 66 to 114 at 8.2 GHz as the Sr doping concentration rises. At the same doping concentration, the Sr-doped Gd$_2$Ti$_5$O$_{15}$ has higher complex permittivity. The calculated reflection loss shows that the Sr-doped Gd$_2$Ti$_5$O$_{15}$ absorber is thinner than the Ca-doped counterpart. The optimal thickness of the Sr-doped Gd$_2$Ti$_5$O$_{15}$ is 0.74 mm with an effective absorption bandwidth of 2.7 GHz, surpassing the existing MAMs. In the next stage, we will plan to modify the frequency dispersion characteristics to broaden the effective absorption bandwidth and further reduce the thickness by adjusting doping concentration and combining with other ceramics. These doped Gd$_2$Ti$_5$O$_{15}$ and related composite ceramics would be very good candidates for microwave absorption applications in the future.

CM01.06.12
Superstructures Driven Through Ordered Chemical Bonding in Unconventional Clathrates—Cs$_8$Zn$_{18}$Sb$_{28}$ and Cs$_9$Cd$_{12}$Sb$_{28}$ Bryan Owens-Baird$^1$,$^2$, Shannon J. Lee$^1$,$^2$, Oleq Lebedev$^3$ and Kirill Kovnir$^1$,$^2$; $^1$Iowa State University, Ames, Iowa, United States; $^2$Amer National Laboratory, Ames, Iowa, United States; $^3$Laboratoire CRISMAT, Caen, France.

Unconventional clathrates, whose frameworks are composed of late row transition metals and pnictide elements (e.g. M = Ni, Cu, Zn, Au; Pn = P, As, Sb), are a promising class of materials for thermoelectric applications. Previous studies have shown that many unconventional clathrates show a disposition to order their frameworks into larger supercells due to the difference in chemical bonding between framework elements. This framework ordering often minimizes bonding interactions within the framework, e.g. M-M interactions. The previously reported clathrates, Cs$_8$Zn$_{18}$Sb$_{28}$ and Cs$_9$Cd$_{12}$Sb$_{28}$, were described to have the arystotpe cubic clathrate-I structure in which all framework sites were mixed occupied by metal and antimony. In our study of these clathrates, we show that the frameworks order into discrete metal and antimony sites, reducing Cd-Cd and Zn-Zn interactions. Cs$_9$Cd$_{12}$Sb$_{28}$ adopts an 8-fold volume increase into a centered cubic superstructure, space group (No. 206), doubling the unit cell length to 24.3027(7) Å. The structure of Cs$_8$Zn$_{18}$Sb$_{28}$ has proven to be more complex and not easily solved through single-crystal X-ray diffraction experiments due to extensive twinning. Electron diffraction of Cs$_8$Zn$_{18}$Sb$_{28}$ has shown intrinsic twinning down to a nanoscale, and still a source of findings, hexagonal MoO$_3$ (h-MoO$_3$) is a metastable material with, as yet, poorly known structure and physicochemical properties. In addition, this work, undoped and Ag-doped h-MoO$_3$ microrods have been synthesized by a scalable soft chemistry method based on the precipitation of ammonium heptamolybdate, while composites of h-MoO$_3$ microrods and graphene or graphene oxide (GO) were synthesized by a slightly different route. In addition, highly crystalline h-MoO$_3$ nanoparticles were obtained by ball-milling of the as-grown microstructures. All the obtained samples were thoroughly characterized by a wide set of complementary techniques including monochromatic X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV-Vis spectroscopy, micro-Raman, micro-photoluminescence, X-ray photoemission spectroscopy (XPS) and X-ray absorption (XAS) with synchrotron radiation.

CM01.06.14
Sintering Behavior of Zinc Oxide Under DC Field by EDXRD Hulya Bicec$^2$, Berra Beyoğlu$^1$, Tevfik Ozdemir$^1$, John Okasinski$^1$ and Thomas Tsakalakos$^1$; $^1$Rutgers Univ, Piscataway, New Jersey, United States; $^2$Dumlupınar University, Kutahya, Turkey; $^3$Argonne National Laboratory, Lemont, Illinois, United States.

In this study, the sintering behavior of zinc oxide (ZnO) under dc field was analyzed. The performed method is called as flash sintering where the assistance of electric field reduces sintering temperature much lower than traditional sintering temperatures. Non-isothermal condition runs under 50V/mm electric field and 250°C/min heating rate led us to the rapid increase in power absorption by specimen between 580°C to 834°C in less than a minute and densification of the specimen increased to >95%. No appreciable grain growth was observed in ex situ SEM analyses. While flash-sintering has been demonstrated in a variety of oxide material systems including ZnO, the mechanism behind this technique is not still fully understood. Here, we report on the results of an in situ time-resolved EDXRD study as a function of electric field and temperature. The densification phenomena of ZnO particulate system has been analyzed at the unit cell level over times scales by using polychromatic x-rays with photon energies up to 200 keV.

CM01.06.15
Hexagonal Molybdenum Trioxide (h-MoO$_3$) as a Multi-Functional Material for Energy Storage, Optoelectronics and Photocatalytic Applications Paloma Almódvar$^1$, María Luisa López$^2$, Carlos Díaz-Guerrero$^1$, Julio Ramírez Castellanos$^2$, José María González Calbert$^1$, Marco Perez$^1$,$^4$, Katharina Lorenz$^4$,$^5$, Silvia Suarez$^3$ and Benigno Sánchez$^2$; $^1$Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Madrid, Spain; $^2$Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid, Spain; $^3$IFFN, Instituto Superior Técnico, Universidade de Lisboa, Bobadela, Portugal; $^4$Instituto de Engenharia de Sistemas de Computadores-Microsystems and Nanotechnology (INESC-MN), Lisboa, Portugal; $^5$FOTOAIR-Ciemat, Unit of Analysis and Photocatalytic Treatment of Pollutants in Air, Avida, Madrid, Spain.

Molybdenum oxides are considered exceptionally functional and adaptable optical and electronic oxides due to their unique physical properties. In particular, molybdenum trioxide (MoO$_3$) is a polymeric material. The thermodynamically stable orthorhombic o-phase is a well-known semiconductor with a widegap of 5.7 eV. However, there is still a source of findings, hexagonal MoO$_3$ (h-MoO$_3$) is a metastable material with, as yet, poorly known structure and physicochemical properties. In this work, undoped and Ag-doped h-MoO$_3$ microrods have been synthesized by a scalable soft chemistry method based on the precipitation of ammonium heptamolybdate, while composites of h-MoO$_3$ microrods and graphene or graphene oxide (GO) were synthesized by a slightly different route. In addition, highly crystalline h-MoO$_3$ nanoparticles were obtained by ball-milling of the as-grown microstructures. All the obtained samples were thoroughly characterized by a wide set of complementary techniques including monochromatic X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV-Vis spectroscopy, micro-Raman, micro-photoluminescence, X-ray photoemission spectroscopy (XPS) and X-ray absorption (XAS) with synchrotron radiation.

CM01.06.16
Electrochemical Li-Ion Intercalation for Control of Electronic Phases in Transition-Metal Oxide Epitaxial Films Takuto Somi$^1$, Kohei Yoshimitsu$^2$ and Akira Ohtomo$^{1,3}$; $^1$Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan; $^2$Materials Research Center for Element Strategy (MCES), Tokyo Institute of Technology, Yokohama, Japan.
Electrochemical Li-ion intercalation is widely utilized as Li-ion battery operation. Apart from the battery application, it can be applied for reversible modulation of physical properties in materials, where content of Li-ion is largely controlled while keeping their host structures. Meanwhile, the large amount of carrier as high as $10^{22}$ cm$^{-3}$ can be modulated, which is enough to control the exotic properties of transition-metal oxides (e.g., metal-insulator transition and superconductivity). Nevertheless, due to a hurdle for homogeneous intercalation to bulk materials, it is limited to apply electrochemical intercalation for control of physical properties.

In this study, we have focused on epitaxial films as host materials, which are advantageous to Li-ion intercalation owing to well-defined structural properties and vast specific surface area. Using pulsed-laser deposition technique, high-quality epitaxial films were grown. A compact three-terminal electrochemical cell was implemented for the electrochemical Li-ion intercalation to the epitaxial films, and successive in-situ resistivity measurements were performed.

First, we have applied this experimental technique to tungsten oxide (WO$_3$), which is a typical band insulator owing to empty W 5d band. When Li ions were intercalated to WO$_3$ epitaxial films, systematic modulation of the electronic properties was verified: resistivity systematically decreased with increasing the amount of intercalated Li-ions (i.e., carrier density), and an insulator-to-metal transition occurred at Li-ion content of 0.24 \cite{1}. Next, we have applied this technique to layered lithium niobate (LiNbO$_3$), which is known to show superconductivity in the Li-deficient phase \cite{2}. As-grown LiNbO$_3$ epitaxial films showed metallic conductivity and no superconductivity appeared above 2 K. On the other hand, after Li-ion deintercalation, Li$_{1-x}$NbO$_3$ films showed superconductivity below 5 K. We also demonstrated that the superconducting transition induced by Li-ion electrochemical reaction was reversible just like the Li-ion battery operation, suggesting that electrochemical Li-ion intercalation was useful for both exploration of electronic phases and operation of next-generation devices utilizing electronic phase transitions of transition-metal oxides.


CM01.06.17
Grain and Grain Boundary Properties of ZnO-Zn$_2$Bi$_{2}$O$_5$-CoO$_{2}$-Cr$_2$O$_3$-CaCO$_3$ Ceramics Using Dielectric Functions Youn-Woo Hong, Man-Jin Ha, Jong-Hoo Paik, Jeong-Ho Cho, Young-Hun Jeong and Ji-Sun Yun; KICET, Jinju, Korea (the Republic of).

ZnO has been applied to various electrical and optical applications such as gas sensors, piezoelectric transducers, phosphors, transparent conducting films, and varistors. To control the figure of merits of these devices it is essential to understand the behavior of defects and interface states in doped ZnO, especially in ZnO varistor. All of these applications are either affected by, or depend on, defects and grain boundary properties according to various dopants (Bi, V, Pr, Co, Mn, Cr…oxides). It is known that cobalt oxide doped to ZnO improves the nonlinear current-voltage characteristics, which is presumably due to the formation of the Schottky-type double barriers at the grain boundaries. Also it is found that the presence of a large Bi, V or Pr ions induces the concentration of native defects of acceptor type in the grain boundary of doped ZnO. However, it is not known about the relationship between the defects and grain boundary properties in the simple five component system ZnO-Zn$_2$Bi$_{2}$O$_5$-CoO$_{2}$-Cr$_2$O$_3$-CaCO$_3$ (ZZCCCa) revealed good nonlinear current-voltage characteristics. In this study, we investigated the effects of CaCO$_3$ and Zn$_2$Bi$_{2}$O$_5$ (newly synthesized liquid phase sintering aid by us for varistor application) additives in ZnO-Cr$_2$O$_3$ (it’s a new varistor system developed by us) on the defects and grain boundary properties using dielectric functions ($\varepsilon_\infty$, $\varepsilon_*$, $\gamma$, $\tan\delta$). It will provide information about the relationship between the formations of donor or acceptor defects at the grain or grain boundary for the double Schottky barrier. Experimentally ZZCCCa sintered at several temperatures in air have two kinds of defects (Zn interstitial and O vacancy) according to its sintering temperature, a single grain boundary (apparent activation energy Ea=0.90–1.2 eV), and a good varistor properties (nonlinear coefficient $\alpha$$>$80). The origin of varistor behavior in this system has been discussed in relation to grain boundary traps and defect chemistry based on the experimental results.

CM01.06.18
Materials Discovery by Chemical Analogy—Role of Oxidation States in Structure Prediction Daniel W. Davies, Keith Butler, Alexandra Iasyev and Aron Walsh; 1University of Bath, Bath, United Kingdom; 2Materials, Imperial College London, London, United Kingdom; 3ISIS Facility, Oxford, United Kingdom; 4UNC Eshelman School of Pharmacy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

The concept of oxidation states has, for many decades, been integral to the way in which chemists think about the coming together of elements to form molecules and extended solids. Oxidation states continue to be a useful heuristic tool across all areas of the chemical sciences. By treating elements in given oxidation states as species in their own right, it is possible to use these as building blocks to create chemically feasible compositions\cite{1}. Oxidation states also play a crucial role in approaches to structure prediction: Tabulated sources like Shannon’s radii and coordination environments as well as recent data-mined probabilistic models\cite{2} can predict the likelihood of a given crystal structure occurring.

The likelihood of an element to adopt a certain oxidation state in a solid, given a certain set of neighbours in a given coordination environment, might often be obvious to the well trained eye of a chemist, backed up by their intuition. However, encoding this information for use in high-throughput searches presents a significant challenge.

In this work, we carry out a statistical analysis of the occurrence of oxidation states in 25,000 ordered, inorganic compounds. These results demonstrate that a large number of elements are only likely exhibit certain oxidation states when other, particular elements are present.

We use the information gleaned from this analysis to construct a screening process that ascribes a likelihood score to suggested element compositions. This screening procedure is implemented in this work to efficiently explore the enormous search space for new ternary transition metal halide compositions. We show how a large number of otherwise sensible looking compositions can be discounted from such a search using our method.

Structure prediction is then carried out for some candidate compositions using a probabilistic model as implemented in the Pymatgen code,\cite{3} in which the energies of the structures found with those suggested by the probabilistic model, in order to assess its performance. Overall, we show how careful consideration of the occurrence of oxidation states can be used as part of a materials design methodology. Our methodology can be applied in a range of contexts and is an important tool in the quest for accelerated materials discovery.


CM01.06.19
Perovskite Electron Emitters—Computational Prediction and Preliminary Experimental Assessment of Novel Low Work Function Cathodes Tianyu Ma, Lin Lin, Ryan Jacobs, Dane Morgan and John Booske; University of Wisconsin--Madison, Madison, Wisconsin, United States.
Commercial W-based thermionic electron emission cathodes have been used in high frequency, high power vacuum electronic devices for decades. However, there is an ongoing need for the development of new thermionic cathode materials that don’t suffer from the shortcomings of traditional W-based cathodes, such as limited emission lifetime due to the continual evaporation of volatile Ba during high temperature operation and non-uniform emission throughout the cathode surface.[1]

Our recent work explored a representative set of 20 perovskite oxides as potential new electron emitting materials by conducting Density Functional Theory (DFT) calculations of the surface work function using accurate hybrid HSE functionals, where we discovered that pure and Ba-doped SrVO$_3$ could exhibit low work functions of about 1.9 and 1.1 eV, respectively.[2] Given the well-known compositional flexibility of perovskites, the question naturally becomes the following: What other perovskites exist that could also have a low work function?

In this work, we have used high-throughput DFT calculations enabled by the MAterials Simulation Toolkit (MAST)[3] to computationally screen over 3100 perovskite oxides in search of new thermionic electron emitters. We screened materials in search of candidates with (1) low predicted work function of less than 2 eV, obtained using the bulk O p-hc band center as a descriptor as informed from previous work[2], (2) high bulk stability in a typical thermionic cathode operating environment of $T = 1273 \text{ K}$ and $p_{(O_2)} = 10^{-8} \text{ Torr}$, (3) metallic electronic structure to allow for facile electronic transport, and (4) low work function surfaces that are also stable and are thus expected to be present on the surface of a real cathode. From this computational search, we have identified 6 new perovskite compounds that are promising new thermionic cathode materials.

In addition to our high-throughput computational search for low work function perovskites, it is crucial to experimentally synthesize and test these promising materials. We successfully synthesized >95% phase pure polycrystalline SrVO$_3$ powders using solution-based precursor salts and high temperature heat treatment in a reducing atmosphere. Additionally, we pressed and sintered the SrVO$_3$ powders into cathode test pellets and obtained work function values using high temperature electron emission measurements and X-ray photoelectron spectroscopy (XPS). These experimental results demonstrate the promise of SrVO$_3$ as a low work function thermionic emission cathode.

References


CM01.06.20

Fracture Damage of Ceramic Substrates Utilizing an Acoustic Emission Method and Frequency Analysis of the Elastic Wave Takuya Ono, Yusuke Daiko, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.

From the strong demand of both higher efficiency and energy saving of the power semiconductor, material shift from conventional silicon (Si) to silicon carbide (SiC) was gradually seen since the late 1980’s. SiC-based power devices have various advantages including high frequency operation, high thermal conductivity, high breakdown voltage and temperature operating capability higher than 200 °C owing to its wide bandgap compared with silicon.[3] High temperature operation leads to decrease the volume of heat sink (cooling system). Ceramics with high thermal conductivity such as AlN and Si$_3$N$_4$ have been used for the insulating substrate. Because of their high power/current densities and wider range of the operating temperature, thermal fracture at those insulating ceramic substrates during prolonged operation is a serious problem. In addition, since the power module consists of various components including a ceramic insulating substrate, Cu electrode and polymer molding, understanding of the start-point of the thermal fracture, e.g. whether at the ceramic substrate itself or at Cu electrode/ceramic interface etc. also becomes a significant issue. Acoustic emission (AE) has been widely used to detect fractures, and frequency of the elastic wave can be obtained by Fourier analysis. Here we show the relationship between the frequency of the acoustic wave and elastic modulus of various substrates.

Four substrates of a silicate glass (70 GPa), Y$_2$O$_3$-stabilized ZrO$_2$ (231 GPa), Si$_3$N$_4$ (300 GPa) and Al$_2$O$_3$ (390 GPa) were used for the AE measurement, the numbers of brackets are its Young’s modulus. Thermal shock fractures induced using an infrared radiation heating (IRH) method[4,5] were recorded, followed by Fourier transform of the acoustic wave decay in order to estimate the wave frequency. In the case of a three-point bending method for crack generation, serious noise due to the friction between substrate and AE sensor was also detected. On the other hand, characteristic frequencies for each substrate were observed using the IRH method with a good reproducibility especially in the frequency ranging from 200 to 300 kHz. A good linear relationship between the Young’s modulus of substrates and corresponding frequency was successfully obtained. We also confirmed the start-point of the fractures at both AlN substrate AlN/Cu interface from the AE frequency shift. These results will be discussed together with a heating/cooling cycle test.

CM01.06.21

The Influence of Crystal Structure in the Development of Complex Nanosized Mixed Iron Oxides by Cation Exchange Alberto Casu¹, Sergio Lentijo Mozol², Davide Deiana² and Andrea Falqui¹, ¹Biological and Environmental Sciences and Engineering (BESE), King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia; ²Centre Interdisciplinaire de Microscoop Electronique, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The extensive field of application of magnetic nanoparticles (NPs) makes them a wide, popular and attractive class of materials that receives an ongoing development, with different compositions and morphologies being proposed to improve the NPs’ magnetic features. In regards to this, cation exchange (CE) could represent a promising approach to obtain complex, modulated magnetic nanostructures, but its application to this class of materials has been sporadic and not always consistent.

To this aim we studied the effect of a post-synthetic CE approach on same-sized magnetite and wüstite NPs by performing in-depth morphological, structural, thermally resolved chemical and magnetic behavior analysis, finally obtaining bi-concave core/shell NPs with mixed Fe/Mn and Fe/Co ferrite shells that still maintained the initial shape and size. The combination of such diverse techniques evidenced unanimously this unexpected result, while also shedding light on the role of the NPs’ crystal structure for CE reactions: given the common size and shape of the initial NPs, the crystal structure of the two phases (non-defective for magnetite, defective for wüstite) was the only variable among the NPs populations that affected the CE and was responsible for the higher percentage of doping cation (Co or Mn) present in the post-CE wüstite NPs. Then, the experimental evidence provided what needed to clarify the mechanisms that drive CE processes in this class of materials, while also offering a solid basis for the interpretation of the dramatic variations observed in the magnetic features of the post-CE NPs. In particular, the evolution of the magnetic features could be attributed to the combination of three separate
The first factor was the main cause of exchange-bias effects, while the introduction of Mn or Co in the shell modulated the net magnetic hardness of the core/shell NPs, leading to magnetically softer or harder NPs, respectively, with respect to the initial NPs. Finally, the presence of ferrimagnetic (magnetcite) or antiferromagnetic (wüstite) cores in the core/shell NPs has a major influence in the net magnetic hardness and saturation magnetization of the final NPs. These results give a new insight on the mechanisms that command CE of nanosized magnetic oxides, while providing a clearer picture over the possible capabilities of CE approach to develop novel, complex magnetic nanostructures.

CM01.06.22  
Rational Design of Semiconductor Heterostructures for Energy Conversion  
Junsang Cho1,2, Erick Braham1,2 and Sarbajit Banerjee1,2; 1Department of Chemistry, Texas A&M University, College Station, Texas, United States; 2Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Lead halide perovskites have rapidly emerged as promising next-generation materials for photovoltaics, light-emitting displays, and other optoelectronic applications owing to their desirable optical and electronic properties. Dimensional control provides a means to tune the optical, electronic, and magnetic properties of semiconducting materials as a result of quantum confinement effects. Ligand-mediated colloidal synthesis methods allow for control over nucleation/growth kinetics and enable precise modulation of nanocrystal dimensions through variation of reaction parameters such as the precursor concentration, reaction temperature, and the electronic and steric parameters of passivating ligands. I will focus on synthetic efforts at establishing dimensional control of semiconductor nanostructures with a particular emphasis on the ligand-mediated synthesis of two dimensional (2D) lead halide perovskite nanocrystals guided by elucidation of crystal growth mechanisms. I will further discuss the design of semiconductor heterostructures for photocatalytic water oxidation that couple multiple polymorphs of vanadium oxide (V2O3) nanowires with semiconductor nanocrystals. The alkyl chain length, branching, ligand concentration, and temperature greatly influence the dimensional modulation of 2D perovskite nanoplanelates (MAPbBr3 and CsPbBr3). Our recent work demonstrates that the crystalline order of the ligand-shell assembly, as dictated by the length of the alkyl chains, the degree of branching, the reaction temperature, and ligand concentration, strongly influences the extent of dimensional confinement attainable for the perovskite nanoplanelates. The denticity, steric bulk, and concentration of the added alkylamine ligands further provide a means of modulating structural dimensionality from 3D CsPbBr3 to 0D CsPbBr3 structures. Machine learning approaches for navigating synthetic landscapes have further been developed and provide control over layer thickness down to a single layer.

The rational design and interfacing of semiconductor heterostructures comprising light harvesting (charge donor) and wide-bandgap semiconductor (charge acceptor) elements is imperative for solar energy conversion within PEC cells wherein incident solar radiation is converted and stored as a chemical fuel. Such heterostructures need to be carefully designed to efficiently harvest a large portion of the incident solar radiation, which requires precise control of energetic offsets (governing the thermodynamic driving forces for charge separation) and the kinetics of charge transfer (determined in large measure by interfacial properties). I will discuss the design of V2O3/quantum-dot heterostructures that simultaneously optimize thermodynamics and kinetics. The ability to tune the V—O connectivity across multiple polymorphs of V2O3, and the specific composition of QDs allows for a broad palette of heterostructures to be systematically developed.

CM01.06.23  
Re Segregation at Interfacial Dislocation Network in a Nickel-Based Superalloy  
Jixue Li, Qingqing Ding, Qian Yu and Ze Zhang; Zhejiang University, Hangzhou, Alabama, United States.

The distribution of Rhenium (Re) in a Ni-based single-crystal superalloy is studied by sub-angstrom resolution transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy. It is found that Re atoms segregate at the tensile stress regions near the interfacial dislocation cores, and the segregation process is facilitated by dislocation pipe diffusion. In situ TEM and scanning electron microscopy (SEM) straining studies reveal that the Re-decorated dislocation networks along the phase boundaries act as mechanical walls that effectively block dislocation motion and crack propagation. Furthermore, the degree of Re segregation can be regulated by thermal treatment; the slower the cooling rate, the higher the concentration of Re at the interfacial properties. I will discuss the design of V2O3/quantum-dot heterostructures that simultaneously optimize thermodynamics and kinetics. The ability to tune the V—O connectivity across multiple polymorphs of V2O3, and the specific composition of QDs allows for a broad palette of heterostructures to be systematically developed.

CM01.06.24  
Sequential Charge Transitions in Ca0.5Bi3+0.5Fe3+O3 and the Electronic Consequences of B-Site Substitution  
Fabio Denis Romero1,2, Takashi Saito1, J. Paul Attfield3 and Yuichi Shimakawa1; 1Institute for Chemical Research, Kyoto University, Kyoto, Japan; 2Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan; 3University of Edinburgh, United Kingdom.

Transition metal oxides with unusually high-valent cations often show unusual structural, magnetic, and transport behavior as a result of their inherent charge instabilities. Additionally, the charge transitions via which these instabilities are relieved often lead to coupling of several fundamental properties. For example, CaFeO3 shows charge disproportionation of the unstable Fe3+ cations (2Fe3+ → Fe3+ + Fe5+) which leads to a structural phase transition due to ordering of the disproportionate cations and a metal-insulator transition.[1] In addition, competing magnetic interactions in the charge disproportionated phase lead to the emergence of incommensurate magnetic order.[2] In BiNiO3, there is an intersite charge transfer transition (Bi3+3Ni3+O3 → Bi5+3Ni5+O3) which is accompanied by significant structural modifications due to the columnar ordering of the Bi5+ and Bi3+ cations.[3]

Recently, we reported the synthesis of Ca0.5Bi3+0.5Fe3+O3, which shows sequential charge transitions of the unusually high valent Fe3+5: first at 250 K there is charge disproportionation from Ca0.5Bi3+0.5Fe3+O3 to Ca0.5Bi3+0.5Fe3+5+3Ni5+O3 with accompanying charge and magnetic ordering and then at 200 K there is intersite charge transfer between Bi and Fe to form Ca0.5Bi3+0.5Fe3+5+3Ni5+O3.[4] These charge transitions are accompanied by significant changes to the structural, magnetic and transport properties of this material.[5] This material is tolerant to substitution of the iron for cobalt enabling the formation of the full Ca0.5Bi3+0.5Fe3+Co3O3 solid solution. This results in an initial sharp suppression of the charge disproportionation transition at x = 0.03 due to the broadening of the oxygen hole peak while the interstitial charge transition remains up to approximately x = 0.67.

References:

CM01.06.25
Influence of Nanoparticle on Microstructure and Magnetic Properties of Bi-Substituted LiZnTi Ferrites with Low Sintering Temperature Fang Xu and Huaiwu Zhang; University of Electronic Science and Technology, Chengdu, China.

Microstructural changes including grain growth and densification in ceramic materials, either through liquid phase sintering or by lowering reaction energy, have a profound effect on the material properties. In this work, Li$_{0.43}$Zn$_{0.27}$Ti$_{0.13}$Fe$_{2.17}$O$_4$ nanoparticles (LZNs) with were prepared by sol-gel method. HRTEM image of the LZNs showed that the spinel structure nanoparticles with ~26 nm average particle size were obtained. As a reaction additive, the LZNs were introduced into a Bi-substituted Li$_{0.43}$Zn$_{0.27}$Ti$_{0.13}$Fe$_{2.17}$O$_4$ (LiZnTiBi) ferrite ceramic to control abnormal grain growth and enhance magnetic properties (sintering temperature is ~920 °C). XRD patterns demonstrated that a pure spinel phase structure composite ceramics were synthesized. This indicated the LZNs can further react with LiZnTiBi ferrite ceramics. Also, SEM images showed that adding LZNs can obviously control abnormal grain growth and reduce pores between grains. More importantly, results of ferromagnetic resonance (FMR) linewidth (ΔH) showed that optimized LZNs additives can reduce ΔH of the LiZnTiBi ceramics. Meanwhile, saturation magnetization (4mM) of the ceramics can be improved by adding moderate LZNs. The doping method reported in this study also provides a referential experience for other low temperature sintering ceramics.

CM01.06.26
Magnetcocaloric Materials Based on Binary and Ternary Mn Compounds—Screening and Testing Joya Cooley1, Joshua D. Bocarsly1,2, Matthew Horton1, Kristin A. Persson1 and Ram Seshadri1,2,5; 1Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, California, United States; 2Materials Department, University of California, Santa Barbara, Santa Barbara, California, United States; 3Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 5Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.

Magnetic refrigeration is accomplished through the magnetocaloric effect (MCE) associated with a reversible temperature change upon application of a magnetic field. The effect originates from cycling materials between two different magnetic states with high and low entropies. In recent decades, this technology has been proposed as an environmentally friendly alternative to traditional vapor-compression technology, obviating the need for chlorofluorocarbon or hydrochlorofluorocarbon refrigerants, and potentially capable of greater efficiency.1,2 The figure of merit for magnetocalorics is the magnetic entropy change (ΔS_M), and it has been recently proposed that compounds with high ΔS_M can be screened using a density functional theory (DFT) based proxy called the magnetic deformation (Σ_M) – a measure of the deformation between relaxed structures with and without spin polarization.3 Several useful Mn-containing binary and ternary compounds have been identified as potential magnetocalorics. We will discuss the synthesis, characterization, and magnetic property measurement of some of these candidate materials.

This research was supported by the National Science Foundation under Grant DMR-1710638. Use of the Shared Experimental Facilities of the Materials Research Science and Engineering Center at UCSB (MRSEC NSF DMR 1720256) is gratefully acknowledged. The UCSB MRSEC is a member of the NSF-supported Materials Research Facilities Network (www.mrfn.org).


CM01.06.27

Refractory ceramics, such as metal carbides, metal nitrides, and metal borides offer superior thermal, electrical, and mechanical properties that significantly outpace metal alloys, oxide-based ceramics, and other comparable materials. The outstanding temperature stabilities (over 3,000 °C) and high hardness (over 30 GPa) of these ceramics and ceramic matrix composites (CMCs), therefore, offer significant promise for ballistic protective armor, industrial tools, and hypersonic engine applications. However, conventional synthesis and composite fabrication methods involve expensive and energy-intensive carbothermal synthesis or sintering that is neither safe nor industrially scalable for mass production. Furthermore, since intrinsic ceramics are brittle and require incorporated reinforcements in order to adequately perform, their processing adds significant engineering complexity and remains poorly optimized for refractory carbides.

We rely on blends of metals and phenolic resins to synthesize near net shape refractory ceramics using a single-step in situ reactive melt infiltration/reaction bonding method in which no pressure is required to compact and densify the composites. The polymer source, which is an inexpensive thermoset with a high char yield and zero oxygen-containing groups, reacts with metals at low temperatures (700 – 1,400 °C) under flowing Ar in a tube furnace and requires 75% less energy input than conventional ceramics synthesis methods. A similar method employs a melamine-rich resin and requires on flowing N₂ to synthesize metal nitride monoliths. To date, our approach has successfully yielded TiC, SiC, Si₃N₄, B₄C, ZrC, ZrN, ZrB₂, and TiB₂ composites in preformed shapes (discs, cones, spheres, etc.). The resulting structures exhibit nanocrystalline grains and high density, and the ceramic monoliths demonstrate high toughness and durability in harsh environments. We reinforce these composites with metals, carbon allotropes, and secondary ceramics in a bottom-up approach in order to enhance their oxidation stability, thermal stress mitigation, and fracture toughness. The resulting customizable and inexpensive refractory composites offer a number of solutions for vital applications in the aerospace, military, transportation, and tooling industries.

SESSION CM01.07: Solid-State Catalysis
Session Chairs: Amy Prieto and Dmitri Talapin
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 203
Water splitting involves the synergistic operation of water oxidation and hydrogen evolution half-reactions and remains a considerable challenge since it requires the concerted transfer of four electrons and four protons. Catalysts that can facilitate both of the half-reactions at low overpotentials are imperative to avoid squandering free energy harvested using a semiconductor in a photoelectrochemical cell, or provided directly in the form of current in a water electrolyzer. Photocatalytic water splitting requires the operation of light harvesting, charge separation, charge transport, and redox catalytic steps that must operate in concert. As such, it is necessary to tune the energetic offsets to establish optimal thermodynamic driving forces for charge transfer. Design and control of interfaces to mediate kinetics of charge transfer. I will discuss the design of compounds with the composition \( \text{M}_n \text{V}_n \text{O}_x \), where \( \text{M} \) is a post-transition metal cation with lone-pairs characterized by intercalative mid-gap states that can accept holes from photoexcited semiconductor quantum dots. Such compounds, accessible through topochemical intercalation of metastable polyoxymetals of \( \text{V}_n \text{O}_x \), have facilitated the design of semiconductor heterostructures with energetic offsets primed to facilitate effective hole transfer upon photoexcitation of the heterostructures, thereby mitigating the longstanding challenge of the anodic photocorrosion of quantum dots. Interfacial design further provides a means of modulating the dynamics of hole transfer, which occurs at \( <1 \) ps timescales. The second half of my talk will focus on discussing the specific electronic structure characteristics of edge sites of MoS\(_2\), that enable them to function as catalysts for the hydrogen evolution reaction. Interfacial hybridization of MoS\(_2\) with n-cistrans provides a means to modulate the electronic structure and enhance catalytic activity. Finally, I will discuss ternary heterostructures that are capable of catalyzing both reactions.

This work was supported by the National Science Foundation under NSF 1627197.

8:30 AM CM01.07.02
Disordered MoTe\(_2\) with Self-Enhanced Catalytic Activity for Hydrogen Evolution
Alexey Ganin and Jessica Meglynn; University of Glasgow, Glasgow, United Kingdom.

Sunlight is widely distributed geographically and provides enough energy in one hour to supply the world’s energy demands for a full year. However, this form of renewable energy is intermittent; thus, current solar energy technologies must be fed into the grid or are otherwise wasted. Recent efforts have therefore been focused on the conversion of excess solar energy into a fuel in the form of hydrogen via water electrolysis. Subsequent oxidation of this hydrogen would allow for the release of energy (and water) without the need for fossil fuels. Due to the diffusivity of solar power, a relatively modest current density of 10 mA cm\(^{-2}\) has been proposed as a benchmark for the comparison of hydrogen evolution reaction (HER) electrocatalysts, which roughly equates to a 10% efficient solar-to-fuels device. \[1\] Layered transition metal dichalcogenides (TMDs) can offer a viable solution for achieving appreciable conversion rates in low currents due to intrinsic and useful feature of any layered material, namely two-dimensionality. \[2\] The 2D nature of TMDs enables a maximum output from the entire surface of a catalyst and allows a simplistic and cheap design of future devices, for example, in form of atomically thin films. A semimetallic 1T\(^-\)-MoTe\(_2\) with the monoclinic structure stands out among chalcogenides of molybdenum due to its remarkable ability to accommodate excess of electrons and thus, presenting an excellent prototype for studies of the role of electrochemical activation on catalytic properties of a 2D material. \[3, 4\] Herein, we report the synthesis, structure and properties of a new disordered MoTe\(_2\) material with self-enhanced catalytic activity for HER that reaches the overpotential value of –187 mV at \( j = 10 \) mA cm\(^{-2}\) after short potential cycling in 1 M H\(_2\)SO\(_4\). The optimisation is coupled with a five-fold increase in turnover frequency and reduced charge transfer resistance as the HER progresses, all while preserving the electrochemically active surface area. By applying a solid state approach to the synthesis of the disordered MoTe\(_2\), we can exclude stoichiometry defects as the cause of the enhanced activity and conclude, in conjunction with electron microscopy, spectroscopy and X-ray diffraction experiments that the improved electrochemical performance is due to the intrinsic activation of the basal plane. The outcome of the studies on optimisation of MoTe\(_2\) thin films using the in operando cycling protocol is discussed as well in connection with how appreciable gains in future energy conversion and storage via HER may be achieved.

References:


8:45 AM CM01.07.03
Faceted Oxide Nanoparticles as Catalyst Supports
Kenneth R. Poeppelmeier\(^1, 2\), Ryan J. Paulf\(^3\), Zachary R. Mansley\(^2\) and Laurence D. Marks\(^2\); Chemistry, Northwestern Univ, Evanston, Illinois, United States; \(^2\)Materials Science & Engineering, Northwestern University, Evanston, Illinois, United States.

Our focus has been on understanding how the metal/oxide interface can modify the activity and selectivity of supported noble metal catalysts. To this end, metal/support interfaces on faceted oxide perovskites have been examined. Specifically, we use the variable strength of interaction between different perovskite oxide supports and noble metal catalysts. Support particles can be produced through sol-gel or hydrothermal methods. Lanthanide scandates (LnScO\(_3\)) were produced through a low-temperature heat treatment of a stoichiometric hydroxide gel in a humid environment.\(^4\) Water vapor was necessary to preserve the higher diffusivity of the gel, but an excess of water vapor led to the formation of secondary phases. The temperature of the reaction was used to tune the Gibb's free energy of reaction and kinetics of particle growth to produce faceted nanoparticles. The lattice parameters of LnScO\(_3\) match well with several noble metals, which allows for a systematic study of how certain support properties (lattice parameter, acidity, etc.) can affect the catalytic performance of these supports. This study synthesizes the way for different surface structures or morphologies to be obtained, which further influence the metal/support interface. Hydrothermal synthesis of SrTiO\(_3\), for example, may produce materials that are controllably terminated with either SrO-rich \(100\),\(^5\) \(\text{TiO}_2\)-rich \(100\), or \(\text{TiO}_2\)-rich \(110\) surfaces.\(^6\) Pt nanoparticles showed a higher selectivity in acrolein hydrogenation towards allyl alcohol when the Winterton shape had a higher ratio of facets to edges or corners, as was the case when supported on SrTiO\(_3\) rather than BaTiO\(_3\), and exploiting the Strong Metal-Support Interaction further improves the selectivity.\(^7\) This library of the different support oxides with controlled surface structure and morphology allows for better control of specific active sites of several noble metals.


9:15 AM CM01.07.04
Electrochemically Driven Non-Congruent Phase Transitions in Ordered Intermetallic Pd-Bi Electro catalysts
Shoji Hall, Du Sun and Yunfei Wang; Johns Hopkins University, Baltimore, Maryland, United States.
The conversion of $\text{O}_2$ to $\text{H}_2\text{O}$ is an important fuel cell reaction for the recovery of renewable electricity from chemical fuels. Alloys of Pt-group metals (PGMs) with transition metals have emerged as catalysts with enhanced activity and durability for the oxygen reduction reaction (ORR). To date, most studies focus exclusively on alloys that adopt a Face-centered cubic (FCC) or Face-centered tetragonal (FCT) crystal lattice. Under ORR operating conditions, these materials evolve from alloys to Pt core-alloy shell materials, in these systems both the alloy core and Pt shell retains the FCC or FCT type crystal structure. Generally, PGM alloys belonging to the lower symmetry FCT structure usually exhibit higher activity than FCC-type alloys of the same composition. However, materials with lower symmetry than FCT crystal structures are not often explored as catalysts, hence there is wide open opportunity to explore new materials.

Here we present the synthesis and interrogation of low-symmetry Pd-Bi based ordered intermetallics for ORR. We found that under ORR operation conditions, $\beta$-Pd$_2$Bi$_3$ (I4/mmm space group) which adopts a tetragonal lattice, transforms to $\alpha$-Pd$_2$Bi (Pnma space group) which adopts an orthorhombic crystal structure; this transformation is mediated by oxidative Bi corrosion under potential cycling. To the best of our knowledge, this is the first report of a material that exhibits an electrochemically driven, non-congruent phase transition among materials with different crystal structures. The resulting phase-converted Pd$_2$Bi is stable and exhibits high performance for ORR. Phase-converted Pd$_2$Bi outperform Pt and Pd metal, reaching mass activities of 2.6 A/mg$_{\text{Pd}}$, which is nearly 10X higher than Pt/C ($-0.3$ A/mg$_{\text{Pt}}$) and Pd/C ($-0.2$ A/mg$_{\text{Pd}}$) at 0.9 V vs the Real Hydrogen Electrode (RHE). The mass activity of Pd$_2$Bi decreases by $-38\%$ after 10,000 cycles, indicating that it is stable. Activation energy ($E_a$) determined by temperature dependent electro-kinetic measurements indicates that the activity enhancement on phase-converted Pd$_2$Bi originates from anion-poisoning resistant behavior. These results establish that PGMs-based ordered intermetallics with low-symmetry crystal structures can be highly active and durable electrocatalysts.
In contrast to oxides, polyoxometalate compounds adopting sophisticated polyhedral structures with a variety of connectivity types and topologies provide a large playground for searching new cathode materials and tuning their electrochemical properties. [1, 2, 3]

We recently designed and synthesized a novel series of vanadium-based AVPO₄F (A = Li, Na, K, Rb) cathode materials adopting the unique KTiOPO₄ (KTP)-type structure using different soft-chemistry approaches including hydrothermal and freeze-drying techniques. The peculiarities of the KTP-type “VPO₄F” framework enabled excellent rate capability particularly demonstrated in Li cells [4]. The material exhibited remarkable capacity retention maintaining more than 75% of the initial specific capacity in Li-ion cells at 40C and an average potential of 4.0 V vs Li/Li⁺. The structural evolution during Li de/intercalation was studied using in-situ synchrotron diffraction and ex-situ electron tomography. The material was found to undergo a sequence of phase transformations with the change of a non-centrosymmetric space group to a centrosymmetric one.

The materials also support reversible intercalation of Na⁺, K⁺ and even Rb⁺ ions maintaining the host structure. The observed electrochemical behaviour and ion transport properties were quite different for Li⁺, Na⁺, K⁺ and Rb⁺ ions. Alkali ion diffusion coefficients measured by PITT were found the lowest for Li⁺ (10⁻¹⁵ – 10⁻¹⁶ cm²/s) and highest for K⁺ (10⁻¹⁴ – 10⁻¹⁴ cm²/s). [5] Moreover, the full de/intercalation of K⁺ in KVOPO₄F occurs at the highest potentials comparing to Li⁺, Na⁺ and Rb⁺ exceeding 4.6 V vs K/K⁺, which states KVOPO₄F as the most high-voltage cathode material for K-ion batteries studied so far. DFT studies revealed extremely low energy barriers for K⁺ and Rb⁺ migration of less than 0.2 eV along the c-axis, which are in accordance with experimentally observed fast ion transport properties.

Thus, the KTP-type “VPO₄F” framework that exhibits an ability to de/intercalate four types of alkali ions opens up new opportunities in designing polyoxometalate cathodes for metal-ion batteries. We will focus on our recent activities on KTP-type fluoride-phosphates considered as promising cathode materials for metal-ion rechargeable batteries.

References:

11:00 AM CM01.07.08
Structural and Physical Properties of Novel Double Perovskites, BaLaBO₆O₅
Andrew Bowser and Corey Thompson; Purdue University, West Lafayette, Indiana, United States.

Double perovskite oxides, A₂BB’O₆ and AA’BB’O₆, are a well-studied set of compounds in solid state chemistry. Their importance in both fundamental and technological research is mainly due to the wide variety of properties they exhibit, and the ability to incorporate nearly any element into their structure. The Ba₂BO₆O₅ compounds have been underexplored until recently, with only limited structural data reported. Interestingly, according to current literature, several of these compounds have been reported to adopt either a hexagonal (P₆₃/mmc or P-3m1) or cubic (Pm-3m) structure, dependent on reaction conditions. Recently, magnetic and physical property studies upon hexagonal-Ba₂Fe₁₋ₓOsₓO₅, synthesized under ambient solid-state conditions have revealed ferrimagnetic behavior with a magnetic ordering temperature of ca. 370 K. Whereas, cubic-Ba₂NiO₅, synthesized under high-pressure show properties of a Dirac–Mott insulator with a magnetic ordering temperature at 100 K. In both these cases, the properties observed can be traced to 3d/5d interactions within the B-site sublattice. We have recently synthesized several novel double perovskite compounds, and their structure and physical properties will be presented.

11:15 AM CM01.07.09
Local Atomic Rearrangement Around the Superconducting CuO₅ Planes Upon Oxidation in the M-1212 Cuprates (M <-> Fe, Mo & W)
Miguel Angel Alario-Franco, Sara Lopez Paz, Xabier Martinez de Irujo and Emilio Moran-Miguelez; Facultad de Quimica, Universidad Complutense, Madrid, Spain.

Superconductivity in cuprates is achieved when holes are doped to an antiferromagnetic Mott insulating parent compound [1]. However, not only a high concentration of holes is required but also an effective charge transfer process from the Charge Reservoir Layer to the superconducting planes [2]. As a result, the critical temperature (Tc) is very sensitive to subtle changes in both local structure and charge distribution between the planes and the charge reservoir block [3].

The M-1212 phases, resulting from total or partial substitution of copper in the chains in the YBCO model compound by other transition metals, are suitable candidates in studying this charge transfer process [4, 5]. In this communication we will present the effect of iron, molybdenum and tungsten substitutions, resulting in Fe-1212, Mo-1212 & W-1212 phases with FeSr₂YCu₂O₇, Mo₀.₃Cu₀.₇Sr₂RECu₂O₇ and W₀.₂Cu₀.₈Sr₂YCu₂O₇ compositions. We have studied the subtle influence of charge balance and compositional order/disorder in both the anion and cation sub-lattices. Besides, we have explored the local atomic rearrangement around the superconducting CuO₅ planes as a function of the oxidation treatment. The ensemble of these results will be presented and discussed.

This work has been supported by REE with Project No. REE: 44-2014, Fundación Ramón Areces, by MINECO with Projects MAT2016-78362-C4-4-R and by CM with Project MATERVENER3CM-S2013/MIT-2753. X.

References:
2. M. Magnuson et al., Scientific Reports 4, 7017 (2014)

11:30 AM CM01.07.10
Improving Charge Transport Properties of Oxide-Based Photoelectrodes for Use in Solar Water Splitting

Among various semiconductor electrodes (photoelectrodes) that have been investigated for solar fuel production, oxide-based photoelectrodes have the possibility of significantly lowering the materials processing costs while also being more stable in aqueous media. However, oxide-based photoelectrodes...
Understanding Metallicity and Magnetism in theories based only on nearest-neighbor interlayer coupling, they compel a closer look at effective second-nearest-neighbor interactions, mediated by


The structural versatility of the tetrahedral vanadate (VO4)3− bridging group provides the opportunity to systematically examine a wide range of low-dimensional magnetic systems with a broad assortment of spin values. The structural and magnetic properties of several novel layered magnetically frustrated manganese vanadate systems will be discussed. Magnetic lattices with mixed corner-sharing and edge-sharing triangular units have recently been found in K2Mn3(VO4)2(OH)2, Mn5(VO4)2(OH)4 and Mn5VO8. The arrangement of triangular [MnO13] building blocks in K2Mn3(VO4)2(OH)2 create a Kagome strip lattice. Mn5(VO4)2(OH)4 contains two unique triangular [MnO13] units formed by the presence of the additional Mn atom, such that every other row of hexagons has an additional Mn atom in the center of each hexagon creating two-dimensional striped triangular lattices. The structure of Mn5VO8 differs from the other two structures, by containing Mn in two valence states 2+ and 3+ distributed over two types of magnetic layers that are alternately stacked in the crystal structure. One layer contains Mn2+ in a Kagome strip lattice and the other contained a mixture of Mn2+ and Mn3+ that form a triangular lattice. For all these systems, neutron diffraction measurements revealed the onset of very complex antiferromagnetic orderings, while inelastic measurements, and density functional theory calculations of structural, electronic, and magnetic ground states. We examine the interplay between electronic properties. Some materials in this family undergo metal-insulator transitions and others host exotic magnetic spin textures such as skyrmions. These properties can be related to clustering of the magnetic moments in the honeycomb sublattice, that become crucial at finite-temperatures and intermediate fields.

The family of ABQn compounds, where A is Al, Ga, or Ge, B is an early transition metal like V, Mo, or Ta, and Q is a chalcogen like S or Se have been studied since the 1970s. They crystallize at room temperature in the F–4m defect spinel structure and display a fascinating array of magnetic and electronic properties. Some materials in this family undergo metal-insulator transitions and others host exotic magnetic spin textures such as skyrmions. These properties can be related to clustering of the B-site atom, crystalline anisotropy, and the electronic correlations present. We study two of these materials, GaVS4 and GaMoS4Se6, using a combination of experimental techniques including high-resolution X-ray diffraction and magnetic measurements, and density functional theory calculations of structural, electronic, and magnetic ground states. We examine the interplay between electronic structure, crystal structure, and magnetic/electronic properties in these systems and develop insights into chemical tuning to optimize functionality.

This research was supported by the National Science Foundation under DMREF Award 1729489. Use of the Shared Experimental Facilities of the Materials Research Science and Engineering Center at UCSB (MRSEC NSF DMR 1720256) is gratefully acknowledged. The UCSB MRSEC is a member of the NSF-supported Materials Research Facilities Network (www.mrfn.org).

References:

4. J. A. Santana-Palacio, K. Kayahan, S. A. Mishra, A. Albina Borisevich, S. Sokrates Pantelides, P. Kent, F. Rebrodo, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee, United States; Department of Chemistry, University of Puerto Rico at Cayey, Cayey, Puerto Rico, United States; Department of Mechanical Engineering and Materials Science, Washington University in St. Louis, Missouri, United States.

Strong electronic correlations, interfaces, defects, and disorder can individually challenge the theoretical methods for predictions of materials properties.
These challenges are all simultaneously present in complex transition-metal-oxides (TMOs). TMO’s interfaces and superlattices are known to exhibit unique electronic properties caused by multiple coupled degrees of freedom and strong electronic correlations. The computational treatment of TMOs remains an outstanding challenge due to the multivalent character of the metal components and the predominant role played by many-body effects (electronic correlations). This challenge is increased at TMO interfaces and superlattices, where the transition-metal ion valence varies sharply. Computational costs drive TMOs out of reach of conventional quantum chemistry methods. On the other hand, the commonly used Density Functional Theory (DFT) approximations, e.g., Local Density (LDA) and semilocal Generalized Gradient (GGA), are not sufficiently accurate and transferable to account for all experimental observations without adjustable parameters. We show [1] that a fundamentally different approach, ab initio diffusion Monte Carlo (DMC), is now a practical solution of the many-electron problem for the full complexity of these systems. Within a single nonempirical theoretical approach, we unambiguously establish the site-specific stability of oxygen vacancies in the (LaFeO3)2/(SrFeO3) superlattice, accounting for experimental data, and predict their migration pathways. In addition, we will describe a number DMC calculations which are currently capable of playing a major role in the elucidation of many-body phenomena complex oxides previously out of reach of theories without adjustable parameters.

Nitride Tuning of Transition Metal Perovskites

Amparo Fuertes; Institute of Materials Science of Barcelona (ICMAB-CSIC), Bellaterra, Spain.

Substitution of nitride for oxide anions is an important method for tuning materials properties in transition metal perovskites, for example, Ca$_x$La$_{1-x}$TaO$_3$, Ca$_x$Ni$_{1-x}$Fe$_2$O$_4$, Ca$_x$F$_{30-x}$Ti$_{42}$O$_{120}$, Sr$_2$FeWO$_6$, Sr$_2$FeWO$_5$N, Eu$_x$Bi$_{2-x}$O$_3$, and Eu$_x$Bi$_{2-x}$O$_3$N. Colossal magnetoresistance (CMR) is one of the main characteristics of CMR materials. However, CMR is not always observed in materials containing metal-oxide nitride substitutions. This paper presents recent research of selected perovskite oxynitrides focusing on the relationships between the synthesis conditions, the oxidation states of the metals, the nitrogen content, the ordering of anions, and the physical properties.

References


Camilo01.09.01

Growth Mechanisms of α-Fe$_2$O$_3$ Nanocubes and Their Influence on Magnetic Properties

Gabriel D. Rocha$^1$, Marcello A. Martínho$^2$, Marco A. Cordeiro$^3$ and Edson R. Leite$^4$; 1Materials Engineering Department, UFSCar, São Carlos, Brazil; 2Chemistry Departament, UFSCar, São Carlos, Brazil; 3LNANO, Campinas, Brazil.

One of the main branches of nanoscience deals with the tailoring of nanoparticles (NPs) shape (e.g., spheres, octahedra, cuboctahedra, cubic structures) due to the possibility of tuning several properties as electrical, optical and magnetic. Likewise, hematite (α-Fe$_2$O$_3$) NPs have a series of fascinating polyhedral structures, which magnetic properties are ruled by NP shape and size, finding fundamental applications in many fields including ferrofluid technology, biomedicine, catalysis and magnetic storage. Accordingly, in this study we provide some insights into the growth process of hematite NCs in the colloidal state, as well as the parameters that affect crystal growth and morphology, which are essential for designing new hematite-based nanostructured functional materials. Many shape and size oleate-capped α-Fe$_2$O$_3$ NPs were synthesized by hydrothermal route under microwave heating. By fine-tuning the amount of surfactant (sodium oleate) and reaction time (450 min), three main structures: spheres, polyhedral, and cubic-like shapes were identified by high-resolution transmission electron microscopy (HRTEM). According to HRTEM observations, the proposed mechanism for the formation of cube-like NPs from spheres is based on a three-step growth process, with the initial formation of a seed or nucleus, and then sphere particles (~7 nm). With the progress of the synthesis, those spheres grow under the oleate groups action and polyhedral NPs are obtained (~12 nm). The second part of the growth mechanism is the oriented attachment of polyhedral NPs, mainly by the coupling of graphite exposed facets, resulting in diamond-like shapes (25-30 nm). Although it was possible to identify many oriented attachments in progress by HRTEM, these structures were only found in a small-time gap (20-25 min of synthesis). Finally, the diamond-like NPs reshape, resulting in the formation of a cubic shape, with small size increasing from monomers in solution. According to the particle shape evolution, we also investigated the dependence of magnetic properties by using a superconducting quantum interference device (SQUID) that revealed the role of NPs shape and size in the magnetic properties of the α-Fe$_2$O$_3$NPs. This knowledge provides fundamental improvements in chemical preparation protocols for the reproducible production of NCs with specific properties and high yields.
until 1% w/w. A secondary phase of FeSbO$_4$ (PDF#74-4588) was indexed from 2% w/w on. For the samples sintered at 1300 °C, the solubility was reached until 4% w/w, and the 5% w/w concentration shows that the secondary phase was also indexed as FeSbO$_4$. SEM analysis show that average grain sizes are 2 µm for 1100 °C and 30 µm for 1300 °C. Electrical measurements were performed after the electroceramics were heat treated in N$_2$ atmosphere at 850 °C by 20 minutes. The results show that for 1100 °C, resistivity reaches $10^5$ Ω cm, while for the higher temperature, it lowers by 2 orders of magnitude. These results suggest that possibly the reaction between the precursor oxides is facilitated at higher temperatures, which favor the electrical properties of hematite. The resistivity values found are comparable with those obtained with Sn-doped hematite, therefore showing the potential of Sb as a dopant.

CM01.09.03
Solventless Synthesis of Copper Antimony Sulfide Materials from Reactive Melts of Metal Xanthate Precursors Tahani Alqahtani, David J. Lewis and Paul O'Brien; University of Manchester, Manchester, United Kingdom.

In recent years, ternary copper antimony sulfides show considerable promise as alternative absorber materials for cost-efficient and scalable photovoltaics due to their high absorption coefficients, optimum band gap and consist of cheap, low-toxicity and earth-abundant elements. The Cu-Sb-S system exist in four ternary phases, which are Cu$_2$Sb$_3$ (chalcostibite), C$_3$Sb$_4$S$_3$ (tetrathedrite), Cu$_3$Sb$_5$S$_7$ (skinnerite) and Cu$_5$Sb$_5$S$_7$ (fematinite). Chalcostibite has been considered as an alternative absorber to the CuInS$_2$ because of the comparable optical properties required for solar absorber materials, with the advantage that antimony is earth-abundant element and less expensive than indium.

Tetrathedrite has been recently attracted a huge amount of attention due to its potential for energy conversion applications. It is highly suitable for thermoelectric materials because of its unique feature in its crystal structure as it has naturally low lattice thermal conductivity. Furthermore, it is an attractive candidate for solar absorber materials as it displays strong absorption in wide spectral range. Partially substituting on the copper, antimony and chalcogen sites has been an active area of research to optimize the thermoelectric properties. These dopants could lead to additional and interesting optical and magnetic properties.

This work, we report a facile simple solvent-less route for the preparation of chalcostibite and tetrathedrite nanostructure phases using metal xanthates. One feature of this approach is the absence of a solvent, which gives the melt route a potential/environmental and economic advantage as compared to other solution-phase routes. The use of metal xanthates is advantageous because they already contain the sulfur required for the preparation of the metal sulfide. Another important advantage of metal xanthates is that they have low decomposition temperature and the by-products of the decomposition are volatile, allowing the clean formation of Cu-Sb-S materials using mild temperature without impurities. The compositions of the obtained materials were adjusted by varying the molar ratio of the copper and antimony xanthate precursors. In addition, zinc and bismuth xanthates were also used for the preparation of the Zn and Bi-v-doped tetrathedrite.

The results obtained from XRD indicate that the solventless pyrolysis of the metal xanthates is advantageous in that it has demonstrated successful formation of the single-phase chalcostibite and tetrathedrite of high purity in short time of amount. Furthermore, incorporation of dopants into the tetrathedrite crystal structure has shown to form the pure phase of tetrathedrite. As the dopant content increase in the samples, the diffraction peaks gradually shifted toward lower angle. The lattice parameter increases linearly with increasing the dopants content in the samples. In addition, the morphology, composition and optical properties of the obtained Cu-Sb-S nanomaterials were also investigated.

CM01.09.04
Multimodal Chemical and Functional Imaging of Materials via Combined AFM/ToF-SIMS Platform Anton V. Ievlev, Matthias Lorenz and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Polarization switching in ferroelectric materials underpins a broad gamut of applications ranging from random access memory, tunneling barriers, data storage, and ferroelectric ceramics. Classically, the polarization switches due to a co-existence of energetically equivalent crystallographic states, that can be altered with an external electric field. To stabilize polarization, charge discontinuity at surfaces and interfaces requires compensation, or screening, to avoid long-range electrostatic fields that destabilize the ferroelectric phase. Most studies consider polarization screening to be chemically inert; leaving the composition of the ferroelectric intact. However, analysis of extant ferroelectric phenomena suggests higher complexity. It is well known that multiple polarization switching cycles can accumulate damage at interfaces, dubbed “ferroelectric fatigue.” Typically, tens or hundreds of thousands switching events are required, and the exact mechanisms remain controversial. Furthermore, polarization-dependent photovoltaic effects in perovskites suggest that even under optimal screening conditions a considerable electric field remains in the material. Thus, switching is associated with high fields, which can chemically alter material composition.

Here we utilize multimodal approach combining time of flight secondary ion mass spectrometry (ToF-SIMS) with atomic force microscopy (AFM) to explore the structure property interplay of ferroelectrics during polarization switching in lead zirconate titanate (PZT, Pb$_2$TiO$_3$) thin films. Using this multimodal imaging platform, we demonstrated that chemical phenomena plays significant role in ferroelectric switching process. Specifically, we found that local ferroelectric switching by the AFM tip, significantly alters the chemical composition in the 3-nm-thick surface layer of the sample, forming reversible concentration wave, of Pb$^+$ ions. Furthermore, investigations of the polarization cycling in the PZT sample with copper electrodes, showed penetration of the copper cations into the structure of PZT. This explains ferroelectric fatigue phenomenon, leading to decrease in spontaneous polarization with sample cycling.

Altogether, explored chemical phenomena associated with ferroelectric switching will enhance fundamental understanding of ferroelectric phenomena and aid in the practical application of ferroelectrics in devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and using instrumentation within ORNL’s Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

CM01.09.05
Magnetic Properties of Novel Tellurides, Tl$_{1-x}$A$_x$Fe$_3$Te$_3$ Robert Compton and Corey Thompson; Purdue University, West Lafayette, Indiana, United States.

Materials with a pronounced magnetocaloric effect (MCE) are promising candidates for magnetic refrigeration technology. The intermetallic TlFe$_2$Te$_3$ phase has several characteristics that make it an ideal system to study. These include a moderate MCE at near room transition temperature (T$_m$ = 220 K), low thermal and magnetic hysteresis, and a low dimensional structure consisting of pseudo-1D chains composed of iron telluride clusters. To become commercially feasible, replacement of thallium with non-toxic elements and a higher magnetic ordering temperature (>300 K) are desirable. Partial substitutions of earth-abundant alkali metals for thallium have been successful. These substitutions have a substantial effect on the magnetic properties, which can be tuned based on the choice of alkali metal. Their interesting structural and magnetic properties will be presented.

CM01.09.06
Study the Synthesis, Crystalline Structure, Morphology and Magnetic Properties in the Ba$_x$Bi$_{1-x}$O$_3$-$V_2$O$_5$ and SnO$_2$-$MgO$-$Sb_2$O$_3$ Systems Elizabeth Chavira$^1$, Jose Hurtado$^{1,2}$, Jorge Barreto$^3$, Jesús Aenas$^3$, Roberto Sato$^3$, Adriana Tejeda$^2$, Joséh Esaú Romero-Ibarra$^2$, Omar Novelo$^2$ and Karla Eriseth$^2$.
Our interest is to study the thermodynamic properties on two systems of oxide materials to reproduce the $\text{Sn}_x\text{SbTe}_5\text{Ba}_2\text{Y}_2\text{Mg}_2\text{O}_{26}$ and $\text{Sn}_x\text{SbTe}_5\text{Ba}_2\text{Y}_2\text{Mg}_2\text{O}_{26}$ superconductors reported in the web site www.superconductors.org.

The two systems $\text{Ba}_2\text{Mg}_2\text{O}_3$ and $\text{Sn}_2\text{O}_3\text{Mg}_2\text{O}_3$, were synthesized, by solid-state reaction at 880°C. It is observed the formation of ternary and binary phases after reaction. Powder X-ray diffraction (XRD) was used to identify those phases.

Thermal Analysis characterization was used to know on what range of temperatures the reaction could occur.

One way to study the thermodynamic properties was the comparison of reaction into a high-alumina (A1O3) crucible, because implies a slow cooling, with the reaction into a Platinum crucible cooled into an ice bath. When the cooling of the products is made into an ice bath (4°C media), a different effect from the air (for the alumina crucible) in the formation of crystalline phases is observed, having a wider range of different crystalline phases in the case a high alumina crucible. The cooling velocity effect was observed in the x-ray diffractograms; for the products cooled in ice bath, some displacements of the experimental x-ray patterns related to the powder diffraction files (PDF) were observed, and in the case of the alumina crucibles, results were aligned with PDF files. For the case of the platinum crucible, an isostructural compound related with $\text{Ba}_2\text{Mg}_2\text{O}_3$ structure was obtained; also, the formation of an isostructural solid solution (Sc:SbO3) in the planes: (110), (101), (200), (111), (210), (211), (220), (002) and (112), with rutile type structure. Due to the size of the ionic radii of $\text{Sc}^{3+}$ and $\text{Sb}^{3+}$ a cationic substitution of $\text{Sc}$ by $\text{Sb}$ forms the solid solution. Cooling rate had a great effect in the stability of the solid solution since when the samples were cooled into the high alumina crucibles this phase disappeared by the lack of conditions to its stability.

A magnetic characterization helped to know the behavior of the system, so the reaction products cooled into the ice bath were studied with an SQUID.

The samples cooled into the ice bath were analyzed by Raman spectroscopy to know the oxidation states and the coordination number of the atoms involved in the solid solution.

A variation of composition for the system $\text{Sn}_x\text{Mg}_2\text{O}_3\text{Sb}_2\text{O}_3$ was studied too, $\text{Sn}_x\text{Mg}_2\text{Sb}_2\text{O}_5$. Two compositions were used, x = 0.15 and x = 0.20. XRD was performed to characterize the products and a thermal analysis.

Changes in weight were found during the reaction period. After XRD, a change in the oxidation state of $\text{Sb}$. An oxide phase formed between $\text{Sb}$ and $\text{Mg}$ ions was found, $\text{MgSb}_2\text{O}_5$, with other antimony oxide ($\text{Sb}_2\text{O}_3$), in both cases. The increase in weight is due to the change in the oxidation state of $\text{Sb}$ and to an amount of oxygen entered to the system. Thermal analysis detected the total change in weight.

CM01.09.08
Temperature Dependence of the Ionic Conduction in the Dy$_{3-x}$Sc$_x$TaO$_7$ (0 < x < 0.2) Solid Solution Jesús E. Ortega, Jesús Arenas, Gustavo Tavízón and José Francisco Gómez; Universidad Nacional Autónoma de Mexico, Ciudad de Mexico, Mexico.

The defect fluorite related crystal structures poses a very wide variety of interesting properties, like structural and electronic [1], some compounds with this crystal structure are ionic conductors. The recent interest in novel ionic conductor materials has been increased in recent years due the development of new devices for some applications like gas sensors or in electronic industry. The novel polycrystalline solid solution Dy$_{3-x}$Sc$_x$TaO$_7$ (0 ≤ x ≤ 0.15) was obtained by standard solid state reaction technique and single-phase compositions formation were confirmed by X-ray diffraction studies. Structural characterization of compounds was made using Rietveld refinements. The electrical measurements were carried out using complex impedance spectroscopy in a wide range of frequencies (102 – 107 Hz) in the 250 °C – 650 °C temperature range, also the electrical measurements were carried out in dc experiments to compare the data. The impedance spectra were modeled using equivalent circuits and the dc conductivity shows an Arrhenius-type behavior. The frequency dependence of the ac conductivity obeys the Jonscher universal power law[2]. The results of the activation energy values obtained for the ac measurements and the behavior of the critical exponent show that the mechanism of electrical conduction is ionic and the charge carrier is the (O2-) oxygen ion. Also, we have found two temperature regions of ionic conduction, the intrinsic and the extrinsic region, differentiate by a change in the activation energy and the critical exponent value.

References:

CM01.09.09
Effect of Cl on the Hydroxylated CrO$_{3}$ Protective Layer of Stainless Steel Kofi Oware Sarfo1, Pratik V. Murkute1, Julie D. Tucker1, Linsey Arnadottir1, Burkan Isgor1 and Yongfeng Zhang2; 1Oregon State University, Corvallis, Oregon, United States; 2Idaho National Lab, Idaho falls, Idaho, United States.

The stainless steel is important materials for nuclear industry applications and is extensively used in light water reactor systems (LWR). The corrosion resistance of stainless steel is attributed to presence of chromium which segregates to the surface to form Cr$_{2}$O$_3$, a strong passive layer that provides corrosion protection for the material. Understanding the surface chemistries of these oxide layers in different conditions provides an essential insight into the stability of these protective layers. Chlorides and other aggressive ions are often part of the water chemistry surrounding stainless steel, but these ions can lead to a breakdown and loss of passivity. In this work, we used density functional theory (DFT) to examine the interactions of chlorine (Cl) and adsorbed water on Cr$_{2}$O$_3$. The work is intended to provide models of the Cr$_{2}$O$_3$ surface in the presence of Cl. Structural and electronic properties of the Cr$_{2}$O$_3$ terminated surfaces but do not affect the order of the most to least stable configurations. However, the inclusion of implicit water decreases the Cl-interactions with the O-terminated surface. This is because the O-terminated surface is slightly more stabilized by the implicit solvent than the Cr and Cr-O terminations. Theoretical and experimental studies suggest this can be modeled using equivalent circuits and the dc conductivity shows an Arrhenius-type behavior. The frequency dependence of the ac conductivity obeys the Jonscher universal power law[2]. The results of the activation energy values obtained for the de measurements and the behavior of the critical exponent show that the mechanism of electrical conduction is ionic and the charge carrier is the (O2-) oxygen ion. Also, we have found two temperature regions of ionic conduction, the intrinsic and the extrinsic region, differentiate by a change in the activation energy and the critical exponent value.

References:

CM01.09.10
Sintering Behavior, Microstructure and Microwave Dielectric Properties of Novel Temperature Stable Li$_3$Mg$_2$NbO$_8$-TiO$_2$ Composite Ceramics Gang Wang and Huaiwu Zhang; State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China.

A novel series of temperature stable Li$_3$Mg$_2$NbO$_8$-xTiO$_2$ ceramics were prepared by the conventional solid-state route. The effects of TiO$_2$ addition on the sintering behavior, phase composition, microstructure and microwave dielectric properties were investigated systematically. The dense microstructure could be obtained in low TiO$_2$ content (x=0.1) samples sintered at 1100 °C. The dielectric constant $\varepsilon_r$ was attributed to the bulk density and TiO$_2$ content.
The variation in $Q \times f$ values is related to the bulk density, and improved $Q \times f$ values could be obtained for Li$_3$Mg$_2$NbO$_6$–0.1TiO$_2$ ceramics. The quality factor $Q$ had a maximum for $x = 0.1$ and the resonant frequency ($f$) value shifted towards positive direction with the increase of TiO$_2$ addition. Notably, Li$_3$Mg$_2$NbO$_6$–0.1TiO$_2$ ceramics sintered at 1100 °C possessed excellent microwave dielectric properties: $Q \times f = 74,000$ GHz, $T_e = -3.4$ ppm/°C, which made the ceramics as promising low loss and temperature stable candidates for millimeter-wave applications.

CM01.09.11

Ternary Vanadium Oxide Bronzes as a Palette for Imagining Metastable Cathode Materials with Improved Multivalent-Ion Storage Capacities

Justin L. Andrews and Sarbajit Banerjee; Texas A&M University, College Station, Texas, United States.

The discovery and investigation of metastable materials has only sparsely sampled the available design space. In this contribution, we explore a systematic approach to identifying metastable phases of interest in the vanadium-oxygen system. In particular, we report on the successful stabilization of several novel polymorphs and discuss their subsequent utilization as cathode materials in Li- and multivalent-ion batteries. A detailed elucidation of structure-function relationships that underpin their much-improved performance over the thermodynamically stable sink of the system, $\alpha$-V$_2$O$_5$, has been performed based on structural characterization, elucidation of electronic structure, and first-principles calculations of diffusion pathways. The first example, $\zeta$-V$_2$O$_5$, can be topochromically stabilized from the ternary quasi-1D $\beta$-M$_n$V$_2$O$_6$ tunnel bronze and has been demonstrated to be far superior to its thermodynamically stable counterpart as a cathode material in both Li- and Mg-ion batteries. In particular, metastable $\zeta$-V$_2$O$_5$ overcomes several challenges associated with $\alpha$-V$_2$O$_5$, mitigating irreversible structural transitions and polaronic confinement effects that are a severe constraint on electrode applications of the thermodynamically stable phase. Mitigating these challenges allows for the unprecedented, fully reversible insertion of up to 3 Li$^+$ per V$_2$O$_5$ as well as the highly reversible insertion of 0.33 Mg per V$_2$O$_5$ at moderately high operating voltages. In a second example, metastable $\gamma$-V$_2$O$_5$ can be stabilized from the ternary $\gamma$-Li$_2$V$_2$O$_6$ phase and shows promising initial results as a cathode in both aqueous and non-aqueous Mg- and Ca-ion batteries. The role of metastability is central to explaining the improved performance of these metastable polymorphs and thereby insight gleaned from a fundamental evaluation of the origins of this behavior provides a glimpse into the importance of structure-function relationships and crystal structure motifs as they relate to metastability, further establishing the potential use of metastable materials as synths for accessing undereexplored compositional space.

CM01.09.12

Interfacial Oxidation and the Photoluminescence of InP-Based Core/Shell Quantum Dots

Michaël Tessier2, Edwin Baquero1, Dorian Dupont1, Valeria Grigel1, Yannick Coppél1, Zeger Hens2, Céline Naryal1 and Fabien Delpech1; 1Laboratory of Physics and Chemistry of Nano-Objects, INSA Toulouse, Toulouse, France; 2Ghent University, Ghent, Belgium; 3Laboratoire de Chimie de Coordination, Toulouse, France.

CdSe based QDs have been intensively studied, however, due to their toxicity Cd-based materials are not acceptable for real-life applications. Indium phosphide (InP) based QDs represent the most advanced alternative without toxic heavy metals. Nevertheless, for industrial applications, the photoluminescence quantum yield (PLQY) and the emission linewidth (FWHM) of InP QDs have to be significantly improved. The analysis of InP specificities shows that in contrast to their CdSe analogues, the InP QDs suffers from a high oxophilicity. This leads a strong tendency to oxidize and results in the formation of an amorphous phosphate layer at the surface of the InP QDs either during the synthesis or the shelling (often with ZnS). The role and the influence of this oxidation on the optical properties (PLQY and FWHM) is still a matter of controversy and the definitive answer has so far been precluded because of the lack synthesis method allowing the access to comparable oxide-free samples. In this presentation, we will describe our new approach to prepare oxide-free InP core and InP/ZnS core/shell QDs. Then, we will compare the structural (using XRD, TEM, MAS NMR) and the optical properties (UV-Vis and PL) of oxidized vs. oxide-free samples. The use of the same InP QDs core for the preparation of the samples provides fully comparable data and will thus allow unraveling for the first time the influence of phosphate at the core/shell interface.

CM01.09.13

Characterization of Crystalline Defects Studied by STEM-in-SEM

Chunyang Zhang1, Jean-Claude Menard2, Julien Guyon1, Jean-Jacques Fundenberger1, Yudong Zhang1, Emmanuel Bouzy1, Cécile Hébert4 and Antoine Guitton1; 1Université de Lorraine, CNRS, Arts et Métiers ParisTech, Metz, France; 2AHEAD Microscopy, Bois d’Arcy, France; 3Labex Damas, Université de Lorraine, Metz, France; 4EPFL-LSME, Lausanne, Switzerland.

Mechanical tests followed by microstructural investigations provide engineers information to computationally predict the mechanical performance of components. Electron microscopy is one of the most well-known techniques for analyzing deformation features of materials allowing understanding their response to exterior solicitations [1]. Two kinds of electron microscopes are generally used and bring complementary information: at macro/meso-scopic scale, Scanning Electron Microscopy (SEM) and at micro/nano-scale, Transmission Electron Microscopy (TEM) [2,3]. Weak Beam Dark Field (WDBF) is a TEM techniques allowing fine characterization of dislocations [4]. Such comprehensive dislocation studies at microscopic scale bring valuable information for understanding macroscopic mechanical response of materials [5]. Full characterization of dislocations is not only synonym of TEM experiments. SEM can access diffraction contrast with Scanning Transmission Electron Microscopy in a SEM (STEM-in-SEM). Briefly, this technique is based on the classical STEM (in a TEM) [6]; the electron beam is scanned and diffraction contrast allows observing defects. Diffraction patterns are acquired from domains below 10 nm in diameter [7]. In this framework, we report here technological challenges such as detector development and sample holder design will be presented. Moreover, first dislocation analyses, which clearly show the full potentialities of this new characterization technique will be discussed.

References:

CM01.09.14

Computationally Aided Discovery of Layered Quinarian Oxyselenoginide P-Type Transparent Conductors

Benjamin A. Williamson3, 2, Gregory J. Limburn1, Geoffrey Hyett1 and David O. Scanlon1, 2, 4; 1Department of Chemistry, University College London, London, United Kingdom; 2Thomas Young University College London, London, United Kingdom; 3Department of Chemistry, University of Southampton, Southampton, United Kingdom; 4Diamond Light Source Ltd., Diamond House, Didcot, United Kingdom.

Despite the major advances in n-type transparent conducting oxides (TCOs), the scarcity and performance of an equivalent p-type TCO has been a stumbling block for the opto-electronics industry for decades. Solid design principles such as the ‘chemical modulation of the valence band’, where the Cu
Composite materials usually exhibit the combined physical properties of their constituents. The result is a material that is superior to conventional monolithic materials. Advanced composites are used in a variety of industrial applications and therefore attract much scientific interest. Here we report on the formation of novel carbon-based nanocomposites via incorporation of graphene oxide (GO) into the crystal lattice of single crystals of calcite (1). Incorporation of a 2D organic material into single-crystal lattices has never before been reported. The resulting nanocomposites were characterized utilizing state-of-the-art characterization techniques such as high-resolution synchrotron powder X-ray diffraction, electron microscopy, aberration corrected high resolution transmission electron microscopy, fluorescence microscopy and nanoindentation tests. Our results show that GO sheets can indeed become incorporated into calcite single crystalline hosts, allowing for the fabrication of graphene-based composite materials with enhanced properties. A detailed analysis reveals a layered distribution of GO sheets entrapped within the calcite host. Moreover, the optical and mechanical properties of the calcite host are altered when a carbon-based nanomaterial is introduced into its lattice. Carbon-based calcite single crystals exhibit new optical properties: in contrast to pure calcite, the hybrid crystals become fluorescent and are spectroscopically characterized by the presence of three lifetimes, one of which is considerably longer than that observed for bare GO in solution. Nanoindentation tests demonstrated that relative to pure calcite the composite GO/calcite crystals exhibit lower elastic modulus and higher hardness.

The results of this study demonstrate that the incorporation of a 2D material within a 3D crystalline lattice is not only feasible but can also lead to the formation of hybrid crystals exhibiting novel properties.


Carbon-Based Nanocomposites—2D Organic Materials within a 3D Lattice Iryna Polishchuk: Materials Science and Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

CM01.09.15


CM01.09.16

Cationic Impurities Modifications of Mayenite Nanocages—Interpretations from DFT Calculations Jian Huang1,1, Loredana Valenzano2 and Gaurav Sant3, 1Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; 2Department of Chemistry, Michigan Technological University, Houghton, Michigan, United States; 3Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Mayenite (i.e., Ca12Al4O33, C12A7), and more specifically its electrode form (C12A7-e-) has attracted attention as a functional material which shows high ionic conductivity, and for its potential in oxidation catalysts, fuel cells, and hydrogen storage. In contrast to anionic substitutions into C12A7, less is known about the effects of cationic substitutions on the properties of C12A7. This study applies DFT methods to rigorously understand the influences of Mg2+, Cu2+, Sr2+, Fe3+, Ir4+, P5+ and V5+ impurities on the structural and electronic features of C12A7 and its electrode variant. Broadly, the presence of impurities and their relation to their ionic radii are noted to influence the lattice parameters and altering charge localization. Impurities also effect mayenite’s cage framework with a major influence in the ‘window’ connecting two adjacent cages. Since the cage conduction band (CCB) depends are related to the presence of framework’s electrons changes into the ‘window’ is considered as a critical factor able to influence conductivity. Different dopants can differently influence the behavior of the trapped anionic electrons. While Mg2+, Sr2+, P5+ and V5+ impurities can still maintain their F+-like attractors nature, Cu2+, Fe3+ and Ir4+ neutralize such a tendency in the cages of electrode. This corresponds to change the conduction mechanism of electrode mayenite from that of hopping electrons to that of band conduction electrons. In other words, the s-electrons are now diffuse over the cages. Interestingly, the insertion of Cu-impurities results in the ‘window’ between two cages to collapse and inducing the formation of a transport channel between two neighboring (Ca-Al-O) cages across the localized interstitial electrons. Such an observation is confirmed by the analysis of electron-localization functions (ELF), procrystal, and non-covalent interactions (NCI) indices. This suggests new means to induce electron coupling between nearest neighbor cages. This last aspect is of particular interest for the engineering of electronic transport properties of mayenite-like electrodes.

The authors acknowledge full financial support for this research provisioned by the University of California, Los Angeles (UCLA) and National Science Foundation (CAREER Award #: 1253269). Access to computational resources was provisioned by: (a) the Laboratory for the Chemistry of Construction Materials (LC2), (b) the Institute for Digital Research and Education (IDRE) at UCLA and (c) the Extreme Science and Engineering Discovery Environment (XSEDE) supported by the National Science Foundation (OCI-1053575 and DMR-130039).

CM01.09.17

Synthesis, Characterization and Magnetic Behavior of α-Fe2O3 and α-Cr2O3 Nanoparticles and Their Composites with Graphite, Graphene and Graphene Oxide—Memory and Exchange Bias Effects Paloma Almodovar1, Carlos Diaz-Guerra1, Julio Ramirez Castellanos2 and José María González Calbet2, 1Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Ciudad Universitaria, Madrid, Spain; 2Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, Madrid, Spain.

Nanocomposites of transition metal oxides with graphene or graphene oxide (GO) have recently received much attention for applications in Li ion batteries (LIBs), supercapacitors, solar cells and photocatalysis. The development of such applications requires new strategies to synthesize these nanocomposites and a detailed characterization of their physicochemical properties. Hematite (α-Fe2O3) is a widely studied semiconductor because of its availability, low environmental impact and corrosion resistance. Cr2O3 is a wide band gap (~3.2 eV) semiconductor with potential uses in LIBs, optical, electronic and magnetic devices. Due to its high specific surface area and electrical conductivity, graphene appears to be an ideal adjuvant for α-Fe2O3 and Cr2O3 to improve their capacity and cycling stability in LIBs anodes.

In this work, α-Fe2O3 and Cr2O3 nanoparticles and their composites with graphite, graphene and GO, were synthesized by a wet chemistry method of hydroxide precipitation at low temperature. The morphology, structure, composition and electronic properties of the samples were investigated by X-ray
Effects of Excess Electrons on the Structure of BiVO₄

As-grown α-Fe₂O₃ nanoparticles show a good crystallinity and an average size of 5 nm, as revealed by HRTEM. Raman and XRD measurements indicate that the synthesis route critically determines the crystallinity and phase composition of the final products. A homogeneous distribution of the nanoparticles on the graphene/GO/graphite sheets was revealed by SEM, EDS and TEM observations. Oxygen 1s core level XPS spectra reveal the existence of oxygen vacancies in the nanocomposites. DC and AC magnetization measurements reveal a superparamagnetic behavior with strong dipolar interactions between the hematite particles in all the samples investigated. Moreover, zero field cooled memory experiments of the thermal variation of the magnetization allowed us to confirm that both the hematite nanoparticles and their composites with graphene and graphite show superspin-glass behavior. The as-grown Cr₂O₃ nanoparticles show dimensions between 15 and 30 nm. Raman measurements indicate that the synthesis route determines the crystallinity of the Cr₂O₃-based nanocomposites, which show superparamagnetic behavior and exchange bias effects according to SQUID magnetometry results. The exchange bias field is as high as 3200 Oe in graphite nanocomposites. Correlation of the obtained results with XAS measurements of the C 1s edge suggests orbital hybridization and electron sharing at the C-Cr₂O₃ interface.

CM01.09.18
The Role of Hydrogen in the Persistent Photoconductivity in Strontium Titanate Zhisong Zhan¹ and Anderson Janotti²; ¹Department of Physics and Astronomy, University of Delaware, Newark, Delaware, United States; ²Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States.

Strontium titanate (SrTiO₃ or STO) is a wide band-gap material (3.25 eV at room temperature) with potential applications in oxide-based electronic devices, such as resistive switching memory. Extremely long persistent photoconductivity (PPC) at room temperature has been observed in annealed strontium titanate single crystals under sub band gap light excitation [M. C. Tarun, F. A. Selim, and M. D. McCluskey, Phys. Rev. Letters, 111, 187403 (2013)]. Annealing studies indicate that hydrogen impurities as well oxygen and strontium vacancies are involved in this effect. Using electronic structure calculations based on density functional theory (DFT) we investigate possible mechanisms behind the PPC effect. We consider both interstitial and substitutional configurations in different charge states, as well as the possible participation of oxygen and strontium vacancies. We present results for formation energies, migration energy and optical absorption peak position due to defects. The results are then used to explain the experimental observations.

CM01.09.19
Effects of Excess Electrons on the Structure of BiVO₄ Iflah Larabi¹, Marciano A. Carneiro² ¹ and Anderson Janotti²; ¹University of Delaware, Newark, Delaware, United States; ²Universidade Federal Fluminense, Rio de Janeiro, Brazil.

Among the available photoelectrochemical materials, BiVO₄ has huge potential to be utilized as a cheap and efficient material. Precisely knowing its band gap and understanding of electron transport in BiVO₄ are crucial for improving its performance, but both aspects of the material are debated, mainly due to its two extant different phases which have similar structures and are close in energy. We use density functional calculations with the PBE, meta-GGA SCAN, and hybrid functionals to study the stability of the different phases of BiVO₄, the effects of excess electrons in its conduction band, changes in local structure with excess electrons, and the possibility of carrier localization through electron-small polaron formation. The obtained results are compared to previous calculations and available experimental data.

CM01.09.20
Synthesis and Characterization of Mayenite Electride - Ti Composites for Thermionic Electron Emission Applications Adam Kuehster¹, Bao Nguyen¹, Luke Uribarri², Gautham Ramachandran¹, John Williams¹ and Kaka Ma¹; ¹Colorado State University, Fort Collins, Colorado, Colorado, United States; ²Lockheed Martin Corporation, Bethesda, Maryland, United States; ³Lockheed Martin Space Systems Company, Palo Alto, California, United States.

Mayenite (12CaO·7Al₂O₃ or C12A7), a typical electrical insulator, can be converted into an electro-active functional material, i.e., mayenite electride (C12A7:2e⁻), with a low work function, chemical inertness, and superconductivity at low temperatures. Mayenite electride has attracted extensive interests due to its application as inexpensive thermionic emission sources. However, pure mayenite electride exhibits brittleness, low fracture strength, and poor machinability. Thus, it is in demand to explore composite materials, such as a mayenite electride-titanium (Ti) composite, that will overcome these drawbacks while retaining the low work function characteristic of the mayenite electride. In the present work, C12A7:2e⁻ - Ti composites (50:50 wt%) were synthesized in a single step via electric field assisted sintering (EFAS). The microstructures of the composite consist of some other calcium aluminate phases (e.g., Ca₅Al₂O₇) in addition to C12A7:2e⁻ and Ti phases. The work function of the composite is approximated 2.5 eV evaluated by thermionic emission current measurement.

CM01.09.21
Structural and Magnetic Behavior in Rhenium-Based Double Perovskites Fang Yuan and Corey Thompson; Purdue University, West Lafayette, Indiana, United States.

Double perovskites, A₂B'B''O₆, have been intensely studied due to their interesting chemical and physical properties. The different B-site cations combination allows for a wide range of novel materials with unique magnetic behavior, from ferromagnets to spin glasses. Our current work is focused on the synthesis, structure, and magnetic properties of Re-based double perovskites, La₂B'ReO₆ (B' = Mg, Co, and Ni). All phases adopt the monoclinic P2₁/c crystal structure and are paramagnetic above room temperature. The Co-and Ni-analogs are ordered below 250 K, while the Mg-analog shows no magnetic phase transition down to 2 K. These results and a comparison to their ruthenium and osmium analogs will be presented.

CM01.09.22

The quantification of atomic transport processes such as solid-state diffusion is important for controlling the processing, properties, and stability of solids in general. Measurements on bulk solids have provided a wealth of information on the nature of diffusing species (vacancies, interstitials, etc.) and their mobility, but it is uncertain to what extent these properties may be extrapolated to the nanoscale. The relative dearth of experimental methods for determining these properties in nanostructures complicates this question.

In this work we use the Pb₅Sb₃Cs cation exchange reaction to quantify the kinetics of ion diffusion in core-shell nanoparticles. Pb₅Sb₃Cs-poor nanocrystals (NCs) provide an ideal model system due to their well-established synthetic chemistry and their relatively simple structure, which facilitates structural
interrogation. Using in-situ x-ray diffraction of 7 nm-diameter PbS NCs as they undergo cation exchange to CdS, we have identified that three processes are important in the conversion of the NCs: an initial surface reaction (chemisorption of Cd) which imposes significant inhomogeneous strains on the underlying PbS; the exchange of the first underlying atomic layer(s) of the NC; and a diffusion-controlled growth of a thick zincblende-phase CdS shell. Quantification of the kinetics of shell growth based on a shrinking-core model show that the activation energy for chemical diffusion of the rate-limiting species lies in the range of 110 kJ mol$^{-1}$, which is in good agreement with prior measurements of the energy of interstitial self-diffusion in bulk CdS. This suggests that, at least for diffusion lengths longer than 1-2 nm, energies of point defects in these simple ionic solids may not be greatly perturbed by the presence of a nearby surface, even under large chemical potential gradients.

Finally, we also discuss some structural peculiarities of these NCs. Previous suggestions of the existence of a metastable rocksalt CdS phase during shell formation are not supported by our experimental results, as we observe a monotonic change in the relative diffraction intensities to those consistent with zinblende CdS, a trend opposite to that expected in rocksalt phase formation. Additionally, an apparent symmetry breaking of the structure of the PbS/CdS NCs (loss of cubic structure) is evidenced by anomalous peak shifts in the diffraction patterns. We show this phenomenon does not indicate a true distortion of the unit cells, and account for it in terms of the kinematical diffraction theory supported by Debye scattering equation simulations. The interfered, of diffracted waves from octahedral Pb and tetrahedral Cd sublattices, which are displaced relative to each other by a non-integer multiple of the unit cell along key directions, is sufficient to give rise to substantial apparent peak shifts. This diffraction effect will be important in reflecting on previous observations of “symmetry breaking” in nanoparticles in general.

**CM01.09.23**

**Dynamic Structural Changes upon Hydrogenation and Dehydrogenation of Mg-Nanoparticles by In Situ Transmission Electron Microscopy and Electron Tomography**

Jochen A. Kammerer$^1$, Xiaoyang Duani$^2$, Frank Neubrech$^2$, Rasmus Schroeder$^1$, 4, Laura Na Liu$^2$, 3 and Martin Pfannmüller$^1$.$^1$Department of General Studies, Tangntional University, Heidelberg, Germany; $^2$Kirchhoff-Institute for Physics, Heidelberg University, Heidelberg, Germany; $^3$Max Planck Institute for Intelligent Systems, Stuttgart, Germany; $^4$Cryo Electron Microscopy, Heidelberg University Hospital, Heidelberg, Germany.

A theoretical capacity of 7.6 wt% hydrogen and favorable hydrogen desorption kinetics turn Mg-based nanomaterials into promising candidates for solid state hydrogen storage$^1$. Furthermore, the excellent plasmonic properties of Mg and the transition to dielectric MgH$_2$ enable dynamic photonic applications$^2$. Hydrogenation and dehydrogenation are accompanied by large volumetric expansion and shrinkage leading to drastic structural changes and thus alter (de)hydrogenation kinetics and plasmonic properties. To be able to steer Mg behavior it is of utmost importance to understand these changes at nanoscale and below. Here, we use Mg nanoparticles (NPs) preparation by electron lithography, which are reproducible in size and shape. This allows a meaningful comparison of pristine and dehydrogenated NPs depending on size. We demonstrate that radiation induced dehydrogenation process and accompanied structural alterations lead to long-term reorganization of the Mg nanostructure. Time resolved electron energy loss spectroscopy and electron diffraction in the transmission electron microscope were used together with time and spatially resolved electron spectroscopic imaging to visualize the dynamic changes of MgH$_2$ and Mg from characteristic bulk and surface plasmon excitations. Furthermore, three-dimensional analysis by electron tomography enables the detailed observation of voids that are formed during dehydrogenation. We investigated Mg NPs with diameters from 100 nm to 350 nm and 40 nm in thickness, covered by 2 nm Ti and 3 nm of catalytic Pd. Volume expansion during hydrogenation and mechanical constrains in $x$-$y$-direction frequently cause twinning in the hydridate, especially in large NPs. Interestingly, the size of the twins clearly exceeds the grain size of pristine NPs. Shrinkage during dehydrogenation is accompanied by the formation of faceted cavities, visualized through the excitation of surface plasmons within the NPs. Surface energy reduction driven coarsening of the initially fine cavity network continues for several days at room temperature after complete dehydrogenation. Thereby, ripening of the network slows down in small NPs faster than in large ones. The transformation to Mg is observed to be rather governed by a large number of small nuclei with a low growth rate than a small number of fast growing nuclei. Our results contribute to understanding the influence of defect structures and orientation relationship between Mg and MgH$_2$ on the structure of the corresponding NPs. The presented methodology and results will enable defined experimental designs to reveal the dynamic processes in MgH$_2$ particles and related structures. Such insights will crucially influence the optimization of materials parameters that determine applications in nanophotonics and hydrogen storage.


**CM01.09.24**

**DFT+DMFT Study on the LaTiO$_3$/LaAlO$_3$ Superlattice—Magnetic Properties near Metal-Insulator Transition**

Jae-Hoon Sim$^1$, Hunpyo Lee$^2$ and Myung Joon Han$^1$; $^1$Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); $^2$School of General Studies, Kangwon National University, Samcheok-si, Korea (the Republic of).

The strongly correlated electron system is of central importance in the condensed matter physics. Among the correlated materials, transition-metal oxide superlattices are extensively studied, due to their novel characteristics and potential applications. The electronic and magnetic properties can be significantly different from their bulk counterpart, showing unexpected interface phenomena, e.g., magnetism, high-temperature superconductivity, correlation induced metal-insulator transition. Importantly, due to the strong couplings in TMO between the charge, spin, orbital, and lattice degrees of freedom, the material properties can be controlled by external perturbations, e.g., pressure, electric/magnetic field, or strain.

Motivated by the previous experiment and density functional theory+U (DFT+U) results$^1$, 2, we have studied LaTiO$_3$/LaAlO$_3$ superlattice. From the previous theoretical study, it was found that the magnetic transition from the ferromagnetic-spin/antiferro-ortorial order to the antiferromagnetic-spin/ferro-orbital phase induced by epitaxial strain. This magnetic transition is not observed in the bulk LaTiO$_3$ compound. While the standard DFT and DFT+U are successful methods to describe real materials, correlated materials are not properly treated with this method, especially near the transition point. To overcome the technical limitation, we performed dynamical mean-field theory calculations combined with the density functional theory, which is one of the successful approaches to study these systems. Under epitaxial tensile strain, we observed unexpected insulator-to-metal transition, followed by magnetic transition$^3$. Our findings demonstrate that not only magnetic but transport properties can be controlled by strain.

We also present the implemented DFT+DMFT method based on the non-orthogonal pseudo-atomic orbitals (PAOs) basis DFT code, OpenMX$^4$. Newly developed methods for analytic continuation, so-called maximum quantum entropy method$^5$, is applied to obtain resulting spectral functions.

**References**

CM01.09.25

Highly-Ordered Hollow Nanochanneled-Silica Nanospheres Prepared Using Sacrificial Copolymer Nanospheres

Yong Ku Kwon, Hyun Jun Lim, Seho Kwon, Minkee Lee and Tae-Yang Jeong; Inha Univ, Incheon, Korea (the Republic of).

Monodisperse hollow mesoporous silica nanospheres were synthesized based on the cationic colloidal polymeric nanospheres. The nanospheres were prepared by the surfactant-free emulsion copolymerization of styrene and butyl acrylate in the presence of a cationic monomer, methacryloyloxyethyl trimethyl ammonium chloride using azobisisobutyramidine hydrochloride as an initiator. The charged polystyrene nanospheres were dispersed in water and mixed with cetyltrimethylammonium bromide and ammonium hydroxide in ethanol. Tetraethylorthosilicate as a negatively charged silica precursor was then added dropwise to achieve rapid hydrolysis onto the cationic surfaces of colloidal particles and allow mesoscopic ordering of the co-self-assembly of tetraethylorthosilicate and cetyltrimethylammonium bromide on the shell phase. The samples were then heated to 600°C to remove the colloidal template, resulting in monodisperse hollow mesoporous nanospheres. These nanospheres were characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction.

CM01.09.26

Synthesis, Optical and Structural Properties of Copper Sulfide, Cadmium Sulfide and Lead Sulfide Nanocrystals for Use in Quantum Dot Sensitized Solar Cells

Peter A. Ajibade; University of KwaZulu-Natal, Pietermaritzburg, South Africa.

Quantum dot sensitized solar cells (QDSSC’s) have attracted numerous research interest in the past decades as alternative to silicon based photovoltaic devices. It has emerged as promising agent in solar energy conversion due to its size-dependent optoelectronic characteristics, facile and low cost fabrication techniques.\(^1\). Their tunable bandgaps, high extinction coefficients, multiple exciton generation effect and large intrinsic makes QDSSC’s distinctive solar cells\(^2\). In this paper, copper(II), cadmium(II) and lead(II) dithiocarbamate complexes were synthesized and characterized by elemental analysis, thermal gravimetric analysis, mass spectrometry, \(^1\)H and \(^13\)C-NMR spectroscopy. The complexes were used as single source precursors to prepare oleyamine, TOPO and HDA capped quantum dots at three different temperatures. The structural properties of the quantum dots were established using FeSEM, HRTEM, FTIR, EDS and XRD. Absorption and photoluminescence spectroscopy was used to study the optical properties of the as prepared quantum dots. HRTEM images shows quantum dots with particle size in the range 4 - 9 nm. The potential of the quantum dots as sensitizers in solar cell fabrication are being evaluated.

References

SESSION CM01.10: Functional Materials by Design
Session Chairs: Daniel Fredrickson and Corey Thompson
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 203

8:00 AM *CM01.10.01

Computational Discovery of Novel Structural and Functional Heusler Compounds

Christopher Wolverton; Northwestern University, Evanston, Illinois, United States.

Heusler compounds are being widely studied for their potential usage in spintronics, shape-memory devices, superconductors, thermoelectrics, topological insulators, etc. The crystal structure and its variants are ubiquitous, with more than 1000 Heusler compounds being reported. However, the phase space for possible Heusler compounds is orders of magnitude larger, raising the real possibility that many new, stable Heusler compounds are still awaiting discovery. We demonstrate a high-throughput computational DFT screening approach for ~200,000 potential Heusler compounds, and use this method to predict hundreds of new stable and metastable Heusler compounds, which we further examine for interesting functional properties. We highlight three distinct examples of computational discovery of Heusler compounds, demonstrating the extraordinary diversity of properties possible with this single structure type: efficient thermoelectrics, off-stoichiometric semiconducting Heuslers, and strengthening precipitates in bcc metals.

8:30 AM CM01.10.02

Predicting the Thermodynamic Stability of Perovskite Oxides Using Machine Learning Models

Wei Li, Ryan Jacobs and Dane Morgan; University of Wisconsin-Madison, Madison, Wisconsin, United States.

The thermodynamic phase stability of a perovskite is a key materials property, the value of which may determine the utility of the perovskite in the given application of interest. The stability typically correlates at least loosely with whether a perovskite is synthesizable, as well as whether it may be expected to degrade (or remain stable) over time under some operational environment, such as a specific working temperature or partial pressure of oxygen. Of the numerous materials families investigated with high throughput DFT methods,\(^1\)\(^2\) perovskite materials stand out as a particularly challenging class of materials for computational screening and property evaluation.\(^3\) When one accounts for the large number of different A- and B-site elements, as well as different typical dopant ratios and combinations, the potential number of unique perovskite compositions may be easily greater than \(10^5\) materials, the full space of which cannot be currently assessed experimentally or with DFT. Accurate machine learning model predictions for a material can be orders of magnitude faster than the corresponding DFT simulations or experiments, allowing them to be used to quickly understand trends in materials properties and inform materials discovery.\(^4\)

In this work, we used machine learning models to predict the stability of a set of nearly 2000 perovskite oxides from the work of Jacobs, et al.\(^3\) We first constructed a set of features based on the properties of the constituent elements of each perovskite composition and well-known empirical perovskite structural descriptors, and performed feature selection routines to select the set of features which produced the best predictions of material stability without significant overfitting. We performed both binary classification (to determine whether material is expected to be stable or unstable) and regression (to predict a numerical value for stability as an energy above the convex hull), and found that an extra trees classifier and kernel ridge regression model performed the best for classification and regression, respectively. The best F1 score for classification was 0.881 (+/- 0.032) and RMSE score for regression
Energetic Upper Bound for Synthesis of New Materials

Muratbahan Aykol, Shyam Dwaraknath, Wenhao Sun and Kristin A. Persson; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Laboratory synthesis of new functional inorganic materials, in particular the metastable ones, designed or discovered on the computer or suggested by theorists is a significant hurdle in materials science. To bridge this gap between computational and experimental worlds, we introduce a new thermodynamic upper bound on the energy scale for the creation of metastable crystalline polymorphs that is based on the entropic dominance of amorphous form of materials. This “amorphous limit” can be computed from first-principles and is found to be remarkably accurate and very sensitive to chemistry and composition in classifying hundreds of inorganic materials in the Materials Project database, from oxides to nitrides to sulfides, as synthesizable or not. The limit is expected to replace constant common, heuristic energetic limits or intuition often used as guidelines in filtering computed materials in materials screening for functional applications.

References:


9:00 AM CM01.10.04

Structural and Thermodynamic Effects in High Entropy Oxides

Colin Freeman1; Gautam Anand2; Christopher M. Handley1; John H. Harding1 and Derek Sinclair1;
1University of Sheffield, Sheffield, United Kingdom; 2University of Warwick, Coventry, United Kingdom.

The functional ceramics community is increasingly exploring complex solid solutions containing multiple cations [1,2] to generate the desired properties and to avoid the need for rare or expensive dopants. These multi-component systems no longer possess regular, periodic lattices with occasional point defects but show variable stoichiometry over nanometre scales, regions of disorder and cluster formation. These features are likely to be key to the properties. Because of the heterogeneous nature of these systems their characterisation can be very challenging as the bulk response must be an average of the different configurations present. Fabrication is also hindered as we move away from conventional processing where enthalpy is the dominant factor and must contend with entropic contributions.

We have performed a range of classical atomic scale simulations to study these systems. These are ideal tools as the atomic level detail explores the local relaxations that can occur around particular atomic configurations and identify issues of clustering. The relatively low cost of the simulations also means it is possible to look at multiple large cells providing the opportunity to actually sample the configurational variation that is present.

Our simulations examine the recently reported high entropy oxide system (Mg,Co,Ni,Cu,Zn)O [3]. We demonstrate that these phase is entropically stabilised over the enthalpy penalty of mixing. By sampling an ensemble of configurations we are able to consider some the average structural and property features the material exhibits and comment on how mixing influences the local atomic behaviour. We also explore the formation of defects and how these might disrupt the material.

References:


9:15 AM CM01.10.05

Theoretical and Experimental Studies on the Mixed Chalcogenide Phases Sb2Se-xTe-x and GeSe-xTe-x

Ralf P. Stoffel and Richard Drönskowski; RWTH Aachen Univ, Aachen, Germany.

Chalcogenide phases, in particular tellurides, are of enormous technological importance nowadays because they serve as, for instance, phase-change [1] and thermoelectric materials [2]. The substitution of tellurium by selenium seems a promising pathway to obtain chalcogenide compounds with new electronic properties. Here we present the results of density-functional theory-based investigations regarding the structural, lattice dynamical and thermodynamic properties of mixed chalcogenide materials in the Sb2Se-x – Sb2Te-x and GeSe-x – GeTe pseudo-binary systems compared with experimental measurements carried out by us.

Crystal structures in the system GeSe-xTe-x have been studied up to pressures above 20 GPa using synchrotron radiation at DESY, Hamburg. The results are supported by theoretical investigations, including lattice dynamical and bonding properties [3]. We found a new orthorhombic structure type forming under pressure which has not yet been reported.

In the Sb2Se-xTe-x system we investigated the crystal structure as dependent from the selenium content x [4]. We focused on the preferred incorporation of selenium into one of the two possible chalcogenide sites of the Bi2Te3 structure type which is the ambient pressure structure up to a selenium content of x = 1.8. This incorporation was investigated additionally by DFT calculation as regards its energetic landscape and the bonding properties by making use of the COHP method as implemented in the LOBSTER code [5]. Additionally, low-temperature heat capacities were measured experimentally and compared to theoretically calculated data [6] using lattice dynamical calculations and the quasi-harmonic approximation [7].

References:

Since the 1960s, the National Aeronautics and Space Administration (NASA) has successfully utilized radiisotope thermoelectric generators (RTGs) as the primary power source for many deep space probes, landers and orbiters for many missions including Voyagers 1 and 2, Cassini and Curiosity. RTGs are commonly used when other forms of on board power are not practical due to low solar flux, day/night cycles and settling of dust, or when they would significantly enable or enhance a mission’s ability to meet its objectives. RTGs are a proven technology and have been demonstrated to have high reliability, redundancy and long life. Historically, the thermoelectric (TE) materials used in the RTGs by NASA have either been based upon Si-Ge alloys or PCTe/TAGS (tellurium, silver, germanium, antimony), with system level conversion efficiencies of −6.5%. The goal of the Advanced Thermoelectric Materials (ATOM) project in the Thermoelectric Technology Development Project at the Jet Propulsion Laboratory (JPL) is to develop TE materials that are capable of providing 20% conversion efficiency across a wide temperature range 400-1275 K. In this paper we’ll highlight the technical progress of the program and pathways to 20% efficiency. Specifically we will discuss the investigation of f-orbital chemistry on the electronic properties of La$_{3-x}$Te$_4$ and their impact on the thermoelectric figure of merit.

10:30 AM CM01.10.08
Antisite Pairs Suppress the Thermal Conductivity of Boron Arsenide (BAs) Qiang Zheng1, Carlos A. Polanco2, Mao-hua Du1, Lucas R. Lindsay1, Miaofang Chi3, Jiqaing Yan1,4 and Brian C. Sales1; 1Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Department of Materials Science and Engineering, University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

As microelectronic devices become faster and smaller, materials with ultrahigh thermal conductivities (κ) are becoming important for new generation electronic devices. Recently, based on first-principles calculations, boron arsenide (BAs) with a zinc blende cubic structure was predicted to possess an unusually high κ at room temperature of over 2000 Wm$^{-1}$K$^{-1}$, comparable to that of diamond [1]. However, the experimentally measured κ of BAs single crystals was only 200–350 Wm$^{-1}$K$^{-1}$, an order of magnitude lower than the predicted value [2-4]. While theoretical calculations revealed that As vacancies even with very low concentration could significantly suppress κ [5] and X-ray photoelectron spectroscopy (XPS) studies suggested possible As-deciency in BAs single crystals [2,3], there has been no direct observation of As vacancies (V$_{As}$) in BAs crystals. Therefore, direct observation and identification of the defect types in BAs that suppress κ become quite urgent for growth of high-quality BAs crystals or films with significantly improved κ.

In this work, we use aberration-corrected scanning transmission electron microscopy (STEM) to investigate the lattice structure and possible defects in BAs single crystals at atomic scale [6]. Rather than finding V$_{As}$, as widely thought to suppress κ of BAs crystals, STEM results showed the enhanced intensity of some B columns and reduced intensity of their neighboring As columns, suggesting the presence of As$_{B}$-B$_{As}$ antisite pairs with significant concentrations. Additional calculations on formation energies confirm that such antisite pair is preferred energetically among the different types of point defects investigated. Using a concentration of 1.88(8)% (6.6±3.0×10$^{17}$ cm$^{-3}$ in density) for the antisite pairs estimated from STEM images, κ of BAs is estimated to be 65–100 Wm$^{-1}$K$^{-1}$, in reasonable agreement with the measured value. Finally, we also propose possible approaches, such as flux growth out of alkali metal-based or Ni-based melts and MBE, to achieve high-quality BAs single crystals or films with high thermal conductivity.

Overall, this combination of computational and experimental methodology offers a more rational and systematic paradigm for targeted synthesis of metal oxides. The future outlook for this “synthesis by design” approach is promising for other binary and ternary oxides with high polymorphism.

The zinc blende cubic BAs and BP, due to their potential ultra-high thermal conductivity calculated through first principle approach, have attracted significant research efforts in the past few years. The crystal growth of these materials, on the other hand, remains a challenge due to incongruent melting/peritectic decomposition nature of BAs/BP, and the low solubility of B in the common metal fluxes. Here, we reported our synthetic efforts to grow the high quality of BAs/BP crystals through chemical vapor transport/metal flux method. We obtained the single domain, and defect-free crystals of BAs and BP up to mm size, evidenced by both single crystal diffraction and scanning transmission electron microscopy (STEM) studies. More importantly, ultrahigh thermal conductivities, ~1000W/mK for BAs and ~500W/mK for BP respectively, have been achieved through time-domain thermoreflectance (TDTR) measurement. The measured experimental thermal conductivity values are also compared with theoretical calculations based on both three phonon (3ph) scattering and three+four phonon (3ph+4ph) scattering process.

Computational driven design of materials has provided guidelines for designing novel materials with desired properties. However, the current computational approaches are not able to predict reaction pathways that pass through intermediate or metastable phases. As a consequence, repeated iteration is usually required to find the reaction conditions needed for realizing targeted materials with desired properties. To address this challenge, we combine theory, computation, and experiments to establish a theoretical framework that guides the synthesis of intermediate/metastable phases [1,2].

This framework has the ability to predict the multistage crystallization, as well as the influence of particle size and solution composition on polymorph stability along reaction pathways. To validate this framework, hydrothermal synthesis of manganese oxide is utilized as a demonstration case. In the experiment, we track the evolution of manganese oxide polymorphs occurring during the synthesis by using in-situ X-ray wide-angle scattering and X-ray absorption spectroscopy. Three synthesis pathways with varying potassium ion concentrations ([K+] = 0, 0.2, and 0.33 M) in the solution were studied. By combining the experimental and computational results together, we find that our computed size-dependent phase diagrams capture which metastable/intermediate polymorphs appear, the order of their appearance, and their relative lifetimes [3]. Furthermore, we demonstrated that the intermediate phases can be isolated from reaction pathways by quenching the reaction to stabilize the phases at room temperature.

Overall, this combination of computational and experimental methodology offers a more rational and systematic paradigm for targeted synthesis of metal oxides. The future outlook for this “synthesis by design” approach is promising for other binary and ternary oxides with high polymorphism.

1:30 PM *CM01.11.01
Structure and Properties of Pnictide Zintl Phases with Rare Earth Cations Susan M. Kauzlarich; University of California, Davis, Davis, California, United States.

Zintl phases have generated a great deal of interest because their structures can be understood using simple electron counting rules allowing for strategic compositional tuning to enable and enhance useful properties for applications in energy conversion and information technologies. We have employed the Zintl concept to introduce new compounds with unique structures to the thermoelectric community. In addition, many of these new compounds also show complex magnetic ordering and colossal magnetoresistance. I will outline our motivation for employing rare earths in pnictide containing Zintl phases and discuss their structures and properties.
K₂SnO₃ and Related New Oxide Structure Types

Rebecca D. McAuliffe, Christopher A. Miller, Shuai Li and Daniel P. Shoemaker; Univ of Illinois-Urbana. Urbana, Illinois, United States.

Our exploratory forays into the K-Sn-O phase space are motivated by the search for Sn²⁺-containing transparent conducting oxides, and have revealed a surprisingly diverse phase space, with many previously-unreported stable and metastable phases. We present techniques for combatting experimental challenges in this system, including deliquescence of certain precursors and a proclivity for beam damage in some products. Among them is K₂SnO₃, a Sn⁴⁺-containing oxide with a unique structure type among oxides. The compound is orthorhombic and reminiscent of an offset hollandite, where open channels hold a row of four K⁺ per channel per cell. The continued discovery of new structure types in ternary tin oxides should remain a priority for the identification of prospective ion conductors and transparent conducting oxides.

2:15 PM CM01.11.03
Structures and Properties of Kesterite-Type Quaternary Chalcogenides
Anthony V. Powell, Panagiotis Mangelas, Alex Aziz, Ricardo Grau Crespo and Paz Vaqueiro; University of Reading, Reading, United Kingdom.

Quaternary chalcogenides of general formula A₂BCO₄, where A, B and C are elements from groups 11, 12 and 14 respectively and Q = S, Se, have applications in solar cells, thermoelectric devices and photocatalysts for water splitting. Thin-film solar cells containing Cu₂ZnSnO₄ have attracted considerable interest, as they have efficiencies of 12.6%. Although this is lower than that of CIGS (CuInGaSe₂) based devices, Cu₂ZnSnO₄ confers the advantage of being composed of Earth-abundant elements, affording significant reductions in materials costs. An emerging body of work suggests the detailed structure of these materials plays a key role in their functionality. Band–gap fluctuations, which reduce solar cell efficiencies, are strongly correlated with the degree of cation disorder, while phase transitions have a marked impact on the transport properties that underlie thermoelectric performance.

The presence of cations with similar atomic numbers hampers analysis by X-ray methods and has led to ambiguity over the detailed structures of members of this family of materials. Using neutron diffraction, we have established that the room-temperature structures of all A₂ZnCoO₄ (A = Cu, Ag; C = Sn, Ge and Q = S, Se) phases are best described in the kesterite (I-4) derivative of zinc blende, which DFT calculations indicate is energetically favoured over the stannite (I-42m) form. However, the detailed structures show a marked dependence on composition. Cu₂ZnGeO₄ phases exhibit partial disorder of Cu and Zn cations within cation planes at z= ¼ and ¾. Disorder is greatly reduced in the tin analogues and the silver-containing phases Ag₂ZnSnO₄ are fully ordered at room temperature. DFT suggests the disordered structure may be considered as a probability-weighted average of two ordered configurations, differing in the stacking sequence of the Cu-Zn planes. Ordering of silver cations is driven by minimization of the inter-plane Zn²⁺-Zn²⁺ repulsions in one of these configurations. The magnitude of this stabilization is reduced with increasing c/a value, and both configurations have a similar probability in the Cu-containing phases, leading to a disordered structure.

On heating, Cu₂ZnSnO₄ transforms at 1123 K, to a wurtzite-stannite-type structure with complete ordering of cations over the tetrahedral sites. The analogous selenide (Cu₂ZnSnSe₄) remains in I-4 at all temperatures to 973 K, despite the signature in thermal analysis data of a phase transition in the region 437 ≤ T/K ≤ 512. These observations are reconciled by Rietveld analysis, which reveals an order-disorder transition to a fully disordered kesterite structure at 450 K. Simultaneously, copper-ions become mobile, conferring phonon-liquid-electron-crystal characteristics, and copper-ion vacancies are created. This leads to marked changes in electron-transport properties: both ρ(T)and S(T) indicate the order-disorder transition is accompanied by a semiconductor to metal transition.

2:30 PM BREAK

3:00 PM *CM01.11.04
Improved Synthesis of Two-Dimensional Covalent Organic Frameworks
William Dichtel; Northwestern University, Evanston, Illinois, United States.

Polymerizing monomers into periodic two-dimensional (2D) networks provides structurally precise, layered macromolecular sheets that exhibit desirable mechanical, optoelectronic, and molecular transport properties. 2D covalent organic frameworks (COFs) offer broad monomer scope but are generally isolated as powders comprised of aggregated nanometer-scale crystallites. Here we control 2D COF formation using a two-step procedure, in which monomers are added slowly to pre-formed nanoparticle seeds. The resulting 2D COFs are isolated as single-crystalline, micron-sized particles. Transient absorption spectroscopy of the dispersed COF nanoparticles provides two or three orders of magnitude improvement in signal quality relative to polycrystalline powder samples and suggests exciton diffusion over longer length scales than those obtained through previous approaches. These findings will enable a broad exploration of synthetic 2D polymer structures and properties.

3:30 PM CM01.11.05
Microstructure—Properties Relationships in MOFs
Rifan Hardian, Marie-Vanessa Coulet and Philip Llewellyn; CNRS-Aix Marseille Univ, Marseille, France.

Metal-Organic Frameworks (MOFs) are a class of porous materials that combine metal oxide clusters with organic linkers. The wide variety of metal precursors and organic ligands allows tuning the properties of this class of materials to be used for gas storage and separation, catalysis, mechanical energy storage, etc. It has been recently proposed that the presence of defects and disorder in MOFs can have an impact on many of their properties [1,2]. In this contribution, the microstructure-properties relationships are studied in two kinds of defective MOFs.

The first example concerns the generation of defects by ball-milling in ZIF-8. It is shown that this kind of post-synthesis modification allows the control of the microstructure and the reactivity. Microstructure is analysed using X-ray diffraction while reactivity toward polar and non-polar molecules is studied using gas and vapour sorption experiments. Although the maximum uptake at high pressure is decreasing with increasing number of defects, the reactivity at low pressure is higher. This indicates that defects induced by ball-milling improve the reactivity which can be of interest for catalytic reactions.

The second example focuses on the influence of the microstructure on the structural flexibility in functionalized MIL-53(Cr) compounds. This MOF family presents the remarkable property of being flexible. This means that one compound exists in at least two crystalline states with distinct pore size and shape: a narrow pore (NP) structure and a large pore structure (LP). The NP/LP transition is reversible and can occur under gas adsorption and desorption or without any guest, that is to say under mechanical pressure or temperature. Functionalization of this compound allows tuning the NP/LP transition temperature. Various functionalized samples that possess different microstructures in terms of crystallite size and strain are studied using differential scanning calorimetry combined with X-ray absorption spectroscopy and X-ray diffraction. It is shown that the microstructure strongly modifies the energies associated with the transition as well as the temperature or pressure at which it occurs. It is thus proposed that microstructure may be used to
Metal-organic framework (MOF) materials containing oxometalate cluster-based nodes, such as oxozirconium or oxocerium nodes, can provide the basis for single-site heterogeneous catalysts, for example, if all nodes are uniformly modified with suitable metal species. However, the application of MOFs for catalysis at high temperatures, particularly in oxidizing environments, is limited, because the instability of the organic linkers under these conditions leads to loss of the MOF structure and aggregation/sintering of the catalytic clusters. Under those conditions, it may be necessary to stabilize the cluster sites. We will discuss methods of stabilizing MOF-derived functionalized and non-functionalized oxometalate clusters by nanocasting with silica, titania, or carbon scaffolds. A silica scaffold, for example, can prevent the oxozirconium clusters in the MOFs NU-1000 or UiO-66 or oxocerium clusters in related cerium-based MOFs from aggregating after the linkers are removed at temperatures between 500 and 600 degrees C. This is in contrast with bare NU-1000 or UiO-66, which shows sintering of the clusters after undergoing the same thermal treatment. The clusters in the nanocast material remain accessible to probe molecules and their Lewis acidity is maintained, keeping them active as catalysts in certain acid-catalyzed reactions. This nanocasting method can also be extended to other scaffolds to support cluster nodes in large-pore MOFs. We will consider synthesis parameters that permit uniform infiltration of the MOF with the scaffold precursors and correlate these to nanocast products that maintain discrete clusters after thermal treatment at 500 degrees C or higher, without formation of extended zirconia or ceria aggregates. Accessibility of the stabilized clusters in the scaffolds is probed by spectroscopic and catalytic reaction methods. Nanocasting, combined with the exceptional tunability of the composition and structure of MOFs, provides a starting point for designing a new generation of highly active and stable heterogeneous catalysts.

Wurtzite (WZ)-derived ternary nitrides are an interesting class of materials promising enhanced optoelectronic functionalities. Peculiar to this category of materials is their capability of accommodating large off-stoichiometries, as we recently demonstrated for the Zn3MoN4-ZnMoN2 system. In the latter case, cation off-stoichiometry enables a continuous tuning of the composition between the two end points, while retaining the WZ structure, through a process that we defined as redox-mediated stabilization. Most of the cations in the periodic table have been reported to form nitrides as either a monometallic or bimetallic compound. To date, an exception to this rule is represented by antimony: M-Sb-N ternary compounds where Sb is acting as an anion are known, however crystalline nitrides where Sb is acting as a cation have not been reported to date. In this contribution, we theoretically predicted and experimentally realized the first ternary antimony nitride where antimony is a cation. A data-mined structure prediction (DMSP) algorithm was used to identify the compound and evaluate the stability of the candidate crystal structures by comparing their density functional theory (DFT) formation energies to the competing phases. Combinatorial RF magnetron sputtering was used as growth technique, to enable access to high nitrogen chemical potential (AQc) and fast screening of deposition conditions. It was found that this metastable compound could be synthesized over a wide range of deposition conditions, showing tunable optical and electrical properties as a function of the Sb content in the cation sub-lattice and growth conditions. The low native n-type conductivity and moderate carrier concentration, coupled with an almost ideal direct band gap (1.7 eV theoretical, ~1.4 eV experimental) make it a promising candidate as a photoactive material. Based on measured values of the ionization potential and the electron affinity, the applicability of this material as a photoactive absorber will be discussed.

References:

Colloidal inorganic nanocrystals offer many advantages for use in photovoltaic devices: controllable synthesis, processability, and tunable band gap energies. Ideal materials for photovoltaics would contain earth abundant, nontoxic elements and would possess ideal band gaps. Copper and iron chalcogenides exhibit these properties. However, many of these compounds are ternary compounds, with interesting bonding between transition metals, main group elements, and chalcogenides, so developing synthetic routes toward nanocrystals of these materials is a significant challenge. We are exploring how the interactions between precursors, surfactants, organic solvents, and temperature in injection-type reactions can affect the reaction pathways toward the ultimate products.

**CM01.12.01**

**Lattice Dynamics of Layered AMg2Pn2: Zintl Compounds**

Wanyue Peng1, Guido Petretto2, Gian-Marc Rignanese3, Geoffrey Hautier4 and Alexandra Zevalkink5

1: Michigan State University, East Lansing, Michigan, United States; 2: Université catholique de Louvain, Louvain-la-Neuve, Belgium.

AMg2Pn2 compounds with the layered CaAl2S3 structure type have received a great deal of attention recently due to their excellent thermoelectric properties. The binary member of this structure type, Mg2Sb2, exhibits the highest peak z ≤ 1.6, due in part to its surprisingly low lattice thermal conductivity. Here, we explore trends in the thermal properties of AMg2Pn2 compounds (Pn = Sb or Bi and A = Mg, Ca, Sr, Ba, Yb, Eu) to elucidate the role that the cation radius and electronegativity in determining the elastic moduli and anharmonicity in this structure type. Temperature-dependent resonant ultrasound spectroscopy and inelastic neutron scattering are used to investigate the elastic moduli and speed of sound, while phonon calculations within the quasi-harmonic reveal mode Grüneisen parameters. The binary compounds Mg2Sb2 and Mg2Bi2 are found to have anomalously soft shear moduli and large mode Grüneisen parameters. We attribute this primarily to the undersized Mg cations, which are too small for the 6-fold octahedral coordination with Sb or Bi, leading to weak interlayer bonds, highly anharmonic transverse acoustic phonon modes, and high rates of phonon-phonon scattering. The consequence is that those compounds with the lowest density in the AMg2Pn2 series are also those with the lowest lattice thermal conductivity.

**CM01.12.02**

**Oxidation-Resistive Two-Dimensional Dihafnium Sulfide Electride with Efficient Electrocatalytic Activities in Water-Based Solution**

SeHyang Kang, Ye Ji Kim and Sung Wng Kim; Sungkyunkwan Univ, Suwon, Korea (the Republic of).

Electrides are exotic ionic crystals where excess electrons are located in cavities as anions. Because of the loosely bound anionic electrons, electrides have been received much attention, exhibiting intriguing physical and chemical phenomena, such as low work function, high electron mobility and excellent catalytic reactivity1,2. However, the electro-active functionalities of electrides have been degraded once oxygen and/or moisture is absorbed, preventing the novel applications for an industry. It is thus highly demanded to discover a thermally or chemically stable electride in ambient or moisture condition. Here, we report the highly oxidation-resistive dihafnium sulfide ([Hf2S]2+2e−) electride with efficient hydrogen evolution electrolysis (HEE) activities over 5,000 cycles in water. We have grown single-crystals [Hf2S]2+2e− electride with floating zone (FZ) melting method. X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) combined with density functional theory (DFT) calculations clarify that [Hf2S]2+2e− electride has two excess electrons per formula unit, which are confined in the Hf-Hf interlayer with dumbbell-like shape. [Hf2S]2+2e− electride shows a state-of-the-art durability against air and water among the existing electrides, retaining the crystal structure and physical/chemical properties over 1 month. Furthermore, Cu-loaded [Hf2S]2+2e− electride shows highly effective HEE performances comparable to the defect-rich MoS2, which is one of the most effective catalyst except Pt for water splitting. Transmission electron microscopy (TEM) observation indicates that the formation of thin native amorphous HfO2 layer, known as oxidation-resistive passivation layer, is responsible for the electro-catalytic activity in water. It is verified that the anionic electrons of [Hf2S]2+2e− electride can migrate to the Cu nanoparticle through the amorphous HfO2. Our findings provide an important insight into the design strategy of new oxidation-resistive electrides and their active functionality in electro-catalysis.


**CM01.12.03**

**Effect of Crystal Structure on Hole Carrier Generation in Wide-Gap P-Type Tin-Niobate**

Akane Samizo1, 2; Naoto Kikuchi3; Yoshihiro Aiura2 and Keishi Nishio1

1: Tokyo University of Science, Tokyo, Japan; 2:National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Transparent conducting oxides (TCOs) are widely used as transparent electrodes in displays and solar cells. However, most of existing TCOs are n-type semiconductors such as ITO (In2O3:Sn) and ZnO. In order to fabricate transparent devices based on p-n junctions, the development of p-type TCOs are required. The reason of the difficulty in development of p-type TCOs is low hole mobility. Since the wide band-gap of TCOs comes from significant contribution of ionistic character to chemical bonds between metal cations and oxygen anions, positive holes at valence band maximum (VBM) are strongly localized around O 2p orbitals. Thus, delocalization of VBM is essential for material design for realizing p-type TCOs. The oxidation of metal cations with ns2 electronic configurations (n: the principal quantum number) such as Pb5+; Sn4+ (hereafter s-orbital-based oxides) have been recently attracted as new candidates for p-type TCOs. The large spatial spreading and isotropic nature of metal s orbitals delocalize the VBM, then low effective mass of holes is expected. However, only a few reports on electrical properties of these oxides exist because of difficulties in hole carrier generation. The s-orbital-based oxides require to anneal in reduced atmosphere in order to prevent oxidative decomposition (eg. SnO changes to SnO2),
which results in a charge compensation of holes by electrons generated by the formation of oxygen vacancies ($V_{o}^{**}$). Therefore, controlling of structural defects, e.g., oxygen vacancies is indispensable for introduction of hole carriers. We focus on Sn$^2+$ oxides, which is more environmental-friendly compared to Pb$^2+$, and succeeded in preparation of p-type Sn$_2$Nb$_2$O$_7$ and SnNb$_2$O$_6$ by sample annealing. The crystal structure of both oxides has a substructure of Nb$_6$O$_{12}$ octahedral, and there are considerable three kinds of native point defects, $V_{o}^{**}$, Sn$^{4+}$-on- Nb$^{5+}$ substitutional defects (Sn$'$Nb), and tin vacancies ($V_{Sn}''$). We found that the hole carriers were generated by Sn$'$Nb in Nb$_6$O$_{12}$ octahedra in both p-type tin-niobates. Although same hole carrier source was found, the carrier generation efficiency of Sn$_2$Nb$_2$O$_7$ was in two orders higher than that of SnNb$_2$O$_6$. In this paper, the amount of each defects and distortion of the crystal structure was discussed by the Rietveld analysis in order to clarify the origin of difference in the carrier generation efficiency. We summarize characteristics of hole carrier generation related to structural defects of two tin-niobates. The findings obtained in this study may bring us detailed mechanisms of carrier generation in Sn$^2+$ oxides, leading to future transparent device applications.

CM01.12.04

Grain Boundary and Discontinuous Precipitation Phenomena in a Multicomponent Alloy Julio C. Spadotto$^2$, Grace Burke$^1$ and Guillermo Solórzano$^2$; $^1$University of Manchester, Manchester, United Kingdom; $^2$PUC-Rio, Rio de Janeiro, Brazil.

Discontinuous precipitation (DP) reaction is a grain-boundary (GB) diffusion-controlled phenomenon driven by migrating GB, acting as fast reaction path under the action of chemical and capillary forces, leaving behind a regularly-spaced array of lamellar precipitates growing cooperatively from the supersaturated matrix. In multicomponent alloy systems containing both substitutional and interstitial solutes normally the DP colonies are constituted of either Cr-rich M$_2$C$_6$ or Cr$_7$N lamellae. However, DP colonies in superaustenitic stainless steel have been observed in which the lamellar σ phase has precipitated at the migrating GB and the additional precipitation of Cr$_7$N has occurred within the colony with increasing ageing time [1]. The present investigation deals with the DP reaction in Alloy 33, with nominal composition (wt.%) 33Cr-32Fe-31Ni-1.6Mo-0.6Cu-0.4N, upon aging at 800 °C. In order to understand the complex DP phenomenon in this alloy, both analytical scanning (SEM) and analytical transmission electron microscopy (TEM) have been used extensively for detailed microstructural characterization. The DP phenomenon in Alloy 33 displays different characteristics from those reported in the literature. After aging at 800 °C for 1 hour heterogeneous precipitation occurred at the GBs, where, in some cases, the initial stages of development of DP colonies were observed. At this stage, dislocations walls marking the original grain boundary position had been observed. Upon aging for 2 hours its verified in some regions of DP colony that the precipitates are connected to migrating GB, but in other regions of the same GB the boundary appears disconnected from the precipitate in a similar fashion as diffusion-induced grain boundary migration (DIBM) topologies. The intergranular precipitates were identified using selected area electron diffraction (SAED) and EDX microanalysis as Cr-rich M$_2$C$_6$ carbide with FCC structure. Based on DP theory, it is expected that the precipitate initially formed at GB grows together with the GB migration. After aging at 800 °C for 5 hours, energy dispersive X-ray spectrum imaging and SAED analyses confirmed that the original GB position is M$_2$C$_6$ in the DP colony, as expected. However, in the same DP colony, a platelet-type precipitate, identified as α-Cr phase with BCC structure, was also observed at the GB. Similar behavior was also observed in a different DP colony: M$_2$C$_6$ precipitation did not occur at the original GB position. In this DP colony, α-Cr phase was also observed along with a phase rich in Cr, Mo, and Fe at reaction front. These results showing different types of precipitates occurring at the early stages of the DP reaction show the complexity of this phenomenon in Alloy 33, and suggest a high entropy system behavior [2].

References: $^1$ S. Zhang et al., Mater. Charact., 137, pp. 244–255, 2018. $^2$ The authors are grateful to CNPq. Thanks are due to Dr Octav Ciuca for the help with the electron microscopes.

CM01.12.06

Unveiling the Nature and Structure of ZnO-Bi$_2$O$_3$ Grain Boundaries Marcelo A. Martinho, Gabriel D. Rocha, Marco A. Cordeiro and Edison R. Leite; UFSCar, São Carlos, Brazil.

Owing to the structural and chemical nature of polycrystalline materials, grain and phase boundaries play a fundamental role in these materials properties by tailoring desired material features. For example, grain boundaries have a tremendous implication in plastic deformation in materials, especially in failure mechanisms such as fatigue, fracture and creep, which are fundamental for the development of new materials, as superplastic ceramics. In spite of the evident importance, the basic understanding of interfaces is still in its beginning, and lacks an essential correlation of its structure and materials properties. In order to provide fundamental insights into the structure and chemical nature of the grain boundary in oxides, Bi$_2$O$_3$-doped ZnO$_2$ system was used. Due to its ample physical and chemical properties (e.g., chemical stability, broad range of radiation absorption and high photostability), ZnO$_2$ materials find place in a myriad of applications (e.g., varistors, photocatalysts, solar cells.). Besides, Bi$_2$O$_3$-doped ZnO$_2$ has been studied as a model for liquid-phase/activated sintering due to the lower temperature in the eutectic (~740 °C). Despite the important studies over the years, the knowledge of the sintering and grain boundary development is based on ex situ studies, which approach could hide fundamental aspects of sintering and grain boundary formation phenomena. In this study, ex situ and in situ studies of sintering and grain boundary formation were performed. Ex situ studies were carried out by using samples produced by oxide mixture (Bi$_2$O$_3$ and ZnO$_2$) followed by conventional sintering. The resulted pellets were polished and the grains revealed by temperature, and then studied by scanning electron microscopy (SEM). On the other hand, in situ studies were carried out by using ZnO$_2$ and Bi$_2$O$_3$ nanoparticles (NP) (10-20 nm), both synthesized by non-hydrolytic route (thermodecomposition of the acetate precursors) under the action of organic ligands (oleylamine and/or oleyl alcohol). Self-organization of ZnO$_2$ and Bi$_2$O$_3$ NPs on amorphous carbon film supported on nickel grids were submitted to in situ heating experiments in a Gatan 628 single-tilt heating holder (with an Inconel-based furnace) in a FEI Tecnai F20 field emission TEM operating at 200 kV. By real-time tracking the NPs sintering and grain boundary holder, it was possible to analyze the structure formation and further grain restructuration and correlation with the ex situ experiments. Moreover, the evolution of grain boundary formation and the final structure were correlated to the complex structures, providing a promising avenue toward the construction of grain boundary phase diagrams.

CM01.12.07

Control of Size Distribution of Surface Nanoparticle Formed by Selective Phase Transition in Sr$_{0.98}$Ti$_{0.95}$Me$_{0.05}$O$_{3-\delta}$ (Me = Mn, Fe, Co, Ni, and Cu) Jun Kyu Kim, Bonjae Koo and WoOchul Jung; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Supported metal nanoparticles (NPs) are of significant importance in heterogeneous catalysis owing to their excellent dispersion and many undercoordinated surface sites. Recently, the in-situ growth phenomenon of metal NPs directly from an oxide support, known as ‘ex-solution,’ has been reported as a new method of decorating oxide surfaces with uniformly dispersed metal NPs. Here, a catalytically active metal is embedded in the crystal lattice of a backbone in oxidizing conditions, forming a solid solution, and then is released (ex-solved) on the surface of the structure as metallic nanoparticles upon exposure to a reducing atmosphere. Compared to conventional nanoparticle synthesis and dispersion techniques, this process is faster, more cost-effective and allows finer and better particle distribution. Furthermore, the sintering of nanoparticles can be prevented by re-oxidation, enhancing the life-time of the supported nanoparticles. Despite extensive research efforts, however, the fundamental mechanisms of the processes remain largely unknown. Accordingly, how to control particle size and distribution precisely are also unknown, despite the fact that these processes are crucial to
render this phenomenon technologically attractive.

In this study, we prepared dense thin-films of 3d-transition metal (Mn, Fe, Co, Ni and Cu) doped and A-site deficient SrTiO3 with highly flat surfaces and observed the ex-solved particles on their surfaces depending on the annealing temperature, oxygen partial pressure, and kind of dopants. SrTiO3 was selected as a model perovskite host due to its superior phase stability in a wide range of temperatures and gas atmospheres, and the thin-film samples were used for reliable and reproducible surface analysis. We found that the nucleation and growth of ex-solved particles took place extremely fast, and their rate gradually increased as the pO2 decreases. Significantly, the lower the pO2 at the same temperature, or the higher the temperature at the same pO2, the greater the number of nuclei, which forms metal NPs with higher density and smaller size. These observations were explained through the classic nucleation theory, suggesting a novel technique to control the size and dispersion of supported metal NPs, which can be readily applied to various applications.

CM01.12.08
Rapid Discovery of Ternary Transition Metal Chalcogenides Ankit Bhutani¹, Julia Zuo¹, Thrivongadam Ranagarajan¹, Piush Behera¹, Awadhesh Narayan¹, Joshua Schliller¹, James N. Eckerstein¹, Santanu Chaudhuri², Lucas K. Wagner¹ and Daniel Shoemaker¹; ¹University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ²University of California, Santa Barbara, Santa Barbara, California, United States; ³ETH Zurich, Zurich, Switzerland; ⁴Illinois Applied Research Institute, Urbana, Illinois, United States.

In order to capitalize on computational modeling and predictions, fast and accurate experimental synthesis and characterization techniques must evolve. In this study, we investigate transition metal chalcogenides using high-throughput experimental techniques, such as temperature and time-resolved in-situ x-ray diffraction, powered by computational predictions. High-temperature in-situ x-ray diffraction accelerates materials discovery by allowing us to watch a chemical reaction in real time and identify new stable/metastable phases. It provides useful insights into the thermodynamics and kinetics of reactions. Transition metal chalcogenides are particularly interesting because of their understudied d-electron correlations which lead to various interesting properties including superconductivity, meta-magnetic metallic behavior, and quantum phase transitions.

I applied such a tandem approach to explore the Ba–Ru–S phase space using a combination of evolutionary algorithms and density functional theory (DFT) to inform traditional and in situ diffraction methods. My work identified a high-temperature polymorph of BaS2, that would have been otherwise missed in ex-situ reactions and did not reveal formation of the predicted candidates BaRu2S2 or BaRuS3 (Bhutani, A. et al. Chem. Mater. 29 (14), 5841–5849 (2017)). I then used this methodology to study several other ternary systems to screen for novel phases. I screened 31 ternary chalcogenide phase diagrams of the form XYZ (X = K, Na, Ba, Ca, Sr, La, K, Bi, Pb; Y is a 3d transition metal; and Z = S or Se), where DFT predicted new compositions (Wagner Research Group, Physics, UIUC). I discovered 9 new phases belonging to the K/Na-Zn/S/Se systems with potential uses as wide band gap semiconductors and found 27 phase diagrams to be “empty” in the case of bulk synthesis (Narayan, A., Bhutani, A. et al. Phys. Rev. B. 94, 045105 (2016)). I complete my study with detailed characterization of new phases using XRD, UV-Vis Spectroscopy, SEM and magnetic and transport measurements.

CM01.12.09
Exceptionally Enhanced Electrode Activity of (Pr,Ce)O2-δ-Based Cathodes for Thin-Film Solid Oxide Fuel Cells Han Gil Seo, Yoonsok Choi and WooChul Jung; Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

We show that an electrochemically-driven oxide overcoating substantially improves the performance of metal electrodes in high-temperature electrochemical applications. As a case study, we overcoat Pt thin films with (Pr,Ce)O2-δ (PCO) by means of cathodic electrochemical deposition process that produced nanostructured oxide layers with a high specific surface area and uniform metal coverage and then examine the coated films as an O₂-electrode for thin-film-based solid oxide fuel cells (TF-SOFCs). The resulting structures were examined by SEM, XRF and ICP-MS. The electrode activity of symmetric cells (cathode|electrolyte|cathode) was analyzed by the AC impedance spectroscopy (ACIS) measurements. The combination of excellent conductivity, reactivity and durability of PCO dramatically improves the oxygen reduction reaction rate while maintaining the nanoscale architecture of PCO layers and thus the performance of the PCO-coated Pt thin-film electrodes at high temperatures. As a result, with an oxide coating step lasting only 5 min, the electrode resistance is successfully reduced by more than 1000 times at 500 °C in air. Based on these observations, furthermore, we successfully designed and fabricated nano-columar PCO films with an enhanced specific surface area and succeeded in achieving high electrode performances. These findings provide useful guidance for design and fabrication of high-performance TF-SOFCs.

CM01.12.10
Oxygen Interstitial Migration in Solids from First Principles—Apatites and Mellitides Steffen P. Grieshammer¹, ¹Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany; ²Helmholtz-Institut Münster, Forschungszentrum Jülich GmbH, Münster, Germany.

Solid state oxygen ion conductors play a crucial role as electrolytes in solid oxide fuel cells (SOFC), solid oxide electrolyzer cells (SOEC) and rechargeable oxide batteries (ROB). In common oxygen ion conductors, like yttria-stabilized zirconia, oxygen transport is enabled by oxygen vacancies, while in recent years oxygen ion conductors where transport is enabled by interstitial ions have gained increasing attention.

In the present study, two examples of oxygen batteries (ROB). In common oxygen ion conductors, like yttria-stabilized zirconia, oxygen transport is enabled by oxygen vacancies, while in recent years oxygen ion conductors where transport is enabled by interstitial ions have gained increasing attention.

In the present study, two examples of oxygen ion conductors with an interstitial mechanism are investigated using density functional theory. Lanthanum apatites with the general formula La₃(BO₃)₂X₃X₆O₁₄ form a hexagonal structure with oxygen ion channels enabling transport along the crystallographic c-direction. Mellitides with the composition Al₂Ga₄O₉ crystallize in a tetragonal layered structure with oxygen interstitials migrating in a layer composed of GaO₆-units. The energies of defect formation and migration of oxygen ions via vacancy and interstitial mechanism are calculated for different compositions. In both types of materials the transport of oxygen ions by a cooperative interstitiality mechanism is favorable compared to vacancy migration. However, the migration energies clearly depend on the ordering of the cations around the migration oxygen ion. For apatites, compositions with X = Mg, Ca, Sr and Ba as well as B-deficient variations are considered. The migration energies are in a range of 0.1 eV to 0.4 eV for interstitialcy migration and more than 1 eV for vacancy migration. In mellitides with the composition La₂₋₅Sr₅Ga₄O₉₋₂ the migration barriers vary in a wide range of about 1 eV depending on the migration direction and the occupation of the surrounding cation positions.

The energies of intrinsic defect disorder for both materials are several eV suggesting that the fraction of ionic charge carriers is determined by the adjusted composition or by impurities in experiments. Experimental results from impedance spectroscopy measurements are used to complement the ab initio results.

CM01.12.12
Light Absorption Coefficient of CsPbBr3 Perovskite Nanocrystals Jerick Maco¹, ², Lieve Balcaen¹, Émile Drieyvers², Qiăng Zhao³, Jonathan De Roo⁴, ¹, André Vertommen¹, Frank Vanhaecke¹, Pieter Getregat¹, ² and Zeger Hens¹, ²; ¹Department of Chemistry, Ghent University, Ghent, Belgium; ²Center for Nano and Biophotonics, Ghent University, Ghent, Belgium; ³Instituut voor Kern- en Stralingsfysica, KU Leuven, Leuven, Belgium; ⁴Department of Chemistry, Columbia University, New York, Belgium.

The concentration of colloidal nanocrystals (NCs) is a key characteristic for any quantitative study on nanocrystals. At present, the concentration of CsPbBr3 NCs is typically quantified by means of an absorption coefficient or cross section obtained from photoluminescence saturation or by
thermogravimetric analysis; two methods that are not accurate and need benchmarking by direct quantification methods. We combined inductively coupled plasma mass spectrometry (ICP-MS), UV−vis absorption spectroscopy and transmission electron microscopy to determine the size, composition, and intrinsic absorption coefficient $\mu_i$ of 4 to 11 nm sized colloidal CsPbBr$_3$ NCs. The ICP-MS measurements demonstrate the nonstoichiometric nature of the NCs, with a systematic excess of lead for all samples studied. Rutherford backscattering measurements indicate that this enrichment in lead cores with a relative increase in the bromide content. At high photon energies, $\mu_i$ is independent of the nanocrystal size. This allows the nanocrystal concentration in CsPbBr$_3$ nanocolloids to be readily obtained by a combination of absorption spectroscopy and the CsPbBr$_3$ sizing curve.

Nanoparticle temperature monitoring using a complete thermodynamic cycle, including detailed molecular dynamics simulations of vacancy migration through the growing nanocrystals, has been combined with a comprehensive analysis of the properties that are determined by the vacancy formation process. This approach has been used to gain insights into the properties of nanocrystals that are relevant to their potential applications in a wide range of fields, including catalysis, electronics, and energy storage.

The use of magnetic nanoparticles (NPs) to convert electromagnetic energy into heat is known to be a key strategy for numerous biomedical applications but is also an approach of growing interest in the field of catalysis. We have shown that, associated to catalytic metals (Ni, Ru), iron carbide NPs submitted to magnetic excitation very efficiently catalyze CO$_2$ hydrogenation in a dedicated continuous-flow reactor. Since a huge gradient of temperature between the self-heated particles and the “cold” environment is expected, nanoscale measurements need developments to correlate the result of catalysis reaction to NPs temperatures, but also to control the process to keep constant the heating power or the NP surface temperature. Thermometric probes have been described at low temperatures with different luminescent species. However, using phosphors to determine high temperatures under harsh experimental conditions remains largely unexplored and highly challenging. At the nanoscale, QDs optical properties offer a rare opportunity to build an innovative complex nano-object integrating heating capacities, catalytic ability and thermal reporting property. The temperature-dependent emission of different QDs (InP@ZnS and CdSe@CdS) have been investigated in this purpose. Peak emission wavelength, intensity, and full width at half maximum were completely described as a function of temperature. We will present here the use of QDs as local temperature probes during the magnetic heating of iron carbides NPs in catalysis conditions. We evidence that the global temperature (measured by a thermal camera) of the catalytic solid is drastically lower than the local temperatures measured by the QDs at the nanoscale.

Quantitative understanding of high temperature oxidation of alloys at the atomic scale to the microscale has remained a challenge and can guide in rational materials design. We employed accurate interatomic potentials and available experimental data to analyze the oxidation mechanism of Ni at high temperature using a complete thermodynamic cycle, including detailed molecular dynamics simulations of vacancy migration through the growing

**CM01.12.13**

*Control of Transition Metal---Oxygen Bond Length Boosts the Redox Ex-Solution in Perovskite Oxide Surface*  
Bongsoo Koo, Kyeoung academia, Yong-Ryun Joo, Siwon Lee, Jun Kyu Kim, Min Ji Seo, Bong-Joong Kim, Jeong Woo Han and Woochul Jung; 2; Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of); 3Pohang University of Science and Technology (POSTECH), Pohang, Korea (the Republic of); 4Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of).

Nano-sized metal particles have been widely used as heterogeneous catalysts for various reactions due to their high surface-to-volume ratios and possibly unique catalytic properties. Particularly when dispersed on oxide supports, their catalytic activities are often greatly enhanced compared to those in pure metal particles. Recently, in-situ growth via metal nanoparticles (NPs) directly from an oxide support, known as ‘ex-solution’, has been reported by multiple researchers in the fields of high-temperature catalysis and renewable energy. When perovskite oxides (ABO$_3$) are used as a hosting framework, transition or precious metals can be dissolved as cations in the B-sites of the perovskite lattice under oxidizing conditions; they can also be ex-solved partially upon subsequent reduction as nano-sized metallic phases decorating the oxide surface. Compared to traditional nanoparticle synthesis and dispersion techniques, this process is faster, more cost-effective and allows finer and better particle distribution. Furthermore, the exsolved metal NPs are deeply soaked into the parent perovskite with a wide particle-substrate interface, leading to enhanced sintering and hydrocarbon cracking resistance. More importantly, its reversibility indicates that catalyst agglomeration can be avoided through re-oxidation, significantly enhancing the lifetime of the supported catalysts. Since the key to this phenomenon is how stable certain cations are in a perovskite lattice, it is obvious that the bond strength between neighboring cations and oxygen ions determines the outcome of ex-solution. To the best of our knowledge, however, there is no atomic-level consideration of the intrinsic stability of a reducible cation surrounded by six oxygen ions in a lattice, and thus a solution that effectively controls the amount or distribution of the exsolved particles is not yet known.

Here, we investigate the influence of the bond length between the B-site transition metal and the neighboring oxygen in a perovskite lattice on surface transition metal ex-solution. Considering dense epitaxial thin films of Sr$_{1-x}$Co$_x$O$_3$ (STC) as a model system, we control the average Co-O bond length through the misfit strain of STC films, and monitor how the surface composition and catalytic reactivity for CO oxidation changes accordingly. Combined theoretical and experimental analyses show that the relatively weak bond strength induced by the elongated Co-O bond in STC drives the Co ex-solution significantly and thus activates the CO oxidation. Based on the observations, we conclusively demonstrated that the tensile strain could be sufficiently increased by introducing a large-sized isovalent dopant, offering a new strategy for activating the ex-solution phenomenon.

**CM01.12.14**

**A Novel Class of Oxynitrides Stabilized by Nitrogen Dimer Formation**  
Sanjae Kim, Seung-Hyub Back and Chong-Yung Kang; 1; 2; 3Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2KU-KIST Graduate School of Converging Science and Technology, Seoul, Korea (the Republic of).

Despite the wide applicability of oxynitrides from photocatalysis to refractory coatings, our understanding of the materials has been limited in terms of their thermodynamics. The configurational entropy via randomly mixed O/N or via cation vacancies are known to stabilize oxynitrides, despite the positive formation enthalpies. Here, using tin oxynitrides as a model system, we show by ab initio computations and experimental characterization that oxynitrides in seemingly charge-unbalanced composition stabilize by forming nitrogen dimers among metal-(O,N)$_6$ octahedra. The nitrogen dimer, (N-N)=, reduces formation enthalpies. Here, using tin oxynitrides as a model system, we show by computationally and experimentally that oxynitrides in seemingly charge-unbalanced composition stabilize by forming nitrogen dimers among metal-(O,N)$_6$ octahedra. The nitrogen dimer, (N-N)=, reduces formation enthalpies.

**CM01.12.15**

**Magnetic Heating Monitoring with Quantum Dots Nanothermometers**  
Celine Navral, Gaelle Muraille, Robert Swain, Benjamin McVey, Bruno Chaudret and Fabien Delpech; Univ of Toulouse, Toulouse, France.

The use of magnetic nanoparticles (NPs) to convert electromagnetic energy into heat is known to be a key strategy for numerous biomedical applications but is also an approach of growing interest in the field of catalysis. We have shown that, associated to catalytic metals (Ni, Ru), iron carbide NPs submitted to magnetic excitation very efficiently catalyze CO$_2$ hydrogenation in a dedicated continuous-flow reactor. Since a huge gradient of temperature between the self-heated particles and the “cold” environment is expected, nanoscale measurements need developments to correlate the result of catalysis reaction to NPs temperatures, but also to control the process to keep constant the heating power or the NP surface temperature. Thermometric probes have been described at low temperatures with different luminescent species. However, using phosphors to determine high temperatures under harsh experimental conditions remains largely unexplored and highly challenging. At the nanoscale, QDs optical properties offer a rare opportunity to build an innovative complex nano-object integrating heating capacities, catalytic ability and thermal reporting property. The temperature-dependent emission of different QDs (InP@ZnS and CdSe@CdS) have been investigated in this purpose. Peak emission wavelength, intensity, and full width at half maximum were completely characterized as a function of temperature. We will present here the use of QDs as local temperature probes during the magnetic heating of iron carbides NPs in catalysis conditions. We evidence that the global temperature (measured by a thermal camera) of the catalytic solid is drastically lower than the local temperature measured by the QDs at the nanoscale.

Quantitative understanding of high temperature oxidation of alloys at the atomic scale to the microscale has remained a challenge and can guide in rational materials design. We employed accurate interatomic potentials and available experimental data to analyze the oxidation mechanism of Ni at high temperature using a complete thermodynamic cycle, including detailed molecular dynamics simulations of vacancy migration through the growing
nanometer-thick NiO oxide layer. The energy profile of all steps including oxygen adsorption, bond dissociation, charge transfer from metal to oxygen, cation vacancy-diffusion, and growth of the oxide interfacial layer are discussed and quantified. Cation vacancy migration in the NiO films becomes the critical process determining the overall oxidation rate. The effect of oxide film thickness, a step-edge, and a crescent on the Ni cation diffusion barrier was predicted which is consistent with experimental observations, and the methods can be applied to models up to several 100 nm size. The atomistic model of NiO used a nonbonded-only potential that involves Coulomb and Lennard-Jones terms. Care is taken that the atomic charges remain close to verifiable internal dipole moments even though covalent bonding contributions are disregarded. The non-bond model of NiO is inherently reactive, enabling changes in morphology and defects. It achieves quantitative agreement with experiment in lattice parameters (-1% deviation) and in bulk modulus (+10% deviation). It is fully compatible with existing parameters for other oxides, metals, solvents, and polymers following the IFF protocol. The parameters are available using both 12-6 and 9-6 Lennard-Jones potentials to achieve compatibility with CHARMM, CVFF and AMBER.

CM01.12.17
Understanding Processing-Property Relationships in Pulsed Laser Deposition of Complex Oxides via Crowd-sourced Database Generation and Machine Learning
Rama K. Vasudevan, Steven R. Young, Robert Patton and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Current methods of material design and synthesis relies largely on researcher intuition and large numbers of iterations in a vast parameter space. Much of the data that can aid in this process is scattered throughout the extant literature, but is scattered, uncollated and unindexed. We present a method to employ text mining through the form of regular expressions in combination with crowd-sourcing, to yield a database of growth condition-functional property information for select oxides grown via pulsed laser deposition. Open source tools facilitate the text mining, automatically annotating the relevant information, while user-led efforts in the form of crowd-sourcing sift through annotated data as well as figures, to compile database entries in an efficient manner. We have produced a database with hundreds of entries, which show growth windows, trends and outliers, and which can serve as a template for analyzing the distribution of growth conditions and provide starting points for related compounds. Basic visualization and machine learning enables correlations to be determined, with an example shown for the narrow growth window of BiFeO3, and a decision tree-based classifier that can predict whether a Tc for a manganite thin film will be in a certain range. These tools and methods will be useful to assisting in mining processing-property relationships, aiding both materials synthesis and materials design, and their integration with first-principles modeling will be critical in completing the materials feedback loop.

The Laboratory Directed Research and Development fund at ORNL is acknowledged. Research was conducted at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility.  

CM01.12.18
New “ZN” Model for Zero Poisson’s Ratio Structures
Alexandre F. Fonseca1, Socrates O. Dantas2-1 and Douglas S. Galvao1; 1State University of Campinas, Campinas SP, Brazil; 2Universidade Federal de Juiz de Fora, Juiz de Fora, Brazil.

Poisson’s ratio (PR) is a measure of a material’s change along its transversal dimensions under the application of an axial strain. Most materials present positive PR, i.e., they laterally shrink (expand) under the application of a tensile (compression) strain. Other materials and structures present, on the other hand, negative PR and are called “auxetic”. Re-entrant polymeric crystals and/or foams are examples of auxetic materials [1]. Even more rare are the materials and structures presenting zero Poisson’s ratio (ZPR) [2]. i.e., materials that neither contract nor expand laterally under the application of an axial strain. Gases and semi-re-entrant honeycomb structures are known examples of ZPR materials [2,3]. Motivated by recent attempts to produce new ZPR structures [4,5], we propose a new type of ZPR structure that is not based on re-entrant honeycomb or hexagonal structures. The proposed structural model is composed of planar structures formed by the junctions/fusions, side by side, of several blocks in the shape of letters “Z” or “N”, which are two parallel bars connected by a diagonal bar, so the name “ZN” model. These diagonal bars are formed by soft, low bending stiffness materials, while rigid, high stiffness materials form the other two parallel bars. We show that such a kind of structure presents ZPR along both orthogonal directions. We discuss the challenges involving the production of these models, how to build a tri-dimensional ZPR structure from our two-dimensional “ZN” model, and the feasibility of having such a ZPR structure at nanoscale.


CM01.12.19
Thermal Properties of 2:1 Bismuth Borate Ceramics—Microscopic Contribution of Lone Electron Pairs for Lattice Expansion Tensors
Mangir Mushref1,2, Hilke Petersen1, Michael Fischer1-2, Mariano Curti2, Cecilia B. Mendive1, Volodymyr Baran1, Anatoly Sensyshyn2 and Thorsten M. Gesing1-2; 1Institute of Inorganic Chemistry and Crystallography, University of Bremen, Bremen, Germany; 2MAPEX Center for Materials and Processes, University of Bremen, Bremen, Germany; 3Crystallography, University of Bremen, Bremen, Germany; 4Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Mar del Plata, Argentina; 5Research neutron reactor ZWE FRM-II, Munich University of Technology, Munich, Germany.

The applications of bismuth-borates require knowledge of thermal expansion coefficients for optical, mechanical and electronic properties. However, to understand the microscopic features leading to macroscopic thermal expansion of bismuth borates is not straightforward as borates mostly show high anharmonic thermal expansion even with negative expansion tensors. Herein we report the thermal expansion of Bi2B6O11 between 4 K and 900 K using temperature-dependent neutron and X-ray powder diffractions and Raman spectroscopy. Thermal expansion was modeled using the Debye-Einstein-Anharmonicity [1,2] fit. The calculated phonon density of states (PDOS) shows two broad continua with a sharp feature at 890(1) cm⁻¹. Comparing the highest frequency of the PDOS the model simulation results in a Debye frequency that represents only the acoustic lower frequency parabolic spectrum. The model also follows six independent thermal expansion tensors of the monoclinic system. The ¹¹B-enriched sample showed a mean B-O bond distance of 138(1) pm within the whole investigated temperature range. Due to stereochemical activity of the 6x⁶ lone electron pair (LEP) of Bi³⁺, four distinctive BiO₆ polyhedra showed different distortions: (i) the Wang-Liebau eccentricity (WLE) parameter [3] for each Bi-atom decreases with increasing temperature, indicating the electron deformation density associated with LEP is a function of temperature as well as the thermal expansion tensors. These phenomena are of fundamental interest to understand temperature-dependent non-linear optical and ferroelectric behaviors of relevant centrosymmetric systems.

Temperature-Dependent Structural and Spectroscopic Investigations of \( (\text{Bi}_{0.83}\text{Fe}_{0.17})\text{FeO}_3 \) Using Neutron Elastic and Light Inelastic Scattering

Andrea Kirsch\(^1\), Manjir Murshed\(^1\),  Ashfaq Haq\(^2\), and Thorsten M. Gessing\(^1\)

\(^1\)University of Bremen; \(^2\)Institute of Inorganic Chemistry and Crystallography, Bremen, Germany; \(^3\)Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; \(^4\)University of Bremen; \(^5\)MAPEX Center for Materials and Processes, Bremen, Germany.

\( \text{BiFeO}_3 \) is one of the widely studied multiferroic materials for interesting properties \([1]\) depending on crystal chemistry \([2]\) and crystalline/particle dimensionality \([3]\). Recently, a \(^{57}\text{Fe} \) Mössbauer spectroscopy and X-ray powder diffraction (XRPD) study revealed a series of \((\text{Bi}_{x}\text{Fe}_{1-x})\text{FeO}_3\) perovskite-type structures, where the Bi-site is partially shared by Fe \([4]\). To further tune the multiferroic property either from electric or magnetic approaches, or simultaneously both directions, the present study reports two compositions \((\text{Bi}_{0.83}\text{Fe}_{0.17})\text{FeO}_3\) and \((\text{Bi}_{0.67}\text{Fe}_{0.33})\text{FeO}_3\). Samples were synthesized by a sol-gel route at 873 K. Starting from X-ray amorphous nano-crystallites heating time and temperature exclusively determine the iron occupancy on the perovskite site \([4]\). The materials were investigated by temperature-dependent neutron time-of-flight powder diffraction at POWGEN (SNS, Oak Ridge, USA) from 10 K to 650 K. A deep minimum has been observed at about 240 K for the change of coordination of Fe-site and O-sites in \((\text{Bi}_{0.67}\text{Fe}_{0.33})\text{FeO}_3\) system, which has been shifted to 260 K for \((\text{Bi}_{0.83}\text{Fe}_{0.17})\text{FeO}_3\). Any anomaly was not observed for the temperature-dependent atomic displacement parameters (ADPs) and thermal expansion. Fitting the ADPs using Debye approach, all three atom-sites showed usual harmonic behavior, leading to a Debye temperature of 288(10) K and 368(13) K for \((\text{Bi}_{0.83}\text{Fe}_{0.17})\text{FeO}_3\) and \((\text{Bi}_{0.67}\text{Fe}_{0.33})\text{FeO}_3\), respectively. Notably, the Bi/Fe and O-sites show significantly a higher frequency shift of two selective modes than those of the stoichiometric \(\text{BiFeO}_3\) perovskite. The damping factors obtained from the simplified Klemens phonon decay model distinguishes between the phonon and magnon contributions to the microscopic heat capacity of the modes.


Investigation of Structural and Magnetic Properties of RT\(_2\)Ga Compounds

George Ahegworovri and Corey Thompson; Chemistry, Purdue University, West Lafayette, Indiana, United States.

Ternary \( \text{RT}_2\text{X} \) compounds \((\text{R} = \text{rare earth, T} = \text{transition metal, X} = \text{Al, Ga, Si, Ge}) \) and their derivatives have been the subject of intense research during recent years. These compounds crystallize in three structure-types, cubic \( \text{MnCu}_2\text{Al} \), orthorhombic \( \text{YPd}_2\text{Si} \), and hexagonal \( \text{GdP}_2\text{Sn} \). In this system, the silicides, germicides, and aluminides are the most studied and little is known about their gallium congeners. \( \text{RPd}_2\text{Ga} \left( \text{R} = \text{La} - \text{Dy} \right) \) is the only gallium compounds that have been studied thus far. These compounds exhibit both ferromagnetic \((\text{R} = \text{Tb})\) and antiferromagnetic \((\text{R} = \text{La} - \text{Gd, Dy})\) properties with an ordering temperature ranging from 2 to 24 K. We have synthesized several new \( \text{RT}_2\text{Ga} \) phases \((\text{T} = \text{Fe, Co, R} = \text{Gd, Tb, Dy})\), with ferromagnetic transitions greater than those exhibited by the \( \text{Pd}-\text{analogs} \). The structural and physical properties of these new ternary compounds will be highlighted in this talk.

Structural Transitions, Jahn-Teller Distortion, Cyclability and Specific Energy in \( \text{PZ}-\text{Type Na}_2\text{MnO}_2 \) (M=Transition Metals) Materials as Candidates for Sodium-Ion Battery Cathode Applications

Uma Garg\(^1\), William C. Rexhausen\(^2\), Nathaniel P. Smith\(^1\), Joshua Harris\(^2\), Deyang Qu\(^2\) and Prasenjit Guptasarma\(^1\); \(^1\)Department of Physics, University of Wisconsin Milwaukee, Milwaukee, Wisconsin, United States; \(^2\)Department of Mechanical Engineering, University of Wisconsin Milwaukee, Milwaukee, Wisconsin, United States.

Development of reliable, high-performance solid state materials for advanced energy conversion and storage is of technological importance for the US economy as well as for a secure, sustainable energy future for humankind. The design of present-day Li and Li-ion batteries have relied on previous studies of composition, crystal structure-property characterization, and device performance. Na-ion cathode materials are potential alternatives to Li-ion materials due to the natural abundance, and low cost, of sodium resources. Recent developments in suitable electrolyte and anode materials have revived interests in the use of newer Na-based compositions and structures as potential battery electrode materials. Here, we report our results on different compositions of layered oxides of the type \( \text{Na}_2\text{MO}_2 \) (where \( \text{M} = \text{a transition element, or a combination of transition elements} \)) as cathodes in coin cells built using a Na anode, \( \text{NaClO}_4 \) electrolyte and Celgard separator in a CR 2032 coin cell assembly. Specifically, we discuss the effect of \( \text{in-situ} \) battery voltage cycling on crystal structure, and on structural transitions, in \( \text{PZ}-\text{type Na}_2\text{MnO}_2 \) (NMFO). We find NMFO to have a reversible capacity of 185 mAh/g, but relatively low cyclability. Our results confirm that NMFO undergoes a structural transition from \( \text{P6}_3\text{mmc} \) to \( \text{P6}_3 \) at 4.3 V while charging, and to a \( \text{Cmcm} \) at 1.5 V while discharging. It is currently believed that the presence of \( \text{Mn(III)} \), a Jahn-Teller active ion leads to a cooperative distortion and structural instability, resulting in a transition from \( \text{hexagonal P2} \) to \( \text{orthorhombic P2'} \) during cycling. We have studied the effect of substitution of additional transition metals in NMFO in an effort to suppress this distortion and structural instability and to increase cyclability. We performed crystal structure refinement on \( \text{ex-situ} \) x-ray diffraction under controlled atmospheric conditions, as well as studies of battery capacity, specific energy, and cyclability at different battery voltage values during cycling. The substitution of additional transition metals is found to lead to an absence of structural transitions during charging and discharging to 4.3 V and 1.5 V, respectively. However, charging at 4.3 V affects the crystallinity of the material as observed by the broadening of x-ray diffraction (XRD) peaks. The cyclability and capacity was found to improve when the cells are cycled in the voltage range 1.5–4.0 V and 2.0 – 4.0 V, with an increase in specific energy from 325 Wh/g to 375 Wh/g when cycled in the 1.5 – 4 V range. Specific energy remains steady up to 100 cycles, pointing to the possibility of higher cyclability. We believe that additional detailed work on the effect of the Mn(III) Jahn-Teller distortion on properties of Na-ion cathode phases can lead to battery materials with improved capacity and cyclability.
CrFeO₃ is a spinel inverse spinel structured crystal with potentially interesting magnetic, electronic, and photophysical properties. The parent materials Fe₂O₃ (magnetite) and Fe₃O₄ (chromite) are naturally occurring minerals each with their own interesting and industrially useful properties. Despite the general interest in the parent compounds, CrFeO₃ is among the least studied of the transition metal spinels. Part of this gap in research lies in the lack of availability of high quality single crystals to study on top of being an unnatural compound. To get around the latter part we can use molecular beam epitaxial (MBE) growth techniques to control the precise stoichiometry and orientation to allow for synthesis of meta-stable or unnaturally layered materials. However, there still remains a lack of suitable single crystal substrates for epitaxial growth of CrFeO₃. MgO (magnesia) has a favorable lattice mismatch of just ~0.34% compressive, but Mg diffusion from the substrate into the overlying film can become significant at deposition temperatures as low as 250°C, creating a tradeoff between crystallization kinetics and intermixing. MgAlO₃ (spinel) is isostructural with CrFeO₃ and more stable against intermixing, but it also has a much smaller lattice constant, and lattice mismatch >5% compressive. Here we report on novel MBE synthesis of CrFeO₃ on spinel and with a variety of similar systems, previously studied. A novel method for estimating cation concentration is presented and scrutinized.

Transmission electron microscopy (TEM) (1) has been used to analyze the material structure in detail and correlated to bulk techniques like x-ray diffraction (XRD). Surface chemistry, surface structure, optical absorption, magnetic properties, out-of-plane lattice constants, and other material properties are examined as a function of reversible cation valence, cation stoichiometry, and growth conditions.

Keywords: Molecular beam epitaxy (MBE), ellipsometry, reflected high energy electron diffraction (RHEED), low energy electron diffraction (LEED), X-ray photoemission (XPS), thin film, stoichiometry, magnetite, Fe₃O₄, chromium, iron, oxygen, Fe₃O₄, magnesite, hematite, semiconductor, optical, X-ray diffraction (XRD), extended x-ray absorption fine structure (EXAFS), x-ray absorption near edge spectroscopy (XANES), Rutherford backscattering spectrometry (RBS)

CM01.12.24
Heterointerface Effects on the Peculiar Growth Characteristics of Brownmillerite SrFeO₂.₅ Thin Film Grown on Perovskite SrRuO₃ and SrTiO₃

The rich properties and broad utilities of transition metal oxides are enabled by the strong coupling among the lattice, charge, spin, and orbital degree of freedom, which basically originates from the strong hybridization between transition metal d and oxygen 2p orbitals. Engineering such complex correlations has thus been recognized as a route for tailoring functional properties of transition metal oxides. In recent years, unprecedented physical phenomena further emerged by manipulating the heterointerface of transition metal oxides, such as two-dimensional free electron gases, which have never been accessed in their bulk equilibrium phases. These new phenomena were born through the interface controls which essentially modify the degree of the orbital hybridization. Basically, such interface structure and/or chemistry could also exert a profound influence on the growth dynamics of oxide thin films on foreign substrates. In addition to controlling the growth process of the thin films by a conventional method, i.e. imposing an epitaxial strain, various interface effects can extend the range of choice for manipulating the growth behavior of oxide thin films. The resulting growth behavior significantly affect the microstructures and physical properties of the thin films correspondingly. Therefore, accurate determination of oxide heterointerface structure is essential for understanding the growth characteristics of oxide thin films and for fabricating the functional devices having desired physical properties.

The interface effect can play a crucial role in controlling the growth behavior of oxide thin films by overcoming the simple epitaxial strain energy. For that purpose, brownmillerite SrFeO₂.₅ (BM-SFO) thin films were grown on SrTiO₃ (STO)(001) and SrRuO₃ (SRO)(001) substrates as a model system, and their microstructures were investigated using first principles calculations and transmission electron microscopy. The BM-SFO thin films grown on both the STO(001) and SRO/STO(001) substrates showed b-axis oriented growth at the interface, as opposed to the a-axis oriented growth predicted simply by the epitaxial strain effect from lattice mismatch with the substrates. They even revealed distinct heterointerface structures and growth processes on the two substrates having the same in-plane lattice parameters, which indicates the presence of additional key factors controlling growth characteristics of the thin films. We found that these discrepancies in the growth processes of the thin films originated from the interface effects governed by the heterointerface structures such as the ‘peculiar transition layer’ as well as the different chemical species and ‘octahedral connectivity’.


CM01.12.25
Diamond-Clad Semiconductor Optical Fibers

Optical fibers are a cornerstone of modern communications and research. The simplest of these fibers, made of silica, guide light with exceptionally low losses, while more complex microstructured or doped silica fibers are capable of advanced photonics. Such structures are immensely useful but have one clear limitation: optical fiber technology has historically been limited to glass. Materials such as semiconductor materials can expand the optical and electronic functionality of fiber technology, but have proven difficult to manufacture because their properties are not compatible with conventional glass drawing processes. High pressure chemical vapor deposition (HPCVD) circumvents this issue by enabling the direct deposition of semiconductor materials into glass capillaries via the thermal decomposition of gaseous precursors. With HPCVD, optical fibers composed of highly pure semiconductor cores, including silicon and zinc selenide, have been synthesized. These fibers possess low optical losses due to their atomically smooth surfaces and infrared transparency and exhibit a range of tunable material properties, opening the way for new functional fibers. Despite broadening the materials base for optical fibers, HPCVD continues to operate with the constraint that materials are deposited into glass templates. Current efforts are underway to replace this glass cladding with materials such as diamond. Diamond possesses a range of extraordinary properties, including high thermal conductivity and wide optical transparency in the IR, making it an ideal cladding for materials such as silicon or zinc selenide fiber. To synthesize diamond claddings, silicon wires are first deposited using HPCVD. Following deposition, the silicon glass is removed by etching in hydrofluoric acid, leaving a bare silicon wire that may be used as a substrate for microwave plasma CVD. Dip-coating and sputtering are then used to seed...
such fibers and enable the deposition of diamond claddings tens of microns thick around the entire fiber structure. Scanning electron microscopy and Raman spectroscopy are used to characterize the diamond, revealing excellent crystallinity. In addition, waveguiding of infrared light has been demonstrated in such fibers.

References

CM01.12.26 Synthesis and Structural Characterization of Non-Stoichiometric Ferrite Nanopowders Keri A. Ledford1, Kenneth Allen1, Jason H. Nadler1, Rick Moore1, David Reid2 and Sarah Lombardo2; 1Georgia Tech Research Institute, Atlanta, Georgia, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

Sol-gel processes, followed by an auto-combustion reactions to synthesize ferrites with tailorable stoichiometry have been investigated. Different compositions were produced by this method, substituting the iron in some of the crystal structure with other metals, including nickel, zinc, copper, manganese, and cobalt. A parametric study was conducted on the different compositions to determine the effects of calcining and leaching on the structure of the material. The as-synthesized, calcined, and leached nanopowders were characterized by x-ray diffraction and transmission electron microscopy.

CM01.12.27 Visible Absorbance Variation in Bismuth-Containing Dion-Jacobson Perovskites Luis J. Smith, Wendy Nason and Raistlin Bittues; Carlson School of Chemistry and Biochemistry, Clark University, Worcester, Massachusetts, United States.

Dion-Jacobson perovskites with the general formula A’A-nBnO3n+1 are of interest due to their photocatalytic, piezoelectric, ferroelectric properties as well as their ability to exfoliate into nanosheets and restack into new heterogeneous materials. Insertion of lead or bismuth into the interstitial sites of the layered niobates can shift the band gap of the material from the UV into the visible region. Incorporation of bismuth is desired to produce an alternative to the known APb2Nb2O7 (A = Cs, Rb) due to toxicity concerns with lead containing materials. However, the band gap energies of the double and triple perovskite layer version appear to depend on the A’ cation and A cation identities and the synthesis and ion exchange pathways when bismuth is part of A’ interstitial site population. The double-perovskite layer version, RbBiNb2O7, is reported to display ferroelectric and piezoelectric properties as well as possess a moderate indirect band gap (2.5 eV). However, when RbBiNb2O7 is acid-exchanged to remove rubidium under typical conditions (6M HNO3 at 60 °C) in preparation for the exfoliation process, the observed band gap of the material is no longer in the visible region, yet acid-exchange at low temperatures preserves the visible region band gap. A new Dion-Jacobson perovskite RbBiKnO3 has been synthesized via high temperature solid state methods using RbBiNb2O7 and KNbO3. The triple-perovskite layer version, RbBiKnO3, maintains an indirect band gap in the visible region (2.5 eV) before and after acid-exchange over a wide temperature range. However, replacement of the interstitial site potassium atoms with sodium results in a band gap in the ultra-violet region even in the rubidium-containing parent form. Results from x-ray diffraction, diffuse reflectance spectroscopy, and 93Nb solid-state NMR spectroscopy will be presented to discuss the evident changes in local structure due the site population variations that drive the band gap changes.

CM01.12.28 Comparative Study on Structural and Optical Properties of InGaN/GaN MQWs Grown by Pulsed MOVPE Mantas Dmukauskas1,2, Tadas Malinauskas3, Rolandas Tornasiunas1, Juras Mickevicius1, Darius Dobrovolskis1, Martynas Skapas4, Sandra Stanionyte5 and Arunas Kadys5; 1Institute of Photonics and Nanotechnology, Faculty of Physics, Vilnius University, Vilnius, Lithuania; 2Department of Characterization of Materials Structure, Institute of Chemistry, Center for Physical Sciences and Technology, Vilnius, Lithuania.

InGaN alloys continue to experience problems of incorporating indium (In) when grown by metalorganic vapor phase epitaxy (MOVPE) [1]. On a theoretical level it should be possible to incorporate higher In concentrations into InGaN alloys, however, current attempts to do so lead to In clustering or even segregation into metallic In, ultimately leading to the deterioration of crystal quality. One of the possible solutions to overcome In segregation is to use growth with metallic (MO) flow interruptions [2]. This method gives extra time for adsorbed atoms to migrate on the surface and either be incorporated to crystal or to desorb. In this work we present a detailed analysis of InGaN multiple quantum wells (MQWs) grown by MOVPE using interruptions of MO flow into the reactor chamber. All samples were grown using Aixtron CCS 3×2 reactor keeping all growth parameters constant except timing of MO flow interruptions from 0s (conventional growth) up to 15s.

X-ray diffraction (XRD) measurements were conducted to evaluate the In mole fraction, composition, homogeneity and crystalline structure of the InGaN QWs. Structure morphology and layers thicknesses of MQWs were studied using transmission electron microscopy (TEM). XRD measurements revealed that In concentration in InGaN MQWs was 9.5 ± 0.5% for all samples and so the desorption of In during the interruptions was found to be minor. TEM measurements showed that the QW, barriers, as well as super-lattice (SL) structure are easily distinguishable by the In fluctuation, which confirms a well-formed crystalline structure. A systematic study of the photoluminescence (PL) intensity on interruption duration was carried out at different temperatures from 10 K up to 300 K. PL intensity increases up to 2 times with blue shift of 54 meV at room temperature with interruption time increase. The FWHM value increase is minor and can be neglected. To determine the extent of the carrier localization effect in MQWs the Gaussian broadening parameter of carrier localization states was evaluated from S-shape temperature dependence of the PL peak. Though, the value of s parameter does not change significantly (21÷24 meV) with increase of interruption duration. To get a better understanding of MO flow interruption influence on In fluctuation in InGaN layers spatially-resolved sub-micrometer scale PL (µPL) measurements were carried out. Extracted areas (grains) having the average values of PL peak position with ± 3 nm deviation represent the carrier localization centers. It was found that increasing the duration of interruption resulted in reduction of the average grain area. Meanwhile, the number of individual grains increased and resulted in a total grain area increase. This leads to a higher density of states and an increase in PL intensity.


CM01.12.29 Atomistic Origins of Shear Strength in 2D Materials Adam R. Hinkle, John F. Curry, Tommas Babuska, Brandon Keick, Michael T. Dugger, Michael Chandross and Nicholas Argibay; Sandia National Laboratories, Albuquerque, New Mexico, United States.
The low-friction behavior of two-dimensional lamellar materials has been reported in dry, inert environments and is known to depend upon the diffusive motion of the lamella and their relative degree of commensurate stacking, as well as temperature. However, no encompassing theoretical framework presently exists to predict macroscopic friction-related properties such as shear strength. We present a simplified, yet unifying model where the frictional behavior of lamellar materials is described entirely in terms of rotational and translational energy barriers, whose values are determined directly from chemically reactive molecular dynamics (MD) calculations. In the specific case of molybdenum disulfide (MoS2), the barrier heights are shown to converge with increasing lamellar flake size, and reveal the most probable activation mechanisms to interlamellar sliding. We evaluate the model's prediction of interfacial shear strength by comparing to related MD shear simulations and thin-film sliding experiments of MoS2, and find strong agreement over a wide range of temperatures.

CM01.12.30
Defect Architecture for Decoupling Carrier Mobility and Lattice Thermal Conductivity in N-Type PbSe Thermoelectric Materials [Chongjian Zhou] and In Chung; 2Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul, Korea (the Republic of); 3School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of).

Structural defects including vacancies, nanoprecipitates, and dislocations can reduce lattice thermal conductivity. However, they also tend to be deleterious to carrier mobility. As a result, the overall effects for improving ZT are often compromised. In fact, developing strategies allowing for strong phonon scattering and high carrier mobility at the same time is a primary task in thermoelectric. In this presentation, we report a high performance thermoelectric system of Pb0.95Sr0.05Sn0.5Si0.5Te3 that includes unique defect architecture. Considering the mean free paths of phonons and electrons, we integrate multiple defects that include point defects, vacancy-driven dense dislocations, and Te-induced nanoprecipitates with different sizes and mass fluctuations. They scatter thermal phonons collectively in a wide range of frequency to give ultralow lattice thermal conductivity of ~0.4 W m⁻¹ K⁻¹, which approaches to the theoretical lower limit. Remarkably, Te alloying increases a density of nanoprecipitates that affect mobility negligibly and disrupt phonons significantly, and it also reduces a density of dislocations that scatter both electrons and phonons heavily, As x is raised to 0.4, electron mobility is increased and lattice thermal conductivity is decreased concurrently. As a consequence, Pb0.95Sr0.05Sn0.5Si0.5Te3 exhibits the highest ZT ~1.5 at 823 K, which is attributed to the significantly enhanced power factor and depressed lattice thermal conductivity, compared with a ZT ~0.9 for Pb0.95Sr0.05Sn0.5Te3 that contains heavy dislocations only. These results highlight the potential of defect engineering to control electrical and thermal transport properties independently.

CM01.12.31
Enhanced Energy Storage Properties of Ba(Zr0.2Ti0.8)O3-0.15(Ba0.7Ca0.3)TiO3 Ceramics with BaO-SrO-TiO2-Al2O3-SiO2-BaF2 Glass [Addition Weiwei Ping1, Wenfeng Liu2 and Shengtao Li; 1Electrical Engineering, Xi’an Jiaotong University, Xi’an, China; 2Department of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China.]

Glass addition BaO-SrO-TiO2-Al2O3-SiO2-BaF2 was employed to improve the microstructures and energy storage properties of the Ba(Zr0.2Ti0.8)O3-0.15(Ba0.7Ca0.3)TiO3 ceramics, which exhibited a large dielectric constant of 3458 at 25 °C under 1 kHz, slim hysteresis loop with the maximum polarization of 12.53 μC/cm² and a remnant polarization of 4.05 μC/cm². Microstructural observation indicated that the average grain size reduced significantly with increasing the glass concentration. Macroscopically the glass ceramics exhibited diffusion phase transition with reduced peak dielectric constant but broad peak with relatively large dielectric constant of around 1000 within the room temperature region. Meanwhile the electrical breakdown strength (BDS) of the glass modified ceramics was nearly quadruple to the pure ceramics form. Energy storage performance of the glass modified ceramics, both 419.4 kJ/m³ calculated from the product of dielectric constant and square of BDS and 192.8 kJ/m³ from the integration of the hysteresis loop strength (BDS) of the glass modified ceramics was nearly quadruple to the pure ceramics form. Energy storage performance of the glass modified ceramics, both 419.4 kJ/m³ calculated from the product of dielectric constant and square of BDS and 192.8 kJ/m³ from the integration of the hysteresis loop strength under the electric field of 9.6 kV/mm, showed significant superiority to that of the pure ceramic form.

CM01.12.32
Building Optical Anisotropy via Polarizability Engineering in Quasi-1D Crystal Structures [Shuyuan Ni; 1Huan Zhao; 2Graham Joe; 1Yucheng Zhou, 1Thomas Orvis1, Huaxiong Huang1, Jad Salman1, Krishnamurthy Mahalingam3, Brittany Urwin3, Jiangbin Wu2, Yang Liu1, Tom E. Tiwald1, Stephen B. Cronin2, Brandon M. Howe2, Matthew Mecklenburg2, Ralf Haiges2, David Singh1, Han Wang2, 1Mikhail A. Kats1 and Jayakanth Ravichandran1, 3Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States; 3Department of Electrical and Computer Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States; 4Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, United States; 1A. Woollam Co. Inc., Lincoln, Nebraska, United States; 5Center for Electron Microscopy and Microanalysis, University of Southern California, Los Angeles, California, United States; 6Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California, United States; 7Department of Physics and Astronomy, University of Missouri, Columbia, Missouri, United States.]

Rational design or discovery of new materials or innovative functionalities in underexplored materials, has been a key contributor to several electronic, photon, and energy technologies. We report the realization of strong optical anisotropy via chemically tuning the polarizability tensor in quasi-one-dimensional (quasi-1D) crystal structures. Optically anisotropic materials are of great scientific and technological importance in photonic and optoelectronic applications. Quasi-1D structures feature long parallel chains with strong intra-chain bonding and weak inter-chain interaction. In contrast to other low-dimensional materials, they offer robust cleavage planes with easily accessible in-plane anisotropy, which is critical for practical application of optical anisotropy. The optical anisotropy is enhanced by considering the constituent ions’ polarizability to maximize the polarizability difference along different axes in the system. We demonstrate two model systems, BaTiS3 and Sr0.7Ti0.3S0.7T0.3, both with hexagonally aligned chains of face sharing TIs6 octahedra. Large single crystals were grown using chemical vapor transport method with iodine as a transporting agent, allowing extensive spectroscopic studies of their inherent anisotropic properties. We report the observation of strong and broadband infrared birefringence, as well as linear dichroism with distinct polarization-dependent optical absorption edges in the mid-infrared spectrum. Notably, the unprecedented birefringence of up to 0.76 in the transparent region of BaTiS6 more than doubles that in any other bulk crystal.

CM01.12.33
Memristor Behavior and Novel Structural Properties in (Ph3As)3(BiI3)3 Mixtures [Graff C. Alexander1, 2Hue Joon Jung2, Patrick Krantz2, Giancarlo Tormen3, 4Mannes van den Waals5, 6K. Jayme McCall7, 8Bruce Wessels7, 8Vinayak P. Dravid7, 8Venkat Chandrasekhar7, 8Chemistry, Northwestern University, Evanston, Illinois, United States; 4Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 5Physics and Astronomy, Northwestern University, Evanston, Illinois, United States; 6Physics and Astronomy, Northwestern University, Evanston, Illinois, United States.]

Heavy metal halide semiconductors have been widely investigated for their optoelectronic properties for photovoltaic and high energy radiation detection applications. Ph3As (Eg = 2.3 eV) and BiI3 (Eg = 1.7 eV) are highly resistive semiconductors that have been exhaustively characterized for device applications but suffer structurally due to their 2D van der Waals structure. Ph3As crystallizes in the CdI2 structure type with layers of fully edge-sharing...
octahedral PbI4 and BiI3 displays an analogous structure with ordered vacancies to compensate for Bi being trivalent. This work focuses on the preparation of (PbI2)(BiI3)
and characterizes the material chemically, electronically, and structurally. Our work predominantly features (PbI2)(BiI3)1.8 which is prepared by the direct reaction of PbI2 and BiI3 to yield dark black crystalline ingots. (PbI2)(BiI3)1.8 displays an absorption edge at 1.7 eV and tuning cooling rate can be used to induce low energy absorption beginning at 1.0 eV. Density Functional Theory calculations demonstrate that this low energy absorption arises as Bi is incorporated into the PbI2 non-vacancy lattice leading to strong mid-gap states. Single crystal X-ray diffraction is deceptive to the true structure as by X-ray (PbI2)(BiI3) appears as a single structural phase. However, transmission electron microscopy (TEM) reveals that while the material has a new structure, it partially phase separates yielding Pb and Bi rich regions while still retaining an overall contiguous structure. (PbI2)(BiI3)1.8 displays consistent and reproducible memristor behavior. As bias is swept perpendicular to the layers (PbI2)(BiI3) behaves as an ohmic resistor and is activated. As bias is reversed a significant current spike is observed as the sample is “switched” on and activated in the opposite direction. This observed “switch” current decays on the time scale of seconds when the bias is held constant, contrasting with other memristor materials that remain in their low resistive states once induced. We propose that this effect is due to observed lattice mismatch between Pb and Bi rich regions as observed by TEM. At these regions some layers terminate abruptly leading to undercoordinated iodine atoms which can be liberated with the appropriate field applied across the material and moved in within their narrow defect regions. These results expose a new class of robust memristor materials with novel optical and structural properties that are ready for further development.

CM01.12.34
Non-Equilibrium Crystallization Pathways of Manganese Oxides in Aqueous Solution
Wenhao Sung1, Daniil Kitchaes2, Denis Kramer3 and Gerbrand Ceder1; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Drexel University, Philadelphia, Pennsylvania, United States; 3Argonne National Laboratory, Argonne, Illinois, United States.

Aqueous precipitation of transition metal oxides often proceeds through non-equilibrium phases, whose appearance cannot be anticipated from traditional phase diagrams. Without a precise understanding of which metastable phases form, or their lifetimes, targeted synthesis of specific metal oxides can become a trial-and-error process. Here, we construct a theoretical framework to reveal the nanoscale and metastable energy landscapes of Pourbaix (E-pH) diagrams, providing quantitative insights into the size-dependent thermodynamics of metastable oxide nucleation and growth in water. By combining this framework with classical nucleation theory, we interrogate how solution conditions influence the multistage oxidation pathways of manganese oxides. We calculate that subtle variations in pH and redox potential can redirect a crystallization pathway through different metastable phases, even when the final equilibrium product remains unchanged. Our theoretical framework offers a predictive platform to navigate through the thermodynamic and kinetic energy landscape towards the rational synthesis of target oxide transition pairs.

CM01.12.35
A Map of the Inorganic Ternary Metal Nitrides
Wenhao Sung1, Christopher Bartel2, Elisabetta Arca3, Sage Bauers3, Bethany Matthews4, Bor-Rong Chen5, Michael F. Toney3, Laura Schelhas4, William Tumas3, Janet Tate3, Andrij Zakutayev2, Stephan Lany4, Aaron Holder1 and Gerbrand Ceder1; 1Lawrence Berkeley National Laboratories, Berkeley, CA, CA, California, United States; 2University of Colorado Boulder, Boulder, Colorado, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4SLAC National Accelerator Laboratory, Menlo Park, California, United States; 5Oregon State University, Corvallis, Oregon, United States.

Exploratory synthesis in novel chemical spaces is the essence of solid-state chemistry. However, uncharted chemical spaces can be difficult to navigate, especially when materials synthesis is challenging. Nitrides represent one such space—where stringent synthesis constraints have limited the exploration of this important class of functional materials. Here, we employ a suite of computational materials discovery and informatics tools to construct a large stability map of the inorganic ternary metal nitrides. Our map connects the ternary nitride clusters into chemical spaces with distinct stability and metastability; and highlights hundreds of promising new ternary nitride spaces for experimental investigation, from which we synthesized 7 novel Zn- and Mg-based ternary nitrides. By extracting the mixed metallicity, ionicity, and covalency of solid-state bonding from the DFT-computed electron density, we reveal the complex interplay between chemistry, composition, and electronic structure in governing large-scale stability trends in the ternary metal nitrides.

CM01.12.36
Revealing the Atomic Kinetics of Phase Transition from 2D Layers to 1D Tunnels in Transitional Metal Oxides
Yifei Yuan1, Bryan W. Byles2, Kun He3, Cong Liu4, Jun Lu5, Khalil Amine6, Ekaterina Pomerantseva7 and Reza Shahbazian-Yassar1; 1University of Illinois at Chicago, Chicago, Illinois, United States; 2Drexel University, Philadelphia, Pennsylvania, United States; 3Argonne National Laboratory, Argonne, Illinois, United States.

MnO2 abundantly exists in the earth’s crust and marine sediment. Based on how its structural units ([MnO6] octahedra) are linked, polymorphic MnO2 is categorized into two types: two-dimensional (2D) layered and one-dimensional (1D) tunnel phases. In general, layered MnO2 can transform into tunnel structures, such as the well known σ-MnO2-α-MnO2 and buserite-todorokite phase evolution. Therefore, layer-to-tunnel (L-T) transition, typical for manganese oxide (MnO2) polymorphs, is the ubiquitous reaction leading to the formation of one-dimensional angstrom-scale tunnels that are extensively applied in catalysis, energy storage and material separation. This transition is also fundamental in the natural formation of Mn-rich marine sediment on the Earth. Current mechanisms explaining the L-T transition are debating, particularly in the critical role of Jahn-Teller distortion of [Mn3+O6] in guiding the behavior of the layered precursors. The lack of fundamental and atomic level understanding of this phase transition leads to poorly controlled synthesis of size-specific tunnels, and also results in difficulty to clarify the role of marine sediments in global trace element cycles.

Herein, we report the first atomic-scale visualization of two novel L-T transition pathways via aberration-corrected scanning transmission electron microscopy, electron energy loss spectroscopy and density function theory calculations. 10 Å-spaced layered buserite is used as the precursor subjected to hydrothermal treatment to enable the L-T transition. By characterizing the atomic structure of the products at different reaction stages, we found that the L-T transition requires multiple steps via formation of intermediate tunnels with large openings, and this stepwise process obeys the numeric rule: one 3+ (2N-1) tunnel → two 3+ N tunnels. The important role of Jahn-Teller Mn3+O6 octahedra in driving the microscopic layer distortion, causing strain concentration and triggering the L-T transition is also demonstrated. We expect these atomic-level discoveries to guide the synthesis of MnO2 nanostructures with controllable and uniform tunnel sizes, and also results in difficulty to clarify the role of marine sediments in global trace element cycles.

CM01.12.37
Extremely Low Thermal Conductivity and High Thermoelectric Performance in Polycrystalline SnSe
YongKyu Lee1, 2 and In Chung1, 2; 1Seoul National University, Seoul, Korea (the Republic of); 2Center of Nanoparticle Research, Institute for Basic Science, Seoul, Korea (the Republic of).

SnSe have emerged as a promising thermoelectric material due to the recent discovery of an ultralow thermal conductivity and ultrahigh thermoelectric figure of merit in its single crystalline form. Since then polycrystalline counterparts have been extensively investigated because of their machinability and probability of large scale applications. However, polycrystalline SnSe samples show much higher thermal conductivity and consequently poor thermoelectric performance. Our work here explores the influence of hydrothermal treatment to enable the L-T transition. By characterizing the atomic structure of the products at different reaction stages, we found that the L-T transition requires multiple steps via formation of intermediate tunnels with large openings, and this stepwise process obeys the numeric rule: one 3+ (2N-1) tunnel → two 3+ N tunnels. The important role of Jahn-Teller Mn3+O6 octahedra in driving the microscopic layer distortion, causing strain concentration and triggering the L-T transition is also demonstrated. We expect these atomic-level discoveries to guide the synthesis of MnO2 nanostructures with controllable and uniform tunnel sizes ideal for specific nanoengineering applications, as well as clarify the geochemical interpretation of marine sediment discoveries for the geological evolution of the Earth.
thermoelectric performance than single crystals. It is in contrary to the general understanding that the polycrystalline specimens show suppressed thermal conductivity due to phonon scattering at the grain boundary. Several reports suggested that higher thermal conductivity of polycrystalline SnSe originates from impurities as induced by powder processing. In this work, we discuss that our synthesis process successfully impurities that can increase thermal conductivity. As a result, we can obtain extremely low lattice thermal conductivity and remarkably enhanced thermoelectric figure of merit in polycrystalline SnSe samples.

CM01.12.38
Multi-Steps Sintering Synthesis Process of Ferrite for Enhancing Magnetic Property
Ning Jia and Huaiwu Zhang; State Key Laboratory of Electronic Thin Film and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China.

The criteria of the synthesis of high-performance bulk ferrite might be very rigor especially for the temperature. Most of the ceramic and ferrite should be sintered at hundreds degree centigrade and for YIG (yttrium iron garnet, original), the sintering temperature should be 1450 °C. The high level of sintering conditions limits the applications of ferrite for instance of co-sintering with silver. In decades, many researchers launched the research in ions doping, adulteration, adding sintering aids, changing the method of sintering. But rare of them considered on optimizing the synthesis process. Therefore, it is highly desirable to design a new synthesis process that allows us to improve it. Here, we study doped Bi-YIG simples synthesized by multi-steps including different sintering tempales and variable steps. The results showed an obvious improvement on soft magnetic properties and low linewidth. Then the multi-steps sintering enables enhancing the carrier mobility and the fusion of grain boundary which makes main effect on the homogenization of grains.

CM01.12.39
Pulsed Laser Deposition of Ti3AlC2 of the New Class of Layered Mn+1AXn Phase Solids
Arundhati Sengupta, Abhijit Biswas and Satishchandra Ogale; Department of Physics and Centre for Energy Science, Indian Institute of Science Education and Research (IISER), Pune, Pune, India.

Mn+1AXn phases (where n = 1–3, M is an early transition metal, A is mostly a group 13 or 14 element and X is carbon/nitrogen) are a new class of layered solids with intriguing chemical, physical, electrical, and mechanical properties arising from basal dislocations. These materials combine metallic and ceramic characteristics exhibiting oxidation/ corrosion resistance, elastic stiffness and low friction coefficient together with high thermal and electrical conductivities and machinability. These features lead to diverse applications such as structural, microelectromechanical, protective coatings, sensors, and electrical contacts. Although very large volume of outstanding work has been done on these systems in bulk by Gogotsi and coworkers as well as others, there is hardly any work on high quality Mn+1AXn and MXene films. Here we report oriented growth of films (~100 nm thickness) of Ti3AlC2, a well-recognized Mn+1AXn phase comprising earth-abundant elements, on substrates such as sapphire, silicon and quartz by pulsed laser deposition (PLD) at moderate temperatures (550–600°C) under vacuum (~10−6 mbar). These deposits were carried out by ablating a Ti3AlC2 target using the 248 nm radiation from a KrF* excimer laser (10 Hz frequency and fluence ~2 J/cm²). PLD technique was chosen for depositing the films because its hyperthermal particle energies enable low-temperature processing which is advantageous over conventional techniques such as chemical vapor deposition. Deposition of Ti3AlC2 films was confirmed by X-ray diffraction, Raman and energy dispersive X-ray spectroscopy (EDS). Preferred orientation of hexagonal Ti3AlC2 film grown on c-cut (006) sapphire was found to be along (103) plane while that on p-type (100) Si and quartz substrates was along (105) plane. Most intense Raman band ~270 cm−1 exhibited by the deposited films corresponds to longitudinal displacements of Ti and Al atoms of A1g symmetry. High energy band around 680 cm−1 corresponds to vibrations in C sublattice. Observed atomic % of Ti, Al and C were 30.8, 20.1 and 49.1, respectively, as per EDS elemental analysis (on films deposited on Si), fairly in accordance with 3:1:2 atomic ratio of Ti:Al:C in Ti3AlC2. Scanning electron microscopic images of the films showed homogeneous deposition. Thickness of films was tuned by varying the number of laser shots in optimizing the electrical conductivity for pertinent device applications.

CM01.12.40
Highly Ordered and Nanostructured Hexagonal Boron Nitride Synthesized through Molten Salt Synthesis Method
Kaiflin Wang1, Metin Örnek1, Sisi Xiang2, Chawon Hwang1, Kelvin Xue2 and Richard A. Haber1; 1Materials Science and Engineering, Rutgers, The State University Of New Jersey, Piscataway, New Jersey, United States; 2Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Hexagonal boron nitride (h-BN) is one of the materials of choice for applications such as electronic insulators, heat sinks, and coatings due to its unique properties of high thermal conductivity, low thermal expansion, high thermal shock resistance, high electrical resistance, and a low dielectric constant. These properties, along with chemical inertness and resistance to wetting by metallic or non-metallic melts, make h-BN a viable material for metallurgical applications of high pressure. However, commercial highly ordered h-BN is synthesized at temperatures of 1800°C or higher, while lower synthesis temperatures through conventional methods result in unstable and less ordered (turbostratic) BN. Molten salt synthesis (MSS) allows precursor reactions to occur in a liquid media, allowing for improved diffusion and reaction kinetics, and therefore reduces synthesis temperatures. Through MSS, highly ordered h-BN was formed at 1000°C, and confirmed through X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FTIR), and high-resolution transmission electron microscopy (HR-TEM). In this presentation, we will address the effect of synthesis conditions including heating temperature, dwelling time, and precursor composition on the formation of BN and its structural ordering. We will also propose a possible reaction mechanism to describe BN formation in molten salt based on thermodynamic considerations.

CM01.12.41
Precursor Dependent Synthesis of Aluminum Oxide Thin Films
Yvonne Afriyie; Washington Univ-St. Louis, Saint Louis, Missouri, United States.

Abstract
Aluminum is an ideal metal for solution-processed oxide dielectrics because it can form polymerized hydroxide networks in aqueous solution and dense amorphous oxide dielectrics by vacuum methods. Atomic layer deposition (ALD) is the traditional vacuum method for thin film deposition, however, ALD is not the most economically feasible method for fabrication due to the high operational cost and limitations in large surface-area applications.1 Solution deposition is a more economical deposition method which is more cost-saving and ideal for large surface area thin film fabrication.2 The behavior of the solution-solid conversion remains an enigma thus the project seeks to understand the thin film transformation from solution to solid in order to fabricate films with optimal properties.3

1. Aluminum oxide (Al2O3) thin films prepared from aqueous solution-deposited cluster precursors have been proposed for use in devices such as high-k dielectrics in solar cell materials.4 The films are fabricated with different Al precursors, spin-coated on a substrate and annealed to high temperatures. The low-temperature range of these films are amorphous and lack long-range order which complicates the analysis by traditional means; however, solid-state nuclear magnetic resonance (ssNMR) can be used to determine the structure of these materials. Herein, a combination of x-ray diffraction (XRD), and NMR techniques are used to elucidate the phase transformation of these thin films as they are annealed to high temperatures.

References
Indium phosphide is the leading Cd-free quantum dot material for application in photoluminescence downconversion display and lighting technologies. To date the performance of InP quantum dots has lagged behind cadmium selenide in terms of both luminescence line width and quantum yield. Extensive studies in our lab have implicated kinetically persistent magic-sized cluster intermediates as a leading contributor to polydispersity in these samples, providing new opportunities for achieving high color purity. Now, using a combination of X-ray emission and solid-state NMR spectroscopy we have studied the evolution of oxidized phosphorus species during both synthesis and shell growth. Correlations of this data with observed ensemble and single particle luminescence will be used to reveal the role of interfacial oxidation on the luminescence properties of InP QDs.

8:30 AM CM01.13.02
Ultrasmall Inorganic Cages Directed by Surfactant Micelles

Tangi Aubert\(^1,4\), Kai Ma\(^1\), Yunye Gong\(^2\), Melik Z. Turker\(^1\), Teresa Kao\(^1\), Peter C. Doerschuk\(^2,3\) and Ulrich Wiesner\(^1\);
\(^1\)Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; \(^2\)School of Electrical and Computer Engineering, Cornell University, Ithaca, New York, United States; \(^3\)Nancy E. and Peter C. Meinig School of Biomedical Engineering, Cornell University, Ithaca, New York, United States; \(^4\)Department of Chemistry, Ghent University, Ghent, Belgium.

Functional silica nanoparticles have become highly relevant materials in the fields of biology and medicine. Ultrasmall fluorescent silica nanoparticles developed in our group (Cdots) have now reached phase 2 of clinical trials for cancer diagnostics. Nevertheless, modern nanomedicine techniques and their increasing complexity today are still in demand for more efficient and multifunctional tools for advanced applications such as theranostics. To this end, new alternative particle geometries have been investigated for targeted drug delivery applications.

In this contribution, we will review some of the recent progress made in our group that ultimately led to the discovery of highly symmetrical dodecahedral silica nanocages, or ‘silicages’ \(^[1]\). Ultrasmall (< 10 nm) silica nanoparticles with tunable geometries can be obtained through their templating with surfactant micelles. The self-assembly of silica clusters on these micelles gives rise to unique and well defined structures. The dodecahedral cage structure in particular is of great fundamental importance. It is the simplest of a set of Voronoi polyhedra suggested to form the smallest structural units of multiple forms of mesoporous silica, yet such highly symmetrical silica cages had never been isolated before. In order to resolve the actual structure of these ultrasmall objects, single-particle 3D reconstruction from tens of thousands of cryo-electron microscopy images was performed using a custom-built ‘Hetero’ machine learning algorithm. We will finally show that cage formation is not limited to silica, but has been observed for other materials including metals and transition metal oxides.

The chemical and practical value of this polyhedral structure may prove immense. Given the versatility of silica surface chemistry one can readily conceive of cage derivatives of many kinds, which may exhibit unusual properties and be useful in applications ranging from catalysis to drug delivery. For example, given recent success in the clinical translation of ultrasmall fluorescent silica nanoparticles with similar particle sizes and surface properties to these cages, one can envisage a range of new diagnostic and therapeutic probes with drugs hidden inside the cages.

Reference:

8:45 AM CM01.13.03
Ultrasonic Melting Synthesis Method for Nanomaterials

Yuanbing Mao; The University of Texas at Rio Grande Valley, Edinburg, Texas, United States.

Bottom-up synthesis of nanomaterials with controllable crystallite size, shape, and composition often enhances the materials performance and provides model systems to aid in understanding nanoscale phenomena. Such benefits are evident in the application of nanomaterials towards heterogeneous catalysis, energy conversion, and environmental remediation, just name a few. Given the intimacy between the structural features and functions of nanomaterials, the development of facile synthetic methods with controllable growth of nanomaterials, especially for those with complex chemical compositions/morphologies, becomes an urgent necessity. Molten-salt synthesis (MSS) method is one of those as a simple, versatile, and cost-effective approach available for obtaining crystalline, chemically purified, single phase powders at lower temperatures and often in overall shorter reaction times with little residual impurities as compared with conventional solid-state reactions. While bulk materials have long been prepared using the flux method, the preparation of uniform nanostructures using the similar MSS technique has only arisen relatively recently, that is, within the current century. Over the years, our laboratory has applied this method to make various nanomaterials, especially those of transition-metal oxides. In this presentation, various examples will be demonstrated, including materials with perovskite, fluorite, pyrochlore and spinel structures, along with relevant growth mechanism studies and the property measurements of these synthesized nanomaterials. Therefore, it is expected that the MSS method will be widely disseminated and broadly adopted as a facile, reliable, scalable and cost-effective approach in synthetic nanochemistry.
understand MXene's properties, the precursor MAX phases have to be studied more in depth, specifically how starting MAX properties affect the consequent MXene properties.

Ti3AlC2 MAX was synthesized using three carbon sources: graphite, carbon lampblack, and titanium carbide. The synthesis was carried out using two routes: an equilibrium and non-equilibrium route. The equilibrium route was conventional high-temperature annealing, while the non-equilibrium route was via self-propagating high-temperature synthesis (SHS). By doing this, optimized synthesis conditions were determined for production of highly pure (>95 at.%) MAX phase materials. The reaction conditions were further varied, including heating rate, holding time, and pre- and post-ball milling treatment. Furthermore, the reaction mechanisms were studied, showing that the initial carbon source and heating rates change the reaction pathway. These additional parameters led to further refinement over the produced MAX phase. The effect of these changes was studied on the final MXene product, showing that there are significant changes in the resultant MXene quality, and consequently the electromagnetic interference shielding, electrical and electrochemical properties. Finally, these findings were applied to a wider variety of different MAX and MXenes, including V, Cr, Hf, and Nb-containing materials in 211, 312, and 413 phases.

9:15 AM CM01.13.05

Transition metal chalcogenide nanoparticles (NPs) have been proposed for applications in batteries, solar cells, and supercapacitors. Many methods have been established for synthesizing Ni NPs and the conversion chemistry to form Ni oxide and phosphides from template Ni NPs is well understood. The sulfidation and selenidation of Ni NPs have been much less explored, however. We report a method for the conversion of Ni template NPs into sulfide and selenide product NPs using elemental sulfur, l-hexadecanethiol, thiourea, trioctylphosphine sulfide, trioctylphosphine selenide, and selenourea. While maintaining molar ratios of 1.6 mmol S/Se precursor : mmol Ni in the Ni NPs, products with phases of NiS2, NiSe2, NiS, NiSe, Ni0.6H2O, NiSn, Ni3Se8, and Ni3S6 were obtained. Trends relating the chemical properties of the precursors to the phases of the products have been identified. While some precursors contained P, incorporation of P was not observed in the products. An increase of the NP size during sulfidation and selenidation is consistent with ripening. The products also can have voids that can be attributed to the Kirkendall effect, which also commonly occurs during oxidation and phosphidation of Ni NPs.

9:30 AM CM01.13.06
Colloidal Semiconductor CdS Magic-Size Clusters—Thermally-Induced Reversible Structural Isomerization Kui Yu; Sichuan University, Chengdu, China.

Here, we report the first pair of structural isomers identified for colloidal nanocrystals which exhibit thermally-induced reversible transformations. The two isomers are CdS magic-size clusters exhibiting sharp absorption peaks at 311 nm and 322 nm. We show that their thermally-induced interconversions follow first-order unimolecular reaction kinetics. We anticipate that our findings on structural isomerism should stimulate attention towards solid-solid transformations and advanced design and synthesis of functional nanomaterials for a diversity of applications enabled by structural transformations.

9:45 AM BREAK

10:00 AM CM01.13.07
Solution-Grown Sodium Bismuth Dichalcogenides—Toward Earth-Abundant, Biocompatible Semiconductors Javier Vela, Bryan Rosales and Miles White; Iowa State University of Science and Technology, Ames, Iowa, United States.

Many technologically relevant semiconductors contain toxic, heavily regulated (Cd, Pb, As), or relatively scarce (Li, In) elements and often require high manufacturing costs. We report a facile, general, low-temperature, and size tunable (4–28 nm) solution phase synthesis of ternary APM2 semiconductors based on Earth-abundant and biocompatible elements (A = Na, Pn = Bi, E = S or Se). The observed experimental band gaps (1.20–1.45 eV) fall within the ideal range for solar cells. Computational investigation of the lowest energy superstructures that result from “coloring”, caused by mixed cation sites present in their rock salt lattice, agrees with other better-known members of this family of materials. Our synthesis unlocks a new class of low cost and environmentally friendly ternary semiconductors that show properties of interest for applications in energy conversion.

10:30 AM CM01.13.08
A New Perovskite-Type Sulfide Semiconductor, SrHfS3, Exhibiting Intense Green Emission at Room Temperature Kota Hanzawa1; Soshi Limura1,2; Hidenori Hiramatsu1,2; and Hideo Hosono1,2; 1Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama, Japan; 2Materials Research Center for element Strategy, Tokyo Institute of Technology, Yokohama, Japan.

Semiconductors that are capable to dope into both of p- and n-types are key components in practical devices such as light-emitting diodes and CMOS transistors. Currently we have critical issues on next-generation device applications such as higher resolution display. To overcome such issues, the most difficult challenge is to develop bright green-emitting sources (λ ≈ 550 nm), which has not been realized even in GaN-based systems. Thus it has strongly been required to explore novel semiconductors with a bandgap of ~2.3 eV exhibiting efficient green emission at room temperature (RT). We focus on exciton in semiconductors due to its highly efficient emission. High ionicity of the chemical bonding is a key factor to obtain high exciton binding energy (BE); for SrF2, with high ionicity, the exciton has a large BE (0.9 eV), while for covalent compounds such as Ge and GaAs the BE is quite small (4 meV for Ge and GaAs). On the other hand, deep CBM and shallow VBM are also required to achieve n- and p-type dopings, respectively. However, the orbitals of low electron-negativity elements such as alkaline earth (AE) and early transition metals (eTM) usually form a shallow CBM level, while energy level of oxygen or halogen-p-orbital is too deep to dope hole. Hence, ionic compounds composed of AE and eTM have not attracted interest as a constituent of semiconductors so far.

Recently, our research group proposed a design concept for eTM-based semiconductors [1]. Our idea is to create non-bonding state at a specific k-point in high symmetry crystal structure. Since the non-bonding d-orbitals of cation form a deeper energy level than that of anti-bonding state between cation d- and anion p-orbitals, the deep CBM is realized in high symmetry crystals. In the same manner, shallow VBM is also obtained due to the formation of the non-bonding p-orbital of anion.

Based on the above consideration, we selected SrHfS3 with a high symmetry perovskite-type structure. The DFT calculations indicate that the CBM and VBM consist of nearly non-bonding state of Hf 5d and S 3p orbitals, respectively. As a result, the deep CBM and shallow VBM as well as the resultant bandgap of 2.2 eV meet our research target. We successfully synthesized polycrystalline SrHfS3 by a solid-state reaction. The optical bandgap was 2.3 eV and photoluminescence (PL) exhibited intense green emission peaking at ~521 nm, which are all consistent with the DFT results and meet all our requirements. It should be noted that the emitting light can be seen by human eyes even at RT. PL arising from defects was not observed, suggesting that concentration of deep defects is quite low.
Controlling the Surface Chemistry of Metal Phosphide Quantum Dots

B. A. Glassy, B. M. Cossairt

unlocking the true potential of these emerging materials.

Metal phosphides, Zn$_2$P$_2$, Cd$_3$P$_2$, InP, are an important class of semiconductor quantum dots (QDs) with applications ranging from light emitting diodes to biomedical imaging.\[1\] The extreme sensitivity of metal phosphide quantum dots to air and moisture require the development of robust surface passivation strategies to truly harness their potential in the above applications. To create such robust surface passivation strategies, a thorough understanding of metal phosphide surface chemistry and interfaces is required.\[2\]

In particular, we have previously demonstrated that the use of classical high-temperature procedures with indium carboxylate precursors induces an indium oxide surface layer that readily forms as a result of decarboxylation processes leading to water-based, in-situ – formed impurities.\[3\] We present here a comprehensive study that elucidates this oxidation mechanism utilizing a novel indium precursor, In(amidinate)$_3$, more reactive than traditional carboxylate or halide indium sources.\[4\] Indeed, while several reports utilizing different phosphorus sources can be found,\[5\] the variation of the indium source has been much less described. Our research has granted insight into the mechanism of oxide formation, including the sources of oxidants arising from previously unconsidered side-reactions. This increased knowledge of ligand and surfactant chemistry is valuable to the further efforts of precise surface control. The possibility to avoid oxidation of the QD surface under the correct conditions will be exposed and we demonstrate the ability to successively grow multiple layers of oxide-free InP surfaces. With lessons in hand, we could go on to create oxide-free InP nanocrystals, allowing us to study surface passivation strategies via a clean, native interface.\[6\] The role of Zn$_2^+$ and Zn precursors played in i) producing robust surface passivation, ii) enhancing key optical properties (emission linewidth, quantum yield) for InP QDs will also be discussed, highlighting the importance that surface chemistry and interfaces play in unlocking the true potential of these emerging materials.

References

Iron germanides (FeGeₓ) is a fascinating class of material that provides several phases with attractive and, in some cases, exotic properties including ferromagnetism (FeGeₓ, Fe₅Ge₃, Fe₃Ge₂…), antiferromagnetism (FeGe₂…), or helimagnetism (B20-FeGe). This latter phase has become the focus of intense interest due to the chiral magnetic ordering at RT which makes them highly relevant for the next generation of magnetic information storage.[1] Despite the attractiveness of nanoscale FeGeₓ structures, there exist only two synthetic approaches for their preparation: chemical vapor transport process to Fe₅Ge₃ at 650°C,[2] and solution phase thermolysis of precursors at high T (>260°C).[3] This latter example provides a proof-of-concept of the relevancy of solution-based strategies. However, the size, the shape or the phase purity are poorly controlled.

We will present herein a novel approach for the preparation of iron-germanium nanocrystals, which relies on the design of single source organometallic precursors that display special features: i) a preformed iron germanium bond, ii) labile substituents to facilitate their removal and iii) low coordinate metal to provide an easy access to FeGeₓ NCSs. We will show how the design of novel organometallic single source precursors allows the synthesis of nanocrystals at the lower temperature ever reported using thermolytic approach, ii) the dramatic influence of the substitution on the germanium atom to control the NCs formation and their magnetic properties.

11:45 AM CM01.13.13
Nano-Grained Hexagonal LaMgAl₁₁O₁₉ Doped with Ce for Optical Applications Ladislav Nadberny, Vaclav Dolezel, Vit Jakes and Katerina Rubesova, University of Chemistry and Technology, Prague, Prague, Czechia.

Due to their isotropic properties, high chemical stability and radiation resistance, aluminates (such as Y₃Al₅O₁₂, MgAl₂O₄, LaAlO₃, LaMgAl₁₁O₁₉) are suitable for use in optical applications for the detection of high-energy sources. One of the main advantages of lanthanum-magnesium hexaaluminate (LMA) is its ability to be doped with high concentrations of transition metals or rare-earth elements (REE) without the need for quenching. Hence, LaMgAl₁₁O₁₉ doped with REE has been investigated for many applications such as solid-state lasers, thermal barriers, w-LEDs, solar panels and non-contact thermometers.

Cerium is frequently used as an optical activator; for example, in mixed oxides, halides or glasses [1]. However, it has rarely been studied as a dopant for LMA, largely because of technological demands involved in preparing such a material by a solid-state method at 1600 °C [2, 3]. Recently, though, sol-gel methods have emerged as a new approach for preparing perfectly homogenous materials at a lower sintering temperature and in a shorter reaction time. We prepared La₆₋ₓCeₓMgAl₁₁O₁₉ with four different non-hydrolytic sol-gel methods La⁺, Ce³⁺, Mg²⁺ and Al³⁺ cations in the form of oxides, carbonates, chlorides and acetates. Two of the methods were based on active polymerization while water-soluble polymers were applied in the others. All these sol-gel methods produced stable solutions, from which white-to-brown fine amorphous and nanocrystalline precursor powders were prepared. These precursors were then pressed into pellets and annealed for 0.1–16 h at 1150–1300 °C in an Ar–H₂ flow. The annealing temperature was several hundred degrees lower than that of a solid-state method.

The phase compositions of the precursor powders and final polycrystalline materials were analyzed by RT-XRD, using Cu-Kα₁,₂ radiations in the range of 5–120° 2θ. The XRD data were matched with the PDF-4 reference database and refined by Pawley and Rietveld analysis. XRD full profile, TEM image analysis and dynamic light scattering were used to describe the relationships between precursor properties (particle size, morphology, crystallinity) and the final phase composition. In addition, we outline the mechanism of LMA phase formation. Finally, the optical activity of cerium in the prepared LMA matrices is shown in UV-Vis photocatalytic excitation and emission spectra.

The Continuous Random Network—A Review
Franz Spaepen, School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

The continuous random network (CRN), introduced by Zachariasen for oxide glasses, became the paradigm for the structure of covalent, directionally bonded amorphous materials. Elemental amorphous Si and Ge, which form one of the simplest CRNs, have been studied for more than fifty years. We will review their structure, thermodynamic properties, phase transformations, flow and structural relaxation. We will revisit some striking features, such as their density being higher than that of the diamond cubic crystal, their negative activation volumes for crystallization, and the bimolecular kinetics of their structural relaxation.

Understanding Indentation Behavior of Oxide Glass from Molecular Dynamics Simulation
Liping Huang, Rensselaer Polytechnic Institute, Troy, New York, United States.

To evaluate the damage resistance of glasses, instrumented indentation using sharp indenters is the method of choice, as it can mimic real-life damage incidents under controlled conditions. Furthermore, indentation provides a useful system to study crack initiation, as unstable crack propagation is prevented by the highly localized stress state. However, unravelling the nature of structural change under indentation is a formidable task in experiment because of the complexity that originates from the atomic-scale disorder of glass, and the experimental difficulties associated with the in-situ investigation at a local scale (tens of microns) under very high stresses. To this end, computer simulations can provide an important complement to experimental approaches. In this work, we carried out large scale molecular dynamics (MD) simulations to investigate the effect of quench pressure during hot compression and chemical composition variation on the response of glass to nanoindentation. A rigid hollow Vickers indenter made of carbon atoms is used to indent the glass sample with a fixed loading rate, during which atoms in the indenter interact with the glass via a repulsive force field. To minimize the boundary condition effects in simulated nanoindentation tests, large samples of several hundred nm in lateral dimensions are used. The indenter angle is varied to study the effect of the indenter sharpness on the deformation of glasses, as what has been done in experiments. Short- and medium-range order of glass structure evolve with the deformation underneath the indenter, which in turn shed light on the degree of densification and pile-up in different glasses.

Connecting Mechanical Properties of Amorphous Polymers to Chain Alignment and Entanglements
Marco A. Galvani Cunha and Mark O. Robbins; Johns Hopkins Univ, Baltimore, Maryland, United States.

Polymer glasses are frequently used in a form of additive manufacturing called fused filament fabrication (FFF). Melts are extruded onto previous layers and form a weld before the temperature drops below the glass transition temperature. Extrusion is typically fast enough to produce significant chain alignment that affects the welds formed by diffusion between layers and leads to a strongly anisotropic amorphous structure. Improved understanding of the structure property relations in printed parts is essential to optimizing FFF for structure-critical parts and FFF offers unique opportunities to create non-crystalline materials with continuously tunable local alignment and entanglement densities.

We have used molecular dynamics simulations of a generic polymer model to examine the relaxation of aligned melts, including the evolution of alignment and the entanglement density in bulk regions and at the interfacial weld. The mechanical properties of the resulting structures are then studied under tensile and shear loading. Local structure determines the initial yield stress while entanglements lead to strain hardening and crazing that strongly affects the total fracture energy. Alignment of chains along the deposition direction means that there are more weak van der Waals bonds in the perpendicular directions. This reduces the yield strength for shear and tensile failure perpendicular to the deposition axis. Alignment and changes in entanglement density also produce profound changes in the strain to failure and ultimate fracture energy. Welded regions are most affected by diffusion during cooling and may be stronger than adjacent bulk material which has higher entanglement density than the weld but is also strongly aligned.

Modeling Slip Statistics and Dynamics in Bulk Metallic Glasses, Granular Materials and Other Systems
Karim Dahmen, Wendelin J. Wright, Dmitry Denisov, Todd Hufnagel, Peter K. Liaw, Peter Schall; John Hopkins University, Baltimore, Maryland, United States.

Slowly strained solids deform via intermittent slips that exhibit a material-independent statistics and dynamics. We compare predictions of a simple model for the plastic deformation, the slip statistics and dynamics, and time series properties to experiments on slowly deformed bulk metallic glasses and granular materials. We highlight measures that can be used to differentiate between different systems and explain connections to other systems with avalanches. Predictions for future experiments will be discussed. The results are important for transferring results across scales and material structures.
Tailoring Glass Structure to Break the Speed Record of Phase-Change Memory

This talk describes our recent success (F. Rao et al., Science 2017) in controlling the amorphous structure of chalcogenide Sc-Sb-Te glass to accelerate its crystallization, reaching an unprecedented operation speed for memory and switch applications. Specifically, we have designed a new phase-change memory alloy with drastically reduced crystal nucleation stochasticity from the parent amorphous phase. The ultrafast transition between the two metastable states accomplishes sub-nanosecond switching for cache-type phase-change random-access memory (PCRAM) technology. This is a milestone in memory materials, because operation speed is currently a key challenge in the amorphous Ge2Sb2Te5 glass. Here we use alloying into the parent glass to speed up the crystallization kinetics by orders of magnitude. The newly designed chalcogenide Sc-Sb-Te alloy enables a record-setting writing speed (as short as ~700 picoseconds) in a conventional PCRAM device, with no requirement for pre-programming or additional device design. This ultrafast crystallization stems from the reduced stochasticity of nucleation via geometrically matched and robust chemical bonds that stabilize crystal precursors in the amorphous state, which are found via ab initio simulations to exhibit long life-times, shortening the incubation time for crystallization. This discovery is an example of physical metallurgy principles in action, using atomic-scale insight into glass structures (bonding configurations and sub-critical nuclei) to control properties. For details, see F. Rao et al., Science 358 (6369), 1423 (2017).

11:00 AM  *CM02.01.06*

The Interaction Between Stress, Light and Chemistry in Glass


Application of mechanical stress to glass causes interesting changes in how it transmits light. This interplay is summarized by the elasto-optic tensor, the key metric for technological applications including zero stress-optic glass, and reduced stimulated Brillouin scattering glass. Fundamentally, these effects are controlled by the glass chemistry, and in particular the nature of the chemical bonds that make up the glass. We will summarize our approach to this problem, which is focused on both an empirical and ab initio approach to the structure-property relations governing the elasto-optic tensor. We will describe the control of the stress-optic response through judicious choice of glass chemistry, and also describe our current progress in understanding and developing glass with reduced stimulated Brillouin scattering. We will include discussion of both average properties and energy-dispersive effects. We will show how these effects may be computed ab initio, with a reasonable trade-off between accuracy and speed, and illustrate a bond-based model we are developing that attempts to put in simple terms the empirical relations we have discovered.

11:30 AM  *CM02.01.07*

Ductility and Residual Liquidity in Metallic Glasses

**Takeshi Egami**1, 2 and Wojciech Dmowski1; 1Univ of Tennessee, Knoxville, Tennessee, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Lack of ductility is one of the major shortcomings of bulk metallic glasses which hamper their wide application as structural material. Ductility is a complex mechanical property which is difficult to characterize precisely. In a sense metallic glass is always microscopically ductile, because applied shear stress can locally liquify glass. But it has no work-hardening, thus often local yielding results in catastrophic shear failure. In order to achieve macroscopic ductility glass must be able to relax local stress concentration before it starts macroscopic shear band or crack. In our view the key is the residual liquidity in glass. The structure of supercooled liquid is heterogeneous, and the frozen-in structure at the glass transition contains weak liquid-like and solid-like regions. It is difficult to assess such heterogeneity directly from the structure itself, but it is possible to characterize it through the structural response to applied stress. We determined the anisotropic pair-density function (PDF) of various metallic glass samples under uniaxial stress by high-energy x-ray diffraction using the spherical harmonics expansion of the structure function $S(Q)$ and the PDF. The measured anisotropic PDF at large distances agrees with the one expected for affine (uniform) deformation which determines the long-range strain $e_{\infty}$. However, at short distances it deviates from the affine deformation, and at the first neighbour the local strain, $e_c$, is smaller than $e_{\infty}$. The deviation from the affine deformation occurs because of local liquid-like regions, so that the ratio $G = e_{\infty}/e_c$, or $\Delta G = 1 - G$, characterizes the strength of residual liquidity in glass. We found that the ratio $e_{\infty}/e_c$ is closely related to ductility. In particular, $G = 0.77$ is the threshold which separates brittle and ductile behaviors. If $G > G$, the samples are brittle, whereas if $G < G$, the samples are ductile. Thus we suggest that the percolation of the liquid-like regions results in ductile behaviour. This new parameter is compared to other criteria for ductility.

1:30 PM  *CM02.02.01*

Network Structures and Dissolution Behavior of Specialty Oxide Glasses

**Richard K. Brow**, Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

Borate, phosphate, and borophosphate glasses have been developed for a variety of technological applications, including fast ion conductors, optical substrates, and biomedical devices. For the latter, compositions are often tailored to control the rate at which physiologically significant ions are released to induce the desired biomedical response. These reaction rates depend on the hydrolysis of bonds that link neighboring glass forming polyhedra as well as the hydration of bonds associated with other metal cations that modify the glass forming network, and so detailed understanding of the glass structure connect composition to design performance. For borate and borophosphate glasses, the network hydrolysis rates decrease with increasing fractions of tetrahedral borate. For phosphate glasses, hydrolysis is not significant in neutral pH physiological conditions, but the hydration rates of metal cations are faster when they are linked to chain-forming P-tetrahedra than when they are linked to a chain-terminating pentahedron. Quantitative and qualitative structural information about Na-Ca-borate, phosphate, and borophosphate glasses, obtained by techniques like nuclear magnetic resonance spectroscopy, Raman spectroscopy, and ion chromatography, will be described and used to explain their bio-functionalit.

2:00 PM  *CM02.02.02*

Progress in Scattering with the Neutron Electrostatic Levitator (NESL) at the Spallation Neutron Source

**Dante Quirinale**, Neutron Technologies Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Progress in Scattering with the Neutron Electrostatic Levitator (NESL) at the Spallation Neutron Source (SNS) is described. The NESL is described as an approach to the scattering of neutrons from condensed matter systems. The NESL measures the dependence of the neutron scattering cross-section on momentum transfer by placing a sample into a strong electrostatic field and recording the scattered neutrons as a function of time and energy. This approach is highly efficient and allows for the rapid measurement of the scattering cross-section for a wide variety of materials. The NESL is useful for studying a wide range of materials, including liquids, glasses, and amorphous solids. The NESL is also useful for studying the dynamics of materials, such as the motion of molecules in liquids and glasses. The NESL is also useful for studying the structural properties of materials, such as the distribution of atoms in a crystal. The NESL is also useful for studying the response of materials to external stimuli, such as temperature and pressure. The NESL is also useful for studying the evolution of materials over time, such as the aging of glasses and the crystallization of glasses and liquids. The NESL is also useful for studying the response of materials to external stimuli, such as temperature and pressure. The NESL is also useful for studying the evolution of materials over time, such as the aging of glasses and the crystallization of glasses and liquids.
There is great interest in a developing understanding of the relationships between structures and dynamics in liquid and glassy systems. Metallic liquids, which exhibit a degree of short and medium range ordering, are well suited to scattering probes, but there are many difficulties associated with selecting the proper furnaces for such studies. The Neutron Electrostatic Levitator (NEL) [1] at the Spallation Neutron Source is a containerless environment developed for challenging systems, including high temperature alloys and undercooled liquids. It provides a high vacuum, high purity, non-contact environment for fundamental studies of materials at wide temperature ranges. Combined with x-ray scattering data and isotopic substitution, the system is well suited to structural characterization of liquids via pair distribution function analysis, as has been successfully demonstrated at the Nanoscale Ordered Materials Diffractometer (NOMAD) [2,3].

A series of upgrades has improved the stability of the levitator and enabled new avenues of exploration. Recently, the system has been operated at the Wide Angular Range Chopper Spectrometer (ARCS) [4] and is currently being commissioned at the Cold Neutron Chopper Spectrometer (CNCS) [5] for high resolution inelastic and quasi-elastic scattering, enabling non-contact probes of excitations in glass forming liquids as well as high temperature self-diffusion measurements. The current capabilities and characteristics of the levitator furnace, progress in inelastic scattering measurements, and early results from the commissioning at CNCS will be discussed.


2:15 PM CM02.02.03

Modern drug delivery increasingly relies on micro- and nano-structures to achieve specific release rate and therapeutic target. The delivery systems modulate drug release via engineering control of the API and drug domains. Recent advances involve the use of functional coating or performance-enabling excipients. The small-scale nature of pores, drug domains, and delivery vehicles demands higher resolution technique to characterize. High-resolution image-based characterization has been broadly utilized in drug product development for fundamental understanding on the process-property-performance interplay and optimizing formulation process and design. It finds applications in various novel drug release systems such as tailoring rate-limiting film coat thickness where the pore formation is critical to control drug release and interrogating the underlying mechanism of in-situ drug nanoparticle formation from amorphous solid dispersions in dissolution media for solubility enhancement. 3D micro-imaging can qualitatively visualize micro-structures, quantify their spatial and chemical distribution, and predict release behavior. In recent years, the emerging image-based numerical simulation has received significant traction and plays an important role in predicting drug release performance. Information-rich 3D images can be converted to characteristic drug transport parameters through intelligent analysis and applied to numerical simulation models to predict release performance. This image-based simulation approach represents a potential paradigm shift in drug design and evaluation, with significantly reduced evaluation time, improved release performance, and lowered in-vitro and in-vivo experiment cost.

2:30 PM CM02.02.04
Nanoscale Imaging of Bulk Bottlebrush Polymers Using Helium-Ion Microscope Nikolay Borodinov; Alex Belianinov; Dongsook Chang; Jan-Michael Carrillo; Matthew J. Burch; Yuewen Xu; Anton V. Levchuk; Bobby G. Sumpter and Olga Ovchinnikova; Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; Kimberly-Clark Corporation, Irving, Texas, United States.

Recently, bottlebrush polymers have attracted significant interest due to their potential applications in drug delivery and electronics. The tunability of their properties, stemming from the diversity of sidechains and their spatial arrangement, have emphasized their industrial potential as compared to the linear macromolecules. In this context, the structural information and organization of these systems play a major role in the rational design of functional bottlebrush polymers. Specifically, direct observation of the molecular organization can reveal inter-chain interaction phenomena and explain the fundamental physical properties of these systems. Here, we report a new method to analyze bulk macromolecular chain arrangement of bottlebrush polymers based on Helium Ion Microscopy ( HIM ). By using the HIM we were able to quantify structural nematic-type ordering in an amorphous polymer bottlebrush system. High-resolution imaging coupled with data analytics has proven to highlight the location and distribution of the polymer backbones, after oxygen plasma-generated height contrast; as well as map changes in the backbone spatial arrangement as a function of thermal annealing. Our experimental findings are corroborated by the coarse-grained molecular dynamics simulations. Overall, this approach can generate clear insights on the internal structure of amorphous materials and provides a complimentary information channel to scattering techniques and theoretical modeling.

This work was performed at the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility. This research used resources of the Oak Ridge Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC05-00OR22725. The authors acknowledge Scott Retterer at the Center for Nanophase Materials Science at Oak Ridge National Laboratory for helpful input and discussion.

2:45 PM CM02.02.05
Correlating Nanoscale Structural Heterogeneity to Glass Forming Ability and Mechanical Properties of Metallic Glasses Soobyun Im; Jared Johnson; Gabriel Calderon Ortiz; Menglin Zhu; Pengyang Zhao; Guen Hee Yoo; Eun Soo Park; Yuzhi Wang; and Jinwoo Hwang; Seoul National University, Seoul, Korea (the Republic of); Materials Science and Engineering, The Ohio State University, Columbus, Ohio, United States.

We determine the nano-to-mesoscale structural heterogeneity in metallic glasses (MGs) using 4-dimensional (4D) nanodiffraction in scanning transmission electron microscopy (STEM). Structural heterogeneity in MGs has been suggested by both experiments and simulations previously. The heterogeneity must involve local structural ordering at the nanoscale, commonly known as medium range order (MRO), some of which has been studied using small electron probes in the past. However, the statistically reliable information on how such MRO constitutes the heterogeneity has remained difficult to determine. Our new approach to determine the MRO and structural heterogeneity involves 4D-STEM, which uses a new-generation pixelated fast STEM detector that allows for the continuous collection of the diffraction patterns from a large area of the MG sample. Using angular correlation and intensity
variance analyses, the diffraction patterns can then be converted to real space maps of the local ordering, which we use to precisely determine the type, size distribution, and volume fraction of MRO. We will present two cases of how the heterogeneity affects the important properties of MGs, one is the glass stability in Ti-based MGs, and the other is the ductility of Zr-based MGs. To connect the structural heterogeneity to ductility, we use a new mesoscale simulation that incorporates the exponentially determined heterogeneity, which can simulate realistic shear band formation and overall deformation that match the spatial and temporal scales of the deformation of real MGs.

3:00 PM BREAK

3:30 PM CM02.02.06
Structure is the Organization Plan of Glasses—But Dynamics Might Bring Deeper Insight
Bernhard Frick1, Henriette W. Hansen1,2,3 and Kristine Niss4; 1Institut Laue–Langevin, Grenoble, France; 2Roskilde University, Roskilde, Denmark; 3Chalmers, Göteborg, Sweden.

It is well known that for a large number of glass forming liquids the static structure factor, S(Q), shows no or only subtle changes when passing from the liquid into the glass. In contrast the dynamic structure factor S(q,ω) of simple or more complex glass forming liquids evidences in the GHz - THz frequency range and close to the glass transition clear and common signatures which have been addressed by several theories over the last decades. In spite of large experimental and theoretical activity in this field the glass transition is still not fully understood. Quasielastic neutron scattering plays a vital role for the experimental investigation of dynamic properties of disordered materials, glasses and undercooled liquids. We will give a brief overview over typical experimental findings near the glass transition and over recent instrumental progress on neutron spectrometers before presenting some examples. We then focus on our recent investigations on simple organic, hydrogen bonded and ionic liquids for which we have probed the dynamics near the glass transition by simultaneous dielectric and neutron spectroscopy. For these simultaneous experiments we have controlled both temperature and pressure which did allow us to map lines in the (P,T)-diagram along which the dynamics is unchanged and therefore is isochronous over a wide time range.

4:00 PM CM02.02.07
Spatially Heterogeneous Dynamics in Metallic Glass Nanowires Imaged by Electron Correlation Microscopy
Debaditya Chatterjee1, Pei Zhang1, Jittisa Ketkaew2, Jan Schroers2 and Paul M. Voyles1; 1Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin, United States; 2Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States.

We have used electron correlation microscopy (ECM) to image the nanometer scale heterogeneities in the relaxation dynamics of the supercooled liquid of a metallic glass forming alloy [1]. The length and time scales of the heterogeneous dynamics are central to the glass transition and influence nucleation and growth of crystals from the liquid. Electron correlation microscopy (ECM) experiments use time-resolved tilted dark field transmission electron microscopy with sub-nanometer resolution for direct measurement of those length and time scales. ECM data on Pt-based metallic glass nanowires above the glass transition temperature (Tg) reveal a relaxation time scale that varies from a few seconds to hundreds of seconds and a length scale that varies from 0.8 to 1.4 nm. They also demonstrate the existence of a ~1 nm thick near-surface layer with an order of magnitude shorter relaxation time than inside the bulk which may influence crystallization of the wires. Additional measurements of the surface layer relaxation time below the bulk Tg and its connection to enhanced surface diffusion in metallic glasses and surface crystallization will be discussed.


4:15 PM CM02.02.08
Kinetic Metallic Glass Evolution Model
Thomas J. Hardin and Christopher A. Schuh; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Metallic glass is a heterogeneous composite on the scale of a few nanometers; the structure of the glass on this scale governs its macroscopic thermomechanical response. This structure evolves in response to thermal and mechanical loading; this evolution is mediated by discrete kinetic events in which clusters of atoms locally rearrange themselves. We present a model of this structural evolution and mechanical response which consists of a thermodynamic state space, density of states, and models for relaxation and shear transformation events which move the glass through that state space. We implement this model in a homogenized statistical sense and compare to homogeneous relaxation and flow data previously in literature; we also implement it in a discrete mesoscale framework. We conclude with a discussion of gaps in the current understanding of the fundamental structure of metallic glass.

4:30 PM CM02.02.09
Atomic-Level Insight into Amorphous Aluminum Oxide Structure—Atomic Simulation vs In Situ Experiment
Marcela E. Trybula1,2, Przemyslaw W. Szafranski1, Pavel A. Korzhavyi1, Nikolay A. Vinogradov2 and Edvin Lundgren3; 1Institute of Metallurgy and Materials Science Polish Academy of Sciences, Krakow, Poland; 2Department of Materials Science and Engineering, KTH-Royal Institute of Technology, Stockholm, Sweden; 3Department of Organic Chemistry, Faculty of Pharmacy, Jagiellonian University Medical College, Krakow, Poland; 4Institute of Metal Physics, Ural Branch of RAS, Ekaterinburg, Russian Federation; 5MAX IV Laboratory, Lund University, Lund, Sweden; 6Synchrotron Radiation Research, Lund University, Lund, Sweden.

Structural disorder in amorphous solids may depend on the method of their preparation. An easily-accessible method is electrochemical anodization of metal surface, which may result in formation of periodic voids, or pores, for example in a well-known Al anodization process [1,2]. These voids, or pores, are thought to derive from the morphological instabilities underlying the initial stage of oxidation [1]. Such nanostructuring can have a profound impact on local structural anisotropy or hierarchical ordering of atom clusters build-up in the structure of the amorphous Al oxide film.

In this contribution, we determine the structural and topological descriptors of bulk alumina to compare them with those obtained from in situ synchrotron-based experiment of porous anodic aluminum oxide scale growth. We also discuss the impact of self-assembling ring structure on chemical and topological short- and intermediate-range ordering in bulk alumina in the light of in situ oxide growth. The interpretation of out of in situ X-ray diffraction data is supported by molecular dynamics simulations and DFT-based calculations. These allowed us to capture physical phenomena accompanying in situ anodic aluminum oxide growth. Obtained calculation results agree well with the available experimental [3] and computational data [4].

Literature:

4:45 PM CM02.02.10
Hierarchical Machine Learning to Decode Structural Origin of Heterogeneous Deformation in Disordered Materials Qi Wang and Anubhav Jain; Lawrence Berkeley National Lab, Berkeley, California, United States.

When subjected to external stimuli such as mechanical loading, atoms in disordered solids respond heterogeneously. Due to lack of representations to resolve the subtle packing difference around atom sites and approaches to deal with the long-range correlation involved, it is hard to quantitatively predict this heterogeneous, site-specific response solely from the structure. Here, by designing a robust hierarchical machine learning framework, we show that it is possible to predict the mechanical heterogeneity in disordered solids a priori, directly from the quenched structural state itself. We encyclopedically create a large pool of 810+ site descriptors, from 40+ sets of structural measures, spanning topological and chemical short- and medium-range order, and develop a novel hierarchical scheme to further extend the studied scale to an unprecedentedly long-range while still retaining good interpretability and generality. Impressive predictability is achieved in a fairly large strain regime, suggesting a long-lived inheritance of the quenched state until later obstructed by shear banding. The framework is robust over a range of compositions and processing conditions and can well detect the site environments tuned by these conditions. We also identify a bag of promising structural signatures unrevealed previously, with their predictability exhaustively benchmarked and discussed. This hierarchical learning framework is general and could potentially be applied to decode structural origin of any site-specific properties in the family of disordered materials.

SESSION CM02.03: Poster Session I: Structure-Property Relations in Non-Crystalline Solids
Session Chairs: Katharine Flores, John Mauro, Tanguy Rouxel and Yunfeng Shi
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM02.03.01
Microstructure Design for Ductile Glass Composite Yanming Zhang, Binghui Deng, Liping Huang and Yunfeng Shi; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

In this work we use molecular dynamics (MD) simulations to investigate glass composites constituted by two brittle model glasses with different stiffness. We show that tuning the stiffness ratio (SR), shape, volume fraction and distribution of the two brittle glass constituents can trigger a brittle to ductile (BTD) transition. Such composite glasses can exhibit high strength, remarkable toughness and some work hardening. The highest failure strain of 80% can be reached in composite glasses as compared to 7% in monolithic model glasses. We also found that mechanical properties of such glass composites will not be deteriorated by introduction of pre-notch. Excellent load redistribution capability introduced by structural heterogeneity is responsible for high ductility in our composite glasses. Through a systematic analysis, we unveil the design principles that lead to the aforementioned BTD transition. We believe the current approach could enhance ductility and broaden the application of glasses as enabling structural materials.

CM02.03.02
Molecular Modeling of Stress Corrosion Behavior Swastik Basu, Liping Huang and Yunfeng Shi; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Glass is well known to be susceptible to stress corrosion cracking caused by chemicals in the environment, a phenomenon that can cause delayed failure of glasses due to growth of pre-existing surface defects in the presence of humidity. The complex macroscopic effects of stress corrosion, like fracture, occur due to microscopic interactions, which demand a study to replicate the microstructural interactions within a model, which should reproduce the macroscopic behaviors. The purpose of this research is to study the stress corrosion behavior of a model metallic glass system with a view towards representing the underlying atomic level mechanisms using a molecular dynamics approach.

CM02.03.03
Liquid Metal Nanoscale Structures as Novel Platform for Characterization of Structural Relaxation of Metallic Glasses Ziyang He1, Chen Liang2 and Chenhao Qian3; 1Economics Department, Columbia University, New York, New York, United States; 2Engineering Department, University of Liverpool, Liverpool, United Kingdom; 3Department of Mechanical Engineering, Jiangnan University, Wuxi, China.

This poster firstly introduces a new microfluidic method for preparing nanostructures of gallium-indium liquid alloy systems. Due to its smaller nanometer size (50-100nm diameter), good self-healing behavior, strong oxide layer formed by spontaneous oxidation, rich changeable nanomorphology driven by voltage variation and large undercooling range, the alloy system has become a good platform for studying amorphous structure transformation and internal structure of liquids using in-situ characterization technology under current conditions. We have successfully discovered the presence of secondary structures in this liquid metal system through in situ TEM lithiation experiments and subsequent nanomechanical and electrical experiments. By comparing the structural relaxation of the same kinetic fragility liquid with or without the oxide layer structure, we found that the oxide layer structure could guide the dynamic non-uniformity of the nano-amorphous system to some extent. At the same time, we are also actively exploring the future application of this alloy system in liquid metal self-healing electrodes, nano-heat pipes, nanoscale self-propelled robots and other industrial fields.

CM02.03.04
Self-Diffusion Mechanism of Atoms in Forsterite Glass Junya Nishizawa and Tomoko Ikeda-Fukazawa; Department of Applied Chemistry, Meiji University, Kawasaki-shi, Japan.

Forsterite glass exists as dust grains in interstellar molecular clouds and young stellar objects [1]. In interstellar molecular clouds, elements such as hydrogen, oxygen, carbon, and nitrogen deposit on dust grains, and form various molecules (e.g., H2O, CO, CO2, NH3, CH4, H2CO, CH3OH, and so on) [2]. These molecules undergo chemical evolutions to organic molecules through various processes on the surface of dust grains [2]. Dust grains are important materials governing the chemical and thermal evolutions in space. However, the transport coefficients of forsterite glass are less conclusive, because forsterite glass is easily to crystallize. To investigate the mechanism of self-diffusion of atoms in forsterite glass, molecular dynamics (MD) calculations were performed.

The MD calculations were performed using an atom-atom potential model with MDXORTO program [3]. The potential parameters were empirically determined by constraining the model to reproduce the experimental results of density, thermal expansion coefficient, and bulk modulus [4]. The transition
point from glassy state of supercooled liquid state ($T_g$) for our potential model is 1567 K. A fundamental orthorhombic cell consisting of 160 MgSiO$_4$ with three-dimensional periodic boundary conditions was used. The glass structure was prepared by quenching the liquid phase from 3000 K to 10 K with 0.4 K/ps in rate. The quenched glass was warmed to 3000 K with the same rate. The MD code was run with NTP ensemble. The pressure was kept at 0.1 MPa. The self-diffusion coefficients of Mg, Si and O were calculated using mean-square displacement (MSD). To investigate the mechanisms of self-diffusion, the temporal variations of pair correlations functions for Mg were analyzed. The result shows that the jumping probability of Mg, which is located at a position with high Si and low Mg densities is high. Because of the strong Si-O bonds in the tetrahedral SiO$_4$ units, the jump of Mg atom (or MgO$_x$ unit) was induced by structural distortion of the surrounded SiO$_4$ units. From analyses of spatial distribution of MSD, it was found that the MSD values of Mg are inhomogeneous at temperatures just below $T_g$. Because the self-diffusion coefficient of Si is significantly low at $< T_g$, the distribution of Si in forsterite glass is inhomogeneous. Therefore, the diffusivity of Mg depends on surrounded Si distribution.

Reference:

CM02.03.06
Methods for Estimating Appearance of Metal-Like Plastic
Sun Chul Jin, Hyungjin Roh, Kiyong Kim and Sunghawn Cho; Samyang, Daejeon, Korea
(the Republic of).

A plastic has a lower specific gravity than glass or metal and has many advantages such as lightweight and good mechanical properties. These thermoplastics are rapidly replacing conventional glass and metal areas in fields such as electronic and automobile parts. Recently, as increasing need for environmentally friendly material, there is an increasing demand for plastic that can feel a metallic appearance similar to a metal without a spray process. For the development of metal-feeling thermoplastics, it is well-known way to use metallic pigment. But because of difference in flowability between metal pigment and plastic, there is an appearance problem such as flow mark and weld-line. This is why metal-feeling plastic can’t be expanded. In order to solve these problems, much research have been studied to control the shape and aspect ratio of metallic pigment and to improve the surface coating of it. However, it is limited to improve the appearance problems such as aggregation and orientation. In addition, there is no effective method for objectively estimating the appearance of the metallic feeling except for flop index. But the flop index can evaluate only the metallic brightness and the degree of defects such as flow mark and weld-line caused by the metallic pigment could not be evaluated. As a result, there is no method of evaluating the appearance that can represent the overall phenomenon caused by the metallic pigment as an objective numerical value. In this research, development of method for estimating appearance of metal-feeling plastic is studied. Through correction of flop index, new index named as ‘T/N. Flop. X’ was developed. Using this index, it is available to objective evaluation and comparison of metal-feeling. And using the CCD camera, it was studied that correlation of sparkle effect, metallic pigment’s orientation and weld-line. Based on these studies, we found out sparkle index that could be explained about orientation and metal-feeling. Additionally we studied about control of metallic pigment for reduce an appearance problem. Orientation is important factor to determine weld-line degree and in a constant direction makes decrease it. We found out factors that could control orientation especially additive having an affinity of polar and non-polar.

CM02.03.07
Amphiphilic Modification of PDMS Surface with PVA/PSBMA Zwitterionic Semi-Interpenetrating Hydrogel for Marine Antifouling
Application
Xingyang Xu, Rongrong Chen and Jun Wang; College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, China.

Marine biofouling is a highly complex process and a worldwide problem which involve a wide variety of species. The common techniques proposed incude heavy metals (Cu$_2$O), or organic biocide, are bring potential harm to marine environment and ecosystem. Therefore, the nontoxic approaches, particularly silicone-included low-surface-energy Fouling Release Coatings (FRCs) may be the alternatives to chemically active coatings and more environmentally friendly AF strategies. In this research, development of method for estimating appearance of metal-feeling plastic is studied. Through correction of flop index, new index named as ‘T/N. Flop. X’ was developed. Using this index, it is available to objective evaluation and comparison of metal-feeling. And using the CCD camera, it was studied that correlation of sparkle effect, metallic pigment’s orientation and weld-line. Based on these studies, we found out sparkle index that could be explained about orientation and metal-feeling. Additionally we studied about control of metallic pigment for reduce an appearance problem. Orientation is important factor to determine weld-line degree and in a constant direction makes decrease it. We found out factors that could control orientation especially additive having an affinity of polar and non-polar.

CM02.03.08
The Effect of Arm Segment Length on Thermally Induced Self-Healing Behavior of Supramolecular Star Poly(ε-caprolactone)s Network
Woojin Lee,1 Dae-Young Won1, Hye-bin Wi2, Jae Woo Chung2 and Seung-Yeop Kwak1;1 Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of);2 Soongsil University, Seoul, Korea (the Republic of).

Supramolecular polymer is comprised of oligomers or polymers that are held together by reversible non-covalent supramolecular interactions. It is capable of responding to damage or crack and restoring the polymer’s performance without affecting the initial materials properties. The healing property of supramolecular polymer network depends on two factors, that is, the first being the supramolecular interactions, and the second being the chain dynamics of the individual polymer chains. In this study, we synthesize the simple supramolecular network consisted of ureidopyrimidinone (UPl) ends functionalized 6-arm star poly(ε-caprolactone)s and investigate the effect of arm length on thermally induced self-healing behavior of the supramolecular star poly(ε-caprolactone)s network. The resulting materials can be healed several times at 90°C during 10 minutes, and even can be healed at 60°C after 40 minutes. We find the compromise number of tie points by supramolecular force and chain dynamics related to sufficient mobility of network. Both supramolecular end clusetery crystal and main chain crystal might affect the mobility of network. For the efficient healing behavior, the crystalline domain of supramolecular polymer network should be collapsed. Thus, the sufficiently thermally induced healing behavior can be achieved through the enhanced mobility of network.

CM02.03.09
Ab Initio Study of the Amorphous Cu-Bi System
David Hinojosa-Romero1, Isaias Rodriguez2, Alexander Valladares2, Renela M. Valladares2 and Ariel
As a pure element, bismuth is a semimetal which possesses several interesting physical properties, not all of them well understood. The recent discovery of superconductivity [1], as predicted by our group [2], and the increasing superconducting transition temperature as the pressure applied increases, are some examples of its particularities. Also, the fact that the amorphous phase is superconductive with a transition temperature several orders of magnitude larger than the crystalline at ambient pressure is unusual [2]. These phenomena have also motivated our predictions for the transition temperatures of Bi-bilayers [3] and the Bi-IV phase [4]. When mixed with other elements, bismuth seems to contribute to the superconducting character of the resulting material. Here we study the binary copper-bismuth amorphous system which is known to superconduct in diverse compositions [5]. Using \textit{ab initio} molecular dynamics and the undermelt-quench method, we generate an amorphous structure for a 144-atom supercell corresponding to the Cu$_{44}$Bi$_{56}$ system. We shall report the calculated electronic and vibrational densities of states for this system and relate them to the superconducting properties of this alloy.


**CM02.03.10 Structural Commonalities in Different Classes of Non-Crystalline Solids—A Pair Distribution Function Analysis**

Isaias Rodríguez$^1$, David Hinojosa-Romero$^1$, Renela M. Valladares$^2$, Alexander Valladares$^2$ and Ariel A. Valladares$^1$; $^1$IIM-UNAM, Mexico City, Mexico; $^2$Physics, Faculty of Science, UNAM, Ciudad de México, Mexico.

In the past decades the research community has explored diverse structures and new fabrication methods of non-crystalline solids. Glassy materials that belong to the semiconductor realm and to the metallic type are the most studied both experimentally and simulationally. The present work investigates common structural trends whenever they exist and different trends among different classes. Amorphous semiconductors display Pair Distribution Functions (PDF) that are very similar among themselves and this indicates that these network forming materials have properties that are alike [1]. Analogously metallic systems have comparable PDFs but different from the network forming materials, as it should be, since the properties between these two classes are very different [2].

Here we pay attention to the Short-Range Order (SRO) and Intermediate Range Order (IRO) of these two classes. In particular, the first peaks of the structures studied are contrasted, while the second peaks are shown to differ considerably. Whereas the semiconductor structures display a simple first and second peak with a near-zero value between them, the metallic systems have a very well defined non-zero value between the first and second peaks and they also display what we have come to identify as an “elephant” second peak [3]. To manifest the uncommonalities with amorphous semimetals we recall calculations carried out by our group for bismuth where the elephant peak does not appear but the non-zero behavior between the first and the second peak is present [3]. The Plane Angle Distribution (PAD) functions are also reported.


**CM02.03.11 Dependence of Modulus on the Annealing Conditions of Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ Bulk Metallic Glass**

Zheng Chen$^1$, Amit Datye$^1$, Jittisa Ketkaew$^1$, Sungwoo Sohn$^1$, Jan Schroers$^1$, and Udo Schwarz$^1$; $^1$Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States; $^2$Department of Chemical Engineering and Environmental Engineering, Yale University, New Haven, Connecticut, United States.

The mechanical properties of bulk metallic glasses are often tuned by annealing, which influences these properties by adjusting the relaxation or crystallization status of the glasses. Here, we studied the modulus of Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ bulk metallic glass (Pt-BMG) annealed at different temperatures in the metastable regime by nanoindentation, where the annealing generates the BMG different fictive temperature and fractions of crystallization. We find the modulus of the investigated BMG samples exhibits a “V” trend: As the annealing temperature increases, we first observe a decrease that is followed by an increase until saturation is reached. This phenomenon can be explained as a result of the combination of the glasses relaxation and the glasses crystallization: Relaxation caused by higher fictive temperatures lead first to higher free volumes, which leads to lower moduli, while past a specific temperature, crystallization generates new, denser phases with higher moduli. The latter finding is confirmed by nanoindentation measurements at which fully amorphous Pt-BMG samples with different fictive temperatures are compared with partially crystalline samples featuring the same fictive temperature.

**CM02.03.12 Theoretical Support to Hydrogen Elimination Monitoring by Ultraviolet Photodissociation Mass Spectrometry Using Density Functional Theory**

Lindsay Morrison, Wenru Chai, Jake Rosenberg, Graeme Henkelman and Jennifer Brodbelt; The University of Texas at Austin, Austin, Texas, United States.

Mass spectrometry (MS) has became an increasingly popular and useful in analyzing structures of proteins. Initially only information of low resolution and of the whole protein in general can be obtained. Many techniques that utilize property differences between parts of the protein to produce signature

---

fragmentation patterns and products have been developed to gain more information on local geometry, such as collision induced dissociation (CID), electron transfer dissociation (ETD), electron capture dissociation (ECD) and ultraviolet photodissociation (UVPD). A new method called hydrogen elimination monitoring (HEM) was invented by Brodbelt et. al, to overcome disadvantage of other methods. For example, CID disrupts protein structure prior to fragmentation therefore higher order structural information is lost and ECD cannot differentiate highly ordered surface regions with internal buried regions. HEM aims finding out higher order structure anywhere in the protein by using hydrogen elimination information after fragmentation to determine the level of hydrogen binding prior to fragmentation, therefore determining local geometry. Experiments have demonstrated that hydrogen elimination correlates strongly to absence of backbone hydrogen bonding yet the underlying process and reason to this correlation is unknown. DFT studies of model peptides at ground state can help in illustrating the process and in providing theoretical support to HEM method.

In the computational study complementary to experimental findings, we used 3 structures of Ala8 peptide models with increasing amount of hydrogen binding: an unstructured linear peptide, a hairpin turn and a helix, to study the thermodynamics as well as the kinetics of the fragmentation process, by finding out the enthalpy change of the fragmentation reaction and the minimum energy pathways (MEPs) for the processes. The thermodynamics show that fragmentation products without hydrogen elimination are much higher in energy compared to products with hydrogen elimination, and therefore extremely unfavorable. The MEPs revealed reasons why the thermodynamic favorable product may not always form. In the unstructured peptide, hydrogen elimination always take place at the same time as the C-C back bone is cleaved. In the hairpin turn and helix structure, however, the MEP show that C-C cleavage takes place first and produces spatial separation that could prevent hydrogen elimination. This finding shows the underlying principle of the correlation between hydrogen elimination and amount of hydrogen binding prior to fragmentation, and therefore supports HEM as an effective method for analyzing protein structure.

CM02.03.13
The Molecular Influence on High Strain Rate Microscale Impact Response of Synthetic Polymeric Materials
Yuchen Sun1, 2, 4, David Veysey1, Alex Hsieh1, Steven Kool1, You-Chi M. Wu1, John P. Mikhail1, A. A. Maznev2, Jan W. Andzelm3, Gregory C. Rutledge1, Timmy M. Swager2 and Keith A. Nelson1, 2, 4, 5
1 Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3U.S. Army Research Laboratory, RDRL-WMM-G, Aberdeen Proving Ground, Maryland, United States; 4Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 5Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The deformation of materials in extreme dynamical environments such as high-velocity microparticle impact is a challenge to understand though important for many areas of science and technology from space exploration to sand erosion. While impact dynamics of macroscale projectiles have been studied in real time using high-speed imaging, investigations of microscale impact have been essentially limited to post-mortem analysis of impacted specimens. Here, we present real-time observations of supersonic microparticle impacts using multi-frame imaging. In a laser-induced projectile impact test, a microparticle is accelerated by laser ablation from a sacrificial gold layer on a glass substrate. These particles can be accelerated into free space with controllable speeds up to 1.0 km/s depending on laser pulse energy and particle characteristics. The particles are monitored in flight and during impact with an ultra-high-speed camera that can record up to 16 images with a minimum interframe time of 3 ns. We investigated the high-velocity impact deformation response of elastomers to further the fundamental understanding of the molecular influences on high strain rate elastomeric response. The types of materials that were synthesized and tested are glassy polymers, graft copolymers, and other materials. We show the dynamic stiffening response of various elastomers including poly(urea urethane) upon impact at strain rates of ~10⁸ s⁻¹ and demonstrate the significance of molecular constitution in the response. These results provide an impetus for modeling the molecular influence on high strain rate microscale impact responses in these polymeric materials.

CM02.03.14
Enhancing the Mechanical Properties of Biodegradable PLA using Ternary Polymer Blends
Xianghao Zuo1, Yuan Xue1, Elena Urquiola2, Ruilin Yin3, Jinhai Tang4 and Miriam Rafailovich1
1 Stony Brook University, Stony Brook, New York, United States; 2Hunter College High School, New York City, New York, United States; 3St. Anthony's High School, South Huntington, New York, United States; 4Hunter College High School, New York City, New York, United States; 5Stony Brook University, Stony Brook, New York, United States.

Acrylonitrile butadiene styrene (ABS) has a similar matrix structure to the styrene acrylonitrile copolymer but has additional distribution of polybutadiene which strengthens it and allows ABS to surpass the properties of traditional commercial polymers. PLA is a 100% biodegradable polymer which can be regarded as a replacement to many current commercial plastics. However, it’s brittleness limited its applications. Commonly, binary blends including PLA and another polymer additives are created to enhance the mechanical properties of PLA, but this has been found to be ineffective due to the poor interfacial reaction between the polymers. Previous studies have determined that a 70:30 PLA: ABS ratio effectively balances the bio-based properties of PLA with the exceptional mechanical properties of ABS. Many have observed that the binary PLA/ABS blend actually has worse mechanical properties than just the PLA alone. Therefore, an efficient compatibilizer with good affinity with both PLA and ABS is a key factor to solve this problem. In our previous work, we have certified that PMMA is miscible with PLA and considering the structure of ABS, we hypothesise PMMA should be an excellent compatibilizer to the blend.

To create the ternary blends, the polymers were added to a C.W. Brabender and then molded into the tensile and impact test shapes using a Carver Hot Press. The blends were also run through an extruder to create filaments for 3D printing. A 286% increase for the molded sample in the impact test was observed when 4% by weight PMMA was used with the 70PLA/30ABS blend. Mechanical tests also showed that this ternary polymer material can maintain high mechanical properties even when 3D printing, as the mechanical properties of the 3D printed surpassed the pure PLA sample and PLA/ABS binary blend by 24.3% and 55.5% respectively. SEM and TEM imaging were used to verify the location of PMMA phase. And contact angle tests show that ABS has a higher affinity with PMMA than PLA.

The ternary blends reached their peak mechanical properties with less than 5% by weight of compatibilizer added, suggesting the economic efficiency of this blend for industrial use. For future study, interfacial properties in the ternary blends could be investigated using secondary ion mass spectrometry (SIMS) analysis to reveal interactions that contribute to mechanical strength.

CM02.03.15
Enhancing Impact Resistance of Polymer Blends via Self-Assembled Nanoscale Interfacial Structures
Xianghao Zuo, Yuan Xue, Yichen Guo and Miriam Rafailovich
1 Stony Brook University, Stony Brook, New York, United States.

We have designed and engineered ternary polymer blends with the mechanical properties comparable to high impact resistant conventional polymers under the guidance of the lattice self-consistent field model. Tow formulas were used to study the mechanical properties. In one system, poly (methyl methacrylate) (PMMA) was used as the compatibilizer for the widely used biodegradable polymer blend, poly (lactic acid) (PLA)/Poly (butylene
where quantized steps with height of $2g_0$ are found in Labyrinth tiling with periodic order along the applied electric field direction, in contrast to the step a set of independent chains with rescaled Hamiltonians [2]. Such transformation leads to an analytical solution of the direct-current conductance spectra, the best focus on the mechanical analysis. Single-edge-notched-tension (SENT) and double-edge-notched-tension (DENT) samples with pre-notch size of tensile experiments and finite element methods analysis.

60 nm and thickness of 200 nm were fabricated in mushroom like shape with head size of ~2 μm using Focused Ion Beam (FIB) on DLC film of ~1.5 μm present an unwonted roll of cracks at the nanoscale as an activator of a fracture resisting mechanism not as an enemy of brittle ceramics through nanoscale flaws when they shrink below a certain critical size and enables to reach almost theoretical strength of the material [1]. Getting ideas from this, here we usually never been reached before the total failure in bulk scale. However, in some theoretical studies, fracture of nanomaterials becomes insensitive to space renormalization method [3], we can address in a non-perturbative way the electronic transport in macroscopic aperiodic Labyrinth tiling based on height of $g_0$ observed in the corresponding square lattices, being $g_0$ the conductance quantum. When this convolution theorem is combined with the real-exponentially localized eigenstates [1]. Nowadays, the study of electronic transport in artificial structures is of great importance in condensed matter physics, because such structures introduce many new physical properties essential for technological applications of atomic-scale devices. In this work, we revisted a previous convolution theorem developed for the Kubo-Greenwood formula in Labyrinth tiling by transforming the original two-dimensional lattice into a set of independent chains with rescaled Hamiltonians [2]. Such transformation leads to an analytical solution of the direct-current conductance spectra, where quantized steps with height of 2$g_0$ are found in Labyrinth tiling with periodic order along the applied electric field direction, in contrast to the step height of $g_0$ observed in the corresponding square lattices, being $g_0$ the conductance quantum. When this convolution theorem is combined with the real-space renormalization method [3], we can address in a non-perturbative way the electronic transport in macroscopic aperiodic Labyrinth tiling based on generalizad Fibonacci chains [4]. Furthermore, we analytically demonstrate the existence of ballistic transport states in such aperiodic Labyrinth tiling. This finding suggests that the periodicity should not be a necessary condition for the single-electron ballistic transport even in multidimensionally fully non-periodic lattices. This work has been partially supported by UNAM-IN114916, UNAM-IN106317 and CONACyT-252943. Computations were performed at Miztli of DGTF, UNAM.


CM02.03.16

Electronic Transport in Aperiodic Labyrinth Lattices

Vicenta Sanchez, Fernando Sanchez and Chumin Wang; Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

The search for a simple and direct relationship between atomic scale arrangement and macroscopic properties of a material constitutes a principal task of the materials science. For example, the Bloch theorem establishes extended electronic wavefunctions and then a ballistic conduction if the atoms of a crystalline material are periodically ordered. At the other extreme, one- and two-dimensional amorphous solids with randomly arranged atoms possess only exponentially localized eigenstates [1]. Nowadays, the study of electronic transport in artificial structures is of great importance in condensed matter physics, because such structures introduce many new physical properties essential for technological applications of atomic-scale devices. In this work, we revisited a convolution theorem developed for the Kubo-Greenwood formula in Labyrinth tiling by transforming the original two-dimensional lattice into a set of independent chains with rescaled Hamiltonians [2]. Such transformation leads to an analytical solution of the direct-current conductance spectra, where quantized steps with height of 2$g_0$ are found in Labyrinth tiling with periodic order along the applied electric field direction, in contrast to the step height of $g_0$ observed in the corresponding square lattices, being $g_0$ the conductance quantum. When this convolution theorem is combined with the real-space renormalization method [3], we can address in a non-perturbative way the electronic transport in macroscopic aperiodic Labyrinth tiling based on generalizad Fibonacci chains [4]. Furthermore, we analytically demonstrate the existence of ballistic transport states in such aperiodic Labyrinth tiling. This finding suggests that the periodicity should not be a necessary condition for the single-electron ballistic transport even in multidimensionally fully non-periodic lattices. This work has been partially supported by UNAM-IN114916, UNAM-IN106317 and CONACyT-252943. Computations were performed at Miztli of DGTF, UNAM.


CM02.03.17

Fracture Tensile Test for Brittle Diamond-Like-Carbon at the Nanoscale

Dahye Shin and Dongchun Jang; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Ceramics are well used in various fields as functional materials and their property range is a way more expanded these days by adding new nanoscale properties. Even though a number of studies have been achieved for investigating electronic, magnetic, optic properties etc. at nanoscale, the fracture behavior is not reached to the same level of evaluation. It is in need of investigating the fundamentals of fracture mechanics for nano-sized ceramic materials to guarantee the reliability of the systems adding to enjoy the newly enhanced nano-properties at the same time. Brittle failure of ceramics is usually mediated by a rapid crack propagation due to the lack of intrinsic crack tolerant mechanism which requires extremely high critical stress for its activation, usually never been reached before the total failure in bulk scale. However, in some theoretical studies, fracture of nanomaterials becomes insensitive to flaws when they shrink below a certain critical size and enables to reach almost theoretical strength of the material [1]. Getting ideas from this, here we present an unwonted roll of cracks at the nanoscale as an activator of a fracture resisting mechanism not as an enemy of brittle ceramics through nanoscale tensile experiments and finite element methods analysis. In situ SEM tensile fracture tests with different crack geometries were carried out. Diamond-like-carbon (DLC) was chosen to be conductive for SEM image quality, isotropic, and brittle material to eliminate any complicate material issues and to make the best focus on the mechanical analysis. Single-edge-notched-tension (SENT) and double-edge-notched-tension (DENT) samples with pre-notch size of 60 nm and thickness of 200 nm were fabricated in mushroom like shape with head size of ~2 μm using Focused Ion Beam (FIB) on DLC film of ~1.5 μm coated on Si wafer. The head part was grabbed and pulled by a self-produced claw-like tip. In short, we observed that the DENT samples were deviated from the expectations based on classical linear elastic fracture mechanics showing 150% higher fracture strength even with 60% of total crack length out of thickness. It is explained by the interaction between the two stress fields of each crack that activates additional fracture resisting mechanism in the neck region of the specimen preventing the whole sample from the failure.


CM02.03.18

Studies of Photo-Thermal Dual Curing Behaviors of Acrylate Monomers with FTIR and Photo-DSC

Hyuck Sik Wang, Seung Hyuk Lee, Seok Hyung Bu and Kigook Song; Kyung Hee University, Yongin-si, Korea (the Republic of).

The photo-curing behaviors of acrylate monomers capable of urethane thermal reaction were investigated using time-resolved FTIR spectroscopy and photo-DSC (Differential Scanning Calorimetry). Faster photo-reaction and lower conversion of acrylate reactions were observed in the thermal-photo dual curing process compared to the photo-curing only process. In the case of the acrylate system with long chain oligomers, faster photo-reaction was also observed in the dual curing process although no difference was found in the degree of conversion of acrylates between two photo-curing processes. The photo-curing process of three acrylate monomers was investigated using ATR-FTIR spectroscopy with a deuterated acrylate compound. In the free-radical terpolymerization, the conversion of three acrylate monomers into terpolymer as a function of time was monitored by observing the characteristic FTIR peaks of each component. In order to identify the acrylate components involved in the free-radical terpolymerization, careful peak assignments were made for the acrylate terpolymer such that characteristic FTIR bands from different monomers chosen for quantitative analysis should not overlap with one...
Carbon dots (C-dots) are a class of low-dimensional carbon-based particles which exhibit a signature photoluminescence (PL) consisting of a red-shifted emission when irradiated with UV-visible light. This photoluminescence (PL) has been explained as either the effects of quantum confinement, or of energy traps on the particle surface. Several groups have reported the synthesis of C-dots directly from the thermal treatment of aqueous solutions of simple sugars (e.g., glucose, sucrose) either in a conventional autoclave or in a microwave oven. These studies have looked exclusively a preparation from low concentration (less than 10 wt% sugar) solutions reacted at rather high temperatures (between 160 to 200 °C). We report the synthesis of fluorescent carbon particles produced from viscous glucose solutions of a much higher concentration heated at much lower temperatures. Analysis by photon correlation spectroscopy (PCS) reveals the particles form immediately with a size (approximately 300 nm) that is nearly 100 times larger than the precursor clusters of sugar but which decrease slightly in size with additional heating. Despite their larger size, PL shows emission similar to that of smaller C-dots but with clear indications of fine structure suggesting a set of discrete surface energy levels likely associated with different functional groups attached to the particle's surface.

References:

Crystallization is a key issue in understanding glass and plays a fundamental role in the development of advanced glass-ceramics. In the absence of catalytic agents, most supercooled liquids crystallize heterogeneously from the external surfaces of a few initial nuclei and slowly crystallize homogeneously in the interior. It is essential to follow the formation of the first nuclei. Is the whole local structure around the cations modified well before crystallization is completed? The precise role of nucleating agents in glass-ceramic formation will likely only be understood by investigating the very first stages of crystallization with a strictly local structural probe having atomic selectivity. The X-ray Absorption Fine Structure (XAFS) technique is quite appropriate to characterize the local structure of specific cations present in glassy samples from the earliest stage of crystal nucleation. In this work, partially crystallized and fully crystallized samples were obtained after treatment at temperatures and times defined in previous studies. The XANES and EXAFS spectra of selected cations ions in the BaO-SiO₂, Ba₂Ti₃O₉, CaMgSi₂O₆ − 9 mol% Fe₂O₃, MgO-SiO₂, NaO-2CaO-3SiO₂ and 2NaO-1CaO-3SiO₂ glassy systems were collected at room temperature by using the transmission and total electron yield modes. A preliminary analysis of the data indeed showed modifications in the local order around some cations as the time of crystallization increased. The results will be fully discussed.

CM02.03.23
Shear Band Nucleation and Propagation in Metallic Glass Matrix Composites Jonathan Gentile1, Douglas Stauffer2 and Jason R. Trelewicz1; 1Stony Brook University, Stony Brook, New York, United States; 2Bruker Nano, Minneapolis, Minnesota, United States.

Metallic glass matrix (MGM) composites combine high-strength amorphous metals with ductile crystalline inclusions to overcome the inherent brittleness of metallic glasses. While the crystalline heterogeneities have been shown to influence the process of shear localization, the underlying mechanisms are not well understood especially since they seemingly operate at disparate length scales. To explore the role of crystalline inclusions in the process of strain delocalization, we employ instrumented nanoindentation, which is particularly suited to study the deformation physics of these composite materials due to its ability to detect individual shear band propagation events and its precise control over plastic zone size. Using nanoindentation, we focus on elucidating three specific phenomena including the onset of plasticity through the formation of shear bands, the propensity for shear localization and its dependence on indentation strain rate, and the nature of shear band propagation. In this presentation, we describe instrumented Hertzian contact experiments that provide additional evidence for enhanced shear band nucleation as the shear band trajectory evolves with indentation depth to encompass the crystalline phase. Additionally, by measuring the fraction of discrete plastic events deriving from shear band plasticity during loading, we outline a transition from discrete to continuous deformation with increasing indentation strain rate, which is consistent with the behavior of monolithic metallic glasses. Through comparison of the propensity for shear localization with microstructural length scales of the MGM composites, we show that the presence of amorphous-crystalline interfaces simultaneously limit shear band propagation and promote a more homogeneous response through the partitioning of shear strain to the crystalline phase.

CM02.03.24
Revealing β-Relaxation Mechanism Based on Energy Distribution of Flow Units in Metallic Glass Zhen Lu1, Wei Hua Wang2 and Hai Yang Bai1; 1Mathematics for Advanced Materials Open Innovation Laboratory (MathAM-OIL), Sendai, Japan; 2Institute of Physics, Beijing, China.

The β-relaxation, which is the source of the dynamics in glass state and has practical significance to relaxation and mechanical properties of glasses, has been an open question for decades. Here, we performed stress relaxation experiments under isothermal and linear heating modes and molecular dynamics simulations to investigate the different β-relaxation behaviors of various metallic glasses and the correlation between β-relaxation and flow units based on the activation energy distribution of flow units. We show that the β-relaxation originates from the flow units in metallic glasses, and the activation energy distribution of flow units modulates the β-relaxation modes such as excess wing, shoulder and peak in their dynamic spectra. A clear picture on the structural origin of β-relaxation and the correlation between activation energy distribution of flow units and β-relaxation behaviors in metallic glasses is proposed, which might be helpful to understand the nature of glasses and glass dynamics.

CM02.03.25
Diffusion and Avalanches in a Mesoscopic Model of Amorphous Plasticity Botond Tyukodi1, 2, Kareem Khirallah1, Damien Vandembroucq2 and Craig E. Maloney2; 1Northeastern University, Boston, Massachusetts, United States; 2PMMH, ESPCI, Paris, France.

Plastic deformation of amorphous materials around the yielding point shows critical properties such as avalanches, diverging correlation lengths and finite size effects. While this criticality is captured by various models, there is less consensus regarding the degree at which critical exponents are robust to the details of the particular system. Here we focus on the robustness of fluctuations in these properties to the main ingredients of amorphous plasticity: elastic interactions and structural disorder. We find that, at short times, neither the details of the elastic interaction kernel, nor the type of the disorder are important when it comes to the critical properties. We find a short term diffusive behavior in our model and the associated diffusion coefficient shows the same finite size scaling as previous particle simulations. We connect the scaling of the diffusion coefficient to the scaling of avalanche sizes and the correlation between β-relaxation and flow units based on the activation energy distribution of flow units. We show that the β-relaxation originates from the flow units in metallic glasses, and the activation energy distribution of flow units modulates the β-relaxation modes such as excess wing, shoulder and peak in their dynamic spectra. A clear picture on the structural origin of β-relaxation and the correlation between activation energy distribution of flow units and β-relaxation behaviors in metallic glasses is proposed, which might be helpful to understand the nature of glasses and glass dynamics.

CM02.03.26
Atomistic Simulation of Nearly Defect-Free Models of Amorphous Silicon—An Information-Based Hybrid Approach Dil K. Limbu1, Raymond Atta-Fynn2 and Parthapratim Biswas3; 1Department of Physics and Astronomy, The University of Southern Mississippi, Hattiesburg, Mississippi, United States; 2Department of Physics, The University of Arizona at Tucson, Arizona, Arizona, United States.

We present an information-based total-energy optimization method to produce nearly defect-free structural models of amorphous silicon. Using geometrical, structural and topological information from tetrahedral networks, we have shown that it is possible to generate structural configurations of amorphous silicon, which are superior to the models obtained from conventional reverse Monte Carlo methods involving structural constraints and total-energy optimization. The new static (i.e. relaxation-based) approach presented here is capable of producing atomistic models with structural properties which are on a par with those obtained from the modified Wooten-Winer-Weaire (WWW) models of amorphous silicon. Structural, electronic, and vibrational properties of the hybrid models are compared with the best dynamical models obtained from using machine-intelligence-based algorithms and efficient molecular-dynamics simulations, reported in the recent literature. We have shown that, together with the WWW models, our hybrid models represent one of the best static models so far produced by total-energy-based Monte Carlo methods in conjunction with experimental diffraction data of amorphous silicon.

CM02.03.27
Metastable Hydrogenated Amorphous Silicon (a-Si:H) as Reversible Programmable Photonic Material Mahir A. Mohammed1, 2, Ripalta Stabile1, 3, Jimmy Melskens2, 3, Wilhelms (Erwin) Kessels1, 4 and Oded Raz2, 3; 1Electrical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands; 2Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 3Institute for Photonic Integration, Eindhoven University of Technology, Eindhoven, Netherlands.
Hydrogenated amorphous silicon (a-Si:H) is known to exhibit light-induced metastable properties that are reversible upon annealing. Although these metastable properties suggest the existence of reversible optical properties of a-Si:H as well, very little is known about this effect. If indeed properly identified and characterized, such reversible optical properties may find application in the reversible programmable photonic integrated circuits (PICs) that can enable multiple functionalities on the same chip, similar to field-programmable gate arrays (FPGAs). However, the required reversible effective refractive index change due to light soaking and annealing has not been reported yet nor has it been thoroughly investigated. Therefore, the effects of prolonged high intensity light soaking and annealing on a-Si:H on the near infrared (NIR) optical properties are studied in this work. A thin-film interferometric technique was developed to detect minute changes probed using a NIR laser source (1465-1575 nm). Using this approach, an increase in refractive index resulted in a reduced value of the sharp reflection minimum and a blue shift for the decrease in refractive index. To detect the changes in optical properties more precisely, double-layered thin films were used: a-Si:H was deposited by inductively coupled plasma-enhanced chemical vapour deposition (ICP-PECVD) on SiO2, which was in turn deposited by PECVD on a crystalline silicon substrate. The a-Si:H deposition temperature was set to 80 °C and 300 °C, such that significantly different structural properties, e.g. hydrogen content and density, could be achieved. An irreversible blue shift was observed during the first cycle of annealing and light soaking after the deposition. However, from the second cycle onwards, a red shift of the spectrum due to light soaking, i.e. reversal of the annealed state was observed. It appeared that the initial irreversible changes are inevitable and only after these changes reversibility is observable. The reversibility was sustained after further cycles of annealing and light soaking. The reversibility appears for both a-Si:H deposited at 80 °C and 300 °C. However, the magnitude of the reversibility for a-Si:H deposited at 80 °C is significantly larger when compared to a-Si:H deposited at 300 °C. This suggests a correlation of the metastable properties of a-Si:H on the hydrogen content and density of the material, i.e. porous films (deposited at 80 °C) are more susceptible to light-induced change than dense films (deposited at 300 °C). The magnitude of the reversibility in refractive index for a-Si:H deposited at 80 °C is estimated to be around 0.03%. Although small, this metastable state could be sufficient for an application in reversible programmable optical switch. These results therefore indicate that a-Si:H has potential in enabling reversible programmable PICs and work to implement this material in a photonic device is currently ongoing.

**CM02.03.28**

**Ag’ Ion Emission from Sharp-Edged Ag’ Ion Conducting Glasses and Two Emission Mechanisms**

Yusuke Daiko, Hiroki Mori, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.

Ion implantation is an effective method for surface modification of materials, and that has been used in various fields such as the semiconductor and metal industries, and bio-technology. In general, a discharged plasma (gas) or liquid (e.g., liquid Ga for a focused ion beam) is used as the ion source so far. However, in these cases, side reactions such as generation of radicals or various ions with different mass, e.g. in the case of H’ emission, H2’ and H3’ etc. are also generated) are unavoidable. Also, ion accelerators are huge and expensive. On the other hand, ion emissions from high ion conductors such as alkali-lead electrolytes have also been investigated because in a good solid electrolyte the mobile ions can move almost as freely as those in a liquid. The emission of O’ ions from O’-ion-conducting yttria-stabilized zirconia (YSZ) was first reported in 1997. Similarly, continuous Ag’ ion emissions for a few days were reported using Ag’-ion-conducting (AgI)0.5(AgPO3)0.5 or RbAg4I5, for AgI-7AgClO4(C12A7) pellets. However, side recombination (generation of radicals or various ions with different mass, e.g. in the case of H’ emission, H2’ and H3’ etc. are also generated) are unavoidable. Also, ion accelerators are huge and expensive.

We have studied ion emissions from various types of ion-conducting glasses [1-3]. One advantage of utilizing glass is its formability for tip sharpening because the electric field strength is proportional to the inverse of the curvature radius of the tip. Here we report Ag’ ion emission from a sharpened Ag’ ion conducting glasses. An aluminum phosphosilicate glasses Ag2O-Al2O3-P2O5-SiO2 show Ag’ ion conductivity of 3×10−5 S/cm at 300 °C, and an ionic current of Ag’ ion emission was successfully observed at 300 °C and 1×10−5 Pa. A good linear correlation is obtained between the log(current) and voltage. At the source of the acceleration voltage, the current of Ag’ ion changes from Ag’ ion to Ag’ ion is eliminated by Schottky model similar to a thermionic emission source.

The relationship between the emission current and voltage is expressed by a space-charge limited current model, in which the current is proportional to the inverse of the curvature radius of the tip. Here we report Ag’ ion emission from a sharpened Ag’ ion conducting glasses. An aluminum phosphosilicate glasses Ag2O-Al2O3-P2O5-SiO2 show Ag’ ion conductivity of 3×10−5 S/cm at 300 °C, and an ionic current of Ag’ ion emission was successfully observed at 300 °C and 1×10−5 Pa. A good linear correlation is obtained between the log(current) and voltage. At the source of the acceleration voltage, the current of Ag’ ion changes from Ag’ ion to Ag’ ion is eliminated by Schottky model similar to a thermionic emission source.

**CM02.03.29**

**Enhancement of Creep Deformation Induced via Proton Implantation for Phosphate Glasses Monitored Utilizing an Electrochemical Indenter Yusuke Daiko, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.**

Intermediate temperature fuel cells (IT-FCs) operating around 400-500 °C have attracted much attention as next-generation energy source owing to their high conversion efficiency and low fabrication cost. Our group successfully prepared a fast proton conducting phosphosilicate glass using conventional melting method, and we confirmed fuel cell operation using H2 and O2 at the intermediate temperature (~5 mW/cm2) [1,2]. Similar to typical oxide glasses, intermediate temperature fuel cells (IT-FCs) operating around 400-500 °C have attracted much attention as next-generation energy source owing to their high conversion efficiency and low fabrication cost. Our group successfully prepared a fast proton conducting phosphosilicate glass using conventional melting method, and we confirmed fuel cell operation using H2 and O2 at the intermediate temperature (~5 mW/cm2) [1,2].

Hydrogenated amorphous silicon (a-Si:H) is known to exhibit light-induced metastable properties that are reversible upon annealing. Although these metastable properties suggest the existence of reversible optical properties of a-Si:H as well, very little is known about this effect. If indeed properly identified and characterized, such reversible optical properties may find application in the reversible programmable photonic integrated circuits (PICs) that can enable multiple functionalities on the same chip, similar to field-programmable gate arrays (FPGAs). However, the required reversible effective refractive index change due to light soaking and annealing has not been reported yet nor has it been thoroughly investigated. Therefore, the effects of prolonged high intensity light soaking and annealing on a-Si:H on the near infrared (NIR) optical properties are studied in this work. A thin-film interferometric technique was developed to detect minute changes probed using a NIR laser source (1465-1575 nm). Using this approach, an increase in refractive index resulted in a reduced value of the sharp reflection minimum and a blue shift for the decrease in refractive index. To detect the changes in optical properties more precisely, double-layered thin films were used: a-Si:H was deposited by inductively coupled plasma-enhanced chemical vapour deposition (ICP-PECVD) on SiO2, which was in turn deposited by PECVD on a crystalline silicon substrate. The a-Si:H deposition temperature was set to 80 °C and 300 °C, such that significantly different structural properties, e.g. hydrogen content and density, could be achieved. An irreversible blue shift was observed during the first cycle of annealing and light soaking after the deposition. However, from the second cycle onwards, a red shift of the spectrum due to light soaking, i.e. reversal of the annealed state was observed. It appeared that the initial irreversible changes are inevitable and only after these changes reversibility is observable. The reversibility was sustained after further cycles of annealing and light soaking. The reversibility appears for both a-Si:H deposited at 80 °C and 300 °C. However, the magnitude of the reversibility for a-Si:H deposited at 80 °C is significantly larger when compared to a-Si:H deposited at 300 °C. This suggests a correlation of the metastable properties of a-Si:H on the hydrogen content and density of the material, i.e. porous films (deposited at 80 °C) are more susceptible to light-induced change than dense films (deposited at 300 °C). The magnitude of the reversibility in refractive index for a-Si:H deposited at 80 °C is estimated to be around 0.03%. Although small, this metastable state could be sufficient for an application in reversible programmable optical switch. These results therefore indicate that a-Si:H has potential in enabling reversible programmable PICs and work to implement this material in a photonic device is currently ongoing.

Intermediate temperature fuel cells (IT-FCs) operating around 400-500 °C have attracted much attention as next-generation energy source owing to their high conversion efficiency and low fabrication cost. Our group successfully prepared a fast proton conducting phosphosilicate glass using conventional melting method, and we confirmed fuel cell operation using H2 and O2 at the intermediate temperature (~5 mW/cm2) [1,2]. Similar to typical oxide glasses, our glass has quite few H’ (OH groups) just after quenching the melt. However, based on originally developed in-situ FTIR measurement, we found a proton implantation into the phosphosilicate glass occurs under fuel cell operating condition [3]. We anticipated such proton implantation affects mechanical properties of the glass. In this study, creep behavior of proton conducting glass in fuel cell atmosphere is reported.

A new electrochemical indentation apparatus was developed, in which we can control measuring conditions including atmosphere (H2, N2, air and relative humidity), temperature, and electrical field. A spherical Inconel 625 indenter was used as an electrode simultaneously, and we evaluated in-situ creep behavior under the proton implantation. Proton conducting glass was prepared by conventional melting method with composition of 7.5Na2O-7.5K2O-35P2O5-50SiO2 (mol%). After polishing the glass with ~1 mm thickness, Pt ring-electrode was sputtered on a side of the glass plate. Atmosphere was controlled by flowing a humidified H2/gas (4%H2-96% Ar), heating up to 200 °C, and applying DC 5 V between the Pt ring and Inconel electrodes. This condition is similar to the anode reaction of fuel cell (H2 -> 2H++ 2e-), and proton implantation occurs. We conducted an indentation creep experiment under the reaction. We also carried out same experiments in N2 atmosphere as comparison. Humidity effects were also investigated using humid gas (relative humidity ~1%)

The phosphosilicate glass showed typical creep behavior in N2 atmosphere at 200 °C. Interestingly, the creep displacement increases remarkably in H2 atmosphere, and we obtained a longer relaxation time for creep in H2 atmosphere compared with that in N2. These results suggest that proton implantation affects significantly for mechanical properties of glass. Results including Raman spectroscopy will be shown and discussed at the presentation.

Polymer resins are used for numerous applications, for example as matrix materials for high performance fiber-reinforced composites. Such structures operate in humid air and liquid water, which may cause swelling and degradation of the material. Because of imperfections in the chain structure such as chain ends, glassy polymer contain molecular sized voids called “free volume”. In addition, macroscopically sized voids are commonly found in polymers. When polymers absorb water, differential scanning calorimetry (DSC) studies have shown that the absorbed water may be classified as free water and bound water. Free water exist when the water molecules occupy free volume and voids. Bound water state exists when the water molecules interact with the polymer chains and form hydrogen bond. In order to examine the influence of voids on water uptake, and the state of water in epoxy, foaming agents were utilized to produce a controllable amount of voids (void contents from 0 to about 50%).

Epoxy specimens containing voids and void-free were prepared. Water uptake experiments were conducted by immersing specimens with and without voids in distilled water at 40 °C. The moisture content was monitored by gravimetric measurements. To examine the state of absorbed water, DSC analysis of dry and water saturated epoxy specimens without and with voids was conducted over a temperature range from -80 °C to room temperature. DSC data was recorded during both the cooling and heating cycles. The state of water absorbed was determined based on analysis of the appropriate transitions recorded.

The free and bound water phase transitions were absent in the dry void-free specimen. In the water saturated void-free specimen, most the moisture absorbed was non-freezable water. In the water saturated medium and high void content specimens, peaks attributed to free and bound water were observed. The contents of free and bound water were estimated from the exothermic peaks in the DSC curves. The bound water peak was much smaller than the free water peak, and decreased with increasing the void content. The area under the free water peak increased with increasing void content.
The effect of surface disorder, load, and velocity on friction between a single asperity contact and a model surface is explored with one-dimensional and two-dimensional Prandtl-Tomlinson (PT) models [1]. We show that there are fundamental physical differences between the predictions of one-dimensional and two-dimensional models. The one-dimensional model estimates a monotonic increase in friction and energy dissipation with load, velocity, and surface disorder. However, two-dimensional PT model, which is expected to approximate a tip-sample system more realistically, reveals a non-monotonic trend, i.e., friction is inert to surface disorder and roughness in wearless friction regime. The two-dimensional model discloses that the surface disorder starts to dominate the friction and energy dissipation when the tip and the sample interact predominantly deep into the repulsive regime. Our numerical calculations address that tracking the minimum energy path and the slip-stick motion are two competing effects that determine the load, velocity, and surface disorder dependence of friction. In two-dimensional model, the single asperity can follow the minimum energy path in wearless regime; however, with increasing load and sliding velocity, the slip-stick movement dominates the dynamic motion and results in an increase in friction by impeding tracing the minimum energy path. Contrary to two-dimensional model, when one-dimensional PT model is employed, the single asperity cannot escape to minimum energy minimum due to constraint motion and reveals only a trivial dependence of friction on load, velocity, and surface disorder. Our computational analyses clarify the physical differences between the predictions of one-dimensional and two-dimensional models and open new avenues for dispersed surfaces for low energy dissipation applications in wearless friction regime.


Infrared microspectroscopy is a powerful technique for obtaining unique chemical information from a variety of biological systems. In general, spatial resolutions are limited by the Abbe diffraction laws to \( \lambda / 2 \) (3-10 µm). In recent years, the development of the AFM-IR technique has allowed for overcoming these diffraction limitations by using an AFM probe as the detector for IR absorption. Using a quantum cascade IR laser (QCL), the molecular vibrations in a sample are excited, leading to thermal expansion of the surface, which is monitored using an AFM cantilever. This technique reduced the spatial resolution of < 10 nm, however, in certain cases this high resolution is not required and the size of an image in AFM-IR is limited by the piezo stage to sub 100 µm. A new technique has been developed that fills the gap between IR microspectroscopy and AFM-IR. This is an optical based technique that still beaks the diffraction limits associated with conventional IR microspectroscopy, and provides sub-micron spatial resolution. Taking advantage of the same fundamental principles that govern AFM-IR, the thermal expansion of a sample surface induced by a QCL IR laser is monitored using a visible probe laser, instead of an AFM probe. This unique technique provides transmission like IR spectra while operating in a reflective regime. The spatial resolution is limited by the diffraction limit of the visible probe laser, while also being independent of the IR wavelength used. This talk with focus on the use of optical based photothermal IR spectroscopy to characterize a variety of materials.

Non-Contact Sub-Micron Infrared Spectroscopy of Non-Crystalline Materials Using Visible Probe Detection Eoghan Dillon\(^1\), Craig Prater\(^1\) and Curtis Marcolt\(^2\); \(^1\)Photothermal Spectroscopy Corp, Santa Barbara, California, United States; \(^2\)Light Light Solutions, Athens, Georgia, United States.

Nanoscale characterization methods play a key role in the analysis, development and optimization of nanoscopic materials and devices. Often several characterization techniques are required to gain a comprehensive understanding of the various material properties of such complex functional materials. Here we introduce the combined analysis of complex nanoscale material systems by correlating infrared scattering-type Scanning Near-field Optical Microscopy (s-SNOM) [1] and nanoscale Fourier Transform Infrared (nano-FTIR) spectroscopy [2] with information obtained by other Scanning Probe Microscopy (SPM) based techniques. For example, the material-characteristic nano-FTIR absorption spectra of a phase-separated PS/LDPE polymer blend identifies sharp material interfaces between the two materials by measuring a line profile across a ca. 1 µm sized LDPE island inside the PS matrix. Near-field reflection/absorption imaging at 1500 cm\(^{-1}\) of the only 50 nm thin film allows to selectively highlight the distribution of PS in the blend, while selective atomic force microscopy (AFM) modes simultaneously map the mechanical properties like adhesion of the different materials [3,4]. Further, results will be presented that correlate the nanoscale near-field optical response of semiconducting samples like graphene (2D) or functional SRAM devices (3D) in different frequency ranges (mid-IR & THz) to Kelvin Probe Force Microscopy (KPFM) and Electrostatic Force Microscopy (EFM) measurements.

Nanoscale characterization methods play a key role in the analysis, development and optimization of nanoscopic materials and devices. Often several characterization techniques are required to gain a comprehensive understanding of the various material properties of such complex functional materials. Here we introduce the combined analysis of complex nanoscale material systems by correlating infrared scattering-type Scanning Near-field Optical Microscopy (s-SNOM) [1] and nanoscale Fourier Transform Infrared (nano-FTIR) spectroscopy [2] with information obtained by other Scanning Probe Microscopy (SPM) based techniques. For example, the material-characteristic nano-FTIR absorption spectra of a phase-separated PS/LDPE polymer blend identifies sharp material interfaces between the two materials by measuring a line profile across a ca. 1 µm sized LDPE island inside the PS matrix. Near-field reflection/absorption imaging at 1500 cm\(^{-1}\) of the only 50 nm thin film allows to selectively highlight the distribution of PS in the blend, while selective atomic force microscopy (AFM) modes simultaneously map the mechanical properties like adhesion of the different materials [3,4]. Further, results will be presented that correlate the nanoscale near-field optical response of semiconducting samples like graphene (2D) or functional SRAM devices (3D) in different frequency ranges (mid-IR & THz) to Kelvin Probe Force Microscopy (KPFM) and Electrostatic Force Microscopy (EFM) measurements.

Our goal is to demonstrate novel approaches to extend the performance limits of organic and/or inorganic composites to high-temperature applications of oil and gas applications. Conventional composite technology has fulfilled increasing materials property requirements by using expensive high-end performance polymers and fillers. Our goal is to demonstrate novel approaches to extend the performance limits of organic and/or inorganic composites to high-temperature applications of up to 400°F, without relying on costly high-end raw materials. Commercial low-cost materials were used to develop high-strength performance composites by extensive application of advanced processing techniques. In addition, we studied the potential applications of developed composites for downhole completions applications through prototype testing.
Material properties were assessed within the 300 to 400°F temperature range by using a compressive strength test, Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). Furthermore, test specimens doped in water and/or downhole fluids to evaluate the effect of prolonged exposure to downhole conditions on mechanical properties. Implementation of out-of-the-box approaches enabled development of low-cost, high-performance systems capable of achieving compressive strengths over 20 ksi at temperatures over 300°F. In-depth processing optimization enabled further improved composite properties. The practical implications of the experiments enabled covering a large number of conventional and unconventional fillers for organic and/or inorganic matrices.

We demonstrated the development of high-strength organic and/or inorganic composites based on low-cost raw materials for high-temperature applications. This novel material-design approach was investigated with advanced material analysis techniques.

CM02.03.38
Moran Emuna1, Yaron Greenberg1, Eyal Yahel1 and Guy Makov; 1Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel; 2Physics, NRCN, Beer-Sheva, Israel.

We present a novel experimental design for high sensitivity measurements of the electrical resistance of samples at high pressures (0-6GPa) and high temperatures (0-1000K) in a “Paris-Edinburgh” type large volume press. Uniquely, the electrical measurements are carried out directly on a small sample, thus greatly increasing the sensitivity of the measurement. The sensitivity to even minor changes in electrical resistance can be used to clearly identify phase transitions in similar samples. Electrical resistance measurements are relatively simple and rapid to execute and the efficacy of the present experimental design is demonstrated by measuring the electrical resistance of Pb, Sn and Bi across a wide domain of temperature-pressure phase space and employing it to identify the loci of phase transitions. Based on these results, the phase diagrams of these elements are reconstructed to high accuracy and found to be in excellent agreement with previous studies. In particular, by mapping the locations of several well-studied reference points in the phase diagram of Sn and Bi, it is demonstrated that a standard calibration exists for the temperature and pressure, thus eliminating the need for direct or indirect temperature and pressure measurements. The present technique will allow simple and accurate mapping of phase diagrams under extreme conditions and may be of particular importance in advancing studies of liquid state anomalies.

CM02.03.39
Structure, Curing Dynamics and Performance of Phthalonitrile Resins
Boris Dyatkin1, Stephen M. Deese1, Tristan Butler1, Naresh C. Osti2, Madhusudan Tyagi1 and Matthew Laskoski; 1Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

High-temperature polymer matrix composites (PMCs) allow great control over various intrinsic properties (e.g. oxidative stability, mechanical toughness, thermal conductivity, etc.) that tailor these lightweights for numerous emerging applications. Despite many available formulations, conventional epoxy and phenolics, which form the matrix backbones of most thermoset composites, require high processing temperatures and cannot adequately withstand fire damage or high temperatures. Our efforts have recently yielded several types of thermosetting polymer resins called phthalonitriles, which are synthesized via a two-step, one-pot nucleophilic displacement reaction between dihaloaromatic compounds and bisphenol, followed by end-capping with 4-nitrophthalonitrile. Several backbone structure variables are available for this resin system, and all of them offer low gelation (150 °C) and final curing temperatures (350 °C). In addition to low processing costs, the resulting thermostats offer high strength and exceptional fire resistance (up to 700 °C). However, existing research efforts have not adequately described the curing process and associated monomer dynamics for these resins; nor have they correlated them with structures and performance of resulting composites. Given that the backbone chemistry of each resin system significantly influences cross-linking and material properties, this information is essential to further optimize materials processing of high-performance phthalonitrile-based PMCs.

We have correlated the microscopic dynamics of three different phthalonitrile resin monomers during different thermal conditions with the morphologies, chemistry, and properties of resulting thermostats. The systems used a resorcilon backbone, a bisphenol A (PEEK-like) backbone, and a reserveratrol backbone. We measured the temperature-dependent monomer dynamics by conducting quasi-elastic neutron scattering measurements of each resin at room temperature, at 135 °C (at the Tg), during the gelation transition, and at 257 °C (fully cured systems), and correlated the extracted mobility and diffusion transformations with rheometry-derived viscosity changes to fundamentally probe the curing process of each system. In turn, these insights provide a proper explanation of the resulting morphology and, in turn, the oxidative stability and tensile strength of each resin system. Our efforts have established greater processing controls over high-performance phthalonitrile thermostats and facilitated their implementation in fiber-reinforced composites, flame-retardant panels, and lightweight airframes.

CM02.03.40
Porous-Carbon Nanotube Aerogels for Ultrafast Charging Supercapacitors and Potassium-Ion Batteries
Wenqi Zhao1, 1, Yibin Li2 and Anyuan Cao1; 1Peking University, Beijing, China; 2Harbin Institute of Technology, Harbin, China.

Energy storage systems with ultrafast charging properties have become a hot topic in recent years along with the increased life rhythm. Supercapacitors are energy storage systems capable of fast charging and discharging, thus generating superior power density. Potassium ion batteries (PIBs) possess a series of advantages as the next generation energy storage systems, such as low cost, large reserves compared to lithium, and high energy density. Porous carbon with high surface area and tunable pore size represents a promising candidate to construct ultrafast supercapacitors; so far most of porous carbon-based electrodes can only be charged to a moderate current density (100-200 A/g), also with significant capacitance loss at increasing rate. Here, we show that a three-dimensional (3D) aerogel consisting of interconnected 1D porous-carbon nanotubes (PCNs) could serve as a freestanding supercapacitor electrode with excellent rate performance (62% retention at 1000 A/g) and high power density (265 kW/kg). The aerogel is formed through a combination of nitric acid doping and controlled air-etching processes. Mechanism study reveals favorable kinetics including a low and linear IR drop, about 85% contribution from electrical double layer capacitance, a very small time constant (0.057 s) and a metallic feature of 1D PCNs by theoretical calculation. The development of rechargeable batteries using potassium ions has recently attracted considerable attention. Here, we chose carbon nanotube (CNT) sponges as scaffolds to load nitrogen doped porous carbon (NDPC) and form hierarchical structures. The obtained 3D CNT/NDPC sponges can work as freestanding electrodes with significantly increased potassium storage capacity and compressive properties. The hybrid sponges achieve high capacity of 420 mAh/g as PIB electrodes, excellent rate capability and stable cyclic performance.

In conclusion, we demonstrated controlled fabrication of 3D freestanding porous electrode materials with ultrafast charging properties in supercapacitors and PIBs. Our pore-creation method, by combining HNO3-doping and air-etching processes, could be extended to other N-containing precursors to fabricate various porous-carbon structures with tunable hierarchical pores. The highly porous 1D nanotube structure has the potential to develop microelectronic and power-supply devices that require fast charging/discharging capability (e.g. within 0.1 seconds).

References
Wenqi Zhao, Hui Zhang, Jie Liu, Lu Xu, Huaiheng Wu, Mingchu Zou, Qian Wang, Xiaodong He, Yibin Li, Anyuan Cao. Controlled air-etching synthesis

Wenqi Zhao, Anyuan Cao, Yibin Li. Carbon nanotube/nitrogen doped porous carbon sponges with high performance for potassium ion batteries. Prepared.

CM02.03.41
Mechanically Strong and Thermally Conductive Ultra-High Molecular Weight Polyethylene Sheets Shengqiang Ren; University at Buffalo, The State University of New York, Amherst, New York, United States.

Ultra-high molecular weight polyethylene (UHMWPE) is of great interest as a next-generation body armor material due to its superior mechanical properties. However, such unique properties depend critically on its microscopic structure characteristics, including the degree of crystallinity, chain alignment and morphology. Here we present a highly aligned UHMWPE and of its composite sheets containing uniformly dispersed boron nitride (BN) nanosheets. The dispersion of BN nanosheets into the UHMWPE matrix increases its mechanical properties over a broad temperature range. Experiments and simulation confirm that the alignment of chain segments in the composite matrix increases with temperature, leading to an improvement in mechanical properties at high temperature. Together with the large thermal conductivity of UHMWPE and BN, our findings serve in expanding the application spectrum of highly aligned polymer nanocomposite materials for ballistic panels and body armor over a broad range of temperatures.

CM02.03.42
Microcellular Materials with Stress-Activated Pores Exhibiting Opto-Mechanical Properties Bilal Abdul Halim, Sheikh Rasel, Reza Rizvi, Navid Namdari and Eranan Hossain; Polymer and Inorganic Composites, Structures and Surfaces Lab, Toledo, Ohio, United States.

Microcellular (1-30µm) and Nanocellular (<1µm) polymers have significantly lower densities relative to the base polymer resulting in improved specific mechanical properties as well as increased impact absorption and thermal insulation. Batch micro- and nano-cellular processes are generally well suited for low volume lab-based studies. The gas sorption within the polymer system tends to swell the polymer, resulting in increased free volume, higher chain mobility and a depressed glass transition temperature (Tg). These porous polymers acquire a static porosity, not quite as applicable or interesting as those with a dynamic porosity. Such a characteristic enables the polymer to mimic several stimuli activated porous systems found in nature, which exist at all length scales. For instance, the regulation of what enters and exits the cell (including oxygen, carbon dioxide, and other molecules and ions) cannot transpire if the cell membrane wasn’t permeable (porous). Another example is the ability of the cuttlefish to use its cuttlebone, which is not exactly a bone, but a calcium carbonate like material that is almost 90% porous. Disjoined from the fish, the cuttlebone floats on water, however, the cuttlefish is able to control the flow of water in and out of the cuttlebone which helps with its buoyancy and structure. Synthetic attempts at systems with dynamic porosity have focused mainly at the molecular-scale and nano-scale. No proven examples of dynamic porosity exist at the micron-scale. This study introduces a fundamental examination of foams composed of the triblock copolymer styrene-ethylene-butylene-styrene (SEBS) which was prepared using batch foaming, where the polymer is put in a pressure chamber using CO2 as the blowing agent, and were then quenched at different temperatures (30°C, 50°C, 70°C, 90°C). These foams exhibit pores that shrink under stress and remain stable with an internal vacuum. Now, the reduced pore size fails to act as a light-scattering site, turning the polymer transparent and recovering back to an almost neat SEBS film. Different characterization techniques were done on foams before and after applying stress, using Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD). The opaque to transparent transition (OTT) was studied using an in-situ optomechanical setup comprised of an LED and a photoreistor while under a dynamic load using a universal testing machine. Each foam at different quenching temperature undergoes OTT at different loads and remains transparent. However, collapsed pores can be re-foamed which was demonstrated through saturating the almost-recovered SEBS for many cycles whilst under getting density measurements and electron microscopy images at each cycle. This behavior can be instrumental in making pressure sensitive films.

CM02.03.43
Unraveling the Solution-State Supramolecular Structures of Donor-Acceptor Polymers and Their Influence on Solid-State Morphology and Charge-Transport Properties Yiqing Zheng1, Jian Pei1, Jie-Yu Wang1 and Lin Zou2; 1Peking University, Beijing, China; 2Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, China.

Polymer self-assembly in solution prior to film fabrication makes solution-state structures critical for their solid-state packing and optoelectronic properties. However, unraveling the solution-state supramolecular structures is challenging, not to mention establishing a clear relationship between the solution-state structure and the charge-transport properties in field-effect transistors. Here, for the first time, it is revealed that the thin-film morphology of a conjugated polymer inherits the features of its solution-state supramolecular structures. A “solution-state supramolecular structure control” strategy is proposed to increase the electron mobility of a benzodifurandione-based oligo(phenylene vinylene) (BDOPV)-based polymer. It is shown that the solution-state structures of the BDOPV-based conjugated polymer can be tuned such that it forms a 1D rod-like structure in good solvent and a 2D lamellar structure in poor solvent. By tuning the solution-state structure, films with high crystallinity and good interdomain connectivity are obtained. The electron mobility significantly increases from the original value of 1.8 to 3.2 cm2 V−1 s−1. This work demonstrates that “solution-state supramolecular structure” control is critical for understanding and optimization of the thin-film morphology and charge-transport properties of conjugated polymers.

CM02.03.44
Toughening PDMS Through Entanglements Deborah Ehrlich, Junpeng Wang and Jeremiah Johnson; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

There is a need for tough PDMS that maintains its optical clarity and high temperature resistance. Fillers increase the modulus, toughness, and tear resistance of PDMS, but diminish optical clarity. Entanglements can be used to improve the mechanical properties of PDMS, without impacting desirable properties. By enhancing entanglements, we can further increase the modulus, toughness, and tear resistance of PDMS elastomers while maintaining optical clarity and high temperature resistance. Here we discuss our efforts to synthesize novel PDMS network architectures with entanglement promoted toughness.

CM02.03.45
Combining Raman Spectroscopy with Rheology to Correlate Physical and Chemical Properties of Polymers Richard A. Larsen1, Frederik Fleissner2, Boris Wezsiha3, Georg Krem2 and Katharina Napp4; 1Anton Paar, Ashland, Virginia, United States; 2Anton Paar OptoTec, Seelze-Lettlert, Germany; 3Anton Paar GmbH, Graz, Austria.

During chemical reactions such as polymerization, the physical as well as chemical properties of a material change. While the viscoelastic properties usually can be characterized with a rheometer, no chemical information is obtained by the mechanical testing. The interpretation of rheometric results often relies on empirical models and a more phenomenological approach. For directly relating the changes in rheological behavior to chemical changes, Raman spectroscopy is employed in-situ with rheology. Raman is a spectroscopic technique based on inelastic light scattering from the sample molecules. By measuring the presence and intensities of molecular vibrations, Raman spectroscopy provides information on the chemical composition and structure of the
The combination of both techniques enables the simultaneous correlation of the mechanical properties and the molecular structure to obtain a better understanding of the sample.

The Anton Paar MCRxx2 (Modular Compact Rheometer) series of rheometers can be easily combined with the Anton Paar Cora Raman spectrometers via an optical fiber probe. For the applications presented here, a high temperature probe with an extended working distance of 10 mm was used to obtain measurements through the lower measurement plate of the rheometer system. To demonstrate the possibilities of a combined Rheo-Raman system, we investigated resin hardening as well as the melting behavior of polyethylene. First, the hardening of an epoxy resin was monitored providing insight into the chemical and physical changes during the reaction. Specifically, the reaction induced changes in the flow characteristics over time were characterized. In the Raman spectrum, the chemical changes can be found in the decrease of vibrational bands belonging to the epoxy group of the reaction component. Secondly, the phase transition from the crystalline to amorphous state in HDPE (High Density Polyethylene) was monitored while the polymer was heated. This resulted in a higher viscosity as well as alteration of vibrational bands in the Raman spectrum reflecting the conversion from a crystalline to an amorphous structure.

Having both viscoelastic and spectroscopic information on a sample provides a more detailed characterization of the observed sample. As a result, sample behavior can be analyzed in all its facets for better quality control as well as optimizing the process properties of materials.

**CM02.03.46**

A Compressive-Sensing Pixelated Direct Detector for 4D-STEM

Benjamin Bammes, Robert Bilhorn and Robert Monteverde; Direct Electron, LP, San Diego, California, United States.

Use of a pixelated detector in scanning transmission electron microscopy (STEM) enables the simultaneous acquisition of both the conventional annular dark-field (ADF) signal and the coherent bright-field (BF) diffraction pattern at every probe position. By detecting the scattering angle of nearly all the primary electrons that interact with the specimen, this “4D-STEM” technique promises to provide much more information about the specimen than conventional STEM using only an ADF detector.

An acute challenge for acquisition of 4D-STEM data is the relatively slow speed of pixelated detectors for capturing the coherent BF signal. Slow acquisition of STEM data introduces deleterious artifacts from specimen drift and thus forces users to acquire a severely limited field-of-view—a significant problem for non-crystalline specimens.

One strategy to improve the speed of these detectors, is to reduce the number of pixels in the pixel array. However, this strategy prevents acquisition of the low- and medium-angle DF signal on the pixelated detector and it may also undersample the BF diffraction pattern and reduce its usefulness for differential phase contrast (DPC) or ptychography. This is especially problematic for complex specimens, such as specimens containing light atoms.

To address this challenge, we have implemented a new compressive-sensing readout mode—called Arbitrary Kernel Row Addressing (AKRA)—on our DE-16 direct detection camera. In AKRA readout mode, the user can specify any arbitrary combination of kernel rows from the detector to readout; all other kernel rows are skipped. By reading out fewer pixels, the detector framerate can be increased, enabling STEM imaging of a larger field-of-view. But since the “missing” pixels are scattering across the detector, the pixelated detector still captures a large area of the BF diffraction pattern and surrounding DF signal, with the “missing” pixels reconstructed using compressive-sensing algorithms. Therefore, AKRA enables fast 4D-STEM acquisition with a large pixelated detector so that rich structural information can be collected for large regions-of-interest of complex specimens.

**CM02.03.47**

Size-Dependent Properties of Nano-Crystalline Oxides

Siu-Wai Chan; Columbia University, New York, New York, United States.

A number of oxides, when prepared in nano-scale crystallites, exhibit a larger than bulk lattice parameter. A couple of these nano-oxides also show decreasing thermal expansion as well as stiffness constants as crystal-size goes beyond 10nm. We will discuss the physics and the materials science behind such an extraordinary behavior and the implications for solid-state chemistry and physics in nanoscale.

**CM02.03.48**

Fluorinated Polyurethane Resin with Fold Shape Structure and the Cavitation Erosion Resistance Performance

Haocheng Yang, Rongrong Chen, Jun Wang, Xuejie Guo and Kazunobu Takahashi; Materials Science and Engineering, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, China.

Cavitation erosion is a common mode of propeller surface damage, which seriously affects the hydrodynamic performance of propeller. In industrial applications, it is a surface treatment technology that effectively improve the cavitation erosion resistance performance by spraying elastomer organic coating on hydraulic components. Fluorinated polyurethane is a good elastomer which not only has excellent mechanical properties, but also has good ability of anti-biofouling. Herein, hydrophobic fluorinated polyurethanes (FPU), which combination of cavitation erosion resistance and biological fouling resistance coating were prepared by using the method of introducing fluorine with perfluoroalkyl ethanol (TEOH-10) for modification of isophorone diisocyanate (IPDI) and controlling the IPDI adding dosage and time. The chemical structure of FPU was investigated by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectrum (NMR) and gel permeation chromatography (GPC). The bonding strength between top coating and metal interlayer is significantly excellent(>4 MPa). Cavitation erosion tests were performed on Ultrasonic bubble generator for 10h. The mass loss of different cavitation time was examined by balance analysis. Surface morphology of the specimens was observed by Contour GTX and scanning electron microscope (SEM), respectively. Six-months marine field test in the Yellow Sea revealed that the FPU coatings exhibited excellent anti fouling/fouling release performance. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

**CM02.03.49**

Cryo-EM Characterization of Chalcogenide Glass Solution Structure

Nikita Dutta and Craig B. Arnold; Princeton University, Princeton, New Jersey, United States.

The unique optical properties of solution-processed chalcogenide glasses have long been of interest for photonic devices; a common test system is arsenic
The goal of this work is to progress the current understanding of structure-property relationships of amorphous carbons. This presentation will review some surface chemistry, and interfacial capacitance. It will better understand how growth parameters like dopant concentration, substrate etc. affect the electrode properties i.e. electrical conductivity, microstructure, wide potential window, mechanical strength, low-temperature deposition (<100 °C), tunable doping level and surface chemistry. Research is needed to better understand how growth parameters like dopant concentration, substrate etc. affect the electrode properties i.e. electrical conductivity, microstructure, surface chemistry, and interfacial capacitance.

The goal of this work is to progress the current understanding of structure-property relationships of amorphous carbons. This presentation will review some of the basic properties of these advanced carbons, investigated using Raman, X-ray reflectivity, AFM, XPS, and SEM. Structure and dynamics of interface between t-C:N and RTILs will be investigated using cyclic voltammetry and electrochemical impedance spectroscopy. RTILs are solvents composed entirely of ions. They have great potential to replace conventional organic solvent/electrolyte systems in energy storage devices because of their remarkable properties like wide electrochemical potential window (~4V), environmentally-benign characteristics (non-volatility, non-toxicity) and excellent thermal and electrochemical stability. To optimally harness the properties of t-C:N, and RTIL-based devices, a comprehensive fundamental understanding of their electrochemical behavior is critical.

Nitrogen incorporated tetrahedral amorphous carbon (t-C:Nx) is diamond-like carbon composed of a mixture of sp2 (graphite-like) and sp3-bonded carbon. It can be deposited at room temperature and makes a great electrode material because of its remarkable microstructural stability, high inertness, wide potential window, mechanical strength, low-temperature deposition (<100 °C), tunable doping level and surface chemistry. Research is needed to better understand how growth parameters like dopant concentration, substrate etc. affect the electrode properties i.e. electrical conductivity, microstructure, surface chemistry, and interfacial capacitance.

The fracture toughness of eight glasses was measured by the surface crack in flexure (SCF) and single-edged precracked beam (SEPB) methods. These include four soda lime silicas including a common plate glass form, two low iron modern forms, and one ancient Roman glass, a fused silica, a borosilicate crown (BK-7) optical glass, and two other borosilicate glasses for armor applications. The historical soda lime silica glass was made in an ancient Roman glass factory that operated in Palestine until 383 AD. This glass was exposed to the environment for almost sixteen centuries. The two SCF and SEPB methods have different susceptibilities to environmentally-assisted slow crack growth, that can be a major interference in measuring fracture toughness in ambient testing environments. A new definition for fracture toughness of glasses is proposed.

The fracture surface energy (γ) and the fracture toughness (KIc) of glass were estimated from the nominal composition by means of a simple approach to govern the average coordination number, the bond directionality, and the atomic packing density.

Intrinsic Ductility of Glassy Solids

Yunfeng Shi; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

8:45 AM

Intrinsic Ductility of Glassy Solids

Yunfeng Shi; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.
Glasses are usually brittle, seriously limiting their practical usages. Recently, the intrinsic ductility of glass was found to increase with the Poisson’s ratio (ν), with a sharp brittle-to-ductile (BTD) transition at ν_{cr}=0.31-0.32. Such a correlation between far-from-equilibrium fracture and near-equilibrium elasticity is unexpected and not understood. Via force-field tuning technique, metallic glasses, amorphous silicon, silica glasses, and polymeric glasses have been investigated, showing BTD transition accompanied by an increase in their Poisson’s ratio. Interestingly, beyond monolithic glasses, the Poisson’s ratio of glassy composites embedded with crystallites also correlate to the intrinsic ductility. The Poisson’s ratio, though defined elastically, reflects the bonding covalency and structural disorder, as well as microstructure heterogeneity.

9:00 AM CM02.04.04
Stresses and Strains in Colloidal Glass 1 Zuoqi Terdik1, David Weitz1,2 and Frans Spaepen1; 1SEAS, Harvard University, Cambridge, Massachusetts, United States; 2Department of Physics, Harvard University, Cambridge, Massachusetts, United States.

Micron-sized hard-sphere colloidal particles can be used to form dense amorphous packings. Due to the large size and slow dynamics of colloidal particles, confocal microscopy can be used to investigate the 3D structure and dynamics of these glasses at the particle level. Previous studies have directly visualized both the inhomogeneous particle level strains in deformed colloidal glasses (i.e. STZs), and surrounding continuum strain fields. Measuring the stress in colloidal glasses during deformation, however, is a significant challenge; due to the large size and thermal interaction energies, colloidal solids have very small elastic moduli, on the order of 10-100mPa. We introduce a new technique, traction force rheology, to directly measure the mechanical response of colloidal glasses while simultaneously visualizing the microstructure using a confocal microscope. The method consists of a bilayer of colloidal glass atop a well calibrated soft polymer gel of slightly greater shear modulus. The composite bilayer is sheared and the shear stresses are inferred from the displacement of embedded tracer particles in the calibrated polymer gel. Using these stress measurements, we show that under cyclic applied shear the colloidal glass goes through a sequence of reversible and irreversible microscopic rearrangements which are related to the spatially correlated heterogeneities in the stress field.

9:15 AM CM02.04.05
High Strain Rate Compression Testing of Amorphous Silica Micropillars Rajaprabhak Ramachandramoorthy1, Jakob Schwiedrzik1, Laszlo Petho1, Damian Frey2, Jean-Marc Breguet1 and Johann Michler1; 1EMPA, Thun, Switzerland; 2Alemnis, Thun, Switzerland.

Mechanical testing of bulk materials at high strain rates is a well-established field of research over the past multiple decades. Recently in the past decade, the field of micromechanics has been established and it is now recognized that a reduction in sample dimensions to the micro- and nano-scale leads to enhanced material properties such as strength and ductility. Until now, the micromechanical experiments such as indentation and micropillar compression has been conducted only at quasi-static strain rates. This limitation of low strain rate testing (~0.1/s) at the microscale arises primarily due to the lack of high strain rate testing platforms capable of simultaneous high-speed actuation and high-speed sensing of microscale displacements and millinewton loads. Thus, the micromechanical properties and the deformation mechanisms for almost every material at strain rates above 0.1/s remains largely unknown. This presentation will report, for the first time, a piezo-based experimental methodology for conducting high strain rate in situ micropillar compression testing at rates up to ~1000/s inside a scanning electron microscope. The strain rate achieved in this study is an increase of approximately four orders of magnitude compared to the current state-of-the-art micromechanical testing. The advantages and unique challenges of conducting micromechanical testing at high strain rates, with a particular focus on wave phenomena, inertia and sample recovery capability at particular strain, will be compared against traditional macroscopic high strain rate tests conducted using kolsky bars. Subsequently, a case study on the high strain rate micromechanical characterization of amorphous silica or glass, a commercially relevant classic material, will be presented. The rate dependent mechanical properties of ~1μm diameter amorphous silica micropillars will be presented as a function of strain rate across eight orders of magnitude, from 0.001/s to 1000/s. Remarkably, the amorphous silica micropillars undergo a unique ductile-brittle-ductile transition in failure mechanism as the strain rate is increased from quasi-static to ~1000/s. The stress-strain curves become serrated at strain rates between 0.01 and 10/s, a typical mechanical response of amorphous materials. Using the extracted velocities of the load drops in the serrated stress-strain curves, analytical calculations based on adiabatic heating and atomistic simulations reported in literature, an explanation for the anomalous plasticity behavior of amorphous silica at different strain rates will be presented. Also, it will be shown, for the first time, that the yield stress increases as the strain rate is increased till 10/s and then saturates as the strain rates are increased further till 1000/s. Finally, a comparison between the macro-scale and micro-scale mechanical response of amorphous silica at high strain rates will be used to demonstrate their startling differences.

9:30 AM CM02.04.06
Effect of Aging and Cryogenic Temperatures on the Mechanical Response of Sputtered Zr-Ni-Al Metallic Glass Nano Structures Julia R. Greer1, Rachel Liontas2, Anthony Kwong3 and Yongwei Zhang4; 1California Institute of Technology, Pasadena, California, United States; 2Intel Corporation, Portland, Oregon, United States; 3IHPC, Fusionopolis, Singapore.

Brittleness of metallic glasses (MGs) is a major drawback for their structural use at bulk scale. It has been shown that when reduced to ~100nm, some metallic glasses undergo a brittle-to-ductile transition and become plastically deformable. To harness this ductility emergent only at nano-scale and proliferate it onto materials with macroscale dimensions, we produced hollow-tube octet-truss nanolattices made out of sputtered NiAlZr with median wall thicknesses of ~10 to ~100nm, which results in a relative density of ~5% and renders them to be 20x lighter than their bulk counterparts. In-situ uniaxial compression experiments conducted inside an SEM reveal a transition from brittle, catastrophic failure in thicker-walled nanolattices (~60 nm) to deformable, gradual, layer-by-layer collapse in thinner-walled nanolattices (~40 nm). We explain the brittle-to-deformable transition as wall thickness decreases in terms of the "smaller is more deformable" material size effect that arises in nano-sized MGs. We further irradiated ZrNiAl nano-architectures with 12 MeV Ni+ ions and found that the thickest-walled nanolattices (~88 nm) withstood irradiation; all other substantially shrunk and collapsed. In-situ nanomechanical experiments reveal significant improvement in mechanical response upon irradiation, with a ~36% increase in average yield strength and enhanced deformability. Irradiated nanolattices deformed via a layer-by-layer collapse in contrast to catastrophic failure in equivalent as-fabricated samples. The field of micromechanics has been established and it is now recognized that a reduction in sample dimensions to the micro- and nano-scale leads to enhanced material properties such as strength and ductility. Until now, the micromechanical experiments such as indentation and micropillar compression has been conducted only at quasi-static strain rates. This limitation of low strain rate testing (~0.1/s) at the microscale arises primarily due to the lack of high strain rate testing platforms capable of simultaneous high-speed actuation and high-speed sensing of microscale displacements and millinewton loads. Thus, the micromechanical properties and the deformation mechanisms for almost every material at strain rates above 0.1/s remains largely unknown. This presentation will report, for the first time, a piezo-based experimental methodology for conducting high strain rate in situ micropillar compression testing at rates up to ~1000/s inside a scanning electron microscope. The strain rate achieved in this study is an increase of approximately four orders of magnitude compared to the current state-of-the-art micromechanical testing. The advantages and unique challenges of conducting micromechanical testing at high strain rates, with a particular focus on wave phenomena, inertia and sample recovery capability at particular strain, will be compared against traditional macroscopic high strain rate tests conducted using kolsky bars. Subsequently, a case study on the high strain rate micromechanical characterization of amorphous silica or glass, a commercially relevant classic material, will be presented. The rate dependent mechanical properties of ~1μm diameter amorphous silica micropillars will be presented as a function of strain rate across eight orders of magnitude, from 0.001/s to 1000/s. Remarkably, the amorphous silica micropillars undergo a unique ductile-brittle-ductile transition in failure mechanism as the strain rate is increased from quasi-static to ~1000/s. The stress-strain curves become serrated at strain rates between 0.01 and 10/s, a typical mechanical response of amorphous materials. Using the extracted velocities of the load drops in the serrated stress-strain curves, analytical calculations based on adiabatic heating and atomistic simulations reported in literature, an explanation for the anomalous plasticity behavior of amorphous silica at different strain rates will be presented. Also, it will be shown, for the first time, that the yield stress increases as the strain rate is increased till 10/s and then saturates as the strain rates are increased further till 1000/s. Finally, a comparison between the macro-scale and micro-scale mechanical response of amorphous silica at high strain rates will be used to demonstrate their startling differences.

Ductility was dependent on specimen size and annealing conditions, with highest ductility of ~150% true strain in ~90 nm wide samples; all annealed.
The fracture toughness of glassy materials, despite its central role in glass science and technology, remains poorly understood. In large part, this is due to the disordered, intrinsically non-equilibrium nature of the glass structure which challenges its theoretical description and experimental determination. By meeting some of these challenges, we show that the notch fracture toughness of metallic glasses exhibits an abrupt toughening transition as a function of a well-controlled fictive temperature $T_f$, which characterizes the glass structure. The ordinary temperature, which has been previously associated with a ductile-to-brittle transition, is shown to play a minimal role. The observed transition is interpreted to result from a competition between the $T_f$-dependent plastic relaxation-rate and an applied strain-rate. Consequently, a similar toughening transition as a function of strain-rate is predicted, which is demonstrated experimentally here. The observed mechanical toughening transition bears strong similarities to the ordinary glass transition and explains previously reported large scatter in fracture toughness data and ductile-to-brittle transitions.

11:00 AM CM02.04.08

Cyclic Shear in a Mesoscopic Model of Amorphous Plasticity Kareem Khirallah, Botond Tyukodi and Craig E. Maloney; Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States.

We present results of a mesoscopic model of amorphous plasticity in which the material is subject to oscillatory shear. We show the existence of a threshold amplitude of the shear. Below this threshold amplitude, eventually all plasticity is exhausted and the material shows a fully elastic response under the periodic shear. The time necessary to reach this fully elastic state diverges as one approaches the critical amplitude. Above the critical amplitude we observe a hysteresis in the stress response. After several cycles the hysteresis reaches a steady state, showing that plasticity never vanishes above the threshold amplitude. Right above the critical amplitude, we observe a strong localization of plastic activity and a diffusive increase of strain and displacement fluctuations. Our results are in good agreement with several recent particle simulation observations.

11:15 AM CM02.04.09

Topological Origin of Strain Induced Damage of Elastomers by Bond Breaking Yikai Yin, Nicolas Bertin, Yanning Wang, Zhenan Bao and Wei Cai; Stanford University, Stanford, California, United States.

Elastomers that can sustain large reversible strain are essential components for stretchable electronics, which enables novel wearable and biological applications. The stretchability and mechanical robustness of unfilled elastomers can be enhanced by adding breakable cross-links, which also causes stress-strain hysteresis indicating strain-induced damage in the elastomer network. However, it remains unclear whether the breaking of the cross-links follows a predictable pattern that can be used to understand the evolution of damage with strain. Through coarse-grained molecular dynamics simulations and topology analyses, we find that bond breaking events are controlled by the evolution of shortest paths between well-separated cross-linkers. We show that the average length of the shortest paths, which is both anisotropic and hysteretic with strain, is the microstructural parameter responsible for damage evolution. These findings provide an explicit connection between the microscopic molecular structures and the macroscopic mechanical behaviors of elastomers, thereby paving the way to the development of physics-based models of elastomers, and providing guidelines for the molecular design of mechanically robust soft materials.

11:30 AM CM02.04.10

Effects of Stress State on Flow and Fracture of Metallic Glasses John Lewandowski; Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States.

The processing and subsequent mechanical behavior of a variety of commercially important materials are affected by the imposed stress state. An earlier review* has summarised the experimentally documented effects of superimposed pressure on deformation under quasi-static conditions, following the classic work of P.W. Bridgman at Harvard University. This will be used to put the effects of superimposed pressure on metallic glasses into perspective. It will be shown that the pressure response of a variety of materials exhibit distinct differences, including metallic glasses, and the potential reasons for these differences will be presented. If time permits, the relevance of such deformation and fracture studies to deformation processing will be overviewed.


SESSION CM02.05: Deformation of Glasses II

Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 200

1:30 PM CM02.05.01

A Study of Shear Band Broadening in Simulated Glasses Darius Alix-Williams and Michael L. Falk; Johns Hopkins University, Baltimore, Maryland, United States.

Two models are proposed to predict the evolution of shear band width as a function of applied strain for simulated glasses mechanically deformed in simple shear. The first model arises from dimensional analysis and an assumption that band broadening is controlled by the strain rate inside the shear band. The second model describes the shear band as a pulled front propagating into an unsteady state, the dynamics of which are described using the effective temperature shear transformation zone (ET-STZ) theory. Both models are compared to three simulated systems: a two-dimensional binary Lennard-Jones glass, a Cu64Zr36 glass modeled using an embedded atom method (EAM) potential, and a Si glass modeled using the Stillinger-Weber potential. In systems across a variety of quench rates. Depending on the case these bands either appear to broaden indefinitely or to saturate to a finite width. The shear band strain rate model appears to apply only when band growth is unconstrained, indicating the dominance of a single
time scale in the early stages of band development. The front propagation model, which reduces to the other model in the early stages of band broadening, also applies to cases in which the band width saturates, suggesting that competition between the rate of shear-induced configurational disordering and thermal relaxation set a maximum width for shear bands in a variety of materials systems.

2:00 PM *CM02.05.02
Dynamic of Shear Bands Initiation in Metallic Glasses—Analysis of a Mg-Based Alloy Using Nano-Indentation Yannick Champion; Centre National de la Recherche Scientifique, St Martin d'Heres, France.

Deformation in metallic glasses occurs by initiation and propagation of multiple thin shear bands. This mode is rather difficult to analyse since a single band propagates early and to a large extent in the specimen leading to catastrophic failure. Exception is for example in confined deformation tests. We used instrumented nano-indentations to perform series of independent experiments at room temperature on a Mg65Cu12.5Ni12.5(Ce75La25)10 metallic glass. Loading part of curves shows serrations which size and duration were measured using an automated procedure. To make analyses consistent, data were considered only in the domain with similar strain rates, in the range of 1 to 0.3 s⁻¹. Times between successive serrations follow a normal distribution that suggests a random occurrence of serrations in the glass. It was then conjectured, that (i) serration occurs through activation of appropriate zone in the glass that should naturally scale with a multiple of an elementary domain size characterizing the deformation mechanism. (ii) As activated zones leading to serration are very few in the glass, the process should fit with rare event dynamics. Actually, serration sizes are well fitted by a Poisson distribution. The model predicts an elementary size which scale with that of the activation volume of 3 atoms, measured from nano-indentation creep tests at constant load in the same series of experiments (Thurseau et al. J. Appl. Phys. 2015). Dynamic of shear bands initiation is then analyzed using statistical approach based on the method proposed by Adam and Gibbs (J. Chem. Phys. 1965).

2:30 PM CM02.05.03
Insight into Shear-Band Affected Zone in Metallic Glasses Through the Measurement of Magnetic Domains Lai Quan Shen and Wei Hua Wang; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Plastic deformation of metallic glasses (MGs) has long been considered to be confined in nanoscale shear band, which usually leads to catastrophic failure and limits their potential applications. Recently, it was found that an affected zone is also involved upon shear banding. Yet, due to technical limitations, the shear-band affected zone (SBAZ), which is critical for understanding shear banding and thus the design of ductile MGs, remains to be precisely identified. Here, by taking magneto-elastic coupling induced magnetic domains as a probe with sufficiently high sensitivity and spatial resolution, we unveil the structure of SBAZ in much more detail. We demonstrate that shear banding is composed of a nanoscale core surrounded by a micron-scale SBAZ with gradient in the strain field, and multiple shear bands interact through the superimposition of the SBAZs. There even exists super-long-range gradual elastic stress field extending hundreds of micrometers away from the shear-band core. Our method and findings enable a visualized insight into SBAZ and provide a comprehensive picture on shear banding, which are important for elucidate the micro-mechanisms for plastic deformation of glasses.

2:45 PM CM02.05.04
Understanding the Mechanisms of Amorphous Plasticity through Molecular Simulation Pemphhi Cao. Michael Short and Sidney Yip; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Using a meta-dynamics method of sampling activated state pathways we study two related plastic responses of a model metallic glass at experimental strain-rate levels beyond the reach of traditional molecular dynamics simulations. The problems are (1) discrete stress relaxation (slip avalanches) in the onset of yielding and subsequent strain evolution, and (2) stress effects on creep rate. In (1) we quantify the yielding response and the role of major and minor avalanches in sustaining serrated plastic deformation. In the case of deformation under a constant stress, problem (2), we demonstrate a nonlinear interplay between non-affine atomic displacement and cooperative shear transformation distortion of local atomic clusters that provides a molecular explanation of the familiar behavior of creep-rate upturn beyond a stress threshold, as well as a mechanism map delineating the effects of stress and temperature. Collectively these findings lead to an understanding of the elementary processes governing deformation and flow of disordered materials and the effects of thermal and stress activations.

3:00 PM BREAK

3:30 PM *CM02.05.05
Improving the Ductility of Metallic Glasses by Heterogeneous Jurgen H. Eckert1; 2; Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; 3Materials Physics, Montanuniversitaet Leoben, Leoben, Austria.

Significant progress has been made in recent years in how to optimize processing conditions for glass formation, net-shape forming and property rejuvenation. However, the details of the correlation between composition, atomic structure, defects and thermo-mechanical treatments for structure modification and their impact on shear banding behavior and failure mechanisms for achieving macroscopic ductility are still not well-understood. Recent work suggests that the intrinsic properties of metallic glasses and composites are strongly affected by the details of short- and medium-range order arrangements and their response to external fields like mechanical deformation or temperature cycling causing heterogeneous stress and strain variation on different length-scales.

This talk explores the diversity that can be achieved in metallic glasses and composites considering structure changes, recovery and rejuvenation mechanisms when the materials are subjected to different casting conditions or thermo-mechanical cycling. The findings will be discussed with respect to short- and medium-range order modulation, local stress and strain states, defect generation and annihilation, and precipitation of secondary phases. The structure changes will be correlated with plastic deformability and failure mechanisms, and the effectiveness of composition tuning and thermo-mechanical processing for plasticity improvement will be discussed to derive guidelines for property optimization.

4:00 PM *CM02.05.06
Spatial-Temporal Characterization of Shear Band in Bulk Metallic Glasses Xie Xie1, 2; Chieh Lo2, Tong Yang2, Junwei Qiao2, Gongyao Wang1, Shigenobu Ogata2, Hairong Qi1, Karin Dahmen5, Yanfei Gao1, 3 and Peter K. Liaw1; 1University of Tennessee, Knoxville, Tennessee, United States; 2National Chiao Tung University, Hsinchu, Taiwan; 3Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 4Taiyuan University of Technology, Taiyuan, China; 5University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 6Osaka University, Osaka, Japan.

Recent research shows that temperature is an important factor for the shear-band operations in bulk metallic glasses (BMGs). Thus, the characterization of shear bands through thermal imaging provides a way to study BMG deformation. Based on recent reports and research progress, the present work develops a kinetic Monte Carlo (kMC) model to investigate and simulate the initiation and propagation of shear bands, which correlates well with the thermograph-
imaging results. These findings are expected to reveal the hidden structural characteristics during the BMG deformation and advance the basic understanding of the deformation mechanism.

Acknowledgements: we would very much appreciate the supports from (1) the Department of Energy (DOE), Office of Fossil Energy, National Energy Technology Laboratory (DE-FE-0011194) with the program manager, Dr. J. Mullen, (2) the U.S. Army Research Office project (W911NF-13-1-0438) with the program managers, Dr. M. P. Bakas and Dr. D. M. Stepp, and (3) the support from the National Science Foundation (DMR-1611880) with the program directors, Des G. Shiflet and D. Farkas.

4:30 PM CM02.05.07
Local Yield Stress Analysis in Simulated 3D Glasses Dhiin Raan1, Sylvain Patinet2 and Michael L. Falck3; 1Johns Hopkins University, Baltimore, Maryland, United States; 2ESPCI, Paris, France.

The ‘Local Yield Stress’ (LYS) method is applied to an atomistic model of as-quenched glasses by shearing local regions. By probing the structure in local shear modes, the LYS method measures the local yield stress as the incremental stress at the onset of a plastic instability. This method has been upgraded to a three-dimensional version with variations in orientations, rotations and triaxiality when locally deformed. This analysis is then utilized to identify the population of ‘Shear Transformation Zones’ (STZs), defined as local atomic clusters that rearrange cooperatively when the material is subjected to shear. These STZs are present in the as-quenched material structure. The population of STZs is correlated with the plastic events observed during a molecular dynamics simulation in which the glass is subjected to shear at the boundaries in order to assess the predictive capability and persistence of the derived STZ population while the material undergoes deformation.

4:45 PM CM02.05.08
Atomic-Scale Homogeneous Plastic Flow of Bulk Metallic Glass Jiaxin Yu1,2, Amit Datye2, Zheng Chen3, Chao Zhou3, Omur E. Dagdeviren3, Jan Schroers4 and Udo Schwarz5,6; 1Key Laboratory of Testing Technology for Manufacturing Process, Ministry of Education, Southwest University of Science and Technology, Mianyang, China; 2Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States; 3Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States.

The onset of yielding and the local plastic flow mechanism of bulk metallic glasses (BMGs) at room temperature have not been fully understood at atomic scale. Further reducing the stressed volumes of BMGs during mechanical testing can decrease the amount of activated shear transformation zones (STZs) under shear stress, which is expected to provide direct insight into the onset of plastic deformation and the material’s atomic-scale flow behavior. In this work, we employed thermoplastic forming to produce atomically flat Pt-based BMG surfaces, whose yield stress, the onset of yielding, and plastic flow at the atomic scale were subsequently studied using atomic force microscopy (AFM)-based nanoindentation. The experiments revealed a much higher yield stress compared to the value obtained by conventional nanoindentation testing, which indicates that the yield stress of BMG strongly depends on the stressed volume in the test, with a smaller stressed volume causing a higher yield stress. Differing from control experiments performed on Pt(111), the plastic flow of Pt-BMG is homogeneous, and no pop-in events are observed. Moreover, the plastic response of Pt-BMG does not exhibit any loading rate dependence, but needs a constant stress to sustain flow. These atomic-scale results are contrasted to the larger-scale model that explains plastic deformation of BMG as originating from the finite STZs activation.

SESSION CM02.06: Poster Session II: Structure-Property Relations in Non-Crystalline Solids
Session Chairs: Katharine Flores, John Mauro, Tanguy Rouxel and Yunfeng Shi
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM02.06.01
Real-Time Observation of Thermally-Induced Structural Changes of Poly(Lactic Acid) Thin Film by Terahertz Spectroscopy Madoka Nakamura, Makoto Okano and Shinichi Watanabe, Keio University, Yokohama, Japan.

PolymERIC materials exhibit intriguing temperature-dependent structural transitions, such as a glass transition at Tg, and a crystallization phase transition at Tc. Since some polymers have relatively low Tg and Tc, the structural change might occur during the productive processes. Since the structure of polymers affects their electrical, mechanical and electrical properties, it is important to characterize the in situ during the productive processes. Recently, it has been demonstrated that the terahertz time-domain spectroscopy (THz-TDS) is a powerful tool to evaluate the structure of polymeric materials[1-5]. In contrast to the conventional methods such as X-ray diffraction, THz-TDS has some clear advantages: (i) Nondestructive and contactless inspection. (ii) Evaluation of Tg[1,3] (iii) Detection of both the amorphous and the crystalline phases[5]. (iv) Prompt measurement within 1 ms. These features allow us to real-time monitor the structural change of the polymeric products. Here, we demonstrate a real-time sensitive monitoring of the thermally-induced structural changes of poly(lactic acid) (PLA) using THz-TDS. PLA is one of the most promising biodegradable polymers for industrial polymer products. Because the PLA has relatively low Tg (~60°C) and Tc (~120°C), its structure easily modified by the heating. Thus, the PLA is a suitable material for investigating the structural changes by the heating with the THz-TDS.

By real-time monitoring the terahertz optical responses of the PLA during the heating, the complicated temperature dependence of the complex dielectric function (ε′) of the PLA was observed. To clarify the structural change of the PLA, we focused on the spectral shape of ε′, especially the absolute value of the slope, |ε′| at 0.5-1.0 THz. We found two characteristic behaviors of |ε′| regarding the structural changes of the PLA: (i) Existence of the inflection point at Tg (ii) Drastic decrease around Tc. Our findings are well explained by the classical Lorentz oscillator model[5]. The former behavior results from the broadening of the vibration mode due to the change in the free volume from the glass to the rubber states[1,3]. The latter one is attributed to the blueshift of the vibration mode accompanied by the phase transition from the amorphous to the crystalline phases[2,5]. Our novel analytical procedure that is based on the Lorentz oscillator model and utilizes |Δε′| as an indicator to evaluate the structure clearly reveals the structural change in the PLA compared with the previous reports [1-5]. Thus, we conclude that our method is promising for proving the structural change of polymeric materials in the productive processes.

CM02.06.02
Beneficial Effects of Oxygen Addition on Glass Formation in a High-Entropy Bulk Metallic Glass Di Cao, Zhaoping Lu and Yuan Wu; University of Science and Technology Beijing, Beijing, China.

Glass-forming ability (GFA) is one of critical scientific problems for the field of bulk metallic glass (BMGs), and how to facilitate glass formation is always a central yet important research theme for this field. Compared with conventional BMGs in the same alloy system, newly developed high-entropy BMGs (HE-BMG) usually show much enhanced thermal stability, but appreciably reduced GFA. In contrast to the conventional wisdom, we found that GFA of the Zr20Cu20Hf20Ti20Ni20 HE-BMG could be enhanced by oxygen microalloying. The underlying mechanism was explored from both thermodynamic and kinetic point of view, and our analysis indicates that the high packing density resulted from addition of small oxygen atoms is responsible for the beneficial effect of oxygen. The current findings not only shed new insights into understanding of glass formation, but also broaden the view for exploring new kinds of HE-BMGs with enhanced properties and low manufacturing costs.

CM02.06.03
ToF SIMS Characterization of Polymer Thin Films—Impact of Molecular Weight Amal Ben Hadi Mabrouk1, 2, 3; 1University Grenoble Alpes, Grenoble, France; 2CEA-LETI, Grenoble, France; 3Sorbonne Universités, Paris, France.

Organic materials have risen to great importance in the world of electronics. Especially polymers have brought new possibilities to the field. With their numerous advantages like thermal stability, etch resistance and flexibility [1], organic compounds are growingly being studied and used for conductive layers, high resolution lithographic and packaging applications. In order to understand the logic behind the development and selection of such materials, it is fundamental to acquire a basic familiarity with the relationships between their structural parameters and physicochemical properties. Chemical depth profiling techniques like time-of-flight secondary ion mass spectrometry (ToF-SIMS) can help identify the relationship between the polymer chemical behavior when being bombarded by primary ions and their structural parameters. ToF-SIMS depth profiling of organic materials has developed rapidly and has been improved by using mainly the “Dual beam” technique which allows the precise tracking of characteristic chemical fragments and the suppression of the accumulated damage during the etching process [2].

In this work we present the characterization of Poly (methyl methacrylate) and Polystyrene thin films with varying molecular weights (2-9.9x10^5 g.mol^-1) by ToF-SIMS measurements. It focuses on the in-depth investigation of the influence of the molecular weight of the mentioned polymers on the efficiency of the sputtering process, at different energies. The characterization was carried out using monoatomic Cesium sources with different energies for sputtering and Bismuth ions sources for analysis. Additionally, roughness measurement using Atomic Force Microscopy (AFM) were performed because the surface topographic change during sputtering is known to be one of the most important factors to affect depth resolution. The experiments show an inversely proportional relationship, with different orders of magnitude, between the sputtering yield volume (nm^3/primary ion) and the molecular weight Mw. This tendency can be related whether to the studied polymers glass transition temperature (Tg) or to the initial solution viscosity.

This work was carried out in the Nano-Characterization Platform (PFNC) at the CEA Grenoble


CM02.06.04
Highly Processable Work-Hardenable Zr-Based Metallic Glass Composites Reinforced by Continuous TiNi Fiber Jie Zhou, Zhaoping Lu and Yuan Wu; University of Science and Technology Beijing, Beijing, China.

Bulk metallic glasses (BMGs) have attracted considerable research activities because of their unique mechanical properties, such as high strength, large elastic limit and high hardness. However, room-temperature brittleness and strain-softening limited their structural applications. Up to now, it has been proved that enhanced plasticity and strong work-hardening ability could be achieved by introducing the concept of transformation-induced plasticity (TRIP) into Zr-based or Ti-based bulk metallic glass composites (BMGCs). Most currently developed TRIP-reinforced BMGCs are fabricated with in-situ formed second phase method, in which homogeneous formation of austenite phase is a big challenge.

To produce work-hardenable BMGCs in a processable way, we designed a series of BMGC reinforced by introducing ex-situ continuous TiNi fibers, which can bring in martensitic transformation (MT) and TRIP effect and eventually leads to the combination of pronounced plasticity and considerable work-hardening ability under both quasi-static and dynamic compressive loading.

In this talk, preparation, microstructure characteristics, mechanical properties and deformation mechanism of BMGCs reinforced by TiNi fibers will be discussed.

CM02.06.05
Combinatorial Temperature Resistance Sensors for the Analysis of Phase Transformations Haitao Zhang1, Yong Xiang1 and Joost J. Vlassak2; 1University of Electronic Science and Technology, Chengdu, China; 2Harvard University, Boston, Massachusetts, United States.

In this work, we describe a sensor array that can effectively measure the resistance of thin films as a function of temperature and composition. The sensor is fabricated in very simple micro fabrication steps. Detailed FEM simulation indicates that the sensor has very high temperature uniformity, which leads to extreme sensitivity and thus the ability to detection of subtle structure change of materials. We have used the sensor to observe structural relaxation, the glass transition, and crystallization of PdCuSi metallic glasses. We also find that the ratio of the resistance of crystallized to as-deposited material is correlated with the glass-forming ability for both PdCuSi and NiZr-based alloys, potentially providing an avenue to the fast screening of good glass formers in complex material systems.

CM02.06.06

Alkali and earth alkaline elements can behave as network modifier or as charge compensator of AlO4- in aluminosilicate glasses and melts. As a function of the role, density, molar volume, viscosity, liquidus and glass transition temperature and more generally, macroscopic properties, can change significantly. But how evaluate or prove this change of role? Recently, Helhen and Neuvillé (2014) have shown by comparing Raman in VV and VH polarization, that a new band appears in the VH Raman spectra when the role of Ca(Na, Mg) changes from charge compensator to network modifier. Furthermore, we have shown in the
XANES spectra at the Ca K-edge, important differences in the Ca pre-edge peaks as a function of this same change of role. Similar behaviour were observed on the Calcium K-edge via XANES spectroscopy (Cicconi et al., 2016) and on the Na, via NMR (Le Losq et al., 2014). During this presentation, we plan to show some new results on XANES, Raman, NMR.

To conclude, by looking at the role of alkaline earth elements in glasses and melts, it is possible to have a better knowledge of the structure of glasses and melts, but also to better understand their influence on redox and nucleation processes.

Reference:

CM02.06.07
Short Range Order in Fluorine Containing CaO-SiO2-CaF2 Glasses from NMR, Neutron Diffraction, and X-Ray Absorption Spectroscopy
Laura A. Swansbury1, 2 and Gavin Mountjoy1; 1University of Kent, Canterbury, United Kingdom; 2Morgan Advanced Materials, Bromborough, United Kingdom.

The glass system CaO-SiO2-CaF2 has been studied to help elucidate the structure of more complex CaO-SiO2-P2O5-CaF2 fluorine-containing bioactive glasses. The CaO-SiO2-CaF2 glass series was synthesized and the glass transition temperature decreased linearly with increasing CaF2 concentrations. Compositional analysis revealed that fluorsilicate losses occurred due to fluorsilicate volatilisation during synthesis. The chemical shift positions in the 29F MAS-NMR spectra became more negative with increasing CaF2 concentrations, becoming more similar to that of pure CaF2. By studying the calcium environment using neutron diffraction and x-ray absorption spectroscopy at the Ca K-edge, reasonably consistent values for Ca-F and Ca-O nearest neighbour distances of approximately 2.3Å and 2.4Å (respectively) could be obtained. However, it was challenging to determine the coordination numbers and disorder in distances of such nearest neighbours.

CM02.06.08
Structure-Property Relations in Amorphous Polymer Derived Ceramics for Electronic Applications
Mehrad Abdass1, Soohyun Im1, Jared Johnson1, Gabriel Calderon Ortiz2, Menglin Zhu1, Nathan A. Oyler2, Michelle M. Paquette1, Paul Ruif1, Ridwan Sakidja2 and Jinwoo Hwang1; 1The Ohio State University, Columbus, Ohio, United States; 2University of Missouri – Kansas City, Kansas City, Missouri, United States; 3Missouri State University, Springfield, Missouri, United States.

We develop a novel methodology for accurate design and fabrication of complex disordered solids using a combination of advanced experimental and computational techniques. Complex disordered solids are non-crystalline materials for which the fundamental building blocks are typically molecules or molecule fragments, and therefore they have great potential for tunable structure and properties for various applications. However, the complex nature and large degree of freedom in their structure impose substantial challenges to the design and optimization of these materials. This presentation will focus on the structural characterization of polymer derived amorphous hydrogenated boron carbide thin films using 4-dimensional scanning transmission electron microscopy (4D-STEM). The 4D-STEM utilizes electron nanoprobes and the new-generation fast pixelated STEM detector, which records the diffraction patterns from individual nanoscale volumes of the material. The fluctuation and angular correlation analyses of the diffraction patterns can provide the unprecedented details of the structural heterogeneity, including the size, distribution, connection, and volume fraction of medium range ordering (MRO). We show that the MRO in amorphous hydrogenated boron carbide can be comprised of the connection and networking of the icosahedral short-range clusters, and the MRO can directly affect the important physical and electrical properties of the films. Our finding is promising as it could greatly expand the breadth of materials-by-design approaches by flexibly tuning the structure of disordered materials to achieve desired properties.

CM02.06.09
In Situ Observation of Shear-Driven Amorphization Process in Silicon Crystals
Scott X. Mao1, Yang He1, Chongmin N. Wang2 and Ting Zhu3; 1University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 2Pacific Northwest National Laboratory, Richland, Washington, United States; 3Georgia Institute of Technology, Atlanta, Georgia, United States.

Amorphous materials are used for both structural and functional applications. An amorphous solid usually forms under driven conditions such as melt-quenching, irradiation, shock loading or severe mechanical deformation. Such extreme conditions impose significant challenges on the direct observation of the amorphization process. Various experimental techniques have been used to detect how the amorphous phases form, including synchrotron X-ray diffraction, transmission electron microscopy (TEM) and Raman spectroscopy, but a dynamic, atomistic characterization has remained elusive. Here, by using in-situ high-resolution TEM, we show the dynamic of the amorphization process of silicon nanocrystals during mechanical straining at the atomic scale. We find that shear-driven amorphization occurs in a dominant shear band starting with the diamond-cubic (dc) to diamond-hexagonal(dh) phase transition and then proceeds by dislocation nucleation and accumulation in the newly formed dh-Si phase. The process then leads to the formation of an amorphous Si (a-Si) band, embedded with dh-Si nanodomains. The amorphization of dc-Si via an intermediate dh-Si phase is a previously unknown pathway of solid-state amorphization.

CM02.06.10
Mineralogical Characterization and Quantification of a Complex Natural Mineral Containing Diatomite after Thermal Treatment
Carolina Cárdenas-Ramírez1, 2, Franklin Jaramillo Isaza1 and Maryory Gomez Botero1; 1Universidad de Antioquia, Medellin, Colombia; 2Sumicol S.A.S, Medellin, Colombia.

In the present work, a thermal treatment of a complex natural mineral containing diatomite was carried out to investigate the effect on its phase transitions and, moreover, to properly identify and quantify such phases. Diatomite is a type of hydrated amorphous biogenic siliceous mineral, primarily opal, from geological deposits and possesses unique properties as highly porous structure, excellent absorption capacity and thermal stability. One of the major problems is distinguishing crystalline cristobalite from some forms of opal which have similar diffraction patterns, the opal phases significantly contain water and these phases are not crystalline in the classical sense, therefore as no long-range ordering exists, it is difficult to identify such phases through conventional XRD techniques. The characterization is even more difficult as typical natural minerals are not pure diatomite. The sample studied for this investigation was calcined in a muffle furnace at temperatures of 600°C, 900°C and 1100°C. The phase evolution and microstructure of the sample were investigated by X-ray fluorescence (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS) and transmission electron microscopy (TEM). Through Rietveld refinement method the phases were quantified. The results showed that the clay minerals in the raw material were kaolinite, quartz, illite and a great amount of amorphous (presumably diatomite). The calcination at 1100°C allowed to crystalize most of the phases other than diatomite, allowing to quantify the amount of diatomite present in the material when compared with the raw sample. No crystallization of diatomite was observed at any of the evaluated temperatures. Besides, it was found by HRTEM that diatomite has a short-range ordering, d-spacings were measured and correlated with possible crystalline phases showing cristobalite/tridymite-like
crystals, even in the raw sample, these crystalline phases correspond to cryptocrystals. These findings allow to improve the understanding of complex natural minerals containing diatomite through the implementation of a systematic use of different characterization techniques for its adequate phase determination and quantification.

CM02.06.11
Amorphous Germanium Material Evaluation for Evanescent Wave Sensors for MWIR and LWIR Sensing Applications
Eveline Postelniciu1, Peter Su1, Danhao Ma1, Raitao Wen2, Ruturaj Pujari3, Ryan Kosciolek4, Venita Boodhoo5, Ron Synowicki5, Jurgen Michel6, Lionel C. Kimerling1, Kazumi Wada7 and Anuradha Agarwal1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2J.A. Woollam Company, Inc., Lincoln, Nebraska, United States.

Room temperature deposited amorphous germanium (Ge) material has been evaluated for evanescent sensing applications in the Midwave and Longwave infrared regions (MWIR and LWIR). The advantage of amorphous Ge is that it can be used to sense a wide variety of organic molecules for both biomedical and environmental sensing and its room temperature processing is very economically efficient. Thin films of amorphous Ge were obtained using various processing approaches: Sputter Deposition, Electron Beam Evaporation (E-beam), and Physical Vapor Deposition (or thermal evaporation).

Films were characterized using X-Ray Diffraction (XRD), Fourier Transform InfraRed (FTIR) Spectroscopy, Wavelength-Dispersive (Electron) Spectroscopy (WDS), Hall Effect measurements, and Ellipsometry. It was shown that Electron Beam Evaporation yielded the purest material, with 96% Ge and 4% carbon contamination, while thermal evaporation showed only around 70% Ge and 30% of the film containing contaminants from the evaporation chamber. Ellipsometry performed on the amorphous Ge samples at a wavelength range of 1.5 to 15 microns showed that the index of refraction, n, of sputtered Ge had a lower range (2.9 – 3.4) than that of E-beam Ge (4 – 4.5). The extinction coefficients for both sputtered Ge and E-beam Ge are in a comparable range, 0 to 0.4, for the same measured wavelength range (1.5 to 15 microns), indicating low absorption losses within the material. X-Ray Diffraction confirmed the amorphous nature of the deposited Germanium. Waveguides utilizing this low loss amorphous Ge within a Si-CMOS compatible platform will be presented.

CM02.06.12
Structural Variation of (Hydrogenated) Amorphous Silicon with Density—A Classical Monte Carlo Study
Enrique Guerrero and David A. Strubbe; Physics, University of California, Merced, Merced, California, United States.

We present computational generation of hydrogenated (a-Si:H) and non-hydrogenated (a-Si) amorphous silicon structures for use in studying the electronic properties of thin-film solar cells, such as "heterojunction with intrinsic thin-layer" (HIT) cells with a-Si:H and c-Si layers. We generate structures using the Wooten-Winer-Weaire (WWW) classical-potential Monte Carlo method using our CHASSM (Computational Hydrogenated Amorphous Semiconductor Structure Maker) code, which implements a WWW scheme that can take into account Si-H bonds. We create structures of various densities and study the effect on structural parameters including bond lengths, bond angles, dihedral angles, and radial distribution functions. Abrupt transitions occur at certain critical densities (different depending on hydrogen content) which suggest crossover between different types of amorphous structures, perhaps even different phases. We investigate mechanical and spectroscopic consequences of these changes. At low densities, voids form, which are likely to constitute defects limiting polymer mobilities and may be implicated in light-induced degradation (the Staebler-Wronski effect). We mathematically characterize the voids using Voronoi polyhedra and persistent homology. We show some refinements of the Monte Carlo randomization process needed to avoid ending in crystalline structures or a class of unphysical excessively coordinated structures.

CM02.06.13
Insight into the Mechanism of Damage Initiation and Fracture of Conductive Polyurethane Nanocomposites
Spencer A. Hawkins1, Evan Sullivan2, Aimee Syred3, 4, Alirea Sarvestani3, 5 and Enrico Ferrari6; 1Physics, University of California, Merced, Merced, California, United States; 2Mechanical Engineering, Mercer University, Macon, Georgia, United States; 3Wright-Patterson Air Force Base, Air Force Research Laboratory, Dayton, Ohio, United States; 4Universal Technology Corporation, Beavercreek, Ohio, United States; 5University of Kentucky, Kentucky, Kentucky, United States.

Polyurethane (PU) is a functional copolymer whose properties bridge the gap between rubber and thermoplastics. Their excellent physical properties, such as flexibility and abrasion resistance along with their high temperature plasticity have made them an ideal structural material for application in aerospace structures, automobiles, electro-machinery vocation, etc. In an attempt to promote the formation of a conductive network within PU, we have developed an experimental technique to decorate carbon nanofibers (CNFs) with silver (Ag) nanoparticles and subsequently blended them with PU. Introduction of a small amount of CNF (coated with Ag) into the PU matrix produced a conductive nanocomposite with higher stiffness and strength compared to that of pure PU but substantially reduced the fracture toughness of the material. Here, we present a systematic and comprehensive study to understand the mechanism of damage nucleation and fracture evolution in Ag-CNF-PU nanocomposites. By mapping the surface of samples using AFM-IR, the onset of damage was monitored prior to realization of plastic deformation during in situ tensile testing. Coupled with the results of DMA analysis, we concluded that strain induced crystallization in PU and polymer debonding from CNF surface are the most detrimental mechanisms that control the fracture toughness of PU nanocomposites. These conclusions were used to develop a model that predicts the mechanical behavior of PU nanocomposites at finite deformations.

CM02.06.14
Mechanical Behavior of Highly Rejuvenated Bulk Metallic Glasses
Jie Pan and Yi Li; Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China.

Rejuvenation of metallic glasses, bringing them to higher-energy states, is of interest in improving their plasticity. However, how to achieve significant flow and rejuvenation throughout a deformed metallic glass remains challenging, and the mechanical behavior of the highly rejuvenated bulk metallic glasses is unexplored. In this presentation, we will reveal the significant improvement in compressive plasticity in a Zr-based bulk metallic glass (BMG) by structural rejuvenation, which is in stark contrast to the ageing induced brittleness. Upon constrained compression on the BMG rods at room temperature, extreme rejuvenation occurs in a large volume of BMG specimens, accompanied with a considerable amount of free volume generation, reduced hardness, Young’s modulus. As a result, shear transformation zones will be easily activated, giving rise to reduced yield strength of 1.37 GPa, much improved compressive plasticity, as well as more homogeneous deformation. The present work reveals the correlation between the deformation behavior and energy state in metallic glasses, which will help us to understand the deformation mechanism of metallic glasses, even disordered systems.

CM02.06.15
Atomistic Modeling of a Photovoltaic Material—Hydrogenated Amorphous Silicon
Raymond Atta-Fynn1, Harsh Arya2, Sominilkumar Rathi2 and Parthapratim Biswas3; 1Physics, Univ of Texas-Arlington, Arlington, Texas, United States; 2Eugenes Inc., San Jose, California, United States; 3Physics, University of Southern Mississippi, Hattiesburg, Mississippi, United States.
Hydrogenated amorphous silicon (α-Si:H) is an important electroactive and photovoltaic material of technological importance that can be quite difficult to model accurately, particularly on a large scale for electronic structure analysis. In this work, we present a novel and efficient approach which couples accelerated classical molecular dynamics with ab initio relaxation to model high-quality, large atomistic models of α-Si:H. Specifically systems containing 10,000 Si atoms and H atomic concentration of 9%-18% were simulated. The models are nearly free of coordination defects and their structural, electronic and nuclear magnetic resonance properties of the models are in good agreement with experimental data. The approach paves the way for the generation of realistic device-size atomistic networks of α-Si:H. Furthermore, the approach can be readily generalized to produce a variety of binary and ternary amorphous networks in two and three dimensions, and amorphous/crystalline heterojunctions to address the physics of photovoltaic devices.

CM02.06.16
Extreme Energy Absorption Through High Rate Deformation of Freestanding Glassy Polymer Thin Films Jinho Hyon1, Ye Eun Song1, Edwin L. Thomas1, Jason Streit2 and Richard Vaia1; 1Material Science and NanoEngineering, Rice University, Houston, Texas, United States; 2Materials & Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, United States.

Of all materials, only polymers exhibit a strongly dissipative melt state. If a set of deformation processes can lead to strong heating of an initially glassy polymer material, large amounts of kinetic energy can be absorbed. Normally at room temperature, glassy polymers undergoing rapid tensile loading craze, crack and then fracture with little overall energy absorption. Here we exploit the higher mobility and lower entanglement density of the chains near the free surfaces of ultrathin films to induce extensive crazing and consequently adiabatic heating by imposing a very high strain rate (~107/s) using a micro-projectile ballistic test. The near-surface thin films effects not only dramatically increase the number of crazes nucleated, but assist their subsequent growth, impingement and the accompanying large adiabatic temperature rise of the deforming film. We employ 3.0 micron diameter spherical silica projectiles propelled at incident velocities ranging from 350-800 m/s to investigate the kinetic energy (KE) absorption. Homopolymer polystyrene (PS) films with different molecular weights and film thicknesses and single component nanocomposite PS grafted nanoparticle (PSgNP) films (~1% v/v NPs with 100's of chains covalently anchored to each NP) show extraordinary high KE absorbed per unit mass of the target film (on the order of several MJ/kg, comparable to the energy density of TNT). Use of a glassy-glassy microphase separated lamellar diblock copolymer (PS-b-P2VP) to create films comprised of just a few parallel lamellae allows strong alteration of the polymer chain conformations while keeping the overall molecular weight (MW) and glass transition temperature (Tg) comparable to the PS homopolymer and grafted NP films. A block copolymer offers the additional energy absorption mechanism required for block mixing if heating takes the sample above the order to disorder transition temperature.

CM02.06.17
Evaluation of Amorphous Alumina as Effective Hydrogen Resistive Coating for Ferritic Steel Xiaohui Yao, Vrinda Soajit, Ju Li and Bilge Yildiz; Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Hydrogen gas (H2) as a promising energy storage media and a clean fuel, plays a central role in future low-carbon infrastructure. Yet the storage and transportation of hydrogen gas is cumbersome due to its high diffusivity, low density and poor compressibility. Long range hydrogen delivery exploiting the existing natural gas pipeline network has been proposed and found feasible when the volume ratio of hydrogen is below 15%. But the high diffusivity of hydrogen results in nearly seven times higher permeation than natural gas. At the same time, the notorious hydrogen embrittlement effect is expected to degrade the mechanical performance of the steel and bring safety concerns. To improve the tolerance of existing pipeline steels toward high concentrations of hydrogen, as in direct transportation of hydrogen gas in these pipelines, a low-cost and effective hydrogen resistant coating is desired to be applied on the inner surface of the steel pipelines. α-Al2O3 is one of the best materials to reduce the permeation of hydrogen. But the formation of crystalline α-Al2O3 requires processing temperatures beyond the tolerance of pipeline steel. In this work, we developed two conformal coatings of amorphous Al2O3 on the surface of ferritic steel with mild formation temperature and evaluated their effectiveness as a hydrogen permeation barrier. An electrochemical testing approach was adopted for this evaluation to mimic the operation condition of hydrogen pipeline, which is featured by the ambient temperature but high H2 activity (equivalent to a high H2 pressure of 30–70 MPa). We found that amorphous Alumina also provides excellent barrier characteristics. Over 200 times permeation reduction factor was found for the coating with only 1/300 of steel thickness. The micro-structure of the two coatings were also compared and found to be critical in the permeation performance. Currently, we are systematically assessing the effect of the microstructure, controllable by synthesis and post-anneal conditions, on the resistance of these layers against hydrogen entry and diffusion. Our result suggests that by properly managing the microstructure of the coating layer, it is possible to utilize the low temperature derived amorphous alumina as an effective hydrogen barrier coating.

CM02.06.18
Ultra-High Strength Above 10 GPa and Short-Range Atomic Order of Amorphous Boron Jessica M. Maita, Gyuho Song, Mariel Colby and Seok-Woo Lee; University of Connecticut, Storrs, Connecticut, United States.

Amorphous boron fiber has been widely used as a reinforcement filler in aerospace resin-matrix composites due to its high strength and high elastic modulus. However, its mechanical properties have not been measured accurately due to its intrinsic issues during fabrication. Amorphous boron is usually produced in single-filament reactors by chemical vapor deposition of boron on tungsten wire, and the final product is a core-shell wire with a tungsten boride core and amorphous boron shell. The diameter of this composite fiber is approximately 100 micrometers, and the thickness of the boron-shell is 40 micrometers. Traditionally, wire tension tests of the composite fiber or hollow amorphous boron fiber have been conducted but would underestimate the strength due to the greater probability of defects that exist along the long wire. Therefore, it is necessary to perform reliable mechanical tests at small length scales. Recent developments in micropillar compression and tension testing enable us to probe mechanical properties of small materials accurately. In addition, the local atomic arrangement in amorphous boron has not been clearly understood because of the complexity in its amorphous structure. Therefore, it is necessary to conduct advanced transmission electron microscopy (TEM) to analyze the local structure at atomic resolution.

In this presentation we will discuss microstructural and mechanical characterization of amorphous boron with high resolution TEM and in-situ scanning selection microscopy (SEM) micropillar compression results. TEM diffraction patterns show a unique set of three halo rings while an amorphous material usually has a single halo ring. The three halo rings imply amorphous boron would consist of the random distribution of crystallites. Fast Fourier transform (FFT) was used to confirm these crystallites consist of short-range ordered boron clusters. We will also discuss micropillar compression results, the yield strength as a function of micropillar diameter. Its ultra-high strength (~13 GPa) will be discussed in terms of its unique microstructure and the intrinsically strong atomic bonding of metallicloid materials. Our results help to provide a deeper understanding of plasticity and fracture processes in amorphous boron and will be useful in the development of mechanically robust boron-fiber composite materials.

CM02.06.19
Mass and Thermotransport in Liquid Ni-Al-Co Alloys Tanvir Ahmed1, William Yi Wang1, Zi-Kui Liu1, Irina Belova1 and Graeme Murch1; 1School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an, China; 2Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; 3School of Engineering, The University of Newcastle, Callaghan, New South Wales, Australia.
Mass and thermotransport properties in liquid Ni-Al-Co alloys are studied over a wide temperature and concentration range by using molecular dynamics (MD) simulations. The calculations are performed by means of equilibrium MD simulations in conjunction with the Green-Kubo formalism and an embedded-atom method (EAM) potential for this system developed by Pun et al. [1]. Results of simulations also allow the description of the temperature and concentration dependence of the thermodynamic factor. Furthermore, the simulations permit analysis of the heat of transport as a function of temperature and composition as well. The complete range of the diffusion properties including Osnag off-diagonal terms and partial properties are estimated for the considered temperature and concentration ranges. Overall, results of this study agree well with previous published experimental and simulation data where available. In addition, for liquid Ni-Al alloys, the calculations are also carried out with a potential [2] for comparison purposes.

References
http://dx.doi.org/10.1080/14786430903258184

CM02.06.20
Mobility of proton Carriers in Porous Conduction Phosphate Glasses Takahisa Oomura1, Takuya Yamaguchi2, Tomohiro Iijiyama2, Satoshi Tsukuda1, Junji Nishi3, Toshihara Yamashita4 and Hiroshi Kawazoe4; 1Tohoku University, Sendai, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 3Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan; 4Kawazoe Frontier Technologies Corporation, Yokohama, Japan.

Proton conduction in phosphate glasses is a historical topic in solid state ionic and glass chemistry because of their potential applications of electrolytes in various devices. A lot of studies have focused on to understand and to improve their proton conductivity. In previous proton conducting phosphate glasses, because the proton carriers were supplied from the residual water that was vaporized and come away from the melt during melting at the temperatures higher than 1000 °C, the proton carrier concentration was limited to 10^9–10^10 cm^-3. We recently developed a proton injection technique that is electrochemical substitution of alkali ions with protons termed as APS. APS enables to achieve extraordinary high proton concentration such as 10^22 cm^-3; therefore, to achieve high proton mobility is only strongly desired in order to realize high proton conductivity.

In this study, we studied the influences of the polymerization degree of phosphate glass network and kinds of alkaline-earth oxides that are typical glass network-modifiers on the proton mobility. As a result, we found that the proton mobility increases with the decreasing polymerization degree of glasses; however, the proton mobility must start to decrease when pyrophosphate ions, P_2O_7^4-, become major component in phosphate network, because the protons are deeply trapped in pyrophosphate ions rather than metaphosphate ions, (PO_3^-). Regarding to the kinds of alkaline-earth oxide modifiers, the proton mobility was higher in the glass containing BaO than the glass containing MgO. The higher proton mobility in the Ba-glass than the Mg-glass was attributed to higher ionicity of the Ba-O bond than the Mg-O bond based on P 2p and O 1s core-level XPS spectra. Based on these understandings, we designed a glass, 36HO_1/2-4NbO_5/2-2BaO-4LaO_3/2-4GeO_2-1BO_3/2-49PO_5/2, and it was prepared by APS using 36NaO_1/2-4NbO_5/2-2BaO-4LaO_3/2-4GeO_2-1BO_3/2-49PO_5/2 as a precursor glass. The proton conductivity of the glass was 1×10^-1 Scm^-1 at 280 °C in dry 5% H_2/N_2, and it was almost constant during keeping at 280 °C over 500 hours. It was also shown that the glass is stable under the condition of fuel cell operation. These properties are favored for the electrolyte in the intermediate temperature fuel cell.

CM02.06.21
Structural Characterization of Oxide Glass-Ceramic Scintillators for Radiation Detection Sarah Lombardo1, 2 and Jason Nadler1; 1Georgia Tech Research Institute, Atlanta, Georgia, United States; 2Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Glass-ceramic nanocomposite scintillators have become an attractive option as radiation detection materials. These materials provide radioisotope detection capabilities at lower cost with improved scalability, stability and mechanical robustness. However, light output required for proper energy resolution is proven a challenge as a result of light scattering from varying refractive indices and crystalline agglomeration present within the non-crystalline glass matrix. Understanding the structure-property relations of oxide glass-ceramic scintillator compositions is crucial for enhancing resolution, as these relations pertain to processing and performance. Analysis of the structure-property relations of oxide glass-ceramic scintillators has been achieved by employing techniques such as scanning and transmission electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy for structural characterization. In addition, photoluminescence and radiation spectroscopy are employed for characterization of performance. These techniques allow for the identification of light output and resolution obtained as a result of heterogeneity, crystal structure, and phase composition present within these non-crystalline materials.

CM02.06.22
Fabrication of High-Dispersed Strawberry-Like P(St-co-MAA)/SiO2: Composite Microspheres and Their Applications in Cementitious Materials Guanzhi Chen1, 2; Yongjiang Xie1, 2; Xinguo Zheng1, 2; Huajian Li1, 2; Quanxiao Dong1, 2; and Shida Li1, 2; 1Railway Engineering Research Institute, China Academy of Railway Sciences, Beijing, China; 2State Key Laboratory of High Speed Railway Track Technology, Beijing, China.

Silica nanoparticles (SiO2 NPs) can be used in cementitious materials to improve their workability and mechanical properties. But avoiding the agglomeration of SiO2 NPs within the cementitious matrix are still the challenges to play the role of them effectively. In this work, the polystyrene-co-methyl acrylic acid (P(St-co-MAA)) latex particles with hydrophilic carboxylic chains grafted from the surface were first fabricated via soap-free emulsion polymerization, and then high-dispersed strawberry-like composite microspheres were prepared with the P(St-co-MAA) latex partially covered by SiO2 NPs through layer-by-layer (LBL) assembly process. The effects of such composite microspheres on the properties of cementitious materials were investigated afterwards.

The surface carboxylic content of P(St-co-MAA) latex particles was measured by conductometric titration. The morphologies of the latex particles and P(St-co-MAA)/SiO2 composite microspheres were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Thermos gravimetric analyser (TGA) and dynamic light scattering (DLS) were employed to characterize the composition and the dispersibility of the composite microspheres, respectively. After adding the composite microspheres into cementitious matrix, the hydration process of the fresh mixture was monitored by cement hydration heat analyzer. Its workability and mechanical properties were tested via conventional methods. The porosity of the hardened specimens was characterized by mercury injection method method.

The results show that the surface carboxylic content of P(St-co-MAA) latex was about 1.5×10^4 mol/g. For the P(St-co-MAA) / SiO2 composite microspheres, SiO2 NPs with the mass ratio about 5.0 wt% were anchored on the latex surface, leaving above 50 % area of the surface uncovered. Such strawberry-like composite microspheres could be easily dispersed in aqueous phase without further treatment where the poly-dispersion index (PDI) was about 0.3. The composite microspheres had no obvious effects on the fluidity of the mortar and the water absorption of the hardened specimen. But it could promote the condensation of the mortar and improve their early compressive strength and flexural strength. Compared to the blank control, the 3d compressive strength of the specimens in which the mass of composite microspheres was 4 wt% of the cement was 5 MPa higher, and the flexural strength
of those was 1 MPa higher. The modified mechanism of the composite microspheres for mortar was proposed.

CM02.06.23
Calorimetric Studies of a New La-Based Metallic Glass Jie Shen and Wei Hua Wang; Institute of Physics CAS, Beijing, China.

We have prepared a La-based MG which exhibits an unique exothermic peak occurring after the glass transition and before the onset of crystallization. The enthalpy change of the La-based MG is large, ~17% of the heat of fusion. Such a large enthalpy change enables the La-based MG to have an increase in the glass transition temperature and the β-relaxation temperature of 17 K and 30 K respectively, and a remarkable increase of the activation energy for the β-relaxation of 71%. The La-based MG exhibits an abnormal α-relaxation which shows no decrease of loss modulus at high temperature. In the stress relaxation and creep measurements, the MG gets a strong retardation with relaxation time extending from 54 s to 480 s and only 2% decrease in length after a high-temperature creep. These thermo-mechanical responses demonstrate the strong nature of its liquid: the fragility index α of the new metallic glass is only 22. The development of this new MG may provide us a new model system for investigating some fundamental issues in glassy field.

CM02.06.24
Amorphous Carbon for Hard Mask with High Etch Resistance Through Bonding Control with Various Doping Elements Min-Woo Jeong, Kun-Tae Kim, Kyung-Tae Jang, Miyoung Kim and Young-chang Joo; Seoul National Univ, Seoul, Korea (the Republic of).

As the area shrinkage of semiconductor devices for high memory density, the high aspect ratio pattern is needed such as 3D NAND flash. To create a vertical pattern with a mask, mask is needed to be thicker for etching it longer. However, a thick mask distorts the shape of the pattern with a shadowing effect. Therefore, it is necessary to have a hard mask that can be made thinner. The vertical structure is fabricated by plasma based dry etching process with hard masks, which have superior etch resistance. Therefore, it is necessary to study the properties of hard mask materials for deeply patterned devices. The hard mask should have higher etch resistant to plasma reactive gas than conventional organic soft mask for deeper patterning. It must also be easily removed after the etching process. These conditions are well satisfied with amorphous carbon, which is the most promising material for hard mask. Carbon has various atomic bonds like sp³ of diamond and sp² of graphite. The difference in carbon bond between the two materials greatly affects the properties such as mechanical and electrical properties. Amorphous carbon is known that the kind of bonding is changed according to doping element and composition. In this study, we have studied how the etch characteristics change with the change of bonding nature of amorphous carbon according to various metal element doping.

Amorphous Carbon (a-C) was deposited on SiO₂/Si substrate by DC magnetron sputter system using graphite solid target for higher purity and lower roughness than common CVD process. Metal element doping was proceeded by using 10 wt% of Si and W pre-doped target. The thin film was analyzed by Raman spectroscopy, XPS and etch characteristics were investigated by ICP etcher. We also examined the mid-range order of the a-C through the radial distribution function (RDF) using the diffraction pattern through TEM analysis. The content of Si and W in a-C was measured by XPS results, 7.39 wt% and 12.2 wt% respectively. As a result of Raman spectroscopy and XPS of doped a-C thin film, the ratio of D peak and G peak (I_D/I_G) and sp³ bonding increased, which means the increase disordered hexagonal graphite structure. Moreover, the I_D/I_G value was further increased when the heat treatment was performed up to 500 °C, which is because carbide is generated more by heat treatment. Because the Si and W form carbide in a-C film, the degree of disorder increased. In addition, when the structure of the thin film was analyzed with RDF, it was confirmed that the sp³ bond was increased with formation carbide. The increased sp³ bonding portion in amorphous C improved etch resistance, which is consistent with the tendency for mechanical performance of diamond like carbon (DLC) having high sp³ bonding. The relationship between mid-range order of doped a-C and its property was confirmed by the microstructure analysis and the measured etch resistance with various doping elements.

CM02.06.25
A String Model for the Boson Peak and Inelastic X-Ray Scattering Data of Amorphous Materials Ernesto Bianchi and Fernando Lund; Univ of Chile, Santiago, Chile.

In a continuum, solid mechanics, approximation, THz vibrations in glasses can be understood as the normal modes of vibrating strings with fixed ends on top of the Debye approximation modes. These strings scatter acoustic waves and, in a multiple scattering formulation, generate an effective (complex) index of refraction, thus describing dispersive, damped waves [1]. The attenuation and velocity dispersion as a function of frequency are qualitatively similar to that observed in glasses through Inelastic X-ray Scattering (IXS); For very low frequencies attenuation grows like frequency squared, consistent with Akhiezer damping. As frequency grows, a frequency to the fourth power behavior takes over, consistent with scattering from small objects (in this case, the strings). Finally, as frequencies around the Boson peak are reached, a new frequency squared behavior appears. The phase velocity is a decreasing function of frequency for low frequencies, and switches over to an increasing function at frequencies around the Boson peak.

The dynamic structure factor S(k,w) corresponding to these acoustic waves is calculated as an explicit function of two variables, wave vector k and frequency w. The resulting formulae provide a specific functional relationship between the Boson peak data and the IXS data. It should be possible to directly test these results, for example with glycerol glass data [2].


CM02.06.26
Cation Glass, Anion Crystal—Disorder and Order in Metal-Sulfide Thin Films Kevin Ye and Rafael Jaramillo; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural disorder in semiconductors is important to characterize reliably because it strongly affects materials performance, for instance by introducing potential fluctuations and electron-hole recombination sites. In a multicomponent material the differing contrast of different elements to particular characterization techniques can lead to misleading and contradictory conclusions about the nature of disorder and even the existence of crystalline volumes. We present a study of highly-disordered Cu-Zn-Sn-S (CZTS) films, deposited by physical vapor deposition at low temperature and post-annealed at different temperatures. We previously reported synchrotron x-ray absorption spectroscopy (XAS) data showing that deposition at low temperature kinetically stabilizes single-phase compositions that are well outside of the narrow solid solution of CZTS at equilibrium [1]. Here we use complementary characterization techniques to understand and quantify structural disorder: XAS (XANES and EXAFS), x-ray diffraction, and transmission electron microscopy. By combining all three techniques and numerical simulations we reach quantitative conclusions about the nature of cation disorder and the kinetics for recrystallization. We find that cations in highly-disordered CZTS are distributed nearly at random while the sulfur anions remain in a well-defined lattice. This phenomenon of cation glass, anion crystal is important to recognize for its signature in different characterization techniques. For optoelectronic devices it may be useful to design light absorbers and windows with widely varying absorption edge energy.
Thermo-Physical Properties of SrO-Al2O3 Binary System Yongxiao Gao1, Zhitao Shan1, Bowen Ruan1, Zhe Zeng1, Haizheng Tao1, Xiujian Zhao1 and Yuanzheng Yue1,2; 1State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China; 2Department of Chemistry and Bioscience, Aalborg University, Aalborg, Denmark.

Owing to the heterogeneous nucleation at the melt-crucible interface, when using the conventional evaluating methods, such as rotating cylinder and maximum bubble pressure method, it is difficult to access the thermo-physical properties in the super-cooled region for poor glass formers. To avoid this phenomenon, here we use the containerless aerodynamic levitator laser-heated technique to measure the thermo-physical properties, i.e., density and viscosity of xSrO-(100-x) Al2O3 (35≤x≤75) binary system in the metastable super-cooled and equilibrium states. According to the average coefficient of thermal expansion (CTE) of melts calculated from the densities, we noticed that the average CTE shows a non-linear and non-monotonic tendency with increasing the content of SrO. In addition, the average CTE of these aluminate melts exhibit two local minimum at the corresponding compositions with the minimum eutectic temperature. At the same time, these eutectic compositions exhibit local maximum of glass forming ability judging from their bigger ratio values of Tg/Tm and higher viscosity at their corresponding melting points.

Design of Non-Oxide Nanocomposite Ceramic Materials with High Fracture Toughness for Extreme Applications Kaijie Ning, Priyatham Tumurugoti, Kade A. McGarrity and Holly Shulman; Inamori School of Engineering, Alfred University, Alfred, New York, United States.

Ceramic materials can possess properties that withstand extreme environments, such as high temperatures, extreme abrasion, ablation, and corrosion. Strong directional bonding, which brings about high elastic moduli and high theoretical strength, also causes these materials to be sensitive to flaws that produce catastrophic failure. The lack of fracture toughness prevents accessing high strength, preventing use of many promising ceramics in load bearing and wear applications. There are a variety of mechanisms that can be implemented to increase fracture toughness. In our work, we focus on developing novel non-oxide nanocomposite ceramic materials targeting improvement of fracture strength through atomic process control of additives, microstructural design, and an advanced 3D reconstruction technique. The boundary phase control, grain shape modification, and second phase reinforcement are of interest for sintering novel structural nanocomposites in order to reveal toughnes mechanism from different scale levels. Preliminary results of powder processing, sintering, microstructural and mechanical characterization of SiC/Si3N4 nanocomposites are reported here. It is expected that the novel designed nanocomposite ceramics would achieve much improved fracture strength compared to the traditional ceramic matrix.

It is reported that negative or no strain rate dependency of the flow stress of metallic glasses appears at high strain rate or low temperature condition[1][2]. We reveal that this curious strain rate dependency is strongly related to the timescale of glass relaxation process from a rejuvenated glass state induced by activation of shear transformation. We use a constitutive model which estimates average residence time of thermal activation process[3]. In the model we assume the relaxation process recovers the activation energy of shear transformation. Our model successfully reproduces the experimental strain rate dependency of flow stress over the wide strain rate and temperature ranges. The negative or no strain rate dependency appears when the timescale of the activation of shear transformation approaches the characteristic timescale of glass relaxation process.


Structure and Properties of Amorphous Thin Films Vary with Nanometric Thickness

International Space Station

as predicted previously, exhibited more 4-coordinated Al sites. These atomistic alterations were expected to change the amorphous thin film’s average effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size control and can deposit conformal and pinhole-free amorphous films of various materials. Amorphous thin films of aluminum oxide deposited by atomic layer deposition method were found to vary structurally as a function of size; thinner films, nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous materials, in contrast to crystalline ones, lack long-range order. Its order decays rapidly with the distance and while the local environment for a particular type of atom is quite similar, it is not identical; these fine changes in the atomistic structure of the materials lead to new and very interesting phenomena which are unique for amorphous materials. Although many aspects of science and technology rely on amorphous materials, much less research is conducted about their structure than on their crystalline counterparts.

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-

References:


Sample-Size and Temperature Effects on Deformation Behavior of Bulk Metallic Glasses

Chandra Sekhar Meduri and Golden Kumar; Texas Tech University, Lubbock, Texas, United States.

Bulk metallic glasses (BMGs) deform plastically through localized shear bands at room temperature. It is well established that shear banding process in BMGs depends on multiple parameters such as, the elastic constants, the sample size and processing, and the testing conditions (temperature, strain-rate, and loading geometry). Studying the effects of these variables and linking them to a unifying flow model is critical for fundamental understanding and potential applications of BMGs. In this work, we study the effects of testing temperature and sample size on nucleation and propagation of shear bands and the fracture surface through bending and tensile testing. Bending experiments show an increase in number of shear bands and plasticity with decreasing temperature. Analysis of fracture morphologies from the high-throughput tensile tests show an increasing contribution of thermal softening (through shear offset) and decreasing contribution of defect development (through coalescence of nanovoids and formation of microcracks) to the final fracture as sample size and/or temperature decreases. The results are discussed in terms of existing models for shear band formation and fracture of BMGs.

Addressing the Achilles' Heels of Amorphous Carbon with Doping—Mechanisms of Thermal and Oxidative Degradation—From Earth to the International Space Station

Filippo Mangolini1, Brandon Krick2, Tevis Jacobs3, Subarna Khanal4, Frank Streller4, J. Brandon McClimon4, James Hilbert4, Somuri Prasad5, Thomas Schaff5, James Ohlhausen5, Jennifer Lukes6, W. Gregory Sawyer7 and Robert Carpick8; 1Texas Materials Institute, Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States; 2Department of Mechanical Engineering and Mechanics, Lehigh
Amorphous carbon materials are used as protective coatings in a wide range of applications owing to their unique mechanical, electrical, and optical properties. However, they suffer from two key environmental limits: insufficient thermal stability, and high reactivity in oxidizing environments. This inhibits their use in many harsh-environment technologies, such as protective coatings for aerospace components, automotive components, advanced manufacturing tools, and next-generation magnetic storage devices. Here we show that doping hydrogenated amorphous carbon films with silicon and oxygen can overcome these environmental limits and we explain the mechanisms by which these benefits occur through fundamental studies, including experiments conducted on the International Space Station.

The thermally-induced structural evolution of silicon- and oxygen-containing hydrogenated amorphous carbon (a-C:H:Si:O) was investigated in situ by X-ray photoelectron and absorption spectroscopy, as well as molecular dynamics (MD) simulations. The spectroscopic results indicate that upon high-vacuum annealing, two thermally-activated processes occur in a-C:H:Si:O: 1) ordering/clustering of sp² carbon; and 2) conversion of sp³ to sp²-bonded carbon. The experimental results are in qualitative agreement with MD simulations performed using the ReaxFF potential. MD simulations also indicate that the higher thermal stability of a-C:H:Si:O compared to hydrogenated amorphous carbon (a-C:H) derives from the lower fraction of strained carbon-carbon sp² bonds in a-C:H:Si:O compared to a-C:H, which are more likely to break at elevated temperatures.

Exposing a-C:H:Si:O to elevated temperatures under aerobic conditions or to the harsh low Earth orbit (LEO) conditions (aboard the International Space Station during the seventh Materials International Space Station Experiments mission) leads to carbon volatilization limited to the near-surface region with the formation of a silica surface layer\(^3\). This prevents the remaining underlying carbon phase from volatilization by reaction with oxygen and/or water in the environment. The incorporation of silicon and oxygen in a-C:H thus enhances the thermo-oxidative stability and resistance to the LEO conditions via a self-protecting route for carbon oxidation by creating an oxygen diffusion barrier. These findings provide a novel physically-based understanding of the superior stability of a-C:H:Si:O in harsh environments compared to a-C:H.


9:45 AM CM02.07.06
Effect of Deposition Rate and Substrate Temperature on Structure and Properties of Sputtered Metallic Glass Thin Films Sachin V. Muley\(^1\), Debaditya Chatterjee\(^1\), Felix P. Lu\(^2\) and Paul M. Voyles\(^3\); \(^1\) Materials Science and Engineering, University of Wisconsin Madison, Madison, Wisconsin, United States; \(^2\) Grainger Institute for Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States.

Physical vapor deposition offers a route to synthesizing glasses with a wide range of thermodynamic and kinetic stability. We have studied the structure and properties of Zr\(_{65}\)Cu\(_{27.5}\)Al\(_{7.5}\) thin films deposited by single target magnetron sputtering as a function of the deposition rate, substrate temperature, and residual pressure of oxygen and water vapor. Films grown starting with a base pressure of 2×10⁻⁸ Torr and low partial pressures of oxygen of 2×10⁻¹⁰ Torr and water vapor of 5×10⁻⁸ Torr exhibited a phase boundary between amorphous and crystalline states as a function of deposition rate and substrate temperature. At a deposition rate of 0.22 nm/s in 3.8 mTorr of process gas (Ar) the films were crystalline at high substrate temperatures (458K, 0.67×Ts/Tg – 498K, 0.73×Ts/Tg), but amorphous at lower substrate temperatures. At a deposition rate of 1.57 nm/s in 3.8 mTorr of Ar, the films were amorphous up to a substrate temperature of 483K (0.70×Ts/Tg). Optimizing over deposition rate and substrate temperature increased the films modulus by 34% and hardness by 11% as compared to liquid-quenched ribbons with same composition, consistent with increased density and improved stability. Fluctuation electron microscopy (FEM) experiments show that the glasses with improved mechanical properties have increased icosaedral medium range structural order. Films grown starting from poorer vacuum (base pressure ~ 5×10⁻¹⁰ Torr) with higher partial of oxygen (2×10⁻⁸ Torr) at 0.22 nm/sec in 3.8 mTorr of Ar were amorphous at substrate temperatures from 295K (0.43×Ts/Tg) to 518K (0.76×Ts/Tg). These observations suggest that enhancing properties and stability in PVD metallic glasses requires optimization of both deposition rate, which governs monolayer residence time, and substrate temperature, which influences surface diffusion. They reiterate evidence from bulk synthesis that glass forming ability is sensitive to incorporation of oxygen. Calorimetric assessment of stability also will be presented.

10:00 AM BREAK

10:30 AM **CM02.07.07**
Fast Dynamics of Metallic Glasses at Low Dimensions Wei Hua Wang; Institute of Physics, Beijing, China.

The dynamics of metallic glasses at low dimensions such as in surface, ultrathin films, nano-scale particles were measured and studied. The dynamics and diffusion with the value of more than 10⁸ times faster than that of bulk are found far below glass transition temperature at the free surface which is more than 100 times faster than that in bulk, higher electrocatalytic activity and unique self-stabilizing catalytic performance over a long-cycling life than the commercial Pt/C catalysts in Pd-based MGs, and generation of the modulated superlattice-like nanostructure modulated nanostructure from the surface to interior, are found. The fast dynamics can be applied to form ultrastable metallic glasses with unique properties at room temperature. The observations have implications for understanding the glassy dynamics, and pave a way for controllable fabrication of unique and sophisticated nanostructure on glass to realize the properties modification.

11:00 AM CM02.07.08
Interfacial Plasticity and Strain Delocalization in Metallic Nanoglasses Jason R. Trelewicz and Bin Cheng; Stony Brook University, Stony Brook, New York, United States.

The ductility and toughness of metallic glasses are classically limited by plastic flow localizing into shear bands, a process which is augmented by the introduction of structural inhomogeneities to produce a more homogeneous plastic response. For example, in metallic glass matrix composites, ductility enhancements have been attributed to the presence of crystallites in the amorphous matrix, although the mechanisms of delocalization relating to shear band nucleation and propagation are still an active area of research. A new class of amorphous alloys that contain amorphous grains separated by “interfaces”, referred to as metallic nanoglasses, have also exhibited the ability to delocalize plastic strain and believed to result from the interfacial regions distributing shear band nucleation. Using molecular dynamics simulations, we explore the process of strain delocalization in nanoglass models produced
via high pressure consolidation of amorphous nanoparticles. Interfaces are identified in the consolidated structures using a new volumetric strain threshold criterion, and generally exhibit a larger free volume and reduced full coalesced fraction relative to the cores of the amorphous grains. Uniaxial tensile simulations are conducted on the nanoglasses with amorphous grain size and relaxation temperature systematically varied to study the conditions for effective delocalization. We find that the presence of interfaces promote distributed plasticity with a grain size effect deriving from preferential localization transpiring within the interfacial regions containing greater excess free volume. Interfacial structural state also plays an important role where relaxation at higher temperatures initiates rejuvenation and in turn, enhanced localization that manifests in the flow curves as a stress overshoot upon the formation of a dominant shear band. Our results demonstrate that finer amorphous grain sizes and interfacial regions with enhanced disorder promote a more homogenous plastic response, thus providing insights into nano-glass deformation that can be translated to alloy design through the consolidation of nanometer-sized glassy particles.

11:15 AM CM02.07.09
Dynamic Mechanical Analysis on the Effect of Room Temperature Aging on Sputtered Zr55Ni25Al20 Metallic Glass Anthony Kwong, Miranda Schwacke and Julia R. Greer; California Institute of Technology, Pasadena, California, United States.

Compared to bulk metallic glasses, the free-volume content is higher in sputtered metallic glasses due to the high cooling rate of the magnetron sputtering fabrication technique. This excess free volume accommodates larger amounts of local shear during deformation and improves the material’s ductility. However, not much research has been done on understanding the impact of room temperature aging on the size and distribution of free volume in sputtered metallic glass.

In our research, we sputtered five μm-thick Zr-Ni-Al onto a Si substrate and used focus ion-beam (FIB) milling to fabricate micro- and nano-sized pillars. The diameter of the pillars ranged from 300 nm to 1.3 μm with heights ranging from 900 nm to 3.9 μm, respectively. Uniaxial pillar compressions were performed on the as-sputtered Zr-Ni-Al. The elastic modulus and yield strength were measured to be 75.5 ± 12 GPa and 2.49 ± 0.24 GPa, respectively. The as-sputtered Zr-Ni-Al was aged at room temperature in a nitrogen dry box for three years and new pillars were fabricated using FIB milling and then tested under uniaxial compression. After aging, the elastic modulus and yield strength increased to 82.5 ± 4.1 GPa and 2.73 ± 0.09 GPa, respectively. To provide insight into this increase in mechanical property, we performed dynamic mechanical analysis (DMA) to determine the storage and loss modulus of the as-sputtered and aged Zr-Ni-Al.

For the DMA experiments, new pillars were fabricated on both the as-sputtered and aged Zr-Ni-Al. These pillars were tested at room temperature at frequencies between 3 and 700 Hz. The peak of the loss modulus corresponds to the activation of β relaxations in the material. For the as-sputtered and aged Zr-Ni-Al, this occurred at a frequency of 440 Hz and 450 Hz, respectively. The higher frequency of the aged metallic glass indicates that the activation energy of the β relaxations is larger. As expected, room temperature aging redistributed the free volume to a more energetically favorable configuration. Thus, even higher energy is required to relax the aged metallic glass. In addition, the magnitude of the loss modulus increased as a function of pillar diameter. The loss modulus ranged from 20 GPa to 100 GPa for pillar diameters ranging between 300 nm to 1.3 μm, respectively. The total free volume in large pillars is greater than that in small pillars, thus resulting in increased loss modulus. The cooperative shear model (CSM) demonstrated that β relaxations are associated with the transition of shear transformation zones (STZs) in an elastic matrix. Utilizing CSM, the volume and activation energy of the STZs can be calculated. These findings elucidate the effect of room temperature aging on sputtered metallic glass and pave the road for future work on quantifying the activation energy and volume of STZs, the rearrangement of which is the mechanism of deformation in metallic glass.

11:30 AM CM02.07.10
Microstructure and Mechanical Properties of Metallic Nanoglasses Prepared by Nanoparticle Consolidation Omar Adjoud and Karsten Albe; TU Darmstadt, Darmstadt, Germany.

Metallic nanoglasses are amorphous materials with microstructural features analogous to nanocrystalline materials, which consist of glassy grains connected by glass-glass interfaces. They can be produced by cold-compaction of glassy nanospheres which are prepared by inert-gas condensation [1,2]. The interfaces are characterized by an excess volume [3], a lack of short range order [4], and a different composition than the glassy grains [5,6].

In this contribution, we present a detailed analysis of microstructure formation of metallic nanoglasses by molecular dynamics simulations. We analyze the atomic structure of the glassy grains and glass-glass interfaces during the consolidation process. Moreover, we discuss the thermodynamics and kinetic stability of anoglasses, structural features of the interfaces, segregation effects and the mechanical response in uniaxial tensile tests. Finally, the computational results are put in the context of experimental findings.


11:45 AM CM02.07.11
Dispersive Diffusion Fit to Heavy-Tail Relaxation in Amorphous Semiconductors and Disordered 2D Materials Matthew Grayson, Jiajun Luo and Lintao Peng; Northwestern University, Evanston, Illinois, United States.

Dispersive diffusion occurs when the diffusion "constant" in the diffusion equation obeys a power law in time. Remarkably, such processes are successful in describing diverse phenomena from dielectric relaxation in glasses to creep in strained polymers to earthquake aftershocks. In the present work two different disordered semiconductor systems - amorphous indium-gallium-zinc-oxide (a-IGZO) and exfoliated 2D black phosphorus (BP) are shown to both obey a variety of dispersive diffusion behaviors, depending upon doping and disorder strength. Transient responses in a wide range of disordered condensed matter systems show a heavy-tail relaxation behavior: the decay time constant increases as time increases, revealing a spectral distribution of time constants. However, the asymptotic behavior of such transients is notoriously difficult to measure due to the extremely rapid decay at short times and the extremely slow and decreasing decay rate at long times. This work introduces a generalized analysis method for arbitrary heavy-tail transients, which accurately fit a finite experimental dataset to one of a continuum of candidate heavy-tail functions. By plotting the transient response versus log-time and taking the derivative, a simple half-maximum line-width analysis of the derivative is shown to predict the asymptotic value within less than 1%. The dispersive diffusion transient fit is a generalized fit that includes the stretched exponential as a limiting case. The line fits and asymptotic predictions are demonstrated using experimental transient responses from historical data on amorphous silicon and amorphous InGaZnO. The remarkable ability to fit heavy-tail transients in the 2D material black phosphorus implies that the low-dimensionality of such crystalline 2D systems suffer from poor screening such that the disorder potential results in behavior that is more akin to dynamics found in amorphous materials.
Sequences of Metastable Phase Formation Determined via Ultrafast Calorimetry

Jörg F. Löfler; Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, Zurich, Switzerland.

Initial phase formation via nucleation and growth plays an important role in the microstructure evolution upon melt solidification. I will report on novel chip-based fast differential calorimetry (FDSC) to determine thermophysical properties at rates of several $10^7$ K/s and thus to reveal the sequence of metastable phase formation during rapid solidification. In such a way we were able to determine new phase transition paths, such as solid-solid phase transformations via melting for a Au-based glass [1]. In addition, with FDSC it is possible to interrupt rapid cooling after a phase transition and then to “up-quench” the frozen structure via heating at ultrafast rates. Using this strategy, we were able to demonstrate for a Mg-based alloy that a transient quasicrystal (QC) phase nucleates first from the melt and then transforms into an equilibrium approximant phase [2]. We assume that such a transition path, which minimizes the free-energy barrier for nucleation, is likely to be a general mechanism for metastable QC-forming systems. We were also able to completely melt the QC phase mixture via suppressing the metastable-to-stable phase transition. In general, FDSC with the corresponding strategy of “up-quenching” a previously frozen structure can generate the discovery of hidden transient phases and thus the construction of metastable phase diagrams. I will show that such studies are not only key to the understanding of crystallization in metallic materials, but are also of great interest in determining nucleation mechanisms in polymeric materials, biological systems, and pharmaceutical substances.


Are Hints about Glass Forming Ability Hidden in the Liquid Structure?

Juan Wang1, Ryogo Suzuki1, Anupriya Agrawal1, 2 and Katharine Flores1, 2; 1Mechanical Engineering and Material Science, Washington University in St. Louis, St. Louis, Missouri, United States; 2Institute of Materials Science and Engineering, Washington University in St. Louis, St. Louis, Missouri, United States.

There has been concerted effort to correlate high temperature structure and dynamics of liquids with glass forming ability of alloys. Despite intense interest, identifying the structural origin of glass forming ability in metallic alloys remains a challenge due to the difficulty of describing the evolution of the long-range disordered structure from the liquid. Here, we report the cluster variance in the liquid as a potential parameter to predict glass formation. We have used molecular dynamics simulations with embedded atom method (EAM) potentials to simulate the quenching of metallic liquids resulting in crystalline, glassy or composite phases. We observe that variance in cluster fraction correlates with crystallization and hence with glass forming ability. We will show that this correlation persists in multiple binary and ternary systems. Further, it is independent of the dominant cluster type as well as the type of EAM potential used. Moreover, EAM potentials used were not custom fitted to get accurate liquid properties.

We also validated our molecular dynamics prediction of glass forming compositions with experiments. Using a high-throughput, direct laser deposition processing method to experimentally evaluate glass formation, the glass forming ability of Zr-Cu, Zr-Ni-Al, Zr-Cu-Al, and Zr-Cu-Ti was consistently found to be greatest where the variance in the fraction of the dominant cluster in the simulated liquid is minimized. The laser deposited alloy libraries further enabled an investigation of the mechanical behavior across the composition range using nanoindentation. Correlations of these properties with the simulated structures will also be discussed.

In Situ Observation of Spinodal Decomposition Process in Silicate Glass

Katsuaki Nakazawa1, Shin-ich Amma2 and Teruyasu Mizoguchi1; 1The University of Tokyo, Meguro-ku, Japan; 2New Product R&D Center, Asahi Glass Co., Ltd., Yokohama, Japan.

Mechanical and optical properties of glasses can be modified by phase separation phenomena. The number of phases, sizes of phases and especially morphologies of phases affect those properties. Morphologies of phases deeply depend on the volume fractions of the separated phases. If the volume fractions of two phases are equal, interconnected structures are fabricated, whereas non-equal volume fractions fabricate the droplet structures. The morphologies of the interconnected and droplet structures can be clearly discriminated. The interconnected structure is composed of two tubular phases which three-dimensionally entangle. The droplet structure is composed of spherical minor phases dispersed in the major phases. The process of phase separation is divided into three stages: initial, middle and final stages. In the case of spinodal decomposition, interconnectional and
amorphous ice, and liquid water observed in experiments. However, amorphous ices are quantum systems and therefore the zero-point vibration free (like states) [2]. In most cases, classical molecular dynamics (MD) simulations are able to reproduce qualitatively many of the transformations between ice, The details of the temporal changes and the coarsening of those phases will be discussed in my presentation.

Theoretical Study on Polymorphic Transformations in Amorphous Ice Rodion Belosludov1, Kirill Gets2, Ravil Zhdanov2, Vladimir Belosludov2 and Yoshiyuki Kawazoe1; 1Institute for Materials Research, Tohoku University, Sendai, Japan; 3Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk, Russian Federation; 4New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan.

Polymorphism, i.e. the presence of more than one amorphous state or phase in amorphous solids and liquids, is of fundamental importance in materials science [1]. Experimental and theoretical studies on very-high-density (VHDA), high-density (HDA) and low-density (LDA) ices have raised questions regarding the nature of the transformation between the amorphous forms of ice. One of the main questions is whether the amorphous ices are thermodynamically continuously connected with liquid states and can be regarded as vitrified liquids (glassy states) or distorted crystalline phases (crystal-like states) [2]. In most cases, classical molecular dynamics (MD) simulations are able to reproduce qualitatively many of the transformations between ice, amorphous ice, and liquid water observed in experiments. However, amorphous ices are quantum systems and therefore the zero-point vibration free energy is large and at low temperatures, it should be taken into account in free energy calculations. The description of various amorphous phases of ices has been performed on a molecular level in order to study the nature of amorphous polymorphism in a water system [3]. The models of very high-, high- and low-density amorphous (VHDA, HDA and LDA, respectively) ices have been modelled and the pressure-temperature phase diagram was constructed for water in the low temperature region using the combination of MD and lattice dynamics (LD) approaches. It was shown that the transformation between the amorphous phases (at positive pressure LDA → HDA, LDA → VHDA, and at negative pressure HDA → VHDA) is sharp and is a real phase transition in the classical sense at low temperatures. At positive pressure the transformation from the metastable phase HDA to the thermodynamically stable phase VHDA is a continuous transition due to kinetic impediment.

REFERENCES

SESSION CM02.09: Relaxation of Glasses
Session Chairs: A. Lindsay Greer and Robert Maass
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 200

8:00 AM %CM02.09.01
Metallic Glasses—Relating Mechanical Properties to the Relaxation Spectrum A. Lindsay Greer; Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, Cambridge, United Kingdom.

Thermomechanical processing (TMP) of metallic glasses (MGs) [1] can take them to states of higher or lower energy, describable in terms of higher or lower fictive temperature \( T_f \). Recently, there has been particular interest in achieving extremely high values of \( T_f \), as the corresponding glasses are expected to show increased plasticity [2]. This presentation moves on to consider how \( T_f \) itself is an inadequate measure. Glasses show a relaxation spectrum as a function of temperature on heating, seen, for example, in the shape of the energy-absorption peaks in dynamic mechanical analysis, or of the sub-\( T_g \) (glass-transition temperature) exothermic peaks in differential scanning calorimetry. In this spectrum, \( \alpha \)-relaxation relates to the formation of different glassy states on cooling at different rates, and describes processes occurring near \( T_g \), \( \beta \)-relaxation occurs below \( T_g \) and there are yet further processes at lower temperature [3]. We examine how the shape of the relaxation spectrum can be tailored by TMP, and how this affects the properties of MGs. We show that, for MGs with a relatively low \( T_g \) and comparing near-ultrastable with higher-energy states, the distinction between \( \alpha \)-relaxation and sub-\( T_g \) \( \beta \)-relaxation can become blurred. By combining processing techniques, for example annealing with cryogenic thermal cycling [4], one can find that a glass is simultaneously more and less relaxed: with higher hardness, yet easier onset of plastic flow. Such combinations are of clear interest in achieving more uniform plastic flow, one of the most important aims for MGs. In explaining such combinations, it is relevant to consider the heterogeneity of the MG, possibly describable as soft-spots in a comparatively rigid matrix. We consider how novel TMP may improve the properties of MGs. We consider how state-of-the-art structural characterization and atomistic modelling can assist in developing a fundamental understanding of how MG properties can be changed by TMP. And we make comparison with other families of glassy materials.


8:30 AM CM02.09.02
Topological Control on Glass Relaxation Xin Li1, Yushu Hu1, John C. Mauro2, Morten Smoedskjær3 and Mathieu Baechy4; 1University of California, Los Angeles, Los Angeles, California, United States; 2Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; 3Department of Chemistry and Bioscience, Aalborg University, Aalborg, Denmark.

Understanding, predicting, and controlling glass relaxation is of primary importance for the manufacturing of substrate glasses used in display applications, as any small variation in volume can result in undesirable pixel misalignment. However, no clear atomistic mechanism of structural and stress relaxation is available to date, which limits our ability to identify optimal glass compositions featuring low relaxation. Here, based on molecular dynamics simulations, we study the relaxation of a series of alkali-free calcium aluminoislate (CAS) and sodium silicate (NS) glasses with varying compositions. We observe that selected glass compositions exhibit minimal relaxation. We investigate the structural origin of this behavior by means of topological constraint theory. Based on this analysis, we demonstrate that minimal relaxation is achieved for isostatic glasses, which are both free of eigenstress and floppy modes. This highlights the crucial role of the atomic topology in controlling the propensity for relaxation.

8:45 AM CM02.09.03
Elastic Properties and Structural Relaxation of a Chain Like Polymer Manon Heili and John Kieffer; University of Michigan, Ann Arbor, Michigan, United States.

We investigate the structural reorganization process in a chain-like polymer, polyvinylidene fluoride (PVDF). A unique optical setup is used combining a miniature tensile tester placed into the optical path of a Brillouin light scattering (BLS) system, to probe the elastic properties of a sample while it is uniaxially strained. BLS yields the adiabatic moduli of the materials, while their isothermal moduli are derived from the measured stress-strain curves. This two-pronged probing approach yields data, which upon detailed analysis provides for unprecedented insights into the distribution of relaxation times associated with various Maxwell elements, as well as evidence for visco-elastic property changes that require descriptions beyond these simple models.

Upon straining, elastic moduli of the polymer drop instantaneously. However, while maintained at a constant strain, the material undergoes stress relaxation during which the load necessary to maintain this elongation decreases. During stress relaxation, both the adiabatic and isothermal moduli reduce, leaning towards the unstrained values. The structure indeed rearranges to optimize molecular packing and maximize the non-bonding interactions. A thermodynamical approach is proposed to correlate the anelastic moduals with the entropic aspects of the structural changes for this polymer.

9:00 AM CM02.09.04
A Microscopic Description of the Anelastic and Structural Relaxation of Metallic Glasses Tianjiao Lei1, Luis Rangel DaCosta1, Yonghao Sun1, 2, A. Lindsay Greer1, Ming Liu1, Zhen Lu1, Wei Hua Wang2 and Michael Atzmon1, 4; 1Materials Science and Engineering, University of Michigan-Ann Arbor, Ann Arbor, Michigan, United States; 2Institute of Physics, Chinese Academy of Sciences, Beijing, China; 3Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 4Nuclear Engineering and Radiological Sciences, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Metallic glasses (MGs) possess high strength and elastic limit, but they also exhibit little macroscopic ductility due to shear band formation. Because of the disordered atomic structure, it is challenging to define defects that accommodate deformation in MGs. From observations in physical analogs, these defects have been identified as shear transformation zones (STZs), which are dissipative and thermally activated [1]. At small strains, STZs are isolated and can be reversed due to back-stress in the elastic matrix upon removal of the applied stress, which results in anelastic behavior. Recently, Ju et al. obtained a quantized hierarchy of STZs for an Al-based MG from quasi-static anelastic relaxation measurements [2]; the volume difference between STZs corresponding to adjacent peaks in the time-constant spectrum equals that of one Al atom. The volume fraction of potential STZs, i.e. atomic clusters capable of shear transformation, increases with size. After annealing at 110 °C for 1 hour, the number of potential STZs decreases, while their time constants increase. Notably, a detailed description of structural relaxation emerges: its dominant effect is on the largest, and therefore slowest, STZs. Cycling to liquid-nitrogen temperature, observed to induce rejuvenation [5], only leads to subtle changes in the anelastic behavior. The effect of the composition x above will be discussed in the context of observations on its effect on ductility [4].


9:15 AM CM02.09.05
β-Relaxation and Its Correlations with Properties in Metallic Glasses Hui Yang Bai, Peng Luo and Wei Hua Wang; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Metallic glasses (MGs) with structures viewed approximately as dense random packing of hard spheres offer a simple but effective model system for the study of relaxations and related issues in glass science. β-relaxation in MGs has been found to be closely bound up with the structural characterstics, formation, glass transition, deformations or flow behaviors, physical and mechanical properties, crystallization, and stability of MGs. We present the state of the art research on various aspects of the β-relaxations in model metallic glass systems and demonstrate the critical importance of these fast relaxation behaviors in understanding deformation, flow behavior, aging and rejuvenation, mechanical and physical properties of metallic glasses. We illustrate that it is an attractive prospect to incorporate the dynamic relaxations insights into the design of MG materials with extraordinary properties.

Reference
Limitations on Localized Motions in Glass-Forming Liquids—A Dynamic Light Scattering Study


The structural relaxation in glass-forming liquids is characterized by a two-step decay process. A rather fast initial relaxation (often referred to as the beta-relaxation) occurs at early times as a result of localized motions that are globally restricted. As a result of this partial decay, the dynamic structure factor displays an intermediate plateau known as the non-ergodic level. At a longer timescale, the remaining structure is able to relax globally through the so-called alpha-relaxation whose relaxation times scales with the liquid's viscosity.

Here, we review dynamic light scattering measurements of the dynamic structure factor in a variety of glass-forming liquids spanning a wide range of fragility indices, both fragile molecular liquids and strong network-forming oxides for which a careful determination of the non-ergodic level has been made. We show that this plateau level increases with decreasing fragility implying that strong network-forming liquids tend to experience less localized structural arrangements than their molecular liquid counterparts.

The Formation of Ultrastable Metallic Glasses on Cold Substrates

Peng Luo, Hai Yang Bai and Wei Hua Wang; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Vitrification from physical vapor deposition is known to be an efficient way for tuning the kinetic and thermodynamic stability of glasses and significantly improve their properties. There is a general consensus that preparing stable glasses requires the use of high substrate temperatures close to the glass transition one, Tg. Here, we challenge this empirical rule by showing the formation of Zr-based ultrastable metallic glasses at room temperature, i.e., with a substrate temperature of only 0.43Tg. By carefully controlling the deposition rate, we can improve the stability of the obtained glasses to higher values. In contrast to conventional quenched glasses, the ultrastable MGs exhibit a large increase of Tg of ~60 K, stronger resistance against crystallization, and more homogeneous structure with less order at longer distances. Our study circumvents the limitation of substrate temperature for developing ultrastable glasses, and provides deeper insight into glasses stability and their relaxation dynamics.

References

Recent Insights into Thermo-Mechanical Energy Storage in Metallic Glasses

Robert Maass; Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Macroscopic properties of metallic glasses, such as Young’s modulus, plastic strain at failure, fracture toughness, corrosion resistance, or the magnetization behavior depend on the structural state of the glass. This has inspired intense research efforts focusing on the control of structural modifications in glasses that are often quantified by the stored excess enthalpy relative to an as-cast reference, rather than by the precise changes of the atomic structure.

Particularly, high enthalpy states have attracted strong interest since they improve the commonly limited room temperature ductility of metallic glasses. In this talk, we will highlight our recent efforts in this topic, paying attention to three different methods on how to store excess enthalpy in monolithic metallic glasses, including a mechanical, thermo-mechanical, and a purely thermal method. Specifically, this means we will discuss 1) how an alternating elastic load leads to energy storage and how this translates to nanoscopic property fluctuations, 2) how alternating elastic loading during cooling to cryogenic temperatures reveals a low temperature loss process that is accompanied by energy storage, and 3) how ultra-fast heating can lead to significant enthalpy storage of initially very relaxed glasses. The latter approach will be combined with in-situ x-ray measurements and atomistic simulations. Our results are discussed in terms of possible underlying mechanisms reflected in the global response.
Atomic Imprinting into Metallic Glasses

11:45 AM CM02.10.03

Spray Drying of Amorphous Nanoparticles

Mathias Steinaecker and Esther Amstad; EPFL, Lausanne, Switzerland.

Amorphous materials can have distinctly different properties compared to their crystalline counterparts. These include different dissolution rates or higher catalytic activity. Additionally, amorphous materials can serve as transient precursors for the formation of certain crystalline materials such as CaCO3. Certain materials have a low propensity to crystallize and hence, they can easily be processed into amorphous structures. Other materials have a high propensity to crystallize and are therefore extremely difficult to process into amorphous structures. To process these materials into amorphous structures without using large quantities of crystallization inhibitors, their crystallization must be kinetically arrested during early stages of their formation. This can for example be achieved through rapid cooling of melts. However, this method cannot be employed to process thermally labile substances that decompose before they melt. To overcome this limitation, we developed a microfluidic spray drier that produces small droplets that possess a very high specific surface area and hence dry very quickly. We use surface acoustic waves to produce droplets in the range of 1-10 um. The atomizer can process aqueous and non-aqueous solutions containing organic and inorganic reagents. The aerosol droplets are rapidly dried in a dedicated drying unit and the dry particles are subsequently deposited on a substrate to analyze the influence of the processing parameters on their structure and morphology.

In this talk, I will demonstrate that materials can be made amorphous if processed in sufficiently small drops that dry quickly, even if the material possesses a high propensity to crystallize and even if it is processed from low viscosity solutions where the mobility is high. I will present the influence of the formation time and processing conditions on the structure and composition of different amorphous materials, including drugs, and inorganic materials and how this knowledge can be used to produce materials with unusual structures and compositions.

11:30 AM CM02.10.04

Processing-Property Relationship for Additive Manufacturing of Metallic Glasses

Punnathat Bordeenithikasem and Douglas Hofmann; NASA Jet Propulsion Laboratory, Pasadena, California, United States.

Additive manufacturing (AM) or 3D printing is a disruptive technology that is revolutionizing the manufacturing industry. Metallic glasses (MGs) are considered for use in metal AM due to their desirable mechanical properties and high cooling rates achieved through the printing process. To ensure that printed MG parts are suitable for their intended applications, a more robust understanding of the processing-property relationship for AM of MGs must be developed by the scientific community. In this presentation, we investigate the feedstock purity, oxidation, and printing parameters on the mechanical and wear properties of printed MG parts, with direct comparisons to cast MG samples.

11:45 AM CM02.10.05

Atomic Imprinting into Metallic Glasses


Molding and imprinting, which are among the oldest and most widely used manufacturing techniques, have recently regained scientific interest with the demonstration of nanomolding and nanoimprinting as surface functionalization methods. Typically, imprinting involves the embossing of a hard mold into a soft material. Due to the convenient adjustability of their degree of softening, thermoplastic polymers had been the material class of choice for most imprint procedures. Metallic glasses, however, have recently been identified as ideal moldable materials, gaining popularity since they combine favorable mechanical and electrical properties. They are particularly promising for small features sizes since their lack of intrinsic structural order with potentially atomic-sized flow units suggests that they may have the ability to conform to a mold’s shape even on atomic length scales. In this presentation, we demonstrate that thermoplastic imprinting of a metallic glass can reproduce surface features with sub-angstrom accuracy through the replication of terraces from a strontium titanate single crystal surface separated by steps of unit cell height as template. The molded metallic glass replicates the ‘atomic smoothness’ of the strontium titanate, with identical roughness to the one measured on the mold even after multiple usages of the mold and with such molded metallic glass surfaces exhibiting an exceptional long-term stability of years. By providing a practical, reusable, and potentially high-throughput approach for atomic imprinting, our findings may open novel applications similar in magnitude to the development of nanoimprinting two decades ago.

SESSION CM02.11: Complex Non-Crystalline Solids

Punnathat Bordeenithikasem and Douglas Hofmann; NASA Jet Propulsion Laboratory, Pasadena, California, United States.

1:30 PM CM02.11.01

Computational Design of Lightweight Structural Materials with Triply Periodic Minimal Surfaces

Zhao Qin and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural materials found in nature, such as wood, bone, insect forewings, bee hive and bird beak, synergistically combine strength, stiffness and toughness with lightweight. In contrast, most manmade engineering materials do not have such multifunctional features. Among many biological materials, the ones with lightweight foam structures serve good examples to provide a variety of mechanical supporting, thermal conservation and impact shielding functions in the animal body and their external protections. Many of the basic building blocks of these lightweight, elastic, and highly dissipative materials can be categorized by triply periodic minimal surfaces (TPMS), such as structures so-called gyroid and Schwarz’ diamond, etc. TPMS have the symmetries in a similar way as crystals but they are composed of a single surface instead of 3D blocks, making their structure and mechanics unique. We try to explore the general mathematical function of TPMS and quasi-TPMS structures and use them as the input geometry to generate solid materials with innovative lattice structures. We theoretically investigate the mechanical property of these structures by using finite element method and molecule dynamics at the different scale levels and combine the modeling work with 3D printing to develop a technique that is capable of producing materials with lightweight
TPMS structures with highly predictive material functions in a consistent and reproducible way. We discover that the structural geometry plays a dominating role in governing the scaling laws of the mechanics of the material density. Our study suggests that these structures can be used as templates to design and make the 3D forms of many 2D materials including graphene, yield structures of 4.6% the density and 10 times the strength of mild steel. We expect such TPMS structures to have high stiffness, toughness, thermal conservation and impact tolerance, as well as lightweight, giving the material a full potential for protection with energy efficiency for production and transportation.

1:45 PM CM02.11.02
Soft Fibrous Materials with Inter-Fiber Adhesion Catalin Picu, Vineet Negi and Ahmed Sengab; MANE, Rensselaer Polytechnic Institute, Troy, New York, United States.

Many soft materials of biological and industrial interest are composed from nanofibers. In such cases, inter-fiber adhesion may produce fiber bundling and organization on scales larger than that of individual components. A type of network structure, entirely stabilized by adhesion, which was not described previously in the literature, emerges. We describe such structures and identify the range of system parameters in which they are expected to occur. Further, we study their mechanical behavior and observe a broad range of tunable properties, including softening in tension, large strain range in which the structure responds linearly to applied strains, and adhesion-dependent elastic moduli. We consider systems with permanent cross-links and systems in which fibers are not cross-linked but interact adhesively and by excluded volume interactions. The application of these results to collagen structures and carbon nanotube buckypaper are discussed.

2:00 PM CM02.11.03
Theoretical and Experimental Investigation of Haze in Transparent Aerogels Lin Zhao1, Elise M. Strobach1, Bikram Bhatia1, Sungwoo Yang2, Amy Leroy1, Lenan Zhang1 and Evelyn N. Wang1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

Transparent aerogel materials integrated in high-performance glazing units hold great promise to reduce building heat loss and improve indoor thermal comfort because of their ultra-low thermal conductivity. One of the primary challenges preventing the adoption of aerogels in windows is their poor visual experience. While the inherent porous structure is vital to suppress heat loss, the refractive index mismatch between the solid skeleton and air causes visible light to scatter and give rise to haze that degrades the contrast of an image when viewed through the aerogel. Previous studies on haze in aerogels relied on direct experimental characterization with little understanding of the underlying mechanisms. In this work, we investigate the haze of transparent silica aerogels using experimental measurement as well as theoretical modeling. We developed a radiative transfer model that can predict the diffuse transmittance, total transmittance, and haze of an aerogel based on its physical properties, i.e., density, mean particle size, and thickness. To validate the model, we fabricated aerogel samples with two different chemical precursors with a wide range of transparency and haze. Comparison of model predictions with experimental results measured using a UV-Vis spectrophotometer showed good agreement across the entire visible spectrum. We then used the validated model to perform a parametric study of haze and found that the haze is most sensitive to the mean particle size. Smaller particle size not only reduces the haze at a given aerogel thickness but also weakens its dependence on thickness. In addition, we developed a complementary approach that prescribes the set of aerogel properties required to achieve certain haze/transmittance targets. We believe this work advances the fundamental understanding of haze in a wide range of transparent porous materials and could help guide material development to achieve optimal optical performance.

2:15 PM CM02.11.04
On the Shape and Size of Voids in Ultra-Large Models of Hydrogenated Amorphous Silicon—A First-Principles Study Duraga P. Paudel1, Raymond Atta-Fynn2, David Drabold3 and Parthapratim Biswas1; 1Department of Physics and Astronomy, The University of Southern Mississippi, Hattiesburg, Mississippi, United States; 2Department of Physics, University of Texas, Arlington, Arlington, Texas, United States; 3Department of Physics and Astronomy, Ohio University, Athens, Ohio, United States.

We present an ab initio study of hydrogen microstructure in pure and hydrogenated amorphous silicon with particular emphasis on the shape and size of voids and the dynamics of hydrogen atoms inside the voids. By using ultra-large models of a-Si, obtained from classical molecular dynamics simulations, with a realistic volume density of voids of 0.1%~0.3%, the dynamics of Si (and H) atoms on the surface of the cavities are studied and their effects on shape and size of the voids are examined using first-principles density-functional calculations. The resulting changes (from the ab initio calculations) are compared with the corresponding data obtained from total-energy relaxation using the Stillinger-Weber potential. The size and shape of the voids are analyzed by examining the three-dimensional distributions of Si/H atoms on the surface of voids using the convex-hull approximation of the void regions and computing the radius of gyration of the corresponding convex-hull regions. A comparison of our results with those obtained from the small-angle x-ray scattering (SAXS) measurements of a-Si/a-Si:H in the Guinier approximation is also discussed.

2:30 PM CM02.11.05
Recent Advances in Thermoplastic Fabrication of Metallic Glasses Golden Kumar and Zhonglue Hu; Texas Tech University, Lubbock, Texas, United States.

Thermoplastic embossing with metallic glasses is considered as a solution for scalable manufacturing for metallic micro- and nano-structures. Despite its potential, embossing faces major challenges such as, limited aspect-ratio, expensive and non-reusable templates, inability to transfer nanostructures to materials other than metallic glasses etc. Significant advances have been made in recent years to overcome these barriers. For example, by reversing from embossing to drawing, assembled nano-tips, nano-wires, and nano-tubes with aspect-ratios exceeding 1000 can be fabricated inexpensively. These nanostructures can be transferred to plastics, semiconductors, quartz, or other metals. Macroscopic structures obtained by machining can be downsized to nanoscale features without using lithography by manipulating the viscous, capillary, and adhesive stresses. The templates can be non-destructively separated from metallic glasses by minimizing the thermal expansion mismatch. Drawing approach can be readily adapted for high-throughput fabrication and testing of nanoscale test specimens, enabling rapid screening of size-effects in mechanical, thermal, and electrical behavior. Recent progress and future directions in thermoplastic fabrication and nanoscale testing of metallic glasses will be discussed.

2:45 PM CM02.11.06
Atomistic Simulations of Amorphous Functional Materials by Combining Machine Learning and DFT Volker Deringer; University of Cambridge, Cambridge, United Kingdom.

Understanding the links between atomic structure, chemical bonding, and macroscopic properties in amorphous materials is a formidable task. Quantum-mechanical atomistic simulations, prominently based on density-functional theory (DFT), have played important roles in this - but are computationally expensive, and can describe complex solids only in small model structures. Novel interatomic potentials based on machine learning (ML) have recently garnered a lot of attention in the computational physics community, as they achieve close-to DFT accuracy but at only a fraction of the cost.
In this talk, I will argue that ML-based interatomic potentials are particularly useful for studying amorphous solids, and that they can be combined with established DFT methods for gaining new insight into this important materials class. I will first describe a Gaussian Approximation Potential (GAP) for amorphous carbon [1], with a brief introduction to the underlying theoretical framework [2], and a special view on what is needed to validate potentials for the amorphous state. I will then present an application to porous and partly "graphitized" carbon structures, which are relevant for applications in batteries and supercapacitors [3]; this includes a new ML strategy for simulating the movement of Li-ions in such materials [4]. Finally, I will present very recent work on amorphous silicon (a-Si), another prototypical non-crystalline material, where ML-driven large-scale simulations have allowed us to generate structural models in good agreement with experimental findings [5], again making steps toward the routine and realistic atomistic modeling and understanding of the amorphous state.

CaO-Al₂O₃ glasses with different CaO content (45-70%) and increases with electron concentrations.
4. The electrical conductivity in C12A7:e glass is enhanced over 5 orders of magnitude by annealing around Tg. No such a pronounced conductivity change has been reported as far as we know.
5. The work function of C12A7:e glass measured by UPS was 3.0eV, which is comparable to metal Li and Ca, but chemically stable.
6. No significant difference in X/neutron RDFs was noted between e-free C12A7 and e-doped C12A7 glasses but striking difference was observed by Resonance Raman scattering.

We explain some of these results by ab initio MD simulation (PNAS 2016) and propose electride glass is a novel type amorphous semiconductor.

4:30 PM CM02.12.04

In this work we characterize the viscoelastic properties of a new class of thermoplastics called polyrotaxane glasses. The polyrotaxane glass macromolecules comprise a polyethylene glycol (PEG) chain threaded by many α-cyclodextrin beads displaying modifiable organic functional groups. X-ray diffraction and calorimetry studies confirm the amorphous nature of these materials. Above the glass transition temperature (Tg), the local cooperative motions of the polyrotaxanes can be probed by various rheological and mechanical techniques. These local motions appear to cease on experimental time scales at Tg, yet secondary relaxations persist even in the apparently frozen state as the material continues to reduce free energy away from equilibrium. We elucidate the effect of chain length and bead density on the fragility and glassy dynamics of these polyrotaxane materials. The fragility of the glasses, which is determined by the extent to which viscosity deviates from the ideal Arrhenius temperature relationship due to the ceasing of local motions as Tg is approached, is characterized by rheological studies above the Tg. Below the Tg, information about the secondary relaxations is obtained by dynamic mechanical analysis. These studies bring us closer to realizing applications for these systems by expanding the scope of our understanding of their mechanical behaviour across a wide range of temperatures and frequencies.

4:45 PM CM02.12.05

Organosilica with bridging organic groups are of great interest in constructing porous materials for liquid chromatographic supports, catalysts, and adsorbents for hazardous materials, non-porous coatings to protect against corrosion or permeation, modified surfaces for composites, and even sunscreens based on nanoparticles bearing bridging organic chromophores to absorb ultraviolet light. While much has been learned of the influence of the bridging group on porosity, far less is known of its effect on the mechanical properties of the amorphous materials. To this end, we have prepared a wide range of organosilica materials as monolithic forms that permit their analysis by mechanical characterization using a Universal testing apparatus and thermal-mechanical properties by dynamic mechanical analyses. Organosilicas with bridging groups that include rigid aromatics, flexible alkynes, and heteroatom functionalized bridges were prepared by sol-gel polymerizations and air dried to afford monolithic xerogels for mechanical testing.
Lithium ion batteries have demonstrated their importance in portable electronics and as alternative to fossil based portable energy in automotive applications. This importance is expected to continue at least in the near and intermediated future. However, in the longer term electrode materials will need improved capacity and charge/discharge rates. As new anode and cathode materials are developed they are typically screened for advantageous properties by assembly into a working battery. This typically involves film fabrication from a mixture of conductive material (e.g. carbon), a binder (e.g. polyvinylidenefluoride), and the active material of interest. How this film is cast onto the current collector, the ratio of the individual components of the film, the drying procedure for the film and the final assembly of the cell can significantly alter the performance of the battery.[3,4] In order to avoid misleading information about the effectiveness of a novel active material many cells are required to validate findings.

Here we present micro-pipet measurements[5,6] which demonstrate the suitability of the technique for probing lithium ion battery materials. Specifically, we probed dispersions of active materials to determine the oxidation and reduction potentials, and the charge capacity of the material. Data obtained on candidate materials by the micro-pipet method was compared to coin cell measurements, to critically assess this technique for characterization of active battery materials.

References:

8:45 AM CM03.01.02
In Situ/Operando Soft X-Ray Spectroscopy of Interfacial Processes in Energy Materials and Catalysis
Yi-Sheng Liu, Liang Zhang and Jinghua Guo; Lawrence Berkeley National Lab, Berkeley, California, United States.

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Synchrotron radiation based x-ray spectroscopic techniques, especially in-situ/operando capabilities, offer unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray characterization technique offers an opportunity to uncover the phase conversion, chemical environment change of elements and other very important information of solid/gas and solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices.

We will present a number of the experimental studies that successfully revealed the catalytic and electrochemical reactions in real time, e.g. solid (Au film)/liquid (water) electrochemical interface, Mg-ion and Li-S batteries, and solid-state hydrogen storage materials [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectra characterization techniques provide the unique information for understanding the real reaction mechanism.

References:

9:00 AM CM03.01.03
Enabling Ultrafast Interfacial Li-Transport in Layered-Oxide Cathodes
Bo-Hun Wen, Ping-Chun Tsai, Menghsuan S. Pan and Yet-Ming Chiang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In order to design electrode materials for optimal combinations of energy and power, it is essential to understand kinetic barriers at all applicable length scales and over a wide range of state-of-charge. Here, using a recently developed single-electrode-particle characterization method,1 we investigate the rate-limiting transport mechanisms in NMC and NCA cathodes. EIS and PITT measurements have been performed on single secondary particles of ~25 μm size, as a function of charge voltage and liquid electrolyte composition. We find that with increasing charge voltage, transport is increasingly limited by surface reaction kinetics; thus increasing the exchange current density is critical to obtaining high capacity utilization at high voltage. Upon performing the single-particle measurements in electrolytes containing salts with different anion groups, we find that electrolytes containing LiTFSI salt have, surprisingly, an order of magnitude higher exchange current density compared to electrolytes containing LiPF6 salt, and that this improvement is retained to high charge voltages. The improved interfacial kinetics lead to a significantly higher materials utilization during fast charge/discharge, in both the single-particle measurements and in experiments on macroscopic composite electrodes. Possible origins of the strong anion species dependence of interfacial kinetics, and interfacial characterization in these systems, will be presented.

This work was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012583. P.-C. Tsai thanks the Ministry of Science and Technology, Taiwan (MOST 104-2917-I-006-006), for financial support.

References:
Interfacial Studies of the Solid Electrolyte Interphase Hans-Georg Steinerueck1, Chuntian Cao1,2, Iwnetim I. Abate1,2 and Michael F. Toney1; 1SSRL Materials Science Division, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 2Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

The solid electrolyte interphase (SEI) is an interfacial layer formed on lithium ion battery (LiB) anode surfaces due to electrolyte decomposition at low potentials outside the electrolyte’s electrochemical stability window, and is a major source for capacity losses. Due to its electrically insulating and solvent diffusion prohibiting nature, its growth is in principle self-limiting. The ideal SEI can thus prevent further decomposition once formed, while allowing for ion conduction. However, in real systems, where electrodes experience volume and morphological changes, continued SEI growth renders LiB cyclability issues. Despite extensive research efforts to investigate the SEI, open questions still remain. These include the SEI formation processes, the SEI composition and thickness, as well as the structure-function relationship to the electrochemical cycling performance.

In a reductionist approach, we utilized simple and well-defined model systems to study SEI formation, growth, and evolution, in order to obtain an atomic scale fundamental understanding of the occurring processes. We have combined in situ x-ray reflectivity (XRR) and ex situ x-ray photoelectron spectroscopy (XPS) to probe the structure and chemistry of the SEI on two different substrates, i.e. oxide terminated crystalline silicon (Si) and pristine silicon carbide (SiC). We used various electrochemical cycling conditions, including galvanostatic, cyclic voltammetry and potential holds, for different electrolytes, such as lithium hexafluorophosphate (LiPF6) in ethylene carbonate (EC)/dimethyl carbonate (DMC). Our results of the thickness, density, roughness, porosity, and composition of the SEI show significant differences between Si and SiC. Specifically, the formation of lithium fluoride (LiF) is significantly suppressed by the presence of a surface oxide, which we attribute to its electrically insulating nature. We compare and contrast our results with recent studies of the electrocatalytic formation of LiF on metal surfaces [1]. Through combining these observations with our findings that the SEI on silicon contains low ion-conductivity lithium silicates, we hypothesize the native oxide is beneficial if a thin and smooth SEI layer is desired, but may be counterproductive if a fast ion-conduction SEI is desired.

Furthermore, we compared our XRR and XPS results with electrochemical data using a cone-cell, which eliminates parasitic currents, and were able to “count” each electron/Li-ion passed into the Si and SEI. Thus, we uniquely disentangled the Si lithiation and SEI contributions to electrochemical current measurements, yielding ultra-sensitive insights into SEI properties. This approach is even more sensitive when a non-active material such as SiC is utilized. [1] Strmcnik et al., Nature Catalysis 2018, 1, 255.

Investigating Molecular Structures at Interface Using Nanogap Surface-Enhanced Raman Spectroscopy Guang Yang1, Robert Sacci1, Ilia Ivanov2, Rose Ruther1, Kevin Hays3, Pengfei Cao2, Gabriel Veith1, Nancy J. Dudney1, Tomonori Saito2, Daniel Hallinan5 and Jagjit Nanda4; 1Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 3Chemical & Biomedical Engineering Department, Florida State University, Tallahassee, Florida, United States.

Understanding the aprotic solution structures at the immediate vicinity of solid/liquid interface (SLI) is critically important for next generation lithium ion battery development. Yet, it is still challenging to investigate the carbonate profiles close to the diffuse layer (about 10 nm) at SLI due to the lack of a highly surface sensitive tool. In this work, we demonstrate the structures of commonly used carbonate solvents (ethylene carbonate (EC) and diethyl carbonate (DEC)) and a carbonate additive (fluoroethylene carbonate (FEC)) in a Li-ion battery electrolyte can be determined at ~17 nm above the electrode surface. This is only enabled by a nanogap surface-enhanced Raman spectroscopy (SERS) technique. SERS stems from the amplification of local electromagnetic (EM) field generated by localized surface plasmons. The local EM-field is extremely intense within metallic nanogap (~10 nm) due to the coupling effect among adjacent nanoparticles. We have developed methods to assemble gold nanoparticles (Au NPs) into large area (cm²) monolayers, which ensures the formation of long-range ordered nanogap arrays. The interparticle gap can be tuned between 1 and 4 nm by surface ligands of different sizes. The SERS enhancement factor (EF) of the carbones in this study was found to depend on the molecular polarizability, with the maximum EF at ~10⁵ found for EC and FEC. Compared to EC, several vibration modes in FEC, such as C=O skeletal deformation, ring breathing band and C=O stretching band, shift to higher frequencies because of the displacement of a hydrogen atom by a much heavier fluorine atom in a methylene bridge. This counterintuitive observation against the commonly used “ball and spring” model in vibrational spectroscopy is mostly due to the increased bond strength in the FEC ring versus that of EC. A second order empirical polynomial of a single indeterminate best describes the correlation between the SERS band and the corresponding mode in the neat solvent.

Acknowledgment

This research was conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, was sponsored by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO). SERS measurements were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

In Situ TEM Studies of Electrochemical Lithium Storage Mechanisms at Nanoscale Reza Shahbazian-Yassar; University of Illinois at Chicago, Chicago, Illinois, United States.

Acknowledgment

This research was conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, was sponsored by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO). SERS measurements were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:45 AM BREAK
Design of safe lithium ion batteries require innovations in advanced characterization of electrochemical reactions at nanoscale. Real time microscopy provides new opportunities to observe and monitor lithium ion storage mechanisms at unprecedented resolutions. We demonstrate the shortage and gaps in the field of lithium ion batteries that require advanced real time microscopy. In particular we show that in-situ transmission electron microscopy (TEM) is fundamental to discover mechanisms of ion conductivity, structural degradation and transformations, and other structural phenomena associate with the behavior of electrodes. Using liquid-cell TEM, we will show the charge and discharge mechanisms in lithium-air batteries depends on the contribution of electrical conductivity and ionic conductivity to allow Li2O2 decomposition. We also show that the oxygen release from oxide cathodes can trigger structural transformations that results in thermal runaway chain events. Using open-electrochemical cell TEM, we demonstrate lithium storage through conversion, intercalation, and alloying mechanisms.

10:45 AM CM03.02.02
Visualizing Intercalation Events in Ultrathin Graphite Electrodes
Madeline Stark, Hailey Kim, Judy Cheng and Scott C. Warren; University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Near the atomic limit, layered materials such as graphite, transition metal dichalcogenides, and black phosphorous demonstrate enhanced transparency, conductivity, and storage capacity, making them attractive electrode materials for battery and optoelectronic applications. To develop sustainable energy storage devices, however, it is critical to understand electrode-electrolyte interactions. In particular, elucidating the mechanisms of intercalation, SEI formation, and ion transport are areas of active research. To explore these processes in-situ, we have developed a planar battery cell that enables us to visualize intercalation events during charge and discharge cycles. In this work, we focus on the electrochemical intercalation of bisulfate into ultrathin graphite as a model for aqueous intercalation. This compound is of interest, since it exhibits well-defined staging and can be reversibly cycled, paralleling battery technologies, but in an aqueous environment. Our work highlights the important factors to consider when designing an electrochemical cell for aqueous intercalation, specifically in a strongly oxidizing electrolyte, and describes a cell design that enables in-situ optical imaging of both bulk and ultrathin graphite. Qualitatively, we image the intercalation process under an optical microscope, and observe intercalation, deformation, and degradation of the material during cyclic voltammetry and galvanostatic cycling. By visualizing the process of intercalation in-situ, we can acquire and analyze complex image sequences to extract information about the rate of ion transport and diffusion in bulk and ultrathin graphite. To correlate optical images with charge transfer, we perform in-situ reflectance measurements as well as Raman spectroscopy at distinct locations in the bulk crystal and on individual graphite flakes. By coupling optical images with in-situ spectoscopic techniques, we gain insight into how intercalation events and charge transfer occur in a bulk crystal compared to a few-layer electrode. In addition, our observation of differences in color and charge transfer between bulk and ultrathin flakes of varying morphologies highlights the importance of understanding the factors that affect intercalation. The presence of edge sites and grain boundaries are of particular interest since they present a likely pathway to initiate intercalation. Defects within the layers can also lead to degradation and non-uniform charging of the material. However, the role that edges, grain boundaries, and defects play in the ion transport mechanism between the layers of ultrathin materials is not well understood. Thus, we can utilize transmission electron microscopy to study these features in individual graphite flakes prior to intercalation. Combining highly-resolved information about intrinsic defects with spatially-resolved dynamics through optical imaging would provide critical insight into the mechanism of intercalation in 2D electrodes.

11:00 AM CM03.02.03
Insertion and Conversion Based Electrochemical Energy Storage Systems—Complementary Insights from Ex Situ, In Situ and Operando Spectroscopy, Diffraction and Electrochemistry Studies
Amy C. Marschilok1, 2, Kenneth Takeuchi1 and Esther Takeuchi1; 1Stony Brook University, Stony Brook, New York, United States; 2Brookhaven National Laboratory, Upton, New York, United States.

Conceptually, there are two related electrochemical storage mechanisms for electrochemical energy storage materials: insertion where an ion inserts into a structure on reduction and then is removed from the structural lattice upon oxidation, and conversion where there is a chemical reaction leading to a new material or phase. For some materials, each of these mechanisms may participate at different stages of the electrochemical redox process, where the kinetics for ion and electron transport can play a deterministic role regarding which process dominates at a particular state of (de)charge. Complementary insights gained from ex situ, in situ, and operando spectroscopy, diffraction and electrochemistry studies will be highlighted in this presentation, emphasizing materials which undergo both insertion and conversion processes.

11:15 AM CM03.02.04
In Situ Investigation of Multi-Step Lithiation of Tin Sulfide
Sooyeon Hwang1, Zhenpeng Yao2, Lei Zhang1, Maosen Fu3, Kai He1, Liqiang Mai1, Christopher Wolverton1 and Dong Saj1; 1Brookhaven National Laboratory, Upton, New York, United States; 2Northwestern University, Evanston, Illinois, United States; 3Wuhan University of Technology, Wuhan, China; 4Northwestern Polytechnical University, Xi'an, China.

Materials adopting two-dimensional (2D) layered structure have been actively explored as electrode for lithium ion batteries since their unique crystal structures is beneficial for lithium ions to be intercalated between layers [1]. Metal chalcogenides which have 2D layered structure have demonstrated intriguing multi-step reaction with lithium ions; for example, it is known that lithiation of tin disulfide (SnS2) takes place via intercalation, conversion, and alloying[2]. As electrochemical properties are highly dependent on how these complicated reactions proceed, investigation of the reaction pathways in in situ analysis is of importance to improve the electrochemical properties of electrode materials. However, thorough understanding of each reaction mechanism of SnS2 is still missing and full scenario of lithiation dynamics remains elusive.

In this work, we examine the dynamic lithiation process of tin disulfide using in situ transmission electron microscopy (TEM) and first-principles calculations[3]. Structural evolutions induced by lithium insertion are reflected in diffraction peak shift, appearance and disappearance of peaks; thus, we could distinguish reaction steps by the modifications in diffraction profiles. We find 4 sequential steps of lithiation reaction: intercalation, disordering, conversion and alloying, which is different from well-known three stages. Disordering step is suggested for the first time. After Li ions are intercalated between S-S layer, rock-salt phase is formed by the disordering of Sn and Li cations. As all the octahedral sites are filled with cations in rock-salt phase, intercalation channel can be restricted. In order for further lithiation, decomposition of rock-salt phase may be inevitable, resulting in a conversion reaction. First principles calculations are conducted not only to elucidate the ground state reaction pathways but to validate the founding from experiments. Due to discrepancies between lithiation reactions at equilibrium state and empirical results, we simulate non-equilibrium reaction pathways using non-equilibrium phase searching method [4]. Calculation results corroborate that rearrangement of cations would not increase the energy of whole system and the formation of rock-salt phase is energetically more favorable than other Li-xSnS2 polymorphs, which is well-matched with real-time TEM observation.

References:
[5] This work is supported by the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy (DOE), Office of Basic Energy Science, under Contract No. DE- SC0012704.
Structural Characterization of the Atomic and Electronic Evolution of Complex Metal Oxides in High-Rate Energy Storage

Measurement of solid-state lithium diffusion coefficients (11:45 AM)

International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

In Situ S/TEM of SnO2 Nano-Clusters for Li-Anodes

Katherine L. Jungjohann, Shalini Tripathi, Subrahmanyam Goriparti, C B. Carter and Narayanav Ravishankar; Sandia National Laboratories, Albuquerque, New Mexico, United States; Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States; Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; Materials Research Center, Indian Institute of Science, Bangalore, India.

For the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

When Lithium Travels in Solid-State Disorder for Novel Device Prototypes to Store Energy, Sense the Environment or Emulate Data

Jennifer L. Hynes, Level 3, Room 300

Next generation of energy storage and sensors may largely benefit from fast Li⁺ ceramic electrolyte conductors to allow for safe and efficient batteries and real-time monitoring anthropogenic CO₂. Recently, Li-solid state conductors based on Li-garnet structures received attention due to their fast transfer properties and safe operation over a wide temperature range. Through this presentation basic theory and history of Li-garnets will first be introduced and critically reflected towards new device opportunities demonstrating that these electrolytes may be the start of an era to not only store energy or sense the environment but also to emulate data and information based on simple electrochemistry device architectures.

In the first part we focus on the fundamental investigation of the electro-chemo-mechanic characteristics and design of disordered to crystallizing Li-garnet electrode architectures with advantages in energy density, scalability, electrode architecture complexity and cost as alternatives to the state-of-the-art high-rate anode materials Li₄Ti₅O₁₂.

The maximum power output and minimum charging time of a lithium-ion battery – key parameters for its use in, for example, transportation applications – depend on structural conductivity. As well, how the discharge/charge rate and capacity can be tuned by varying the composite electrode structure, ionic transport within the active particles represents a fundamental limitation. Thus, to achieve high rates, particles are frequently reduced to nanosize dimensions despite this being disadvantageous in terms of volumetric packing density as well as cost, stability, and sustainability considerations. As an alternative to nanoscaling, we show that complex niobium tungsten oxides with topologically frustrated polyhedral arrangements and dense nm-scale particle morphologies can rapidly and reversibly intercalate large quantities of lithium.

Multielectrode redox, buffered volume expansion, and extremely fast lithium transport approaching that of a liquid lead to extremely high volumetric capacities and rate performance as very recently reported in both the literature and presented at this conference. As a complement, we have now performed high-resolution structural and operando spectroscopy to provide detailed insight into the chemical and physical evolution of SnO₂ nanocrystalline hollow nanoparticle clusters in a battery to elucidate the mechanisms of lithium storage.

Characterisation of these phenomena and complex material evolution will be presented with structural and chemical insights from operando X-ray diffraction and multi-edge X-ray absorption spectroscopy as well as neutron diffraction and nuclear magnetic resonance spectroscopy. The direct measurement of solid-state lithium diffusion coefficients (D₃Li) with pulsed field gradient NMR demonstrates room temperature D₃Li values of 10⁻¹²–10⁻¹¹ m²·s⁻¹ in the niobium tungsten oxides, which is several orders-of-magnitude faster than typical electrode materials and corresponds to a characteristic diffusion length of ~10 μm for a 1 minute discharge. Materials and mechanisms that enable lithium ion transport in minutes have implications for high power applications, fast charging devices, all-solid-state batteries, and general approaches to electrode design and material discovery.

X-Ray Tomography Studies of Ceramic Solid Electrolytes for Solid-State Battery Applications

Munekazu Motoyama, Takayuki Yamanoto and Yasutoshi Iriyama; Nagoya University, Nagoya, Japan.

All solid-state batteries are promising solutions for high energy density storage devices. Absence of volatile liquid elements in the system mitigates the safety hazards encountered in conventional batteries. Ceramic electrolytes have showcased outstanding ionic conductivities and high shear modulus, however have stability and processing challenges still exist. While theoretical studies suggested that solid electrolytes with shear moduli greater than 8.5 GPa can mitigate Li dendrite formation, recent experiments have shown contradictory results. So far, the studies to understand the failure mechanism in ceramic electrolytes have been primarily surface based ex-situ characterization/imaging techniques. Toward the goal of understanding processing-structure relationships for practical design of solid electrolytes, the present study tracks structural transformations in solid electrolytes processed at three different temperatures (1050, 1100, and 1150 °C) using synchrotron X-ray tomography. A subvolume of 300 μm3 captures the heterogeneity of the solid electrolyte microstructure while minimizing the computational intensity associated with 3D reconstructions. While the porosity decreases with increasing temperature, the underlying connectivity of the pore region increases. Solid electrolytes with interconnected pores short circuit at lower critical current densities than samples with less connected pores. These insights provide insight into the importance of microstructure on device performance.

Multi-Modal Characterization of Li10GeP2S12 Solid Electrolyte Stability in Solid-State Lithium Metal Batteries

Andrew L. Davis1, Kevin N. Wood2, Regina Garcia-Mendez2, Kuan-Hung Chen3, Eric Kazyk4, Jeff Sakamoto5, Glenn Teeter2 and Neil P. Dasgupta1;1 Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2 National Renewable Energy Laboratory, Golden, Colorado, United States; 3 Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Solid-state batteries based on ultra-high ionic conductivity solid electrolytes are a promising technology to increase battery lifetime and capacity, and reduce safety concerns associated with usage of a flammable liquid electrolyte. In recent years, sulfide solid electrolytes such as Li10GeP2S12 (LGPS) have achieved ionic conductivities comparable to or higher than that of traditional liquid electrolytes. Despite these promising breakthroughs, viable high capacity and high energy density sulfide solid-state batteries have proved elusive. The small electrochemical stability window of sulfide electrolyte materials leads to undesirable reactions at the electrode/electrolyte interface against both high voltage cathode materials and Li metal anodes. This forms a solid electrolyte interphase (SEI), which dramatically degrades battery performance. To gain a deeper fundamental understanding of the dynamic evolution of the SEI, as well as its spatially varying composition and phase, the LGPS-Li metal interface was characterized by electrochemical measurements, operando X-ray photoelectron spectroscopy (XPS), in-situ auger spectroscopy, scanning electron microscopy (SEM), and optical microscopy. This allowed for quantitative evaluation of time dependent degradation of the interface, which occurs due to the evolution of a variety of decomposition by-products. Operando XPS was used to correlate distinct decomposition products with corresponding increases in overpotential. In-situ Auger, SEM and optical Mapping of the surface shows spatial inhomogeneities leading to preferential lithium plating and corresponding Li10GeP2S12 breakdown. By performing complementary electrochemical measurements of bulk solid-state batteries employing Li metal, electrochemical signatures associated with interfacial degradation can be identified. Using these techniques and the new mechanistic insights gained, rational interfacial design strategies are identified that can provide a pathway to limit interfacial instability and improve battery performance.

In Situ Scanning Electron Microscope Observations of Li Plating/Stripping Reactions on Oxide Solid Electrolytes

Munekazu Motoyama, Takayuki Yamanoto and Yasutoshi Iriyama; Nagoya University, Nagoya, Japan.

The theoretical capacity of Li metal anode (3860 mAh g−1) is more than ten times greater than those of other practical anodes such as graphite and LiTiO2 for lithium ion battery. However, Li dendrites cause short-circuit in liquid electrolytes during cycles of Li plating/stripping. On the other hand, since inorganic solid electrolytes (e.g. Li2Zr2O7) have been expected to prevent dendrite growth, all-solid-state-lithium battery (SSLB) has been regarded to innovate battery technology and enable the use of Li metal anode. Hence, it is important to obtain the fundamental understanding of Li plating/striping processes on solid-state electrolytes. We have studied the Li plating/stripping reactions with lithium phosphorous oxyxinitride (LiPON) glass electrolyte and Li4La2Zr2Ta2O12 (LLZ(Ta0.4)) coated with thin current collector (CC) films of Cu, Ni, W, and Pt. The Li nucleation sites are supposed to exist at solid/solid interfaces in “lithium-free”-thin-film SSLB [2]. Hence, the nuclei must push either electrode or electrolyte to create their own spaces. This process is associated with generation of significant strain energies. This study applies an in-situ scanning-electron microscope (SEM) observation technique to the investigation on the Li nucleation/growth and dissolution processes with various CC films (Cu, Ni, W, Pt, Au). Cu, Ni, and W are unable to form specific alloy phases with Li and Au form alloy phases with Li. The top and bottom surfaces of a Li4La2Zr2Ta2O12 sheet (Ohara Co.) were coated with 2.5-μm-thick LiPON layers by RF magnetron sputtering. Additionally, a LLZ(Ta0.4) plate (Toshiba Manufacturing Co. Ltd.) with a thickness of 0.5 mm was used as an electrolyte [3]. A current collector film (i.e. Cu, Ni, W, Pt, Au) was deposited on the top LiPON surface and LLZ(Ta0.4) surface by pulsed laser deposition (PLD). A Li film with a thickness of 2 to 3 μm was deposited within an area of 9.0 mm in diameter on the other side of a cell as the counter electrode by vacuum evaporation. The results of dynamic observations of Li plating/stripping and Li alloying/dealloying on LiPON and LLZ(Ta0.4) coated with thin metal CC films via an in-situ SEM technique will be discussed.

The authors gratefully acknowledge JSPS 17H04894 and ALCA-SPRING for the financial supports.

Multimodal X-Ray Characterization of Operating Electrochemical Energy Storage Systems

Johanna N. Weker; SLAC National Accelerator Lab, Menlo Park, California, United States.

The shift from fossil fuels toward clean, renewable energy will require significant improvements in rechargeable battery technology for electric vehicles. Current battery technology limits electric vehicles to a short travel range, slow recharge, and costly price tag. Li-ion batteries promise the high specific capacity required to replace the internal combustion engine with a number of possible earth abundant electrode materials; however, setbacks such as capacity fading hinder the full capability of these rechargeable batteries. In the search for better electrode materials, multimodal X-ray characterization spanning many relevant length scales during typical battery operation is vital in understanding and overcoming the failure mechanisms of these materials. We will discuss our multimodal approach combining information from high resolution X-ray microscopy and spectra-microscopy, micro- and nano-tomography, X-ray diffraction, and X-ray absorption spectroscopy to track electrochemical, morphological, and structural changes in the electrode material in real time during typical battery operation.

Revealing Nanoscale Passivation and Corrosion Mechanisms of Reactive Battery Materials in Gas Environments

Yuzhang Li and Yi Cui; Stanford University, Stanford, California, United States.

Lithium (Li) metal is a high-capacity anode material (3,860 mAh g⁻¹) that can enable battery chemistries beyond Li-ion. However, Li metal is highly reactive and repeatedly consumed when exposed to liquid electrolyte (during battery operation) or the ambient environment (throughout battery manufacturing). Studying these corrosion reactions on the nanoscale is especially difficult due to the high chemical reactivity of both Li metal and its surface corrosion films. Here, we directly generate pure Li metal inside an environmental transmission electron microscope (TEM), revealing the nanoscale passivation and corrosion process of Li metal in oxygen (O₂), nitrogen (N₂), and water vapor (H₂O). We find that while dry O₂ and N₂(99.9999 vol%) form uniform passivation layers on Li, trace water vapor (~1 vol%) disrupts this passivation and forms a porous film on Li metal that allows gas to penetrate and continuously react with Li. To exploit the self-passivating behavior of Li in dry conditions, we introduce a simple dry-N₂ pretreatment of Li metal to form a protective layer of Li nitride prior to battery assembly. The fast ionic conductivity and stable interface of Li nitride results in improved battery performance with dendrite-free cycling and low voltage hysteresis. Our work reveals the detailed process of Li metal passivation/corrosion and demonstrates how this mechanistic insight can guide engineering solutions for Li metal batteries.


Operando Characterization of Lithium Metal Plating and Stripping Using Grazing Incidence Small Angle X-Ray Scattering

Robert M. Kasse¹,², Natalie R. Geise³, Hans-Georg Steinrueck² and Michael F. Toney³; Materials Science and Engineering, Stanford University, Stanford, California, United States; ²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Chemistry, Stanford University, Stanford, California, United States.

Emerging technologies such as electric vehicles, which rely on high energy density batteries, necessitate the development of advanced materials to replace those currently being used in traditional lithium ion devices. Anodes employing lithium metal are the most promising given their high specific capacity (3,860 mAh/g) and low electrochemical potential (~3.04 V vs SHE). However, lithium metal is highly unstable with large irreversible capacity losses occurring during plating and stripping due to electrolyte decomposition and formation of electrochemically inactive ‘dead’ lithium. To allow for the intelligent design of lithium protection strategies, a fundamental understanding of the plating and stripping behavior is needed, particularly during the first cycle.

These dynamic processes occurring during battery operation require operando characterization. Thus, we have performed grazing incidence small angle X-ray scattering (GISAXS) during the lithium plating and stripping process in order to probe the morphology of plated lithium. Investigating the surface of a copper film in an operating lithium-copper cell, we are able to determine the lithium metal growth mechanism and particle growth rates as a function of relevant battery parameters including electrolyte composition and cycling protocol. The nucleation and growth mechanism is very sensitive to electrolyte impurities and cycling protocol, due to the different solid electrolyte interphase (SEI) formed on the copper surface under different conditions. Fluorine-containing SEI components formed at high potentials due to impurity decomposition create a more uniform current distribution leading to monodisperse columnar growth of Li metal, compared to nonuniform deposition in a baseline electrolyte. A fundamental understanding of the effect of such parameters on lithium plating can be used to engineer high energy density batteries with enhanced safety and cycle life.

Multiscale Modeling and In Situ Visualization Analyses of Electrodeposition in Nanostructured Electrolytes

Snehashis Choudhury and Lynden Archer; Cornell University, Ithaca, New York, United States.

Electrochemical cells based on alkali metal (Li, Na) anodes have attracted significant recent attention because of their promise for producing large increases in gravimetric energy density for energy storage in batteries. To facilitate stable, long-term operation of such cells a variety of structured electrolytes have been designed in different physical forms, ranging from soft polymer gels to hard ceramics, including nanoporous versions of these ceramics that host a liquid or molten polymer in their pores. In almost every case, the electrolytes are reported to be substantially more effective than anticipated by early theories in improving uniformity of deposition and lifetime of the metal anode. These observations have been speculated to reflect the effect of electrolyte structure in regulating ion transport to the metal electrolyte interface, thereby stabilizing metal electrodeposition processes at the anode. In this work, we create and study model structured electrolytes composed of covalently linked polymer grafted nanoparticles that host a liquid electrolyte in the pores. The electrolytes exist as freestanding membranes with effective pore size that can be systematically manipulated through straightforward control of the volume fraction of the nanoparticles. By means of physical analysis and direct visualization experiments using advanced optical microscopy, we
report that at current densities approaching the diffusion limit, there is a clear transition from unstable to stable electrodeposition at Li metal electrodes in membranes with average pore sizes below 500 nm. We show that this transition is consistent with expectations from a recent theoretical analysis that takes into account local coupling between stress and ion transport at metal-electrolyte interfaces.

References:

4:45 PM CM03.04.05

Coupling Operando Techniques for Unravelling the Electrochemical and Structural Mechanism of High-Performance Lithiated Nitrides as Negative Electrode Material for Li-Ion Batteries Nicolas Emery and Jean-Pierre Pereira-Ramos; ICMPE-GESMAT UMR 7182, Thiais, France.

Comprehension of redox processes and their influence on structural properties of electrode materials is a key point to improve Li-ion batteries efficiency. The rise of operando techniques leads to a better insight into these reactions due to the real-time observation of the process. In this work, we will mainly develop two examples of lithiated transition metal nitrides studies where different operando techniques were combined. Our group has clearly demonstrated layered lithiated metal nitrides can be considered as genuine Li intercalation compounds and possible negative electrode materials for Li-ion batteries [1-2]. In particular attractive properties for optimized Co and Ni contents in the Li-M-N system were proved with for instance Li$_2$Ni$_{0.5}$N exhibiting a specific capacity of 200 mAh g$^{-1}$ and an excellent cycle life. After a precise determination of the chemical composition using NRA technique, its structural mechanism under operation was studied and solved using operando XRD upon successive discharge-charge cycles [2]. A solid-solution behaviour is shown with a very limited volume variation, less than 1% which well explains electrochemical features. A superstructure is mandatory to clearly describe the operando XRD data set recorded here. Indeed, the presence of vacancies in the Li$_2$N planes allows a slight displacement of interlayered nickel ions cell inducing a negligible swelling process of the host lattice in line with a remarkable cycle life. With a specific capacity of 280 mAh g$^{-1}$ at C rate available around 1.2 V vs Li$^+$/Li, a 3D Li$_7$MnN$_4$ has been proved to be a credible alternative to LiTi$_2$O$_4$ for moderate to high power applications. The redox-mechanism and structural response upon a full electrochemical oxidation/reduction cycle have been studied using XAS and XRD in-situ operando techniques. The charge curve composed of two successive plateaus and a continuous potential increase, is well explained by two dihedral domains and a solid-solution behaviour [3]. After a MCR-ALS analysis of the Mn K-edge absorption spectra data set, three different environments related to three different Mn oxidation states involved in redox processes were isolated [4]. Using the simple concept of coordination charges and comparison with available data for appropriate reference oxides, the oxidation states of each environment were ascribed and fully explained the achieved specific capacity. By combining these two methods, a comprehensive scenario has been proposed to explain the attractive electrochemical performances of Li$_x$MnN$_4$ with the role of Mn $^{5+}$, Mn $^{6+}$ and Mn$^{7+}$ ions here stabilized by the nitride framework.


SESSION CM03.05: Batteries I
Session Chairs: Neil Dasgupta and Matthew McDowell
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 300

8:15 AM *CM03.05.01

Correlative Imaging of Electrochemical Devices Over Multiple Time and Length Scales Paul Shearing; University College London, London, United Kingdom.

Electrochemical device is a term used to describe a group of technologies including fuel cells, batteries, electrolyser and super-capacitors. Whilst many of these technologies are already in common daily usage, for example Li-ion batteries that power our mobile phones, in the future electrochemical devices will play an increasing role in our lives – from fuel cells that can power our homes to high performance batteries for our cars.

At a microscopic length scale, these devices can be considered as one of a general class of porous materials, whereby the physical microstructure will influence a range of phenomena, including diffusion, catalysis and conductivity – our ability to engineer these microscopic features to maximize performance can be translated to substantial improvements in macroscopic device design. At macroscopic length scales the robustness of device design will influence the system energy and power density and its ability to safely store/convert energy over extended periods of time.

As these materials are likely to evolve over time, in response to range of processing and environmental conditions (sintering, corrosion, failure etc); understanding how these changes in microstructure can be linked to understanding of degradation and failure is pivotal to improving device lifetime and safety.

Over the past 10 years the increasingly widespread use of X-ray imaging and tomography has revolutionized our understanding of these materials; with increasing sophistication researchers have been able to characterize samples over multiple time and length scales from nm to mm and from ms to days. Here we consider examples of our work to explore these materials in three and “four” dimensions, to examine materials evolution with time. We will explore case studies that utilize both laboratory and synchrotron X-ray sources across a range of spatial and temporal domains, and examine how improvements in these imaging techniques, alongside correlative spectroscopy, is providing unprecedented insight into these materials and devices.

8:45 AM CM03.05.02

Monitoring Capacity Losses Through Operando X-Ray Diffraction in Lithium Metal Anodes Natalie R. Geise$^1$, Robert M. Kasse$^2$, Hans-Georg Steinrueck$^2$ and Michael F. Toney$^2$; Chemistry, Stanford University, Stanford, California, United States; $^2$Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; $^3$Materials Science, Stanford University, Stanford, California, United States.

The rise of electrochemical devices has been propelled by the extraordinary properties of Li-ion batteries which have revolutionized our daily lives. However, the limited voltage capability and high cost of current anode materials, such as graphite, has informed research in lithium metal batteries (Li-MBs). In these devices, lithiation involves nucleation and growth of a reduction product at the metal-electrolyte interface. Here, we present operando X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) techniques for elucidating the structural and chemical evolution of lithium metal anodes in Li-MBs.
Li-metal is a promising, high-capacity anode that can be incorporated into Li-ion, Li-S, and Li-air battery systems to meet the need for energy-dense batteries. Coulombic efficiency losses remain a major challenge to adoption and commercialization. These losses are driven mainly by loss of lithium to the solid electrolyte interphase (SEI) and into metallic lithium deposits that become electrically disconnected ('dead' Li) due to complex morphological changes. While protection methods, such as coatings and electrolyte additives, have yielded improved efficiencies, fundamentally understanding how these improvements are realized will allow for optimization of their design.

Here, we have developed a method of monitoring lithium metal in the anode through plating and stripping cycles via operando X-ray diffraction (XRD). We obtain quantitative results on the reversible lithium metal, dead lithium development and evolution with cycling, and lithium corrosion. Our results show the lithium metal efficiency, measured through XRD, is higher than the electrochemical Coulombic efficiency measurements. Additionally, the contribution of ‘dead’ lithium to the overall Coulombic efficiency varies much more across electrolytes and cycling conditions than the SEI does. This new experimental methodology and the understanding on the origins of capacity loss in lithium metal anodes which it enables will lead to better-designed protection layers and electrolytes which improve anode performance.

9:00 AM CM03.05.03
Plan-View Operando Video Microscopy of Li Metal Anodes Adrian J. Sanchez, Kuan-Hung Chen, Eric Kazyak and Neil P. Dasgupta; University of Michigan Ann Arbor, Ann Arbor, Michigan, United States.

Improving the safety and performance of Li metal anodes is key to enabling next generation batteries such as Li-Air and Li-Sulfur. However, the mechanisms governing poor performance of Li metal anodes are not fully understood, which hinders our ability to characterize, diagnose, and rationally design solutions to problems including dendrite growth and low Coulombic efficiency. In situ and operando analyses are well suited to study the mechanisms of battery degradation, as they avoid any sample alteration due to the disassembly of a cell.

Herein, we present a multifunctional operando visualization platform that synchronizes optical recordings with cycling electrochemistry. This platform was initially used to understand the origins of the “peaking” behavior exhibited in the voltage traces of Li symmetric cells [1]. However, by limiting the viewing angle to a cross sectional perspective, the impact of electrode surface variations, including microstructure, flaws, and chemical inhomogeneities cannot be fully accounted for. To address this, in this study, a plan view optical visualization cell was designed that maintains a highly uniform current distribution along the electrode surface and avoids mechanical deformation of the electrode. This enables correlation of dendrite nucleation location to surface features. Dendrite nucleation and pitting nucleation density are quantified as a function of current density on a Li metal surface. Additionally, the impact of pitting on the performance of a Li metal anode is directly observed. The impact of surface modifications on Li plating, including protective coatings and mechanical deformation, are also quantified. Finally, the knowledge generated on the coupled morphological and electrochemical behavior of Li metal deposition will be discussed as a potential pathway to develop battery failure diagnostics.


9:15 AM CM03.05.04
In Situ/Operando Grazing Incidence Small Angle X-Ray Scattering of Model Oxide Nanostructures for Li-Ion Battery Conversion Electrodes Jae Jin Kim1, Byeongdha Lee1, Chun Zhou2, Hyo Seon Suh2, Anil Mane1, Jeffrey Elam2, Paul Nealey2, Paul Fenter2 and Tim Fister2; 1Argonne National Laboratory, Lemont, Illinois, United States; 2The University of Chicago, Chicago, Illinois, United States.

Conversion reactions in Li ion batteries, such as the electrochemically-driven phase separation of a transition metal oxide into metal nanoparticles and lithium oxide species, are well-known to have specific capacities far beyond typical intercalation materials. However, these types of reactions invariably suffer from irreversibility and hysteresis due to their substantial volume change and kinetic barriers. Oxides also tend to have substantially lower redox potentials than thermodynamically expected values, limiting their practical use. Given the complex network of metal-rich and lithia domains evolved during lithiation, interfacial processes must play a critical role in the nucleation of the overall conversion reaction and charge/mass transport. In contrast to the complex network of nanoparticle that form during lithiation, we have studied electrode surfaces with periodic tungsten oxide waves, whose dimensions can be tuned to test the mechanical and kinetic properties of conversion reactions. Our fabrication approach uses the selective growth of ALD on block copolymers, in this case producing arrays of oxide nano-cylinders or their inverse, a film with periodic hole patterns. These electrodes are well-suited for grazing incidence small angle X-ray scattering (GISAXS), which can be used to assess the size, density, and spacing of the electrodes during the reaction. Using operando GISAXS, we find that nanoscale (50 – 80 nm) oxides undergo conversion reactions at 1.4 – 1.7 V, which is close to the theoretical value (1.65 V) and well above the discharge plateau of 0.8 – 0.9 V for micron-sized bulk powders. Insights from this study can bring a new perspective on enhancing the energy density and reversibility of conversion reactions and provide strategies for improving their overall performance.

9:30 AM CM03.05.05
Reaction with Larger Ions Avoids Fracture in a Conversion Battery Material—In Situ TEM Investigation Matthew G. Booher1, 2, Baolin Wang1, 2, 3, Marc Papakyriakou1, 4, Shuman Xia1, 3, Ting Zhu1, 2, 3 and Matthew McDowell1, 2, 3; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 3The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Demand for cheap energy storage systems has led to growing interest in the development of sodium- and potassium-ion battery systems. Conversion and alloying-type electrode materials with high specific capacity are attractive options for these batteries, but the larger volumetric expansion during reaction with sodium and potassium compared to lithium is thought to limit cycle life. The nanoscale reaction mechanisms of many electrode materials with Na+ and K+ ions are unknown, however, and they must be investigated to understand how to engineer Na and K-battery materials to undergo minimal mechanical damage due to volume changes. In this study, in situ transmission electron microscopy (TEM) experiments are used to examine the nanoscale transformations of cube-shaped FeS2 nanocrystal electrode materials as they undergo reaction with Li+, Na+, and K+. Although the FeS2 nanocrystals underwent a conversion-type reaction via a two-phase mechanism with a sharp reaction front in all cases, fracture was only observed to occur during lithiation, despite the larger volumetric changes associated with sodiation and potassiation. This difference was ascribed to dissimilar shapes of the two-phase reaction fronts during the reaction processes. Specifically, reaction fronts during lithiation were found to retain rectangular shapes with sharp corners, while sodiation and potassiation caused the reaction front to take an oval shape with blunted corners. Chemomechanical modeling of stress evolution during reaction showed that the differences in the evolution of the shape of the two-phase reaction front led to higher tensile stress concentrations and particle fracture during lithiation. The results indicate that even though larger volumetric expansions take place in Na- and K-ion battery materials, these volume changes may be managed through understanding and control of nanoscale reaction mechanisms and do not necessarily cause failure of individual particles.

9:45 AM BREAK
Designing advanced battery interfaces requires visualizing ionic, electronic, and redox pathways that indicate how local surface activation and site-specific differential reactivity impact ion-intercalation and interfacial evolution with cycling. This presentation will discuss new in-situ analytical tools based on the scanning electrochemical microscope (SECM) that incorporate functions for imaging surface redox reactivity, spectroelectrochemistry, and ionic transfer reactions for species such as Li⁺, Na⁺ and K⁺ at interfacial and bulk nanostructures in non-aqueous electrolytes.

In ionic measurements, the principle is based on SECM probes that integrate mercury micro- and nano-cap electrodes on which alkaline ions can be detected by means of fast-scan anodic stripping voltammetry. The probe potential provided chemical specificity while the probe current enables the measurement of ionic fluxes with excellent stability and linearity. We will demonstrate how these probes were used for the measurement of ion insertion sites on graphene, graphite, and silicon nanostructures. When combined with redox modes using the SECM (e.g. feedback), these probes provide a comprehensive view of how interfacial processes impact charge transfer across operating interfaces.

Complementing these powerful measurements, we will discuss how the combination of SECM with Raman spectroscopy via colocalized and simultaneous measurements of operating electrodes enables real-time correlation of electrochemical and structural information. We will show how our system is used for simultaneous imaging and time-resolved experiments of interfaces of interest for energy storage, such as redox polymers and graphene with a resolution of ~1 micron, sub-second resolution, and high signal to noise ratio. We hope our techniques will contribute to a new understanding of interfacial processes on battery structures, allowing the measurement of ionic reactivity, and elucidating the impact of interfacial processes on single reacting sites. SECM mapping reveals aspects of surface reactivity that are lost during averaging in conventional battery testing.

References:

10:45 AM CM03.06.02
Cryo-Electron Microscopy for Battery Materials Yanbin Li and Yi Cui; Stanford University, Stanford, California, United States.

Cryo-electron microscopy (cryo-EM) received the 2017 Nobel Prize in Chemistry for its ability to elucidate the nanostructure of biomolecules in their native state, revolutionizing the field of structural biology. Here, we pioneer an approach to utilize this powerful technique to enable new discoveries for batteries. (Y. Li*, Y. Cui, et al. Science 2017, DOI: 10.1126/science.aam6014) and show that cryo-EM can potentially have a similar impact in materials science.

Whereas conventional transmission electron microscopy (TEM) studies are unable to preserve the native state of chemically-reactive and beam-sensitive battery materials (e.g. Li metal) after operation, such materials remain pristine at cryogenic conditions. It is then possible to atomically resolve individual Li metal atoms and their interface with the solid electrolyte interphase (SEI). We observe that dendrites in carbonate-based electrolytes grow along the <111> (preferred), <110>, or <211> directions as faceted, single-crystalline nanowires. These growth directions can change at kinks with no observable crystallographic defect. Furthermore, we reveal distinct SEI nanostructures formed in different electrolytes that explain why certain additives lead to better performance. With cryo-EM, we open up exciting new opportunities for scientific discovery, which will be critical for providing fundamental insight to battery materials design.


*Denotes equal contribution

11:00 AM CM03.06.03
Electrochemical Interfacial Properties Revealed by Synergistically Combining Ambient Pressure XPS with Theory Ethan J. Crumlin1,2; Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3CESR, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal
role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. In particular, I will discuss how we synergistically combine this powerful experimental technique with DFT theoretical insight to reveal a mechanistic understanding of electrochemical interfaces. I will highlight some of our recent investigations into CO2 adsorption phenomena on various metals. In situ APXPS and DFT together provide a comprehensive understanding of the initial adsorption processes and how oxygen and water transform CO2’s adsorption behavior. Additionally, I will highlight how theory/modeling has enhanced our knowledge of in situ/operando solid/liquid APXPS investigations including electrochemically promoted dissolution and the interaction of a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

11:30 AM CM03.06.04
Illuminating the Oxygen Cathode Interface of the Non-Aqueous Metal Oxygen Battery Iain Aldous and Laurence Hardwick; Univ of Liverpool, Liverpool, United Kingdom.

Improving energy storage, beyond Li-ion batteries, is an important opportunity to provide solutions for varying applications. A family of emerging battery chemistries are non-aqueous metal oxygen cells. Ideally, the cathodic reactant (oxygen) is provided from the atmosphere and electrochemically reduced in the presence of alkali metal cations to form reduced oxygen species (ROS) such as peroxides and superoxides. On charge, the formed ROS are then electrooxidised and the oxygen returned to the atmosphere and alkali metal cations reduced at the alkali metal anode to form alkali metal (Li, Na, K and Ca). Combining electrochemistry and spectroscopy has provided an understanding of how to control this mechanism through the solvation of O2, LiO2, NaO2, and CaO2. This is achieved via the manipulation of the local chemical environment of these species within the electrolyte. Additives such as water and organic redox mediators can be used to great effect in increasing capacity, rechargeability and decreasing the over potential of the system.

This talk will focus on the group’s research and findings on how to manipulate the direction of the oxygen reduction reaction in non-aqueous metal-oxygen batteries. Using in situ/in situ surface enhanced Raman spectroscopy and UV/Vis spectroscopy to characterise the electrochemical reactions occurring at the cathode interface demonstrates the group’s findings. Discussion will touch upon how oxygen electrochemistry relates to the electrode substrate and as well as the use of electrolyte additives.

References:

11:45 AM CM03.06.05
Electrofied Solid/Liquid Interface Studied by Nanoelectrical and Nanoelectrochemical Atomic Force Microscopy Zhuangqun Huang1, Peter De Wolf1, Antoine Dujardin1, 2, Bede Pittenger1 and Thomas Mueller1; 1Bruker Nano Surfaces, Goleta, California, United States; 2Cellular Microbiology and Physics of Infection Group, Lille Centre for Infection and Immunity, CNRS UMR8204, INSERM U1019, Lille Regional Hospital University Centre, University of Lille, Institut Pasteur de Lille, Lille, France.

Atomic force microscopy (AFM) has been adopted for in situ and in operando electrical and electrochemical (EC) studies with nanometer resolution at electrofied solid-liquid electroactive interfaces. Recent developments include PeakForce EC-AFM for topographic and nanomechanical imaging during EC reactions on the surfaces of Li ion battery anodes,1,2 and PeakForce scanning electrochemical microscopy (SECM) for the simultaneous acquisition of local EC and conductivity information at electrified solid/liquid interfaces of nanoparticle-catalysed photoelectrodes for water splitting.2–3 In this work, we introduce these recently-developed techniques with a variety of examples in energy, biological, and semiconductor applications.

We have also developed DataCube SECM to provide highly-dimensional, big-data results allowing us to perform in-depth data mining for improved theoretical insight to reveal a mechanistic understanding of electrochemical interfaces. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. In particular, I will discuss how we synergistically combine this powerful experimental technique with DFT theoretical insight to reveal a mechanistic understanding of electrochemical interfaces. I will highlight some of our recent investigations into CO2 adsorption phenomena on various metals. In situ APXPS and DFT together provide a comprehensive understanding of the initial adsorption processes and how oxygen and water transform CO2’s adsorption behavior. Additionally, I will highlight how theory/modeling has enhanced our knowledge of in situ/operando solid/liquid APXPS investigations including electrochemically promoted dissolution and the interaction of a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

References:

Solar-to-fuel technology promises to play a key role in realizing a carbon-neutral future by enabling renewable fuel processing for capacity-independent storage beyond current battery technologies [1]. Metal oxide catalysts enable the two-step thermochemical cycle by catalyzing the reduction of H₂O and CO₂ to produce H₂ and CO. Currently, ceria is the reference material due to its rapid kinetics, crystallographic stability, and abundance [1]. To address the low fuel production of ceria, doping with tetravalent cations and co-doping with 3+/5+ combinations are used to enhance oxygen release and thus increase maximum fuel yield [2]. However, the reaction mechanisms and kinetics of oxygen vacancy formation in doped-ceria are still unclear, and this understanding will be crucial to developing improved redox materials that will make solar-to-fuel technology economically viable.

This novel investigation utilizes in situ Raman spectroscopy under redox cycling schemes to illuminate the reaction mechanisms of oxygen vacancy formation and annihilation in 10mol% doped ceria solid solutions of the composition Ce₀.₉(Me)₀.₁O₂ with Me= La, Zr, Hf, Nb and in co-doped Ce₀.₉(Me)₀.₁O₂(NO)₀.₅O₂. In-situ Raman spectroscopy was utilized to study the chemical reduction of doped-ceria materials under H₂ atmosphere up to 900 °C and the redox cycling under alternating reducing H₂ and oxidizing CO₂ atmospheres at a constant temperature of 800 °C.

Results revealed that the peak corresponding to the triply degenerate F₂g stretching mode of the cation and oxygen ions in the cubic fluorite structure of ceria shifts to lower frequencies and decreases in intensity during reduction; these changes correspond to chemical expansion with the reduction of the cation and an increase in the oxygen vacancy concentration. Additional vacancy bands also appear at different positions depending on the dopant choice and indicate how each dopant cation facilitates the formation of oxygen vacancies.

Raman spectroscopy confirms that catalytic oxygen vacancy concentration determines the fuel yield of this process: samples with the highest fuel yield also had the largest shift of the peak corresponding to the triply degenerate F₂g when heated, suggesting the highest oxygen vacancy concentration and thus the highest oxygen storage capacity. This model experiment not only provides crucial preliminary results for understanding the mechanisms of oxygen vacancy formation in doped ceria catalysts but also provides an experimental template for future investigation of reaction mechanisms of other electrochemical materials. By utilizing Raman spectroscopy to understand the redox mechanisms of various materials, as was done in this experiment, materials scientists can optimize doping to engineer the redox performance of materials for a variety of applications.

In this work, we elucidate the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer of flat band potential and the charge carrier concentration. The highest photocurrent was found for distinguished concentrations of the iron group metal, demonstrating that this combinatorial approach is very useful in the search for high performance water splitting photoelectrodes.

In this context, improved understanding of these complex surface interactions will aid the development of highly efficient light absorbers as well as the integration of effective passivation and catalyst layers for these materials.

Photoelectrochemical (PEC) water splitting is a promising approach to provide carbon neutral power and renewable fuels. The chemical transformation of water into oxygen and hydrogen takes place at the surface of catalysts and photoactive materials. Consequently, the activity, efficiency, and reaction pathway are critically controlled by the material surface properties. Under PEC operating conditions, surface properties strongly depend on the surrounding environment, and they may be altered in the course of the reaction. Thereby, absorption of molecules can modify the chemistry at the surface, for example by influencing the kinetics of reactants, products, or reaction intermediates, but they can also directly impact the electronic transport properties of the photoactive material by effectively acting as surface trap states. In this context, improved understanding of these complex surface interactions will aid the development of highly efficient light absorbers as well as the integration of effective passivation and catalyst layers for these materials.

In this work, we elucidate the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer of photogenerated charge carriers in polycrystalline BiVO₄ thin films—a promising material for solar water splitting. The charge transfer between adsorbates and BiVO₄ is monitored in situ Kelvin probe measurements under dry nitrogen, humid nitrogen, and oxygen environments at atmospheric pressure. To gain complementary insight into the relationship between surface interactions and interfacial charge transport characteristics, we employ photoconductive AFM under the respective in situ conditions. By combining these complementary techniques, we demonstrate that adsorbed oxygen acts as a surface trap state for electrons, which enhances the built-in potential and depletes the BiVO₄ layer, resulting in an increase of the measured surface photovoltage. Furthermore, we have recently demonstrated that the low intrinsic bulk conductivity of BiVO₄ limits the electron transport through the film, and that the transport mechanism can be attributed to space charge limited current (SCLC) in the presence of trap states. By analyzing the SCLC, we estimate that the contribution of water adsorbed oxygen to the total number of shallow traps is as large as 40%. For humid environments, our results are consistent with the adsorption of water as an oriented dipole layer, which does not induce a surface charge transfer but partially inhibits the adsorption of oxygen at the surface. Disentangling the individual effects of oxygen and water on surface band alignment and charge carrier trapping underpins the importance of trap state passivation for efficient transport of photogenerated charge carriers in BiVO₄.


2:30 PM CM03.07.05
Disentangling the Role of Surface Chemical Interactions on Interfacial Charge Transport at BiVO₄ Photoanodes Johanna Eichhorn1, Christoph Kastl1, Adam Schwartzberg1, Ian D. Sharp1 and Francesca Maria Tomà2; 1The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Walter Schottky Institut and Physik Department, Technische Universität München, Munich, Germany.

Photoelectrochemical (PEC) water splitting is a promising approach to provide carbon neutral power and renewable fuels. The chemical transformation of water into oxygen and hydrogen takes place at the surface of catalysts and photoactive materials. Consequently, the activity, efficiency, and reaction pathway are critically controlled by the material surface properties. Under PEC operating conditions, surface properties strongly depend on the surrounding environment, and they may be altered in the course of the reaction. Thereby, absorption of molecules can modify the chemistry at the surface, for example by influencing the kinetics of reactants, products, or reaction intermediates, but they can also directly impact the electronic transport properties of the photoactive material by effectively acting as surface trap states. In this context, improved understanding of these complex surface interactions will aid the development of highly efficient light absorbers as well as the integration of effective passivation and catalyst layers for these materials.

In this work, we elucidate the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer of photogenerated charge carriers in polycrystalline BiVO₄ thin films—a promising material for solar water splitting. The charge transfer between adsorbates and BiVO₄ is monitored in situ Kelvin probe measurements under dry nitrogen, humid nitrogen, and oxygen environments at atmospheric pressure. To gain complementary insight into the relationship between surface interactions and interfacial charge transport characteristics, we employ photoconductive AFM under the respective in situ conditions. By combining these complementary techniques, we demonstrate that adsorbed oxygen acts as a surface trap state for electrons, which enhances the built-in potential and depletes the BiVO₄ layer, resulting in an increase of the measured surface photovoltage. Furthermore, we have recently demonstrated that the low intrinsic bulk conductivity of BiVO₄ limits the electron transport through the film, and that the transport mechanism can be attributed to space charge limited current (SCLC) in the presence of trap states. By analyzing the SCLC, we estimate that the contribution of water adsorbed oxygen to the total number of shallow traps is as large as 40%. For humid environments, our results are consistent with the adsorption of water as an oriented dipole layer, which does not induce a surface charge transfer but partially inhibits the adsorption of oxygen at the surface. Disentangling the individual effects of oxygen and water on surface band alignment and charge carrier trapping underpins the importance of trap state passivation for efficient transport of photogenerated charge carriers in BiVO₄.

Carbon dioxide is one of the major contributors to global warming and the possibility of recycling this greenhouse gas is gaining attention within the scientific community. The electrochemical reduction of CO₂ (CO₂RR) is an attractive way to utilize this greenhouse gas by converting it into a broad range of useful fuel such as alcohols and hydrocarbons. The development of highly active electrocatalysts for CO₂RR is a national priority, which requires a better understanding of the fundamental reactions on various metal surfaces, along with the development of analytical tools that allow for the quantification of the reaction products. We have designed and built a comprehensive electrochemical mass spectrometry (DEMS) setup consisting of an electrochemical flow cell coupled to an MS, which demonstrated to be an excellent and versatile tool for testing the performance of electrocatalysts. The DEMS setup allows us to study the electrocatalysts under real operating conditions and to correlate the performance of the electrocatalysts with the structure of the catalyst surfaces. In this talk, we will discuss our recent results on the electrocatalysis of CO₂RR on Au, Pt, and Pt/C catalysts, and we will present a novel method for the simultaneous detection of volatile species produced during the electrocatalysis reactions.
Christopher Hahn1 and Walter Drisdell2; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Stanford University, Palo Alto, California, United States; SLAC National Accelerator Laboratory, Menlo Park, California, United States.

The primary challenge in electrochemical CO2 reduction lies in tuning the catalytic selectivity for desired solar fuels products. Molecular-scale knowledge of the catalytic mechanism for CO2 reduction is required, ideally for systems with controlled morphology that can be directly compared to first principles calculations. Achieving this control is difficult, as CO2 reduction competes with hydrogen evolution and only proceeds with appreciable efficiency at high current densities, and suffers from mass transport limitations due to low solubility of CO2. I present a new electrochemical flow cell system designed collaboratively in the Joint Center for Artificial Photosynthesis (JCAP) at Lawrence Berkeley National Laboratory and SLAC National Accelerator Laboratory, which uses a fast liquid flow design to enable grazing incidence X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) of a smooth planar catalyst surface (top 2-4 nm) during operation. These measurements characterize the chemical state, local electronic structure, and long-range atomic structure of the catalyst surface as a function of electrochemical conditions, including full catalytic chemistry at high current density. I demonstrate the surface sensitivity and electrochemical control of the technique, and present early data on model CO2 reduction catalysts.
Conducting redox polymers have been investigate massively as an efficient cathode material. Herein we synthesis a series of quinone substituted PEDOT conducting redox polymers and investigate the effect of electron withdrawing substitutions on the redox potential of quinone in the PEDOT backbone in two electrolyte 0.1M LiClO4/MeCN a. Electron withdrawing substitutions leads to an increase of the redox potential of quinone in LiClO4/MeCN. The conductivity of PEDOT backbone is hindered by the lithiated reduced quinone. In-situ uv-vis and EQCM is used to probe the exact PEDOT doping onset potential, confirming that conductivity of quinone is hindered by lithiated reduced quinone. In situ EQCM proves that mass change in the PEDOT doping region involves cation repulsion and dopants anion uptake.

**CM03.09.04**

**Effect of Coating on Lithiation in LiMn2O4**

Kimberly Bassett1, Robert W. Burton2, Siddharth Desphande2, Tim Fister1, Kim Ta1, Jennifer Esbenshade1, 

Kamila Wiaderek1, Karen W. Chapman2, Jeffrey Greeley2 and Andrew Gewirth1,

1University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Purdue University, West Lafayette, Indiana, United States; 4Argonne National Laboratory, Lemont, Illinois, United States.

We utilize in-operando powder X-ray diffraction (XRD) coupled with Rietveld analysis and density functional theory (DFT) calculations to describe how a Au coating affects the degree of lithiation available in bulk LiMn2O4 (LMO) and to explore the electronic interactions between the active material and its coating.

Lithium-ion batteries enable the portable electronics industry and appear increasingly in electric and hybrid vehicles. However, capacity fade in Li-ion cathodes remains a barrier between current technologies and longer-lasting devices and vehicles. LMO is a cathode active material that experiences limited life-times due to (1) a Jahn-Teller distortion which incites the formation of the tetragonal phase below 3 V vs Li/Li+, (2) Mn2+ dissolution into the electrolyte, and (3) electrolyte degradation at high potentials. Many approaches have been developed to protect LMO from these mechanisms, such as bulk or surface doping and deposition of protective coatings on the electrode surface.

Previously we deposited a Au coating via electroless deposition onto LMO.[1] The Au-coated LMO exhibited higher capacity after prolonged cycling likely due to a decrease in Mn dissolution. However, the effect of the coating on the initial capacity of LMO is unclear.

XRD results show that the Au-coated LMO exhibits smaller lattice parameters than uncoated LMO at low voltages (3.5 V vs Li/Li+) at which lithiation should be complete. The smaller lattice parameter suggests less Li+ has intercalated into Au-coated LMO compared to uncoated LMO. Integration of the cyclic voltammograms further supports this observation because Au-coated LMO passes less charge in comparison to uncoated LMO. DFT calculations suggest that Au coatings in the LMO surface make a partially delithiated surface more thermodynamically favorable, even at potentials where fully lithiated domains are expected. Chemical bonding analysis shows enhanced hybridization between Au and LMO at partially delithiated surfaces, including strong Au-O bonding character below the Fermi level. The partially oxidized Au leads to less electron density available to complete lithiation.


**CM03.09.06**

**In Situ Optical Spectroscopy During Electrochemical Coloration of WO3 Thin Films**

Simon Burkhardt1, 2, Jan Luka Dornseifer1, 2, Alexander Günter Strack1, 2, Matthias T. Elm1, 2, 4, Bernhard Lani-Wayda1 and Peter J. Klar1, 2, 

1Institute of Experimental Physics I, Justus Liebig University Giessen, Giessen, Germany; 2Center for Materials Research (LaMa), Justus Liebig University Giessen, Giessen, Germany; 3Mathematical Institute, Justus Liebig University Giessen, Giessen, Germany; 4Institute of Physical Chemistry, Justus Liebig University Giessen, Giessen, Germany.

Various applications for tungsten trioxide (WO3) thin films can be anticipated. Key applications include the employment of such films in electrochromic devices or lithium-ion batteries. For example, tungsten trioxide based “Smart Windows” already have been launched commercially. Nevertheless, optimization is still desirable in order to improve decisive product properties or to substitute critical materials such as tungsten itself. In particular, the former requires a very deep understanding of the electrochemical and optical properties of WO3 thin films under operating conditions. Furthermore, a correlation of properties and morphology needs to be established as the film morphology strongly affects charge transfer, charge transport, and coloration dynamics. To simultaneously investigate electrochemical and optical properties, a specially designed electrochemical cell has been used.[1] It enables us to perform in-situ optical experiments in the application of electrochemical methods. Results from spatially and temporally resolved transmission spectroscopy during potentiostatic coloration of amorphous and polycrystalline WO3 thin films reveal a significant impact of the thin film morphology on the concentration dependent lateral diffusion of protons. The impact of morphology on results from in situ transmission spectroscopy and in-situ Raman spectroscopy during electrochemical impedance spectroscopy is also investigated.


**CM03.09.07**

**A Study of Direct Methane Oxidation at Ceria/Gas Electrochemical Interface**

Yoonseok Choi1, JeongDo Yoo1, Han Gil Seo1, Hyun You Kim2 and WooChul Jung3, 

1MSE, KAIST, Daejeon, Korea (the Republic of); 2MSE, Chungnam National University, Daejeon, Korea (the Republic of); 3MSE, Uppsala, Sweden.

Direct-methane-fueled solid oxide fuel cells has received great attention for near-term realization of the high-efficiency energy conversion advantages even in the absence of a hydrogen delivery infrastructure. In particular, essentially all of the successful demonstrations in the related studies included ceria, either doped or undoped, as a component. However, limited understanding of the electrochemical oxidation of methane on ceria surface hinders implementing the electrode performance comparable to hydrogen fuels. Therefore, the aim of this study is to identify the electrochemical oxidation pathways of methane (CH4) on ceria surface through applied combined theoretical and experimental analyses. The identification of the predominant species on ceria surface coupled to the mixed valence of Ce3+ and Ce4+ can be a key to clarify the reaction mechanism. Here, we propose a real-time analysis of surface adsorbates and lattice ions during the methane electrooxidation using ambient pressure X-ray photoelectron spectroscopy. We combine the AP-XPS results with AC impedance spectroscopy (ACIS) and density functional theory (DFT) calculations for atomic-level mechanisms to understand the overall processes.

**CM03.09.08**

**Multi-Dimensional Electrochemical Characterization at Sub-100 nm Length Scale**

Omur F. Dageviren, Tyler Enright, Aaron Mascaro, Yoichi Miyahara and Peter Grutter, 

McGill University, Montreal, Quebec, Canada.

Simultaneous characterization of surface structure and local electrochemical properties is essential to establish correlations between mechanical and electrochemical material properties. In this work, we demonstrate that multi-dimensional electrochemical material characterization at sub-100 nm length scales
can be routinely achieved by combining atomic force microscopy (AFM) and scanning electrochemical microscopy (SECM). We use an amplitude modulation based AFM technique to modulate the distance between the scanned probe and the substrate [1]. Using a quartz tuning fork as our oscillator integrated with a pulled pipette allows the robust operation at small oscillation amplitudes [2, 3]. The pipette is filled with electrolyte and a back electrode inserted into the pipette allows for electrochemical measurements. We exhibit the robustness of combined electrochemical measurements on different surfaces and along interfaces. Moreover, our experiments elucidate the variation of local electrochemical properties of surfaces previously assumed to be pristine. We are also able to resolve electrochemical properties across grain boundaries due to the spatial resolution afforded by our operation architecture. Most importantly, our technique enables characterization of electrochemical properties across conducting/non-conducting interfaces. Also, our technique allows for the simultaneous measurement of local electrochemical properties and topography as a function of time, which opens a new pathway for corrosion studies of materials at nanometer length scale. All in all, we demonstrate a novel approach that facilitates robust operation of a scanning electrochemical microscope with AFM feedback while revealing electrochemical properties with sub-100 nm spatial resolution as a function of time at a selected potential landscape.


CM03.09.09
Why Does Oxide-Derived Silver Work so Well as an Electrocatalyst for CO2 Reduction? An EXAFS Study
Nienke Fing1, Marijn Blommaert1, Thomas Burdyny1, Anirudh Venugopal1, Alessandro Longo2 and Wilson Smith1; 1Delft University of Technology, Delft, Netherlands; 2European Synchrotron Radiation Facility, Grenoble, France.

To be fully able to take advantage of the current rise in electricity production, we have to find means to convert the electricity in fuels for both mobile (e.g. automotive and airline) and storage applications. With electrocatalysis, we can directly use renewable electricity to convert carbon dioxide and water into valuable products such as carbon monoxide, hydrogen, ethanol, and methane. One of the main bottlenecks for this technology is to find suitable electrodes that can act as efficient, stable and selective catalysts in the electrochemical reduction of CO2.

Due to the vast possibilities in choice for electrocatalyst, we use in operando techniques such as extended X-ray absorption fine-structure spectroscopy (EXAFS) to study the difference between highly active and less active catalysts, to see if any electronic, structural or compositional changes may promote the enhanced activity. In particular, we studied the difference between a pure silver film and oxide-derived silver, a nanostructured catalyst with improved CO2 reduction performance. We found that the presence of trace amounts of oxygen in the oxide-derived silver improves the reactivity of the silver. We found a direct correlation between the faradaic efficiency (or selectivity) of carbon monoxide and the amount of oxygen present in these catalysts. The faradaic efficiency relation does not scale with electrochemical surface area, ruling out other explanations for the enhanced selectivity that are related to mass transfer limitations. Earlier studies based on X-ray photoelectron spectroscopy (XPS) were not able to identify this oxygen, most likely because in ultra-high vacuum conditions, the silver self-reduces to Ag0. This in operando EXAFS study shows how vital the participation of in situ and in operando techniques is to properly understand electrochemical systems.

CM03.09.10
In Situ XANES and PDF Analysis of Electrochemical Cycling of Defective δ-MnO2 Nanosheet Electrodes
Madeleine N. Flint, Peng Gao, Robert Koch, Alec Ladonis and Scott Mixture; Kazuo Inamori School of Engineering, Alfred University, Alfred, New York, United States.

The roles of defects in electrochemical charge storage in 2-D oxides remain largely unexplored. MnO2 nanosheets exhibit an interesting defect, where reduction of MnVI causes displacement of the MnVII out of the plane of the nanosheet, forming a “surface Frenkel” defect. The defect content dramatically impacts the capacitance, where defects improve charge storage by factors of 2 or even 3 times. In-situ XANES data showed an increase in MnII content with increasing charge state (15% for a sample with 20% cation defects, and 17% for a sample with 27% cation defects), confirming that the Faradaic redox reaction is the main charge storage mechanism. Comparing XANES and CV loop calculations indicates that the change in Mn oxidation state upon charging is a function of the overall defect content, with higher defect content yielding proportionally less Mn reduction to the trivalent state. This result suggests that the Mn vacancies serve as new sites for K+ intercalation without changing the average Mn oxidation state. The XANES data corresponds well to our synchronous X-ray PDF study, which shows a reversible expansion of ~0.5 to 1% of the in-plane lattice spacing upon charging.

CM03.09.11
High-Temperature Thin-Film Calorimetry
Hendrik Wulfmeier, Alexander Omelchenko and Holger Fritz; Clausthal Univ of Technology, Goslar, Germany.

Thermodynamic properties of thin films may differ significantly from bulk counterparts due to e.g. increased impact of surface energy or grain boundary densities. As a consequence, sophisticated approaches to determine phase transformation temperatures and enthalpies of thin films and thin-film systems are indispensable. Moreover, numerous film deposition processes include high-temperature steps which require the applicability of calorimetry at high temperatures. A topical example is the deposition of active materials for thin-film batteries which is carried out at temperatures of up to 1000 °C [1]. The thin-film calorimeter (TFC) presented here takes advantage of the extraordinarily high temperature sensitivity of piezoelectric resonators which show increased thermal insulation and, thereby, improved sensitivity. Further, the detectable amount of heat is as low as about 1 mJ. Finally, improvements of the TFC system are done by application of free-standing piezoelectric resonators which show increased thermal insulation and, thereby, improved sensitivity. Materials investigation is done on the one hand by focusing on well known systems such as tin films to confirm the functionality of the TFC system. On the other hand, promising materials for thin-film batteries are investigated. One example is Li(NixMnyCoz)O2 (NMC, x+y+z=1) where the number of phase transformations between room temperature and 850 °C depends on the atmosphere applied. Temperatures and enthalpies of the phase transformations are extracted. Obviously, the presence of air suppresses the Jahn-Teller effect and, thereby, a phase transformation at high temperatures. Aluminum doping increases the stability of NMC which becomes evident from increased phase transformation temperatures.

The Effect of Illumination on the Geometric Structure of Water Molecules on GaN(0001) Surface

Masahiro Sato1, Yuki Imazeki2, Katsushi Fujii3, Yoshihiko Nakano4 and Masakazu Sugiyama1,1 Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan; 2Department of Electrical Engineering and Information Systems, The University of Tokyo, Tokyo, Japan; 3RIKEN, Tokyo, Japan; 4Global Solar Plus Initiative, The University of Tokyo, Tokyo, Japan.

First principles calculation has become a powerful tool for materials design in many fields [1]. However, theoretical design of photocatalysts has met with limited success, due to the lack of adequate modeling criteria: although photogenerated carriers accumulate at the semiconductor surface under continuous illumination, the effect of “semiconductor surface charging” on the photocatalytic activities have not been studied in detail. Thus, in our previous work, in order to handle the charged surface, we used the effective screening medium method, [2] in conjunction with density functional theory (DFT) calculations. We have modeled H atom adsorption on GaN surface and showed that the apparent adsorption energy decreases with decreasing surface electron density. In this contribution, we study in more detail the effect of illumination on the geometric structure of water molecules on GaN surface by both DFT calculations and infrared absorption spectroscopy.

The effect of UV illumination was modeled by adding excess holes to the GaN surface. The computational results show that both H atoms and -OH adsorbed on the GaN(0001) surface prefer the on-top site. Interestingly, when excess holes accumulate on the surface at low surface coverage, the hollow site becomes the most stable site for -OH even at moderate surface charge density around 10 μC/cm². On the other hand, in the case of H atoms, the on-top site remains the most stable site. At higher surface coverage (~ 1 ML), as the surface electron density decreases, the number of H atoms and -OH adsorbed on the surface decreases, i.e., the number of water molecules in the intact form increases. The number of dissociated water molecules roughly follows the “extended electron counting rule”; the maximum number of H atoms and -OH on a single Ga atom is around 3/4 - n, where n is the number of excess holes per Ga atom. In addition to the change of the geometric structure of the water wetting layer, a significant change in the O-H stretching frequency of the -OH on Ga atom is observed. The O-H stretching frequency shifts downwards as the surface electron density decrease, at the rate of ~ 2 cm⁻¹/μC/cm². Transmissin and ATR-FT(NIR) experiments are conducted to confirm this frequency shift. Although quantitative measurement of the O-H stretching frequency shift is difficult due to the strong absorption of bulk water, in line with the computational results, the red shift of the O-H stretching frequency upon UV illumination is observed. Considering the fact that water splitting involves bond cleavage, these results, which demonstrates that bond strengths change according to surface charging, indicate that surface charging has a large effect on photocatalytic reactions and should be taken into account when modeling the semiconductor/electrolyte interface.


CM03.09.13 Charge Transfer Dynamical Processes at Graphene-Transition Metal Oxides/Electrolyte Interface—Insights from In Situ Raman Spectro-Electrochemistry

Sanju Gupta and Sara B. Carrizzosa; Western Kentucky University, Bowling Green, Kentucky, United States.

Hybrids consisting of supercapacitive functionalized graphene (graphene oxide; GO reduced graphene oxide; rGO) and graphene nanosheets (MLG, electrochemically reduced GO; ErGO) and three-dimensional graphene scaffold (rGOHT; hydrothermally prepared) decorated with cobalt nanoparticles (CoNP), nanostructured cobalt (CoO and Co₃O₄) and manganese (MnO₂) oxides, assembled electrochemically facilitate chemically bridged interfaces with tunable properties. Since Raman spectroscopy can capture variations in structural and chemical bonding, Raman spectro-electrochemistry in operando i.e. under electrochemical environment with applied bias is employed to probe graphene/metal bonding and dynamic processes, 2) monitor the spectral changes with successive redox interfacial reactions, and 3) quantify the associated parameters including type and fraction of charge transfer. The transverse optical (TO) and longitudinal optical (LO) phonons above 500 cm⁻¹ belonging to CoO₃, CO₃O₄, MnO₂, and carbon-carbon bonding occurring at 1340 cm⁻¹, 1590 cm⁻¹ and 2670 cm⁻¹(belonging to D, G, and 2D bands, respectively, are analyzed with applied potential. Consistent variation in Raman band position and intensity ratio reveal structural modification, combined charge transfer due to localized orbi-tal re-hybridization and mechanical strain, all resulting in finely tuned electronic properties. Moreover, the heterogeneous basal and edge plane sites of graphene nanosheets in conjunction with transition metal oxide ‘hybrids’ reinforce efficient surface/interfacial electron transfer and available electronic density of states near Fermi level for enhanced performance. We estimated the extent and nature (n- or p-) of charge transfer complemented with Density Functional Theory calculations affected by hydration and demonstrate the synergistic coupling between graphene nanosheets and nanoscale cobalt (and manganese) oxides for applied electrochemical applications.

CM03.09.14 Replicating Bulk Electrochemistry in Multimodal Liquid Cell Microscopy

Khim Karki1, Julio A. Rodriguez Manzo1, Daan H. Alsem1, J. Tyler Mefford2, Jungjin Park3, William Chaehr4 and Norman Salmon1; 1Hummingbird Scientific, Lacey, Washington, United States; 2Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Liquid electroanalytical measurements performed inside the transmission electron microscopy (TEM) and synchrotron X-ray microscopy (XRM) are becoming more common and are used to study a wide range of electrochemical reaction-systems at the nanoscale. This approach has already started to produce new insights on the dynamics and structural changes during processes as lithium ion insertion/extraction, dendrite formation, metal nucleation, and metal corrosion. Despite the power of this approach, the challenges associated with replicating bulk-scale electrochemistry data in the environmental cell microcopy platform are well-known. First, the hardware components are not best optimized to perform in the reduced scale environment. Second, the chips configurations such as sizes and aspect ratios of different electrodes suitable for various electroanalytical measurements are poorly designed. Here, we present an operando liquid cell TEM/XRM microscopy platform that enables true electroanalytical measurements using some model compounds, mimicking bulk behavior.

The studies presented here are performed using electrochemical cells, which consist of two microfabricated chips sandwiched with electron transparent SiNx membranes for viewing in TEM/XRM. Using a new developed hardware system with a specialized configuration of working, counter and reference electrode, we performed cyclic voltammetry studies in 0.1M CuSO₄ and 20 mM K₃Fe(CN)₅/20 mM K₃Fe(CN)₆ in 0.1M KCl solutions. In the former case the copper deposition and stripping occurs at the working electrode at distinct redox peaks and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. In the latter case, the redox reaction of 20 mM ferrocyanide/ 20 mM ferricyanide in 0.1M KCl at different voltage scans show reversible electrode reaction during both the forward and reverse scans, elucidating bulk behavior. We will also present results where we compare this result to energy systems. These results and methodologies demonstrate that minimizing artefacts as well as optimizing the hardware for small volume and limited diffusion cell geometries allow mimicking the bulk data, which can be further implemented in the quantitative measurements of broader electrochemical systems.
Electrochemical concepts were recently identified as a novel route for low power voltage control of interfacial magnetism [1]. For this, electrolyte-gated structures are utilized, in which changes of magnetism can occur via capacitive and/or redox effects. Up to now, however, the underlying mechanisms at the electrode/electrolyte interface that are triggered by the applied voltage are often controversial. Solid state-, gel- and liquid electrolytes can all be utilized [1–4]. Liquid electrolytes offer a high ionic mobility and, due to electric double layer charging, an enhanced electric field at the interface. Therefore, they are favorable for achieving room-temperature effects at low voltage [4].

We present large electrochemically induced changes within several nanometers of FeOx/Fe films at room temperature utilizing a liquid alkaline electrolyte. In situ anomalous Hall effect and in situ ferromagnetic resonance demonstrate that large changes in magnetization can be achieved when applying merely 1 V. With those magnetic methods, integral magnetic changes are probed. Kerr microscopy is a powerful tool to probe and visualize the magnetic microstructure, but has not been applied during electrochemical operations yet. We designed an electrochemical cell for a Kerr microscope which allowed us, for the first time, to resolve the local impact of electrochemical redox reactions on the magnetic domain characteristics. Significant changes of the magnetic domains and the magnetization curve are observed in FeOx/Fe thin films. Changes of Fe metal thickness as well as the oxide transformation are discussed as possible key factors for the occurring phenomena.

DOI: 10.1016/j.pmatsci.2017.02.002

DOI: 10.1103/PhysRevB.87.224411

DOI: 10.1038/nmat4134

DOI: 10.1063/1.4942636


8:00 AM CM03.10.01
In Situ Observation of Magnetic Changes During Electrochemical Reactions of FeOx/Fe Nanostructures Jonas Zehner, Kenny Duschek, Ivan Soldatov, Nicolas Perez, Andreas Petz, Sebastian Faehler, Rudolf Schafer, Kornelius Nielsch and Karin Leistner; IFW Dresden, Dresden, Germany.

We study thermal and mechanical properties of five Li-ion electrode materials using in situ time-domain thermoreflectance (TDTR) and picosecond acoustics during charge/discharge cycles with Li+ ions. The conversion NiO and Fe2O3 electrodes show irreversible thermal conductivity and mechanical modulus loss of up to 80% and 40% after the first cycle. The intercalating V2O5 and TiO2 electrodes exhibit reversible thermal conductivity switching as a function of Li+ content without the irreversible thermal conductivity and mechanical modulus loss. The alloying Sb electrode shows thermal conductivity switching but the switching contrast gradually decreases with cycling. We attribute these large differences in the thermal and mechanical switching properties to the existence of Li+ pathways in the crystal structure of electrode materials. While the irreversible thermal conductivity and mechanical modulus loss of conversion electrode materials are caused by the lattice disordering and loss of crystal structure of electrodes by Li+ ion penetration, the Li+ ion pathway and the crystal structures of the intercalating electrodes are maintained during cycling. This study emphasizes the role of Li+ ion pathways of the electrode materials and their thermal and mechanical properties during cycling with Li+ ions.

8:15 AM CM03.10.02
Thermal Conductivity Changes of TiO2, V2O5, NiO, Fe2O3 and Sb During Electrochemical Cycling with Li+ Ions Jungwoo Shin1, Sanghyeon kim1, HoomKee Park2, Ho Won Jang2, David G. Cahill3 and Paul V. Braun1; 1University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

We study thermal and mechanical properties of five Li-ion electrode materials using in situ time-domain thermoreflectance (TDTR) and picosecond acoustics during charge/discharge cycles with Li+ ions. The conversion NiO and Fe2O3 electrodes show irreversible thermal conductivity and mechanical modulus loss of up to 80% and 40% after the first cycle. The intercalating V2O5 and TiO2 electrodes exhibit reversible thermal conductivity switching as a function of Li+ content without the irreversible thermal conductivity and mechanical modulus loss. The alloying Sb electrode shows thermal conductivity switching but the switching contrast gradually decreases with cycling. We attribute these large differences in the thermal and mechanical switching properties to the existence of Li+ pathways in the crystal structure of electrode materials. While the irreversible thermal conductivity and mechanical modulus loss of conversion electrode materials are caused by the lattice disordering and loss of crystal structure of electrodes by Li+ ion penetration, the Li+ ion pathway and the crystal structures of the intercalating electrodes are maintained during cycling. This study emphasizes the role of Li+ ion pathways of the electrode materials and their thermal and mechanical properties during cycling with Li+ ions.

8:30 AM CM03.10.03
Operando Probing of Phase Transformation in Li2TiO3 Using Electronic Conductivity and Its Applications in Neuromorphic Computing Yiyang Li1, Elliot J. Fuller, Yuping He, Sapan Agarwal and A. A. Talin; Sandia National Laboratories, Livermore, California, United States.

Electrochemical ion insertion yield phase transformations in many transition metal oxides, and such materials are used as electrodes in lithium-ion batteries. Based on nucleation theory, phase transformation initiates from a supersaturation of ions. This metastable or unstable ion concentration in the miscibility gap begins nucleation and growth. While this behavior is accepted from nucleation theory, it is very difficult to quantify and observe in electrochemical insertion materials because operando techniques typically do not possess the sufficient temporal resolution (< 1 sec) and sensitivity to both the ion concentration and the crystal phase to capture the supersaturation and subsequent phase transformation process.

Operando measurement of electronic conductivity possess high temporal resolution (up to megahertz) and is extremely sensitive to small changes in conductivity that correspond to differences in ion concentration or crystal phase. We use lithium insertion into a TiO2 thin film as a model system to measure the changes in electronic conductivity as a function of ion concentration and phase separation. TiO2 transforms from a lithium-poor anatase phase to a lithium-rich titane phase upon lithium insertion. Lithium insertion into either solid solution anatase or solid solution titane increases the electronic conductivity by reducing Ti4+ to Ti3+. On the other hand, the titane phase has a lower conductivity than anatase; therefore, during the anatase-to-titane phase transformation, the electronic conductivity drops despite an overall increase in the lithium concentration. We further confirm this relationship between doping, phase transformation, and conductivity using operando Raman spectroscopy.
Because lithium doping and the anatase-to-titanate phase transformation have opposite contributions to the electronic conductivity, we are able to temporally distinguish between the two behaviors. In particular, we note that the electronic conductivity momentarily rises a few seconds after lithium is inserted, corresponding to the supersaturation of lithium dopants. Over the course of several minutes, the conductivity drops because of some conversion of anatase to titane and the restoration of each phase back to their equilibrium lithium concentrations. This *operando* electronic conductivity measurement is able to directly capture this nucleation and growth process and shows that lithium diffusion and doping is much faster than the phase transformation in Li$_2$TiO$_3$. We demonstrate how lithium insertion in the solid solution anatase can be used as a non-volatile redox transistor for neuromorphic computing. More broadly, we demonstrate an *operando* method to probe supersaturation, nucleation, and growth with extremely high sensitivity and temporal resolution.

**SESSION CM03.11: Batteries II**

**Session Chairs: Matthew McDowell and Jagjit Nanda**

**Wednesday Morning, November 28, 2018**

**Hynes, Level 3, Room 300**

8:45 AM CM03.11.01

**Combined TXM/Acoustic Study of Sudden Pouch Cell Expansion** Daniel Steinpart and Clement Bommier; Princeton University, Princeton, New Jersey, United States.

Gas formation during lithium ion battery cycling can be both subtle and dramatic. In some cases it a slow degradation of the electrolyte solvent during cycling due to impurities, over charge, over discharge, or a cumulative combination of all three. In other cases it can be sudden and dramatic expansion due to auto-catalytic cathode decomposition, SEI decomposition, or again, a combination of these and other factors.

In this study we combine electrochemical acoustic signal interpretations with in operando transmission x-ray microscopy to determine the sequences and rates associated with various gassing modes in lithium ion pouch cells.

9:00 AM CM03.11.02

**Simultaneous Operando Measurements of the Local Temperature, State of Charge and Strain Inside a Commercial Lithium-Ion Battery Pouch Cell** Stephen J. Harris1, Zhili Feng2 and Yang Ren3; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3APS, Argonne National Laboratory, Argonne, Illinois, United States.

A high energy X-ray diffraction technique is employed in a new way to make operando through-thickness measurements inside a large format commercial Li-ion pouch cell. The technique, which has a sub-mm in-plane spatial resolution, simultaneously determines the local temperature, the local state of charge of each electrode separately (as opposed to the global average state of charge determined electrochemically), and the local in-plane elastic strain in each current collector, all without embedding any intrusive sensors that could alter battery behavior. As both thermal strain and mechanical strain develop during the charge-discharge cycling of the pouch cell, a novel approach developed herein makes it possible to separate them, allowing for measurement of the local temperature inside the battery. The operando experiment reveals that the temperature inside the cell is substantially higher than the external temperature. We propose that mechanical strain is due primarily to load transfer from the electrode to the current collector during lithiation, allowing determination of the local binder adhesion to its current collector. Detailed local SOC mapping illustrates non-uniform degradation of the battery pouch cell. The possibility for 3D measurements is proposed. We believe that this new approach can provide critically needed data for validation of detailed models of processes inside commercial pouch cells.

9:15 AM CM03.11.03

**Interrogating Electrolyte Decomposition Reactions in Advanced Batteries with Collector-Generator Measurements and Molecular Probes** Maureen Tang, Oliver Harris and Sophia Lee; Drexel University, Philadelphia, Pennsylvania, United States.

One of the most serious lifetime problems for established Li-ion and emerging “Beyond-Li” batteries is electrolyte degradation from unwanted side reactions. Electrolyte reduction into insoluble products causes formation and growth of the solid electrolyte interphase (SEI) and has been well-studied. However, both oxidation and reduction can also result in soluble gaseous or liquid products, which then can migrate to the opposite electrode and contribute to electrochemical activity. Such inter-electrode ‘communication’ reactions may be detrimental to battery lifetime; for example, dissolution of transition metals from the cathode and their deposition at the anode is known to accelerate capacity fade [1]. However, communication can also be beneficial when harmful products generated from the cathode are consumed by reduction at the anode [2]. Controlling chemical communication between electrodes for improved battery lifetime requires better understanding of the chemical reactions that generate soluble products. Electrochemical methods are particularly advantageous because they can directly assess the redox activity of reaction products. In particular, four-electrode generator-collector measurements such as the rotating ring-disk electrode (RRDE) are commonly used to quantify reaction selectivity in fuel cell catalysis. Despite their utility, these methods are seldom applied to nonaqueous battery research.

In this work, we apply generator-collector measurements and other electroanalytical techniques in order to understand how chemical communication between electrodes affects cell lifetime. In one application of our approach, the RRDE is used to probe mechanisms of transition metal incorporation into the SEI and their effect on through-film electron transport [3]. By using convection to control electrode cross-talk, we observe the presence of Mn contaminants from an upstream cathode at the downstream anode. Electrochemically interrogating the SEI with functionalized ferrocene mediators demonstrates that the through-film mediator reduction is much more sensitive to mediator functional group than size, indicating preferential partitioning into the organic SEI layer. Continuum-scale models to interpret the voltammetry show that incorporation of dissolved transition metals increases both the density and the activity of active sites within the SEI. We conclude that the inner, inorganic layer is responsible for preventing charge transfer through the SEI while the outer, organic layer is minimally important. Our model reconciles contradictory observations from the literature and identifies the most important components of a functional battery interface. Future work will discuss this mechanism in greater detail as well as our development of improved methods for studying these and related reactions.


9:30 AM CM03.11.04

**Using In Situ and Operando Methods to Characterize Phase Changes in Charged Lithium Nickel Cobalt Aluminum Oxide Cathode Materials** Eric
Lithium nickel cobalt aluminum oxide cathode materials (Li\textsubscript{x}Ni\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{3} – “NCA”) are seeing increasing use in demanding energy storage applications due to their high energy storage capacity. However, these materials can experience undesirable thermal runaway in real life applications, leading to catastrophic failures. In this presentation, I will review our work investigating the atomic scale changes that occur in NCA during thermal excursions. These studies will mostly focus on the use of in-situ transmission electron microscopy (TEM) but will include information gleaned from complementary probes such as in-situ x-ray diffraction and x-ray absorption. We have used these approaches to understand how thermal excursions can lead to bulk oxygen loss from the structure, how this oxygen loss is correlated with the movement of the transition metal ions, and how these movements lead to a series of structural changes from the spinel structure to the ‘disordered spinel’ structure to the rock-salt structure on the surface of the particles. Environmental TEM also allows us to explore how we can tune the surface activity, leading to the suppression of both oxygen loss and the initiation of the phase transitions. Finally, we will show how operando TEM approaches using electrochemical liquid-cell methods can lead to further insights into the relationship between lithium extraction and surface structural changes.

10:00 AM BREAK

10:30 AM *CM03.12.01
Probing Interfacial Charge Transfer Limitations of Sulfide Solid Electrolytes for All Solid-State Battery Applications Y. Shirley Meng1,2, 1University of California, San Diego, La Jolla, California, United States; 2Sustainable Power and Energy Center (SPEC), La Jolla, California, United States.

All-solid-state battery (ASSB) technology has its unique capabilities, among them the potential ability to enable the Li metal anode, operate at high voltage, along with improved safety. Among the known solid electrolytes, sulfides have shown promise due to facile battery fabrication, demonstrated high ionic conductivity, and ductility. Even though current sulfide solid electrolytes enable room temperature ASSB operation, their performance is still limited in terms of energy efficiency, power density, and the issue of dendritic growth of lithium at high current densities. All of those problems are closely related with solid-solid interfaces that arise in an ASSB. In this talk, we discuss and highlight the importance of probing and understanding interfacial phenomena with some of the advanced diagnosis techniques. Controlling and optimizing interfacial phenomena are crucial to overcome the performance obstacles to creating practical ASSB devices.

11:00 AM CM03.12.02
Operando XPS and In Situ SAM Measurements of Solid Electrolyte Interphase Formation at Lithium/Solid Electrolyte Interfaces Kevin N. Wood1, Andrew L. Davis1, K. X. Steier1, Shriram Santhanagopalan3, Chunmei Ban3, Sehee Lee4, Neil P. Dasgupta2 and Glenn Teeter3; 1Colorado School of Mines, Golden, Colorado, United States; 2University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4University of Colorado Boulder, Boulder, Colorado, United States.

Solid electrolytes such as Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12}(LPS), Li\textsubscript{10}GeP\textsubscript{2}S\textsubscript{12}(LGPS), and related materials show great promise for battery applications, with the potential to enable lithium-metal anodes and improve safety relative to conventional liquid electrolytes. On the other hand, many solid electrolytes are unstable against metallic lithium, and little is known about the chemical evolution of the solid electrolyte interphase (SEI) during cycling. The lack of detailed knowledge about SEI formation and evolution hinders the rational design of novel solid electrolytes with superior ionic conductivity, coupled with passivating SEI layers that facilitate interfacial charge transfer. Here we report on recent efforts to develop and apply novel operando X-ray photoelectron spectroscopy (opXPS) techniques that enable compositional and chemical-state analysis of battery interfaces during cycling. OpXPS measurements are implemented via the ‘virtual electrode’ approach, in which electrons are supplied to or extracted from an exposed interface using either an electron gun or ultraviolet light source, eliminating the need for a physical electrode and current collector. This approach enables real-time, in situ XPS measurements of an electrode/electrolyte interface under electrochemical operating conditions. Initial opXPS measurements probed the formation and evolution of the SEI between LPS and metallic lithium and documented chemically resolved overpotential losses associated with specific SEI phases during electrochemical cycling. These results are compared with experiments LGPS, and recent extensions of the virtual-electrode approach, including opXPS measurements on full cells, real-time in-situ scanning Auger microscopy (SAM) results, and the use of a low-energy Li\textsuperscript{+} ion gun to drive interfacial electrochemistry, are also described.

11:15 AM CM03.12.03
Lithium-Electrolyte Interface Characterization in All-Solid Batteries with Operando Electron and X-Ray Microscopies Natalie Seitzman1, Harvey Guthrey2, Johanna N. Weker1, Heather A. Platt1, Mowafak Al-Jassim2 and Svitlana Pylypenko1; 1Colorado School of Mines, Golden, Colorado, United States; 2SLAC National Accelerator Laboratory, Menlo Park, California, United States.

All-solid batteries offer increased theoretical capacity and wider voltage windows over traditional lithium-ion systems. Additionally, replacing flammable liquid electrolytes with a solid material provides a significant safety improvement, making solid electrolytes particularly attractive for electric vehicle applications. Lithium dendrite propagation at electrolyte surfaces, a micro- to nano-scale phenomenon, can be severely detrimental to battery lifetime. A greater understanding of fundamental processes at the lithium/anode electrolyte interface is therefore critical for the success of solid-state lithium battery systems.
Characterization of this interface comes with challenges, which include the extreme reactivity of lithium metal, narrowing the scope of experiments that can be conducted with conventional laboratory techniques, such as scanning electron microscopy (SEM). In this work, we developed operando SEM to provide high-resolution visualization of Li-Li$_2$PS$_3$ electrolyte and lithium metal electrode surfaces during cycling, and windowless EDS enabled identification of resultant lithium dendrites within the electrolyte. However, the near-surface nature of SEM and the reactivity of lithium ions to the electron beam complicate the analogy between laboratory experiments and practical batteries. Integration of surface observations from SEM with x-ray tomography experiments-in which a battery or symmetric cell can be analyzed whole—was used to increase the reliability of SEM data and to probe all anode-electrolyte interfaces at both the micro- and nano-scale.

At the micro-scale, operando X-ray computed tomography investigation revealed the same pattern of lithium migration with applied current in a sample that is more reflective of a realistic battery. Further, X-ray transmission microscopy (TXM) was utilized due to improved spatial resolution allowing the study of nano-scale features, with resolution closer to that of SEM but without reactivity of the sample to the beam. Our approach, combining SEM and X-ray operando studies, revealed lithium growth through cracks and pores in the Li-Li$_2$PS$_3$ ceramic material and demonstrated the influence of inhomogeneities in the lithium anode on dendrite growth at the electrode-electrolyte interface.

11:30 AM *CM03.12.04
Elucidating Ion Transport and Charge Transfer Behavior at Solid-Solid Interfaces via STEM Miaofang Chi; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Understanding transport behavior in solid-solid heterogeneous interfaces represents one of the most challenging problems in electrochemical systems. Sluggish ion transport and cycling instability are frequently observed at interfaces and the exact origins are unclear. These interfaces are composed of two materials with dissimilar lattice structures, distinctive chemical potentials, and can experience different responses to external stimuli. Multiple interfacial phenomena are often involved, including electrochemical and chemical reactions, elemental inter-diffusion, phase transformation, mechanical integrity, and interfacial space charge. These phenomena are spatially confined and are often correlated, complicating the mass and charge transfer behavior at interfaces and imposing challenges in their characterization. Scanning transmission electron microscopy (STEM) represents an ideal platform for studying interfacial behavior owing to its unprecedented spatial resolution. Recent new developments in STEM-based in situ and functional imaging is creating new opportunities to elucidate interfacial charge transfer behavior not previously feasible. This talk will highlight our recent studies conducted to probe the stability of solid-solid electrochemical interfaces using atomic-resolution in situ STEM and electron energy loss spectroscopy (EELS). Two systems, LiPON-Li and LLZO-Li will be compared and discussed. Observations show that while both LiPON and LLZO form a passivation layer when contacted with Li metal, their formation mechanism and equilibrium thicknesses differ significantly. Further, different responses are detected between the grain bulk and grain boundary when contacted with Li metal under an external bias; LLZO grains tend to be stable under a high external bias while grain boundaries are more prone to chemically reaction with Li. These results provide valuable insight toward the design of stable and conductive interfaces in Li metal batteries. This presentation will also focus on the application of new STEM-based techniques as applied to battery research, and will emphasize recent developments in 4-D STEM-based differential phase contrast imaging and EELS-based vibration spectroscopy.

Acknowledgement
Research sponsored by the Materials Sciences and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). Microscopy performed as part of a user project at Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

1:30 PM *CM03.13.01
X-Ray and Optical Spectroscopy and Imaging of the Electrode/Electrolyte Interface on Intermetallic Anodes Robert Kostecki, Philip N. Ross, Hans Bechtel, Jinghua Guo, Liang Zhang, Atetegeb Haregewoin and Ivana Hasa; Lawrence Berkeley National Lab, Berkeley, California, United States.

Intermetallic anodes e.g., Si, Sn, Sb have received significant attention as a viable alternative to graphitic carbon as the negative electrode in lithium-ion batteries due to its high capacity and availability. These electrodes can theoretically store charge nearly an order of magnitude higher than graphite. However, several problems have been identified that limit its utility including large crystallographic expansion upon lithiation, which translates to particle cracking, particle isolation, and electrode delamination issues, as well as electrolyte side reactions, which affect electrochemical performance and lifetime of these electrodes in battery cells.

The key problems that have hindered practical application of intermetallic anodes in commercial Li-ion batteries are: (i) the large volume changes during cycling, which results in cracking and decrepitation of the active material, and loss of electronic connectivity and mechanical integrity in the composite electrode, (ii) inherent non-passivating behavior of silicon in organic electrolytes, which results in large irreversible capacity loss and gradual electrolyte consumption during the electrode operation. However, despite extensive research in the past four decades, the intrinsic behavior and the corresponding barriers to implementation of silicon anodes have in Li-ion systems have not been fully understood and remedied. This study involves diagnostic evaluations of silicon composite electrodes as well as studies of the properties of the individual components and their interfaces. Unraveling the basic function and operation of the SEI layer on Si, Sn, Sb and their binary and ternary alloys with transition metals to elucidate interfacial charge transfer behavior not previously feasible. This talk will highlight our recent studies conducted to probe the stability of solid-solid electrochemical interfaces using atomic-resolution in situ STEM and electron energy loss spectroscopy (EELS). Two systems, LiPON-Li and LLZO-Li will be compared and discussed. Observations show that while both LiPON and LLZO form a passivation layer when contacted with Li metal, their formation mechanism and equilibrium thicknesses differ significantly. Further, different responses are detected between the grain bulk and grain boundary when contacted with Li metal under an external bias; LLZO grains tend to be stable under a high external bias while grain boundaries are more prone to chemically reaction with Li. These results provide valuable insight toward the design of stable and conductive interfaces in Li metal batteries. This presentation will also focus on the application of new STEM-based techniques as applied to battery research, and will emphasize recent developments in 4-D STEM-based differential phase contrast imaging and EELS-based vibration spectroscopy.

Acknowledgement
Research sponsored by the Materials Sciences and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). Microscopy performed as part of a user project at Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.
Understanding the Many Length Scales of Ion Insertion Solids  

William Chueh; Materials Science and Engineering, Stanford University, Stanford, California, United States.

The availability of low-cost but intermittent renewable electricity (e.g., derived from solar and wind) underscores the grand challenge to store and dispatch energy so that it is available when and where it is needed. Redox-active materials promise the efficient transformation between electrical and chemical energy and are at the heart of carbon-neutral energy cycles. Understanding design rules that govern materials chemistry and architecture holds the key toward rationally optimizing technologies such as lithium-ion batteries and solid oxide fuel cells. Electrochemical reactions involved in these technologies span diverse length and time scales, ranging from Ångström s to meters and from picoseconds to years. As such, establishing a unified, predictive framework has been a challenge. The central question that motivates our research is, “can we understand and engineer redox reactions at the levels of electrons, ions, molecules, particles and devices using a bottom-up approach?” In this talk, I will discuss how we integrate synthesis, fabrication, in-situ characterization, modeling and data analytics to understand molecular pathways and interfacial structure, and to bridge fundamentals to energy storage and conversion technologies by establishing new design rules.

2:30 PM BREAK

SESSION CM03.14: Batteries III  
Session Chairs: Miaofang Chi and Stephen Harris  
Wednesday Afternoon, November 28, 2018  
Hynes, Level 3, Room 300

3:30 PM *CM03.14.01  
Revealing Li-Ion Battery Processes Using Operando Neutron Depth Profiling and NMR Methods  
Anne Co, Danny Liu, Jose Lorie Lopez, Daniel Lyons, Lei Cao and Philip Grandinetti; Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States.

Rechargeable Li-ion batteries (LIBs) have been the predominant energy storage for a wide range of portable devices like cell phones, laptops and digital electronics. Non-destructive methods such as neutron depth profiling (NDP) and solid state NMR are ideal for probing Li complex formation, accumulation and transport within the battery material during charge/discharge. Currently, our work is focused on understanding the effect of an electrochemical event to the materials’ storage properties using NDP and NMR techniques in operando. Specifically we report our recent work on the preferential Li nucleation, Li trapping, Li transport in intermetallic materials like Li,Sn, Li,Si, and Li,Al, and evidence of formation and accumulation of a Li,Sn metastable phase that is correlated to capacity fade.

4:00 PM CM03.14.02  
Operando and Three-Dimensional Visualization of Ion Depletion and Lithium Growth by Stimulated Raman Scattering Microscopy  
Qian Cheng, Lu Wei, Wei Min and Yuan Yang; Columbia University, New York, New York, United States.

Visualization of ion transport in electrolyte provides fundamental understandings of electrolyte dynamics and electrolyte-electrode interaction, shedding light on material designs to enhance device performance, such as batteries and fuel cells. However, this task is extremely challenging for existing techniques due to their inability to capture the low ionic concentration (<1 M) and the fast dynamics (1-10 s) of the electrolyte. Here we show that an emerging Stimulated Raman Scattering (SRS) microscopy offers the required spatial (sub-micrometer optical resolution), temporal (faster than 1 s per frame) and chemical (around mM) sensitivities to address this challenge. In Raman, [Li+] can be probed by either Li+-solvent interaction, or vibrational mode in the anion which has the same concentration as Li+ due to electroneutrality. Utilizing this technique, we examined and provided evidence for a long-lasting question: How does Li+ concentration correlate with and contribute to the uneven deposition of lithium metal? A three-stage lithium deposition process is uncovered, each corresponding to no-depletion, partial-depletion and full-depletion regime of Li+ respectively. Further analysis reveals a previously uncharacterized spatial heterogeneity of Li+ concentration near lithium surface, and a positive feedback mechanism between the inhomogeneous growth of lithium and the local ionic concentration or flux. Finally, we demonstrate that Li,P,O, based artificial solid electrolyte interface (SEI) is effective in homogenizing Li+ concentration near lithium surface and suppressing the dangerous dendritic growth of lithium, which provides new insights into battery safety. This study shows that SRS microscopy is a powerful technique for imaging ion transport and will open various applications in materials and energy fields.

4:15 PM CM03.14.03  
Solvent Dynamics at Electrode Interfaces—Analysis of SEI Formation Pathways and Electric Fields Using Vibrational Spectroscopy  
Jarred Olson, Patrik Johansson, David Castner and Cody Schlenker; University of Washington, Seattle, Washington, United States.

At an electrode interface, redox mechanisms associated with electrolyte solvent breakdown into components of the solid-electrolyte interphase (SEI) layer are often invoked to rationalize the cycling performance of battery materials. Mechanisms of SEI formation frequently include the release of gas, whose composition serves as an indicator of subsequent chemical structures comprising the SEI. Recently, our group monitored reduction of fluoroethylene carbonate (FEC) and ethylene carbonate (EC) electrolyte solvents on silicon nanoparticles using interface-sensitive vibrational sum frequency generation (SGF) spectroscopy in tandem with electrochemistry. We observe SGF signatures that suggest carbon monoxide (CO) evolution on nano-Si proceeds at distinct lithiation potentials for different electrolyte solvents. FEC appeared to preferentially follow a 2-electron reduction pathway regardless of the degree of lithiation (potential) of silicon. However, EC appeared to be more sensitive to the degree of Si lithiation, reducing to CO only at the highest lithiation state of Si. Upon prolonged reduction of EC, we additionally observe the formation of poly(EC), which is soluble in carbonate-based electrolytes and appears to form through the release of CO2. The results of this study validate previous computational descriptions of FEC and EC reduction, as well as provide insight on a failure mechanism EC-based electrolytes impart upon Si anodes.

The phenomena responsible for the aforementioned SEI-formation processes is the intense electric field magnitude at the electrode interface. Quantification of the local field at the electrode/electrolyte junction has remained an elusive endeavor due to the lack of a reference material that is calibrated against known value. Vibrational Stark effect spectroscopy, a method historically used to characterize the strength of electric fields in enzyme active sites, commonly utilizes the C=O group as a calibrated field reporter. Thus, carbonate-based electrolyte solvents (all of which contain the C=O group) provide amendable conditions for operando characterization of electric fields confined within the electrochemical double layer. Recently, we calibrated the
sensitivity of EC, FEC and diethyl carbonate (DEC) to electric fields, demonstrating that their responsivity to an arbitrary field follows a linear trend. Referring results of the DEC/LiCoO$_2$ junction as a model system, we estimate that the field localized within the electrochemical double layer is in the MV/cm range before electrochemical cycling is induced, providing a lower boundary of field strengths prior to electrochemical cycling. As the progress of high-voltage electrode storage materials advances, understanding interfacial fields may provide new avenues for improving electrolyte stability by tailoring the interface electrostatics.

4:30 PM CM03.14.04

Electrode-Electrolyte Reactivity Trends and Coatings Screening at Positive Electrodes in Li-Ion Batteries Livia Giordano$^1$, Pinar Karayaylali$^1$, Yang Yu$^1$, Yu Katayama$^1$$^{3,4}$, Soo Kim$^1$, Yirui Zhang$^1$, Nenian Charles$^1$, Sokseihua Muy$^1$, Filippo Maglia$^2$, Isaac Lund$^3$ and Yang Shao-Horn$^1$; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2BMW Group, München, Germany; 3BMW Group Technology Office USA, Mountain View, California, United States; 4Department of Applied Chemistry, Yamaguchi University, Ube, Japan.

Understanding the electrochemical reactions at the interface between the positive electrode and the organic electrolyte is crucial for the rational design of Li-ion batteries towards improved capacity retention and cycle life. Commonly used positive electrodes, such as layered intercalation oxides, exhibit different degrees of chemical reactivity with carbonate-based electrolytes [1, 2], yet a comprehensive understanding of the reaction mechanisms and the parameters governing the interfacial reactivity is still lacking. Here we employed density functional theory calculations to study the reaction mechanism and reactivity trends for organic solvents at the surface of oxides. We found that solvent dissociation is thermodynamically more favorable than electrophilic attack, nucleophilic attack and dissociation with oxygen extraction from the oxide surface on layered oxides. We showed that the dissociation is accompanied by an interfacial charge transfer, where the solvent molecule is oxidized and the transition metal oxide is reduced. Solvent dissociation became thermodynamically more favorable on oxide surfaces with transition metal ions from left to right in the periodic table or by increasing transition metal oxidation state in the oxides upon delithiation, where greater solvent dissociation was found as the oxide Fermi level was lowered into the oxide O 2p band [3]. Similar driving force was found for the dissociation of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diphenyl carbonate (DPC) additive [4]. The predicted trends can explain the reactivity and the interfacial compositions observed experimentally for LiCoO$_2$, LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (NMC) and Ni-rich NMC. These findings were used to identify a design principle for the screening of coating materials which can prevent the dissociation of organic carbonates.


SESSION CM03.15: Poster Session II: In Situ Investigation of Electrochemical Materials

Session Chairs: Neil Dasgupta and Matthew McDowell

Wednesday Afternoon, November 28, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

CM03.15.01

Development of a Method to Characterize Active Sites in Photocatalysis Using In Situ Transmission Electron Microscopy Noah Glachman$^1$, Noah Geller$^1$, Alexander Shea$^1$, Khim Karki$^2$, Daan H. Alese$^1$, Julio A. Rodriguez Manzo$^2$, Norman Salmon$^2$, Deep M. Jariwala$^3$ and Eric A. Stach$^1$$^{3,4}$; 1Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2BMW Group, München, Germany; 3BMW Group Technology Office USA, Mountain View, California, United States; 4Nanoscale Characterization Facility, Philadelphia, Pennsylvania, United States.

Hydrogen gas has the potential to be a clean source of sustainable energy due to its high energy density. However, greenhouse gas emissions are still a major byproduct of current hydrogen production methods. Photoelectrochemistry provides a promising, environmentally friendly route to hydrogen production; however, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting reaction are currently poorly understood. Further understanding of the chemical physics governing the active hydrogen evolution sites would allow for better design of photoelectrochemical devices and thus lead to improved reaction efficiencies. This will overcome one of the major barriers impeding this promising technology. We have developed a unique in-situ photoelectrochemistry transmission electron microscope (TEM) liquid cell sample holder which can be used to characterize these reactions in real time at nanometer length scales. In order to provide accurate, quantitative information, it is necessary to accurately deposit the photocatalyst of interest onto microfabricated electrodes. In this research, a precise sample deposition technique utilizing an inkjet printer has been developed along with stable suspensions of known photocatalysts, leading to site-specific deposition onto the electrode chips. These experiments will investigate the mechanisms by which selected photocatalysts induce water splitting and allow for the identification of defect features that serve as the active sites. Specifically, this experimental design allows for correlation between L-V characteristics and real time, high magnification imaging and spectroscopy, elucidating information about photocatalytic mechanisms at the nanoscale. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS$_2$ flakes. These experiments will lay the groundwork for the use of this novel experimental design to investigate a wide variety of photoelectrochemical systems using this in-situ approach.

CM03.15.02

In Operando Optical Microscopy and Vertex Delay Cyclic Voltammetry for Direct Observation of Lithium Dendrite Regimes Noah Hart; NICE, Mountain View, California, United States.

Understanding the mechanisms of lithium dissolution/deposition has benefited significantly from in-operando microscopy. Recent work has used optical microscopy to explore dendritic growth. Existing designs face lithium strips across from each other, with the optical instrument placed in the plane of the strips. This work presents a system that cycles lithium from the edge, rather than the face. By limiting electrochemical activity to an edge, (a) the entire electrochemical process on the electrode surface is within the optical instrument's depth of field, (b) tight control of current density can be achieved and (c) the removal of a native layer can be easily and reliably replicated, offering a high purity lithium surface unaffected by shelf-life. This system allows for unambiguous identification of which deposition/dissolution phenomena are occurring in the cell at different current densities and cycle life.

Optical observations are paired with cycling and cyclic voltammetry with vertex delays (CV). A simple V=IZ relationship is used to convert current-
controlled cycling and voltage-controlled CV, showing how directly these two regimes translate. CV is then used to explore a voltage controlled environment for the investigation. With CV a milder voltage environment can be imposed, reducing the reaction complexity and the cell can be observed via current response. This allows for a clear delineation of different reaction regimes, where kinetic, electronic and diffusion limitations are expressed clearly via current rate and regimes can run their course, independent of the requirements of cell cycling. Decoupling the reaction from a controlled current allows for more dramatic changes in the scale of the reactivity, as one regime takes over from another, with a current response that reflects their distinct bottle-necks. The optical cell allows different dendrite deposition/dissolution regimes to be unambiguously identified and studied, validating shifts between regimes and correlating them to the electrochemical response.

CM03.15.03
Asymmetric Dynamics of Ion Insertion/Extraction of Lithium Battery Electrodes by Electro-Autocatalyst and Electro-Autoinhibitor Jihyun Hong1,2, Hongbo Zhao3, Jungjin Park4, Kapil Lim1,2, William Gent6,6, Samanbir Kalirai1,4, Michael F. Toney2, William Chueh1,2 and Martin Bazant1,2,6, MSE, Stanford University, Stanford, California, United States; 2Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 3Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4The Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 5Department of Chemistry, Stanford University, Stanford, California, United States; 6Department of Mathematics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Reversible insertion and extraction of a guest ion into the host crystal is the fundamental reaction underpinning insertion electrochemistry and has been widely applied to store energy and tune catalysts. It has been considered that the ion extraction and insertion reactions are reversible and following near-equilibrium paths for charge and discharge of lithium ion batteries, respectively. However, recent studies have revealed that the dynamics of the ion extraction and insertion can be altered by current density (reaction rate) and reaction direction in a phase-separating compound, Li1-xFePO4, using operando characterization techniques such as X-ray diffraction (XRD) and X-ray microscopy. We recently demonstrated that the kinetics of the reactions at solid-liquid interface governs the uniformity of ion insertion/extraction reactions by electro-autocatalyst and autoinhibitory. Here, we first show the asymmetric dynamics of ion insertion and extraction of a model solid-solution compound, lithium transition metal oxides. Combining population dynamics theory, operando XRD and scanning transmission X-ray microscopy (STXM), we show that the non-constant reaction kinetics results in the heterogeneous delithiation and homogeneous lithiation, which eventually affects the fast-charging capability of lithium ion batteries.

CM03.15.04
Controlling Interfacial Properties of Solid-State Lithium Batteries Using Atomic Layer Deposition Kirit Joshi1, Francisco Javier Quintero Cortes2, John Lewis2 and Matthew McDowell1,2, 1Georgia W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Solid-state lithium batteries (SSLiBs) could enable improved safety and higher energy density compared to traditional lithium-ion batteries due to the use of metal anodes without dendrite growth. However, successful implementation of solid electrolytes within batteries is contingent upon controlling the chemical, mechanical, and electronic properties at solid electrolyte/electrode interfaces. SSLiB interfaces can exhibit poor wetting properties, leading to interfacial void spaces and high impedance. Furthermore, many solid electrolytes are chemically unstable in contact with electrodes. This project aims to stabilize traditionally unstable interfaces between lithium metal and ceramic electrolytes through the use of atomic layer deposition (ALD) of thin film oxide protection layers. It is expected that these protection layers will improve wetting properties and prevent or slow detrimental anode-electrolyte interactions. A custom ALD instrument has been designed and constructed for this project. This fully-automated instrument allows for the deposition of ternary oxides with atomic precision. It features pneumatic control of valves, a custom LabVIEW Virtual Instrument interface, and real-time pressure feedback control. This instrument is ideal for coating nanometer-scale films on either bulk solid electrolyte pellets or on powder. The custom reactor is used to coat NASICON-type solid electrolytes, including Li1-xAlxTi2-x(PO4)3, with oxide thin films (Al2O3, ZnO). These NASICON materials are shown to readily react in contact with Li metal. The effect of these ALD protection films on electrochemical behavior and lifetime are compared to that of uncoated materials to determine whether the ALD coating improves battery performance and stability. Ultrathin oxide layers are found to improve the stability of the solid electrolytes in contact with Li during galvanostatic cycling. In particular, the ALD layers are shown to substantially extend the time to failure during cycling and to alter degradation pathways within cells. In conjunction with other students, ex situ and in situ characterization is used to uncover the evolution of these layers during cycling. These results are important for the development of stabilized, high-conductivity solid electrolytes for solid-state batteries.

CM03.15.05
Enhancing In Situ Far-Infrared Spectroelectrochemistry Sensitivity with Gold Nanostructures Luciano J. Macedo and Frank N. Crespilho; São Carlos Institute of Chemistry, University of São Paulo, São Carlos, Brazil.

Organometallic structures are fundamental building blocks in life, being crucial components of biological systems such as metalloproteins and far-infrared (FIR) spectroscopy plays a fundamental role in the identification and investigation of metal-ligand bond vibrational modes in these organometallic structures. Due to the possibility of investigating the influence of the redox state of the metal on the structural behavior, in-situ spectroelectrochemistry using this region of the electromagnetic spectrum is applied; however, this analytical approach is limited due to the low sensitivity of optical components available to date even when synchrotron light is used as source of infrared radiation. To address this issue, we utilized the surface-enhanced infrared absorption (SEIRA) effect to promote more sensitivity in the spectroscopic analyses, using surfactant-free gold nanostructures in order to avoid the interference from organic matter. As probe, we used well-known redox active organometallic probes, whose iron-carbon, iron-nitrogen, and iron-sulfur bonds vibrational modes are active in the FIR region. Thus, we observe an enhancement of the signal from these vibrational modes in the FIR spectrum when these gold nanostructures are in close interaction with these probes. Also, this absorption enhancement benefits the use of this approach in aqueous medium electrochemistry, probing more clearly the role of the metallic atom redox state on the whole organometallic structure. Based on these observations of such control of the vibrational modes in the FIR spectroscopy by electrochemistry, this approach might also be helpful to further investigate organometallic interaction with biological relevant molecules such as metalloproteins.

CM03.15.06
In Situ Study of the Reaction Processes and Mechanisms of Nanocatalysis by Enhanced Raman Spectroscopy Chen Wang; Xiamen University, Xiamen, China.

In-situ dynamic monitoring of nanocatalytic processes is of significant importance for the insightful understanding of reaction mechanisms and structure-activity relationships. Raman spectroscopy can provide fingerprint structural information. However, its sensitivity is too low to achieve the in-situ detection of trace amount of surface species on catalysts. To solve this long-standing problem, we develop a SHINERS-satellites strategy which can be used to in-situ track the nanocatalytic processes based on shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). In the SHINERS-satellites strategy, nanocatalysts are assembled on shell-isolated nanoparticles (SHINs), leading to the formation of SHINERS-satellites nanocomposites (Au core-silica shell-
Catalyst satellites. The Au cores can generate strong electromagnetic field to enhance the Raman signals of the species adsorbed on the catalysts, while the silica shells can isolate the influence of the Au cores on the catalysts and reactions. Therefore, SHINERS-satellites strategy can be used to in-situ detect the trace amount of active species and intermediates during nanocatalytic reactions. It is a general strategy and can be used for different kinds of nanocatalysts including monometal, bimetal, trimetal, oxide, etc. With SHINERS-satellites strategy, the reaction processors of CO oxidation on Pt- and Pd-based nanocatalysts are in-situ monitored. The intermediates including active oxygen species, Pt-C, Pd-C, etc. are in-situ detected, and the reaction mechanisms as well as structure-activity relationships are revealed at a molecular level. Furthermore, SHINERS-satellites strategy has also been used in the in-situ study of catalytic hydrogenation using the conversion of pNTP to pATP as a probe reaction. Direct spectroscopic evidences for the hydrogen spillover at interfaces are obtained, and the influence of the interfacial structures on the hydrogen spillover and reaction pathways has been revealed. At the same time, the transportation of hot electrons generated on plasmonic nanomaterials in different materials has been studied using SHINERS. It is found that hot electrons can only be transferred via semiconductors and then trigger photocatalytic reactions. This study provides not only a new strategy for the in-situ study of nanocatalysis but also molecular information of the reaction mechanisms and structure-activity relationships, thus greatly helps the rational design and development of highly efficient nanocatalysts.

CM03.15.07
Characterizing the Mechanical Failure of Solid Electrolytes Through Operando X-Ray Tomography Jared Tippens, Matthew McDowell, Francisco Javier Quintero Cortés, John Lewis, Christopher Saldana, John Miers and Haipeng Qiao; "School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; "George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Solid state batteries have attracted growing interest due to their increased safety and potentially high energy density when compared with traditional lithium-ion batteries with liquid electrolytes. Solid electrolytes have been shown to offer a greater resistance to lithium dendrite growth when using a lithium metal anode, but recent studies demonstrate that metal growth and mechanical degradation can still occur when using a ceramic ion-conducting membrane. The low fracture toughness of ceramic solid electrolytes suggests that they are susceptible to mechanical failure, particularly after cracks are initiated in the material. While several studies have been conducted to characterize the mechanical properties of solid electrolytes, little work has been done to characterize and understand the fracture process during electrochemical charging. In this work, we use operando x-ray tomography with a lab-scale computed tomography (CT) instrument to investigate the mechanical degradation process in Li1.5Al0.5Ge1.5(PO4)3 (LAGP), a NASICON-type solid electrolyte during cycling. NASICON electrolytes have garnered interest due to its high ionic conductivity. A symmetric cell with lithium metal electrodes was cycled galvanostatically, and 3D images were collected showing the morphology of the solid electrolyte at different stages of electrochemical cycling. A voxel resolution of 18 μm was obtained, allowing for thorough characterization of the microstructural evolution during the experiment. Through this methodology, the locations of crack initiation and the process of crack growth can be tracked voxel by voxel as a function of the number of galvanostatic cycles. The results show the potential for using this non-invasive method to investigate the mechanical degradation behavior of various solid electrolytes. This information paves the way to future studies in which protection layers between the electrolyte and mechanical failure could be applied to prevent or retard mechanical failure in solid electrolytes to prolong battery life.

CM03.15.08
XPS on Li Battery Related Compounds—Analysis of Inorganic SEI Phases and a Methodology for Charge Correction Kevin N. Wood, Sang-Don Han, Andrew L. Davies, Yun Xu, Andriy Zakutayev, Neil P. Dugaspta and Glenn Teeter; "National Renewable Energy Laboratory, Lakewood, Colorado, United States; "University of Michigan, Ann Arbor, Michigan, United States; "San Diego State University, San Diego, California, United States.

Accurate identification of chemical phases associated with the electrode and solid-electrolyte interphase (SEI) is critical for understanding and controlling interfacial degradation mechanisms in lithium-ion-containing battery systems. To study these critical battery materials and interfaces, X-ray photoelectron spectroscopy (XPS) is a widely used technique that provides quantitative chemical insights. However, due to the fact that a majority of chemical phases relevant to battery interfaces are poor electronic conductors, phase identification that relies primarily on absolute XPS core level binding-energies (BEs) can be problematic. Charging during XPS measurements leads to BE shifts that can be difficult to correct. These difficulties are often exacerbated by the coexistence of multiple Li-containing phases in the SEI with overlapping XPS core levels. To facilitate accurate phase identification of battery-relevant phases (and electronically insulating phases in general), we propose that BE separations between core levels present in a particular phase (e.g. BE separation between the O 1s and Li 1s core levels in Li2O) should be used as an additional constraint in order to significantly improve reliability of phase identification. This approach is applied to XPS data acquired from six battery-relevant inorganic phases including lithium metal (Li0), lithium oxide (Li2O), lithium peroxide (Li2O2), lithium hydroxide (LiOH), lithium carbonate (Li2CO3) and lithium nitride (Li3N). To demonstrate the practicality of this approach, we apply the charge-correction methodology to ex-situ and operando XPS data acquired on solid electrolytes and Si anodes materials.

CM03.15.09
Origin of Contraction Force in Artificial Muscle Based on Conducting Polymers Keiichi Kaneto, Fumito Hata and Sadahito Uto; Osaka Institute of Technology, Osaka, Japan.

Artificial muscles are interested in the application to human friendly robots, because of the noiseless and simple structure for complicated motions. Among various materials, conducting polymers are superior in operation voltage, magnitude of deformation and contraction force. These features originate from the mechanism of deformation, as well as the high electrical conductivity, flexibility and toughness of conducting polymers. Electrochemical oxidation and reduction of conducting polymers induces the electrochemomechanical deformation (ECMD) by insertion and exclusion of ions. It has been shown that the magnitude of deformation is determined by the total volume of inserted bulky ions, being up to 40% and larger than skeletal muscle of 25%. The contraction force is several tens MPa, being larger than that of skeletal muscle of 0.4 MPa. However, little is known about the origin of contraction force. The strain of ECMD in the polymer films was measured in-situ as the function of tensile stress using a laser displacement meter. The strain decreased with increasing the tensile stress, which gave the EC stress-strain curve. In this talk, the origin of EC contraction force is discussed based on EC stress-strain relationships as well as structure-activity relationships are revealed at a molecular level. Furthermore, SHINERS-satellites strategy has also been used in the in-situ study of catalytic hydrogenation using the conversion of pNTP to pATP as a probe reaction. Direct spectroscopic evidences for the hydrogen spillover at interfaces are obtained, and the influence of the interfacial structures on the hydrogen spillover and reaction pathways has been revealed. At the same time, the transportation of hot electrons generated on plasmonic nanomaterials in different materials has been studied using SHINERS. It is found that hot electrons can only be transferred via semiconductors and then trigger photocatalytic reactions. This study provides not only a new strategy for the in-situ study of nanocatalysis but also molecular information of the reaction mechanisms and structure-activity relationships, thus greatly helps the rational design and development of highly efficient nanocatalysts.

CM03.15.07
Characterizing the Mechanical Failure of Solid Electrolytes Through Operando X-Ray Tomography Jared Tippens, Matthew McDowell, Francisco Javier Quintero Cortés, John Lewis, Christopher Saldana, John Miers and Haipeng Qiao; "School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; "George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Electrochemical reduction of CO2 is a promising approach towards reducing the atmospheric CO2 levels and converting CO2 to usable fuels. While a variety of electrocatalysts have been developed for CO2 reduction, a major challenge remains in minimizing co-evolution of hydrogen as well as maintaining a sufficiently high CO2 concentration in the electrolyte. Herein we report the effect of CO2 bubbles on the current density and product distribution mix during CO2 reduction. We compare and contrast against standard approaches using CO2 atmospheres and demonstrate high faradaic efficiency towards carbonaceous products using copper catalyst, as well as a sustained higher current density and propose broader implications towards scaling up.

CM03.15.10

CM03.15.07
Characterizing the Mechanical Failure of Solid Electrolytes Through Operando X-Ray Tomography Jared Tippens, Matthew McDowell, Francisco Javier Quintero Cortés, John Lewis, Christopher Saldana, John Miers and Haipeng Qiao; "School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; "George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Electrochemical reduction of CO2 is a promising approach towards reducing the atmospheric CO2 levels and converting CO2 to usable fuels. While a variety of electrocatalysts have been developed for CO2 reduction, a major challenge remains in minimizing co-evolution of hydrogen as well as maintaining a sufficiently high CO2 concentration in the electrolyte. Herein we report the effect of CO2 bubbles on the current density and product distribution mix during CO2 reduction. We compare and contrast against standard approaches using CO2 atmospheres and demonstrate high faradaic efficiency towards carbonaceous products using copper catalyst, as well as a sustained higher current density and propose broader implications towards scaling up.

CM03.15.10
One of the biggest obstacles in the way of battery technology development is the limited amount of information that one can obtain from the battery mechanism without taking it apart. Here we are presenting a novel nondestructive battery assessment technology that is capable of obtaining crucial information from batteries even when the cells are encased in conductive material. One important application is commercial-type cell-phone batteries, which can be analyzed with this method. The technique is based on measuring the magnetic susceptibility of active ingredients inside an electrochemical cell that is affected by the oxidation of the materials to give insights into the state of charge (SOC) of the battery, its failure mechanisms and the current distributions. The technique has been demonstrated on various cell types, defects, chemistries, and current level. The measurement is fast (a couple of seconds), and could be adapted to a range of cell types. Overall, it is hoped that this new noninvasive methodology will provide much-needed tools for the development of new battery materials and cell designs that address current and future needs.

CM03.15.11
Rechargeable Li-Ion Cell State of Charge and Health by In Operando Inside-Out Magnetic Resonance Imaging
Mohaddese Mohammadi, Alexej Jerschow and Emilia Silletta; New York University, New York, New York, United States.

CM03.15.12
In Situ Identification of High-Efficient Phosphide-Based Catalysts for Bi-Functional Overall Water Electrolysis
Sung-fu Hung; Chemistry, National Taiwan University, Taipei, Taiwan.

CM03.15.13
In Situ TEM Investigation of 3D Vertical RRAM Array
Min-Ci Wu, Tsung-Eong Hsieh and Wen-Wei Wu; Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

CM03.15.14
Mechanical Behavior of Silicon Dioxide (SiO2) Thin-Film Coatings During Electrochemical Lithiation/Delithiation Cycling
Subhajit Rakshit, Akshay Shailendra Pakhare and Siva P. Nadimpalli; Mechanical Engineering Department, New Jersey Institute of Technology, Newark, New Jersey, United States.

CM03.15.15
In Situ Measurement of the Effect of Stress on Chemical Diffusion Coefficient of Large Volume Change Electrodes
Siva P. Nadimpalli, Rajasekhar Tripureni and Subhajit Rakshit; New Jersey Inst of Technology, Newark, New Jersey, United States.

CM03.15.16
Bismuth as Rechargeable Lithium-Ion Battery Anode—A Fundamental Study Using In Situ Synchrotron XRD and In Situ TEM
Yifei Yuan1, Wentao Yao1, Vitaliy Yurkin1, Lu Ma2, Tongchao Liu2, Farzad Mashayek1, Jun Lu2, Khalil Amine2 and Reza Shahbahzan-Yassar1; 1University of Illinois at Chicago, Chicago, Illinois, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.
than current graphite anode. Among these materials, bismuth provides a high theoretical volumetric capacity of 3800mAh/cm^3 when it alloys with Li\(^+\) to form Li\(_3\)Bi. Yet, its further development has been hobbled by the unclear alloying mechanisms with Li\(^+\). In this work, we carry out real-time study of the (de)alloying kinetics of Bi nanomaterials working as a LIB anode combining both in situ synchrotron XRD and in situ TEM. In situ synchrotron XRD reflects the phase transition information of the ensemble of many Bi nanoparticles, while in situ TEM demonstrates the structural evolution of single Bi nanoparticle at both high spatial resolution and high temporal resolution. Both two methods reveal that the Li-Bi alloying is a two-step process featuring two two-phase reactions with formation of Li\(_3\)Bi as the intermediate phase. More importantly, our work reveals an energetically favorable lithiation pathway along Bi-(012) planes during the Bi-Li\(_3\)Bi phase transition process, which is further theoretically understood by DFT calculations. The fundamentals discovered in this work are expected to further guide the design of Bi-based electrode materials for battery performance enhancement in the future.

**CM03.15.17**

**Carrier Transfer from N-Type GaN Photoanode to Island-Like NiO-Catalyst for Water Oxidation Evaluated by Photoluminescence**

K. Koike\(^1\), Katsushi Fujii\(^1\), Kayo Koike\(^1\), Takenari Goto\(^2\), Shinichiro Nakamura\(^2\), Takayo Ogawa\(^1\) and Satoshi Wada\(^1\); \(^1\)RIKEN, RAP, Wako, Japan; \(^2\)RIKEN, Baton Zone Program, Wako, Japan.

The island-like NiO catalyst loaded on n-type GaN single crystal photoanode works perfectly to prevent the anodic corrosion \(^1\). The mechanism of NiO catalyst is, however, not fully understanding. Carrier transfer from GaN photoanode to NiO catalyst is expected for the prevention. The carrier transfer direction between the GaN surface and NiO-islands was proposed from our experiments recently \(^2\).

In this report, the in-situ and ex-situ photoluminescence (PL) was used for the evaluation of the carrier transportation. The samples were island-like NiO-loaded n-type GaN and bare n-type GaN. The 325.0 nm He-Cd laser was used as the excitation light. The light was used for both PL and photoelectrochemical water splitting for the in-situ measurements. The electrolyte was 1.0 mol/L NaOH aqueous solution.

The major PL peaks of n-type GaN at room temperature (RT) are near-band-edge luminescence (XL) and deep-yellow luminescence (YL). From the ex-situ PL results, the intensities of XL and YL were similar for both island-like NiO-loaded and bare n-type GaN when the excitation intensity was relatively high at about 1.0 W/cm\(^2\). The XL intensity of island-like NiO-loaded GaN decreased more than that of the bare n-type GaN when the excitation intensity was changed to 0.9 mW/cm\(^2\), whereas the YL intensities were similar for both samples. This 0.9 mW/cm\(^2\) excitation intensity is close to our commonly used photoelectrochemical excitation of 100 mW/cm\(^2\) Xe lamp.

During the photoelectrochemical reaction, the XL intensity of the bare n-type GaN decreased from the intensity without the reaction. The amount of XL intensity decreasing was much larger than that for YL. For the PL results of island-like NiO-loaded GaN, the XL intensity did not change and the YL intensity showed small decreasing with photoelectrochemical reaction from that without the reaction. The in-situ intensity change from the ex-situ intensity shows that the holes of bare n-type GaN are mainly used for the XL at the process without the photoelectrochemical reaction. On the other hand, the holes in the GaN of the island-like NiO-loaded GaN moves to the island-like NiO and would be consumed at the NiO by thermal recombination even without the photoelectrochemical reaction. The holes at the NiO are probably used for the water oxidation before the thermal recombination at the photoelectrochemical reaction. This probably shows that the holes in NiO can move more smoothly from the electrode to the reactant in the electrolyte than that in the bare GaN.


**CM03.15.18**

**In Situ Optical Absorption Spectroscopy for Investigating Point Ionic Defects Concentration and Kinetics in Mixed-Ionic-Electronic-Conductor Thin Films**

Dmitri Kalaev\(^1\), Clement Nicollet\(^1\), George F. Harrington\(^1,2\) and Harry L. Tuller\(^1\); \(^1\)Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; \(^2\)Kyushu University, Fukuoka, Japan.

Mixed ionic electronic conducting (MIEC) oxides are extensively used as electrodes in energy, electronics and catalysis applications. In particular, point ionic defects concentrations in MIECs bulk and surface and their kinetics properties are important parameters in the design of solid oxide fuel cell electrodes. Typically, the point ionic defects properties are measured electrically as function of oxygen partial pressure change to reveal the defect model. The electrical measurement can be disadvantageous, in some cases, if the contacts alter significantly the material properties or if the electrical conductivity dominates over the ionic one. Additionally, there is an increased interest in using MIEC thin films in electronics and catalysis applications that impose an additional challenge for characterizing them by other classical impedance spectroscopy and other electrical measurement techniques.

We demonstrate how the ions with optical absorption, occurring naturally or inserted on purpose in the MIECs, can be used for the characterization of the point ionic defects concentrations and kinetics in the oxides thin films. The examples will include praseodymium substituted ceria (PCO) and praseodymium oxide thin film. In these materials the praseodymium ions can have different valence states showing significant visible light absorption in one of the states. The praseodymium ions concentration and changes in their valence state can be measured, in-situ, at elevated temperatures and under a controlled oxygen partial pressure.

Applying the optical measurement technique allows, among other, to measure the oxygen vacancies ordering associated phase transition in praseodymium oxide thin film, measured previously by thermal gravimetric analysis. Finally, measuring the properties of the point ionic defects from optical absorption in heterostructures of an interchanging layers of epitaxial PCO and SrTiO\(_3\) thin films enables to study the effect of the space charge regions widths on the ionic defects concentration and the effect of a strain, induced by a lattice mismatch between the materials, on the ionic defects kinetic properties.
in situ synchrotron diffraction and X-ray absorption spectroscopy to unravel the underlying sodium storage mechanism and charge compensation behaviour is presented.

Model systems for multivalent-ion insertion can also include hybrid batteries with two mobile metal ions in the electrolyte, where a metal like Mg is plated at the negative electrode, while Li- or Na-ions are inserted at the positive electrode [2,3]. This presentation summarizes some recent results on the underlying working mechanisms in such hybrid batteries as revealed by in operando diffraction using synchrotron radiation in combination with X-ray photoelectron spectroscopy (XPS).


8:30 AM CM03.16.02

**In Situ Focused Ion Beam-Scanning Electron Microscope Study of Microstructural Evolution of Single Tin Particle Anode for Li-Ion Batteries**

Xinwei Zhou1, Tianyi Li1, Yi Cui2, Yuzi Liu1 and Likun Zhu1; 1Department of Mechanical and Energy Engineering, Indiana University-Purdue University Indianapolis, Indianapolis, Illinois, United States; 2Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois, United States.

In this study, we developed an approach to build a single particle battery in the chamber of focused-ion beam-scanning electron microscope (FIB-SEM) to monitor the microstructural evolution of a single Sn micro-particle during cycling. The experiment was performed within a ZEISS Nvision FIB-SEM at the Center for Nanoscale Materials, Argonne National Laboratory. A tin particle was attached to the tungsten probe by carbon coating using FIB deposition as positive electrode. The lithium metal was placed on the top of SEM stage as negative electrode. One drop of ionic liquid electrolyte (ILE) was placed on the top of lithium metal. The ILE was made by dissolving the lithium salt, lithium bis (trifluoromethylsulfonyl) imide (LiTFSI), in a solvent of 1-butyl-1-methylpyrrolidinum bis (trifluoromethyl-sulfonyl) imide (P3,6TFSI). The tungsten probe and the SEM stage were connected to a Keithley 6430 sub-femtoamp remote sourcemeter. Galvanostatic mode was used in all electrochemical cycling with a current of 300 pA. The particle was immersed in the ILE drop during cycling and lifted out for imaging at different states of charge. The particle was polished by FIB before imaging to remove ILE on the surface. Our results show the formation and evolution of cracks during lithiation, evolution of porous structure during delithiation and volume change during cycling. The electrochemical performance and the microstructural evolution of the Sn micro-particle during cycling are correlated.


8:45 AM CM03.16.03

**Probing Electrochemical Phase Transformation Kinetics by In Situ TEM**

Kai He; Clemson University, Clemson, South Carolina, United States.

In *situ* transmission electron microscopy (TEM) as a fast-growing technique has attracted tremendous attention in diverse scientific research because it can acquire dynamic information and allow for mechanistic understanding of various physical and chemical processes and materials systems [1]. Specifically, the advancement of *in situ* TEM in chemically reactive environments has enabled the direct real-time observation of electrochemical reactions in electrode materials for lithium ion batteries [2]. Previous studies have found different types of electrochemical reactions with lithium via various mechanisms such as intercalation, alloying, and conversion, which confirmed the lithiation processes following the thermodynamic reaction pathways. In addition to that, we would like to utilize *in situ* TEM imaging and spectroscopy approaches to build direct correlations between microstructure and electrochemistry on atomic to nanoscale and reveal the kinetics of phase transformations during the electrochemical reactions. We primarily focus on transmission metal oxides and sulfides with a large number of openings in their crystal framework, such as the spinel (FeOx) and 2D layered (CuS) structures [3, 4], to accommodate the uptake of guest Li ions. Although it is generally believed that these materials should follow the conversion reaction, we found the intermediate lithiated phases resulted from the intercalation reactions at the beginning; and more importantly, such phase transformations are sensitive to the reaction kinetics that are common in realistic battery coin cells. With further performance tests of coin-cells at various charging rates, we are able to explicitly establish the relationship that crosslinks the structure evolution, electrochemical properties, and the reaction pathways on the atomic level, and address the importance of the effects of kinetics and dimensionality on the phase transformation. Our findings provide insights into understanding phase transformation mechanisms in spinel and layered structures, and also show implications for improving performance in future design of battery electrodes.

References


9:00 AM CM03.16.04

**Investigation of Dynamic Phase Transformation of Selenium-Doped Germanium Anode during (De)Lithiation Processes Using In Operando Synchrotron X-Ray Diffraction**

Tianyi Li1, Yi Cui2, Xinwei Zhou1, 2, Melissa Meyerson1, Alan Guo1, Charles Mullins1, Yang Ren1, Qi Liu1, Yongzhu Fu3 and Likun Zhu2; 1Department of Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; 2Department of Mechanical and Energy Engineering, Indiana University Purdue University Indianapolis, Indianapolis, Indiana, United States; 3Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States; 4Argonne National Laboratory, Argonne, Illinois, United States.

Germanium (Ge) is an attractive candidate for high-capacity Li-ion battery anode due to its high theoretical capacity of 1384 mAh/g (for the charged
Li$_2$(Ge$_4$ phase), low operation voltage, fast bulk Li diffusion, and high electrical conductivity. However, the major challenge in the development of Ge anode is the large void that is formed in the reaction scheme, which could result in particle enlargement and electrode delamination from the current collector, thereby leading to rapid loss of specific capacity. Klavetter et al. recently reported that selenium (Se) doped Ge (GeSe) forms an inactive phase that buffers the volumetric expansion of Ge which provides better cycling life and performance [1]. Therefore, it is essential to understand the mechanisms and dynamic phase transformation that occur during battery cycling processes.

The in-operando experiment conducted by Lim at al. has shown crystal Li$_2$Ge$_4$ as the final product of lithiation and amorphous Ge at the end of Delithiation [2]. However, the crystalline change of GeSe anode material is still unclear which needs further investigation. In this study, we examined and compared the dynamic phase evolution of Ge and GeSe electrodes made of micro-particles (~5 μm in diameter) via Synchrotron X-ray diffraction (XRD) at the beamline 11-ID-C of the Advanced Photon Source at the Argonne National Laboratory. To investigate the crystalline evolution of Ge and GeSe particles, a synchrotron X-ray diffraction with a wavelength 0.1173 Å was employed to obtain diffraction data of the electrodes during in-operando condition to monitor and quantify crystalline change of active materials. Similar to Lim’s results, Li$_2$Ge$_4$ was observed as the single crystalline at the end of lithiation and no crystal Ge peak was found at the end of delithiation process for Ge. However, GeSe became amorphous at the end of the first lithiation and no crystal phase was observed thereafter. We believe that the different phase evolution is caused by the formation of a network of Li-ion super-conducting and inactive Li-Ge-Se phase at the beginning of the lithiation process.

Solid-state reactions underpin virtually all aspects of materials synthesis, operation of batteries and fuel cells, as well as ionic information technology devices. However, despite extremely high significance, these processes were traditionally studied only on the macroscopic level or via scattering techniques, providing only average information. Recent advances in scanning transmission electron microscopy (STEM) allow the visualization of solid-state transformations in materials, including those induced by electron beam influence and temperature, in real time with atomic resolution. However, the existing analytical tools allow extracting only a very small (and insufficient) portion of relevant physical and chemical information from the experimental data. Here we demonstrate a deep learning framework for full data analysis of the atomic defect dynamics and evolution from dynamic STEM data and illustrate its application for STEM “movies” from graphene and WS$_2$. The developed framework allows us to create a library of defects, map chemical transformation pathways at the atomic level, including detailed transition probabilities, and explore subtle distortions in local atomic environment around the defects of interest. In particular, we were able to extract parameters of diffusion for the sulfur vacancies and transition probabilities associated with switching between different configurations of defect complexes consisting of Mo dopant and sulfur vacancy in WS$_2$(arXiv:1803.05381), as well as to analyze evolution of topological defects in graphene. Overall, our approach allows an unprecedented insight into the nature and mechanisms of solid-state reactions and electron-beam-matter interactions on the atomic level.

9:30 AM CM03.16.05

Deep Learning of Solid-State Reactions on Atomic Level Maxim Ziatdinov, Ondrej Dyck, Artem Maksov, Andrew Lupini, Stephen Jesse and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

SESSION CM03.17: Battery Cathodes

Session Chairs: Andrej Singer and Chongmin Wang

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 300

10:00 AM CM03.17.01

Structural Analysis of Layered Li$_2$RuO$_3$ via Operando X-Ray Absorption Spectroscopy and X-Ray Diffraction Kipil Lim$^{1,2}$, Jihyun Hong$^{1,2}$, William Gent$^1$, Peter Csernica$^1$, Iwemien I. Abate$^{1,2}$, William Chueh$^1$ and Michael F. Toney$^1$; Stanford University, Stanford, California, United States; SLAC, Menlo Park, California, United States.

In the last decades, lithium-ion batteries (LIB) have significantly contributed to technological progress [1]. Recently, Li-excess layered materials are attracting interest since they exhibit high energy densities and capacities significantly higher than the commercially available layered NMC oxides [2]. Unlike conventional layered oxides where the only redox center is transition metal cations, an oxygen anion redox in the Li-excess layered material plays an important role to achieve high capacity [3]. Even though several research groups have suggested theories and tried to explain the mechanism of anion redox, the anion redox in the Li-excess layered material is still not fully understood. Understanding the electronic structural evolution of the Li-excess layered oxide is the key to understand the mechanism of the anion redox. Recently, our group reported a strong coupling between the anion redox and the transition metal migration into the Li layer during cycling in the Li$_{1+x}$[Ni,Co,Mn]$_2$O$_3$ material [4]. Their simulation predicted a reshuffling of the electronic states by the migrated transition metal and the oxidized oxygen, and the hypothesis was proved by the resonant inelastic X-ray spectroscopy (RIXS) analysis which showed a distinctive feature at the oxygen K edge spectra. Therefore, understanding the precise crystal structure is important to explain RIXS feature and understand the nature of anion redox. To build upon this work, we have selected Li$_2$RuO$_3$ as a model system, due to its good electrochemistry properties and the presence of only a single transition metal. In this work, we present how different synthesis conditions dramatically impact the properties of Li$_2$RuO$_3$. We present a combination of advanced techniques, including operando X-ray absorption spectroscopy (XAS), operando extended X-ray absorption fine structure (EXAFS), and high-resolution synchrotron X-ray diffraction to obtain a complete picture of the electronic and structural changes during cycling. This accurate structural information will be compared with the RIXS analysis to identify the mechanism of the anion redox in the Li$_2$RuO$_3$ material.

Using oxygen redox reactions to obtain higher capacity in Li-ion batteries (LIBs) is an intriguing route. Despite numerous experimental and theoretical attempts to unravel the electronic origin of oxygen redox behavior, whether the oxidation of oxygen occurs via the formation peroxo-like species or depletion of electrons from non-TM-bonding states is still, however, an open question. It is also unclear how the electron-depleted oxygen states manifest themselves in experimental observations. In this study, using Li-rich layered 4d/5d transition metal oxides and three dimensional cationic disordered cathodes as model systems, we performed density functional theory (DFT) and *ab-initio* molecular dynamics (AIMD) simulations to investigate the structural response of oxygen matrix to delithiation. The oxygen K-edge X-ray absorption near-edge spectra (XANES) were modeled using Bethe-Salpeter Equation (BSE) approach and compared with experiments, from which the oxygen redox mechanism is uncovered. This work demonstrates the effectiveness of combining experimental core-level spectroscopy with first-principles simulations to unambiguously identify the signature of oxygen reactivity, and has profound implications in understanding and exploiting the oxygen capacity in Li-rich LIB systems.

**10:30 AM CM03.17.03**

**Investigating the Nanoscale Heterogeneity of Solid Electrolyte Interphase on Amorphous Silicon from Tip Enhanced Raman Spectroscopy (TERS)**

Jagjit Nanda1, Guang Yang2, Dmitry Voylov3, Michael Naguib2, Rose Ruther1, Gabriel Veith1 and Alexei Sokolov2; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Tulane University, New Orleans, Louisiana, United States; 3The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

A key challenge of using silicon as an anode in a Li-ion battery is the dynamic nature of the solid electrolyte interphase (SEI) layer that constantly breaks and reforms due to the enormous volume changes during electrochemical cycling resulting in the loss of lithium inventory. Recent literature studies report a highly heterogeneous and multiphase nature of SEI that evolves under continuous electrochemical cycling. In this work, we report Tip Enhanced Raman Spectroscopic (TERS) study of SEI on cycled amorphous silicon (a-Si) for the first time. Amorphous silicon anode (50 nm in thickness on copper current collector) was cycled in a commercial lithium-ion battery electrolyte (1M LiPF6 in EC/DEC: 1:1 vol). TERS analysis on cycled amorphous silicon sample indicates that the nanometer scale SEI “islands” are unevenly distributed on the Si anode surface. Even for the same SEI “island”, the composition is different from point to point with inter-point distance smaller than 10 nm. In addition, the TERS spectra and mapping obtained from a-Si of differing cycle numbers suggests different SEI local compositions. The a-Si cycled for once (denoted as 1X a-Si) has rich local SEI species containing poly(ethylene oxide) (PEO) - like oligomer and lithium ethylene dicarboxylic (LEDIC, (CH2OCOOL)2). In sharp contrast, the bulk chemical information of the SEI for 1X a-Si probed by FT-IR only indicates the existence of the Li2CO3. Moreover, different vibrational modes from the same species such as LEDIC have differing TERS activity. This is due to different alignments of the enhanced near field vector versus the Raman scattering tensor of the given vibrational modes. The SEI on 5X a-Si is dominated by the LEDIC species, although Raman bands assigned to PEO oligomer and carboxylate compounds also show up. For 20X a-Si, the dominant species in the SEI is carboxylate compounds. The bands between 1450 cm-1 and 1650 cm-1 which are related to the =CO stretching and C=O stretching modes were analyzed in details for the first time. Due to its excellent spectral resolution on this type of compound, as compared to its IR counterparts, TERS is capable of probing the conformational change of the carboxylates upon their coordination to Li+ cations with nanoscale spatial resolution in sample plane.

**Acknowledgement**

This research was conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, is funded by Asst. Secretary Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO).

**10:45 AM CM03.17.04**

**Multiscale Heterogeneity in Single Particles of Li-Ion Battery Cathodes Visualized with X-Ray Imaging**

Jordi Cabana; University of Illinois at Chicago, Chicago, Illinois, United States.

The existing performance limitations of Li-ion batteries can be tracked to slow transport and irreversibilities in the changes undergone by the electrode materials, often coupled with mechanical events. Tools that provide insight into the onset and propagation of these transitions are critical to identify the mechanisms of electrochemical function. This information must be generated at the level of single particles, where irreversibilities trigger degradation of the electrode architecture. Synchrotron-based X-ray microscopy currently combines high spatial resolution with a suite of possible mechanisms of chemical contrast, such as diffraction and spectroscopy. In this talk, we will discuss recent developments to image, using X-rays, electrochemical reactions in single particles of battery electrodes, with a focus on the prospects of capturing and assessing the relevance of time-resolved phenomena using *operando* measurements. These measurements avoid relaxation of components from the kinetically controlled functional state to one that is more stable under open circuit conditions. The talk will highlight the new fundamental insight generated by the tools, involving mechanisms of transformation and local dynamics of heterogeneity.

**11:00 AM CM03.17.05**

**An Operando Study of Rechargeable MnO2 Cathodes for Low Cost, High Energy Density Aqueous Batteries**

Joshua W. Gallaway1, Gautam Yadav2, Damon Turney2 and Sanjoy Banerjee; 1Northeastern University, Boston, Massachusetts, United States; 2City College of New York, New York, New York, United States.

This talk will outline the complex cycling pathways of electrolytic manganese dioxide in alkaline electrolyte, as studied by *operando* characterization in "real world" electrodes of high areal capacity. The alkaline MnO2 system is one of the safest and most inexpensive battery materials ever discovered, and is well known in primary batteries. Deeply cycling MnO2 has the potential to provide battery storage of high safety, high energy density, low toxicity, and low cost, for applications such as intermittent renewable generation backup at the scale of the power grid. Deep cycling is defined as reduction through nearly all of the theoretical capacity from Mn(IV) to Mn(II), or 617 mAh/g-MnO2, while remaining reversible. Modification of MnO2 by Bi is known to impart rechargeability, through a cycling pathway with the layered polymorph δ-MnO2 as the end member.[1-3] The molecular mechanism of this effect has previously been unknown, and typically works well only in thin electrodes of low areal capacity, lessening the potential for use in applications. However, it has recently been reported that modification by both Bi and Cu imparts rechargeability even in thick electrodes, promising high impact if this chemistry is successfully developed into practical batteries.[4]

The MnO2 proton insertion reaction involves both unit cell dilatation and multiple phase changes, which are often spatially inhomogeneous throughout the electrode.[5] We use the correlation of energy dispersive X-ray diffraction (EDXRD) to a multiscale electrochemical model to demonstrate that a phase
change to MnOOH leads to spinel formation, but this reaction is suppressed with Bi. EDXRD using high energy white beam photons allows spatially-resolved diffraction to be collected in real time within batteries through the cell containment. We further demonstrate two distinct regimes of Mn(OH)₂ formation, with Bi causing a shift from amorphous to highly crystalline discharge product. These phenomena have not previously been observed through ex situ analysis. We further use a cell modified for X-ray transparency to follow the concentrations and redox states of Mn, Bi, and Cu spatially, in real time. This is done via operando X-ray fluorescence mapping (XRF) and micron-sized spot XANES (μ-XANES). All experiments were performed on electrodes with areal capacities of ~20 mAh/cm². Modeling indicates that such cathodes have potential to result in high energy density aqueous, rechargeable batteries when paired with zinc anodes meeting the requirements for a collection of emerging applications, namely grid-scale electrical storage.[6]

References

11:45 AM CM03.17.06
Cation Ordering and Oxygen Release in LiNi₀.₅Mn₁.₅O₄ (LNMO)—In Situ Neutron Diffraction and Performance in Li-Ion Full Cells Burak Aktekin1, William Brant1, Mario Valvo1, Fernando L. Marzano2, Wolfgang Zipprich1, Daniel Brandell1 and Kristina Edstrom1; 1Department of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden; 2Scania CV AB, Södertälje, Sweden; 3Volkswagen AG, Wolfsburg, Germany.

LiNi₀.₅Mn₁.₅O₄ (LNMO) is a promising spinel-type positive electrode for lithium ion batteries as it operates at high voltage and possesses high power capability. However, rapid performance degradation in full cells, especially at elevated temperatures, is a problem. There has been a considerable interest in its crystal structure as this is known to affect its electrochemical performance. LNMO can adopt a P4/mnn (cation ordered) or Pfdm (cation disordered) arrangement depending on the synthesis conditions. Most of the studies in literature agree on better electrochemical performance for disordered LNMO [1], however, a clear understanding of the reason for this behaviour is still lacking. This partly arises from the fact that synthesis conditions leading to disordering also lead to oxygen deficiency, rock-salt impurities and therefore generate some Mn³⁺ [2]. Most commonly, X-ray diffraction is used to characterize these materials, however, accurate structural analysis is difficult due to the near identical scattering lengths of Mn and Ni. This is not the case for neutron diffraction. In this study, an in-situ neutron diffraction heating-cooling experiment was conducted on slightly Mn-rich LNMO under pure oxygen atmosphere in order to investigate relationship between oxygen atmosphere and oxygen deficiency. The study shows that the first time that there is no direct relationship between oxygen loss and cation disordering, as disordering starts prior to oxygen release. Our findings suggest that it is possible to obtain samples with varying degrees of ordering, yet with the same oxygen content and free from impurities. In the second part of the study, highly ordered, partially ordered and fully disordered samples have been tested in LNMO|LiTFSI(O) full cells at 55 °C. It is shown that differences in their performances arise only after repeated cycling, while all the samples behave similarly at the beginning of the test. The difference is believed to be related to instabilities of LNMO at higher voltages, that is, in its lower lithiation states.


1:30 PM *CM03.18.01
Nucleation of Dislocations and Their Dynamics in Layered Oxides Cathode Materials During Battery Charging Andrei Singer; Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

Lithium-rich layered oxides (LRLO) are among the leading candidates for the next generation cathode material for energy storage, delivering 50% excess capacity over commercially used compounds. Despite excellent prospects, voltage fade has prevented effective use of the excess capacity, and a major challenge has been the lack of understanding of the mechanisms underpinning the voltage fade. I will present our recent results, where using operando three-dimensional Bragg coherent diffractive imaging, we directly observe the nucleation of a mobile dislocation network in LRLO nanoparticles. The dislocations form more readily in LRLO as compared with a classical layered oxide, suggesting a link between the defects and voltage fade. We show microscopically how the formation of partial dislocations contributes to the voltage fade. The insights allow us to design and demonstrate an effective method to recover the original high voltage functionality. Our findings reveal that the voltage fade in LRLO is reversible and call for new paradigms for improved design of oxygen-redox active materials.

2:00 PM CM03.18.02
In Situ Synchrotron X-Ray Diffraction Studies on the P2- Manganese Based Sodium Layered Oxides—Structural Evolution During Cycling Elena Gonzalez1, Wesley Dose2, Neeraj Sharma3, Teofilo Rojo1, 3 and Miguel Angel Muñoz-Marquez2; 1CIC Energigune, Miñano, Spain; 2Chemical Sciences and Engineering (CSE) Division, Argonne National Laboratory, Lemont, Illinois, United States; 3Departamento de Química Inorgànica, Universidade do País Vasco UPV/EHU, Bilbao, Spain; 4School of Chemistry, University of New South Wales, Sydney, New South Wales, Australia.

Na-ion battery research has been under focus lately due to its advantages in specific applications such as large scale power grid systems [1,2]. Among the candidates of cathode materials, layered oxides with the general formula: NaTMO₂ (TM = Cr, Mn, Fe, Co, Ni, etc.) exhibit one of the largest theoretical capacities along with simple crystal structures.[3,4]

Co- and Ni- free P2-manganese based systems possesses excellent cathode characteristics for Na-ion batteries due to combination of environmentally benign, economically favorable transition metals and high capacity, although some issues such as the Jahn-Teller distortion effect, ascribed to Mn³⁺, has to
be taken into account.[5] The importance of considering this issue has been widely studied by our group,[6,7] as well as mitigation strategies – such as doping with electrochemically active (Fe)[8] and inactive elements (Ti).[9]

Here we report the in situ synchrotron X-Ray diffraction study we have carried out to shed light on the relationship between electrochemical performance and structural evolution of different P2- Na2-xMnxFe2O4 phases (0.1≤x≤0.67) upon cycling. Lattice parameter evolution, phase fractions and sodium content in the crystal structure as a function of the charge/discharge process and at different current rates will be shown. The effect of dopants such as Ti and the mitigation of structural changes during cycling will be examined in detail.

References

2:15 PM CM03.18.03

In Operaando Tracking Ion Intercalation into 2D MXenes in Aqueous Electrolytes

Qiang Guo1, Xin Li1, Weiwei Sun1, Michael Naguib3, Stephen Jesse1, Paul Kent1, 2, Arthur P. Baddorf1 and Nina Balke1, 1Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Department of Physics & Engineering Physics, Tulane University, New Orleans, Louisiana, United States.

Super capacitors have drawn considerable attention for a variety of applications in portable electronics, grid and transportation systems due to their rapid power delivery and an almost unlimited cycle life. To enhance the energy stored, the intensive efforts have been devoted to exploring new electrode materials, new electrolytes, and novel cell configurations. In search for new electrode materials, two dimensional (2D) transition metal carbides-MXenes, are of particular interest owing to their excellent electrical conductivity and high volumetric capacitance[1][2]. The mechanism for high capacitance was essentially described as intercalation pseudo-capacitance arising from redox reactions of the Ti atoms. Similar to graphite or other electrode materials, MXene electrodes also show a significant change in volume when ions are intercalated. This electro-chemo-mechanical coupling can be used to get unprecedented insight into ion intercalation pathways with lateral resolution of 10’s of nm using Scanning Probe Microscopy (SPM) techniques. In this communication, we introduce contact resonance SPM which allows to extract mechanical properties and its changes under electrochemical control when ions are intercalated into MXenes.[3][4]. Therefore, it is of great importance to explore the different intercalation contributions with varying aqueous cations to the mechanical properties variations of material itself, which is required to evaluate the electrochemical long-term stability of electrode materials. Of special interest to boost energy storage is the intercalation of multivalent ions which suffers from sluggish intercalation and transport kinetics due to its ion size. By combining electrochemical dilatometry and contact resonance atomic force microscopy, the synergistic effects of smaller ion size cation and larger ion size cation are demonstrated to improve charge storage to maximize the utilization of electrode volume, as well as tune mechanical and actuation properties of Ti3C2 MXene.[5][6] Our results have important implications for quantitatively understanding the charge storage processes in intercalation compounds and provide a new path for studying the mechanical evolution of a variety of electrochemical energy storage materials.

The experiments and sample preparation in this work were supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The facilities to perform the experiments were provided by the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

References

2:30 PM CM03.18.04

In Situ and Ex Situ Electron Microscopy and Spectroscopy Diagnosis Guided Designing of Electrode Materials for Better Battery

Chongmin N. Yang, Pacific Northwest National Laboratory, Richland, Washington, United States.

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of energy storage materials. Both ex-situ and in-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass and charge transport, providing insights as how active materials failure during the cyclic charge and discharge of a battery. In particular, I will broadly cover the frontier of the current understanding of the interfacial process in an electrochemical cell. In perspective, my presentation will target to stimulate this field of research to re-check what has been understood and what need to be done to tackle the technical challenges facing the application of the layer structured cathode and high capacity silicon based anode.

3:00 PM BREAK
With an increasing demand for higher energy and power density of lithium ion batteries (LIBs), the coupled electrochemical-mechanical degradation of electrode materials becomes a more pressing problem. In particular, fracture and delamination of electrodes can occur during repeated charging and discharging of LIBs. An improved understanding of the mechanical behavior of electrode materials, which often evolves with the state-of-charge and cycle number, is therefore necessary for improving the performance and durability of the next generation LIBs. In this presentation, we will provide an overview of our recent work on using three complementary measurement techniques: (1) in situ electrochemical nanoindentation; (2) peel adhesion and cohesion test; and (3) electrode curvature measurement to help understand several coupled effects between mechanical and electrochemical behavior of materials on the performance and durability of high capacity electrodes. Examples include Si/polymer binder porous composite electrodes, lithium metal electrodes, and inorganic/polymer composite solid-electrolytes. The suite of complementary in situ mechanical characterization techniques can also be used to investigate mechanical behavior of a wide range of electrochemical energy storage materials under realistic working conditions.


2. Jiazhi Hu, Yikai Wang, Dawei Li, and Yang-Tse Cheng, "Effects of binder-silicon interfacial strength on the electrochemical performance and durability of silicon composite electrodes for the next generation lithium-ion batteries," J. Power Sources (under review).


Silicon is considered as a promising anode material for the next generation lithium-ion battery due to its high capacity at nanoscale. However, silicon expands up to 300% during lithiation, which induces high stresses and leads to fractures. To design silicon nanostructures that could minimize fracture, it is important to understand and characterize stress states in the silicon nanostructures during lithiation. Synchrotron X-ray microdiffraction has proven to be effective in revealing insights of mechanical stress and other mechanics considerations in small-scale crystalline structures used in many important technical applications, such as microelectronics, nanotechnology and energy systems. In the present study, an in situ synchrotron X-ray microdiffraction experiment was conducted to elucidate the mechanical stress states during the first electrochemical cycle of lithiation in single-crystalline silicon nanowires (SiNWs) in a lithium-ion battery test cell. Morphological changes in SiNWs at different levels of lithiation were also studied using scanning electron microscope (SEM). It was found from SEM observation, that lithiation commenced predominantly at the top-surface of SiNWs followed by further progression towards the bottom of the SiNWs gradually. The hydrostatic stress of the crystalline core of the SiNWs at different levels of electrochemical lithiation was determined using the in situ synchrotron X-ray microdiffraction technique. We found that the crystalline core of the SiNWs became highly compressive (up to ~325.5 MPa) once lithiation started. This finding helps unravel insights about mechanical stress states in the SiNWs during the electrochemical lithiation, which could potentially pave the path towards the fracture-free design of silicon nanostructure anode materials in the next generation lithium-ion battery. The in situ synchrotron X-ray submicron diffraction methodology as a probe of stress and thus reliability of the novel silicon nanowire anode in Li-ion battery described is also novel and could lead to enable next generation, more robust Li-ion battery technology and thus enable next generation applied energy technologies for the world.

Silicon metal anode can serve as a host-free electrode, and thus has the highest theoretical capacity compared to traditional graphite-based electrodes as well as advanced lithium-alloying anodes. The major challenge with the lithium anode is highly dendritic deposition, resulting in 'mossy' electrode and internal short-circuits. A part of underlying failure mechanisms is attributed to mechanical degradation of solid electrolyte interphase (SEI). Recent theoretical and experimental studies suggest that surface films with high elastic modulus and mechanical stability may mechanically suppress the dendrite formation. Stable lithium plating/striping with ionic liquid (IL) electrolytes, which are known to form inorganic SEI supports the suggestion. This background motivates to develop an experimental platform to measure elastic moduli of SEI formed with various electrolytes. However, most previous experimental approaches are limited to the atomic force microscopy (AFM) indentation. The approach has several sources of uncertainties such as substrate influence and inaccurate contact area due to low thickness and roughness of SEI. As a result, reported elastic modulus of SEI has several orders of magnitude variation.

In this work, we use strain induced elastic buckling instability for mechanical measurement (SIEBIMM) approach to measure the plane strain elastic modulus of SEI formed with IL electrolytes. SEI layers (~80 – 200nm) on polydimethylsiloxane (PDMS) substrates are prepared by letting thermally evaporated lithium thin films react with IL electrolytes. The formation of SEI result in large enough compressive residual stress induce elastic buckling. In situ AFM measures the thickness of SEI and the characteristic wavelength of the buckling topography to extract the plane strain modulus. The
Hydrogen is steadily emerging as the next generation fuel owing to its high gravimetric energy density (143 kJ kg⁻¹) and environmentally benign nature.

Research, Bangalore, India.

The potential advantages of lithium (Li) metal anodes have been widely touted (lowest reduction potential, etc). However, the poor stability of Li metal / liquid electrolyte interfaces leads to chronic problems, such as dendrite formation and capacity loss. The possible impact of mechanical effects on interface stability and dendrite formation is difficult to probe directly. In this study, stress evolution during lithium plating and stripping was monitored with precise in-situ measurements. The data obtained with different film thicknesses made it possible to separate the stresses associated with the lithium metal and the solid electrolyte interphase (SEI). Ex-situ morphological characterization also provided additional information. The results show that significant stresses are created in the SEI films. A basic model of the experiments provides further understanding of the stress contribution from the SEI. An analysis of the relationship between stress in the SEI and morphological stability is also presented.

**SESSION CM03.20: Electrocatalysis**

**Mechanistic Insights into the Promotional Effect of Ni Doping on Mo and W Carbide Systems @NPGC for Highly Enhanced Overall Water Splitting**

Soumyabrata Roy1, 2, Debabrata Bagchi1, 2, Saurav C. Sarma1, 2 and Sebastian C. Peter1, 2; 1New Chemistry Unit, Jawaharlal Nehru Centre For Advanced Scientific Research (JNCASR), Bangalore, India; 2School of Advanced Materials (SAMat), Jawaharlal Nehru Centre For Advanced Scientific Research, Bangalore, India.

Hydrogen is steadily emerging as the next generation fuel owing to its high gravimetric energy density (143 kJ kg⁻¹) and environmentally benign nature. The electrocatalytic process of H₂ generation involves various mechanistic steps at the catalyst surface (adsorption, desorption, spilling and electron transfer) which govern a catalyst’s activity. Transition metal (Mo, W) carbide systems are well known for electrocatalytic hydrogen evolution reaction (HER) due to their optimum proton adsorption energy (del GHads) and good electrocatalytic stability. However, there is still huge scope for improving the activities of carbide systems in terms of electrical conductivity, current densities and onset potentials for HER. We have adopted a one-step in-situ synthetic method to form Ni-doped WC and MoC nano-systems dispersed on nitrogen and phosphorus doped graphitic carbon (NPGC). The catalysts, both Ni-doped WC and MoC, have shown multi-fold improvement in activity both in terms of current densities and onset values than the undoped ones. While the NPGC enhances the electrical conductivity of the catalyst, Ni, as evident from theoretical calculations, optimises the d-band centre and free energy for proton adsorption to yield high activities. Three different percentages of Ni (5:1, 5:2 and 5:3-W/Mo:Ni precursor ratio) were doped to study the promotional effect of Ni doping. Interestingly, the doping percentage and the primary carbide phase was modulated by the extent of milling of the precursors, owing to the differential Ni-diffusion into the carbide lattice. The best electrocatalytic HER activity was observed in the non-ball milled Ni-doped MoC sample (Mo-Cr-Ni(5:1) _NB) with an onset overpotential of 120 mV and a current density of 130 mA/cm² at -370 mV (v RHE), stable up to 10000 cycles. However, the WC-Ni(5:1) BM sample showed the best activity among WC samples with a similar onset but a lesser current density of 90 mA/cm². The electronic interactions of Ni with the metal carbide motifs and the nature of the graphitic carbon were studied through XAFS, XPS and Raman studies. Both samples showed enhanced OER activity in alkaline medium with good onset values of about 1.5 V (v RHE) and current densities as high as 150 mA/cm² at 1.86 V with good stability. Thus their activity as overall water splitting catalysts triggered us to fine tune the electrolyte pH for both HER and OER activities to construct a H₂/O₂ electrolyzer with a minimum Eₘₚ between them as bifunctional catalysts. The activities of the best MoC and WC catalysts are comparable to commercial Pt/C for HER and better than IrO₂ in case of OER. The electronic and structural roles of Ni in enhancing the catalytic activity has been studied through DFT calculations, XPS and in-situ quick EXAFS studies. These studies elucidate, in real time picture, how the adsorption energies of intermediates and reaction kinetics are modulated at different catalytic sites with the promotional effect of Ni doping.

**Spectroscopic Observation of an Electrochemically Inert CO Sub-Population on Cu Electrodes Under CO Reduction Conditions in Alkaline pH**

Charumi M. Gunathunge1, Vincent Ovalle1, Yawei Li2, Michael Janik1 and Matthias Waegeler1; 1Chemistry, Boston College, Chestnut Hill, Massachusetts, United States; 2Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Copper is the only pure metal capable of reducing carbon dioxide to hydrocarbons at significant rates in an aqueous electrochemical environment. Therefore, it is a prototypical catalyst for the electroreduction of carbon dioxide to various economically valuable hydrocarbons, such as methane and ethylene. Surface-adsorbed CO has been identified as a common on-pathway intermediate to hydrocarbons and re-reduction correspond to the potential-
determining step of the overall process. While CO can adsorb on different adsorption sites (e.g. top or bridge) on the Cu surface, in situ spectroscopy of the copper/electrolyte interface has mostly been focused on atop-bound CO. Herein, we combine a combination of interface-selective infrared (IR) and Raman spectroscopies and DFT calculations to study the reactivity and surface dynamics of atop- and bridge-bonded CO on Cu electrodes. We show for the first time that (1) a fraction of the atop-bound CO population shifts to bridge sites when the total surface coverage is lowered below the saturation coverage (2) in contrast to atop-bound CO, bridge-bonded CO is electrochemically stable against reduction at a potential of -1.75 V vs. SHE. Our DFT calculations further reveal an unfavorable effect of the interfacial electric field on the activation barrier for the reduction of bridge-bonded CO as the underlying mechanism of the observed reactivity. In systematic pH studies, we further identify a pH-induced reconstruction of the Cu surface under operating conditions as the likely origin of the conversion of CO from atop- to bridge-sites. We will further discuss the implications associated with the co-existence of the two distinct CO populations on the electroreduction of atop-bound CO.

8:30 AM *CM03.20.03
Operando XAFS Measurements of Water Splitting Photocatalysts Takashi Hisatomi1 and Kazunari Domen1-2; 1University of Tokyo, Tokyo, Japan; 2Center for Energy & Environmental Science, Shinshu University, Nagano-shi, Japan.

Water splitting using semiconductor photocatalysts has attracted much attention as a means of renewable hydrogen production on a large scale [1]. When a particulate semiconductor photocatalyst absorbs a photon, an electron is excited from the valence band to the conduction band, and a positive hole is left in the valence band. These excited electrons and holes can drive reduction and oxidation reactions on each photocatalyst particle, respectively. To drive the water splitting reaction efficiently, it is necessary to load nanoparticles metals and metal oxides, denoted as cocatalysts, on the photocatalyst as active sites for the hydrogen evolution reaction and the oxygen evolution reaction. Otherwise photoexcited electrons and holes just recombine without contributing to the reaction. It is also important to suppress backward reactions such as formation of water from product hydrogen and oxygen and the oxygen reduction reaction. The authors’ group has developed rhodium chromium oxide (RhCrO3) as cocatalyst effective for the overall water splitting reaction [2-5] and has revealed the structure and working mechanism.

Al-doped SrTiO3 (SrTiO3:Al) loaded with a rhodium chromium oxide (RhCrO3) as a cocatalyst (RhCrO3/SrTiO3:Al) decomposes water into hydrogen and oxygen with an apparent quantum yield of 56% at 365 nm [6]. The activity of the photocatalyst starts to decreases in 10 h when the reaction is conducted at an atmospheric pressure; however, loading of cobalt oxide species (CoOx) drastically improves the durability. It is suspected that CoOx species serves as an oxygen evolution cocatalyst and extracts holes from the photocatalyst to prevent oxidative dissolution of the Cr component in the RhCrO3 cocatalyst. In order to discuss the function of the cocatalyst species, the X-ray absorption fine structure (XAFS) of RhCrO3 and CoOx species loaded onto SrTiO3:Al were investigated operando, i.e., in water under UV light irradiation.

In this talk, recent progress and understanding of the structures, chemical states, and functionality of the cocatalysts are to be discussed


9:00 AM CM03.20.04
Visualizing Electrochemical Reactions at the Nanoscale by In Situ TEM Huidun L. Xin, M. Ge and Yong Chu; Brookhaven National Laboratory, Upton, New York, United States.

Over the past five years, we have witnessed a rapid growth in liquid and gas flow holders for TEM and X-ray microscopes. These holders have enabled direct imaging of material transformations in liquid and gaseous environments with submicron-scale to atomic-scale spatial resolution. In particular, research regarding electrode materials in lithium ion batteries and nanocatalysts in heterogeneous catalysis has greatly benefited from the emergence of these capabilities. Despite their initial success in in-situ battery studies, similar class of problems in electrocatalysis has been rarely addressed using existing liquid electrochemical holders. In this talk, I will showcase the capability of direct nanoscale visualization of electrochemical formation and degradation of electrocatalysts utilizing an operando TEM liquid holder and I will also discuss existing challenges that the in-situ EM field need to address.

The research used resources of the National Synchrotron Light Source II and the Center for Functional Nanomaterials, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The research used resources of the National Synchrotron Light Source II and the Center for Functional Nanomaterials, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The electron microscopy experiment was performed at the Center for Functional Nanomaterials. This research is also partially supported by Laboratory Directed Research and Development (LDRD15-037) program at the Brookhaven National Laboratory.

9:15 AM CM03.20.05
Uncovering Biaxial Strain Effect on Kinetics of Metal Nanoparticle Catalyst Exsolution on Thin-Film Perovskite Oxides Jianue Wang1, Alexander K. Opitz1,2, Roland Blien1, Xiaohui Yao1, Guolini Vardar1, Dongha Kim1, Irawkanari Waluyo1, Adrian Hunt1, Ethan J. Crumlin2 and Bilge Yildiz1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Institute of Chemical Technologies and Analytics, Vienna, Austria.

Environment-friendly approaches are being advanced to synthesize carbon-neutral fuels. Some of these technologies rely on catalytically highly active nanoparticles that are supported on oxides. These nanostructured catalysts exhibit enhanced activity towards desired reactions due to their high specific area, and thus, increase the efficiency of the respective system. A recent advance in such catalyst design is to exsolve catalytic metal nanoparticles at the surface of a supporting oxide. Unlike traditional deposition techniques, the nanoparticle catalysts from exsolution are anchored in the parent oxide. This strong metal-oxide interaction makes the exsolved nanoparticles more resistant against particle agglomeration as compared to the deposited ones. In addition, the exsolved particles also open up the possibility of regeneration of catalysts.

While being an exciting and promising pathway for high-performance oxido-metal composite catalysts, the approach towards exsolution has thus far been an empirical one, without a clear understanding and control of the underlying mechanisms to optimize catalyst composition, size and dispersion. Studies in the literature indicate that the exsolution products depend on both the surface chemistry (i.e. stoichiometry and composition) and bulk chemistry (i.e. composition and extended defects) of the parent oxide. However, it remains unclear how these parameters affect the exsolution process.

In this work, we aim to uncover how biaxial strain affects the exsolution process. Our hypothesis is that elastic strain in thin films can alter the reducibility (oxygen stoichiometry) and surface composition, and thereby affect the metal exsolution process. We quantify the strain effect on the materials'
reducibility and on surface cation composition. \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) thin films are employed as model systems due to the well-studied defect chemistry of LSF64, and the possibility to solve metallic Fe on the surface without decomposing the perovskite lattice. Biaxial strain is introduced by growing LSF64 thin films epitaxially on substrates with different lattice constants. In-situ ambient pressure X-ray spectroscopy is employed to probe defect chemistry, surface composition, and exsolution rate on LSF64 thin-film samples at different temperatures. Coupling surface chemistry with morphological information from atomic force microscopy, we found that in-plane biaxial strain can be a powerful tool in optimizing both the onset temperature of exsolution as well as the particle dispersion of the exsolution products. The observed strain dependence of exsolution advances our abilities to control them and enhance the performance of catalysts for clean energy technologies.

9:30 AM BREAK

10:00 AM CM03.21.01
In Situ Evidence of a Segregation Driven Metal-Insulator Transition at the Surface of an Epitaxial Semiconducting Manganese Thin Film Arthur P. Baddorf, Rama K. Vasudevan, Hemant Dixit, Alexander Tselev, Valentino Cooper, Panchapakesan Ganesh and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

We have established the ability to alter the conductivity and magnetism of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) film surfaces by tuning the degree of Ca segregation and the termination, which determine the Jahn-Teller distortion. This is of interest since doped manganese oxides (manganites) exhibit a rich response to an electric field, mixing electron and ionic transport and resulting in structural or electronic phase transitions. Manganites are consequently intriguing components in electrocatalysts, memristors, sensors, and solid oxide fuel cells. Interfaces, which play a key role in applications, introduce strain, off-stoichiometry, surface cation segregation, changes to octahedral rotations and Jahn-Teller coupling which open opportunities to tailor properties.

We have grown \( \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3 \) films by pulsed laser deposition and examined the surface structure, composition, and metallicity with in-situ studies using scanning tunneling microscopy and spectroscopy (STM/S), x-ray photoelectron spectroscopy, and first principles computation. Background oxygen pressure during growth has a strong effect on surface structural and electronic features. Deposition at 20 mTorr O2 leads to a predominantly B-site (MnO2) terminated surface with less A-site (La,Ca)O termination. Increasing the O2 pressure modestly to 50 mTorr produces mixed termination and atomically imperfect surfaces. Both growth modes result in excess Ca at the surface, with greater segregation at higher growth pressures.

STM images show that B-site surfaces have bulk surface structure, whereas A-site terminations are reconstructed. STS demonstrates that both surfaces are metallic (gapless) even though the film bulk remains semiconducting. Density functional theory (DFT) provides understanding of how two experimentally observed structural conditions lead to metallicity. First, computation reveals that the bulk ferromagnetic (FM) ordering is replaced by antiferromagnetic (AFM) ordering with increasing Ca concentration in the top layer and is more stable for 50% Ca as observed in experiments due to segregation. Second, DFT finds that \( (\text{La},\text{Ca})\text{O} \) reconstructed surfaces, where half of apical oxygen are present, are insulating with a band gap of \( \sim 0.8 \) eV. This apical oxygen increases the electron-phonon coupling, specifically a Jahn-Teller distortion, leading to insulating behavior. This information can enable better control over of manganate interfaces in a number of applications.

Research was sponsored the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and the Office of Science Early Career Research Program. Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

10:15 AM CM03.21.02
In Situ Negative Cs HRTEM Imaging of Topotactic Phase Transformation from Perovskite SrFeO3 to Brownmillerite SrFeO2.5 Yadaong Xing1, Kyeong Tae Kang2, Zhen Wang1, Bumsuk Park1, Jinsol Seo1, Jong Chan Kim1, Hu Young Jeong3, Donghoon Jang3 and Sang Ho Oh1; 1Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); 2Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of); 3School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

SrFeO3, a candidate oxide electrode for solid oxide fuel cell, undergoes topotactic phase transformation reversibly to SrFeO2.5 at relatively low temperatures compared to other known similar class of materials due to the small difference in Gibbs free energy between the two phases. The phase transition is referred to as topotactic as the cation sublattice remains almost unchanged while oxygen ions (or vacancies) diffuses through the lattice along the specific crystallographic channels to modify the local coordination and valence states of cations. Previously X-ray diffraction and sequential STEM HAADF imaging have been used to characterize the phase transition of this type of materials. However, neither of these methods can directly observe the channeling of oxygen vacancies, which is extremely difficult due to the low scattering power of oxygen atoms. Here, we report in situ high resolution transmission electron microscopy observation of the phase transition of a 30 nm-thick SrFeO3 epitaxial thin film to SrFeO2.5 brownmillerite phase at elevated temperatures in a Cs-corrected TEM (Grand ARM300F) operated at 300 kV. The TEM lamellas were prepared by focused ion beam milling and attached on the Si MEMS chip for heating using a DENSsolutions Wildfire TEM holder. By using negative spherical aberration imaging (NCSI) technique, we successfully imaged all types of atomic columns in SrFeO3 over a quite large area, which makes it possible to observe the oxygen vacancy channeling and formation and growth of SrFeO2.5 brownmillerite phase during heating. Although real-time NCSI HRTEM movies clearly resolve the oxygen columns, it is still difficult to measure local concentration of oxygen vacancy and sublattice change by looking at dynamically varying oxygen intensity, because of the topotactic phase transformation. We have applied several analysis methods to quantitatively measure the intensity of oxygen columns and cation sublattices to visualize local dynamic motion of transition process. Besides, the inverse Fourier filtered image formed by selecting the reflections from brownmillerite phase visualizes the dynamic motion of phase distribution. It was observed that brownmillerite SrFeO2.5 phase forms and grows from many different locations simultaneously, resulting in the formation of anti-phase boundaries at junctions.

10:30 AM CM03.21.03
Dynamic Control and In Situ Measurements of Oxygen Nonstoichiometry and Phase of Layered Cuprate-Based Thin Films by Electrochemical Pumping Chang Sub Kim and Harry L. Tuller; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Three major criteria are essential for a good solid oxide fuel cell (SOFC) electrode: 1) mixed ionic and electronic conductivity, 2) electrocatalytic activity towards oxygen surface exchange reaction, and 3) chemical and chemo-mechanical stability. Conventional method of assessing these electro-chemo-mechanical properties requires doping different concentrations of aliovalent cations and/or controlling atmosphere. These, however, are constrained by...
solubility limits of dopants, the range of oxygen partial pressures readily experimentally achievable, and require knowledge of the applicable defect chemistry model. In this study, we control and measure oxygen defect types, concentration, and phases of oxygen by electrochemical pumping of oxygen into and out of the film utilizing a Nernst cell of the form Pt/YSZ/PCO. Two cell geometries are examined, including (1) deposition of PCO films on yttrium stabilized zirconia (YSZ) single crystal substrates (300-500 microns thick) and (2) the deposition of PCO films on highly resistive substrates (e.g. Al$_2$O$_3$ or MgO) and subsequent coverage with a YSZ film to pump oxygen. In this work, the chemical expansion of Pr$_x$Ce$_{1-x}$O$_{2-y}$ (PCO) shows the ability to reversibly release and take up substantial amounts of oxygen, even in the high oxygen partial pressure regime (ambient air down to about p$_{\text{O}_2}$ $\approx$ 10$^{-5}$ bar). While strain values of the order of 1 percent are achievable via chemical expansion and contraction, this results in dimensional changes of only on the order of 1-10 nm depending on the thickness of the PCO films. Such levels of chemical expansion are, however, sufficiently large to observe by optical means [2].

To achieve reasonable signal to noise ratios in measuring such small displacements, measurements benefit from periodic adjustment of the oxygen activity within the PCO films, achieved by electrochemical pumping of oxygen into and out of the film utilizing a Nerst cell of the form Pt/YSZ/PCO. Two cell geometries are examined, including (1) deposition of PCO films on yttrium stabilized zirconia (YSZ) single crystal substrates (300-500 microns thick) and (2) the deposition of PCO films on highly resistive substrates (e.g. Al$_2$O$_3$ or MgO) and subsequent coverage with a YSZ film to pump oxygen. In this work, the chemical expansion of Pr$_x$Ce$_{1-x}$O$_{2-y}$ (PCO) shows the ability to reversibly release and take up substantial amounts of oxygen, even in the high oxygen partial pressure regime (ambient air down to about p$_{\text{O}_2}$ $\approx$ 10$^{-5}$ bar). While strain values of the order of 1 percent are achievable via chemical expansion and contraction, this results in dimensional changes of only on the order of 1-10 nm depending on the thickness of the PCO films. Such levels of chemical expansion are, however, sufficiently large to observe by optical means [2].

To achieve reasonable signal to noise ratios in measuring such small displacements, measurements benefit from periodic adjustment of the oxygen activity within the PCO films, achieved by electrochemical pumping of oxygen into and out of the film utilizing a Nerst cell of the form Pt/YSZ/PCO. Two cell geometries are examined, including (1) deposition of PCO films on yttrium stabilized zirconia (YSZ) single crystal substrates (300-500 microns thick) and (2) the deposition of PCO films on highly resistive substrates (e.g. Al$_2$O$_3$ or MgO) and subsequent coverage with a YSZ film to pump oxygen. In this work, the chemical expansion of Pr$_x$Ce$_{1-x}$O$_{2-y}$ (PCO) shows the ability to reversibly release and take up substantial amounts of oxygen, even in the high oxygen partial pressure regime (ambient air down to about p$_{\text{O}_2}$ $\approx$ 10$^{-5}$ bar). While strain values of the order of 1 percent are achievable via chemical expansion and contraction, this results in dimensional changes of only on the order of 1-10 nm depending on the thickness of the PCO films. Such levels of chemical expansion are, however, sufficiently large to observe by optical means [2].

To achieve reasonable signal to noise ratios in measuring such small displacements, measurements benefit from periodic adjustment of the oxygen activity within the PCO films, achieved by electrochemical pumping of oxygen into and out of the film utilizing a Nerst cell of the form Pt/YSZ/PCO. Two cell geometries are examined, including (1) deposition of PCO films on yttrium stabilized zirconia (YSZ) single crystal substrates (300-500 microns thick) and (2) the deposition of PCO films on highly resistive substrates (e.g. Al$_2$O$_3$ or MgO) and subsequent coverage with a YSZ film to pump oxygen. In this work, the chemical expansion of Pr$_x$Ce$_{1-x}$O$_{2-y}$ (PCO) shows the ability to reversibly release and take up substantial amounts of oxygen, even in the high oxygen partial pressure regime (ambient air down to about p$_{\text{O}_2}$ $\approx$ 10$^{-5}$ bar). While strain values of the order of 1 percent are achievable via chemical expansion and contraction, this results in dimensional changes of only on the order of 1-10 nm depending on the thickness of the PCO films. Such levels of chemical expansion are, however, sufficiently large to observe by optical means [2].
two times larger than that of 50Ca glass at 350 °C. The relationship between alkaline-earth cation species and proton implantation rates will be discussed from the viewpoint of the local structure around the metal cations.


11:30 AM CM03.21.07
Sub-Micron Resolution X-Ray Spectroscopy and X-Ray Fluorescence Imaging at the NSLS-II SRX Beamline
Andrew Kiss, Juergen Thieme and Yong Chu; National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States.

The NSLS-II is a recently built and commissioned synchrotron designed to accommodate experiments that require highly coherent and high brilliance X-rays. The generated X-ray light has a very low emittance of 0.6 mm-rad and 8 pm-rad in the horizontal and vertical directions, respectively, as well as a position stability of less than 10% of the source size in the horizontal and vertical. The ring current has been steadily increasing to provide more X-ray flux, with a current value of 375 mA and a design goal of 500 mA. Based on these storage ring parameters, NSLS-II is an ideal synchrotron for X-ray microprobe experiments. The Sub-micron Resolution X-ray Spectroscopy (SRX) beamline at NSLS-II 5-ID has been specifically designed to utilize the strengths of NSLS-II for sub-micron X-ray spectroscopy and X-ray fluorescence (XRF) imaging. Kirkpatrick-Baez (KB) mirrors focus the X-ray beam down to a sub-micron spot for high spatial resolution X-ray absorption near-edge structure (XANES) spectroscopy and XRF imaging experiments. Monochromatic X-rays ranging from roughly 4.5 to 25 keV illuminate the sample and enable XANES across a wide range of elements from titanium up to plutonium. The undulator source produces enough brilliance for roughly 10^13 ph/s at the sample, data collection time is minimized. The high X-ray flux combined with fly-scan sample motion, allow XRF imaging to be rapidly collected. This is necessary for and enables *in situ* experiments which can provide researchers more realistic conditions for their samples. Combining spectroscopy and imaging techniques allow scientists to nondestructively investigate the elemental and chemical state of their samples.

This presentation will introduce current applications of research performed at the SRX beamline, focusing on material science and energy materials, such as Li-ion batteries.

1:30 PM *CM03.22.01
Detailed Investigation of the Interfacial Electrolyte/Electrode Reactions and the Effect of Additives in Li-Ion, Li-Sulfur and Li-Air Batteries by Operando ec-(S)TEM

The high demand for new energy storage nanomaterials has created the need for novel experimental techniques that can provide real-time information on the dynamic structural changes and reactions that occur locally at the electrode/electrolyte interface inside the battery. The development of *in situ* liquid electrochemical stages for (transmission) electron microscopy (ec-(S)TEM) enables fabrication of a "nano-battery" to study the details of electrochemical processes under operando conditions. However, the high complexity of electrochemical processes during battery cycling requires careful calibration of the system to circumvent *e*-beam damage and to control the side electrochemical reactions [1]. Here we demonstrate the application of this "nano-battery" approach to rechargeable Li-ion, Li-sulfur and Li-O2 batteries. The full operation of these complex systems is yet not fully understood and typically involves multi-step electrochemical reduction/oxidation reactions, which often lead to lithium dendrite formation. There are many strategies to improve the interfacial stability of the Li anode and control/suppress Li dendrite growth, which is highly dependent on nature of electrolyte itself, such as mixture of different electrolyte solvents, salts and additives (e.g. HF, LiNO3 etc). In one example, we investigate the role of electrolyte additives on the initial stages of Li depositionstripping and the SEI layer formation. Under operando ec-(S)TEM conditions we can explore the role of the moisture that typically causes fast degradation of the electrolyte but here is used as a "catalyst" that controls the interfacial electrode/electrolyte reactions. With careful calibration of the water content, we obtain precise control of the interfacial reaction mechanism, which leads to suppression of the Li dendrite, increases Coulombic efficiency and to uniform Li grain growth [2]. Similar mechanisms have been observed with LiNO3 as an additive to control the mechanism of nucleation, growth and suppression of Li metal dendrites in Li-S batteries.

References:


[3] This work was primarily supported by JCESR, an Energy Innovation Hub funded by DOE-BES. The development of the operando stage was supported by the Chemical Imaging LDRD Initiative at PNNL. PNNL is a multi-program national laboratory operated by Battelle for the U.S. DOE under Contract DE-AC05-76SL01830. A portion of the research was performed at the EMSL user facility sponsored by DOE-BER and located at PNNL. The multi-target tracking algorithm is supported by NSF-1334012.

2:00 PM CM03.22.02
In Operando Investigations of the Surface Behavior of Cu Electrodeposition Suppressor Additives PEG and PPG
Ryan Rooney1, Kevin Schmitt1, Frank von Horsten2, Ralf Schmidt3 and Andrew Gewirth1; 1University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Atotech Deutschland GmbH, Berlin, Germany.

Fabrication of microelectronics relies on the dual-Damascene process in order to create metal interconnects within dielectric materials. These interconnects allow for electrical connection between nanometer sized transistors and global-scale electrical contacts. The process allows for precise trench and via formation by lithographic techniques and superconformal filling by copper (Cu) electrodeposition. Superconformal filling is accomplished by tailored electrolytes including sulfuric acid, Cu salt, and different types of organic additives.

Suppressors are an important type of additive which prevent over-deposition on substrate surfaces, promoting growth within a trench/via. PEG and PPG are...
commonly used suppressor additives. In this talk we report on the surface behavior of PEG and PPG using Raman, in-situ surface enhanced Raman spectroscopy (SERS), and in-situ electrochemical quartz crystal microbalance (EQCM) measurements. Raman and SERS are used to determine the conformational behavior of PEG and PPG as pure materials, in solution/suspension, and at a roughened Cu surface in-situ during Cu electrodeposition. For both PEG and PPG, a clear spectroscopic trend emerges of increased intensity in higher wavenumber modes in the CH stretching region as the environment is changed from pure material to solution to surface. The spectral changes associated with PEG are larger than those associated with PPG, suggesting that the relatively more hydrophilic PEG undergoes more conformational changes with surface association relative to the more hydrophobic PPG. Calculations show that the observed spectroscopic trend is associated with increased gauche character in the polymer backbone. In-situ EQCM measurements show PEG only adsors to the surface in the presence of Cl\textsuperscript{-}, consistent with previous studies of PEG. Alternately, PPG adsorbed to the surface with and without Cl\textsuperscript{-}, likely again because of the increased hydrophobic character associated with the molecule.

2:15 PM CM03.22.03
Revealing the Initial Stages of Metal Electrodeposition, Atom by Atom Richard Beanland\textsuperscript{1}, Haytham Hussein\textsuperscript{1}, Houari Amari\textsuperscript{2, 1}, Reinhard Maurer\textsuperscript{1}, Jon J. Peters\textsuperscript{1}, Mark Newton\textsuperscript{1} and Julie MacPherson\textsuperscript{1}; \textsuperscript{1}University of Warwick, Coventry, United Kingdom; \textsuperscript{2}Engineering, University of Liverpool, Liverpool, United Kingdom.

Electrochemical deposition has yet to realize its full technological potential, despite its widespread use in many areas. Since it takes place in a liquid electrolyte very little is known about its initial stages, which occur at the atomic level. Many potential applications require precise control at this scale, such as energy storage and conversion electrodes for water splitting, fuel cells and electrochemical reduction of carbon dioxide. Here, we use scanning transmission electron microscopy to obtain snapshots of gold electrodeposition with a time resolution of tens of milliseconds, returning to examine the same areas time and again after each new electrodeposition. Being careful to quantify and account for electron-beam induced effects, we track the movement and behaviour of individual nanoparticles and indeed individual atoms. We show the importance of electrochemically driven atom transport, atom cluster formation, reassembly and growth into nanoparticles as well as deconstruction and atomic fluxes across the electrode surface via atom bridges. These show the limitations of existing models of growth, which typically assume the need for a critical particle size above which subsequent growth occurs irreversibly with direct atom addition.

2:30 PM CM03.22.04
Defect Formation, Coarsening and Morphological Instability of Passivating Oxide Film by Environmental Transmission Electron Microscopy Xiaoxiang Yu\textsuperscript{1}, Ahmet Gulec\textsuperscript{1}, Christopher Andolina\textsuperscript{1}, Judith C. Yang\textsuperscript{1}, John H. Perepezko\textsuperscript{1}, Peter W. Voorhees\textsuperscript{1} and Laurence D. Marks\textsuperscript{1}; \textsuperscript{1}Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; \textsuperscript{2}Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States; \textsuperscript{3}Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

We report the results of in-situ and ex-situ transmission electron microscopy observations on the early stage oxidation of Ni-based alloys. At moderate temperature (~700 °C), an epitaxial rock-salt oxide Ni\textsubscript{1-x}Cr\textsubscript{x}O initiated at the surface of Ni-Cr and Ni-Cr-Mo alloys progressing by a layer-by-layer mode. Fast surface diffusion and slow bulk transportation of cations created vacancies firstly in the oxide film of Ni-Cr, coarsened into Kirkendall voids and then diffused to the metal-oxide interface, driven by the metal/oxide misfit stresses. The voids eventually formed cavities along the metal-oxide interface. For Ni-Cr-Mo alloys, Kirkendall voids were inhibited by the fast formation of metastable Ni\textsubscript{2-x}Cr\textsubscript{x}O\textsubscript{3} (corundum structure) phase after the growth of rock-salt oxide. The results indicate that Mo doping may stabilize the cation vacancies and inhibit the Kirkendall voids formation by promoting the nucleation of corundum structure. Density functional theory calculations confirm that the thermodynamic driving force of phase transformation from rock-salt to corundum structure is increased by 0.6 eV per Mo atom.

At higher temperature (above 800 °C), however, the intrinsic morphological instability of rock-salt oxide thin film manifested due to surface stress. The nonlinear instability began at step edges by forming thicker regions and then retreated toward the thicker portion of the film, in effect “eating” a layer out of the thin film. Density functional theory calculations and continuum modeling of the elastic instability support the model for the process. Collectively, our results provide new and deeper insights into defect formation, coarsening and morphological instability of protective oxide thin film during early stage oxidation, which is critical for better understanding and designing corrosion resistant alloys.

2:45 PM CM03.22.05
First Principles Approach to Model Electrochemical Reactions—Understanding the Fundamental Mechanisms Behind Mg Corrosion Mira Todorova\textsuperscript{1}, Sadarsan Surendralal and Jorg U. Neugebauer; Max-Planck-Institut fuer Eisenforschung, Duesseldorf, Germany.

Ab-initio modelling using density functional theory (DFT) provides important insights into reactions at electrochemical interfaces. Observation of reactions under conditions of applied potential presents, however, a major challenge. The reason is the lack of an easily available method within commonly used DFT codes with periodic boundary conditions, which allows tuning the electrode potential. Utilising concepts from semiconductor physics we developed a novel potentiostat design. The new approach can be easily implemented in all existing periodic DFT codes. The potentiostat controls the electrode potential of the system by tuning the excess charge of the working electrode. Employing this method, we study the Mg(0001)/H\textsubscript{2}O interface under anodic polarisation conditions. The high corrosion rate under these conditions is a key obstacle to the technological application of Mg and its alloys. However, despite decade long numerous experimental and theoretical studies the mechanism behind the infamously fast corrosion rate could not be resolved. Our new approach allows to observe “in situ” the corrosion reactions at the Mg surface, such as dissociation events, proton transfer and H\textsubscript{2} evolution. Based on these insights we identify a novel and hitherto not considered reaction mechanism and explain the origins of the anomalous hydrogen evolution.


3:00 PM BREAK
Hierarchical semiconductor nanostructures have been widely investigated as solutions to energy and environmental problems due to their excellent energy storage mechanism. Furthermore, several reports have shown that MXenes can be oxidized naturally in various environments [2], therefore direct in situ/operando experiments possible or thinkable.

In this work, soft X-ray absorption spectroscopy (XAS) at the O K-edge and Ti L-edge has been applied to Ti₃C₂Tx MXenes to study the oxidation state of Ti in various environments. The dried pristine Ti₃C₂Tx MXenes have been characterized in vacuum by XAS in total electron yield mode (TEY) and X-ray photoemission electron microscopy (X-PEEM). The X-PEEM is a powerful technique to record spatially resolved XA spectra at the Ti L-edge and O K-edge on individual MXene flakes. To evaluate the effect of solvation on the MXene oxidation state, Ti₃C₂Tx MXenes dispersed in water have also been studied in situ using silicon nitride membrane-based flow cell to enable good soft X-ray transmission. For dispersed samples, XA spectra at the Ti L-edge and O K-edge were recorded in total fluorescence yield (TFY) mode.

Finally, XAS characterization of Ti₃C₂Tx MXenes deposited on gold-coated silicon nitride membrane enabled measurement under applied potential. In situ characterization of Ti₃C₂Tx MXenes under different bias voltages in 1M sulfuric acid at the Ti L-edge were performed. Partial fluorescence yield (PFY) measurements have been performed for these in-situ measurements.

The present work demonstrates that soft XAS can be applied to characterize MXenes in various conditions, which may provide new insights towards the understanding of their electrochemical charging mechanism. Advantages and limitations of the various XAS detection modes will also be discussed.

References:
mixed diffusion-reaction regime at high dose rate, with the flower like structure resulting from unstable growth at the corners of the initial hexagonal plates. Finally, results from liquid phase SEM experiments suggest that the inter-grown plates form mainly by means of monomer addition. These findings provide a systematic and comprehensive view of hierarchical ZnO growth.

4:15 PM CM03.23.04
Real-Time USAXS and WAXS Studies of Morphology Evolution in 3D Nanoporous Gold During Electrochemical Dealloying


Nanoporous (NP) metals with bicontinuous ligament/pore morphology are attractive for various applications including (electro)catalysis, actuation, sensing, plasmonics and electrochemical energy storage. Those NP metals are commonly produced by (electro)chemical dealloying, during which the less noble component of a parent alloy is selectively etched away and a 3D framework is left behind. In this talk, I will present a fundamental study on microstructural and crystallographic evolutions during electrochemical dealloying in combination with in situ and operando Ultra Small Angle X-Ray Scattering (USAXS) and Wide Angle X-Ray Scattering (WAXS) experiments that we have developed to measure structural change on several length scales in real-time. The experiment was realized with the simultaneous WAXS/SAXS capability of the University of Pennsylvania’s multi-detector Dual Source and Environmental X-Ray Scattering (DEXS) facility. By controlling the voltage and measuring charge transferred, the length scale evolution of the system can be matched with the extent of dealloying. In addition, Weissmüller et al. have investigated the morphological similarities of nanoporous metal electron density and a Cahn’s spinodal decomposition model based on a Gaussian Random Field.1,2 Using this model, we can map an autocorrelation function derived numerically to the USAXS data and glean important system parameters such as specific surface area and pore to void ratio. This information can also be used to visually reconstruct the nanoporous framework as it evolves through the dealloying process.


SYMPOSIUM CM04

Ultrasound Probes for Advanced Materials Characterization and Development
November 26 - November 29, 2018

Symposium Organizers
Kimberley Hall, Dalhousie University
Ajay Srimath Kandada, Italian Institute of Technology
Carlos Silva, Georgia Institute of Technology
Cathy Wong,

Symposium Support
Photon etc.

* Invited Paper

SESSION CM04.01: Hybrid Lead-Halide Perovskites
Session Chair: Carlos Silva
Monday Morning, November 26, 2018
Hynes, Level 2, Room 201

8:30 AM *CM04.01.01
Ultrafast Electron-Phonon Coupling in Emerging Semiconductors Xiaoyang Zhu; Columbia University, New York, New York, United States.

In this lecture, I will briefly introduce our recent efforts in understanding electron phonon coupling in molecular, nano, and hybrid semiconductors. Electron phonon coupling is essential to a broad range of charge carrier processes, such as polaron formation, Auger scattering, and charge carrier recombination. They are also responsible for electronic phase transitions and emergent properties, e.g., charge density waves and superconductivity. Our experimental strategy is to target excited state dynamics in the most direct way possible, using, e.g., femtosecond two-photon photoemission spectroscopy, optical Kerr-effect spectroscopy, and two-dimensional spectroscopies, to directly observe many-body events in the time domain. These experiments have led to recent understanding of coherent and incoherent mechanisms in exciton fission in organic semiconductors, direct and phonon-mediated Auger recombination in a bulk semiconductor, charge separation at van der Waals interfaces of transition metal dichalcogenides, and polaronic screening in lead halide perovskites. Such fundamental understandings are leading to new design principles for nano, molecular, and hybrid semiconductors.

9:00 AM CM04.01.02
Exciton Dynamics in Colloidal Metal Halide Perovskite Nanocrystals and Nanoplatelets Matthew N. Ashner1, Seung Kyun Ha1, Katherine Shulenger2 and William Tisdale2; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Metal halide perovskites are a promising class of materials for a variety of applications such as solar cells and lasers. In particular, perovskites are highly defect tolerant, an effect that has been attributed to screening of charge carriers due to lattice deformations, among other mechanisms. Like other inorganic
semiconductor materials, quantum confinement causes changes in the behavior of excited charge carriers, such as a transition from free carriers to excitons as the dominant excited state. Quantum confined perovskites can be synthesized in a variety of forms, including cubic nanocrystals and nanoplatelets with a thickness of 1-3 unit cells. The nanoplatelets exhibit strong quantum confinement effects, while the cubic nanocrystals are more weakly confined due to the small exciton Bohr radius of ~5 nm. In this work, we use femtosecond transient absorption and femtosecond stimulated Raman spectroscopy to simultaneously investigate ultrafast exciton and lattice dynamics in colloidal perovskite nanocrystals and nanoplatelets. We discuss how exciton formation, energetic relaxation, and the role of lattice interactions in these processes, vary between the weakly and strongly quantum-confined regimes.

9:15 AM *CM04.01.03
Ultrafast Spectroscopy of Semiconductor Nanostructures Tonu Pullerits; Chemical Physics and NanoLund, Lund University, Lund, Sweden.

Nanowire semiconductor structures have a rich spectrum of properties related to quantum confinement which are not available in the corresponding bulk materials. Size-tunable spectrum is, perhaps, the best known and understood such property. Here we investigate dissipation and transport dynamics of various semiconductor nanowire systems and their composites. We have studied colloidal quantum dots, plasmonic metal nanoparticles, hybrid and all inorganic perovskite nanocrystals and Ruddlesden-Popper 2D perovskites. We apply a set of modern ultrafast techniques like photocurrent and fluorescence detected coherent 2D spectroscopy, transient terahertz and absorption spectroscopies revealing detailed information about photoexcitation dynamics.

As an example. Photo-generated charge carrier dynamics in Ruddlesden-Popper 2D perovskites with linear (n-BA) and branched (iso-BA) butylamine as capping cations were studied by using transient absorption and time-resolved photoluminescence spectroscopies. Both n-BA and iso-BA perovskites consist of mixed-phase 2D quantum wells with various layer thicknesses, where the photo-generated charges undergo inter-phase charge transfer from thinner quantum wells to thicker ones. By shortening the spacer from n-BA to iso-BA, the transfer rates are significantly increased, which can also diminish the charge accumulation in thin quantum wells induced by the unbalanced electron and hole charge transfer rates. Under high excitation intensity, the shorter spacing cation is found to further facilitate transport, which can compete with fast high-order carrier recombination and consequently improve the charge transfer efficiency. Intriguingly, we observe the existence of extra bulk 3D phases embedded within iso-BA perovskites, which can efficiently collect the confined charges within 2D phases and then transport them with faster carrier mobility and slower recombination rates.

9:45 AM BREAK

10:15 AM *CM04.01.04
Ultra-Fast and Ultra-Slow Processes Depict the (Defect) Photo-Physics of Metal-Halide Perovskite Semiconductors Annamaria Petrozza; Istituto Italiano di Tecnologia, Milano, Italy.

Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects. Here, first I will present our results on the role of structural and point defects in determining the nature and dynamic of photo-carriers in metal-halide perovskites. Then, I will discuss our understanding of key parameters which must be taken into consideration in order to evaluate the susceptibility of the perovskite crystals (2D and 3D) to the formation of defects, allowing one to proceed through a predictive synthetic procedure. Finally, I will show the correlation between the presence/formation of defects and the observed semiconductor instabilities.

10:45 AM CM04.01.05
Charge Carrier Recombination and Lattice Interactions in Bismuth-Based Perovskites Lissa Eyre, Robert L. Hoye, Tudor H. Thomas, Hannah J. Joyce and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

A promising class of lead-free perovskites for photovoltaic applications include the bismuth halides, such as MA3Bi2I9, BiOI, and Cs2AgBiBr6 [1]. Although these materials have been predicted to display defect tolerance, much like lead-halide perovskites, and already display improved stabilities and long charge carrier lifetimes, the power conversion efficiencies of the corresponding devices have lagged behind the lead-based perovskites. Potential reasons for this are being explored, for example, the disconnected nature of the bismuth halide octahedra in the crystal structure, which limits carrier mobility, and the lower levels of absorption due to indirect bandgaps [2]. We probe the behaviour of excited states in many bismuth-halide compounds with various effective dimensionalities using ultrafast transient absorption, Raman, and terahertz spectroscopy. The importance of phonons in carrier transport and hot carrier cooling is also investigated. Our findings are consistent with previous reports of strong coupling between phonons and electronic states [3]. Overall, this work indicates that bismuth-based materials have the potential to be used in efficient optoelectronic devices, but there is a need to account for the effects of strong carrier-phonon coupling and localisation of electronic states on carrier momentum and scattering rates. We therefore present charge carrier-lattice interaction strength as an important design criterion for efficient next-generation solar cells.


11:00 AM *CM04.01.06
Charge-Carrier Dynamics in Metal Halide Perovskites for Photovoltaics Laura Herz; University of Oxford, Oxford, United Kingdom.

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 21%. Yet the optoelectronic properties underpinning their performance are still the subject of debate. Here, ultrafast optical-pump THz-probe photoconductivity spectroscopy has proven to be an outstanding tool to unravel the dynamics of charge carrier recombination, and probe charge-carrier mobility mechanisms. Metal halide perovskites (stoichiometry AMX3) are particularly attractive light absorbers because their properties can be tuned through facile modification in composition and structure, e.g. throughsubstitutions of the organic A cation (e.g. methylammonium versus formamidinium), the metal M cation (e.g. Pb2+ or Sn2+) and the halide X anion (e.g. I3-). Introduction of hydrophobic cations that are too large to be incorporated into the perovskite structure, has also recently been explored, leading to electronic confinement in materials of lowered dimensionality, and better photostability.

We demonstrate how such changes affect parameters essential for photovoltaic operation, discussing the influence of composition, structure, doping and dimensionality on fundamental properties such as electronic bandstructure, charge-carrier recombination and charge-carrier diffusion lengths. We further...
discuss distinct charge-carrier recombination and scattering mechanisms and their dependences on composition and temperature.


SESSION CM04.02: Hybrid Perovskites and Nanostructures  
Session Chair: Matt Graham  
Monday Afternoon, November 26, 2018  
Hynes, Level 2, Room 201

1:30 PM *CM04.02.01  
Investigation of Electronic and Structural Dynamics in Metal-Halide Perovskites with Ultrafast Spectroscopy Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

Metal-halide perovskites have emerged as promising solution-processable semiconductors for optoelectronic applications. These materials show unexpectedly high luminescence yields, long carrier lifetimes under operating conditions. Facile changes in composition during fabrication can be used to control their optical properties, and the nature of electronic states. Recently, the ad-mixture of monovalent cations to the precursor solution has been demonstrated to maximize the luminescence yields and device performance, which harvests photon-recycling effects. The properties and dynamics of the perovskites’ electronic states are controlled by their crystal structure and symmetry. Strong spin-orbit coupling was predicted to introduce Rashba-type state splitting in the electronic band structure. In combination with the soft crystal structure of the perovskite lattice, it is likely that dynamic changes occur in the electronic states during their lifetime. So far, it is not understood how such effects change after optical excitation and how they proceed during relaxation of electronic states.

In this talk I will present how we use spectroscopic techniques to study the dynamics of electronic states and crystal structure in metal-halide perovskites on ultrafast timescales. I will report results on layered and bulk lead-halide perovskites, but also on sustainable lead-free variants. I will discuss how the crystal structure affects the properties of electronic states, and how we can use these changes to create novel optoelectronic devices.

2:00 PM *CM04.02.02  
Ultrafast Non-Contact Probes of Carrier Transport and Dynamics within Semiconductor Nanostructures and Interfaces Matthew C. Beard; Chemical and Nanoscience Center, National Renewable Energy Laboratory, Golden, Colorado, United States.

Solar photoconversion in semiconductors is driven by charge generation via photon absorption, charge transport, and charge separation at the interface of the semiconductor and contacting layers. Thus, the carrier dynamics – charge separation and recombination across junctions – represent a key-determining factor in the photoconversion performance. We have developed several non-contact probes based on ultrafast spectroscopy of carrier dynamics within bulk semiconductors, nanostructures and semiconductor interfaces. Isolating spectral signatures and/or the carrier dynamics that are specific to junctions and not just the interface or bulk is challenging. We developed transient photoreflectance (TPR) as an innovative time-resolved spectroscopic probe that can directly monitor carrier dynamics within and across such junctions. In the TPR method, the change in reflectance (of a broadband probe from a specific interface is monitored as a function of pump-probe delay (Fig. 1). The reflectance can be modulated by either photogenerated free-carriers due to band filling, and/or by transient fields due to electro-optic effects when charges are separated. The spectral nature of the reflected beam provides quantitative information about the built-in field; thus, TPR is a non-contact probe of the electric field at that interface. It will present recent studies of Pb-halide perovskites single crystals, thin films, and nanostructures and semiconductor nanowires.

2:30 PM CM04.02.03  
Observation of Multiple Excitonic Dipole Oscillations in Semiconductor Nanocrystals Using Phase-Locked Interference Detection Hirokazu Tahara, Masanori Sakamoto, Toshihara Teranishi and Yoshishiko Kanemitsu; Kyoto University, Uji, Japan.

Multiple excitons in semiconductor nanocrystals (NCs) are extensively studied for advanced optoelectronic devices such as quantum dot based solar cells, photodetectors, and lasers [1,2]. In particular, carrier multiplication process via multiple excitons is investigated to clarify a fascinating mechanism that enhances the photon-to-current conversion efficiency, i.e., multiple exciton generation. In this process, excitonic coherence is considered to play an important role as predicted in theoretical investigations of the coherent superposition of single and multiple excitons [3]. However, the generation process of multiple excitons still remains unclear. Since multiple excitonic coherence appears only within the ultrafast time regime, the coherent signal is hardly observed by using conventional spectroscopic techniques. Therefore, an advanced spectroscopic technique detecting ultrafast signals is required to observe the multiple excitonic coherence.

In this study, we report on the direct observation of multiple excitonic dipole oscillations in PbS/CdS core/shell NCs by our newly developed spectroscopic technique that employs phase-locked interference detection in transient absorption measurements [4]. Since a stable phase-locked pulse pair was used as pump pulses, transient absorption signals for various time interval between the pulse pair enabled us to monitor the profiles of excitonic dipole oscillations. The transient absorption signals showed the oscillations with higher harmonic orders of the pump photon energy that was set to the single exciton resonance energy. Furthermore, the harmonic dipole oscillations exhibited a clear correlation with the generation probabilities of multiple excitons. These results show that the multiple excitonic coherences, i.e., higher harmonic dipole oscillations, are formed in the NCs. We clarified that the decay profiles of the dipole oscillations are determined as a function of the number of excitons. It is notable that the frequency of higher harmonic dipole oscillations are comparable to that of the dipole oscillation of high-energy hot excitons. This result shows that the harmonic dipole oscillations can also play an important role in the reverse process, i.e., multiple exciton generation from a single hot exciton to multiple excitons in the ground state. Part of this work was supported by JST-CREST (JPMJCR16N3) and JSPS KAKENHI (18K13481).

Quantum confinement of 2D graphene nanomesh[1], 1D graphene nanoribbons[2] and 0D graphene quantum dots[3], has paved the way for the development of promising field of nanographene optoelectronics. In this context, the synthesis of molecular graphene via bottom-up processes permits to obtain monodisperse nanographene, with defined physical and chemical properties[4]. The luminescence features exhibited by molecular graphene[5], in particular, has made these carbon-based materials of great interest for plasmonic and photonic applications, among others.

Here, we demonstrate that the stimulated emission signal of a newly synthesised and very luminescent (absolute PL quantum yield 79%) nanographene molecule, namely dibenzothiophene-sulphonilene (DBOV 1) can be optically switched in the ultrafast time regime both in solution and in the solid state. We will show that such an effect can be achieved by taking advantage of the overlap between the stimulated emission signal and the absorption of intermolecular polaronic-like species.

References

3:00 PM BREAK

SESSION CM04.03: Nanostructures
Session Chair: Matt Graham
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 201

3:30 PM *CM04.03.01
Understanding the Features in the Ultrafast Transient Absorption and Two-Dimensional Electronic Spectra of Colloidal CdSe Quantum Dots Howe-Siang Tan; Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore, Singapore.

We present a model to explain the various features of the transient absorption (TA) and two-dimensional electronic spectrum (2DES) of colloidal CdSe semiconductor quantum dots (QDs). The measured TA and 2DES spectra consist of contributions by the ground state bleach (GSB), stimulated emission (SE) and excited state absorption (ESA) processes associated with the three lowest energy transition of the QDs. We model the shapes of the GSB, SE and ESA spectral components after fits to the linear absorption. The spectral positions of the ESA components take into account the bieaxotropic coupling energy. In order to obtain the correct weighting of the GSB, SE and ESA components to the TA and 2DES spectra, we enumerate the set of coherence transfer pathways associated with these processes. In 2DES, various other features provide information on the inhomogeneity and homogeneity of the sample under study. We use the nodal line slope (NLS) that separates the positive and negative peaks in the 2DES spectrum to characterize the homogeneous and inhomogeneous linewidths of colloidal CdSe QDs ensembles. With a combination of experimental measurements from linear absorption, transient absorption and 2DES spectra, we devise a simulation process to quantify the ratio between the inhomogeneous and homogeneous contributions to the linewidth-broadening effects of CdSe QDs ensemble.

4:00 PM CM04.03.02
Physical Origins of the Transient Absorption Spectra and Dynamics in Thin-Film Semiconductors—The Case of BiVO4 Jason K. Cooper1, 2, Sebastian Reyes Lillo1, Lucas Hess2, Chang-Ming Jiang2, Jeffrey B. Neaton1 and Ian D. Sharp1, 2; 1Lawrence Berkeley National Lab, Berkeley, California, United States; 2Joint Center for Artificial Photosynthesis, Berkeley, California, United States; 3Walter Schottky Institut and Physik Department, Technische Universität München, Garching, Germany.

Transient absorption spectroscopy offers a unique perspective on the photogenerated carrier lifetimes of materials through the ultrafast evolution of the transient difference spectrum taken in transmission and/or reflection geometries. However, the related spectroscopic features can be challenging to interpret accurately and as such the related kinetics may be convoluted in overlapping signals of unknown origin. By co-collecting both transmission and reflection signals we extract the differential absorption of the material. We use a combination of ground state optical properties and the temperature dependent difference spectra of a model system, bismuth vanadate, to obtain an accurate model of the time dependence of the transient spectrum. From this, we have obtained the temporal evolution of the free carrier density from which a kinetic model was developed enabling a unique perspective on the governing recombination mechanisms. Importantly, the lattice temperature has been shown to play a critical role in the optical response at time delays past 10 ps. Additionally, spectral features related to coherent optical and acoustic phonons have also been identified. This comprehensive approach to analyzing and modeling the TA spectra offers a generalizable basis for understanding the complex pump-probe data, reveals thermal heating artifacts that are frequently erroneously assigned to long-lived photocarriers, and offers a path to eliminating ambiguity in analysis of photocarrier dynamics in solid state systems.

4:15 PM CM04.03.03
Plasmon-Induced Demagnetization and Magnetic Switching in Nickel Nanoparticle Arrays Mikko Kaina1, Francisco Freire-Fernández2, Jorn P. Witteveen2, Tommi K. Hakala1, Päivi Törnä1 and Sebastiaan van Dijken2; 1CSIC-ICMAB, Bellaterra, Spain; 2Department of Applied Physics, Aalto University, Espoo, Finland.
In heat-assisted magnetic recording (HAMR), a plasmonic noble metal nanoantenna acts as a near-field transducer (NFT) that reduces the switching field of high-anisotropy materials via local heating [1]. Excitation of the NFT at the plasmon resonance frequency efficiently transfers optical energy to a nanoscale region, enabling local switching at a reduced magnetic field. Noble metal nanoantennas placed on ferromagnetic films have been used for nanoscale confinement of all-optical switching (AOS) [2]. Experiments on pure ferromagnetic metals demonstrate that, despite stronger ohmic damping, they also support surface plasmon resonances. This raises the question if one could nanostructure the magnetic medium itself to trigger magnetic switching via local enhancements of the optical field. To study the effect of plasmon resonances on magnetic switching, we considered ferromagnetic nanoparticles of uniform size and shape. Plasmon resonances in single ferromagnetic nanoparticles are rather broad, several hundreds of nanometers [3]. Yet, ordering of the particles into a periodic array significantly narrows the spectral response. In this geometry, hybridization between LSPRs and the diffracted orders of the array produces intense surface lattice resonances (SLRs) that give rise to enhanced optical absorption and light-matter interaction that can be ascertained from their enhanced magneto-optical properties [4]. We report on the manipulation of magnetization by femtosecond laser pulses in a periodic array of cylindrical nickel nanoparticles. By performing experiments at different wavelengths, we show that the excitation of collective surface lattice resonances triggers demagnetization in zero field or magnetic switching in a small perpendicular field. Both magnetic effects are explained by plasmon-induced heating of the nickel nanoparticles to their Curie temperature. Model calculations confirm the strong correlation between the excitation of surface plasmon modes and laser-induced changes in magnetization [5].


8:45 AM *CM04.04.01
Excitonic Effects in Single Layer MoS2 Probed by Two-Dimensional Electronic Spectroscopy

Margherita Maiuri1, Stefano Dal Cont1, Mattia Russo1, Junjia Wang2, Giancarlo Soavi2, Dumitru Dumcenco2, Andras Kis3, Andrea C. Ferrari2 and Giulio Cerullo1
1University of Cambridge, Cambridge, United Kingdom; 2Politecnico di Milano, Milano, Italy; 3University of Cambridge, Cambridge, United Kingdom; 4Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Atomically thin Transition-metal dichalcogenides (TMDs) have promising physical properties [1,2]. Because of the strong quantum confinement effects, Coulomb interaction is poorly screened in single-layer (1L) TMDs, so that the excitons created by photo-excitation have large binding energy, up to several hundred meVs [3]. The spectrum of 1L-MoS2 is characterized by two peaks of excitonic nature at 1.9 eV and 2.05 eV, the so-called A and B excitons. They arise from optical transitions between the spin–orbit split top valence band and the bottom conduction band, around K and K'. Although, exciton dynamics in 1L TMDs have been largely studied in the last years [4], the complete understanding of the mechanisms leading to the ultrafast excitons formation and coupling is far to understood.

Here we exploit two-dimensional electronic spectroscopy (2DES) to track the sub-ps excitonic interactions within MoS2. 2DES is an interferometric-based optical technique that allows to fully resolve the non-linear response of a material. It employs a sequence of three delayed short pulses impinging on a sample to provide a series of two-dimensional excitation/detection correlation energy maps at different delays, offering a unique combination of high temporal and spectral resolution. We perform 2DES measurements on a chemical vapor deposition grown 1L-MoS2 sample, at 77K and room temperature,
using sub 20-fs visible (1.75-2.3 eV) pulses, covering both A and B transitions.

In 2DES maps we distinguish two types of contributions: the signals along the diagonal line of the excitation/detection map, and the ones out of the diagonal (cross-peaks). At early times (<20fs), we observe instantaneous positive diagonal peaks appearing at the A/A and B/B excitation/detection energies, reflecting the bleaching of the excitonic transitions, as well as two cross-peaks at the A/B and B/A coordinates, indicating correlations between A and B excitons. At later times (40-60fs) we notice a marked elongation of both A and B diagonal peaks, associated with an ultrafast (100fs) spectral diffusion. For times >200fs a strong decrease of the peaks intensity is observed. While the build-up of the diagonal peaks is instantaneous (within our temporal resolution of 20fs), we can clearly resolve the formation of the lower cross-peak, at A/B excitation/detection point. The dynamic of the lower A/B cross-peak, which is completely masked and thus impossible to observe in transient absorption measurements, cannot be simply explained in term of a phase space filling effect, but it is a strong signature that exciton dynamics in 1L-MoS₂ is dominated by more complex interactions. Our results, combined with theoretical modeling, will shed new light on the origin of exciton dynamics in 1L TMDs.

References

9:45 AM CM04.04.02

Ultrafast Dynamics of 2D Materials Studied by Transient SHG Microscopy

Hyunmin Kim; DGIST, Daegu, Korea (the Republic of).

Recently, time-resolved pump-probe spectroscopy has been extensively exploited to study ultrafast carrier dynamics of 2D materials in a femtosecond scale time resolution. In this work, we introduce a transient second harmonic generation (tr-SHG) microscopy to study the electron/phonon dynamics of atomically thin MoS₂ materials. A time-dependent sequential tr-SHG imaging on electron/phonon dynamics was monitored using a tr-SHG microscopy composed of a pump beam tuned to the A-exciton (680 nm) and a probe beam (1040 nm) generating a SHG at 520 nm having a submicron scale lateral resolution. We do believe that the tr-SHG microscopy would suggest a new way to study ultrafast carrier physics of low dimensional materials and their hybrids in a more advanced spatiotemporal fashion.

9:30 AM CM04.04.03

Observation of Chiral Phonons in Monolayer 2D Materials

Hanyu Zhu1, 2, Jun Yi1, MingYang Li2, Lifang Zhang3, Jun Xiao4, Chih-Wen Yang5, Robert A. Kaindl1, Lain-Ling Li1, Yuan Wang1, 2 and Xiang Zhang1, 2, 5University of California, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 4Nanjing Normal University, Nanjing, China.

Chirality is often found in systems with structural inversion symmetry breaking. Previously, for bosonic collective excitations in solids, chirality was only theoretically predicted but never observed. We experimentally show that phonons can exhibit intrinsic chirality in monolayer tungsten diselenide. The chiral phonons have significant implications for electron-phonon coupling in solids, lattice-driven topological states, and energy-efficient information processing. We identified the phonons by the intervalley transfer of holes through hole-phonon interactions during the indirect infrared absorption. The chirality was confirmed by the transient infrared circular dichroism arising from pseudo-angular momentum conservation. From the spectrum we further deduce the energy transferred to the phonons, which agrees with both the first principle calculation and the double-resonance Raman spectroscopy.

9:45 AM BREAK
Excitonic Quantum Gates in Two-Dimensional Materials

Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 201

1:30 PM *CM04.05.01
Ultrafast Momentum-Resolved Phonon Spectroscopy—Direct Observations of Electron-Phonon Coupling and Nonequilibrium Phonon Dynamics in the Time-Domain
Bradley Siwick1, 2, 3, Mark Stern1, 3, Martin Otto1, 3, Laurent Rene de Cotret1, 3 and Mark Sutton1, 3; 1Physics, McGill University, Montreal, Quebec, Canada; 2Chemistry, McGill University, Montreal, Quebec, Canada; 3Center for the Physics of Materials, McGill University, Montreal, Quebec, Canada.

The nature of the couplings within and between lattice and charge degrees of freedom is central to condensed matter and materials physics. These interactions are essential to phenomena as diverse as superconductivity, charge density waves and carrier mobility in semiconductors and metals. Despite their fundamental role, detailed momentum-dependent information on the strength of electron-phonon coupling (EPC) and phonon-phonon coupling (PPC) across the entire Brillouin zone has proved elusive. This talk will describe a new technique, ultrafast electron diffuse scattering (UEDS), that provides such information. By exploiting symmetry-based selection rules and time resolution, different phonon branches can be distinguished even without energy resolution. Specific applications of UEDS to 2D materials will be presented, demonstrating that UEDS patterns map the momentum-dependent relative EPC and PPC strength as well as carrier screening effects through their profound sensitivity to photoinduced changes to the phonon system.

2:00 PM CM04.05.02
Probing Lifetimes and Hydrodynamic Transport in Quantum Materials
Jennifer Coulter and Prineha Narang; School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

The field of topological materials with strong electron-electron interactions is well established and has been the subject of research over the past few decades. In parallel, the field of photonics has made tremendous progress in connecting spatio-temporal ultrafast measurements to new quantum materials, including 2D plasmonics and Moiré structure localized potentials, to theoretical predictions. The study of the interplay between topological properties, optical properties and ultrafast dynamics in these materials has recently started to receive attention. Experimental demonstrations in a set of Dirac and type-II Weyl semimetals, materials where electrons effectively interact as massless relativistic particles (Weyl fermions) and in 3D the conduction and valence bands touch at isolated points, have shown evidence of a viscous electronic transport regime. In this regime, electron-electron scattering dominates over impurity scattering and other momentum-relaxing processes so that momentum is quasi-conserved and electron flow can be described using the formalism of hydrodynamics. This leads to a variety of surprising behaviors such as breakdown of the Wiedemann-Franz law, appearance of electron vortices, and tunable viscosity via magnetic field. Understanding these physical processes in materials is of both fundamental and practical importance, yet these problems pose unique theoretical and computational challenges. The simultaneous contribution of processes that occur on many time and length scales, not only make direct computational approaches very difficult, they also make comparisons with experimental observations challenging. Here we report a new microscopic model of this behavior using a combination of ab initio scattering methods and fluid dynamics techniques. Our work establishes a connection between the observed hydrodynamic phenomena in Weyl semimetals, crystal structure and symmetry and their experimentally observed dynamical properties.

2:15 PM *CM04.05.03
Excitonic Quantum Gates
Eric R. Bittner; University of Houston, Houston, Texas, United States.

Entangled photons offer an exquisite probe to correlated dynamics within a material system. In my talk, I shall discuss some recent experiments and our theoretical investigations into developing an input/output scattering theory approach that connects an incoming photon Fock state to an outgoing Fock state, treating both the internal (material) and photon dynamics on a consistent footing. As proof of concept, we show how entangled photons can probe the inner workings of a model system undergoing spontaneous symmetry breaking.

2:45 PM BREAK

3:15 PM CM04.05.05
Photoinduced Phase Transition in Strained Manganite Films Studied by Ultrafast Optical Single-Shot Spectroscopy
Yu-Hsiang Cheng1, Samuel W. Teitelbaum1, Jingdi Zhang1, Feng Jin1, Xuelian Tan1, Wenbin Wu1, Richard Averitt1 and Keith A. Nelson1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2University of California San Diego, La Jolla, California, United States; 3University of Science and Technology

SESSION CM04.05: Ultrafast Probes for Material Science
Session Chair: David Cooke
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 201

1:30 PM *CM04.05.01
Ultrafast Momentum-Resolved Phonon Spectroscopy—Direct Observations of Electron-Phonon Coupling and Nonequilibrium Phonon Dynamics in the Time-Domain
Bradley Siwick1, 2, 3, Mark Stern1, 3, Martin Otto1, 3, Laurent Rene de Cotret1, 3 and Mark Sutton1, 3; 1Physics, McGill University, Montreal, Quebec, Canada; 2Chemistry, McGill University, Montreal, Quebec, Canada; 3Center for the Physics of Materials, McGill University, Montreal, Quebec, Canada.

The nature of the couplings within and between lattice and charge degrees of freedom is central to condensed matter and materials physics. These interactions are essential to phenomena as diverse as superconductivity, charge density waves and carrier mobility in semiconductors and metals. Despite their fundamental role, detailed momentum-dependent information on the strength of electron-phonon coupling (EPC) and phonon-phonon coupling (PPC) across the entire Brillouin zone has proved elusive. This talk will describe a new technique, ultrafast electron diffuse scattering (UEDS), that provides such information. By exploiting symmetry-based selection rules and time resolution, different phonon branches can be distinguished even without energy resolution. Specific applications of UEDS to 2D materials will be presented, demonstrating that UEDS patterns map the momentum-dependent relative EPC and PPC strength as well as carrier screening effects through their profound sensitivity to photoinduced changes to the phonon system.

2:00 PM CM04.05.02
Probing Lifetimes and Hydrodynamic Transport in Quantum Materials
Jennifer Coulter and Prineha Narang; School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

The field of topological materials with strong electron-electron interactions is well established and has been the subject of research over the past few decades. In parallel, the field of photonics has made tremendous progress in connecting spatio-temporal ultrafast measurements to new quantum materials, including 2D plasmonics and Moiré structure localized potentials, to theoretical predictions. The study of the interplay between topological properties, optical properties and ultrafast dynamics in these materials has recently started to receive attention. Experimental demonstrations in a set of Dirac and type-II Weyl semimetals, materials where electrons effectively interact as massless relativistic particles (Weyl fermions) and in 3D the conduction and valence bands touch at isolated points, have shown evidence of a viscous electronic transport regime. In this regime, electron-electron scattering dominates over impurity scattering and other momentum-relaxing processes so that momentum is quasi-conserved and electron flow can be described using the formalism of hydrodynamics. This leads to a variety of surprising behaviors such as breakdown of the Wiedemann-Franz law, appearance of electron vortices, and tunable viscosity via magnetic field. Understanding these physical processes in materials is of both fundamental and practical importance, yet these problems pose unique theoretical and computational challenges. The simultaneous contribution of processes that occur on many time and length scales, not only make direct computational approaches very difficult, they also make comparisons with experimental observations challenging. Here we report a new microscopic model of this behavior using a combination of ab initio scattering methods and fluid dynamics techniques. Our work establishes a connection between the observed hydrodynamic phenomena in Weyl semimetals, crystal structure and symmetry and their experimentally observed dynamical properties.

2:15 PM *CM04.05.03
Excitonic Quantum Gates
Eric R. Bittner; University of Houston, Houston, Texas, United States.

Entangled photons offer an exquisite probe to correlated dynamics within a material system. In my talk, I shall discuss some recent experiments and our theoretical investigations into developing an input/output scattering theory approach that connects an incoming photon Fock state to an outgoing Fock state, treating both the internal (material) and photon dynamics on a consistent footing. As proof of concept, we show how entangled photons can probe the inner workings of a model system undergoing spontaneous symmetry breaking.

2:45 PM BREAK

3:15 PM CM04.05.05
Photoinduced Phase Transition in Strained Manganite Films Studied by Ultrafast Optical Single-Shot Spectroscopy
Yu-Hsiang Cheng1, Samuel W. Teitelbaum1, Jingdi Zhang1, Feng Jin1, Xuelian Tan1, Wenbin Wu1, Richard Averitt1 and Keith A. Nelson1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2University of California San Diego, La Jolla, California, United States; 3University of Science and Technology
Our findings suggest CE-LFR is a promising route for sensitive characterization of nanoscale structured materials. We show the CE-LFR is applicable for this double resonance greatly increased the light-matter interaction and hence the LFR signal. We have achieved a 47-fold increase in the LFR intensity.

Ultrafast Direct Electron Transfer at Organic Semiconductor and Metal Interfaces

The ability to control direct electron transfer can facilitate the development of new molecular electronics, light-harvesting materials and photocatalysis. However, it has been rarely reported and the molecular conformation-electron dynamics relationships remain unclear. Here, we describe direct electron transfer at buried interfaces between an organic polymer semiconductor film and a gold substrate, by observing the first dynamical electric-field-induced transition. After resonant excitation of the inter-site d-d transition at 1.55 eV, we observed a persistent change in reflectivity at the same frequency (1.55 eV), i.e. the spectral weight transfer to a Drude component at far-IR due to the insulator to metal transition, as confirmed by THz conductivity measurements. In a 30 nm thin film, the volume fraction of the photoinduced metallic phase grew with laser shots and saturated after ~20 shots. Besides the steady-state reflectivity, the transient reflectivity traces also changed shot-by-shot. There was a fast decay component which decreased with shots and eventually disappeared when a full metallic state was established at high fluences. Comparing with earlier transient reflectivity studies on the insulator to metal transition in other manganites, we believe the fast decay within first picosecond represents the recovery dynamics of the insulating phase from the photoinduced metallic phase. Based on that, we conclude parts of the photoinduced metallic phase stay persistently while other parts return back to the insulating phase in less than a picosecond. We also estimated the ratio of insulating and metallic phase in the thin film shot-by-shot.

Effect of Epitaxial Etresses on the Time Dynamics of Photoexcited Charge Carriers in InGaAs Based Superlattices

Epitaxial InGaAs films are promising material for creating photoconductive antennas for the generation and detection of THz radiation. The main disadvantage of such films is the low resistivity. This leads to a high dark current. To increase the resistivity, different approaches are used: ion implantation, epitaxial growth in low-temperature mode with doping with beryllium atoms, introduction of strained ErAs layers, etc. Another problem of InGaAs is the relatively long lifetime of the photoexcited charge carriers.

In this work the method of the carrier lifetime decrease was shown via creating of the epitaxial stress in InGaAs films. 3 types of superlattices were grown by molecular beam epitaxy: InGaAs/GaAs/InAs/InGaAs (SL1), InGaAs/GaAs/InAs (SL2), InGaAs/GaAs/InAs/InGaAs (SL3). Structure of the superlattices is a 30 period of the photoconductive layer (InGaAs) and insulator layer (InAlAs and InAs) with overall thickness ~ 500 nm. This layered system was selected to create epitaxial stresses in photoconductive layer.

XRD asymmetric scanning method ω−2θ was used to characterize epitaxial deformations. There were no stresses in SL1 sample. In SL2 samples epitaxial deformation value was ε = -0.0019, which correspond to compression deformation in InGaAs layer. In SL3 epitaxial deformation value in InGaAs layer was ε = -0.0053.

Optical-pump-probe reflectivity measurements were used for carrier dynamics investigation. Carrier dynamics was performed in wide power range. Carrier lifetime decrease on picosecond time scale was shown with decrease of the pump fluence. In addition, contribution of the nonlinear processes as two photon absorption and free carrier absorption to carrier dynamics was demonstrated. In SL3 sample with higher epitaxial stresses, decrease of the contribution of the TPA and FCA (characterized by ω parameter on time scale) on carrier dynamics was observed. For SL3 parameter ω=0.15 ps was minimal, which is contribute to laser pulse duration and carrier lifetime was 2.73 ps. That result shows, that increasing epitaxial stresses decreasing influence of nonlinear processes on carrier dynamics in InGaAs photoconductive layer and decreasing carrier lifetime.

The work was supported by Ministry of Education and Science of Russian Federation (State task no. 3.7331.2017/9.10 and grant no. 14.Z50.31.0034).

Microcavity Enhancement of Low-Frequency Raman Scattering from CsPbI3 at Room Temperature

Raman spectroscopy is a powerful laser based nonlinear optical technique for identifying chemicals and characterizing materials that has been adapted for both CW and ultra-fast pulsed excitations. Raman spectra can provide insight into numerous properties, including morphology, stress/strain, crystallinity, doping level, conductivity, local temperature, and polarizability, whether in bulk, thin film, monolayer or nanostucture form. Modern laser filters, based on volume holographic gratings amongst other approaches, now make it relatively straightforward to obtain CW Raman spectra much closer spectrally to the dispersion relation and to the vibrational modes associated with the nanostructural dimensions of the material, with broad applications to chiral purity of organics, biomolecular assemblies, hybrid organo-metal halide perovskites, and semiconductor super-lattices. However, the signal strength from LFR is typically very weak. Here we show that introducing a film of material into a photonic crystal structure, in this case a 1D optical microcavity consisting of two distributed Bragg reflector (DBR) mirrors, greatly enhances the LFR signal. This is the first demonstration of Cavity Enhanced LFR (CE-LFR).

In particular, we situated thin films of CsPbI3, which in some forms are Halide Perovskites, into a microcavity prepared from stacks of ZnS and CaF2 alternating layers. The resultant microcavities had a Quality Factor Q = 25. A TiO2 layer with a gradient in thickness was also located between the DBRs to enable tuning of the cavity resonance from a wavelength of 490 nm to 545 nm. We investigated the effect of cavity tuning on the LFR intensity. We observed that the width of the cavity peak is sufficiently broad to resonate both the incident laser and the scattered LFR peak from the CsPbI3 film. This double resonance greatly increased the light-matter interaction and hence the LFR signal. We have achieved a 47-fold increase in the LFR intensity. Our findings suggest CE-LFR is a promising route for sensitive characterization of nanoscale structured materials. We show the CE-LFR is applicable for both CW Raman and pulsed ultra-fast ISRS spectroscopy modalities.
Investigation of GHz Mechanical and Thermal Behavior of Confined Liquids with Molecular Resolution

We thank the Council of Scientific and Industrial Research (CSIR), the Department of Science and Technology (DST) and the Defence Research and Development Organization for financial assistance. We also acknowledge the DST for a J.C. Bose fellowship.

Femtosecond transient absorption (fs-TA) and Ultrafast Raman Loss Spectroscopy (URLS) have also been applied to reveal the excited state dynamics of bis(phenylethynyl)benzene (BPEB), a model system for one-dimensional molecular wires that have numerous applications in opto-electronics. It is known from the literature that in the ground state BPEB has a low torsional barrier, resulting in a mixed population of rotamers in solution at room temperature. For the excited state this torsional barrier had been calculated to be much higher. Our femtosecond TA measurements show a multi-exponential behaviour, related to the complex structural dynamics in the excited electronic state. Time-resolved, excited state URLS studies in different solvents reveal mode-dependent kinetics and picosecond vibrational relaxation dynamics of high frequency vibrations. After excitation, a gradual increase in intensity is observed for all Raman bands, which reflects the structural reorganisation of Franck-Condon excited, non-planar rotamers to a planar conformation. The time dependent peak positions of high frequency vibrations provide additional information: a rapid, sub-picosecond decrease in peak frequency, followed by a slower increase (as shown in figure 2), indicates the extent of conjugation during different phases of excited state relaxation. This study expands our understanding of the excited state of BPEB and analogous linear pi-conjugated systems, and may thus contribute to the advancement of polymeric “molecular wires”.

We thank the Council of Scientific and Industrial Research (CSIR), the Department of Science and Technology (DST) and the Defence Research and Development Organization for financial assistance. We also acknowledge the DST for a J.C. Bose fellowship.

Investigation of GHz Mechanical and Thermal Behavior of Confined Liquids with Molecular Resolution

The phenomenon of liquid structuring near interfaces is related to the liquid/interface interaction forces at distances of some molecular dimensions [1, 2]. Despite the fact that this universal structuring effect plays a key role in various fields such as heat transport, particle transport through biological membranes, nano-fluidics, microbiology and nanomechanics, the experimental investigation of liquid structuring remains challenging.

In this context, we have adapted the experimental technique of ultrafast time-domain Brillouin scattering (TDBS) [3,4] to investigate high-frequency longitudinal acoustic and thermal properties of ultrathin liquids confined between solid surfaces of different types. We will present results of TDBS used to determine the mechanical properties of ultrathin liquids with a subnanometric resolution of the liquid thickness gap. Fourier analysis of the recorded TDBS signals for different liquid thicknesses yield the value of the longitudinal speed of sound and attenuation at GHz frequencies. The TDBS thermal background recorded at different thicknesses gives insight on the evolution of the thermal properties of the sandwiched liquid structure following a variation of the liquid thickness gap. We will present several results obtained with different types of liquids (glycerol, 8CB liquid crystal, ionic liquids) highlighting in some cases liquid structuring at long distances > 10 nm at the vicinity of the solid interface, as well as thermal frustration linked to the confinement of the thermal phonons in a liquid gap dimensions matching the thermal phonons mean free path.

This pioneering TDBS experimental scheme is a first step towards the mechanical and thermal understanding of confined liquids measured through GHz ultrasonic probing.


Developing Time-Resolved Electronic Sum Frequency Generation to Probe Energy Transfer in Organic Thin Films

Organic semiconductors (OSC) represent a broad class of materials for the development of both novel electronics made exclusively from organic materials as well as the augmentation of existing inorganic semiconductors (ISC). However, incorporation of OSCs into devices on the market has been slow, in part due to a lack of understanding of fundamental processes whose function critically depend on the structure of interfacial junctions between layers in a device. To study these structure-function relationships a technique is needed with the ability to in situ monitor charge and energy transfer between the active layers of a functional device. To this end, we have developed electronic sum frequency generation (ESFG) for study of charge transfer both within purely OSC devices as well as from thin OSC films to ISC. ESFG is uniquely suited for the study of the inaccessible junctions in such devices given its interfacial selectivity in media containing a center of inversion. ESFG also has the advantage of being a purely optical technique, giving it the ability to...
study these transfer processes in functioning devices under ambient conditions. By developing heterodyne-detected ESFG (HD-ESFG) for the study of thin films, our group has been able to both resolve the phase of the measured \( \delta \phi \) spectrum and greatly increase our detection efficiency. HD-ESFG allows us to add an additional pump beam before our HD-ESFG probe, realizing time resolved ESFG (TR-ESFG) in order to track dynamics of energy and charge transfer at buried interfaces in working devices. We work demonstrates that TR-ESFG is a strong candidate in the growing list of techniques being developed to answer questions of charge and energy dynamics in OSC-ISC devices.

9:30 AM *CM04.06.04
Ultrafast Electron Solvation Dynamics at the Origin of an Electrochemical Reaction Chain Julia Stähler; Fritz Haber Institute of the Max Planck Society, Berlin, Germany.

The formation dynamics of localized electronic states in molecular films near metal electrodes, including their propensity to act as precursor states for chemical reactions, is of example crucial for a detailed understanding of charge transport and degradation effects in batteries. We investigate the formation dynamics of small polarons and their role as intermediate electronic states in thin films of dimethyl sulfoxide (DMSO) on Cu(111) using time- and angle-resolved two-photon photoemission spectroscopy. Upon photoexcitation, a delocalized DMSO electronic state two monolayers from the Cu surface is initially populated, followed by a dynamic increase in binding energy and electronic state localization. This formation of a small polaron occurs on a 200 fs timescale, consistent with localization due to vibrational dynamics of the DMSO film. This localized state is a precursor state for an extremely long-lived surface-bound electronic state with a lifetime of several seconds and, thus, thirteen orders of magnitude longer than the small polaron. Moreover, experiments in oxygen atmosphere show that these trapped, long-lived electrons react with \( \text{O}_2 \) at the DMSO surface, likely forming \( \text{O}_2^- \). Our findings highlight the importance of interfacial electronic states near metal surfaces for electrochemical reactions despite their femtosecond lifetimes, as they are crucial precursors for long-lived, reactive states of solvents and electrolytes.

10:00 AM BREAK

10:30 AM *CM04.07.01
Nonlinear Terahertz and Optical Spectroscopy of Advanced Materials—Fundamentals and Applications Keith A. Nelson; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

New developments in nonlinear terahertz spectroscopy have revealed important new insights into quantum material behavior and have opened up new possibilities for practical applications including advanced material characterization and control. Terahertz field interactions with electronic, lattice, and spin degrees of freedom have all been exploited in recent measurements. Terahertz-induced responses including quantum material phase transitions, colossal Stark shifts, and magnetization control will be illustrated. Terahertz-frequency electron paramagnetic resonance (EPR) including two-dimensional terahertz magnetic resonance will be discussed.

Time-resolved transient grating measurements of acoustic and thermal responses, in which crossed optical pulses generate an interference pattern at the sample whose spatial period determines the acoustic wavelength or the thermal transport length scale, have been conducted for some time, with applications already developed including noncontact metrology of thin films in microelectronics. Recently the measurements have revealed nondiffusive thermal transport kinetics, which provides fundamental insight into the phonons that carry thermal energy and which is a key consideration in nanoscale chemical reactions, is for example crucial for a detailed understanding of charge transport and degradation effects in batteries. We investigate the formation dynamics of small polarons and their role as intermediate electronic states in thin films of dimethyl sulfoxide (DMSO) on Cu(111) using time- and angle-resolved two-photon photoemission spectroscopy. Upon photoexcitation, a delocalized DMSO electronic state two monolayers from the Cu surface is initially populated, followed by a dynamic increase in binding energy and electronic state localization. This formation of a small polaron occurs on a 200 fs timescale, consistent with localization due to vibrational dynamics of the DMSO film. This localized state is a precursor state for an extremely long-lived surface-bound electronic state with a lifetime of several seconds and, thus, thirteen orders of magnitude longer than the small polaron. Moreover, experiments in oxygen atmosphere show that these trapped, long-lived electrons react with \( \text{O}_2 \) at the DMSO surface, likely forming \( \text{O}_2^- \). Our findings highlight the importance of interfacial electronic states near metal surfaces for electrochemical reactions despite their femtosecond lifetimes, as they are crucial precursors for long-lived, reactive states of solvents and electrolytes.

11:00 AM CM04.07.02
Ultrafast Anharmonic Phonon Scattering in PbTe Probed via Terahertz Emission Spectroscopy Burak Guzelturk1, 2, Mariano Trigo2, David A. Reix1, 2 and Aaron Lindenberg1, 2; 1Stanford University, Stanford, California, United States; 2SLAC National Accelerator Laboratory, Menlo Park, California, United States.

We report on the first direct and real-time measurement of ultrafast anharmonic phonon scattering in PbTe. Among IV-VI semiconductors, PbTe is an important system for infrared (IR) optoelectronics and thermoelectrics. For the latter, low lattice thermal conductivity has been identified as a key for efficient thermoelectric functionality, yet its origin has not been fully understood to date. Theoretical works supported by inelastic neutron scattering measurements pointed to the crucial role played by strong anharmonic phonon scattering between optical and acoustic phonons [1]. Also, ultrafast anharmonic scattering rates were estimated for PbTe underpinning its intrinsic impeded acoustic phonon transport [2]. However, no experimental study to date was able to time-resolve anharmonic phonon dynamics in PbTe.

Here, we observe far-IR electromagnetic radiation within the terahertz (THz) window emitted by PbTe upon ultrafast photo-excitation. This radiation emerges due to buildup of an ultrafast photocurrent close to the surface of the material and leads to the coherent excitation of IR-active optical phonons within the system. In this way, coherent detection of the radiated fields on femtosecond time-scale enables a mode-selective probe of phonon dynamics [3].

We observe that within the first ps following photo-excitation, the bare TO phonon mode (at 0.93 THz) splits into two; a higher energy mode around 1.4 THz and a lower energy mode between 0.4 – 0.8 THz. These new modes develop due to strong anharmonic coupling between TO and longitudinal acoustic (LA) phonons as theoretically predicted before [1, 2]. By monitoring the ultrafast anharmonic phonon scattering processes in real-time, we find the associated scattering rate to be \( (1 \text{ps})^{-1} \) which is in good agreement with the theoretical predictions [2, 4].


11:15 AM CM04.07.03
Ultrathin THz Waveplate as Characterized by Ultrafast Electron Pulse Edwin Sie, Clara M. Nyby and Aaron Lindenberg; Stanford University,
Manipulation of light polarization is indispensable to obtain control over the electronic properties in quantum materials. Here we show that we can change the polarization of light in the THz regime by using an ultrathin, nanometer-thick topological Weyl semimetal. We characterize the change of THz polarization using an ultrafast electron beam streaking that traverses a circular motion with respect to the THz beam. This finding offers a new promising way to enhance control over optoelectronic devices in nanometer scale.

11:30 AM *CM04.07.04
Transient Terahertz Spectroscopy—Femtosecond Dynamics of Low Energy Quasiparticle Excitations David Cooke; McGill University, Montreal, Quebec, Canada.

Terahertz pulses are coherently detected electromagnetic transients with a bandwidth spanning the 1 - 100 meV energy gap. These single cycle, phase stable pulses are powerful tools to examine low energy quasiparticle excitations in materials. Being perfectly synchronized to a fs laser pulse train, they can be used in a optical pump-THz probe geometry to time-resolve the kinetics of these excitations after optical injection or perturbation. The resulting time-energy maps can be used to determine fs dynamics of free charges, phonons, excitons, collective excitations and energy gaps resulting from many-body correlations. In this talk I will review the techniques for transient terahertz spectroscopy, specifically two-color laser plasma based sources capable of continuous coverage of the entire THz band in a single cycle pulse. I will discuss the application of transient terahertz spectroscopy to study a variety of condensed matter systems including semiconductor nanoparticles, organometallic halide perovskites and correlated electron systems. In addition, new methods of generating high field THz pulses have opened the possibility of coherently driving these quasiparticle excitations resonantly. I will discuss the current methods for generation of high field THz pulses, and some applications for controlling electron dynamics. Finally, the prospect of using shaped terahertz fields for quantum control experiments will be discussed, employing a novel pulse shaper demonstrated recently in our group. Proof of principle experiments will be discussed.

SESSION CM04.08: Ultrafast Imaging—Techniques and Applications
Session Chair: Sean Roberts
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 201

1:30 PM *CM04.08.01
Imaging Ultrafast Dynamics on the Nanoscale with Terahertz Scanning Tunneling Microscopy Frank A. Hegmann; University of Alberta, Edmonton, Alberta, Canada.

The ability to directly probe ultrafast phenomena on the nanoscale is essential to our understanding of excitation dynamics on surfaces and in nanomaterials. Recently, a new ultrafast scanning tunneling microscope (STM) technique that couples terahertz (THz) pulses to the scanning probe tip of an STM was demonstrated (THz-STM), showing photoexcitation dynamics of a single InAs nanodot with simultaneous 0.5 ps time resolution and 2 nm spatial resolution under ambient conditions [1]. Operation of THz-STM in ultrahigh vacuum now makes it possible to spatially-resolve subpicosecond dynamics of single molecules [2] and silicon surfaces [3] with atomic precision. Coherent control of THz-pulse-induced tunnel currents in THz-STM has also been demonstrated [3,4]. Even through THz-STM can be performed with THz-induced tunnel currents corresponding to less than 1 electron per THz pulse on average [2], extreme transient tunnel current densities of 10^7 A/cm^2 through single silicon atoms on a Si(111)-(7x7) surface have been observed, corresponding to about 500 rectified electrons tunneling in 0.5 ps across the junction [3]. This was attributed to nonequilibrium tunneling dynamics and penetration of the THz field through the metallic-like Si(111)-(7x7) surface. However, more detailed models may be required to better understand the subpicosecond tunneling dynamics induced in materials by THz-STM. This talk will discuss how THz-STM works and how it can provide new insight into ultrafast dynamics on the atomic scale, which is essential for the development of novel silicon nanoelectronics and molecular-scale devices operating at terahertz frequencies.


2:00 PM CM04.08.02
Time-Resolved (Far-) Infrared Spectroscopy at the Nanoscale Stefan Mastel, Tobias Gokus, Max Eisele and Andreas Huber; Neaspec GmbH, Martinsried, Germany.

Time-resolved optical spectroscopy from the mid- to far-infrared spectral range (0.1 – 100 THz) is a powerful tool to study the dynamics of low-energy elementary excitations in solid state systems, e.g. phonons, plasmons, and excitons on ultrafast timescales. With the development of time-resolved terahertz spectroscopy, ultrafast spectroscopy in the infrared has even reached the ultimate sub-cycle temporal limit [1,2]. In contrast to the achievements regarding the temporal resolution, the spatial resolution of far-field terahertz studies is limited by diffraction to the length scale of the probing wavelength (3 μm – 3 mm), making it impossible to access the intrinsic local response of single nanoparticles, nanodomains, or nanocrystals. To circumvent this fundamental limit, time-resolved infrared and THz spectroscopy has recently been combined with scattering-type Scanning Near-field Optical Microscopy (s-SNOM).

S-SNOM bypasses the diffraction limit, enabling optical measurements with extreme subwavelength spatial resolution down to 20 nm. s-SNOM employs the local field enhancement (hotspot) at the apex of an externally-illuminated sharp metallic atomic force microscopy (AFM) tip. In close proximity to a sample surface, the optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically-tip-scattered light yields nanoscale resolved near-field images and spectra simultaneous to topography. By combining s-SNOM and time-resolved IR spectroscopy, for the first time, this approach enables a detailed analysis of charge-carrier dynamics in single layer materials [3,4], semiconductors [5], single nanoparticles [6], and even strongly-correlated materials [7] with femtosecond temporal and nanometer spatial resolution.

This talk will present the recent highlights in the field of ultrafast infrared spectroscopy and time-resolved terahertz time-domain spectroscopy (THz-TDS) in combination with the resolving power of s-SNOM. In addition, we introduce our first commercially available and ready-to-use THz-TDS near-field
spectroscopy system and show measurements on various test samples, such as graphene, h-BN and functional SRAM device. We achieve a spatial resolution of < 15 nm at a probe center-wavelength of 300 μm, surpassing the spatial resolution of conventional far-field terahertz spectroscopy by a factor > 2000.


2:15 PM CM04.08.03
Ultrafast Imaging of Charge Carrier Dynamics on Semiconductor Surfaces (Ebrahim Najaﬁ), 1-2, 1California Institute of Technology, Pasadena, California, United States; 2Chemours Co, Wilmington, Delaware, United States.

The spatiotemporal dynamics of nonequilibrium carriers reveal the excitation and relaxation pathways in materials. Here we report the ultrafast imaging of photoexcited carriers generated on the silicon surface by a femtosecond laser pulse. We use the scanning ultrafast electron microscopy (SUEM) technique to investigate the evolution of these carriers in space and time as the semiconductor proceeds to the ground state. We find that carrier transport after optical excitation follows the super-diffusion model with the diffusion coefficient that linearly increases with the laser fluence. However, this trend reverses at high excitation fluences. We attribute this anomaly to the generation of a large electric field by the spatial separation of photoexcited carriers, which strongly opposes carrier super-diffusion. This is evident in the second moment of the carrier distribution, obtained from the SUEM images, which reveals expansions and contractions in the carrier density. The numerical simulation of the drift-diffusion equation supports this interpretation. Our finding shines a new light on the dynamics of hot carriers in highly perturbed semiconductors by directly imaging their progression toward the ground state.

2:30 PM BREAK

3:30 PM *CM04.08.04
Spatial and Temporal Imaging of Multi-Scale Interfacial Charge Transport in Two-Dimensional Heterostructures (Libai Huang), Purdue University, West Lafayette, Indiana, United States.

Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using organic and nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional (2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial charge transport. Here we investigate the formation and transport of CT excitons in van der Waals (vdW) heterostructures based on semiconductor transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision of 50 nm.

We have recently imaged the transport of interlayer CT excitons in 2D organic-inorganic vdW heterostructures constructed from WS$_2$ layers and tetracene thin films. To investigate driving force for exciton dissociation, we perform measurements on heterostructures constructed with different WS$_2$ thickness ranging from l layer to 7 layers. Photoinduced luminescence (PL) measurements confirm the formation of interlayer excitons with a binding energy of ~ 0.3 eV. Electron and hole transfer processes at the interface between monolayer WS$_2$ and tetracene thin film are very rapid, with time constant of ~ 2 ps and ~ 3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal coexistence of delocalized and localized CT excitons, with diffusion constant of ~ 1 cm$^2$s$^{-1}$ and ~ 0.04 cm$^2$s$^{-1}$, respectively. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

We have also studied the interlayer charge transfer and recombination in WS$_2$-graphene and WS$_2$-WSe$_2$ heterostructures. We have demonstrated broadband photocarrier generation directly from interlayer CT states in WS$_2$-graphene heterostructures. Lifetime of the CT excitons has been found to be strongly dependent on interlayer stacking in epitaxial grown AA and AB stacking WS$_2$-WSe$_2$ heterostructures.

4:00 PM CM04.08.05

In this paper, we integrate a combination of modern and complementary ultrafast diffuse reflectance based spectroscopy and microscopy techniques to discuss the ultrafast photophysics of efficient photovoltaic materials including Cu$_2$BaSn$_x$Se$_{1-x}$ (CBTSSe) chalcogenides$^1$ for the first time. CBTSSe is a recently introduced alternative to Cu(In,Ga)(S,Se)$_2$ and Cu$_2$ZnSn$_x$Se$_{1-x}$ (CZTSSe). Ultrafast diffuse reflectance measurements enable direct examination of charge carrier processes in opaque device-relevant structures$^2$, highly light absorbing/scattering materials$^3$ or thin films deposited on metal substrates all of which cannot be studied using conventional transmission based pump-probe spectroscopy schemes. Based on broadband diffuse reflectance transient absorption spectroscopy the fingerprints of photocarrier absorption, GSB bleaching and electronic states in the vis-near IR region are investigated. Moreover, pump-probe microscopic imaging in the diffuse reflectance mode enables to localize the photoexcitation patterns and early charge carrier kinetics within the grains of only a few hundreds of nanometers and localize the kinetics of photogenerated carriers in each grain.

The CBTSSe films deposited on Mo-coated glass substrates, are studied similar to the configuration found in functional devices. We spectrally resolve a sharp ground-state bleaching (GSB) peak for CBTSSe films, formed around the band edge transition. The combination of narrow GSB peak width measured, coupled with the sharp steady state UV-Vis diffuse reflectance band edge, PL emission at the band edge and intensity independent PL shape, all point to a reduction in shallow defects and band tailing in CBTSSe relative to CZTSSe films. Furthermore, we have shown that the unique sensitivity of pump-probe microscopy and sharp electronic transitions allow for detection of small S/Se stoichiometry variations, $\Delta S \leq 0.3$, in Cu$_2$BaSn$_x$Se$_{1-x}$—Sex grains—i.e., features that are largely unresolved for ensemble spectroscopy or luminescence measurements. By noting the sharp band edge transition, we show that the band tailing issue (prevalent for CZTSSe) is largely resolved for CBTSSe. The charge carrier relaxation resolved in CBTSSe single grains, or over an ensemble of grains, however, remains faster compared to CZTSSe, pointing to the need to perhaps better understand deep traps within this absorber family. Such deep defects and fast carriers relaxations, would still impact the photocurrent and open circuit voltage of the CBTSSe devices/films examined.
Recent advances in experimental techniques that probe ultrafast dynamics and coherent effects at quantum material interfaces pose a theoretical challenge in predicting such dynamics ab initio with high spatial and temporal resolution simultaneously. Typically, computational predictions of transport phenomena employ either i) stochastic approaches, tracking particle dynamics, or ii) probabilistic approaches, describing the evolution of particle distribution functions. The Boltzmann Transport Equation (BTE), is of the latter kind, and provides the most general description of semi-classical transport. The BTE is a non-linear integro-differential equation in six dimensions which is typically solved either in the time and space-independent form, or using a number of limiting assumptions such as the single-mode relaxation time approximation. Here, we present a general theoretical and computational framework for carrier transport, which solves the full BTE using all its phase space degrees of freedom (i.e. with both real and reciprocal space resolution). Further, our method allows us to resolve contributions to the carrier distribution as a function of individual scattering events – which is often what ultrafast experimental techniques probe. We extend our framework to capture the dynamics of Peierls’ phonon BTE, making it possible to compare our results with picosecond acoustic measurements as well as the more recent coherent phonon spectroscopy techniques. Finally, analyzing the resulting surface fluxes of generated carriers we can draw direct comparisons with techniques probing Surface Acoustic Waves in the GHz range.
Mapping Atomic Motions with Ultrabright Electrons—Fundamental Space-Time Limits to Imaging Chemistry

Dwayne Miller1, 2; The Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany; 2Departments of Chemistry and Physics, The University of Toronto, Toronto, Ontario, Canada.

Watching atomic motions on the primary timescales of chemistry has been a long held objective. It would enable the direct observation of barrier crossing processes related to transition state concepts that link chemistry to biology. There are not only extraordinary requirements for simultaneous spatial-temporal resolution but equally important, due to sample limitations, also one on source brightness. Taking the problem to be an imaging problem, as one makes the shutter speed shorter and shorter, a brighter and brighter source is needed to maintain image contrast. With the development of ultrabright electron and x-ray sources capable of literally lighting up atomic motions, this experiment has been realized and refined to provide a general tool for probing structural dynamics on par with conventional pump-probe spectroscopy. The first studies focused on relatively simple systems. Further advances in source brightness have opened up even complex organic systems and solution phase reaction dynamics to atomic inspection. A number of different chemical reactions will be discussed from electrocatalysis with conserved stereochemistry [Jean-Ruel et al JCP B 2013], intermolecular electron transfer for organic systems [Gao et al Nature 2013; Liu et al Chem Phys Lett 2017], metal to metal electron transfer [Ishikawa et al, Science 2015], to the recent observation of coherently directed bond formation using the classic I3- system, in a process analogous to a quantum Newton’s cradle [Xian et al Nature Chem 2017]. New insight into the nuclear motions involved in spin transitions will be similarly related to coupling between electronic surfaces. These studies have discovered that there exist coherently directed bond formation using the classic I3- system, in a process analogous to a quantum Newton’s cradle [Xian et al Nature Chem 2017].

Understanding charge generation mechanism in organic solar cells is of great importance to further device optimisation. Currently, the nature and magnitude of the binding energy of charge-transfer states (CTS), an intermediate state which is critical for following charge separation process, are still under debate. Here, we demonstrate a new method for determining the dissociation energy of CTSs for a range of devices with various molecular energy levels and disorder using temperature-dependent pump-pulse photocurrent spectroscopy. We observe that dissociation of CTSs is a temperature-dependent process, from which we determine the binding energy by measuring a single activation energy over a wide temperature range. We propose a simple qualitative picture to explain the observation, based on the direct split between the bound CTSs and free carriers after charge transfer. The activation energy falls within the range of 90 ± 50 meV. Surprisingly, this binding energy does not greatly depend on the material composition or the driving energy (~150 meV) for variation) for charge separation. Such observations in the studied benchmark polymer:fullerene systems as well as polymer:non-fullerene acceptor systems reveal unexpected similarities in the energetics of CTSs formed in different electronic environments. This makes our results of general importance for understanding the photophysics at the heterojunction interface for further development of organic photovoltaics. To a broad aspect, this technique might be used for ultrafast in-operando studies of efficiency-loss states in a variety of optoelectronic devices.

Excitonic Effects in Zinc-Porphyrins Arrays Studied by Sub-25-fs UV Pulses

Jiangbin Zhang1, 2, Yifan Dong2, Andreas Jakowitz1, Akshay Rao1, Richard H. Friend1 and Artem Bakulin1; 1University of Cambridge, Cambridge, United Kingdom; 2Imperial College London, London, United Kingdom.

Synthetic porphyrins are largely exploited for artificial light-harvesting and optoelectronics due to their efficient role in energy transfer processes as donor or acceptor molecules [1]. Zinc-porphyrins (1Zn) have been used to synthesize arrays of dimers (2Zn) and hexamers (6Zn) to mimic the interactions of photosynthetic pigments [2]. The 2Zn-arrays revealed evident changes, as splittings and broadening, in the Soret absorption band (ca 415nm, S2 state) [2]. In porphyrins, an ultrafast S2→S1 internal conversion (IC) process occurs on a picosecond timescale due to the changes in the conformational configuration. Indeed, we observe that the recovery of the GSB for both 2Zn and 6Zn cases is faster with respect to the 1Zn one, thus reducing the yield of the triplet state formation. For the 1Zn case, the S1 state undergoes inter-system crossing to long-living triplet states with high efficiency. In the arrays this relaxation pathway is modified by the presence of possible dark states due to the changes in the conformational configuration. Indeed, we observe that the recovery of the GSB for both 2Zn and 6Zn cases is faster with respect to the 1Zn one, thus reducing the yield of the triplet state formation. For the 1Zn case, the S1 state undergoes inter-system crossing to long-living triplet states with high efficiency. In the arrays this relaxation pathway is modified by the presence of possible dark states due to the changes in the conformational configuration. Indeed, we observe that the recovery of the GSB for both 2Zn and 6Zn cases is faster with respect to the 1Zn one, thus reducing the yield of the triplet state formation.

Coherent Exciton-Vibrational Dynamics and Energy Transfer in Conjugated Chromophores

Sergei Tretiak; Theoretical Division and Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The role of coherence signifying concurrent electron-vibrational dynamics in complex natural and man-made systems is currently a subject of intense experimental and theoretical studies. Particularly, gaining control of this phenomenon is important for energy and charge transport when designing functional materials for various technologies, ranging from sensing, imaging, solar energy harvesting, to future optoelectronic devices. Using our Non-adiabatic EXcited-state Molecular Dynamics simulations (NEXMD) framework, we study ultrafast dynamics and exciton transport in several distinct molecular systems. These simulations reveal a ubiquitous pattern in the evolution of photoexcitation spanning dynamics of multiple electronic states. Symmetries of the excited state wavefunctions define specific form of the derivative non-adiabatic coupling driving non-adiabatic quantum transitions, which leads to a collective asymmetric vibrational excitation coupled to the electronic system. This promotes subsequent wave-like evolution of the excited state wavefunction preserving specific phases and amplitude relations across the ensemble of trajectories, facilitating efficient energy funneling. Proposed simple model explains appearance of coherent exciton-vibrational dynamics due to non-adiabatic quantum transitions, which is universal across multiple molecular systems studied. Observed relationships between spatial extent/properties of electronic wavefunctions and resulting electronic functionalities allow us to understand and to potentially manipulate excited state dynamics and energy transfer pathways in a number of organic molecular materials.

The Impact of HOMO-HOMO Offset on Charge Separation in Small Molecule Nonfullerene Organic Solar Cells

Safakath Karuthedath, Julien Gorenflot, Ru Z Liang, Pierre M. Boujuje and Frédéric Laquai; King Abdullah University of Science and Technology, Thuwal, Jeddah, Saudi Arabia.

Non-fullerene organic solar cells (NF-OSC)s now outperform fullerene-based solar cells by their higher power conversion efficiency (PCE) at similar photovoltaic layer thicknesses. However, to compete with other emerging technologies, energy losses after photon absorption need to be minimized. This raises the question: what is the minimum energy difference required to ensure quantitative exciton dissociation at the DA heterojunction? We address this issue in this communication and present the influence of $\Delta E_{\text{U}} = \text{HOMO}_{\text{donor}}-\text{HOMO}_{\text{acceptor}}$ for three different small molecule nonfullerene organic solar cells using DR3:TDDB (DR3) as electron donor blended with different small molecule acceptors, namely IC-C6-6DT-IC (ICC6), O-IDTBR, and IEICO, which gradually decrease the energy offset. We find a PCE of 8.7%, 6.4%, and 0.5% for ICC6 ($\Delta E_{\text{U}}$: 0.7 eV), O-IDTBR ($\Delta E_{\text{U}}$: 0.45 eV), and IEICO ($\Delta E_{\text{U}}$: 0.25 eV) blends under 1 sun condition, indicating a correlation of performance and energy offset. Sub-picosecond to nanosecond (ps-ns) transient absorption (TA) spectroscopy exposes: DR3:ICC6 exhibits charge generation in 20 ps, whereas in DR3:O-IDTBR charges are generated up to 500 ps. In contrast, in DR3:IEICO blends energy transfer (EnT) outcompetes charge transfer, explaining the poor PCE and indicating, the HOMO energy offset is insufficient for charge transfer and separation. In line with the device efficiency, the yield of long-lived carriers remaining at 7 ns after excitation is 65%, 44%, and <10%, respectively, for ICC6, O-IDTBR, and IEICO blends. Our results shine light on the minimum energy offset required for charge separation in all small molecule nonfullerene organic solar cells.

Impact of HOMO-HOMO Offset on Charge Separation in Small Molecule Nonfullerene Organic Solar Cells

Anna Kohler; University of Bayreuth, Bayreuth, Germany.

The mechanisms by which excitons dissociate highly efficiently in some donor-acceptor systems are still not fully understood. In this talk I aim to highlight differences and similarities that exist between the delocalisation of holes along a conjugated polymer backbone and electrons in a more or less ordered (small molecule) acceptor domain, and their impact on the overall dissociation efficiency.

References:
3. Ultrafast Spectroscopy of Loss Processes in Nonfullerene Acceptor Bulk Heterojunction Solar Cells

Sergei Tretiak; Theoretical Division and Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The development of novel nonfullerene acceptors has recently boosted the power conversion efficiency of organic bulk heterojunction solar cells beyond an impressive 14%. However, it remains unclear which NFA structures are best to reduce further energy (voltage) and carrier (current) losses, as a precise understanding of the complex interplay between NFA structure and photophysical processes in blends and devices is still lacking. Here, we discuss for selected material systems, how the molecular structure affects the photophysics, specifically the charge separation and energy losses, which we study by ultrafast transient spectroscopy. As one example, we present BHJ systems that systematically vary in the energy offset between donor and acceptor. By using ultrafast transient spectroscopy, we demonstrate that after photoexcitation, singlet energy transfer can compete very efficiently with charge transfer, leading to low free carrier yields, and thus poor device performance. Furthermore, we show that the acceptors’ quadrupole moment is an important parameter to consider in the design of NFAs, as it determines the charge separation efficiency and simultaneously affects the open-circuit voltage of devices. Finally, we investigate the bias dependence of the device photocurrent by time-delayed collection field (TDCF) experiments and thereby identify reasons for low fill factors (FF) in polymer and small molecule / NFA systems. Specifically, we demonstrate that the fill factor is determined by two parameters: firstly, the field dependence of interfacial charge separation and secondly, non-geminate recombination of free charges competing with carrier extraction. In fact, depending on the NFA structure, field-independent charge separation is observed and thus high FFs can be achieved, if extraction of carriers kinetically outcompetes non-geminate recombination. However, other NFA structures exhibit low fill factors as charge separation is bias dependent and / or non-geminate recombination of charges competes with carrier extraction. Based on our spectroscopic insights and theoretical modeling of interface energetics and charge separation, we propose general design rules for NFAs that promise further reduction of quantum efficiency and energy losses.

The Impact of HOMO-HOMO Offset on Charge Separation in Small Molecule Nonfullerene Organic Solar Cells

Safakath Karuthedath, Julien Gorenflot, Ru Z Liang, Pierre M. Boujuje and Frédéric Laquai; King Abdullah University of Science and Technology, Thuwal, Jeddah, Saudi Arabia.

Non-fullerene organic solar cells (NF-OSC)s now outperform fullerene-based solar cells by their higher power conversion efficiency (PCE) at similar photovoltaic layer thicknesses. However, to compete with other emerging technologies, energy losses after photon absorption need to be minimized. This raises the question: what is the minimum energy difference required to ensure quantitative exciton dissociation at the DA heterojunction? We address this issue in this communication and present the influence of $\Delta E_{\text{U}} = \text{HOMO}_{\text{donor}}-\text{HOMO}_{\text{acceptor}}$ for three different small molecule nonfullerene organic solar cells using DR3:TDDB (DR3) as electron donor blended with different small molecule acceptors, namely IC-C6-6DT-IC (ICC6), O-IDTBR, and IEICO, which gradually decrease the energy offset. We find a PCE of 8.7%, 6.4%, and 0.5% for ICC6 ($\Delta E_{\text{U}}$: 0.7 eV), O-IDTBR ($\Delta E_{\text{U}}$: 0.45 eV), and IEICO ($\Delta E_{\text{U}}$: 0.25 eV) blends under 1 sun condition, indicating a correlation of performance and energy offset. Sub-picosecond to nanosecond (ps-ns) transient absorption (TA) spectroscopy exposes: DR3:ICC6 exhibits charge generation in 20 ps, whereas in DR3:O-IDTBR charges are generated up to 500 ps. In contrast, in DR3:IEICO blends energy transfer (EnT) outcompetes charge transfer, explaining the poor PCE and indicating, the HOMO energy offset is insufficient for charge transfer and separation. In line with the device efficiency, the yield of long-lived carriers remaining at 7 ns after excitation is 65%, 44%, and <10%, respectively, for ICC6, O-IDTBR, and IEICO blends. Our results shine light on the minimum energy offset required for charge separation in all small molecule nonfullerene organic solar cells.

Reference
Interfacial Energy and Charge Transfer for Photon Up-Conversion and Down-Conversion

Aaron P. Moon, Aaron Le, Jon A. Bender, Daniel E. Cotton, Emily K. Raulerson, Inki Lee and Sean T. Roberts; Chemistry, University of Texas at Austin, Austin, Texas, United States.

The negligible spin-orbit coupling in many organic molecules creates opportunities to alter the energy of excited electrons by manipulating their spin. In particular, molecules with a large exchange splitting have garnered interest due to their potential to undergo singlet fission (SF), a process where a molecule in a high-energy spin-singlet state shares its energy with a neighbor, placing both in a low-energy spin-triplet state. When incorporated into photovoltaic and photocatalytic systems, SF can offset losses from carrier thermalization, which account for ~50% of the energy dissipated by these technologies. Likewise, compounds that undergo SF’s inverse, triplet fusion (TF), can be paired with infrared absorbers to create structures that upconvert infrared into visible light. However, integrating materials that undergo SF or TF with existing electronics is challenging as this necessitates interfaces that can readily transfer spin-triplet excitations between these materials and bulk semiconductors, such as silicon. In this talk, I will summarize work investigating energy transfer dynamics in two key interfaces for SF and TF devices. First, I will describe work investigating how the local ordering of perylene diimide (PDI) molecules at a silicon surface impacts triplet energy transfer from PDI to silicon. We find small changes in the ordering of PDIs from their bulk structure due to strain at the silicon surface can shift their triplet energy by a few hundred meV, substantially impacting the driving force for triplet energy transfer. Second, I will discuss measurements characterizing triplet energy transfer from near-infrared absorbing PbS nanocrystals to TF materials covalently bound to their surfaces. We find PbS nanocrystals are decorated with a number of surface states. While some of these states facilitate triplet energy transfer to surface-bound molecules, others hinder it by trapping excitations. Throughout the presentation, an important theme will be use of key spectroscopic techniques, such as broad-band electronic sum frequency generation (ESFG), to visualize interfacial states involved in energy transfer between organic and inorganic systems.

MPP004.10/EP05.13.01

MPP004.10/EP05.13.02

MPP004.10/EP05.13.03
Singlet fission (SF) is a process that can occur in select organic molecules where a singlet exciton splits into two lower energy triplet excitons. While the intersystem crossing of singlets to triplets is typically slow in organic molecules, due to small spin orbit coupling singlet fission does not require a flip in spin and can be exceptionally fast compared to intersystem crossing. The SF process requires two chromophores whose triplet states should be approximately half of the singlet state’s energy to conserve energy. This process has applications in photovoltaics where thermalization of high energy excitations accounts for a major loss channel and limits the maximum performance of such devices. Utilizing materials that undergo efficient SF can potentially mitigate the losses these above band gap excitation experience — high energy excitations can be down converted into lower energy excitations before thermalization can occur. Perylenediimides (PDIs) are a robust class of dye molecule employed as commercial pigments that contain the proper energetics for SF. These molecules form crystalline domains in the solid state that can be readily tuned by functionalization of the molecules, thereby allowing the structure-function relationship of SF and intramolecular geometry in the solid state to be explored. The intramolecular geometry of SF chromophores has been shown to have a strong connection to the SF rate chromophores that undergo SF. A collection of PDIs with different solid state packing structures were evaluated for potential use as SF chromophores in polycrystalline thin films. Employing a combination of ultrafast femtosecond and nanosecond spectroscopy we identify the formation of triplet state spectral features and identify the SF rates for these materials. Extracted experimental rates deviate from theoretical predictions by approximately three orders of magnitude which may be attributed to differences in energetic landscape of the polycrystalline films and the dimer employed in the calculation. A series of temperature dependent spectroscopic experiments were utilized to examine the energetic requirements of SF in these polycrystalline thin films.

Singlet Fission is the process whereby one photon creates two triplet excited states. If both triplet states could be harvested by a single-junction solar cell, the solar cell efficiency would increase by up to 1/3. There has been much academic and industrial interest in developing new materials for singlet fission, but to date no material has proved ideal.

Carotenoids are the most widespread of the natural pigments, important for photosynthesis, vision, human health and industry. Work on astaxanthin [1,2] (the pigment which colours lobsters) shows that carotenoids are good candidates for singlet fission sensitizers for solar cells: they have strong absorption and fast (<100fs) singlet fission, independent of energetic driving force. There are hundreds of naturally occurring carotenoids and each of them can form a range of different dimer or aggregate structures (eg H- or J-aggregates).

To determine how carotenoid structure affects singlet fission, and how to exploit carotenoids or other polyene-type systems as singlet fission sensitizers, we use model systems to create identical dimer structures of a range of carotenoids. The model systems are made of synthetic ‘maquette’ proteins that hold the carotenoids in a specific dimer geometry. I will describe details of the photophysics of singlet fission in polyenes, showing that singlet fission is surprisingly robust to changes in conformation and does not depend on either the aggregate or intramolecular structure.


The electronic structure and exciton dynamics of organic molecules can change dramatically upon aggregation. The exciton dynamics of molecules in solution and in thin films of aggregates can be measured using transient absorption spectroscopy, but the exciton dynamics of intermediate aggregation states during thin film formation are typically unknown since measurements cannot be performed quickly enough to collect accurate transient absorption spectra of these species. By increasing the speed of data collection, the exciton dynamics of evolving material systems can be measured. A novel implementation of transient absorption spectroscopy is introduced that can measure transients with up to a 45 ps pump-probe time delay in one shot. The exciton dynamics measured during the solution deposition of a thin film is validated by comparing the initial exciton dynamics of the solution and the final exciton dynamics of the dry film to traditional transient absorption measurements. The exciton dynamics of intermediate aggregation states will be presented for the first time. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for a particular application.
Probing Single Molecular Dynamics at Ultrafast Time Scales and in Nanoscale Volumes

Niek F. van Hulst1, 2; 1ICFO - Institute of Photonic Sciences, Castelldefels, Spain; 2ICREA - Catalan Institute for Research and Advanced Studies, Barcelona, Spain.

Tracing of individual molecules both in space and in time, provides super-resolution images of intra- and inter-molecular dynamic processes, all beyond the ensemble [1,2]. A host of important dynamic processes occurs on fs-ps timescale, such as electronic relaxation/dephasing, energy & charge transfer, vibrational relaxation, photo-dissociation-ionization, photo-isomerization. Yet capturing fast dynamics is fundamentally limited by the ns lifetime of the detected fluorescence. For the ensemble, fs-ps resolution is conventionally obtained by transient absorption and 2D electronic spectroscopy (2D-ES). Here first, we challenge ultrafast transient absorption of a single molecule and have set out to probe the non-linear ultrafast response of the single molecule using a broadband laser in an effective 3-pulse scheme with fluorescence detection. 2D-ES of single molecules is getting into reach [3]. Next, stimulated emission has the advantage of coherence and unity quantum efficiency, compared to fluorescence. Moreover depleting the excited state rapidly reduces photodissociation. Thus, we have set out to directly detect the stimulated emission from individual molecules and Qdots at ambient conditions, to disentangle ultrafast charge dynamics in the excited state, on fs-ps timescale [4]. Finally, we enhance the sensitivity and resolution using the local optical near-fields of plasmonic nano-antennas. Critical to the optimal coupling and enhancement is the positioning of the molecule at the local nanoscale hotspot of a resonant antenna. We apply deterministic scanning and stochastic mapping of the nanoscale plasmon-molecule interaction, to optimize the coupling strength and ultrafast interaction [5,6]. We apply the enhancement to photosynthetic complexes, LH2 [7], to detect first single FMO complexes at room temperature and assess their photon correlation.

The presented nanoscale ultrafast spectroscopy on individual molecules is of direct importance for pathway-specific detection of energy transfer and charge separation, directly & locally in light-harvesting systems [1].

Acknowledgements

This research was funded by ERC Adv.Grant 670949-LightNet; MINECO Severo Ochoa SEV-2015-0522, FIS2015-69258-P and FIS2015-72409-EXP; the Catalan AGAUR (2017SGR1369), Fundació Privada Cellex, Fundació Privada Mir-Puig, and Gencat CERCA program.

References

Reference:
2. Cong Mai et al., PRB, 90, 041414(R) (2014).

CM04.11.03
Measurement of Ultrafast Carrier Dynamics in Graphene/Copper System
Cheng Dong, Weigang Ma and Xing Zhang; Department of Engineering Mechanics, Tsinghua University, Beijing, China.

Understanding of ultrafast carrier dynamics between graphene and metals at high frequencies is of great significance in graphene-based devices operating in high frequencies. Hence, we used femtosecond laser pulse-pump technique to study the energy coupling between graphene and copper, by monitoring the optical property change of graphene and copper, within 10 picoseconds after excitation of the pump beam. Sample is composed of single layer graphene grown on copper by chemical vapor deposition method. The pump beam of 400 nm is to excite the sample, and the probe beam of 800 nm is to monitor the total reflectivity change of this graphene/copper system. We observed two peaks and two valleys in measured total reflectivity signals, which reflects the optical properties. And then a slow increase in the total reflectivity signals is observed, which is dominated by the copper optical property changes. We developed a four temperature model to calculate the carrier temperature evolution of graphene and copper (phonons and electrons), and considering the energy coupling between graphene and copper is dominated by phonons. The theoretical results modulates the measured signal well. The energy coupling between graphene electrons and phonons, and energy coupling between graphene and copper are extracted from the modulation. These two energy coupling parameters provide understanding of graphene/metal-light interactions in ultrashort time domain, and provide foundation of graphene-based device applications.

CM04.11.04
Carrier Dynamics and Charge Transfer in CdSxSe1-x Lateral Nanoribbon Heterostructures
Freeman Statum, Biswadev Roy and Marvin H. Wu; Mathematics and Physics, North Carolina Central University, Durham, North Carolina, United States.

Ternary CdSxSe1-x semiconductors exhibit direct continuously composition-tunable bandgaps in the visible region and are thus of interest for applications involving emission and detection of light. Lateral nanoribbon heterojunctions offer large surface areas, short carrier diffusion lengths and lower cost of growth compared to bulk films. We characterize the evolution of photo-generated charge carriers in individual CdSxSe1-x nanoribbons using ultrafast optical spectroscopy and time resolved millimeter wave photoconductivity. Static confocal photoluminescence (PL) microscopy of these nanoribbons, which are produced through the vapor – liquid – solid technique using gold nanoparticle catalysts, show variations of ~80 – 120 nm in the locations of the PL peaks in adjacent regions due to spatially varying compositions. PL lifetime mapping via time –correlated single photon counting showed shorter lifetimes (~100 ps) in the central portion of the wider bandgap region, compared to regions near the interface. These shorter lifetimes, combined with wide field static PL measurements that show emission from the narrow bandgap region after excitation in the wider bandgap region, are consistent with transfer of photoexcited carriers. Higher (sub-picosecond) temporal resolution transient absorption (TA) microscopy measurements result in lifetimes matching those obtained via PL, TA and PL measurements with spatially separated excitation and TA probe or PL emission locations show evidence of asymmetric carrier diffusion near the interface. Time resolved photoconductivity decay curves from ensembles of nanoribbons show a system response limited nanosecond lifetime decay consistent with PL measurements, but also show a weak longer lived (~ 50 ns lifetime) component that may correspond to a small population of weakly trapped carriers not observed in PL or TA measurements.

CM04.11.05
Ultrafast Excited State Absorption in Chromophore-Functionalized Chiral Polybinaphthalenes
Jonatas Siqueira¹, Marcelo G. Vivas², Cleber Mendonça¹ and Leonardo de Boni¹; ¹Institute of Physics of São Carlos - University of São Paulo, São Carlos, Alabama, United States; ²Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas, Poços de Caldas, Brazil.

The study of ultrafast chirality dynamics in the excited state has received considerable interest over the past years. Chiral polymers show particularly interesting properties for applications in emerging field of chiral photonics. Chromophore-functionalized polybinaphthalenes are an interesting class of chiral polymers given their high chirality in the ground state. Chromophore-functionalized polybinaphthalenes show a tree-like structure: they are composed of a rigid, rod-like backbone to which flexible chromophores are attached. This tree-like supramolecular architecture, the chromophores (branches) are attached to a rigid backbone (trunk), diminishes and even excludes dipolar interactions between the chromophores. In a previous study on donor-embedded polybinaphthalenes, it was demonstrated that they are a very interesting class of polymers since the dipolar interactions between the chromophores are excluded in these materials and chiral contributions are present. The spectral depletion and ultrafast dynamics of excited state absorption of four different chromophore-functionalized polybinaphthalenes, were characterized by femtosecond absorption transient spectroscopy as a first step towards the characterization of their chirality dynamics in the excited electronic state. In order to better understand the origin of chirality in this class of polymers, we aim at studying their chirality in the excited state. An initial study in this direction was the characterization of their excited state absorption and dynamics via femtosecond transient absorption technique for four chiral polybinaphthalenes. Excited state absorption (ESA) spectroscopy at femtosecond time scale was carried out to measure the relaxation times and absorption spectra of their electronic excited states. Femtosecond time-resolved ESA experiment was implemented using 150-fs pulses (775 nm) from a regenerative Ti:sapphire. ESA spectra and dynamics measurements were performed using the pulse at 387.5 nm (second harmonic of 775 nm) as a pump pulse and a white light continuum (400 - 700 nm) as a probe. We obtained excited state characteristic deactivation times shorter than 100 ps and characterized the spectral dependence of their excited state absorption. The data obtained in this study will assist us in the characterization of the chirality ultrafast dynamics on the electronic excited state of this novel class of chiral polymers.

CM04.11.06
High Contrast Photothermal (PT) Phase Imaging in the Mid-Infrared Exceeding Sub-Diffraction Limited Spatial Resolution
Panagis Samolis¹,², Shyamsunder Erramilli¹,²,³,⁴ and Michelle Y. Sander¹,²,³; ¹Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; ²Photonics Center, Boston University, Boston, Massachusetts, United States; ³Division of Materials Science and Engineering, Boston University, Boston, Massachusetts, United States; ⁴Department of Mathematics and Physics, North Carolina Central University, Durham, North Carolina, United States.

Mid-infrared (mid-IR) spectroscopy and imaging has attracted significant interest as a label-free method for material analysis based on the presence of characteristic vibrational resonances in the molecular fingerprint region. However, most mid-IR photothermal (PT) spectroscopic imaging systems so far have mostly focused on extracting amplitude information from the sample. Here, we present how characterization of phase images can result in enhanced spatial resolution and imaging contrast based on the different thermal properties of the imaging target and its surrounding environment. In a heterodyne measurement configuration with a lock-in amplifier, phase details of single particles are resolved below the spatial sub-diffraction imaging limit of the optical system in a spectral window where the amplitude images don’t show much contrast.
In the presented PT pump-probe microscopy configuration, a nanosecond pulsed mid-IR beam excites the absorption resonance of the sample while a near-IR beam is used to probe its thermo-refractive response. By detecting the scattered probe intensity in the far field with sensitive detector technology, sub-diffraction limited imaging resolution can be achieved circumventing more complex mid-IR detectors.

In traditional mid-IR imaging, if the surrounding medium and the imaging target feature similar absorption properties, this generally limits the contrast, spatial resolution and chemical specificity. Here, we demonstrate the capabilities of PT phase imaging for highly sensitive detection of weakly absorbing single particles embedded in a medium that is also resonant at the excitation wavelength.

The PT signal of our system is acquired by lock-in detection, which allows background-free detection of small modulations in the probe beam intensity with high signal to noise and enables detection of amplitude and phase signals. We investigated the phase signal of 1 μm melamine beads embedded in an 8CB liquid crystal. We demonstrate that high phase contrast can be obtained due to the different thermal properties of the imaging target and its surrounding environment even in a spectral regime where absorption of the bead and the liquid crystal is similar. By investigating the phase signal, we are able to detect the presence of single absorbers smaller than the diffraction limited spot size with high contrast and enhanced spatial resolution, in an absorbing medium. This method provides a promising pathway to detect weakly absorbing signals in an overcrowded spectral region where high absorptive signals can mask weaker contributions, which is attractive for highly sensitive chemical sensing, detection of hazardous trace materials and biological tissue analysis.

CM04.11.07
Identification of Reactive Species in Photoexcited Nanocrystalline BiFeO3 Powder by Transient Absorption Spectroscopy

Wegdan Ramadan and Detlef Bahnemann
1 Physics Department-Faculty of Science, Alexandria University, Alexandria, Egypt; 2Institut für Technische Chemie, Leibniz Universität Hannover, Hannover, Germany; 3Laboratory “Photoactive Nanocomposite Materials”, Saint Petersburg State University, Saint Petersburg, Russian Federation.

BiFeO3 (BFO) is a multiferroic semiconductor that combines antiferromagnetic and ferroelectric order well above room temperature. It has a direct band gap energy lies within a range of 2.3 to 2.8 eV hence, it can harvest visible light of the solar spectrum and an indirect band gap around 1.8 eV. The position of the conduction band, E_C, and valence band, E_V, makes it suitable for the oxidation of water and many other organic pollutants. Combining such desired properties in a simple ternary compound that comprises echo friendly and cost effective elements makes it easier to utilize it towards sustainable energy harvesting application. However, fundamental studies about photo charge carrier dynamics of BFO nanoparticles are still lacking. BFO nanocrystals having particle size ~70 nm were synthesized using sol gel method. In this work, charge carrier dynamics of BFO colloid have been investigated by means of diffuse reflectance transient absorption spectroscopy. Nanosecond transient absorption were performed at two excitation wavelengths; 335 nm (3.4 eV) that is higher than the band gap and at 532 nm (2.33 eV) which is around the bang gap energy. Measurements were carried out in the presence of methanol-N2 saturated atmosphere as a hole acceptor and in presence of N2Na2S2O8 in an alkaline medium, by using NaOH as electron acceptor. By quenching electrons using Na2S2O8 we were able to deal with holes as electrons will be quenched by the persulfate and holes will remain in the particles. Measuring the initial signal height immediately after the laser pulse, two transient absorption maxima can be observed; one sharp maximum centered at around 550 nm and a broad one around 750 nm. To relate the observed transient absorption signals to possible trapped charge carriers, we performed the same measurements in a N2-methanol environment to investigate the changes in the transient spectra. In the presence of methanol, the absorption peak at 550 nm significantly decreases, while the absorption at 750 nm remained unchanged. This indicates that the first absorption maximum can be attributed to trapped holes, which react rapidly with N2–methanol hence the decrease in the spectrum. The same set of measurements when carried out at excitation wavelength of 355 nm and the same behavior was obtained. The observed peak at 750 nm could be related to the indirect band gap which is around the same wave length. This result contradicts what was reported previously by Yasuhiro et. al. who attributed the strong absorption peak at 540 nm to the optical transition of the photoexcited electrons to the higher conduction band. The optical transient absorption of the electrons could not be clearly identified hence, more experiments still need to be carried out.
**In Situ TEM of Formation Processes of Dislocation Loops in Tungsten Under Irradiation—Comparison Between Electron and Self-Ion Irradiations**

Kazuto Arakawa, Shimane University, Matsue, Japan.

Nuclear-fission and fusion materials are degraded primarily due to the accumulation of radiation-produced lattice defects, such as point defects (self-interstitial-atoms (SIAs) and vacancies) and point-defect clusters (dislocation loops and cavities). In order to precisely predict the lifetimes of nuclear materials, accurate understanding of the origins of the defect accumulation—generation of defects and their subsequent dynamics—is crucial.

In-situ transmission electron microscopy (TEM) is a powerful technique for probing defect dynamics, in response to external stimuli such as irradiation under heating or cooling. As the irradiation sources for the in-situ TEM, electrons and ions are available. In the electron irradiation, only point defects are generated as the primary damage via knock-on displacement. In contrast, in the ion irradiation, point-defect clusters are also generated as the primary damage, which is called “collision cascade”, like neutron irradiation.

In the present study, we focus on the formation process of SIA dislocation loops in tungsten under irradiation. So far, we have revealed that the SIAs [1] and loops are intrinsically highly mobile and the loop-formation process must be governed by extrinsic “stabilizers” for them. In this study, we examine the loop stabilizers for 2000-keV electron irradiation using a high-voltage electron microscope in Osaka University in Japan and 500-keV W⁺ self-ion irradiation using an ion-accelerators combined microscope in the JANNuS-Orsay facility in France. Through the comparison between these results, we try to extract the effects of collision cascade on the loop stabilization.

References


**Hot-Electron Mediated Atomic Diffusion in Proton-Irradiated MgO**

Cheng-Wei Lee and Andre Schleife; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Ionizing charged-particle radiation has exciting potential to modify material properties. In particular, swift heavy ions are known to either exacerbate or mitigate damage. Controlling the modification of a material using radiation relies on a quantitative understanding of fundamental interactions between particle radiation and target material.

Since high-energy projectiles significantly drive the electronic system of the target out of equilibrium, standard atomistic simulations based on the Born-Oppenheimer approximation are no longer valid. Therefore, knowledge of non-equilibrium electron-ion physics becomes crucial: Directly after excitation by the projectile ion, the electronic system of the target is in a highly excited, non-thermalized state. Subsequent thermalization and cooling takes tens to hundreds of femtoseconds and tens of picoseconds respectively, depending on the dominant scattering mechanism and the target material. However, it is currently not well understood whether and how non-thermalized excited carriers, as well as thermalized hot carriers, affect atomic diffusion, which is the critical knowledge to understand material property change via irradiation.

In order to achieve a quantitative description of atomic diffusion under particle radiation, we propose a parameter-free first-principles simulation framework that bridges time scales from ultrafast electron dynamics directly after impact, to atomic diffusion in the presence of hot electrons. First, we simulate electronic excitations during ion irradiation using real-time time-dependent density functional theory. We then extract the probability of finding electrons in excited electronic states as occupation numbers and use them as constraint in DFT-based nudged-elastic band simulations to compute migration barrier in the presence of hot carriers.

Here we apply this framework to magnesium oxide under proton irradiation [1]. We compare the migration barrier of an oxygen vacancy in the presence of (i) non-thermalized hot electrons, (ii) thermalized Fermi-distributed electrons, and (iii) an ionized oxygen vacancy. We found that in all three cases, the migration barriers are lower than for the electronic ground state by 1.33, 0.34, and 1.07 eV respectively. Neither thermalized hot electrons nor ionization of the point defect can fully explain the enhanced diffusion under non-equilibrium conditions, hinting at a novel hot-electron mediated diffusion mechanism. Furthermore, our quantitative simulations show that this mechanism strongly depends on the projectile-ion velocity, opening the possibility of turning it on or off by varying the kinetic energy of the particle radiation. We predict that this should facilitate direct experimental observation of this effect and significantly advances current understanding of non-equilibrium electron-ion dynamics in materials under energetic particle radiation.


**Helium Irradiated Cavity Formation and Defect Energies in Ni-Based Binary Single-Phase Concentrated Solid Solution Alloys**

Cheng-Wei Lee and Andre Schleife; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Binary single-phase concentrated solid solution alloys (SP-CSAs), including Ni₈₀Co₂₀, Ni₈₀Fe₂₀, Ni₈₀Cr₂₀, Ni₈₀Pd₂₀, and Ni₈₀Mn₂₀ (in atomic percentage), were irradiated with 200 keV He⁺ ions at 500 °C. He cavity size and density distribution were systematically investigated using transmission electron microscope. Here we show that alloying elements have a clear impact on He cavity formation. Cavity size is the smallest in Ni₈₀Mn₂₀ but the largest in Ni₈₀Co₂₀. Alloying elements could also substantially affect cavity density profile. In-depth examination of cavities at peak damage region (~ 500 nm) and at low damage region (~ 300 nm) demonstrates that cavity size is depth (damage) dependent. Competition between consumption and production of vacancies and He atoms could lead to varied cavity size. Density functional theory (DFT) calculations were performed to obtain the formation and migration energies of interstitials and vacancies. Combined experimental and simulation results show that smaller energy gap between interstitial and vacancy migration energies may lead to smaller cavity size and narrower size distribution observed in Ni₈₀Mn₂₀ compared with Ni₈₀Co₂₀. The results of this study call attention to alloying effects of specific element on cavity formation and defect energetics in SP-CSAs, and could provide fundamental understanding to predict radiation effects in more complexed SP-CSAs, such as high entropy alloys.
Under neutron or ion irradiation point defects and defect clusters are formed within the displacement cascades or by diffusion of defects under irradiation fluxes. The properties of these clusters have significant impact on the evolution of the microstructure under irradiation conditions. Furthermore, solutes within the alloys may affect the defect behaviour (their relative stability and their mobility) due to their more or less large interaction with them. Atomic simulation allows to investigate properties of point defect clusters. DFT calculations are the most accurate available method to determine the impact of substitutional atoms representative of the alloying elements on the stability and mobility of clusters in particular for self interstitial clusters the mobility of which can be quite complex. The results we will present focus on Fe dilute alloys representative of reactor pressure vessel steels, tungsten representative of fusion divertors and zirconium representative of fuel cladding materials. The different possible structures small SIAs clusters can adopt will be discussed, in particular the sessile and non parallel configurations in Fe, as well as the interstitial dislocation loop. The later has been experimentally observed when they are large enough. The dependence of solute interactions as a function of solute size, chemistry or magnetism will be discussed, as well as synergy effects between solutes. Furthermore, the formation of interstitial clusters in the displacement cascade obtained by molecular dynamics (using different EAM potentials) debris will be presented.

The data we obtained are essential / fundamental / necessary to model microstructure evolution using for instance kinetic Monte Carlo simulations.

11:00 AM CM05.02.02
Hydrogen Promoted Vacancy Diffusivity in Cu—First-Principles and Molecular Dynamics Study
Jumping Du1, 2, W.T. Geng3, 4, Kazuto Arakawa2 and Shigenobu Ogata2, 4; 1Center for Elements Strategy Initiative for Structural Materials, Kyoto University, Kyoto, Japan; 2Department of Mechanical Science and Bioengineering, Osaka University, Osaka, Japan; 3University of Science and Technology Beijing, Beijing, China; 4Department of Materials Science, Faculty of Science and Engineering, Shimane University, Shimane, Japan.

The agglomeration of vacancies, which acts as one of the void nucleation and growth mechanisms, may cause ductile fracture in pure metals and radiation-damaged materials. It has been believed that diffusion of vacancy in metals is suppressed in hydrogen environment. The fact that excess hydrogen can enhance greatly the self-diffusion of atoms in metals has been explained by the appearance of superabundant vacancies, because the vacancy formation energy decreases substantially with increasing H concentration, while individual vacancy diffusion is supposed to be slowed down. Previous computational and theoretical studies suggest that the trapped H atoms in a H-vacancy complex impede the diffusion of vacancy by increasing the energy barrier of vacancy jumping. However, by performing first-principles calculations of appearance probability of vacancy-H configurations, the activation energy and attempt frequency of possible vacancy jumping pathways in face-centered cubic Cu, we find at certain H concentrations and temperatures, the diffusivity of vacancy jumping. However, by performing first-principles calculations of appearance probability of vacancy-H configurations, the activation energy and attempt frequency of possible vacancy jumping pathways in face-centered cubic Cu, we find at certain H concentrations and temperatures, the diffusivity of vacancy jumping increases with increasing H concentration. This effect is found to be stronger in pure Cu than in Cu-H alloy, and it is attributed to the fact that the presence of H atoms in the Cu lattice increases the energy barrier for vacancy hopping.

11:15 AM CM05.02.03
Formation Mechanism of Radiation-Induced Re and Os Precipitation in W and Their Influences on Mechanical Properties
Hong-Bo Zhou, Yu-Hao Li, Ying Zhang and Guang-Hong Lu; Department of Physics, Beihang University, Beijing, China.

Tungsten (W) is one of the most promising candidates for plasma facing materials (PFMs) in future fusion reactors. Rhenium (Re) and Osmium (Os) are not only the typical alloying elements but also the main productions of transmutation in W-PFMs. More importantly, Re and Os will aggregate and precipitate in W under high energy radiation, which substantially enhance the radiation hardening and embrittlement, leading to the great concerns for the life-limiting of W-PFM. So far, the formation mechanism of Re/Os-rich clusters in W as well as their influences on the mechanical properties remains to be fully elucidated.

We have investigated the interaction between Re/Os and defects in W using a first-principles method in combination with thermodynamic models in order to explore the precipitating mechanism of Re/Os under irradiation. It is found that the presence of defects can significantly reduce the total nucleation free energy change of Re/Os, and thus facilitate the nucleation of Re/Os in W. Kinetically, self-interstitial atom is shown to be easily trapped by substitutional Re/Os, and form W-Re/Os mixed dumbbell. Such W-Re/Os dumbbell combining with the substitutional Re/Os atom will transform to high stable Re/Os-Re/Os dumbbell, which can serve as a trapping centre for subsequent W-Re/Os dumbbells, leading to the growth of Re/Os-rich clusters. Consequently, an interstitial-mediated migration and aggregation mechanism for Re and Os precipitation has been proposed.

To shed light on the effects of transmutation elements on the mechanical properties of W, we further have investigated the influences of Re on the motion of 1/2<111> screw dislocation in W. It is found that the influence of Re on the dislocation motion is directly related to the distribution of Re in W. For the state of Re dispersed distribution, the addition of Re will reduce the generalized stacking fault energy (GSFE) for both 1/2<111>-[112] and 1/2<111>-[110], and improve the ductility of W. However, the influence of Re clusters (for the state of Re aggregation) on the dislocation motion is significantly different from that of dispersed Re. The presence of Re clusters will substantially increase the Peierls stress and energy, inhibiting the dislocation mobility. This will significantly exacerbate the irradiation hardening of W. Therefore, the radiation-induced precipitation of transmutation elements will degrade the mechanical properties of W.

11:45 AM CM05.02.04
Investigation of Hydrogen Isotope Distribution in Unirradiated and Neutron Irradiated Zircaloy-4 via Atom Probe Tomography
Elizabeth J. Kautz and Arun Devaraj; Pacific Northwest National Laboratory, Richland, Washington, United States.

Tritium is a radioactive hydrogen isotope (^3H) used in various applications. Since tritium is not naturally abundant, it must be artificially generated with Tritium Producing Burnable Absorber Rods (TPBARs), which are specifically designed to produce and capture H when irradiated with neutrons. At the center of each TPBAR, there is a lithium aluminate (LiAlO2) ceramic pellet that produces tritium upon neutron irradiation, which is then absorbed by a Zircaloy-4 tube that surrounds the LiAlO2 pellet [1]. Currently the amount of H absorbed by the Zircaloy-4 getter, and the hydrate phases formed are not well understood [2]. In order to improve predictive models and inform materials processing and design decisions, improved understanding of mechanisms responsible for hydrogen absorption and distribution in the Zircaloy-4 getter is needed. The overall goal of this work is to measure hydrogen isotopic ratios
and spatial distribution in the Zircaloy-4 getter exposed to various environments in order to provide insight into how hydrogen is absorbed in the tritium production process. In this work, comparison of atom probe tomography results from as-received, hydrided, deuterided, and tritiated Zircaloy-4 samples was performed and compared to results from neutron irradiated Zircaloy-4. Data revealed several overlapping peaks in mass spectra, and non-uniformity in hydrogen distribution after exposure to hydrogen and deuterium gases. Additionally, sample preparation procedures and user-selected experimental parameters for pulsed-laser atom probe were studied in order to determine how various parameters impact hydrogen background, and hydrogen isotope content in all Zircaloy-4 samples analyzed. Laser energies of 80-200 pJ at a pulse rate of 125 kHz were studied, and we found that measured hydrogen concentration decreased with increasing laser energy at a given pulse frequency. The work presented here is intended to serve as a baseline for application of atom probe tomography for the challenge of hydrogen isotope quantification in Zircaloy-4, with implications to other hydrogen-sensitive metal alloy systems.

References:


SESSION CM05.03: Chemical and Polymeric Changes Under Ionizing Radiation
Session Chairs: Kazuto Arakawa and Hidehiro Yasuda
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 202

1:30 PM CM05.03.01
Structural and Electronic Changes in Prototypical Catalysts upon X-Ray Irradiation Anna Rescigno1, Amber Thompson2, Alex M. Ganose3, David O. Scanlon1 and Claire Murray4, Imperial College London, London, United Kingdom; 2University of Oxford, Oxford, United Kingdom; 3University College London, London, United Kingdom; 4Diamond Light Source, Didcot, United Kingdom.

Interactions of X-rays with crystalline matter can induce a wide range of changes. Whilst some knowledge is available for biological systems and extended solids, practically nothing is known on the effect of ionising radiation on small molecules. However, they form the basis of a range of important technologies, e.g. catalysis. In small molecule crystals radiation damage can be understood as a three step process. Primary damage is caused by the direct interaction of the incident radiation with the sample. This is followed by secondary damage through electrons as well as species which are created during the initial damage. Finally, an extended collapse of the structure can occur based on a combination of a significant number of damage processes caused by energy deposition in the crystal.

Modern characterisation techniques make extensive use of X-rays to gain information on the properties of matter. Particularly modern microfocused laboratory sources and synchrotrons with their increased radiation dosages and often lower X-ray energies present a challenge. The move towards ever more powerful X-ray sources has increased the urgency to understand the influence of radiation damage. Whilst the observation of radiation damage in itself is useful to design strategies to prevent it, it is of even greater importance to understand the why and how of radiation damage in these materials. Lessons learned from radiation damage studies can in turn give vital information to understand a material’s overall behaviour and stability.

Here, a combination of synchrotron-based X-ray powder diffraction (PXRD) and laboratory-based X-ray photoelectron spectroscopy (XPS) is used to provide insights into changes to the structure, to local chemical environments, and to the electronic structure of small molecular crystals. By combining results from both of these advanced techniques, structural changes can be directly correlated to changes of the chemical state of the metal, which also manifests itself in variations in the valence structure. A range of prototypical catalysts is investigated, based on the general formula of $\text{M}_{x}\text{COD}_{y}\text{X}_z$, where $\text{M}=\text{group 8-11 metals}, \text{COD}=\text{cyclooctadiene}$, and $\text{X}=\text{Cl, Br}$. By using appropriate timescales, the effects of radiation are followed continuously over long periods of time giving an insight into how radiation damage progresses. In order to understand the experimental observations in more detail, theoretical results from density functional theory calculations are employed. Differences in the behaviour of the materials will be discussed in the context of both structural and chemical characteristics.

The combination of diffraction and spectroscopy provides a powerful new way of following X-ray photon exposure effects on both structure and electronic structure. The characterisation processes developed are applicable beyond small molecule catalysts and the insights gained can be extended to other material systems, and inspire further investigations.

1:45 PM CM05.03.02
Evaluating Radical Initiators for Secondary Electron Optimization in Hafnium Oxide-Methacrylate EUV Photoresist Yasiel Cabrera, Eric Mattson, Kolade Oyekan, Yuxuan Wang and Yves J. Chabal, Department of Material Science, The University of Texas at Dallas, Richardson, Texas, United States.

Inorganic-organic hybrid nanoclusters are molecular compounds that have excellent photochemical properties for the newly emerging extreme ultraviolet lithography (EUVL). In particular, these systems have recently come into the spotlight of research due to their achievements in both high etch resistance and photosensitivity abilities thanks to their functional inorganic metal-oxide cores when exposed to ionizing radiation. In this work, we uncover the fundamental mechanisms of photoresists composed of hafnium-oxide core with terminal carboxylic acid ligands. A combination of in situ infrared (IR) spectroscopy and residual gas analyzer (RGA) measurements, together with density functional theory (DFT) provide mechanistic insight into each step of processing of the HMAA system: post-application bake (PAB), 90 eV electron irradiation, and post-exposure bake (PEB). To understand the role of ligands on electron-induced chemistry, we added co-ligand to the HMAA system -- hydroxobenzoic acid (HBA), and phenylacetic acid (PAA) -- and monitored the amount of alkyl CH produced after electron irradiation. We find that co-ligand films enhance crosslinking reactions, particularly for lower energy electrons (20eV). IR spectroscopy shows that similar amounts of CH are produced in the two systems, and analysis with RGA suggests that the ring radicals that are generated upon decarboxylation behave differently; we see the benzyl radical being released in the gas phase for PAA, while for HBA no phenyl radical is detected suggesting participation within the film.

2:00 PM CM05.03.03
When materials are atomic species-, site- or electronic orbital-selectively excited by photons with variable energy, bond breaking or reaction between specific atoms take place. It was confirmed in our group that a platinum silicide, PtSi, was successfully formed at the platinum/silicon oxide interface kept at room temperature under 25–200 keV electron irradiation. This result shows that the reaction cannot be induced by simple thermal annealing under no-electron-irradiation conditions and takes place by bond breaking of Si-O and simultaneous bond formation of Si-Pt under electron irradiation. In the present study, the synthesis of platinum silicide at the platinum/silicon oxide interface by photo-excitation was investigated using synchrotron-radiation photo emission spectroscopy and transmission electron microscopy. After photo-excitation by 80 eV photons, valence band spectrum of silicon did not change, and remarkable changes were not recognized also in Pt4f7/2 core level spectrum. On the other hand, in the case of photo-excitation by 140 eV photons, peak near the Si 3p level in the Si valence band spectrum shifts to higher energy, and a peak originating from Si3p-Pt5d bonds appears near the Fermi level. In Pt4f7/2 core level spectrum, the peaks shift to higher energy by 1.2 eV and are similar to those which are obtained from PtSi. These results indicate that valence band and Pt4f7/2 core level spectra remarkably change during PtSi formation. As mentioned above, it was confirmed that Si 2p core level excitation plays an important role in P2SiH silicide formation by reaction between silicon and platinum on Pt/SiOx thin film interface, because the binding energy of Si 2p is approximately 99 eV. In order to produce Si-Pt bonds preferentially from Si-O-Pt bonds, simultaneous breaks of Si-O and O-Pt bonds and the consequent desorption of oxygen atoms and formation of Si-Pt bonds may be required by photo-excitation. It is suggested that a core level excitation mechanism related to the Knotek and Feibelman mechanism may play an important role in silicide formation within the solid.

2:30 PM CM05.03.04
Damage Efficiency of High-Energy Ions in Ultrathin Polymer Films
Raquel S. Thomaz1, Jean-Jacques Pireaux3, Christina Trautmann2 and Ricardo M. Papaleo1; 1Catholic Univ of Rio Grande do Sul, Porto Alegre, Brazil; 3Materials Research, GSI Helmholtz Centre, Darmstadt, Germany; 2Université de Namur, Namur, Belgium.

In this contribution, we present recent results by our group aiming the investigation of the fundamental problem of damage efficiency of high-energy ions in polymers, under the spatial confinement conditions of ultrathin films. The identifiability and understanding of possible size-effects on the damage efficiency of energetic ions is crucial for several topics of interest, from radiation resistance and stability of nanomaterials and devices to biological damage at small scales. We followed the changes in radiation effects in two polymers (PMMA and PVC) as the thickness of supported films is systematically reduced from ~ 200 nm down to ~2nm to identify critical thicknesses below which the efficiency starts to deviate from bulk values. Two types of experiments were conducted using ions in an energy range from 2 MeV up to 2 GeV: one involving cratering produced by single ion impacts and another on measurements of bond-breaking rates, based on XPS spectroscopy investigations and average effects of high-fluence irradiations. Cratering efficiency decreases strongly with thickness below a critical size as large as 40nm in PMMA. Bond-breaking cross sections, in contrast, were insensitive to thickness reductions in both polymer films, even in layers as thin as 5nm. We will discuss why spatial confinement affects differently the damage efficiency of distinct types of effects, considering the degree of importance of long-range, cooperative effects of excited material along the ion tracks, and the changes in the radial profiles of deposited energy by secondary electrons in very thin layers.

2:45 PM CM05.03.05
Radiation Damage and Failure in Rubbers and Rubber Composites—Effect of Network Polydispersity
Alirea Sarvestani1,2; 1Ohio University, Athens, Ohio, United States; 2Mechanical Engineering, Mercer University, Macon, Georgia, United States.

Irradiation is recognized as one of the major environmental factors affecting the performance, strength, and durability of polymeric compounds. However, the underlying mechanism by which radiation alters the internal structure of rubbers is not well understood. It is known that ionization initiates a variety of chemical reactions in polymers. Among others, crosslinking and scission are the most important effects that markedly change the mechanics and durability of elastomers. Depending upon the radiation structure of polymers and radiation intensity, the chains may either crosslink, with a resulting increase in the network modulus, or undergo rupture that leads to degradation and softening of the network. Scission is an oxidative process that presumably happens due to direct rearrangement of a backbone into two separate entities or loss of a side-group and consequent rearrangement. Crosslinking, on the other hand, in an abstraction process that occurs when two chains join and form a larger macromolecule. Hydrogen abstraction, for example, often takes place between two irradiated polymer chains providing a potential site for crosslinking between them. We developed a continuum micromechanical model that predicts the change in mechanical properties of (filled) elastomers subjected to high-energy radiation (e.g., gamma-rays, UV, or electron beams) and finite deformations. The model demonstrates that polydispersity in internal structure of rubber network controls the elasticity, strength, and durability of rubbers subjected to irradiation. Accordingly, damage starts from scission of short strands and continues with radiation time, coupled with the magnitude of applied deformation.

3:00 PM BREAK

3:30 PM CM05.04.01
The Effective Thermal Conductivity of U-10Mo Fuels with Fission (Xenon and Krypton) Gas Bubbles Present
Rafi Iasir1, Nickie J. Peters2 and Karl D. Hammond3; 1Nuclear Engineering Program, University of Missouri, Columbia, Missouri, United States; 2University of Missouri Research Reactor Facility, Columbia, Missouri, United States; 3Chemical Engineering, University of Missouri, Columbia, Missouri, United States.

Uranium alloyed with 10 wt% molybdenum (U-10Mo) is currently being developed as a potential high-density low-enrichment uranium (LEU) fuel for research nuclear reactors. Given the lower melting points of metals compared to ceramic fuels, control of the temperature—and therefore knowledge of the thermal conductivity—is important to reactor design and operation. Fission generates gas bubbles, metallic precipitates, and solutes in the fuel matrix which can change the thermal conductivity and cause swelling of the fuel. We studied the impact of distributed fission gas bubbles on the effective thermal conductivity of irradiated U-10Mo fuel using a two-dimensional finite element method (FEM). The effective thermal conductivity of the materials is calculated by solving the heat equation on a two-dimensional domain and estimating the mean temperature and heat flux. The effects of both intra- and inter-granular fission gas bubbles are discussed. A distribution representative of a gas bubble superlattice is used as a model of intra-granular bubbles, compared to less-uniform bubble arrangements. For inter-granular bubbles, the bubbles’ spatial and size distributions were estimated from a two-dimensional scanning electron microscopy (SEM) image of fission gas bubbles that had collected on grain boundaries. The obtained results are compared
with theoretical models and experimental results. The results show that the pressure inside the bubbles has minimal influence on the overall conductivity. The overall conductivity of a xenon-krypton mixture typical of fission gas is also negligibly different than that of pure xenon. Bubble arrangement is also insignificant unless a relatively wide bubble-free path through the metal exists. However, the area fraction of xenon bubbles has a significant impact on the overall thermal conductivity.

3:45 PM CM05.04.02

Simulating Electronically-Driven Structural Dynamics in Silicon with Two-Temperature Molecular Dynamics and Electronic Temperature Dependent Forcefields

Robert Darkins1, Pui-Wai Ma2, Samuel Murphy2 and Dorothy Duffy4; 1Dept. of Physics and London Centre for Nanotechnology, University College London, London, United Kingdom; 2Department of Engineering, Lancaster University, Lancaster, United Kingdom; 3Culham Centre for Fusion Energy, Abingdon, United Kingdom.

The structural evolution of materials following ultrafast laser irradiation is generally classified by two distinct regimes. At relatively low fluences thermal processes dominate, as energy transferred to the ions via electron-phonon coupling results in melting on thermal timescales. In contrast, at high fluences the dynamics are dominated by non-thermal processes. These processes drive the electrons out of thermal equilibrium with the nuclei, producing hot, transient electronic states that modify the interatomic potential energy surface. Such non-thermal processes can induce melting on sub-picosecond timescales. Two temperature molecular dynamics (2T-MD) has proved to be a very successful methodology for modelling the low fluence regime, with excellent agreement between modelling and ultrafast electron diffraction experiments. The modifications to the potential energy surface induced by high fluences have, however, proved more challenging for classical simulations. Such effects can be included in 2T-MD by the development of electronic temperature dependent forcefields that capture the dynamic effects of the modifications of the potential energy surface due to the electronic excitations. However, as the potential energy surface changes dynamically during such simulations, care must be taken to ensure energy conservation. We have developed a rigorous formulation of two-temperature molecular dynamics that ensures energy conservation in simulations that employ electronic-temperature-dependent forcefields. We have also developed an electronic-temperature-dependent forcefield for silicon that faithfully reproduces the ab initio-derived thermodynamics of the diamond phase for high electronic temperatures, and the structural dynamics observed experimentally under highly nonequilibrium conditions. We will present the details of the modelling methods, the electronic temperature dependent forcefield and the calculated atomistic dynamics of laser irradiated silicon films.


4:15 PM CM05.04.03

Nanohillock Chain Formation under Grazing Angle SHI Irradiation by Molecular Dynamics Simulations

Henrique Vazquez Muinos2, M. Schleberger1 and Flyura Djurabekova1; 1University of Helsinki, Helsinki, Finland; 2University of Duisburg-Essen, Duisburg-Essen, Germany.

It was shown previously that in layered crystals such as SrTiO3 or Mica, SHI irradiation under grazing incidence can produce chains of hillocks/grooves on the surface of the material [1-3]. These structures could be explained by the fact that at a small angle incidence, the ions travel long distances through high or low electron density pockets, giving rise to higher or lower local stopping power along the ion trajectory [1]. This hypothesis assumes that the electronic thermal conductivity does not wash away the inhomogeneities of the local energy deposition before it is transferred to the lattice, allowing the formation of the nanohillocks due to local melting. We develop a new approach to simulate SHI grazing incidence irradiation and apply it to verify the aforementioned hypothesis.

The new approach calculates the energy locally deposited by the ion based on the electronic density along the trajectory using CasP code and simulates the electronic energy redistribution and transfer to the lattice according to the two-temperature model. This energy is added to the atoms and simulated with Molecular Dynamics (MD), producing structural changes in the material such as hillocks or grooves. Simulations in SrTiO3 shows that low angle irradiation produces strongly modulated electronic energy deposition along the ion track and that the electronic thermal conductivity is not capable of washing away the initial temperature inhomogeneities. As a result, regions with higher energy deposition show stronger melting and give rise to nanohillocks. The simulated hillocks have similar length, interdistance and height as in the experiments and shows dependence on the irradiation angle and crystal structure. The hillocks and grooves observed on the surface are associated with molten and sublimated material, respectively.

This new method allows for the first time to simulate grazing angle SHI irradiation realistically, taking into account the modulation of the stopping power due to the local electron density. The good agreement with experiments not only shows that the proposed method is capable of describing correctly the low angle SHI irradiation, but also strongly supports the hypothesis that the hillock chains form due to the varying local electron density. The good agreement with experiments not only shows that the proposed method is capable of describing correctly the low angle SHI irradiation, but also strongly supports the hypothesis that the hillock chains form due to the varying local electron density along the ion track.


4:30 PM CM05.04.04

Nanoscale Thermal Transport in Ion Irradiated Sapphire—Picosecond Time Domain Thermoreflectance

Baurzhan Muminov1,2, Azat Abdullaev1, Durkhan Alimzhанов1, Jacques O’Connell1, Vladimir Shkurakov2 and Zhandos Utegulov1; 1Department of Physics, School of Science and Technology, Nazarbayev University, Astana, Kazakhstan; 2Department of Mechanical Engineering, University of California, Riverside, Riverside, California, United States; 1Centre for HRTEM, Nelson Mandela University, Port Elizabeth, South Africa; 2Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna, Russian Federation.

Sapphire (α-Al₂O₃) is radiation resistive candidate inert matrix fuel host material for fusion reactors, as well as for fusion reactors and for space station applications. The control of radiation-induced thermal conductivity degradation is a critical issue for nuclear and fusion reactor system design and validation.

We have studied nanoscale thermal conductivity k degradation in sapphire single crystals as a result of swift heavy ion (Xe, 167 MeV, ion fluence range 10¹¹ – 10¹² cm⁻²) and slow light (He, 40 keV, 10¹⁵ cm²) ion irradiation. Cross-plane near-surface thermal transport measurements made by an ultrafast optical pump-probe technique called picosecond time domain thermo-reflectance (TDTR) [1, 2] were found to be in satisfactory agreement with semi-analytical thermal conduction modeling. The decay in through-plane k at high modulation frequencies in swift heavy ion (SHI) irradiated
A1O3 demonstrates a complex interplay between heat penetration depth, phonon mean free paths, spatial extent of SHI-induced latent tracks [3], and amorphization [4]. We demonstrate that TDTR is critical for the analysis of SHI-irradiated sapphire, especially at higher doses, even if virgin sapphire does not demonstrate modulation frequency-dependent thermal conductivity. We also establish using modulation frequency-dependent TDTR that variation in k across slow light ion (SLI) irradiated/virgin subsurface sapphire regions can be spatially profiled on the scale of hundreds of nanometers. Comparing the effects of SHI and SLI irradiations on thermal conductivity of sapphire, we conclude that SLIs tend to impart less damage to the structure and cause less decay of thermal transport even at high ion doses than HSIs do. Funding by MES RK research grant (AP05130446) and state-targeted program (BR05236454) is acknowledged.

References:

4:45 PM CM05.04.05
Uncertainty Quantification and Validation of Multiscale Models of the Effective Thermal Conductivity of UO2 during Reactor Operation Michael R. Tonks1, Jie Lian2, Marina Sessim1 and Xueyang Wu1; 1University of Florida, Gainesville, Florida, United States; 2Rensselaer Polytechnic Institute, Troy, New York, United States.

The microstructure of UO2 changes significantly during reactor operation, including the generation of point defects, defect clusters, fission product formation, and more. These microstructure changes cause the thermal conductivity of UO2, which is already low, to decrease even further. As part of the US Nuclear Energy Advanced Modeling and Simulation program, multiscale modeling and simulation have been used to develop a model of the thermal conductivity of UO2 that is a function of the fuel microstructure. While this model has been shown to perform well in fuel performance simulations, further validation is needed. In this project we perform uncertainty quantification on both the mesoscale and macroscale thermal conductivity models. We then compare the predicted thermal conductivity distribution to the measured thermal conductivity of UO2 samples fabricated to have various microstructures.

SESSION CM05.05: Multiscale Simulation and Characterization of Radiation Damage Session Chairs: Chu Chun Fu and Thomas Schuler Tuesday Morning, November 27, 2018 Hynes, Level 2, Room 202

8:30 AM CM05.05.01
Strategies for Optimal Construction of Markov Chain Representations of Atomistic Dynamics and Their Application to Irradiated Materials Danny Perez and Thomas Swinburne; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

A common way of representing the long-time dynamics of materials is in terms of a Markov chain that specifies the transition rates for transitions between metastable states. Such chains can either be analyzed directly, used to generate trajectories using kinetic Monte Carlo, or upscaled into mesoscale models such as cluster dynamics. While a number of approaches have been proposed to infer such a representation from direct molecular dynamics (MD) simulations, challenges remain. For example, as chains inferred from a finite amount of MD will in general be incomplete, quantifying their completeness and propagating these uncertainties to observables of interest is extremely desirable. In addition, making the construction of the chain as computationally affordable as possible is paramount. In this work, we simultaneously address these two questions. We first quantify the local completeness of the chain in terms of Bayesian estimators of the yet-unobserved rate, and its global completeness in terms of the residence time of trajectories within the explored subspace. We then systematically reduce the cost of creating the chain by leveraging an accelerated MD method, namely Temperature Accelerated Dynamics. We maximize the increase in residence time against the distribution of states in which additional MD is needed and the temperature at which these are respectively carried out. Using examples of defects that are relevant to the evolution of irradiated materials, we demonstrate that our approach is an efficient, fully automated, and massively-parallel scheme to efficiently explore the long-time behavior of materials.

9:00 AM CM05.05.02
Electronic Effects in Self-Ion Irradiated Tungsten—From Ab Initio to Experiment Andrea Sand1, Rafi Ullah1,4, Kai H. Nordlund1 and Alfredo A. Correa1; 1Department of Physics, University of Helsinki, Helsinki, Finland; 4CIC nanoGUNE, Donostia-San Sebastián, Spain; 1Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, California, United States; 2Departamento de Fisica de Materiales, UPV/EHU, Donostia-San Sebastián, Spain.

Primary radiation damage from collision cascades has been simulated with molecular dynamics methods for several decades, yet despite early understanding that electronic effects may be significant in the highly non-equilibrium processes, such effects have proved difficult to incorporate into atomistic cascade simulations.

State-of-the-art cascade simulations now routinely include the energy losses caused by electronic stopping, but this is generally implemented through the use of a non-local friction term, with a cut-off velocity below which the stopping is considered negligible, and hence disregarded. However, in energetic cascades, the atoms with threshold velocities number in the thousands, and as a result the total energy losses change significantly with small changes in the cut-off value. We demonstrate the sensitivity of predictions of the primary damage to the choice of this essentially non-physical threshold parameter. Direct comparisons to in-situ ion irradiation and ion beam mixing experiments can be used to guide simulation methods, and we show that it is possible to find agreement for a number of cases. However, such comparisons are not possible in all materials, due to either a lack of reliable experimental data, or to the fundamental limitations of observing very small defects directly in an electron microscope. Hence there is a need to improve the treatment of electronic effects in molecular dynamics in order to increase the predictive capacity of cascade simulations.

A model for including electron-ion interactions without the use of a threshold, under a unified framework over the whole energy range relevant to cascade dynamics, has been suggested [A. Caro and M. Victoria, Phys. Rev. A 40 (1989)], but only recently implemented by Tamm and Correa [https://github.com/LLNL/USER-EPH] with a parametrization for nickel. The model describes both the electronic stopping in the high-energy regime, and electron-phonon coupling in the low-energy regime, with the magnitude of the coupling varying due to the local electronic density experienced by the ion.
As a first step towards realizing such a model in the fusion-relevant material tungsten (W), we have performed real-time dependent density functional theory (DFT-PES) calculations of the energy losses of a W projectile in W. We show by direct comparison to experimental ion implantation ranges that the electronic stopping obtained in the <100> channel, predicted by TDDFT to be only a third of the value given by SRIM, is in fact in very good quantitative agreement with experimental values. These results provide evidence of the validity of the TDDFT method even for the heavy ion W, and open the way for constructing an electron density-dependent model of the electron-ion interaction for cascade simulations in W.

**9:15 AM *CM05.05.03**  
**Kinetics of Point Defects Under Irradiation—From Atomic to Cluster Scales**  
Thomas Schuler¹, Luca Messina², –¹, Maylise Nastar¹, Pascal Bellon¹, Robert S. Averback² and Dallas Trinkle³, ¹SRMP, CEA Saclay, Saclay, France; ²KTH, Stockholm, Sweden; ³MatSE, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Materials under irradiation experience an engaging competition between interrelated kinetic phenomena, namely the point defect creation rate and the long range diffusion, precipitation and elimination of atoms and defects. The modeling of such competition is hindered by the largely different time scales involved, hence requiring a multi-scale approach. We developed KineCluE, an open-source code that allows for computing cluster transport coefficients from atomic jump frequencies. These cluster transport coefficients—along with other parameters such as dissociation rates—can then be used as input parameters to cluster-based models such as cluster dynamics or object kinetic Monte Carlo to simulate micro-structure and point defect evolution over long timescales with accurate cluster kinetics. We employed this methodology to study and quantify the time-dependent effect of dilute solute additions on the fraction of inter-cascade recombined point defects. We found that point defect-solute flux coupling leads to a critical irradiation dose above which the solute effect vanishes, which was already observed experimentally. From this insight, we devised a general methodology to identify candidate solutes which increase point defect recombination under irradiation over extended periods of time. KineCluE also allows to take into account the effect of temperature, local strain, concentration and ballistic mixing on cluster kinetic properties. Some of these features will be presented in this talk.

**9:45 AM BREAK**
Many astrophysical observations indicate that standard model particles compose only 5% of the matter in the universe. Understanding the nature of dark matter and dark energy, the remaining 85%, is of fundamental importance to cosmology, astrophysics, and high energy particle physics. There are a number of attempts for direct detection of dark matter particles via an elastic interaction with detector nuclei. Astronomical observations indicate that dark matter forms a halo around our galaxy that is static or rotating much slower than the stars. Since our sun rotates around the center of the galaxy at a speed of 220 km/s, dark matter particles would, if they do interact with ordinary matter, give a momentum corresponding to this velocity to ordinary matter nuclei. Assuming dark matter particle masses of the order of 1 GeV/c^2, this would correspond to recoil energies of a few 100 eV, a typical ion irradiation energy. To date, the detectors developed could detect dark matter particles with masses > 10 GeV/c^2. In our recent work [1], we showed that potential dark matter particles in the mass range down to 200 MeV/c^2 could be detected by new kinds of single-electron resolution single crystal semiconductor detectors. The detector response can be calibrated with molecular dynamics simulations of low-energy self-recoils in the material. Moreover, since the threshold displacement energy depends on crystal direction, while the dark matter particles do not follow Earth’s rotation around its axis, the response of a single crystal detector should vary with the time of day. In this work, we used classical and time-dependent density functional theory molecular dynamics to calculate the response of the semiconductor detectors to dark matter recoils as a function of crystal direction, and using an analytical model translated this into a dependence of the signal on the time of the day. The diurnal variation could be a major benefit for distinguishing a dark matter particle signal from that of conventional particle physics standard model particles.

classification offers a path forward to the high-throughput irradiation defects quantification needed for reactor lifetime prediction and more efficient alloy development.

This research is funded by the U.S. Department of Energy Office of Nuclear Energy’s Nuclear Energy Enabling Technologies program project CFA 16-10570, Office of Fusion Energy Sciences under contract DE-AC05-76RL01830, and by the Molecular Foundry which is supported by the Office of Basic Energy Sciences, under Contract No. DE-AC02-05CH11231.

SESSION CM05.07: Mechanical Properties and Stresses Under Irradiation
Session Chairs: Pär Olsson and Hiroyasu Tanigawa
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 202

1:30 PM *CM05.07.01
Macroscopic Stresses and Strains Produced by Micorscopic Radiation Defects in Reactor Components
Sergii Dadarey1, 2, Daniel Densham2, Patrick Hurh2 and Steve Roberts2; 1UK Atomic Energy Authority, Abingdon, United Kingdom; 2Department of Materials, University of Oxford, Oxford, United Kingdom

Predicting macroscopic strains, stresses and swelling in power plant components exposed to irradiation from the observed or computed defect and dislocation microstructure is a fundamental problem of fusion power plant design that has so far eluded a practical solution. We have discovered that the problem can be addressed and solved using the fact that elasticity equations involve no characteristic spatial scale and hence admit a mathematical treatment that is an extension to that developed for the evaluation of elastic fields of defects on the nanoscale. Strains, stresses and swelling can be determined using either the integral equation formalism where the source functions are defined by the density of relaxation volumes of defects, or they develop a general finite element method (FEM) implementation, applicable to a broad range of predictive simulations of strains and stresses induced by irradiation in materials and components of any geometry in fission or fusion nuclear power plants.

2:00 PM CM05.07.02
Microstructural and Micromechanical Investigation of Irradiation Effects in Beryllium
Vabicxay Loushen1, 2, Chris Densham2, Patrick Hurh2 and Steve Roberts2; 1UK Atomic Energy Authority, Abingdon, United Kingdom; 2Department of Materials, University of Oxford, Oxford, United Kingdom

Beryllium is an essential material for reflectors and moderators in material testing nuclear reactors, plasma facing and neutron multiplier material for fusion reactor designs (ITER, DEMO), candidate material for target components in near-future multi-megawatt accelerator particle sources (LBNF), and is under extensive investigation by fission, fusion reactors and proton accelerator facilities communities. Current work reports experimental results obtained on the beryllium sample irradiated at Fermi National Accelerator Laboratory, USA, by 120GeV protons over 7 years at about 50°C up to 0.5 dpa, and beryllium samples implanted with He ions at 50 and 200°C. The microstructure was investigated by SEM/EBSD, STEM/EDX and Atom Probe Tomography, and irradiation induced hardening was measured by nanoindentation experiments.

Microstructural investigations revealed a highly inhomogeneous distribution of impurity elements in both unirradiated and irradiated conditions. Impurities were mainly localized in precipitates, and as segregations at grain boundary and dislocation lines. Low levels of Fe, Cu, Ni, C and O were also found to be homogeneously distributed in the beryllium matrix in non-irradiated state and after proton irradiation. In the proton irradiated beryllium, up to 440 appm of Li, derived from transmutation, was homogeneously distributed in solution in matrix.

Extremely high variation of nanoindentation hardness data was observed for grains with different crystallographic orientation in non-irradiated areas of the beryllium sample. After irradiation, the average hardness was increased, while anisotropy of hardness was decreased. Significant effect of irradiation on fracture properties of beryllium was noticed. The proton irradiated sample was deformed during the post-irradiation handling. Investigation of the produced cracks indicates that proton irradiation at 0.3 dpa level changes the fracture mode from transgranular cleavage to predominantly grain-boundary cracking. In the He implanted samples, microcantilevers were fabricated by focused ion beam milling and loaded via a conventional nanoindenter. Cantilevers were pre-notched so that the fracture properties of grain boundaries and basal cleavage plane, in both as-received and irradiated states, can be compared. Fracture load of both grain boundary and cleavage cantilevers increased significantly after irradiation. Deflection to fracture was found to be lower for cantilevers pre-notched in the basal cleavage plane, but the difference between two types of cantilevers was smaller in irradiated state.

2:15 PM CM05.07.03
Tensile Deformation and Fracture Mechanism of Irradiated RAFM Steel
Hiroyasu Tanigawa1, Masami Ando1, Yutai Kato1, Naoyuki Hashimoto1 and Takuya Nagasaka1; 1National Institutes for Quantum and Radiological Science and Technology, Rokkasho, Japan; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Reduced-activation ferritic/martensitic steels (RAFMs), such as F82H (Fe-8Cr-2W-0.2V-0.04Ta), has been developed as the structural material of fusion in-vessel components which will suffer from high dose irradiation of 14 MeV fusion neutron. The most concerned issue of RAFM steel is hardening and embrittlement which appears as the loss of plasticity and ductile-brittle transition temperature (DBTT) shift by low-temperature irradiation below 350 degrees C. The mechanistic understandings of the phenomena are essential for the prediction of those irradiation induced mechanical property changes, and the impacts of microstructure feature changes have been investigated.

RAFM steels are fully tempered martensitic steels which have microstructures contain prior-austenitic grain (PAG) boundaries and MX precipitates which formed during normalization, martensite packet, block, and lath boundaries which formed during cooling, and M23C6 which formed during tempering. High-density dislocation in the matrix and fine precipitates on various boundaries gives the steel high irradiation and heat resistance. It has been reported that the major microstructural feature of RAFM steels irradiated at low temperatures is dislocation loop formation and evolution. However, this dislocation-loop evolution is not enough to explain hardening level which was observed in irradiated RAFM based on the Orowan equation. In this study, the impact of three-dimensional morphology of martensite blocks, which is the minimum microstructural unit corresponds to the mechanical property, are discussed to investigate the deformation and fracture mechanism of irradiated RAFM steels. The three-dimensional SEM and EBSP analyses on tensile deformed unirradiated F82H, micro-tensile test on a single block in FIB, and TEM microstructural analyses on irradiated F82H are conducted.
The impact of material mechanics on the tensile property, such as stress triaxiality, is discussed to interact the observed mechanical property and microstructure.

2:45 PM CM05.07.04
Micromechanical Study of Radiation and Temperature Effects on Localized Properties of SiC-SiC Fiber Composites Yevhen Zayachuk1, David E. Armstrong1, Arthur Hussey1, Christian Deck2 and Peter Hosemann3; 1University of Oxford, Oxford, United Kingdom; 2General Atomics, San Diego, California, United States; 3University of California, Berkeley, Berkeley, California, United States.

Silicon carbide ceramics is a candidate material for the use in novel accident tolerant fuel (ATF) cladding designs. It is suggested to be used in the form of SiC-fiber reinforced SiC-matrix composite, and therefore in order to reliably predict behavior of fuel cladding it is necessary to understand mechanical properties of the individual constituents of the composite – matrix, fibers and, crucially, interphases, as well as how they are modified by radiation fields and elevated temperatures that fuel cladding is exposed to during the reactor’s operation.

Micromechanical techniques are uniquely suited for determination of such localized properties, which can be rationalized by coupling the mechanical data and the microstructural information obtained by microscopy tools. In this contribution we present the results of the microcantilever fracture (at the interphases, within fibers and in the bulk matrix), fiber push-out and nanoindentation tests on SiC-SiC fiber composite. Samples were irradiated with Si and Ne ions up to 3.9 dpa at the temperatures of up to 750°C. Micromechanical tests were performed in the temperature range of up to 700°C.

Microstructure was investigated using transmission electron microscopy (TEM), with texture information obtained with transmission Kikuchi diffraction (TKD). It was found that in the matrix the preferred grain growth direction is <111>, while in the fibers no texture was observed. Both matrix and fiber feature extensive twinning.

Hardness of matrix and fibers, as measured by nanoindentation, didn’t noticeably change as a function of dose, indicating that radiation damage in bulk SiC is minor. At the same time, cantilever testing indicated that the fracture strength of the interphase noticeably increased with the increase of dose, indicating that pyrolytic carbon that forms an interlayer is strongly affected by irradiation. On the other hand, measurements at elevated temperatures showed that the properties of matrix material significantly change with temperature – hardness decreases from ~45 GPa at room temperature to ~25 GPa at 700°C, and fracture strength decreases from ~22 GPa to ~12 GPa.

TEM was used for imaging of the crack paths in the cantilevers after fracture. It was found that in the matrix fracture is transgranular, while at the interphases it is following the fiber-interlayer boundary.

Fiber push-out measurements showed that there is a significant difference in the interfacial shear strength of the interphases, depending on where within a bundle the tested fiber is – changing from ~120 MPa at the periphery of a bundle to ~70 MPa in the center.

Experimental findings are discussed with the emphasis on the synergy of micromechanical and microstructural characterization, and how these enable better understanding and prediction of the properties of SiC fiber composites in advanced fission and fusion designs.

3:00 PM BREAK

SESSION CM05.08: Electronic, Optical and Magnetic Changes Under Irradiation
Session Chairs: Pär Olsson and Brandon Sorbom
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 202

3:30 PM CM05.08.01
Electrical Characterization of He-Ion Irradiated Pd/n-SiGe Schottky Diode Mamor Mohammed; Département de Physique, University Cadi Ayyad, Faculté Polydisciplinaire Safi, Safi, Morocco.

There has been considerable interest in integrating high speed and novel devices made from Si1-xGex materials, since the alloy is compatible with the silicon based technology. Ion implantation is now a common process in the mature semiconductor industry and is widely used during several electronic devices fabrication steps. In particular, ion implantation is used to improve the fast switches and the performance of photodiodes. Moreover, it is well known that ion implantation into semiconductor materials has a profound influence on the structural and electronics properties of their surface and subsurface region. The ion implantation induces structural and electronic changes, which governs the characteristics of metal contacts formed on the semiconductor. In this presentation, we report on the electronic properties of He-ion irradiation induced defects, as determined by deep level transient spectroscopy (DLTS). In addition, we present the results obtained on temperature-dependent of the Schottky barrier height (SBHs) fabricated on He-ion irradiated n-Si0.9Ge0.1, and the impact of this irradiation on the conduction mechanism in Pd/n-Si0.9Ge0.1 Schottky barrier diodes (SBDs). The electrical properties of He-ion irradiated Pd/n-Si0.9Ge0.1 Schottky diodes were studied in a wide temperature range (100-300 K). It was found that the current flow is controlled mainly by thermionic emission. The Schottky barrier height (Φ_b) and ideality factor (n) of Pd/n-Si0.9Ge0.1 Schottky diode have been studied as a function of temperature. A decrease of Φ_b and an increase of n with decreasing temperature are observed. Additionally, linear dependence between the so-called temperature factor T_0 and temperature as well the well-known linear correlation between SBHs and ideality factors, Φ_b (n), are observed and explained in terms of inhomogeneities due to the presence of He-ion irradiation induced defects and traps with associated energy level localized in the gap.

3:45 PM CM05.08.02
Radiation Damage Effects on High-Temperature Superconductors in Fusion Conditions Brandon N. Sorbom1, Penghui Cao2, Zach Hartwig2, Stephen Jeep3, Leigh Ann Kesler3, Michael Short2, Nick Strickland2, Dennis Whyte2 and Stuart Wimbush3; 1Commonwealth Fusion Systems, Cambridge, Massachusetts, United States; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Robinson Research Institute, Lower Hutt, New Zealand.

Recent advances in high temperature superconductors (HTS) have opened up a new parameter space for the design of tokamak fusion pilot plants. While previously the maximum on-axis field in a superconducting tokamak was limited to ~6 T, HTS allows tokamaks to be designed with on-axis fields in
excess of 10 T, leading to smaller reactor designs, such as the ARC concept from MIT. For these designs, it is critical to determine the lifetime of modern HTS materials, e.g. Barium Copper Oxide (REBCO) high temperature superconductors (HTS) such as the BARAC (Barium/REBCO) accelerator magnets. This damage has historically been quantified as the number of displacements per atom (dpa). While dpa can be used as a rough predictor of radiation effects, the irradiation conditions also play a key role in microscopic damage formation and macroscopic property changes, as demonstrated by recent work. As HTS is irradiated, a variety of changes occur within the superconducting crystal lattice, and competing effects on the achievable critical current density \( J_c \) of the superconductor emerge. On one hand, \( J_c \) can be lowered by the displacement of atoms and creation of defect clusters through the suppression of the critical temperature, amorphization of the lattice, degradation of intergrain current transfer, and disordering of intrinsic pinning sites. On the other hand, \( J_c \) can be increased by point defects and defect clusters acting as artificial pinning centers. The combined effect of these mechanisms can be a net increase or decrease in \( J_c \). In order to better understand the microstructural changes that influence the macroscopic superconducting properties such as \( J_c \), HTS samples (2G REBCO from SuperPower) were irradiated with 1.2 MeV proton beam in the DANTE accelerator facility at MIT. The degradation of these samples was then characterized under a wide variety of HTS operating conditions at the Robinson Research Institute in New Zealand. In order to guide and interpret the experimental studies, a simulation workflow was developed by combining DARY (a binary collision approximation code), SRIM and MCNP (Monte Carlo codes for ions and neutrons/gammas, respectively), and LAMMPS (a molecular dynamics code). These simulations were performed to compare different ion energies and incident particle directions to determine the mechanisms behind the observed experimental results.

4:15 PM CM05.08.03 Effects of Ionizing Irradiation on Ferroelectric Thin Films Steven J. Brewer1, Samuel C. Williams2, Hanhan Zhou3, Jacob L. Jones3, Ryan Rudy4, Maunel Rivas5, Ronald G. Poluektov6, Evan Glaser7, Cory D. Cress7 and Nazann Bassi-Gharb8; 1George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 3Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; 4U.S. Army Research Laboratory, Adelphi, Maryland, United States; 5U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

In recent years, the continuous thrust toward developing microelectronic devices with greater autonomy, reduced footprint size, and large-scale interconnection has necessitated high-performance materials capable of fulfilling multiple functional roles. Ferroelectric materials, and specifically lead zirconate titanate (PZT), boast large dielectric, polarization, and electromechanical responses, making them ideal for microelectromechanical system (MEMS) sensors and actuators, energy harvesters, multilayer ceramic capacitors (MLCC), ferroelectric logic elements and relays, etc. However, many of the most compelling applications for these types of devices – space travel, satellite communications, nuclear energy, and unmanned reconnaissance – require sustained operation in extremely demanding radiation-hostile environments. Radiation, both ionizing and displacive, has been shown to substantially degrade the functional responses of ferroelectric thin films, thus rendering the development of techniques for increased radiation tolerance of these materials critically important.

In this work, a multifaceted investigation towards understanding radiation interaction with PZT thin films and strategies towards increasing radiation hardness was undertaken. Specific focus was placed on an array of critical interfaces and interactions in the ferroelectric material and device. Specifically, we address the role of the electrode material, microstructural feature (columnar vs. equiaxed grains), the effects of doping (with Mn) modifying the mobility of internal interfaces (domain walls) and point defects, and crystallization interfaces. Furthermore, a phenomenological model was developed to quantify functional behavior with total ionization dose (TID), relying on the fact that radiation induces defects and defect interactions that modify functional material response. Fitting of functional response trends as a function of TID with the phenomenological model yields two important parameters describing (i) the global susceptibility to radiation-induced induced degradation by induced defects and (ii) the rate of defect saturation in the material. Extraction and comparison of these parameters allows for quantification of defect interactions as a function of microstructural and compositional variations in ferroelectric thin films.

4:30 PM CM05.08.04 Radiation Damage in REBCO Materials for Compact Fusion Reactors Rebecca Gray and Samuel Murphy; Lancaster University, Lancaster, United Kingdom.

The advent of High Temperature Superconducting magnetic tapes has accelerated the development of compact nuclear fusion reactors. The Rare-Earth Barium Copper Oxide (REBCO) high temperature superconductors (HTS) offer high field strengths to be accessed at high temperatures (>70 K). During reactor operation high energy neutrons ejected from the plasma will damage the tapes ultimately limiting their lifetime. Experimental observation of the damage process at cryogenic temperatures is tricky without highly specialised facilities that are not currently available. Atomistic simulation of the damage cascades enables informed choices of magnetic tapes to be made. As a first step to simulating the cascades, we present a new empirical pair potential for an idealised REBCO material based on the Buckingham form fitted using thermal expansion coefficients from Density Functional Theory (DFT). Using the new potential, we determine threshold displacement energies in YBa2Cu3O7 as a function of the atom type and direction. Finally, we perform radiation damage cascades at the operational temperature and compare with similar simulations performed at the temperature where experimental data is available. A detailed comparison of the remnant defect’s population and distributions at different temperatures enable us to discuss the relevance of the available experimental data to operational conditions.

4:45 PM CM05.08.05 Charge Equilibration and Electronic Stopping for Silicon Projectiles in Silicon Cheng-Wei Lee and Andre Schleife; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Energetic-particle radiation is of technological interest for applications in nuclear energy, electronics in outer space, medicine, and fundamental research. As a result of the irradiation, damage forms and ultimately determines materials properties. Understanding the effects of highly energetic particle radiation is important, e.g. for improving radiation hardness and ion implantation to create quantum bits. While damage caused by irradiation is commonly simulated using Monte Carlo methods, including SRIM, this approach has severe limitations: The accuracy is poor for low projectile kinetic energies, for which band structure effects of the target compounds dominate. In addition, SRIM inherently assumes the target to be amorphous and overcoming this, e.g. using molecular dynamics simulations of primary knock-on atom events, requires accurate parametrizations of two-temperature models to account for the effect of electronic excitations.

This highlights that developing an understanding of the underlying interactions between charged, energetic particles and a material from first principles is highly important to predict evolution and dynamics of defects. Ehrenfest molecular dynamics and real-time time-dependent density functional theory have recently been shown to successfully describe electronic stopping during the early stages of radiation damage for light projectiles. At the same time, its capability to predict electronic stopping for heavy ions remains mostly unexamined.

Here we report our recent work on using this technique to compute electronic stopping of heavy (silicon) projectiles traversing silicon bulk crystals. We
Found a pronounced dependence of electronic stopping on the initial charge state of the projectile ion, which was not observed for light projectiles. Our analysis shows this can be explained by accounting for dynamics of charge equilibration in the target, and we explicitly study the influence of the impact parameter as well as contributions of core and valence electrons. From our simulations we demonstrate that off-channeling trajectories as well as semi-core electrons are needed for a direct comparison to experiment.

Developing a consistent framework based on first principles is an essential part of a multi-scale simulation approach that can accurately predict damage formation after particle irradiation. Incorporating electronic friction, e.g. by deriving accurate parameters from our first-principles simulations, into classical molecular dynamics leads to predictive accuracy. With the growing interest in swift-heavy ion particle radiation that creates strong electronic excitations, the capability of predicting across a large projectile kinetic energy range is crucial. Finally, the strong dependence on the initial condition observed in our simulations may suggest a way to control the magnitude of electronic stopping and, thus, damage, e.g. in nanometer-thin films by varying the initial charge state of the projectile ion.

9:00 AM CM05.09.01
Study the Effects of Localized Spot-by-Spot High Dose MeV Au and Ag into Silica John D. Demaree2 and Daryush Ilia1; 1Fayetteville State University, Fayetteville, North Carolina, United States; 2Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

In this work we have studied the change in the optical properties of Infrasil (Heraeus high-purity optical quality fused quartz silica) before and after spot-by-spot implantation of 0.785 MeV Au and 1.450 MeV Au ions using a National Electrostatics SSDH-2 tandem accelerator. The ion beams were focused to spots roughly 2mm in diameter, and after a given fluence was delivered, the substrate was moved stepwise in horizontal and vertical directions in 0.5 mm increments across an area roughly 8mm x 8mm. The fluence delivered in each overlapping spot was calculated to produce a uniform total implantation doses of Au, Ag, and (sequentially) Au + Ag ranging from 10^16/cm^2 to 10^17/cm^2. The effects of this high dose spot-by-spot method on the optical absorption were then compared with traditional raster scan implantations, in which the beam is swept over the entire area quickly, and the entire area is implanted at once. We, also, used 3D wide area microscopy and 3D laser microscopy to study the optical changes in the silica due to this spot-by-spot high dose MeV ion implantation.

The uniformly implanted area, several millimeters by several millimeters across, was studied before and after annealing, using optical absorption photo spectrometry to assess the optical change in the material and evidence of Au and Ag nanocluster formation. Rutherford Backscattering Spectrometry (RBS) was used to confirm the implantation dose and the uniformity of the implanted area. We have observed, specifically in spot-by-spot Au implanted silica, evidence of a quadrupole interaction which produces widening of the Au nanocluster absorption band beyond 530nm, and which has been seen in past studies using traditional raster scanning followed by annealing. Also, an ordered change in the index of refraction of the host by 3D microscopy correlated to the stepwise implantation in horizontal and vertical directions in 0.5 mm increments, producing 3D embedded optical structures. In this presentation we will compare the results obtained for both spot-by-spot implantation of Au and Ag into Infrasil with past raster scan implantations, and comment on the effect of this method on nanocluster formation and growth, as well as possible changes in the surface topography and 3D-well defined change in the index of refraction of this glassy material.

9:15 AM CM05.09.02
Use of Pure Iron and Fe-15Cr-16Ni Model Alloy to Study the Impact of Self-Ion Energy, Displacement Rate and Irradiation Temperature on Charged Particle Simulation of Void Swelling Aaron J. French, Frank A. Garner and Lin Shao; Nuclear Engineering, Texas A&M University, College Station, Texas, United States.

Void swelling of iron-base alloys under neutron irradiation is known to be very sensitive to a wide variety of material and environmental variables. Additional sensitivities arise using charged particle simulation. To enhance the credibility of charged particle simulation of neutron-induced swelling it is necessary to isolate and quantify those variables associated with ion simulation from those that are material-specific or involve segregation and phase stability, especially under the influence of surface effects, injected interstitials and segregation along ion-induced gradients in dpa rates that are characteristic of ion irradiation. Additionally, it is important to assess the impact of the much higher rates of atomic displacement used in ion irradiation compared to neutron irradiation.

First, we used pure annealed bcc Fe as a model system to avoid complexity associated with radiation-induced segregation and precipitation, studying only void swelling and dislocation changes. Two sets of irradiations were conducted on iron. The first set involved irradiations with Fe ion energies of 1, 2, 3.5 and 5 MeV, all at comparable dpa rate (1x10^-4 dpa/s) and attained dpa peak level of 100 dpa, in order to separate the separate but synergistic effects of surface and injected interstitial on swelling. Moving from lower to higher ion energy the surface and injected interstitial effects were therefore progressively separated. These two effects are both known to be sensitive to the dpa rate and to contribute to the temperature shift phenomenon.

In the second iron set the synergistic effects of temperature and displacement rate on swelling, expressed in the well-known “temperature shift” concept, was studied, using 5 MeV Fe ions at peak dpa rates of 3x10^-3, 1x10^-4, and 3x10^-4 dpa/s, to peak dpa values of 50, 75 and 100 dpa, and at irradiation temperatures of 375, 425, 475, and 525°C, respectively.

Finally, we repeated the temperature shift experiment on a pure annealed fcc Fe-15Cr-20Ni model alloy, but shifting the temperature range from 475 to 650°C, based on previous ion studies conducted on this alloy. The specimens used were drawn from the same batch used for dpa rate studies conducted in the FFTF fast reactor at 420°C where a transient shift was observed with changes in dpa rate. The lack of minor solutes (Si, P, C, especially) in this alloy preclude precipitation, but did result in some segregation of major elements along the ion depth profile.

The results provide significant insight on the complexities of using charged particle simulation at accelerated dpa rates to study neutron-induced void swelling, especially with respect to the temperature shift and transient shift phenomena.

9:30 AM CM05.09.03
Dynamics of Graphene Milling Under the Helium and Neon Ion Beams Alex Belianinov, Songkil Kim, Anton V. Ievlev, Ivan Vlassiouk, Matthew J. Burch, Ondrej Dyck, Xiahan Sang, Raymond R. Unocic, Sergei V. Kalinin, Stephen Jesse and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Graphene has been investigated thoroughly due to its excellent electronic, mechanical and thermal properties. This 2D material can be modified structurally, electronically and doped chemically, to utilize in the design of functional devices. Advances in ion beam-based imaging and nanofabrication techniques have offered a pathway to precisely manipulate 2D materials and offer a roadmap to create junctions, nanoribbons, and introduce dopants for new types of electronic devices. Helium ion microscope (HIM) offers “direct-write” capabilities, packaged in a machine capable of both imaging and nanofabrication with Helium and Neon gases, thus making it an excellent candidate for processing a wide range of 2D, and conventional materials.

However, despite graphene’s properties, and existing tools to take advantage of them; challenges remain in the development of workflows that can yield high-performance 2D electronic devices; where the damage at edges and the basal plane is minimized during the milling process.

In this study, we explore graphene milling by the helium and neon ion beams in order to control material’s electronic and mechanical properties. We demonstrate localized formation, growth and coalescence of nanopores, by investigating different levels of defects in graphene via Scanning Transmission Electron Microscopy. Using advanced image data analytics, we illustrate different dynamic behaviors of graphene milling depending on the material’s initial conditions. This work provides in-depth understanding of the graphene milling as it occurs, laying a foundation to develop new pathways to manufacturing 2D material based electronic devices.

Acknowledgement
This work was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy (DOE) Office of Science User Facility.

9:45 AM BREAK

SESSION CM05.10: Irradiation-Induced Ordering and Disordering
Session Chairs: Bertrand Radiguet and Michael Short
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 202

10:15 AM CM05.10.01
Influence of the Enthalpy Landscape on the Irradiation-Induced Disordering of Minerals Mathieu Bauchy1 and Anoop Krishnan; 1University of California, Los Angeles, Los Angeles, California, United States; 2Department of Civil Engineering, Indian Institute of Technology Delhi, New Delhi, India.

Under irradiation, minerals tend to experience an accumulation of structural defects—which can ultimately lead to a disordered atomic network. Despite the critical importance of understanding and predicting irradiation-induced damage, the physical origin of the initiation and saturation of defects remains poorly understood. Here, based on molecular dynamics simulations of α-quartz, we show that the topography of the enthalpy landscape governs irradiation-induced disordering. Specifically, we show that such disordering differs from that observed upon vitrification in that, prior to saturation, irradiated quartz accesses forbidden regions of the enthalpy landscape, i.e., those that are inaccessible by simply heating and cooling. Furthermore, we demonstrate that damage saturates when the system accesses a local region of the enthalpy landscape corresponding to the configuration of an allowable liquid. At this stage, a sudden decrease in the heights of the energy barriers enhances relaxation, thereby preventing any further accumulation of defects and resulting in a defect-saturated disordered state.

10:30 AM CM05.10.02
Atomic Scale Modeling of the Effect of Forced Atomic Reactions on the Thermodynamic and Kinetic Properties of Fe-Based Alloys Under Irradiation Liangzhao Huang1, Luca Messina2, Thomas Schuler1 and Maylise Nastar1; 1DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, GIF-sur-Yvette, France; 2Nuclear Engineering, KTH Royal Institute of Technology, Stockholm, Sweden.

Irradiation drives materials far from equilibrium. Under sustained atomic reactions such as ballistic mixing forcing exchanges between neighboring atoms, standard thermodynamic and kinetic methods do not apply because of the loss of the microscopic detailed balance. However, the resolution of the microscopic Master Equation describing the transitions between different on-lattice configurations allows us to compute the dynamic chemical short range order (SRO) under stationary conditions. The latter depends on the atomic jump frequencies and is compared to the results of atomic kinetic Monte Carlo simulation. From the dynamic SRO computed by this theoretical approach, we define effective atomic jump frequencies, compute point defect flux coupling, and predict the solute redistribution. We analyze the effect of temperature and irradiation conditions (including ballistic mixing and recombination) on the thermodynamic and kinetic properties of a few iron-based binary alloys.

10:45 AM CM05.10.03
Irradiation-Accelerated Phase Transformations for Low-Temperature Phase Diagram Development Julie D. Tucker, Fei Teng, Li-Jen Yu, Emmanuel Marquis1, Jia-Hong Ke2 and David Srorouster1; 1Oregon State University, Corvallis, Oregon, United States; 2University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 3Brookhaven National Laboratory, Upton, New York, United States.

Low-temperature phase data is essential for long-term applications at intermediate temperatures such as energy production. Experimental data below 500°C is limited due to the long times needed for most phases to develop. First principles techniques are supporting the need for low temperature phase data but still require validation by experiments. Irradiation generates extra point defect, enhancing kinetics at lower temperatures and can be a tool for accelerating phase transformations. In this study, we use ion beam irradiation to enhance the formation of an ordered Ni1Cr phase in the Ni-Cr-Fe system. Commercial alloys, such as alloys 625 and 690, are susceptible to mechanical property changes with thermal aging due to this ordered phase. Model and commercial alloys have been isothermally aged up to 10,000 hours and characterized via nanoindentation, atom probe tomography, synchrotron X-ray diffraction and transmission electron microscopy. Additionally, these alloys have been irradiated to 1.5 or 6 dpa to quantify the role of irradiation in accelerating the ordering kinetics. Preliminary results indicate change in stoichiometry do not change the ordering rate only the amount of ordered phase formed. Also, proton irradiation tends to accelerate the ordering process while Ni^+ ion irradiation do not lead to ordering at the dose rates explored.
Theoretical Prediction of Void Superlattice Formation under Irradiation

Yongfei Zhang, Yipeng Gao and Jian Gan; Idaho National Laboratory, Idaho Falls, Idaho, United States.

Void and gas bubble superlattices have been widely observed in various types of materials under irradiation, with the formation mechanisms still open for debate. Here, rate theory based theoretical analysis coupling thermodynamics and kinetics show that the superlattice forms by superposition of vacancy concentration waves that develop upon the instability of a uniform field. The symmetry of superlattice is governed by anisotropic interstitial diffusion, and the superlattice parameter depends on the irradiation condition including temperature and dose rate. Dependent on the nature of anisotropic interstitial diffusion, various types of void superlattices are theoretically predicted including planar ordering, simple cubic, face-centered-cubic and body-centered-cubic. The theoretic predictions on both the superlattice symmetry and parameters are demonstrated by atomic kinetic Monte Carlo simulations and are consistent with previous experimental observations. The developed theory can be used to guide experimental design for tailored microstructure using irradiation. It may also have general applications in cases involving spontaneous phase transition and anisotropic diffusion reaction.

1:30 PM ~CM05.10.05

Atomic Scale Quantification of Intergranular Segregation in Ferritic Thermally Aged or Irradiated Alloys and Steels

Bertrand Radiguet1, Philippe Pareige1, Allaia Akhatova1, Leifeng Zhang1, Patrick Todeschini2 and Frederic Christien2; 1Université de Rouen Normandie, Groupe de Physique des Matériaux, Saint Etienne du Rouvray, France; 2EMSE, Saint Etienne, France.

Phosphorous intergranular segregation can lower the cohesion between grains, resulting in steel embrittlement. Low alloyed bainitic steels used to build nuclear reactor pressure vessel (RPV) generally contain a small amount of phosphorus (in the range of 100 ppm). Continuous exposure to a low neutron dose rate irradiation at intermediate temperature (~300°C) results in radiation embrittlement of RPV steel. Since intergranular segregation of phosphorous can contribute to this embrittlement it is important to understand the effects of ageing conditions (temperature, irradiation dose), material composition and the grain boundary (GB) nature on the intensity of phosphorous intergranular segregation. Regarding to literature sources, it was revealed that the intergranular segregation values may strongly vary among different GBs. However, there is a lack of systematic studies in this field.

In order to get an accurate and representative description of the effect of GB nature different techniques are combined in this work. Atom Probe Tomography (APT) technique is utilized as the main tool and it is compared to Auger Spectroscopy for validation. GB geometry is determined from Transmission Kikuchi Diffraction (TKD) map. Firstly, this approach is validated on a Fe-0.034at%P-0.01at%C model alloy. It is shown that radiation-induced segregation caused by phosphorous interstitial complex is the dominant mechanism in under irradiation at 450°C with 10 MeV Fe5+ ions at a dose rate of 3 10^-5 dpa/s. Also a higher phosphorous segregation at curved GBs in comparison with the straight one was found. This work has also shown that GBs with high Miller index planes has significantly higher phosphorous segregation than low index GB planes.

In a second step the approach is applied to a real RPV steel thermally aged or ion irradiated. APT analyses revealed that there was a considerable element segregation (C, P, Mn, Mo, Cr, Si, Ni, …) for all boundary types. By taking into consideration all segregated chemical species, both interstitial and substitutional segregations were discussed with regard to GB types. Besides, the element segregation at carbide/matrix interfaces was also quantified. Comparison between as received and aged materials will be given.
Plastic deformation of metals and alloys containing light impurity atoms (for example, nitrogen or carbon) is often accompanied by jerky flow in mechanical tests at elevated temperatures (up to 400°C), with numerous load drops (serrations) appearing on the load–elongation curve. This phenomenon, known as the Portevin-le-Châtelier effect, is due to Dynamic Strain Aging (DSA) occurring in the material because of the interaction of solute atoms with mobile dislocations, temporarily arrested at obstacles. DSA in many cases leads to the reduced ductility and toughness, decreased ability to cold roll, etc. Irradiation leads to the appearance of radiation defects and their interactions with impurity atoms, reducing the concentration of these atoms in solid solution. These interactions significantly decrease the DSA process. It was shown [1] that with increasing irradiation dose of mild steel, the critical temperature for the onset of DSA serrations increased and the temperature range of “blue brittle” behavior narrowed. More precise understanding of the nature and magnitude of radiation defect interactions with the dislocations responsible for DSA can therefore help to mitigate its effects. 

The present work is devoted to investigations of the effect of irradiation with neutrons and alpha particles on the mechanical properties and stored energy characteristics of Arno-iron. Tensile samples were irradiated with neutrons (maximum fluence 6×10¹⁸ n/cm², E>2.35 MeV, T<50°C) in the experimental WWR-K reactor core (6 MW water-pool nuclear research reactor) and alpha particles with an energy of 50 MeV in an isochronous cyclotron U-150 to a helium concentration of 10²⁵ at. % at ≈100°C. Uniaxial tensile tests were carried out in the temperature range of 20-300°C with two nominal strain rates, \( \dot{\varepsilon} = 8.33\times10^{-4} \text{s}^{-1} \) and \( \dot{\varepsilon} = 1.67\times10^{-5} \text{s}^{-1} \). For each test temperature, the value of the critical strain energy density \( (W_c) \) was determined. In some cases, images of the surfaces were taken during tensile tests to study the features of deformation localization using digital image correlation approach. As a result of the experiments, mechanical and energy characteristics were obtained, and DSA parameters were determined as a function of irradiation. It was determined that irradiating Arno-iron with neutrons and alpha particles suppressed DSA, decreased the amplitude of serrations, and increased the activation energy of the DSA process and the critical strain when serration occur on the curves. Decreasing DSA intensity led to increase in the plasticity and We of the material. Optical metallography and electron microscopy were used to study the evolution of radiation and deformation defects. The obtained experimental data can be used in the development of theoretical models of deformation aging, as well as the finding the ways and methods to reduce the negative effects of irradiation on structural materials.


2:15 PM CM05.01.03 Accelerated Materials Testing in Low Earth Orbit Kevin Heath and Lindsay Farrell: Alpha Space Test and Research Alliance, LLC, Houston, Texas, United States.

Alpha Space (AS) provides a turn key service that allows for testing of materials in an extreme environment, space. The AS Test Platform, the Materials International Space Station Experiment Flight Facility (MISSE), provides an environment that cannot be easily duplicated on the earth. The MISSE provides testing of materials in a vacuum, while simultaneously exposing the material to a radiation environment, UV-A through UV-C light, atomic Oxygen, and temperature cycling. The MISSE-FF allows for oxidation testing of a material utilizing atomic Oxygen, which is highly reactive with all materials. Ultra-violet light degradation testing on the MISSE-FF of polymer materials or coatings is provided at an accelerated rate, because the MISSE-FF exposes the materials to UV light at Air Mass Zero. The full extent of UV-A through UV-C is applied to the sample to determine degradation, which cannot be attained in the atmosphere because air absorbs 95% of the UV-B and almost 100% of UV-C wavelengths. The MISSE-FF provides radiation testing across the full spectrum of the naturally occurring radiation spectrum, Gamma Rays through proton/neutron emissions, to determine degradation of materials. The MISSE-FF provides the ability to limit the amount of molecular contamination that can occur with the samples being tested, providing a true test of the material. Thermal Cycling provided by the MISSE-FF occurs sixteen times a day, providing an accelerated test of the interface between the coatings and the substrate they are applied upon. The thermal cycling of samples on the MISSE-FF occurs between -60 Deg. C and 120 Deg. C per cycle, controllable using various different mounting structures to keep within the sample temperature parameters. Testing with the Alpha Space MISSE-FF provides the test environment described above simultaneously, mimicking the actual effects on materials by providing a real world environment that cannot be obtained in a cost effective manner in an earth bound laboratory. The MISSE-FF flight environment tests the cross-coupling effects on materials of the various input parameters from radiation, oxidation, UV, and temperature cycling. Testing of materials on the MISSE-FF is a continuous opportunity, with sample installation and removal on a six month to twelve month cycle. This continuous testing allows for Alpha Space to provide visual degradation data via high resolution pictures during the extended test period on orbit, and sample return for final comparisons between the virgin sample witness plates and the post test samples. Alpha Space will also provide guidance to determine the best way to isolate the various effects of the environment on samples by isolating the input variables.

2:30 PM BREAK

SESSIOCM05.12: Microstructural Stability Under Ionizing Irradiation
Session Chairs: Kazuto Arakawa and Camille Flament
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 202

3:30 PM CM05.12.01 Enhanced Twin Stability Against Irradiation in Nanotwinned Solid Solution Alloys Jin Li1, Dongyue Xie2, Sichuang Xue1, Cuncai Fan1, Youxing Chen1, Haiyan Wang1, Jian Wang1 and Xinghang Zhang1, 1Purdue University, West Lafayette, Indiana, United States; 2University of Minnesota, Minneapolis, Minnesota, United States; 3University of Nebraska-Lincoln, Lincoln, Nebraska, United States.

Face-centered cubic (FCC) metals are in general vulnerable to high-energy ion irradiation. Twin boundaries have been shown to improve the irradiation tolerance of FCC metals. However, nanotwins in monolithic metals are unstable during irradiation. In this study, we show that Fe solute can drastically improve irradiation stability of twin boundaries in Ag. By adding merely 1 at.% of Fe solute atoms into Ag matrix, ultra-high-density twins with an average twin thickness of ~3 nm form in Ag. In situ Kr ion irradiation studies show that defect size and density in Ag:Fe have been significantly reduced comparing with monolithic coarse-grained Ag and nanotwinned Ag. Furthermore, these extremely fine twins survived heavy ion irradiations. Density function theory calculations suggest that Fe solutes stabilize nanotwins by pinning twin boundaries. The mechanisms of enhanced radiation tolerance enabled by solute-twin boundary networks are discussed.

3:45 PM *CM05.12.02 Microstructural Evolution of Fe – 10 wt.% Cr Alloy Irradiated by Fe Ions with Carbon Implantation Camille Flament; DEN-Service de recherches
Because of their high resistance to swelling and low ductile-brittle transition temperature, high chromium ferritic-martensitic (F-M) steels are promising candidates for structural materials of Gen. IV fast neutron reactors and for fusion. The presence of carbon in F-M steels can lead to the precipitation of carbides which may have significant impact on their mechanical properties. Submitted to high neutron flux, the study of their stability under irradiation is a crucial point for reactors lifetime. In order to better understand the mechanisms induced or enhanced by irradiation at fine scale, Fe-Cr model alloys representative of F-M steels have been widely studied. It is well-known that alloys with more than 10 wt.% of Cr are interesting for their resistance to corrosion but display brittleness at temperature below 500°C and after irradiation due to the precipitation of α’ phase [1-3] Nevertheless very few studies deal with the characterization of Fe-Cr-C model alloys and the evolution of carbides under irradiation. This study proposes to characterize high purity Fe – 10 wt.% Cr alloy irradiated at high flux up to a damage of 110 dpa (SRIM2008 calculations (K.-P.)) with Fe ions at 300°C with C implantation, a way to simulate the enrichment in C observed in steels after years of irradiation in reactor. Observations by TEM after irradiation emphasize the coexistence of a\textsubscript{100}<100> and 1/2a\textsubscript{0}<111> dislocation loops homogeneously distributed in the matrix as well as carbides in high density. The mean size of carbides is about 20 nm and they are homogeneously located in intragranular position in the irradiated zone. Observations in HR-TEM show two different morphologies and crystallographic structures: spherical carbides are compatible with M23C6 with a face-centered cubic structure whereas ellipsoidal carbides display an orthorhombic structure close to the one of M6C. APT analyses confirm the enrichment in C to about 0.5 wt.% and show segregation of Cr and C in the habit plane of dislocation loops. No α’ precipitation is observed certainly due to the high density of sinks and C atoms implanted. This irradiated microstructure is compared to an un-irradiated Fe – 10Cr – 0.076C (wt.%) kept at room temperature for ten years. In that case, coarse intergranular carbides (> 200 nm) and finer intragranular carbides (< 150 nm) are observed. Selected area electron diffraction in TEM on several carbides show a face-centered cubic structure with a lattice parameter compatible with M\textsubscript{23}C\textsubscript{6}. Even though the C amount is different between both alloys, it is interesting to note that irradiation with C implantation creates a lot of small clusters of defects which enable a finer and denser microstructure of precipitates in Fe-Cr alloys compared to annealing in Fe-Cr-C alloys. It may impact the mechanical properties of alloys.


4:15 PM CM05.12.03
Stability of Carbides in Fe-Cr-C Systems Under Irradiation—An Ab Initio Based Study
Chu Chun Fu1, Maylise Nastar1, Elric Barbe1-2 and Thomas Schuler1;1 DEN-Service de Recherches de Métallurgie Physique, CEA, Université Paris-Saclay, Gif Sur Yvette, France; 2DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, Gif-sur-Yvette, France.

Fe-Cr steels are promising candidates for structural materials in advanced fission and future reactor reactors. Possible presence of carbides in these systems is well known to have significant impact on their mechanical properties. Further, the stability of the carbides can be modified due to irradiation, as shown experimentally. We address in this study mechanical, thermodynamic and kinetic properties of M\textsubscript{6}C and M\textsubscript{23}C\textsubscript{6}, being respectively the most relevant carbide in Fe-Cr-C alloys. It is known experimentally that distinct fracture mode occurs on these carbides, intra-precipitate for the former and interfacial for the latter. Under irradiation, partial amorphization and dissolution of M\textsubscript{23}C\textsubscript{6} have been observed experimentally, together with the emergence of new carbide phases, changing mechanical properties of the materials. To understand these features, density functional theory (DFT) calculations are applied to investigate the energetics, elastic moduli, and fracture properties of these carbides, as functions of the chemical composition (Fe versus Cr and the carbon concentration) in the carbides. Then, in order to evaluate the impact of irradiation, the stability of the carbides due to point-defect production and diffusion and the ballistic mixing are determined.

4:30 PM CM05.12.04
Additively Manufactured 316L Stainless Steel Behaviour Under Ion Irradiation
Anne-Hélène Puichaud1, Camille Flament1, Fernando Lomello2, Aziz Chniouë3, Marie Loyer-Pros1, Hicham Maskrot1, Frédéric Schuster1 and Jean-Luc Béchade2;1 DEN-Service de Recherches de Métallurgie Physique, CEA, Gif-sur-Yvette, France; 2DEN-Service d'Etudes Analytiques et de Réactivité des Surfaces, CEA, Gif-sur-Yvette, France; 3CEA, Université Paris-Saclay, Gif-sur-Yvette, France.

Additive manufacturing (AM) is being extensively developed as a promising technology, and already exploited in various industries in particular in biomedical and aerospace applications ([1], [2]). However, the use of AM materials in nuclear applications still requires an in depth understanding of the materials response to irradiation, and little work has been done to date [3]. The long term objective of this work is to investigate potential applications of additively manufactured materials, here 316L type stainless steel, suitable for nuclear applications. Stainless steel cubes were fabricated by selective laser melting (SLM) using commercial 316L powder, with AM fabricated materials studied as built, after a heat treatment (HT) and after a hot isostatic pressing (HIP). We performed an in depth microstructural characterisation of the as built, heat treated and HIP materials before irradiation using SEM, EBSD, TEM and nanoindentation. Fe²⁺ ion irradiations of the samples were then performed at the Joint Accelerators for Nano science and Nuclear Simulation (JANNuS, Paris Saclay, France) up to 3 dpa at 550 °C. Finally, microstructures and irradiation behaviours of the AM materials were compared to cold work 316L austenitic stainless steel. The first results of the unirradiated materials show a high microstructural anisotropy for the AM as built and HT materials with elongated grain in the direction of fabrication and a close to α fibre texture. The HIP samples however present more equiaxial grains and a loss of the α fibre texture, closer to conventional 316L. Nanoporosity and segregation of elements (Mo, Si and Mn) were observed in the as-built and HT materials while the HIP samples did not show porosity but presented a high density of precipitates. The microstructure and microchemistry of the irradiated materials were examined using a combination of TEM techniques to establish in particular the void swelling and precipitation behaviour under ion irradiation. The first microstructural characterisations at low dose show apparition of nanocavities, precipitates and a high density of dislocations.

CM05.13.01
Enhancement of Photoluminescent Properties in PBAT/MEH-PPV Blends Provoked by Gamma Radiation for Application in 3D Dosimetry João L. Souza1, Thiago Schimitberger1 and L.O. Faria2; 1Nuclear Engineering, UFMG, Belo Horizonte, Brazil; 2Materials, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte, Brazil.

When using high energy clinical beams for diseases treatments, the determination of the dose distribution versus tissue depth curves, before the patient irradiation, is significant for radiotherapy planning. The procedure allows medical physicists to accurately predict the dose that will only be enough to eliminate a tumor, without affecting the tissues near the region of treatment. In this context, the developing of 3D dosimetric systems capable to previously determine the dose distribution along the tissues affected by the radiation beam is a worldwide field of investigation. Nowadays, the best dosimetric systems commercially available for the gel-based dosimeters such as PGD (Polymer Gel Dosimeter) and FGD (Fricke Gel Dosimeter). These gel dosimeters are tissue equivalent, with no angular dependence and with millimetric spatial resolution. Most 3D dosimeters are made of a continuous uniform medium which polymerizes upon irradiation. However, the small dose working range of these dosimeters (1-50 kGy) is a problem to be solved. In this work we investigate a new polymeric blend that, by means of radiation damage, can be proposed as a 3D photoluminescent radiation detector, which could operate in a much larger absorbed dose range (1 to 500 kGy). In this context, we have developed a polymeric blend made of poly(butylene adipate-co-terephthalate) copolymers (PBAT) and poly[(2-methoxy-5(2'-ethylhexyloxy)-p-phenylenevinylene) copolymer MEH-PPV. Films of PBAT are non-photoluminescent polymers. However, after exposure to high doses of gamma radiation it shows high photoluminescence (PL) output, proportional to the exposed radiation dose. When excited with blue LED, its PL intensity at 490 nm (green) can be used for high gamma dose dosimetry [1]. MEH-PPV is a naturally photoluminescent polymer that, when in solution, undergoes a gradual color change, from red to colorless, when exposed to high gamma doses ranging from 0.5 to 500 kGy. Films of PBAT/MEH-PPV have been recently proposed for 2D high dose dosimetry [2]. In this paper we have produced blends of PBAT/MEH-PPV mixed with a plasticizer in order to produce 3D dosimeters, by using DINCH - 1,2-Cyclohexane dicarboxylic acid disononyl ester plasticizer. After gamma irradiation, the 3D samples in a cylinder form, changes its color from orange (lower doses) to light green (higher doses), for doses ranging from 1 kGy to 500 kGy, respectively. FTIR data revealed that the radio-induced aromatic amines in the binary system are responsible for the observed PL at 500 nm. The PL emission spectra demonstrate that the color change in the 3D polymeric cylinders is a combination of the variation in the green color intensity of PBAT with the decreased red color intensity of MEH-PPV. UV-Vis spectrometry, DSC and DRX analysis are used to complement the discussion about the radio-induced photoluminescent properties. PBAT/MEH-PPV blends are good candidates for 3D dosimetry and bio-imaging devices.

CM05.13.02
Ionising Radiation Effects in UK Nuclear Waste Glasses—An Assessment of Key Processes Aaron R. Daubney1, 2; 1Dalton Nuclear Institute, Whitehaven, United Kingdom; 2Chemistry, University of Manchester, Manchester, United Kingdom.

The current understanding of glass behavior after exposure to a multitude of ionizing radiation fields (including alpha, beta and gamma) is under development by a growing international research effort. Understanding the physical mechanisms which cause deleterious (and sometimes even preferential) changes to a glass microstructure will underpin future policy for the disposal of high-activity nuclear wastes. By using ion beam and gamma irradiation facilities, an assessment of microstructural changes and their relation to glass mechanical and thermodynamic properties will be made.

Through coordinated research efforts, a picture of long-term glass behavior (over hundreds to thousands of years) is generated and so an understanding of key mechanisms and their application to amorphous, metastable materials such as glass are crucial. This agreement of physical mechanisms involved during multi-particle radiation fields and their relative impact to glass structure will also underpin atomistic simulations of glass corrosion processes.

CM05.13.03
Impact of Stored Mechanical Energy in Carbon Onion Resilience Under Space Radiation Gaurab Panda1, Virginia M. Ayres1, Harry Shaw2, Kan Xie1 and SK Bay3; 1Michigan State University, East Lansing, Michigan, United States; 2NASA Goddard Space Flight Center, Greenbelt, Michigan, United States; 3Bahcesehir University, Istanbul, Turkey.

Nano-carbons are a promising new approach to resolve lubrication challenges in space including vacuum, radiation and non-terrestrial temperature regimes. Planar graphite, while an excellent lubricant on earth, undergoes structural collapse in vacuum and knock-on collision generated amorphitization in response to heavy ions, a key component of the solar wind. Space lubrication candidates: carbon onions and multi-walled carbon nanotubes have shown robust performance in vacuum environments and are under investigation by our group and others for radiation and temperature resilience [1, 2, 3].

The responses of carbon onions with increasing polygonal character due to increasing temperature growth conditions were investigated under heavy ion irradiation at the Facility for Rare Isotope Beams (FRIB) at Michigan State University. The heavy ions used in these experiments were primary beams of fully stripped Calcium-48, and Argon-40 with 140 or 70 MeV per nucleon kinetic energies. Stored elastic energy, and layer number were investigated using analysis of pre- and post- irradiation high-resolution transmission electron microscope (HRTEM) images. The study indicated that as the radiation dose increased, the carbon onions tended to store more mechanical energy, which reproduces a mechanical property of growth at a higher temperature. A key consequence was that rearrangements were enabled that included conversion of radial onions to planar graphite when the starting point material had sufficiently high stored mechanical energy. Increase in number of layers was not consistent and average numbers did not show much change. However, individual specimens and standard error of the mean values could support the interpretation of an increase.

Layer rearrangement could have both positive and negative implications for the tribological performance of carbon onions in a heavy ion space environment. Ongoing rearrangements into structures that retained the excellent tribological features of the originals would be a self-healing way of dealing with radiation-induced defects. However, rearrangements that resulted in the formation of planar graphite could have negative consequences for tribological performance. This suggests that for space lubrication applications, lower temperature synthesis carbon onions, while less polygonal and more defective, are more resilient to heavy ion radiation.

Computational Design of Radiation Damage Tolerant Single-Phase Alloys Penghui Cao, Miaomiao Jin and Michael Short; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Understanding and predicting radiation damage are of central importance to develop radiation-tolerant structural materials for current and advanced nuclear systems. Single-phase solid solution alloys constitute attractive choices due to their promising mechanical properties and radiation tolerance. Here, by examining radiation-induced defect production and evolution in single-phase Ni-Fe alloys, we show that radiation damage resistance directly correlates with thermodynamic mixing energy. Defect numbers and sizes appear to first decrease with increasing Fe concentration, but then start to increase at the vicinity of equiatomic concentrations. The observation in damage reduction is further ascribed to the increasing heterogeneity of point defect migration across a complex potential energy landscape that results in enhancement of defect recombination. This new insight into the dynamical evolution of radiation defects implies a thermodynamic criterion for designing radiation-tolerant materials.

Photoirradiation-Induced Reversible Lattice Expansion in W-Doped TiO2 Through the Change of Its Electronic Structure Fan Feng1, Weiyi Yang1, Shuang Gao2, Linggang Zhu2 and Qi Li2; 1Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; 2Graduate School at Shenzhen, Tsinghua University, Shenzhen, China; 2Beihang University, Beijing, China.

The capability of reversible crystal lattice dimension changes on the order of 0.1% or above by external stimulations of applied force or voltage to impose external mechanical or electric forces on atoms forming the lattice had been observed in a lot of types of materials, including oxides, metals, polymers, and carbon nanостructures, which could be utilized as actuators or sensors for various technical applications. As an external stimulation, photoirradiation had been found to be effective to lead to reversible changes in materials, such as photocatalysis, photochromism, photoisomerization, and surface morphology change. In these processes, photoirradiation interacts with materials and electrons are excited internally to induce subsequent changes. If these photogenerated electrons could be designed to cause the material’s internal electronic structure to change reversibly, it should also result in a reversible crystal lattice dimension change by light irradiation.

Recently, photostriiction had been reported in several perovskite oxides due to the combination of the photovoltaic effect and the converse piezoelectric effect or the nonequilibrium of phonons. Here, we report that reversible lattice expansion comparable to those by applied force or voltage (on the order of 0.1% or above) can be induced by the on and off of UV-irradiation in an oxide of W-doped TiO2 nanotube array through the reversible changes of its electronic structure change. This photoirradiation-induced reversible lattice expansion may also be present on other material systems by proper material design if they possess one component able to produce electrons upon photoirradiation and the other component able to accumulate photogenerated electrons to induce lattice changes and release them after the photoirradiation is off. Reversible optical, electric, and magnetic property changes could also be expected due to their reversible internal electronic structure changes. Various potential applications may be found for this kind of materials, including nanoscale, photo-driving actuators or detectors.

Ionization Induced Carbon Phase Changes in Graphite Lenore S. Miller1, John D. Demaree2, Kristophor D. Behlen2, Zhang Tong1 and Daryush Ila1; 1Fayetteville State University, Fayetteville, North Carolina, United States; 2Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States; 3SURVICE Engineering Company, Belcamp, Maryland, United States.

We have studied changes in the surface of graphite before and after MeV ion bombardment, to assess the effect of ionization on the carbon phase and atomic bonding of carbon in HOPG, using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and 3D laser microscopy. We observed the hexagonal carbon ring structure of graphene sheets in graphite using AFM, to assess any changes in carbon bond length or distortion of the hexagonal lattice due to the passage of the heavily ionizing particles. Rutherford Backscattering Spectrometry (RBS) in conjunction with XPS were used to identify impurities in the material and at the surface, and their potential impact on graphite surface properties. RBS was used because most impurities are significantly heavier than carbon, and therefore they can be easily detected and quantified without any need for substrate background subtraction. XPS was used to confirm the RBS findings, identify any differences in the distribution of impurities in the bulk and at the surface of the material before and after MeV implantation. Ion induced changes in carbon bonding, including the transformation of graphitic sp2 bonding to amorphous or diamond-like sp3 bonds were measured using Raman spectroscopy, as well as using X-rays excited C KLL to characterize the carbon phase in various high purity HPOG bombarded transformation which may be explained by rapid thermal quenching following ion-induced excitation.

Accelerated Testing of Carbon Fiber-Reinforced Shape Memory/Epoxy Polymer Composites in Low Earth Orbit Space Joon Hyoek Jang1, Seok Bin Hong1, Jungyu Kim2; Nam Seo Goo3 and Woong-Ryeol Yu1; 1Seoul National University, Seoul, Korea (the Republic of); 2Kyung Hee University, Yongin, Korea (the Republic of); 3Konkuk University, Seoul, Korea (the Republic of).

Carbon fiber reinforced shape memory polymer composites (CF-SMPCs) have been researched for space structural materials due to their high mechanical properties, lightweight, excellent shape deformability, and self-deployment properties. Long term durability of CF-SMPCs in the space environment should be guaranteed for their successful applications to aerospace engineering. In low earth orbit (LEO) space region, there are many factors, such as high vacuum, ultraviolet radiation (UV) and atomic oxygen(AO), that affect polymer matrix composites. Therefore, a predictive method is required to predict long-term properties of CF-SMPC considering these harsh environments and thus to design proper CF-SMPCs for aerospace engineering. In this study, CF-SMPCs made of CF and epoxy shape memory polymers were studied, focusing on their life prediction. First, acceleration tests were developed by exposing CF-SMPCs to LEO space environments (i.e., high vacuum, UV and AO) at elevated temperature in space environment chamber. Then, their storage moduli were measured using dynamic mechanical thermal analysis. Using time-temperature superposition principle (TTSP), a master curve was constructed to predict the long-term behavior of CF-SMPCs in LEO space. The long-term storage modulus was predicted by the linear product of the shift factors for time – three LEO environments and time - temperature superposition. Finally, a predictive model was developed to evaluate the durability of CF-SMPCs in aerospace.
In this talk, the experimental results (APT, STEM, XRD) obtained on multilayers of different wavelengths before and after thermal ageing at different interdiffusion in a bulk material. Diffusion kinetics are wavelength-dependent at this scale, different wavelengths have to be experimentally tested in order to extrapolate results for operating temperatures in the range of 400-550°C lead to long term ageing (thermal or irradiation ageing). This process is governed by thermodynamics and diffusion. Thus, to predict microstructural evolutions, an important step is to gain a better understanding of the diffusion kinetics properties in FeCrNi Austenitic stainless steels are candidates for both structures (316 L(N) steels) and cladding (AIM1-type steels). The 60-year life demonstration design and the decay of satellite peaks intensity thanks to XRD.

Analytical techniques for thin films
Synthetic modulated structures

Corrosion Protection Coatings for Depleted Uranium Volodymyr Lobuz, Martin Hruby, Peter Cernoch, Jiri Paneck, Tomas Chmela and Pavel Krupicka, Institute of Macromolecular Chemistry AS CR, Prague, Czechia; UIP PRAHA a.s., Prague, Czechia.

The depleted uranium is still an indispensable material in numerous areas, from healthcare to arms industry; however its range of applications is limited by high reactivity and susceptibility to corrosion. The current state of art for the storage of depleted uranium stands on expensive and sophisticated procedures, as alloying with up to 20% of molybdenum or encapsulation in aluminum or steel containers. This project aims the reduction of the production costs and simplification of the technology for production and processing of depleted uranium based materials. Within current study we develop the coatings on depleted uranium stored for further reprocessing or already used in various radiation shielding applications. For lower radiation doses, up to 100 kGy, the coatings are based on polymer materials, either in form of polymeric paints from poly(2-butyl-2-oxazoline), poly(2-phenyl-2-oxazoline), series of polyesters, or as two-component curable systems: polyurethanes based on isophorone diisocyanate (ID) with Kralos (K) or Polycarbonate (PC). The coatings were reinforced with inorganic fillers (e.g. modified graphene) to prevent the diffusion of water vapor and oxygen and stabilized with hindered amines BHT or Timuvin 123 for radical scavenging.

The polyurethane layers were exposed to radiation from depleted uranium, and various doses of gamma or β radiation, and their chemical composition, thermal stability and mechanical properties were investigated by FTIR, EPR, TGA/DSC, and micro-hardness indentation. The gamma irradiation improved the thermal stability of polyurethane ID-K, but reduced for ID-PC; the glassing temperature is decreased for all polyurethane samples after every irradiation cycle. The hard polyurethane sample ID-K after irradiation become even harder and stiffer and demonstrated increased intensity of the hydroxyl (3600 cm⁻¹), carboxyl (1740 cm⁻¹) ether and ester (1500-1600 cm⁻¹) bands of FTIR spectra, usually assigned to oxidation products. It was assumed, that ID-K sample undergoes oxidation and additional cross-linking. The softer ID-PC polyurethane remained unchanged. For higher radiation doses (in range of hundreds of MGy or higher) the entirely inorganic coating, based on low melting SnF₂-SnO-P₂O₅ glass is developed. The glass powder is sprayed on the metal surface, melted at 450°C to form the uniform layer, aged at 150°C for relaxation of strains and cooled to ambient temperature. The material contains 40 wt. % of tin, used for radiation shielding together with lead and copper.

Acknowledgements:
Financial support was provided by the Ministry of Industry and Trade of the Czech Republic (grant # FV10164).

CM05.13.09 Effects of X-Ray Irradiation on Amorphous Oxide Semiconductor Thin-Film Transistors Solah Park and Jang-Yeon Kwon; Yonsei University, Incheon, Korea (the Republic of).

In recent years, digital x-ray detectors have been used in the medical device market for miniaturization, portability and rapid information transmission. When driving indirectly, electric signal is amplified by using hydrogenated amorphous silicon Thin Film Transistors (a-Si:H TFT) on the detector panel. At this time, the detector panel is continuously exposed to the x-ray, and the elements therein are also affected by the x-ray. The trend of x-ray detector market requires a high mobility device because it requires effective detection with low x-ray dose. TFT technology using oxide semiconductors (mobility of 10 cm²/Vs) has already been applied to AMOLED in the field of display. It is a suitable alternative to solve problems such as low mobility and device reliability of existing a-Si:H TFT (mobility of 0.5 cm²/Vs). The application of oxide TFT technology in medical devices can give many advantages in the construction of digital X-ray radiography system structure that can realize high resolution and high aperture ratio based on high mobility. Therefore, it will make a great contribution to the development of smart medical device system. For this, the ionizing radiation effect studies are needed to utilize oxide semiconductor TFTs in medical devices. There is a lack of research on how each semiconductor device is affected by x-ray and how long it will last. Therefore, it is necessary to investigate the change of device characteristics after x-ray irradiation, and to study the lifetime and recovery of devices.

In this presentation, we investigated the effects of typical silicon and oxide TFTs used in displays on x-ray irradiation. In particular, we have investigated the effects of different crystalline states (amorphous or crystalline) on silicon and oxide, respectively. We investigated the effect and mechanism of each device according to x-ray dosage. This result is expected to contribute to the study of x-ray radiation damage due to the difference in crystal structure between silicon and oxide TFT and to develop medical industry (Radiography, Fluoroscopy, Dental etc.) and electronic device with tolerant in x-ray environment. Furthermore, it is expected to contribute greatly to research on x-ray industry technology for non-destructive testing (NDT) of facilities and buildings.

CM05.13.10 Experimental Determination of Diffusion Kinetics After Thermal Aging of FeCrNi Nanolayers Solène Rouland, Bertrand Radiigue, Alain Billiard and Philippe Pareige; 1Normandie Univ, UNIROUEN, INSA Rouen, CNRS, GPM, Rouen; France; 2Institut FEMTO-ST, UMR 6174 CNRS, Univ. Bourgogne Franche-Comté, UTBM, Montbéliard, France.

GEMMA (GEneration IV Materials Maturity) European project aspires to validate structural materials and welded joints selected for GenIV demonstrators (e.g. ASTRID) under operating conditions by reliable conditions and simulations.

Austenitic stainless steels are candidates for both structures (316 L(N) steels) and cladding (AIM1-type steels). The 60-year life demonstration design and operating temperatures in the range of 400-550°C lead to long term ageing (thermal or irradiation ageing). This process is governed by thermodynamics and diffusion. Thus, to predict microstructural evolutions, an important step is to gain a better understanding of the diffusion kinetics properties in FeCrNi model alloys. At the typical range operating temperatures, diffusion properties of this ternary system aren’t known for the moment either after thermal or irradiation ageing.

To investigate interdiffusion at low temperature under reasonable time, it has been shown [1] that decomposition or homogeneization of the stacking of composition modulated nanolayers can be used. This kind of material is synthesized by magnetron cosputtering of metallic targets at UTBM (France). Interdiffusion coefficients as a function of annealing time at low temperatures can be extracted from [2] - concentration profiles amplitude evolution obtained by elemental analysis techniques as Atom Probe Tomography (APT) and STEM-EDS/EELS ; - the decay of satellite peaks intensity thanks to XRD. These sinusoidal modulations in composition can be described by their wavelength, corresponding to twice a layer thickness, and their amplitude. As diffusion kinetics are wavelength-dependent at this scale, different wavelengths have to be experimentally tested in order to extrapolate results for interdiffusion in a bulk material.

In this talk, the experimental results (APT, STEM, XRD) obtained on multilayers of different wavelengths before and after thermal ageing at different temperatures will be presented. The diffusion coefficients deduced from experimental results will be given.

CM05.13.11
Effect of Alloying Elements on Stacking Fault Tetrahedra (SFT) in Ni Alloys
Gaurav Arora, Dilpuneet S. Aidhy and Anus Manzoor; University of Wyoming, Laramie, Wyoming, United States.

Formation of stacking fault tetrahedra (SFT) has been widely observed both experimentally and in molecular dynamics (MD) simulations in Ni. Using MD simulations, we show that SFT formation is arrested under tensile strain. This observation is explained by our density functional theory (DFT) calculations that show the decrease in the binding energy of SFT with increasing tensile strain. These predictions are qualitatively validated in Ni-Pd alloys. In particular, adding a large atom such as Pd leads to elongation of the Ni-Ni bonds; our MD simulations indeed show no SFT formation in Ni-Pd alloys. The lack of SFT formation has also been observed in irradiated Ni-Pd systems compared to pure Ni. We further elucidate the effect of strain on the energetics of loop and void formation. In particular, we find that while the vacancy binding energy is negative for SFT, it is positive for voids and loops. However, despite positive binding energy, voids are very difficult to form due to high formation energies. For example, the formation energy of a 10-vacancy void is approximately 9 eV. Thus, our results indicate that vacancy clustering and cluster sizes could be significantly reduced via choosing larger sized alloying elements and by applying tensile strain.

CM05.13.12
Object Kinetic Monte Carlo Modelling of Microstructure Evolution Under Irradiation in Zirconium Based on Atomistic Modelling of Point Defect Clusters
Christophe Domin1, Benjamin Christiaen1, Ludovic Thuanet2, Antoine Ambard1 and Alexandre Legris2; 1EDF R&D, Mèze-Sur-Loing, France; 2UMET, Université de Lille, Villeneuve d’Ascq, France.

Zirconium alloys are used to manufacture fuel cladding as well as fuel assemblies of pressurized water nuclear reactors. Under irradiation, they can show a dimensional change commonly called growth. Experimental observations have shown that above a threshold dose, these alloys are subject to accelerated growth called “breakaway”. It has been established that the irradiation formation of <c> and <a> dislocation loops is responsible for the growth of irradiated zirconium alloys and that the appearance of <c> loops is correlated with this growth acceleration. In order to improve our understanding of the nucleation mechanisms of the <c> loops, object kinetic Monte Carlo modelling based on atomic simulations is used. Atomic-scale calculations based on the density functional theory (DFT) and empirical potentials are used to determine the properties of vacancy and self-interstitial clusters: stability and eigenstrain. In particular, DFT simulations have put in evidence the possible existence of different defect clusters (including non planar defects) with different properties prior to the formation of loops. These objects have been included, in addition to displacement cascade debris, in object kinetic Monte Carlo modelling of the microstructure evolution under irradiation. The calculated growth is compared to available experimental results.

SESSION CM05.14: Surface Effects of Ionizing Radiation
Session Chairs: Fabio Di Fonzo and Chu Chun Fu
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 202

8:15 AM CM05.14.01
Kinetic Study on the Evolution of Nanoceramic Coatings Under Heavy Ions Irradiation
Matteo Vanazzi1, 2, Luca Ceseracciu1, Marco Beghi2, Gaelle Gutierrez2, Celine Caber1, Jing Hu1, Meimei Li1 and Fabio Di Fonzo1; 1Istituto Italiano di Tecnologia, Milan, Italy; 2Energy Department, Politecnico di Milano, Milan, Italy; 3CEA, Paris-Saclay, France; 4Argonne National Laboratory, Argonne, Illinois, United States.

In order to qualify innovative materials for structural components and coatings, their radiation resistance must be assured. In this framework, irradiations studies with neutrons present overwhelming complications related to cost, availability and experimental time needed to reach significant levels of radiation damage. Ions irradiation has been proposed as a valid alternative to produce comparable and accessible data. Specifically, heavy ions in the MeV energy range are quite appropriate to simulate neutrons due to the low Electronic to Nuclear Stopping Power (ENSP). However, the comparison of the relative effects for neutrons and heavy ions presents intrinsic difficulties and many data are required to make it reliable. In the previous studies, we have reported on the evolution of amorphous-nanoceramic Alumina (Al2O3) coatings under heavy ions irradiations. The material was irradiated up to 450 displacements per atom (dpa), showing a general radiation-induced crystallization trend. In this work, we employ 12 MeV Au ions to irradiated Al2O3 coatings up to 3 dpa. In opposition to earlier experiments, we here concentrate on the low dpa regime, to evaluate carefully the first stages of crystallization and to obtain radiation damage values more compatible with neutrons tests. Moreover, irradiations are now performed at different temperatures (namely 400, 500 and 600 °C) in order to decouple the thermal contribution from the radiation-induced effects. A comprehensive analysis of the irradiated samples is accomplished by X-Ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Scanning-TEM (STEM) and Nano-indentation (NI). Generally, the evolution seems strictly temperature-dependent, with no structural changes at 400 °C. For the higher temperatures, results show again an intense crystallization process - even at very low dpa levels - with the formation of different crystalline phases, in relation to the test conditions. A preliminary kinetic model is proposed, based on the experimental data, and the grain-growth-related parameters are calculated. From a mechanical point of view, an evident size-effect is manifested. The formation and growth of nanometric crystalline domains increase rapidly the hardness, in accordance with the Hall-Petch relationship. In particular, for the initial stages of irradiations, an inverse Hall-Petch mechanism is observed, with a reported maximum hardness of approximately 27 GPa (ultra-hardness). To support and confirmed these evidences, irradiation tests are repeated with in-situ TEM tandem apparatus. Further tests are carried out with 1 MeV Kr ions on free-standing Alumina films, to collect dynamically microstructural changes and phases transformation. To conclude, an extensive characterization campaign is performed on ions irradiated-Al2O3 coatings. Tuning different experimental conditions (like temperature, dpa, ions), a consistent and coherent picture of the Alumina evolution under irradiation is produced.

8:30 AM CM05.14.02
Analysis of Helium Segregation on Surfaces of Tungsten at Different Levels of Helium Ion Irradiation
Lin Hu1, Asanka Weerasinghe1, Karl D. Hammond2; 1Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Chemical Engineering, University of Missouri-St. Louis, Columbia, Missouri, United States; 3Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

Plasma facing components (PFCs) in nuclear fusion reactors are exposed to intense plasma heat and particle fluxes. The implantation of helium (He) atoms into these materials impacts significantly the evolution of their surface morphology and near-surface structure. In tungsten (W), a promising PFC material because of its thermomechanical properties, interstitial He atoms are very mobile and aggregate to form clusters of various sizes. Small, mobile helium clusters (Heₙ; 1 ≤ n ≤ 7) are attracted to the tungsten surface due to an elastic interaction force that drives surface segregation, and their diffusional transport
mediates the dynamics of surface morphology and near-surface microstructure.

Here, using atomistic simulations based on a reliable many-body interatomic potential, we explore helium segregation on surfaces of tungsten that has been exposed to different levels of He ion irradiation. At higher helium fluence, mobile helium clusters are subjected to cluster-defect interactions in addition to cluster-surface interactions, which complicate cluster dynamics beyond the dilute limit of helium content in the PFC material. We characterize in detail configurations generated by large-scale molecular-dynamics simulations of implanted helium evolution in plasma-exposed tungsten with W(100), W(110), W(111), and W(211) surfaces facing the plasma. We examine the effects of varying helium fluence due to increased plasma exposure of the tungsten PFC by performing systematic molecular-statics computations of small helium cluster energetics near the above low-Miller-index W surfaces as a function of distance (depth) of the cluster center from the surface on a grid of lateral locations on the surface. We analyze the defect interactions that mediate the energetics of small helium clusters migrating to the surface, taking into account that the migrating cluster also is subjected to the stress fields generated by larger helium bubbles, as well as other small clusters, and quantify the strength of these interactions for different levels of He irradiation. The outcome of this analysis is the systematic parameterization of mobile helium cluster energetics at varying levels of He irradiation through functional forms that include contributions from cluster-cluster and cluster-bubble interactions as well as cluster-surface interactions. Such parameterizations are important for developing atomistically-informed, hierarchical multiscale models of helium cluster dynamics in PFC materials.

8:45 AM CM05.14.03
Harsh Environments of Fast Neutrons and Extreme Temperature Effects on Amorphous Fe-Based Nano-Coatings on Steel Substrate

Ilyas
Savklyivzlyzov,2* Enver Koray Akgözan1, Zhong Zheng1 and Nikolaos Simos1;1 Süleyman Demirel University, Turkey; 2Süleyman Demirel University, Turkey; *Rutgers, The State University of New Jersey, Picataway, New Jersey, United States; Brookhaven National Lab, Upton, New York, United States.

Protective coatings on next generation nuclear reactor steels shows safe operation behavior at high temperatures and fast neutrons. The integrated studies include fast neutron irradiation, macroscopic post-irradiation evaluation, scanning electron microscopy and energy dispersive X-ray diffraction (EDXRD) to investigate irradiation-induced macroscale physio-mechanical changes in the nano-coating/substrate structures. At extreme temperatures, phase evolution and effect on crystallization/amorphization is mapped with EDXRD technique throughout the coating. With modest neutron doses of ~2x1019 n/cm2, the loss of ductility in an amorphous Fe-alloy coating on a steel substrate due to high temperature is prevented. At the higher neutron dose of ~2x1019 n/cm2, radiation-induced embrittlement behavior is observed on Fe-alloy nanostructured coating with macroscopic stress-strain analysis which implies ductility loss in the coating-substrate structure. Neutron irradiation displayed remarkable oxidation resistance of the protective Fe-based amorphous coating, which is attributed to the formation of the FeB phase in the coating. In-situ 3D space resolved EDXRD study revealed an increase amorphous-to-crystalline transition in the amorphous Fe-alloy at elevated temperatures. On the surface of the coating, mostly α-Fe phase is observed but these α-Fe phase transformed into γ-Fe phase close substrate interface. This phenomena is attributed to carbon diffusion from steel substrate to Fe based coating at high temperature annealing process. Electron microscopy was carried out to sustain the radiation-induced suppression of crystallization in the amorphous Fe-alloy nanostructured coating.

9:00 AM CM05.14.04
Nanoceramic Coatings—An Enabling Technology for Future Generation Nuclear Systems

Fabio Di Fonzo, Erkka J. Frankberg, Francisco Garcia Ferré, Daniele Iadicicco, Boris Paladino and Matteo Vanazzi; Istituto Italiano di Tecnologia, Milano, Italy.

In the framework of conceptually innovative nuclear reactors, next generation systems are meant to outperform current ones, by providing disruptive solutions in terms of non-proliferation, fuel cycle efficiency, radioactive waste management and safety. However, the development of future power plants is directly linked to the availability of suitable materials. The greatest challenges in this sense arise from the extremely harsh environments and the intense radiation fields to which materials will be exposed during operation. Among the other candidates, ceramic coatings are a promising solution to tackle these issues. Indeed, the deposition of ceramic coatings on traditional structural materials can provide surface engineering without affecting structural integrity. It is worth highlighting that protective coatings are already being considered as a near-term option for accident tolerant fuel (ATF) for Light Water Reactors (LWRs) while, in the case of Generation-IV (GIV) concepts and fusion systems, coatings could be used to mitigate high-temperature corrosion and tritium permeation. Here, we present a brief summary of the activities performed by the Center for Nano Science and Technology of the Istituto Italiano di Tecnologia, on the materials for advanced nuclear systems. Engineered coatings are grown on relevant structural alloys such as 1515-Ti, EUROFER-97, ZIRLO® and Zircaloy-4. Coatings are designed and processed by different methods, namely Pulsed Laser Deposition (PLD) and Magnetron Sputtering (MS). In respect to GIV systems - specifically Lead reactors - Alumina (Al2O3) layers have been characterized as anti-corrosion radiation-resistant barriers. In particular, the compatibility of PLD-grown Al2O3 in molten Lead has been proven in up to 5000 hours exposure time tests, without degradation. For what concerns fusion reactors, Yttria (Y2O3) as well as Alumina coatings have been evaluated as possible solutions against Lead-Lithium corrosion and Tritium permeation. Indeed, the obtained Tritium permeation reduction is in the order of 106-107 while the requirements indicate reduction values of about 1000. Nevertheless, Al2O3 coatings have been tested also under heavy ions irradiation, at damage levels relevant for fusion and fast reactors. The ceramic film has preserved again its integrity and stability, evolving structurally from an amorphous to an almost-completely crystalline state. Last but not least, a combined approach has been investigated for ATF claddings. An optimized multi-layered structure of metallic Chromium and transitional metal oxides has been tested in autoclave systems, simulating standard and accidental condition. Results show a strong improvement in terms of high temperature oxidation resistance. To conclude, engineered coatings represent promising candidates to face the major issues related to future nuclear technologies and allow the design of innovative and economically attractive power plants.

9:15 AM CM05.14.05
Studies of Electron Beam Damage on γ-FeOOH Nanoparticles

Yulia Trushkina, Cheuk-Wai Tai and German Salazar-Alvare all; Stockholm University, Stockholm, Sweden.

It is known that electron beam in transmission electron microscopy (TEM) can cause a damage of a material in various ways, i.e. a change of surface and structure of a specimen. In the case of lepidocrocite (γ-FeOOH) nanoparticles, electron beam damage is an obstacle to obtain full information about the structure from TEM measurements.

In this work we study lepidocrocite whiskers (2.5×6×200 nm2) prepared through oxidation of a green rust precursor. TEM observations show that within 10 minutes lepidocrocite structure undergoes changes under electron irradiation starting at electron dose 171 e/Å2/s. Analysis of the final structure indicates that the structure dehydroxylates topotactically to produce maghemite (γ-Fe2O3).

In this talk I will present the investigation and quantification of beam damage on lepidocrocite nanoparticles. Results from high-resolution TEM and EELS (e.g., thickness change vs dose) with and without cooling will be presented. We suggest that beam damage mechanisms for lepidocrocite nanoparticles are displacement damage and heating.
Nanoscale Chemical Phenomena Using HIM-SIMS

Axel Belianinov, Songkil Kim, Artem Trofimov, Matthew J. Burch and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The key to advancing materials in a broad range of scientific sectors is to understand, and subsequently control, (i) the structure as well as (ii) the chemistry of surfaces and interfaces. However, significant gaps in characterization techniques hamper simultaneous chemical and physical characterization of materials with high spatial resolution and high chemical sensitivity. This work will illustrate recent nanoscale results on imaging and chemical analysis of conductive and nonconductive surfaces using a tool that combines high-resolution imaging and milling with high spatial resolution chemically sensitive approaches – a Helium Ion Microscope (HIM) with a secondary ion mass spectrometer (SIMS). This multimodal chemical imaging methodology transcends inherent individual instrument limitations, data volumes, and complicated analyses originating from an ex-situ combinatorial approach.

Data will be presented on conductive and non-conductive chemical standards as well as scientifically relevant organic-inorganic perovskite (HOIPs) materials. Ionization efficiency, sputtering, fragment detection, and other salient features of the HIM and the SIMS tools will also be presented and discussed. Overall, a combined HIM-SIMS platform offers significant potential to visualize and map active interfaces, by intertwining imaging, nanoscale elemental characterization, and data analytics; to better grasp the physical properties of materials and the mechanistic physics-chemistry interplay behind their properties.

Acknowledgements

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

9:45 AM BREAK

SESSION CM05.15: Radiation Resistant Material Design
Session Chairs: Chu Chun Fu and Yanwen Zhang
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 202

10:15 AM *CM05.15.01
Current Understanding of Irradiation-Induced Defect Production and Microstructural Evolution in Tunable Concentrated Solid-Solution Alloys
Yanwen Zhang1, Shijun Zhao1, Yuri Osetsky1, Hongbin Bei1 and William J. Weber2, 1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Multicomponent concentrated solid solution alloys (CSAs) offer tunable chemical complexity. The random arrangement of multiple elemental species on a regular lattice (fcc or bcc) results in unique site-to-site lattice distortions and local disordered chemical environments. Control of chemical complexity can be achieved by substituting transition metal elements within the same period or the same group. The requirements for an alloy system with increasing chemical complexity (e.g., variation of electronic structure disorder or magnetic frustration) can be fulfilled, for example, in fcc Ni with addition of other elements, primarily 3d-transition metals (e.g., Cr, Mn, Fe, and Co). The composition of this fcc CSA system (e.g., binary, ternary, quaternary and quinternary) can be at or near equatomic concentrations, or at concentrations with one or two elemental species in large variation within solubility limits. In the case of high entropy alloys (HEAs), e.g. NiCoFeCrMn and NiCoFeCrPd, extreme chemical complexity leads to substantially reduced electron, phonon and magnon mean free paths; modified coupling strengths; and complex formation energies and migration barriers. In contrast to traditional dilute alloys, these energies have broad distributions. Moreover, defect–defect interaction strengths, such that interstitials, vacancies and defect clusters produced by displacement collisions, may create their own distributions that can be strongly affected by the intrinsic site-to-site complex disordered states. Recent results [1-5] show that tuning compositional disorder in CSAs represents a powerful tool to dramatically affect defect energetics that ultimately enhances radiation tolerance. In this presentation, current understanding on defect dynamics and microstructure evolution will be discussed through closely integrated theoretical, computational, and experimental studies.

Work supported by the Energy Dissipation to Defect Evolution Center (EDDE), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.

References

10:45 AM CM05.15.02
Absorption of Radiation-Induced Point Defects at Crystal/Amorphous, Metal/Covalent Interfaces
Sanket S. Navale and Michael J. Demkowicz; Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

We use atomistic simulations to investigate the interaction of radiation-induced point defects with interfaces between crystalline metals and amorphous covalently-bonded solids. We select the gold (Au)/silicon (Si) binary system as a model material and construct interface models along different facets of crystalline Au and with amorphous Si (a-Si) created at different quench rates. We compute formation energies of vacancies and helium interstitials as a function of position relative to the interface and find that Au/a-Si interfaces are strong traps for defects originating from both Au and a-Si. Our work suggests that crystal/amorphous, metal/covalent interfaces, such as those found in iron/silicon oxycarbide (FeSiOOC) composites may be as affective at removing radiation-induced point defects as interfaces in polycrystalline metals composites.

11:00 AM *CM05.15.03
Helium Nanochannels and Future Prospects for Damage-Free Helium Outgassing from Metals
Michael J. Demkowicz; Texas A&M University, College Station, Texas, United States.

Work supported by the Energy Dissipation to Defect Evolution Center (EDDE), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.
In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.

11:30 AM CM05.15.04

Displacive Annihilation of Point Defects in Body-Centered-Cubic Metals Qing-Jie Li1, Ju Li2 and Evan Ma1; 1Johns Hopkins University, Baltimore, Maryland, United States; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.

11:45 AM CM05.15.05

Nanotube/Nanowire as Effective Defect Sinks in Metals—Atomistic Simulations and In Situ Ion Irradiation Transmission Electron Microscopy Kang Pyo So1, Penghui Cao1, Yang Yang1, JongGil Park2, Mingda Li1, Jing Hu1, Meimei Li1, Young Hee Lee1, Michael Short1 and Ju Li1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Sungkyunkwan University, Suwon, Korea (the Republic of k). Arjuna National Laboratory, Argonne, Illinois, United States.

In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.

SESSION CM05.16: Crafting Materials with Ionizing Radiation
Session Chairs: Pär Olsson and Jeroen Van Kan
Thursday Afternoon, November 29, 2018
Hynes, Level 2, Room 202

1:30 PM CM05.16.01

Formation of Porous Silicon by Means of Low Energy Oxygen Bombardment Angelica Hernandez, Rene Asomoza-Palacio, Georgina Ramirez and Yuriy Kudriavtsev; CINVESTAV, Mexico City, Mexico.

In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.

1:45 PM CM05.16.02

Focused MeV Proton Beams for 3D Nano-Lithography and DNA Nanofluidics in Resist and Graphene Jeroen A. Van Kan1 and Tanmoy Basu1; 1Centre for Ion Beam Applications, Department of Physics, National University of Singapore, Singapore, Singapore; 2Centre for Advanced 2D Materials, Faculty of Science, National University of Singapore, Singapore, Singapore.

In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.

In this talk, I will present the recent finding that helium (He) implanted into certain metal nanocomposites spontaneously forms networks of elongated channels, rather than a field of isolated, equiaxed precipitates. Thanks to many years of prior research—performed in large part using ion implantation and ion beam analysis facilities—we now have a complete explanation for the physical mechanisms underlying this surprising departure from classical He behavior in metals. I will explain these mechanisms and, on their basis, discuss prospects for technological applications of metal nanocomposites as He-resistant materials to be used in nuclear energy.
The main weak point is the ion source performance, i.e. the brightness is typically several million times less compared to electron beam sources. Recent tests with on-chip ion sources have shown great potential, opening up the way to improve the ion beam brightness by a million times. In this talk I will give an update on defect formation in graphene using different ion species and different energies (1 keV – 2 MeV). As well as an update on the applications into PBW, especially in the area of nanofluidics where we developed a new platform to image single stranded DNA molecules, used in large scale genomic mapping. Finally I will discuss our progress in the development of our new ion source, aiming for single digit nanometer proton beam spot size.

We kindly acknowledge NRF-Singapore for their support: NRF-CRP13-2014-03 and NRF-CRP13-2014-04.

2:15 PM CM05.16.03
Blister Formation at Subcritical Doses in Tungsten Irradiated by MeV Protons
Inbal Gavish Segev1, Ido Silverman1, Guy Makov2 and Eyal Yahel1; 1NRCN, Beer-Sheva, Israel; 2Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel; 3SNRC, Yavne, Israel.

Tungsten samples were irradiated by 2.2 MeV protons at the Soreq Applied Research Accelerator Facility (SARAF) to doses of the order of 10^17 protons/cm^2 which are below the reported critical threshold for blister formation derived from keV range irradiation studies. Large, well-developed blisters are observed indicating that for MeV range protons the critical threshold is at least an order of magnitude lower than the lowest value reported previously. The effects of fluence, flux, and corresponding temperature on the distribution and characteristics of the obtained blisters were studied. FIB cross sections of several blisters exposed their depth and structure.

2:30 PM CM05.16.04
Feedback-Based Automated Fabrication in a Scanning Transmission Electron Microscope
Ondrej Dyck1, 2, Sergei V. Kalinin1, 2 and Stephen Jesse1, 2; 1Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

In recent years, a surprising number of electron beam-induced transformations have been observed in the scanning transmission electron microscope (STEM). Such transformations set the stage for harnessing the electron beam as a fabrication tool at the atomic scale, however most of these demonstrations are performed “by hand”. In the development of a tool set for atomic manipulation, feedback-based automated beam control and real-time image analysis are needed to improve the consistency, throughput, and executability of various processes. Here, we present the development of feedback-based tools which interface with the microscope through a custom scan control system. We demonstrate automation-enhanced control of crystallization, amorphization, and dopant movement. To accomplish this, we must address the challenge of detecting material alterations while concurrently attempting to manipulate the material. Because the same electron beam is used for imaging and manipulation we explore techniques to generate meaningful sample information during manipulation and use rapid, sparse scanning coupled with real-time image analysis to extract sample information with minimum beam exposure. These experiments represent the first steps toward transforming the modern STEM from a characterization to a fabrication platform.

2:45 PM CM05.16.05
Towards a Vertical Nanopillar-Based Single Electron Transistor—A High-Temperature Ion Beam Irradiation Approach
Xiaomo Xu1, 2, Karl-Heinz Heinig3, Wolfhard Möller1, Ahmed Gharbi1, Raluca Tiron1, Hans-jürgen Engelmann4, Lothar Bischoff5, Thomas Pruefer1, René Hübner1, Stefan Facsko1, Gregor Hlawacek1 and Johannes von Borany1; 1Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany; 2Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

We propose an ion irradiation based method to fabricate a single Si nanocrystal embedded in a Si(001)/SiO2/Si nanopillar layer stack as a prerequisite for manufacturing a CMOS-compatible, room-temperature Si single electron transistor. After either 50 keV broad beam Si+ or 25 keV focused Ne+ beam from a helium ion microscope (HIM) irradiation of the nanopillars (with diameter of 35 nm and height of 70 nm) at room temperature with a medium fluence (2×10^16 ions/cm^2), strong plastic deformation has been observed which hinders further device integration. This differs from predictions made by the Monte-Carlo based simulations using the program TRIDYN. We assume that it is the result from the ion beam induced amorphisation of Si accompanied by the ion hammering effect. The amorphous nano-structure behaves viscously and the surface capillary force dictates the final shape. To confirm such a theory, ion irradiation at elevated temperatures (up to 672 K) has been performed and no plastic deformation was observed under these conditions. Bright-field transmission electron microscopy micrographs confirmed the crystallinity of the substrate and nanopillars after HT-irradiation. When a semiconductor material such as silicon is heated above its amorphisation critical temperature during ion irradiation, it stays crystalline due to an interplay between ion damage and dynamic annealing process. Viscous flow does not occur for the crystalline nano-structures and the shape remains intact. This effect has been observed previously mainly for swift heavy ions and energies higher than 100 keV. Such high-temperature irradiation, when carried out on a nanopillar with Si/SiO2/Si layer stack, would induce ion beam mixing without suffering from the plastic deformation of the nanostructure. Due to a limited mixing volume, single Si-NCs would form in a subsequent rapid thermal annealing process via Oswald ripening and serve as a basic structure of a gate-all-around single electron transistor device.

This work is supported by the European Union’s H-2020 research project ‘IONS4SET’ under Grant Agreement No. 688072.

3:00 PM BREAK

SESSION CM05.17: In Situ Studies of Radiation Damage
Session Chairs: Grace Burke and Pär Olsson
Thursday Afternoon, November 29, 2018
Hynes, Level 2, Room 202

3:15 PM CM05.17.01
In Situ Studies of Nanoporous Niobium During Dealloying and Irradiation
Maria Kosmidou1, Nicolas J. Briot1, Nathan J. Madden2, Remi Dingreville3, Jessica A. Krogstad4, Khalid Hattar1, John Balk1 and Azin Akbari1; 1University of Kentucky, Lexington, Kentucky, United States; 2University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States; 3Sandia National Laboratories, Albuquerque, New Mexico, United States.

Nanoporous materials are potentially advantageous in radiation environments, due to the high amount of ligament surface area that can act as a sink for...
defects produced during irradiation. A special technique, thermal dealloying in vacuum, is utilized for the formation of nanoporous refractory metals. In-situ thermal dealloying experiments in the TEM are performed on Nb-Mg alloys for fabrication of nanoporous niobium (np-Nb), where the precursor alloy composition range and dealloying temperature are the main parameters for controlling morphology and residual Mg in the final nanoporous structure. Subsequently, heavy irradiation of np-Nb at different energies and varying total ion dose are performed on samples inside the TEM, creating defect structure within ligaments, as well as possible changes in the overall porous network structure. This presentation will address the formation of np-Nb and its behavior during heavy ion irradiation, with emphasis on the ability of nanoporous structures to accommodate radiation damage.

3:30 PM CM05.17.02
**In Situ Measurement of the Dislocation Density of Steel During Plastic Deformation Using Ultrasound**

Vicente Salinas1,2, Claudio Aguilar3, Rodrigo Espinoza1, Fernando Lund4 and Nicolás Mujica1; 1Physics Department, Universidad de Chile, Santiago, Chile; 2Núcleo de Matemáticas, Física y Estadística, Facultad de Ciencias, Universidad Mayor, Santiago, Chile; 3Departamento de Ingeniería Química, Biotecnología y Materiales, Universidad de Chile, Santiago, Chile; 4Departamento de Ingeniería Metalúrgica y Materiales, Universidad Técnica Federico Santa María, Valparaíso, Chile.

We report results of local measurements of the speed of transverse waves in 304L steel under standard testing conditions, continuously as a function of applied load. The result, as expected, is independent of stress in the elastic regime, but there is a clear change, consistent with a proliferation of dislocations, as soon as the yield strength is reached. To interpret the results, we use a theoretical model that changes the wave speed on the interaction of elastic waves with oscillating dislocation segments. The relevant formulae quantitatively relate the change in wave velocity with dislocation density Λ and segment length L, thus obtaining a continuous relation between dislocation density and externally applied stress.

The experimental results are compared in some detail with similar measurements obtained with aluminum [1]. The change in velocity as a function of applied stress is smaller in steel than in aluminum, consistent with a higher Peierls barrier.

The theory can be worked out replacing the dislocation segments by dislocation loops [2]. Similar formulae result, in which the dislocation segment length is replaced by the dislocation loop radius. Available STEM images of dislocation loops in FeCrAl after neutron irradiation [3] suggest a density of dislocation loops sufficient to provide a measurable signal. Ultrasound could thus become a non-destructive measuring tool for dislocation density in fuel cladding alloys.

References:

3:45 PM CM05.17.03
**A New Solid Solution Approach for the Study of Self-Irradiation Damage in Non-Radioactive Materials**

Tsivi Templeman2, Michael Shandalov1, Yuval Golan3 and Eyal Yahel4; 1Physics, NCNR, Beer-Sheva, Israel; 2Materials Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel.

We present a new method to produce a model system for the study of radiation damage in non-radioactive materials. The method is based on homogeneous incorporation of 229Th ions in PbS thin films using a small volume chemical bath deposition (CBD) technique. Controlled doping of the thin films with minute amounts of a-emitting radioactive elements such as thorium is expected to provide a unique path for studying self-irradiation damage in materials without the need of sealed enclosures, such as gloveboxes and hot cells.

We developed CBD process for controlled doping of PbS thin films with active 229Th and stable 232Th isotopes [1]. The 229Th-doped films were characterized using x-ray powder diffraction (XRD), which indicated a single phase material. Film morphology and thickness were determined using scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) mapping in the analytical transmission electron microscope (A-TEM), x-ray photoelectron spectroscopy (XPS) depth profiles and a-aautoradiography indicated that the Th ions were homogeneously distributed throughout the films, suggesting Pb substitution by Th ions in the crystal lattice. Electrical resistivity studies were performed and decay-event damage accumulation was measured, followed by isochronal annealing, which presented two defect relaxation stages and additional sub-stages [2]. Photoluminescence (PL) studies of emissive defect states created in the bandgap due to self-irradiation are on the way. This is the first report on self-irradiating damage studies in IV-VI semiconductors and the resulting films present a novel method for the analysis of dilute defect systems in materials.

References:

4:00 PM CM05.17.04
**In Situ Irradiation of Carbide Based Hybrides—Challenges and Differences**

Karl R. Whittle1, Tanagorn Kwannmar2, Glynn Cobourne1, W Mark Rainforth3 and Philip D. Edmondson1; 1University of Liverpool, Liverpool, United Kingdom; 2The University of Sheffield, Sheffield, United Kingdom; 3Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Binary carbide hybides based on TiC and SiC, with mixed properties of both single carbides, have been proposed for application within nuclear reactor cores. For such applications to be viable, their response to irradiation induced damage, must be more fully understood. To achieve this a selection of different TiC-SiC mixtures have been irradiated in situ, at the IVEM facility at Argonne National Laboratory, followed by high resolution electron imaging and diffraction at the University of Liverpool, and Oak Ridge National Laboratory. This analysis has indicated that there is a behavioural change with variation in composition, with increasing TiC content giving rise to a system that is more resilient to increasing levels of damage.

4:15 PM CM05.17.05
**In Situ Characterization of Single Ion Strikes in Single Crystal Silicon**

Anthony Monterrosa, James Stewart, Patrick Price, Remi Dingreville and Khalid Hattar; Sandia National Laboratory, Albuquerque, New Mexico, United States.

Understanding the evolution of damage cascades caused by energetic particle strikes has proven difficult for experimental studies. Individual cascade events occur over an extremely limited spatial and temporal scale, which has left most of their exploration to modeling efforts. However, recent in-situ transmission electron microscopy developments have been used to close this gap, allowing for detailed experimental studies of damage cascades. In-situ and ex-situ irradiations were performed at the Sandia Ion Beam Laboratory with Au ions ranging from 46 keV to 1 MeV on single crystal silicon to explore a wide range of cascade morphologies. Procession electron diffraction (PED) was used to experimentally measure the changes in volumetric strain induced by single cascade events by measuring changes in the diffraction spot area. The experimental results were coupled with a molecular dynamics (MD), which simulated the radiation damage events and provided the size, shape, and composition of the defect damage, along with virtual selected area electron
diffraction (SAED) patterns. Information from a single damage cascade can be acquired through direct comparison between the experimental diffraction patterns and the virtual SAED patterns. Additionally, the coupling of the in-situ ion beam with a dynamic transmission electron microscope (DTEM) can provide the unique capability to experimentally probe the collapse of the damage cascade on a nanosecond timescale.

4:30 PM *CM05.17.06
Using Advanced Analytical TEM to Study Irradiation-Induced Microstructural Evolution in Fe- and Ni-Base Alloys Grace Burke1 and Joven Lim2; 1Materials Performance Centre, University of Manchester, Manchester, United Kingdom; 2UKAEA Materials Research Facility, Didcot, United Kingdom.

The requirement to predict long-term behavior of alloys used in nuclear power systems requires the ability to generate high irradiation-induced damage levels in these alloys and the ability to characterise the nanoscale changes in the microstructure leading to changes in mechanical properties. These nanoscale changes in microstructure lead to the evolution of a variety of features including solute-enriched clusters, segregation, precipitation and defects that directly affect the properties of materials. Neutrons, ions and protons all promote these nanoscale changes. Thus, the ability to generate high dose damage levels using ions or protons represents a potential route to producing microstructures that have similar characteristics to those generated by neutrons. The characterisation of these nanoscale features provides data essential for fundamental modelling efforts. This presentation will discuss advanced analytical electron microscopy studies of microstructural evolution in several Fe-base and Ni-base alloys.

CM05.18.01
Particle Irradiation Induced Defects in High Temperature Superconductor Prashanta M. Niraula1, Eiman Bokari1, Shahid Iqbal1, Lisa Paulius1, Matthew Smylie2, Ulrich Welp2, Wai-Kwong Kwok1 and Asghar Kayani1; 1Physics, Western Michigan University, Kalamazoo, Michigan, United States; 2Argonne National Laboratory, Lemont, Illinois, United States.

Particle irradiation technique can be used to induce defects in High Temperature Superconductor (HTS) such as Y$_2$Ba$_2$Cu$_3$O$_{7-x}$ (YBCO). These defects can act as pinning centers to restrict the motion of magnetic flux vortices, which as a result can increases the critical current density ($J_c$). Depending on the mass and energy of the particle and the properties of the target material, irradiation enables the creation of defects with well-controlled density and topology, such as points, clusters, collision cascades or linear tracks. Furthermore, irradiation allows for the combination of defects with different morphologies or to add to pre-existing defects at densities that are interesting for vortex pinning, all without changing the chemistry of the sample. This creates the so-called mixed pinning landscapes that have proven very effective in high magnetic fields. In this work, HTS coated conductors containing Barium zirconate nanorods as pre-existing defects were irradiated with 50 MeV copper ions at angles of 0°, 15° and 30° from the crystallographic c-axis. We observed moderate enhancement of $J_c$ at 5 K at high fields in samples irradiated at 30° and a suppression in others.

CM05.18.02
Photoluminescence Properties in Aliphatic-Aromatic Biodegradable Polymers Induced by Low Energy Radiation Elisete L. Cunha2, Thiago Schmitberger2, Victor A. Rosas1 and L.O. Faria1; 1Materials, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte, Brazil; 2Nuclear Engineering, Federal University of Minas Gerais, Belo Horizonte, Brazil.

Poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable aliphatic-aromatic copolyester. The radio induction of photoluminescence (PL) properties in PBAT, after exposure to high doses of gamma radiation, was firstly reported by T. Schimitberger et al. (2014). The material shows the highest photo-stimulated luminescence emission when excited with a light-emitting diode (LED) source at wavelengths ranging from 370 to 405 nm. These new PL properties may have great potential for applications in in vitro imaging of human cancer, bio-imaging devices and radiation dosimetry. However, most of these applications are possible just for biocompatible materials. For comparison purposes, the irradiations were performed under air and O$_2$(g) atmospheres. PL emission, UV-Vis and FTIR spectrometry were used to characterize the relationship between UV doses x PL Intensities and to reveal the mechanisms behind the post-irradiation PL character in PBAT samples. Peak fitting of FTIR data using Gaussian lines indicates the radio induction of molecules attached to aromatic hydrocarbons via chain scission. The high quantum yield emission of UV-induced PL near 500 nm, observed in PBAT, is a very interesting finding because it involves the development of a new cheap biodegradable photoluminescent polymer that could find applications in radiation dosimetry and bio-imaging.

References


CM05.18.03
Vertical Nanowires Enhanced X-Ray Radiation Damage of Cells Qingxuan Li, Liyuan Zheng and Ming Su; Northeastern University, Boston,
Cell behavior is affected by nanostructured surface, but it remains unknown how ionizing radiation affects cells on nanostructured surface. This abstract reports an experiment investigation of X-ray radiation induced damage of cells placed on an array of vertically aligned silicon nanowires. X-ray photoelectrons and secondary electrons produced from nanowire array are measured and compared to those from a flat silicon substrate. The cell functions including morphology, viability, adhesion and proliferation have been examined and found to be drastically affected when cells are exposed to X-ray radiation, compared to those sitting on flat substrate and those only exposed to X-ray. The enhanced cell damage on nanowires upon X-ray exposure is attributed to nanowire enhanced production of photoelectrons including Auger electrons and secondary electrons, which have high escaping probability from sharp tips of nanowires. The escaped photoelectrons ionize water molecules and generate hydroxyl free radicals that can damage DNAs of cells. An inference of this work is that the contrast in scanning electron microscopy is useful in assessing the effects of nanomaterials for enhanced X-ray radiation therapy.

CM05.18.04
Study on H in Fe/W Interface by DFT Calculation Jinnming Shi and Naoyuki Hashimoto; Hokkaido University, Sapporo, Japan.

In the development of fusion reactors, tungsten (W) and reduced activation ferritic/martensitic (RAFM) steel are strong candidates as divertor and structure materials of blanket. Many researches have devoted a lot of effort on the radiation effect on W as well as on RAFM steel. Obviously, W component should be connected to RAFM steel in reactor, thus the cohesion properties between W and RAFM steel play an important role in their performance. In this study, a Fe(001)/W(001) interface configuration is built as a model for the cohesion between RAFM steel and W. The mono-vacancy and the dissolution behavior of H in the interface region are studied. This work is conducted by density functional theory (DFT) calculation. And all calculations are implemented by GPAW, a DFT calculation code. Results show that, in the interface region, the lattice of Fe and W are different from in bulk materials. The vacancy formation energy (Ev) in W side in interface region is smaller compared it in bulk W, while the Ev in Fe side in interface is slightly higher than it in bulk Fe. From Fe side to W side, the dissolution energy of hydrogen in interface increases which indicates that the H prefers to stay in Fe side and the H in W side could diffuse to Fe side since no sink effect of the interface is found. And, the effect of vacancy and H atom on strength of the Fe/W interface is investigated. Vacancy in interface region make the strength of interface decrease. At most cases, H atom also make the strength of interface decrease.

CM05.18.05
Study of Nanopatterning Formation Dynamics by Ion Beam Bombardment on GaSb Angelica Hernandez, Rene Asomoza-Palacio, Miguel Avendaño and Yuriy Kudriavtsev; CINVESTAV, Mexico City, Mexico.

Abstract: In this work we have studied the formation of ordered nanostructures on the surface of gallium antimonide (GaSb) under ion irradiation. The substrate temperature was varied from room temperature (RT) up to 300 °C. The GaSb surfaces were bombarded by using a polyatomic bismuth ion beam (Bi^{m+}), from where Bi1+ and Bi3+ were selected as the incident ions, respectively. The energy beam utilized was 15 and 30 keV, whilst the angle of incidence was chosen to be 0° or 45°. Different morphologies were observed for 45° angle of incidence and elevated substrate temperature depending on ion fluences. The morphological characteristics of nano dot patterns formed at normal incidence of the ion beam, were studied by atomic force microscopy (AFM). Also, the chemical and structural properties were characterized for micro Raman. We carried out a detailed study of the effects of substrate temperature, ion fluence, type of incident ion, energy beam and angle of incidence on the morphological characteristics of nano dot patterns.

CM05.18.06
The Effect of Radiation Fluence on the Performance of a High Voltage CMOS Monolithic Active Pixel Sensor Using TCAD Simulation Tuan A. Bui, Haip Tran, Geoffrey Reeves, Patrick W. Leech and Anthony Holland; School of Engineering, RMIT University, Melbourne, Victoria, Australia.

Pixel semiconductor detectors with position sensitivity have played a critical role in the success of high energy physics experiments. Located only a few centimeters from the collision point of the beam at the innermost layer of the ATLAS detector system, the pixel detectors and their electronics have been required to withstand a high fluence of radiation. This paper presents a simulation using computer aided design (TCAD) of the effect of variation in the flux of ionizing radiation on the performance of a high voltage complementary metal-oxide-semiconductor (HV-CMOS) monolithic active pixel sensor (MAPS). The simulation has been performed using an existing TCAD model of a single pixel HV-CMOS MAPS with an on-pixel source follower amplifier [1]. The model was based on the impact of a minimum ionization particle which generated ~280000 electron-hole pairs in a thickness of silicon of 300μm when fully depleted at 120V bias [1]. The present work has expanded the modeling of the behavior of the detector by examining the effect of variation in the fluence of radiation on the range 10^13 - 10^16 n_{eq} cm^{-2}. The induced radiation damage has been simulated using a 3-level trap model for a p-Si detector [2] to investigate the degradation in the performance of the detector as a function of varying fluence. The simulations of single event upset have also been performed on the NMOS and PMOS transistors which were used to implement the on-pixel readout circuit.


CM05.18.07
Induced Order-Disorder Transformations in Fluorite Based Oxides Michelle R. Moore1, Maulik K. Patel1-2, Susan Morgan1, David Hambly1, Kurt Sickafus1, Gianguido Baldi2 and Karl R. Whittle1; 1School of Engineering, University of Liverpool, Liverpool, United Kingdom; 2Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 4Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupelec, Gif-sur-Yvette, France; 5National Nuclear Laboratory, Seascale, United Kingdom.

Fluorites and fluoride-related materials are of interest within the nuclear context, primarily due to the use of UO2 as the predominant fuel in reactors, along with pyrochlore/zirconolite/fluorite being a key waste form for actinide immobilisation. This study examines the radiation damage response of fluoride-derivative structures within the Sr2O−H2O system. Such oxides, for example δ-Sr6H4O12, γ-Sr5H3O12 and β-Sr5H2O3, exhibit distortion away from the ideal fluorite crystal lattice undergoing an order-to-disorder transformation upon irradiation. Samples of γ-Sr6H4O12 and β-Sr5H2O3 were irradiated by 400 keV Ne and 600 keV Kr under cryogenic conditions with fluences between 1x10^16 to 1x10^17 ions cm^{-2}. Irradiations by 400 keV He were undertaken on δ-Sr6H4O12 and γ-Sr5H3O12 samples at 500°C, at fluences of 1x10^16 and 1x10^17 ions cm^{-2}.

Analysis of the induced changes has been undertaken using grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy and electron imaging/diffraction, to elucidate the order to disorder transformation. The results will then be compared with similar transitions in other nuclear-related oxides, such as the pyrochlore-disordered fluorite transformation.
CM05.18.08  
Irradiation Behavior of Multi-Layer Coatings on ZIRLO for Accident Tolerant Fuel Cladding  
Jamie K. Nansen1, Maulik K. Patel1, Yongqiang Wang2 and Karl R. White1; 1School of Engineering, University of Liverpool, Liverpool, United Kingdom; 2Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The continued development of accident tolerant fuels/coatings is a key driver in the continuing nuclear renaissance, in a bid to minimize the chances of an event similar to Fukushima Daiichi repeating. As a consequence of this we have examined a range of multi-layer coatings based on Nb, Al, and C, focusing in particular on how they behave under ion irradiation as a proxy for neutron damage expected within a core. Once irradiated these coated samples underwent oxidation testing at 360 °C, modelling the conditions expected within a PWR. The coatings were irradiated with 400 keV Kr and 150 keV C, both at 300 °C, across a range of fluences, up to 9 x 10^16 ions cm^-2. The damaged materials were subsequently analysed using electron microscopy (SEM, EDX, and TEM) coupled with grazing incidence X-ray diffraction (GIXRD) and Raman spectroscopy. Results indicate there is significant improvement over uncoated ZIRLO under the same conditions, suggesting the possibility of use within a reactor core.

CM05.18.09  
Broad-Beam Simulations of Si+ Ions in Stacked Si/SiO2: Heterostructures for Meta-Stable SiOx Formation  
Christoffer Fridlund1, Kai Nordlund2 and Flyura Djurabekova 1, 2, 3; 1University of Helsinki, Department of Physics, Helsinki, Finland; 2Helsinki Institute of Physics, Helsinki, Finland.

There is no easy way to commercially manufacture Single Electron Transistors (SET) at large scale. A method for creating the nanostructures needed for operating SETs at room temperature (RT), is to use low energetic broad-beam irradiation (25 to 60 keV) inducing atom-mixing over the interfaces in a stacked Si/SiO2/Si semiconductor structure. An excessive amount of Si atoms are transferred into the SiO2 matrix from the surrounding Si layers. By controlling the fluence of the broad beam, it is possible to control the atomic density profile of the Si atoms along the axis of the irradiation.

The excessive Si in the SiO2 layer, give rise to a difference in the atomic density profile around the interfaces, and meta-stable SiOx is formed in these regions. When the system is annealed, Si nanoclusters form through self-assembly towards the center of the SiO2 slab. Both the size and the location of the nanocluster is crucial for flawless operation of the SET at RT. The diameter of the SET should be around 2 nm, and the tunneling distances should be in the range of 1.5 nm to 2.5 nm both above and below the nanocluster. A 7 nm thick SiO2 slab with 25 nm c-Si on top and 20 nm c-Si below, are cut into pillars for the simulations. We use Molecular Dynamics (MD) to simulate the 25 keV Si+ broad-beam conditions in various Si/SiO2 systems. The annealing process is simulated with Kinetic Monte Carlo (KMC) based on the density profiles from the MD simulations. The Stillinger-Weber-like Watanabe potential was used to simulate Si-Si, Si-O, and O-O interactions. The interactions of the kinetic ions were handled by the universal repulsive ZBL potential. To speed up the MD simulations, we allowed 10 ion cascades to develop consecutively (1.5 ps each), all ending with a temperature quench back to RT, alternated by a longer relaxation run (5.0 ps). Repeating the steps until the desired fluence of 1.5E16 cm^-2 was achieved.

During irradiation, the systems are shrinking along the beam direction. This is in good agreement with experiments done on similar pillars at RT. However, while the dynamics in the experiment most likely come from sputtering effects, the dynamics of the simulations are a combination of both sputtering and the hammering effect, caused by short simulation times, not allowing the system to recrystallize inbetween the ion cascades. Coordination analysis indicate some overcoordination of the O, but this is expected due to the meta-stable SiOx. Reference simulations of pure Si pillars generate the same general shape change.

The work has been funded by Svenska Kulturfonden and the European Union's Horizon 2020 research and innovation program under grant agreement No 688072.

CM05.18.10  
Influence of Temperature on Nanofabrication Using Swift Heavy Silver (Ag+) Ion Irradiation on GaSb  
Satish Kumar1, 2, Ajit K. Mahapatro2 and Pusparshree Mishra1; 1DRDO, Solid State Physics Laboratory, Delhi, India; 2University of Delhi, Delhi, India.

 Gallium antimonide (GaSb) nanostructures have stimulated interest because of unique quantum confined nanoscale properties. GaSb has low band gap and high hole mobility, which makes it a suitable candidate for various potential applications such as high frequency electronics, low power consumption electronics, near to mid infrared optoelectronics, and gas/chemical/bio-sensing devices etc. Ion irradiation technique has been effectively used to fabricate several kinds of nanostructures such as nanofibers or nanodots etc. The growth of semiconductor nanostructures in a controlled manner is the key for the development of future optoelectronic devices. This technique is versatile, cost effective, well controlled and reproducible for the spontaneous fabrication of different shapes of semiconductor nanostructures.

This work presents the fabrication of GaSb nanodots using swift heavy silver (Ag+) ion irradiation with ion fluence range from 1x10^12 to 1x10^16 ions/cm^2 under normal incidence at two different temperature (300K and 77K). The GaSb epitaxial layers were grown on semi-insulating gallium arsenide (GaAs) (001) substrates using molecular beam epitaxy (MBE). The surface morphology and crystalline quality of pristine and silver ion irradiated GaSb samples were characterized using atomic force microscopy (AFM) and Raman spectroscopy techniques respectively. The AFM micrograph of pristine GaSb sample shows that the surface is featureless and smooth with minimum rms (root mean square) surface roughness of 1.51 nm. Room temperature irradiation on GaSb samples clearly indicates the formation of well defined nanodots. The nanodots seem to be uniformly distributed over the surface and they coalesce with each other give rise to bigger dots for increasing ion fluences. Over a certain ion fluence (1x10^15 ions/cm^2) a smooth surface is observed. The presence of nanodots was also observed on irradiated GaSb samples using similar parameters at low temperature (77K) ion irradiation. However, the nanodots at 77 K are not well developed and are irregularly shaped as compared to the 300 K ion irradiation. The smoothening of irradiated surface starts at earlier ion fluence (6x10^15 ions/cm^2) for 77K compared to 300K samples (1x10^14 ions/cm^2). The dot morphology at the two different temperatures are analyzed by considering the different rates of surface diffusion of adatoms. Raman spectrum for pristine GaSb sample indicates good crystalline quality of epitaxial layer. The LO and TO phonon modes are found to shift to lower wave numbers with increasing ion fluence for irradiated GaSb surfaces at both temperature (77K and 300K). This is due to the presence of tensile strain in irradiated GaSb samples. Raman analysis reveals higher disorder in silver irradiated GaSb samples at 77K compared to 300K samples.

CM05.18.11  
Defect Formation on Ultrathin Films with Highly Charged Ions  
Ardak Ainabayev1, Masahito Niibe3, Mititaka Terasawa4 and Zinetula Z. Lugnapin1, 2; 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan; 4Laboratory of Advanced Science and Technology for Industry, Kouto, Japan.

Irradiation of ultrathin films by highly charged ions (HCl) offers a very shallow modification of the surfaces by easily controlling the density and the size of defects by changing fluence of ions (ion current and irradiation time) and the potential energies of bombarding ions. Defect formation in the samples of ultrathin films such as graphene, graphene oxide, and MoS2 by HCl irradiations were studied. Highly-charged ions
(HCl) Xeq+ (q = 22, Ekin=400 keV), were used to irradiate ultrathin films at National Nuclear Center, Astana, Kazakhstan, using a DC-60 cyclotron accelerator. Since the mechanisms of defect formation, charge neutralization and screening during HCI interaction with graphene are not clear and require further investigations [1], the study of the irradiated samples was conducted using Raman spectroscopy, atomic force microscopy (AFM), and NEXAFS (Near-Edge X-ray Absorption Fine Structure). The Raman spectroscopy (Horiba) study of the irradiated samples was conducted by a 632 nm laser wavelengths and 100x objective with a laser spot size of ~1 μm, 2 mW power and atomic force microscopy (AIST NT) measurements were carried out in a tapping mode by SUPERSHARP SILICON™ AFM probes for high resolution. NEXAFS spectroscopy measurements were carried out at the NewSUBARU BL09A beamline of the New SUBARU SPring8 LASTI facility at the University of Hyogo, using total-electron yield (TEY) method and without uncompleted correction of energy.


CM05.18.12
Influence of Temperature, Humidity and Light-Intensity on the Conductivity of Solution-Processed Zinc Oxide Thin Films
José B. Cantuária2, Giovani Gozzi1 and Lucas Fugikawa Santos1,2; 1São Paulo State University, Rio Claro, Brazil; 2IBILCE, São Paulo State University, São José do Rio Preto, Brazil.

Zinc oxide (ZnO) is a n-type transparent semiconductor which can be processed by low cost techniques, as spray-pyrolysis and spin-coating, and can be applied as active layer in a variety of electronic devices, including photodetectors and thin films transistors (TFTs). Electrical properties of ZnO TFTs, as threshold voltage, charge carrier mobility and on/off ratio, are strongly affected when the device it is exposed to room conditions. The current explanation to these effects considers the adsorption of atmospheric oxygen molecules, which acts as traps of charge carriers (electrons). In the current work, we studied the influence of environmental parameters, as temperature, humidity and light irradiance, on the electrical conductivity of spin-coated ZnO thin films. The experiments were performed using ZnO thin films with aluminum electrodes in a planar structure. The electrical current with the device biased at a fixed d.c. voltage was measured as a function of the exposure time to light from a filament/discharge lamp which simulates the solar spectrum (visible and UVA and UVB ranges). Variations on the film conductivity were interpreted as a consequence of adsorption-like and desorption-like processes of charge carrier traps, as atmospheric oxygen. As standard, we considered that desorption-like (adsorption-like) processes improves (reduces) the electrical conductivity and, as consequence, the device electrical current. We obtained that a desorption-like process dominates at the beginning of device irradiation (increasing the electrical conductivity) and, after a maximum current is reached, an adsorption-like process dominates, decreasing the electrical current until to a steady state is achieved. The concentration of carrier traps was determined from the current vs. time curves using the Henry model of adsorption and we verified that adsorption/desorption rates are exponentially dependent on time. The initial adsorption/desorption rate and the time constant of each exponential process were determined and used to evaluate the influence of the environmental parameters. This evaluation was performed using a Plackett-Burman experimental design analysis. The factorial analysis shows that the irradiance is the main factor which influences the adsorption/desorption rates. Environmental factors as the temperature and the humidity influence the overall device conductivity, however, do not presented significant influence on the adsorption/desorption rate, which is basically dependent on the irradiance in the observed range.

SYMPOSIUM EP01
TUTORIAL: Introduction to Pyroelectric, Piezoelectric, and Ferroelectric Materials
November 25 - November 25, 2018

* Invited Paper

TUTORIAL
Introduction to Pyroelectric, Piezoelectric and Ferroelectric Materials
Sunday Morning, November 25, 2018
Hynes, Level 2, Room 201

Polar materials continue to be an important class of functionality for modern applications that provides direct and indirect convolution of structure and chemistry from the atomistic to the macroscopic level. This tutorial will introduce researchers to the basic physics of polar response, its connection to fundamental structure and symmetry, synthesis of polar materials and characterization methods. Topics will also cover the connection between polar properties and desirable functionality in application such as sensing and optoelectronic properties. This tutorial will then culminate with hands-on exercises to explore the functionality, synthesize ability, and characterizability of polar materials in the Materials Project.

8:30 AM
Fundamentals of Pyroelectric, Piezoelectric, and Ferroelectric Materials Susan Trolier-McKinstry; The Pennsylvania State University

10:00 AM BREAK
Optimization of Si/ZnO/PEDOT:PSS Tri-Layer Heterojunction Photodetector by Piezo-Phototronic Effect Using Both Positive and Negative Piezoelectric Charges Fangpei Li, Wenbo Peng, Zijian Pan and Yongning He; Xi'an Jiaotong University, Xi'an, China.

Piezo-phototronic effect has been extensively introduced to improve the performances of optoelectronic devices by utilizing external-strain-induced positive or negative piezoelectric charges (piezo-charges) to modulate the generation, separation, transportation, and recombination of charge carriers. However, in most cases till today, only the piezo-charges with one polarity (i.e., positive or negative) are effectively utilized. In this work, we fabricated an n-Si/n-ZnO/p-PEDOT:PSS tri-layer heterojunction photodetector (HPD) and systematically investigated the piezo-phototronic effect on its performances simultaneously utilizing both positive and negative piezo-charges for the first time.

In experiment, the photo-responses of the HPD to 405 nm and 648 nm laser illuminations under different externally applied compressive strains indicate the existence of an optimized compressive strain to achieve the maximized enhancements. For example, the photoresponsivities to 405 nm and 648 nm laser illuminations are gigantically improved, and reach 0.218 A/W (under -10.73‰ compressive strain) and 0.012 A/W (under -6.52‰ compressive strain), respectively. Compared to photoresponsivities under strain free condition, the enhancements achieve over 3000% and 1800%, respectively. Other figure of merits as a function of compressive strain, such as photocurrent and specific detectivity, also exhibit a similar optimizing tendency.

The optimizing phenomena are due to the positive and negative piezo-charges at n-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interface, respectively, that introduce different adjustments to the local energy band diagrams which have either enhancing or weakening effects on the behaviors of photo-generated carriers. Under a relatively small compressive strain, the enhancing influences play a dominant role so the photo-responses are improved. As strain rises, some weakening influences outgrow others, therefore the photo-responses are degraded. This competition mechanism is a combined result of both positive and negative piezo-charges, and eventually produces an optimized modulation to the photo-responses of the HPD. Theoretical validation is implemented by finite element analysis simulations and simulation results show that the strain-induced variations in energy band diagrams in the vicinity of the n-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interfaces are both in good accordance with the proposed working mechanisms.

This work not only presents the utilization of both positive and negative piezo-charges to optimize the performances of the HPD by the piezo-phototronic effect, but also provides a deep understanding of how the piezo-charges of two opposite polarities work together in one optoelectronic device, hopefully proposing the idea of introducing the piezo-phototronic effect into three-/multi-layer devices in future applications.
of 80 nm serves as bottom electrode for the CGO electrostrictor. The direct deposition yields impressive electrostrictive performances (50 m^4/C^2) and long term stability for CGO films of ca. 1 μm in thickness.

References:

9:00 AM EP01.01.03
First-Principles Studies of the Effects of Oxygen Vacancies on the HfO2-Based Ferroelectric Tunnel Junction Jinho Byun, Taewon Min and Jaekwang Lee, Physics, Pusan National University, Busan, Korea (the Republic of).

Owing to the recent advances in the oxide growth technology, ferroelectricity has been stabilized even in a few nm-thick films, which makes it possible to realize the oxides-based ferroelectric tunneling junction (FTJ) combining the quantum-mechanical tunneling phenomena and switchable spontaneous polarization into novel device functionality. Among various ferroelectric oxides, HfO2 is the most promising material for FTJ devices since it has the great advantage of complementary metal-oxide-semiconductor (CMOS) process compatibility. Despite this considerable attention, the influence of oxygen vacancies on the tunneling current has not been clearly understood yet. Here, using first-principles density functional theory calculations, we explored the role of interfacial oxygen vacancy on the tunneling current in the Ti/HfO2/metal devices at the atomic scale. We find that the tunneling current in defective HfO2 is enhanced by over three orders of magnitude compared to plain HfO2 thin film. Our results show that the modulation of electronic properties via interfacial oxygen vacancy has a significant impact on HfO2-based FTJ device performance.

This research was supported by the MOTIE (Ministry of Trade, Industry & Energy (#10080643) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (2018R1A2B6004394)

9:15 AM EP01.01.04
Dynamical Mean Field Theory Investigation of Piezoresistive Thin-Film Rare Earth Compounds Contacted to Metal Electrodes Ivan Rungger1*, Evgeny Plekhanov2, Deblina Banerjee2, Andrea Droughe2, Dennis News6, Cedric Weber2 and Glenn J. Martyna4; 1National Physical Laboratory, Teddington, United Kingdom; 2Kings College London, London, United Kingdom; 3University of the Basque Country, San Sebastian, Spain; 4IBM Thomas J Watson Research Center, Yorktown Heights, New York, United States.

The emerging piezoelectric transistor technology is based on heterostructures combining piezoelectric materials and piezoresistive thin films acting as ON/OFF switches and memories. Rare earth piezoresistive compounds such as SmS, SmSe and SmTe exhibit a reversible metal-insulator phase transition driven by either light, voltage or pressure, which can be applied by the piezoelectric. For device applications the contact with the metal electrodes critically affects switching behaviour in nanoscale piezoresistive materials, which has not been studied so far. Here we present first principles calculations to model these phase transitions both in the bulk and in nanoscale thin films used in transistor applications, and predict how switching can be induced by mechanical and electrical means in nanoscale devices. Importantly, density functional theory with semi-local exchange correlation functionals cannot correctly treat the strongly correlated electrons in the f-orbitals of Sm. We overcome this limitation by using our recent implementation of the dynamical mean field theory, and show good agreement with experimental data for the electrical and mechanical switching properties.

9:30 AM EP01.01.05
Three-Dimensional Interconnected Piezoelectric Ceramic Foam Based Composites as Flexible, High-Performance Piezo/Pyroelectric Materials for Concurrenrt Mechanical and Thermal Energy Harvesting Sulin Zhang1, Qing Wang2, Guangzu Zhang3 and Peng Zhao1, 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2Huzhong University of Science and Technology, Wuhan, China.

Flexible Piezoelectric (PZT)-polymer composites with superior piezoelectric effect have received much attention for a wide range of applications, particularly in energy harvesting. However, classical PZT-polymer composites with low-dimensional ceramic fillers suffer from low piezoelectricity, owing to the poor load-transfer efficiency from the polymer matrix to the active ceramic fillers. The fundamental mechanics is that the load-transfer efficiency for these composites scales with the rigidity of the polymeric matrix to that of the ceramic fillers, a value typically on the order of 10^-5. Here we introduce a cost-effectively producible ceramic-polymer composite consisting of three-dimensional (3-D) interconnected piezoelectric microfoams in polydimethylsiloxane (PDMS) matrix. The resulting composite breaks the conventional scaling law of the load-transfer efficiency, and enables continuous strain and heat transfer, giving rise to exceptionally improved piezo and pyroelectric effects as compared to those based on low-dimensional ceramic fillers. The 3-D composite is also mechanically flexible, robust, and durable, able to sustain thousands of thermomechanical cycles without noticeable degradation, while yielding stable piezo/pyroelectrical signals. We further demonstrate that combining the piezo and pyroelectric effects of the 3-D composites enable concurrent mechanical and thermal energy harvesting. These attributes, along with the scalable production, make the 3-D composite attractive to a wide range of applications in soft robotics, wearable electronics, and artificial muscles and skins, etc.

9:45 AM EP01.01.06
Potential Ferroelectric Binary Oxides Beyond Hafnia Rohit Batra1,2, Huan Tran1, Brienne Johnson, George Rossetti1, Jacob L. Jones1 and Rampi Ramprasad1; 1University of Connecticut, Storrs, Connecticut, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States; 3North Carolina State University, Raleigh, North Carolina, United States.

In the past couple of years, there have been extensive empirical and theoretical efforts to elucidate the surprising phenomenon of ferroelectricity recently discovered in hafnia (HfO2) thin films (~30 nm) [1-5]. While the origin of this unexpected ferroelectric (FE) behavior is associated with the formation of the metastable orthorhombic Pca21 phase owing to unusual thermodynamic or processing conditions [2,4], the most critical lesson to be learned from the example of hafnia is that even binary oxides can be FE if low-lying metastable (or noble) phases are present. Thus, in this contribution, we extend the findings from the case of hafnia to discover new FE binary oxides, as opposed to the traditionally explored class of perovskite-structured oxides, using computations. We employed a combination of structure search methods, first principles computations and group-theoretical considerations to find at least six simple oxides as potential ferroelectric candidates. Among them, a previously unexplored candidate, CaO2, was successfully synthesized in the polar Pca21 phase, in accordance with our theoretical predictions. Furthermore, the high occurrence (~40 %) of low-energy polar phases among the oxides considered in this work strongly advocates the possibility of discovery or engineering ferroelectricity in many more simple oxides beyond hafnia.

References:


perovskites [3], as well as new classes of ternary V-VI-VII semiconductors based on Bi and Sb chalcohalides [4,5] that encompass photocatalysts, Rashba distortions and how they can be controlled to enable novel functionality. Applications areas to be discussed will include thermoelectric devices that incorporate high levels of phonon anharmonicity (e.g. SnSe [2]), photovoltaic cells based on photoferroic semiconductors (e.g. Pb and Sn halide perovskites [3]), as well as new classes of ternary V-VI-VII semiconductors based on Bi and Sb chalcohalides [4,5] that encompass photocatalysts, Rashba semiconductors, and topological insulators.


11:00 AM EP01.01.08
Kinetic Monte Carlo Simulations of Organic Ferroelectrics Tim Cornelissen, Indre Urbanaviciute and Martijn Kemerink; Linköping University, Linköping, Sweden.

Organic ferroelectric materials are emerging as a class of materials that may find application in a broad range of fields; for instance, they might solve the ‘missing memory’ problem in printed electronics. However, a full understanding of their switching kinetics on all length and time scales is still lacking. A variety of computational models have been employed to tackle this problem and to study different aspects of organic ferroelectrics. However, these are usually restricted to idealized morphologies or short time scales.

In contrast, we have developed an electrostatic model that, when used in kinetic Monte Carlo simulations, can reproduce the ferroelectric properties and kinetics on experimental time scales and for realistic 3D morphologies. We apply this model on the prototype small molecular ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA).

We simulate hysteresis loops and depolarization curves and find a good agreement with experiments. Like the experiments, the dependence on frequency and temperature of our model results can be interpreted in the framework of thermally activated nucleation limited switching. Specifically, we find two different modes of switching, each associated with their own kinetics and energetics. One mode corresponds to a full rotation of the dipoles, while the other mode only flips the component along the polarization axis. The existence of these two modes is confirmed by molecular dynamics simulations. Both simulation methods find that the second mode has a lower coercive field and thus is the one occurring in polarization switching experiments.

We also investigate the effect of structural disorder on the ferroelectric properties. When the disorder in the system is increased, the retention time decreases dramatically, while the coercive field remains mostly unchanged. For device applications a high retention time and moderate coercive field is required. Aside from providing a detailed insight into polarization switching processes on experimental length and time scales, our model thus is also able to provide guidance in improving the performance of ferroelectric devices.

11:15 AM EP01.01.09
Lone Pair Engineering for Multi-Functional Polar Semiconductors Aron Walsh; Imperial College London, London, United Kingdom.

Beyond the group oxidation state (V), post-transition metals can adopt a lower (V-2) oxidation state, which is associated with a metal s² lone electron pair. Solid-state lone pairs, as found in the compounds formed of ions such as In(I), Sn(II), Sb(III), and Te(IV), are linked to the formation of asymmetric local coordination environments and non-centrosymmetric crystal structures [1]. Lone pairs underpin the physical properties of many piezoelectric, pyroelectric and ferroelectric materials.

I will discuss progress in the understanding of structure and reactivity of lone pair containing compounds, including the driving force for structural distortions and how they can be controlled to enable novel functionality. Applications areas to be discussed will include thermoelectric devices that incorporate high levels of phonon anharmonicity (e.g. SnSe [2]), photovoltaic cells based on photoferroic semiconductors (e.g. Pb and Sn halide perovskites [3]), as well as new classes of ternary V-VI-VII semiconductors based on Bi and Sb chalcohalides [4,5] that encompass photocatalysts, Rashba semiconductors, and topological insulators.


Sulfurization, an anion substitution to oxide materials is considered a progressive route for designing new multi-functional materials artificially and realization of unusual physical properties which do not exist in nature. Sulfur among the other anions has got major attraction due to its isoelectronic nature and large ionic radius compared to oxygen. However, the sulfurization to polycrystalline perovskite other than bulk single crystal perovskite oxides is rarely reported due to the synthetic limitation. Despite this an alternative feasible synthetic route is developed to better understand the structural and physical properties sulfur is doped quantitatively at atomic level. Sulfur doped ferroelectric perovskite [Pt(Zr,Ti)O3] is grown epitaxially by employing the thiourea (CH2,N2,S) solution at various mole ratio using sol gel method. Microscopic analyses of electronic and crystal structures reveal that oxygen ions are substituted by sulfur atoms with tetragonal distortion. In response to this structural phase transition, macroscopic ferroelectric polarization is enhanced, although a band gap is reduced. More details of theoretical calculations and experimental results will be presented in conjunction with a discussion about the potential usage of our synthetic technique in aspect of novel material design.


Nanostructured composite materials have the potential to overcome challenges in many areas of materials research, which cannot be addressed by more conventional single-phase materials. The unique properties of these composite materials often arise due to unique phenomena that occur at the interface between the phases being coupled. An additional control is the anisotropy of the individual phases and the resultant composite, which can be used to control the magnitude and direction of composite properties. For example, ferroelectric and ferromagnetic materials can be combined to form composites with enhanced multifunctional exchange coupling properties. Here, I will present on these composite materials prepared using the electrospinning technique, generating materials with controllable anisotropy and resultant properties. Specifically, Janus type nanofibers, where two phases are coupled longitudinally, are used to create an anisotropic building block that allow access to both surface and bulk properties of each phase. This novel architecture is linked to an anisotropic interface between the coupled phases, and a model is developed relating fiber composition to interfacial area and resulting functional properties. Applications of these composites as zero-power magnetic field sensors will also be presented.

Enhancement of Ferroelectricity in Perovskite Oxides by Sulfurization Muhammad Sheeran, Ill Won Kim, Chang Won Ahn and Tae Heon Kim; Department of Physics and Energy Harvest Storage Research Center, University of Ulsan, Ulsan, Korea (the Republic of).

Ferroelectric HfO2 Growth from HfCl4 –ZrO4 Solid Solution for Stress/Strain Induced Grain Formation and Defect Control at Oxide-Semiconductor Interface Mahmut Sami Kavrik1, Evgenii Chagarov1, Michael Katz2, Norman Stanford2, Albert Davydov2, Min-Hung Lee2 and Andrew Kummel2; 1University of California, San Diego, La Jolla, California, United States; 2National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 3National Taiwan University, Taipei, Taiwan.

Recent findings in ferroelectric HfO2 and discovery of negative capacitance may provide unexpected improvements in CMOS due to scalability of HfO2 and ease of integration. Ferroelectricity can be induced into thin film HfO2 via doping (Al, Y, Gd, Si), but the composition window for each dopant is narrow, sometime only +/-2%. Conversely, Zr doped HfO2 has a broad stoichiometry window (+/- 15%) in which ferroelectricity can be stabilized. The mechanism for stability of the phases of HfO2, ZrO2, and HZO (H2O,Zr/2O3) were investigated with DFT-MD to determine the origin of large process window of ferroelectric phase for the binary HfZrO oxides. It was shown that for all three oxides although the bulk states of the monoclinic phase (m°) are more stable than either the orthorhombic ferroelectric (“f”) phase or tetragonal (“t”) phases and even the surface free energy does not favor f-phase formation. Instead, the higher surface area per unit cell induced by the stress/strain due to post annealing of the amorphous oxide with a crystalline capping layer such as TiN can favor the orthorhombic f-phase since it has a larger area per unit cell than the monoclinic phase; the only requirement is that epitaxial crystallization occurs over at least 5 unit cells of the capping layer. Consistent with this hypothesis, high resolution TEM images of TiN/HZO/Si gate stacks shows regions of epitaxial alignment between HZO and TiN. To improve the consistency of HZO ferroelectric gates, a new method of deposition was developed. The conventional method of Zr doping into HfO2 employs consecutive ALD cycles of ZrO2 and HfO2 in a nanolaminate structure from separate precursors. This process may limit intermixing of the Hf and Zr when the oxide is scaled to 1.5 nm as required for commercial CMOS devices. Furthermore, this process can limit the defect control at the oxide semiconductor interface due to necessity of the precise control of the oxidant between two precursors to maintain precise stoichiometry. Control of oxidant for growth of HZO on SiGe is particularly challenging since oxidant doping must be differentially controlled at the interface to avoid GeOx formation; for example, O3 intermittent dosing during growth of HZO on SiGe has been show to lower the interface defect density. In this work, an alternative method was investigated in which HfCl4 and ZrCl4 solid mixture was employed; this relies upon the vapor phase composition being a function of the solid-state composition. Ferroelectric Hf-ZrO2 was grown in Ni/HZO/TiN/Si structure from single solid mixture precursor abd >25Å/cm2 polarization was observed in 6 nm HfZrO2 grown from single solid mixture. In second step, ferroelectric Hf-ZrO2 on SiO2/Ge(001) was grown from single solid mixture precursor and MOSCAPs were fabricated. Electrical analysis revealed low defect interface formation with Dit of <3x1012 and low leakage current density of <1x10-10 (A/cm2) similar to the control HfO2 devices on SiGe.

ZnO-Activated Low Temperature Reactive Sintering of High Coercive Field Lead Zinc Niobate Based Piezoelectrics Michael Brova1, 2, Beecher H. Watson1 1, Elizabeth Kupp1, 2, Mark Fanton1, Richard Meyer1 and Gary L. Messing1, 2; 1Material Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; 2Materials Research Institute, The Pennsylvania State University, State College, Pennsylvania, United States; 3Applied Research Laboratory, The Pennsylvania State University, State College, Pennsylvania, United States.

A major limitation of many high performance relaxor-based ferroelectric materials is their Curie temperatures. The recently developed Pb(1-x)Zn(x)O3-Pb(Zn1/3Nb2/3)O3-PbTiO3 perovskite solid solution has a high rhombohedral to tetragonal phase transition temperature (Ts) and Curie temperature (Tc), while also possessing a large piezoelectric charge coefficient (d33), mechanical quality factor (Qm), and coercive field (Ec). In order to lower the sintering temperature and minimize number of heat treatments necessary to fabricate PIN-PZN-PT ceramics, we investigated reactive sintering of ZrO-doped PIN-PZN-PT. Reactive sintering reduced the required processing temperature from 1150°C to 800°C when compared to traditional sintering. ZrO-doping stabilized the perovskite phase, reduced the sintering temperature, and significantly increased the reaction and densification. This effect is attributed to a modification in the defect chemistry of PIN-PZN-PT perovskite and an intermediate pyrochlore phase. Electromechanical properties of reactively sintered ZrO-doped PIN-PZN-PT ceramics are compared with those synthesized by conventional sintering.
Influence of Anneal Parameters on Strained TiN Layers in Ferroelectric HfO2 Capacitors

Terary lead-based (Pb(In0.53Nb0.47)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT) ferroelectric ceramics are leading candidates for next-generation textured piezoelectrics. Fabrication of those bulk textured ceramics requires high sintering temperatures of ~1200°C-1250°C to initiate epitaxial growth and long hold times to achieve full texture development. Holding at high sintering temperatures presents a significant challenge because of the volatility of certain constituents (e.g., PbO) and the limitation of developing multilayered actuators, requiring the use of platinum electrodes. In this work, we explore new doping strategies (such as CuO) to reduce the sintering temperature and through reactive sintering to initiate epitaxy at lower temperatures. The effects of CuO doping on the kinetics of perovskite phase formation and reactive sintering were studied using in situ x-ray diffraction as well as diffraction analysis on samples heated under isothermal conditions. Reactive sintering conditions of CuO-doped PIN-PMN-PT ceramics were explored by isothermally treating ceramic green bodies at temperatures below 900°C, with a relative density of 95-97% achieved at remarkably low temperatures of 790°C for 6.7 h. Using a reactive sintering approach, we adapted a reactive templated grain growth (RTGG) system using BaTiO3 microcrystal platelets to seed the phase transformation of the PIN-PMN-PT perovskite at much lower temperatures than previously demonstrated in the TGG process (~1200-1250°C).

References:

3:30 PM DISCUSSION TIME
integration of single-crystal functional oxides films onto the flexible substrates is rare because of the challenging fabrication process. Functional oxides, showing a rich variety of complex emergent properties including memristive effects, photovoltaics, multiferroic effects and so on, have become promising high-tech functional materials beyond their traditional role as dielectrics. Therefore, integration of functional oxides thin films and flexible substrates would add a wide range of exciting applications to the flexible electronics library. Here, we demonstrate a successful fabrication of single-crystal form ferroelectric oxides films on PET flexible substrates. We will discuss the lift-off of the ferroelectric films from the growth substrate by etching a water-soluble sacrificial layer SrAl2O4 layer, the transfer of those 2D single-crystal membranes onto the PET substrates and the functional electronic properties of the resulting ferroelectric thin films/PET flexible memristors. Moreover, we will show the transfer of other oxides films using the same lift-off method and discuss some potential interesting applications like flexibe bulk photovoltaic devices and so on.

SESSION EP01.03: Poster Session I: Growth and Characterization of Piezoelectric, Pyroelectric and Ferroelectric Materials
Session Chairs: David Ginley and Abdelilah Sloui
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP01.03.01
Flexible Robust and High-Density FeRAM from Organic Ferroelectric Nano-Lamellae by Self-Assembly
Menglan Guo1, Jianyong Jiang1, Jianfeng Qian1, Chen Liu1, Jing Ma1, Ce-Wen Nan1 and Yang Shen1,2; 1School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; 2Center for Flexible Electronics Technology, Tsinghua University, Beijing, China.

Ferroelectric memory device is endowed with high data storage density by nanostructure designing, while the robustness of ferroelectrics is also impaired. Especially for flexible memories based on organic ferroelectrics, low Curie point limits their thermal endurance and stability. Herein, we fabricate a ferroelectric random access memory (FeRAM) based on ferroelectric lamellae by self-assembly of poly(vinylene fluoride-co-trifluoroethylene). The FeRAM exhibits high data storage density and promoted thermal stability. Written data shows enhanced thermal endurance and little volatilization after thermal cycles. These results provide a novel strategy for improving robustness of organic flexible FeRAMs.

EP01.03.02
Effects of Post-Draw Processing on the Structure and Functional Properties of Electrospun PVDF-HFP Nanofibers
Adriano A. Conte1, Khosro Shirvani1, Wei Xue1, Xiao Hu1 and Vince Beachley1; 1Biomedical Engineering, Rowan University, Glassboro, New Jersey, United States; 2Mechanical Engineering, Rowan University, Glassboro, New Jersey, United States; 3Physics, Rowan University, Glassboro, New Jersey, United States.

The current surge in wearable electronics has initiated a need for alternative energy sources. Energy harvesters that employ piezoelectric materials are capable of harnessing the mechanical energy from muscular contractions to power portable devices. The present study examined the properties of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) nanofibers fabricated from conventional electrospinning, and an automated track collector system that contains a post-drawing component. The polymer solution was originally processed by means of the traditional technique, flat-plate electrospinning, which produced a fiber arrangement with random orientations. When carrying out mechno-electrical testing and analysis these fibers yielded negligible voltage. The solution was subsequently processsed employing a post-drawing electrospinning procedure, exclusive to our research laboratory, that permitted fiber alignment and individual nanofiber post-drawing immediately upon collection, prior to total solvent evaporation. Fibers that endured post-drawing displayed an increase in crystal alignment in the direction of the fiber axis (verified by polarized FTIR), and resulted in higher voltages than undrawn fibers and fibers from the traditional electrospinning method. It was examined that fibers produced by means of the post-drawing technique, with varying draw ratios (DR=Final length/Initial length) including DR-2 and DR-3, exhibited improved piezoelectric characteristics. Mechanical properties of the nanofibers were also enhanced as a result of post-drawing. This investigation suggests that the post-drawing practice results in PVDF-HFP nanofibers that are more suitable for piezoelectric applications than conventionally electrospun nanofibers.

EP01.03.03
Epitaxial AIN Thin Film for High Performance Surface Acoustic Wave Devices
Junning Gao, Jianbai Jiang and Guoqiang Li; School of Materials Science and Engineering, South China University of Technology, Guangzhou, China.

Aluminum nitride is a wide bandgap piezoelectric semiconductor that has superior hardness and thermal conductivity. It also has the electromechanical coupling factor and dielectric constant that fit perfectly for the band width needed in bulk acoustic wave (BAW) filters which serve at tremendous quantity in smart phones. Over the years, polycrystalline thin films of AIN have been used almost exclusively as the piezoelectric substrate in commercial BAW filter products. It is also a potentially outstanding candidate for commercial surface acoustic wave (SAW) devices. However, a major disadvantage for polycrystalline AIN used in SAW devices is the existence of grain boundaries which increase insertion loss and pass band ripple. The main stream SAW filters choose LiNb(Ni)O3 single crystalline wafer as the piezo-substrate at present. To realize the full potential of AIN in SAW devices, it is necessary to refrain the negative influences of the grain boundaries, which make high quality single crystalline or epitaxial AIN highly desirable. This presentation will talk about the results of a study on the SAW devices fabricated on epitaxial AIN thin films. The films were grown on (0001) sapphire substrates by metalorganic chemical vapor deposition. The film was a c-axis oriented single crystalline AIN thin film with high density of AIN (0002) facets. The film thickness was around 100 nm. The SAW devices with center frequencies of 355 MHz and 714 MHz both exhibit much suppressed pass band ripples and improved out of band rejections comparing to those on polycrystalline thin films. It is therefore verified that the epitaxial form of AIN is better suited for high quality SAW devices.

EP01.03.04
Atomic-Scale Growth of GdFeO3 Perovskite Thin Films by a Novel Bimetallic Precursor
Christoph Bohr1, Pengmei Yu2, Mateusz Scigaj2, David Graf1, Cornina Hegemann1, Thomas Fischer1, Mariona Coll3 and Sanjay Mathur1; 1Institute for Inorganic Chemistry, University of Cologne, Cologne, Germany; 2Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC, Campus UAB, Barcelona, Spain.

Multiferroic thin films of GdFeO3 are of significant importance due to their G-type antiferromagnetic behaviour and thus potential candidates for magnetic storage devices. Fabrication of single-phase GdFeO3 films is challenging due to demixing into homometallic oxides and formation of thermodynamically preferred Gd2Fe4O9. Herein we report the first selective synthesis of epitaxial GdFeO3 perovskite films through atomic layer deposition of a bimetallic precursor [GdFe(OBu)2(C5H4N)] on SrTiO3. Based on the preformed Gd-Fe bonds in the molecule, phase pure GdFeO3 films were accessible by atomic
HfO₂ films had multidomain structures composed of ferroelectric PbTiO₃. The engineering of nanoscale ferroelastic structures has attracted significant attention in the last few years. These nanostructures are reconfigurable and possess non-volatile properties, making them attractive for applications that harness the changes in electronic properties that arise at the ferroelectric-ferroelastic domain walls. applications of CeO₂-HfO₂ solid solutions have been reported in high-k dielectrics, high-k gate dielectrics, and ferroelectric switching.

Lead zirconate titanate Pb(Zr,Ti)O₃ (PZT) is a ferroelectric material with excellent dielectric and piezoelectric properties. PZT films have been prepared using various fabrication techniques such as sol-gel process, metal organic decomposition, and pulsed laser deposition. Recently, hydrothermal method has attracted increased attention because it could produce homogeneous and malleable, especially when using a high-alkaline medium and surfactant.

Lead zirconate titanate Pb(Zr,Ti)O₃ (PZT) is a ferroelectric material with excellent dielectric and piezoelectric properties. PZT films have been prepared using various fabrication techniques such as sol-gel process, metal organic decomposition, and pulsed laser deposition. Recently, hydrothermal method has attracted increased attention because it could produce homogeneous and malleable, especially when using a high-alkaline medium and surfactant.

Layer deposition experiments. The suppression of phase separation was validated by X-ray diffraction and X-ray photoelectron spectroscopy. Furthermore, magnetic properties of the material were determined by temperature dependent magnetization measurements and demonstrated comparable results as reported for thin films. Based on these results, the presented bimetallic precursor is suitable for the fabrication of high performance magnetic data storage devices.

**EP01.03.05**

**Fabrication of Ferroelectric CeO₂-HfO₂ Solid Solution Thin Films and Their Characterization**

Takahisa Shirai1, Sujin Choi1, Takao Shimizu2, Takanori Kiguchi1, Hiroshi Funakubo2 and Toyohiko Konno2; 1Tohoku University, Sendai, Japan; 2Tokyo Institute of Technology, Yokohama, Japan.

Lead zirconate titanate Pb(Zr,Ti)O₃ (PZT) is a ferroelectric material with excellent dielectric and piezoelectric properties. PZT films have been prepared using various fabrication techniques such as sol-gel process, metal organic decomposition, and pulsed laser deposition. Recently, hydrothermal method has attracted increased attention because it could produce homogeneous and malleable, especially when using a high-alkaline medium and surfactant.

Applying an out-of-plane dc biased voltage to the domain and superdomain patterns reveals that the ferroelastic structures in PbTiO₃ are electrically very malleable, especially when a high-alkaline medium and surfactant are added into the PZT precursor solution to dissolve the precursor source in the aqueous solution and to control the crystal growth, respectively. After hydrothermal reaction with stirring, PZT particles were separated from liquid phase and followed by rinsing and drying several times. When the surfactant was not added into the reaction solution, large-sized PZT particles with rough surfaces were synthesized. On the other hands, nano-sized PZT particles with facet were synthesized by adding the surfactant and it was confirmed that the added surfactant had the effect of inhibiting the growth of the certain faces of particles. The simple spot pattern in the electron diffraction pattern revealed that this nano-sized PZT particle synthesized by the surfactant-assisted hydrothermal method at 230°C had high crystallinity and it was a single crystal. Unlike conventional fabrication techniques with high temperature crystallization process above 600°C, PZT nanocrystals with high crystallinity were obtained by the surfactant-assisted hydrothermal synthesis.

**EP01.03.06**

**EP01.03.07**

**Engineering Domain and Superdomain Architectures in PbTiO₃ Thin Films**

Eric Langenberg1, David Burgallo Ferrón2, Megan E. Holtz3,4, Hanjong Paik1, Elias Ferreiro-Vila2, Eva H. Smith1, Hari P. Nair1, David Muller2, Gustau Catalán3, Neus Domingo4, Francisco Rivadulla2 and Darrell G. Schlenk1,2; 1Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2CQUS-University of Santiago de Compostela, Santiago de Compostela, Spain; 3School of Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; 4Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, Barcelona Institute of Science and Technology, Bellaterra, Barcelona, Spain; 5Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York, United States.

The engineering of ferroelastic structures has attracted significant attention in the last few years. These nanostructures are reconfigurable and non-volatile, making them attractive for applications that harness the changes in electronic properties that arise at the ferroelectric-ferroelastic domain walls or novel (nano-)electromechanical devices based on ferroelastic switching. Here, we study the interplay between epitaxial strain, film thickness, and electric field in the creation, modification, and design of distinct ferroelectric-ferroelastic domain and superdomain architectures in the archetype PbTiO₃ thin films. The suppression of phase separation was validated by X-ray diffraction and X-ray photoelectron spectroscopy. Furthermore, magnetic properties of the material were determined by temperature dependent magnetization measurements and demonstrated comparable results as reported for thin films. Based on these results, the presented bimetallic precursor is suitable for the fabrication of high performance magnetic data storage devices.
stability, however, of the electrically written a/c superdomain structures strongly depends on strain: under low tensile strain they are stable for days, whereas at moderate tensile strains they rapidly convert into a/a2 superdomains—the same equilibrium state as the a/a2-grown films.

EP01.03.08
Fabrication and Properties of Multiferroic Composites by PLD for Voltage-Driven Magneto-Optic Spatial Light Modulator Yuichi Nakamura, Naohide Kamada, Taichi Goto, Hironaga Uchida and Mitsuteru Inoue; Toyohashi University of Technology, Toyohashi, Japan; JST PRESTO, Kawaguchi, Japan.

Spatial light modulators (SLMs) are devices to control the amplitude, phase and polarization of light and are an important component of such as optical communication and optical computing systems. Magnetooptic SLM (MOSLM) using Faraday rotation can modulate light through the direction of magnetization with ultra-high speed and robustness. A voltage-driven MOSLM, which is composed of piezoelectric and magnetic materials, can be driven with relatively low power consumption. The structure in which columnar magnetic materials are embedded in the piezoelectric material is expected to increase the modulation of light easily by changing the magnetization direction of the magnetic layer. In this way, the MOSLM, simultaneous growth of the piezoelectric material such as Pb(Te1/2Zr1/2)O3 (PTZ) and BaTiO3 (BTO) and a magnetic rare earth iron garnet (Bi:RIG) is needed. In this study, we investigated the growth conditions for obtaining the aligned BTO film on nonmagnetic single crystalline Gd3Ga5O12 (GGG) substrate and Bi:RIG/BTO composites.

At first, we checked several materials which can grow epitaxially on GGG substrate by pulsed laser deposition (PLD) method since it would be required to form columnar structure by simultaneous growth technique. As a result, we found that the (111) oriented BiFeO3 (CFO) film could be grown on GGG (111) substrate. Furthermore, the CFO film preferentially oriented in the (111) plane could also be grown on CFO buffered GGG (111) substrate. Pole figure analysis of this sample revealed that the (111) oriented CFO film has two in-plane orientations in the plane. This means that this aligned film of CFO/GGG is not single crystalline feature but polycrystal with two specific crystal alignments. However this would not be a crucial issue to grow columnar structure by simultaneous growth; the relation between CFO and Bi:RIG crystal at the interface may be kept since the columnar size is usually several 10 to 100 nm order and would be smaller or comparable to the that of CFO grain. The detail about the composite films of CFO and Bi:RIG using this CFO buffered GGG substrate will be discussed. This work was supported in part by the Grants-in-Aid for Scientific Research (S) 26220902, (B) 16H04329 and Strategic international research network promotion program No. R2802.

EP01.03.09
Structural, Magnetic and Electrical Characterization of Nanoscale Ba(Ti1-xFex)O3—Stoichiometric Control Over a Multiferroic Oxide Using a Near-Room Temperature Non-Aqueous Synthesis Method Julien Lombardi1, Stephen O'Brien1 and Zheng Gai1; City College of New York, New York, New York, United States; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Low temperature chemical solution processing of nanocrystalline perovskite oxides can be attractive due to the ability to (i) enable precise control over stoichiometry and structure in the product and (ii) offer thin film integration options in device electronics for which high temperatures are not suitable. Ba(Ti1-xFex)O3 is a useful system for the exploration of multiferroic properties as a function of structure, based upon a model of interstitial substitution of the B site cation. A series of iron-substituted barium titanate nanocrystals were synthesized using a hybrid sol-gel synthesis method, known as gel-collection, at 60°C. The as-prepared nanocrystals are fully crystalline, uniform in size (~8 nm) and dispersible in polar organic solvents. The synthesis method could effectively control Fe substitution over a full range of x = 0.0, 0.1, 0.2, 0.3, 0.5, 0.75 and 1.0, enabling a systematic study of the relative effect of Fe addition to the parent BaTiO3 compound. In the case of x = 0.0-0.3, a model of Fe doping suffices with predictable trends in magnetic and dielectric behavior. In the case of x = 0.5 and up, Fe impacts the structure. Powder X-ray diffraction (XRD) initially indicated single phase nanocrystalline samples for x < 0.3. PDF analysis… size and morphology of the nanocrystals was analyzed by the transmission electron microscope (TEM) showing uniform shape and size (~8 nm) nanocrystals. Magnetic characterization (both magnetic hysteresis loops and zero field and field cooling measurements) was carried out on a magnetic properties measurement system (MPMS) and showed increased magnetization with increasing Fe ion concentration. Frequency dependent dielectric measurements were performed at room temperature on spin coated 0-3 nanocomposites of BTF and polyvinyl-pyrrolidone and show stable dielectric constants at 1 MHz of 27.0, 26.0, 24.6, 24.5, 23.6, and 22.2 for BTF samples with x = 0, 0.1, 0.2, 0.3, 0.5, and 0.75 concentrations respectively. The decrease in dielectric constant with increasing Fe concentration is due to the contribution of the electrons in the d orbital leading to a more leaky material.

EP01.03.10
Engineering Growth of Magnetostriective Thin Films by Pulsed Laser Deposition for Magnetoelastic Coupled Future Voltage Controlled Spintronic Devices Rajesh Kumar Rajagopal1, J. Arout Chelvane2 and Venimadhav Adyam1; IIT Kharagpur, West Bengal, India; Defence Metallurgical Research Laboratory, Hyderabad, India.

Multiferroic devices, consisting of coupled ferromagnetic and ferroelectric phases, are of great importance in the drive towards creating faster, smaller and more energy efficient voltage control magnetic random access memory (MRAM) devices for information storage and communication technologies. Such devices require a strong magnetoelastic coupling between the ferromagnetic and the ferroelectric interface, this is obtained by using large magnetostriiction materials as a ferromagnetic layer. Magnetostriective Fe based amorphous alloys of Fe50Co17Si12B10 (FeCoSiB) and Fe51Ga19 (GdFe) amorphous alloys are of great interest for their ultra high saturation magnetization, low coercivity, and high magnetic permeability. Wide varieties of the growth techniques are available for the fabrication of thin films, among the methods, pulsed laser deposition (PLD) is a thin film growth technique which has the advantage of stoichiometric transfer of the elements on to the substrate. By understanding the growth of amorphous thin film by PLD has the advantage of the in-situ growth of high quality epitaxial ferroelectric materials are grown at high temperature, and magnetostriactive materials can be are grown on top of the ferroelectric thin film.

In this present study, we have prepared the highly magnetostriective FeCoSiB and GdFe thin films deposited on the Si substrate using PLD. The prepared films show the soft ferromagnetic property with coercivity of 25 Oe as given in the Fig. 1(a). Pulsed laser deposition induced uniaxial anisotropy in the GdFe thin shown in Fig. 1(b). The thickness dependent composition variation of the thin film was analysed using Auger electron spectroscopy. We also present the growth of this alloy on oxide substrates, magnetotransport characteristics and magnetic domain by Magnetic force microscopy (MFM).

EP01.03.11
Growth of Orientation-Controlled (K,Na)NbO3 Thick Films at 240°C by Hydrothermal Method and Their Piezoelectric Applications Hiroshi Fujikubo1, Akinori Tateyama1, Yoshishiro Itou1, Yoshiko Nakamura1, Takao Shimizu2, Yuichiro Orimo3, Minoru Kurosawa4, Hiroshi Uchida4, Takahisa Shirasuna5, Takamori Kiguchi1, Toyohiko Konno6 and Nobuhiro Kumada3; Tokyo Institute of Technology, Yokohama, Japan; Sophia University, Tokyo, Japan; Tohoku University, Sendai, Japan; Yamazaki University, Koufu, Japan.

(K, Na)NbO3 has a relatively high piezoelectric property among lead-free piezoelectric materials with high environmental adaptability. Their films have been prepared by various methods. Hydrothermal method can prepare (K, Na)NbO3 films at low temperature [1-3] and feasible to control film composition that has been pointed out to be difficult for various preparation methods due to high deposition temperature and vapor pressure of K and Na elements. In this study, orientation-controlled (K,Na)NbO3 films with 1-100 μm in thickness were prepared by hydrothermal method and their crystal structure,
Polymer piezoelastic materials are wildly used in wearable smart devices as they are flexible lightweight, stretchable, environment-friendly and chemically stable, and poly(vinylidenefluoride-co-trifluoroethylene) (P(VDF-TrFE)) is a representative piezoelectric polymer. To construct piezoelectric polymer fibers, electrospinning is a versatile technique. Compared to randomly distributed electrospun fibers, aligned P(VDF-TrFE) fibers possess better electrical properties and larger proportion to mechanical stimuli. Here, we demonstrate a simple dynamical mechanical induced process which enables the formation of large-scale highly aligned electrospun P(VDF-TrFE) fibers obtained under low rotation speed. And the resultant fibers exhibit enhanced mechanical and piezoelastic properties and can be further used as wearable motion sensors.

We collect the initial P(VDF-TrFE) fiber using low speed rotating drum. The as-spun P(VDF-TrFE) fibers still contain residual solvent, thus they are easy to deform under applied external force. The electrospun P(VDF-TrFE) thin film is then peeled off the aluminum foil and mounted in the clamps of a linear travel stage driven by a controller for the following mechanical stretching process. As a result, the initial orientations can be globally unified, which leads to the alignment of a large amount of electrospun P(VDF-TrFE) into highly oriented fiber bundles. The ~80% aligned P(VDF-TrFE) fibers are further twisted into bundles and yarns and made into wearable sensors to monitor the bending angle of the elbow. The output signal for bending 45°, 90°, and 135° are 10.6 mV, 20.3 mV, and 42.5 mV, respectively. Furthermore, multiple P(VDF-TrFE) fiber bundles can be used in a combined way to monitor the direction of arm swing.

**References**

(XRD), atomic force microscopy (AFM), and spectroscopic ellipsometry in order to determine what thickness of ScN would produce the least amount of these domain variances. Preliminary XRD coupled scans show highly oriented ScN on Al2O3 with glancing angle scans showing no additional phases present in the ScN film. AFM surface analysis showed root mean square (RMS) roughness between 0.433 nm and 0.911 nm for films between 0.5 nm and 10 nm, corresponding to one to two monolayers of roughness. Additionally, thin films of Al1−xScxN films were deposited both on bare substrate and with the additional ScN wetting layer, at similar thicknesses to the ScN thin films. These were also characterized using XRD, AFM, and spectroscopic ellipsometry to determine the effect of the ScN thickness and domains on the Al1−xScxN film crystallinity and piezoelectric properties.


EP01.03.15 Magnetron Sputter Deposition of Pyroelectric PZT Thin Films—From Simulation to Experiment Peter K. Petrov1, Andrey Berenov1, Ryan Bower1, Sarah Fearn1, Roger Fecher1, Lars Allers2, Philippa Stephens2, Brian Moffat1, John Phair1, Valery Volpys1, and Andrey Kozylev4; 1Imperial College London, London, United Kingdom; 2Korus Technology Ltd, Newington, United Kingdom; 3Pyreos Ltd, Edinburgh, United Kingdom; 4St Petersburg Electrotechnical University “LETI”, St Petersburg, Russian Federation.

Thin films of lead zirconate titinate (PbZr1−xTiO3 - PZT) are of considerable interest for a range of applications, including piezoelectric MEMS (with x=0.52) and pyroelectric thermal IR sensing (with x=0.30 [1]). Thin films of PZT (x=0.15 to 0.42) have in the past been grown onto platinum Si substrates by sputtering from multiple metal targets [2], but there are considerable technological benefits to deposition from a single ceramic target [3].

This paper will discuss the process of magnetron sputter deposition of PZT thin films from a single ceramic target. We used Monte-Carlo simulation method based on the algorithm, presented in [4], to describe the sputter atoms transport process and their delivery on the substrate. The modeling was carried out taking into account the geometry and dimensions of the deposition system, and the sputter target erosion zone. A complementary SIMS analysis of the PZT sputter target was carried out to identify the type of sputtered particles (e.g. single atoms, binary compound, clusters), which were further used in the simulation process.

Finally, we will present the structural and electrical properties of the sputtered PZT films (e.g. crystal structure, stoichiometry, dielectric permittivity, loss, pyroelectric coefficient etc.) and discuss their dependence on the existence of particular species in the gas phase during the sputtering process.

Acknowledgements
This work was supported by Innovate UK under Project “Advanced manufacturable sputtering of high performance pyroelectric thin films (HiPer-Spy)”, Ref No: 103525.

References

EP01.03.16 Initiated Chemical Vapor Deposition of Multilayered P(VDF-TrFE) Thin Films—Controlling the Chemical Composition Along the Thickness Omid M. Moradi1, Ali Tufani1, Gozde Ozaydin Ince1, 2, 3 and Ibrahim B. Misirlioglu4, 5, 2; 1Materials Science and Nanoengineering, Sabanci University, Istanbul, Turkey; 2Nanotechnology Research and Application Center (SUNUM), Sabanci University, Istanbul, Turkey; 3Center of Excellence for Functional Surfaces and Interfaces (EFSUN), Sabanci University, Istanbul, Turkey; 4Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey; 5Integrated Manufacturing Technologies Research and Application Center, Sabanci University, Istanbul, Turkey.

Fabrication of ferroelectric polymers at lower temperatures, thickness control and film conformity in polymeric multilayer structures are required for full integration of the ferroelectric polymers to the modern integrated devices. Also, designing of multilayer ferroelectric films requires precise control over the deposition parameters.

We use Initiated Chemical Vapor Deposition (iCVD) method to deposit 10-30 nm ferroelectric layers and fabricate multilayer poly [(vinylidenefluoride-co-trifluoroethylene) [P(VDF-TrFE)] thin films. We control the thickness of the layers and control the chemical composition in each layer along the thickness. Also, the change in dielectric constant and dielectric loss at moderately low and high frequencies for each multilayer configuration will be discussed. Hence, we report the frequency dependency of dielectric constant, loss tangent, imaginary electric modulus of multilayered thin films.

EP01.03.17 Multiferroic Polaron in Doped Perovskite Oxides Takahiro Shimada, Tao Xu, Takayuki Kitamura and Hiroyuki Hirakata; Kyoto Univ, Kyoto, Japan.

Control over the electron behaviors is essential for the quest of the unusual coexistence of seemingly conflicting physical properties in condensed matter science. Although the coexistence of ferroelectricity, conductivity and magnetism in a single-phase material has attracted considerable attention due to the fundamental interest and tremendous technological promise, the mutually exclusive mechanisms among them hinder the discovery of multifunctional conducting multiferroics. Here, we propose a novel material design approach for electron engineering, by which we realize an unusual coexistence of these conflicting properties. We demonstrate from first-principles that the appropriate mechanical strain turns the excess electrons in doped BaTiO3 from free carrier configuration to localized polaronic state through the modulation of electron-phonon coupling. The resulting localized spin-polarized electron survives the host ferroelectricity and consequently manifests itself as multiferroic polaron. The multiferroic properties coexist with the electronic carrier configuration to localized polaronic state through the modulation of electron-phonon coupling. The resulting localized spin-polarized electron.

EP01.03.18 Theoretical Prediction of Piezoelectric and Thermodynamic Stability of New LiNbO3-type Al(Sc,In,Tl)O3 Kaoru Nakamura; CRIEPI, Yokosuka, Japan.

LiNbO3 structure, belongs to the space group of R3c, is frequently referred as “strained perovskite structure”. Recently, many compounds have found to be possible to form LiNbO3-type structure under the high-pressure condition, and some of them were quenchable phase. By systematic first-principles prediction of piezoelectricity and phase stability of possible combination of A-site and B-site ions, we have found new Al-based LiNbO3-type piezoelectric materials. Dynamical stability analysis on AlScO3, AlInO3, and AlTlO3 showed no unstable phonon mode. Formation energies of each compound were predicted to show negative value at high pressure. Predicted piezoelectric constants e33 and d33 of each compound were larger than those of LiNbO3.
Especially, $e_{33}$ and $d_{33}$ values of AlTiO$_3$ were anomalously large to be 10.7 C/m$^2$ and 56.6 pC/N. By utilizing the formalism of density functional perturbation theory, piezoelectric constants of each compound were decomposed into elastic and dielectric contribution from each atom. As a result, large piezoelectricity of Al(Sc,In,Tl)O$_3$ was found to be originated in the large strain-displacement coupling.

EP01.03.19
Effects of Structure Parameters on Piezoelectricity in Wurtzite Materials—First-Principles and Statistical-Learning Calculations

Hiroyoshi Momida and Tamio Oguchi; Osaka Univ, Osaka, Japan.

Piezoelectric wurtzite materials such as ZnO and GaN have recently received a lot of attention as piezotronics and piezo-phototronics device materials. The wurtzite-type piezoelectric materials, especially AlN, have another advantage of applicability in high-temperature environments such as sensors in automobile engines, because their noncentrosymmetric crystal structures are thermodynamically stable even at high temperatures. However, the piezoelectric constants of wurtzite-type materials are generally much smaller than those of the perovskite-based materials such as Pb(Zr,Ti)$_3$O$_5$ by a few orders. It remains a challenge to explore better piezoelectric wurtzite materials, and there have been many reports aiming to enhance piezoelectricity by element doping into parent materials. Among the wurtzite materials, the highest piezoelectricity has been experimentally discovered for ScAl$_2$N (about 25 pC/N for $x \sim 0.5$). Novel low-cost materials, which are superior to ScAl$_2$N, have not been synthesized yet as there are no clear and general material-design criteria practically usable for enhancing the piezoelectricity of wurtzite materials.

In this study, we calculate longitudinal piezoelectric constants ($e_{33}$) of more than a dozen binary wurtzite materials, which are listed in a structure database, by using the first-principles methods, and we investigate possible correlations between the piezoelectric constants and several material parameters using the statistical-learning methods [1]. As a result, it is theoretically shown that wurtzite materials with high $e_{33}$ generally have small lattice constant ratios ($c/a$) almost independent of constituent elements, and approximately expressed as $e_{33} \propto c/a - (c/a)_{b}$ with ideal lattice constant ratio ($c/a$)$_b$. We find that this relation also holds for highly-piezoelectric ternary materials such as the calculated $e_{33}$ values of ScAl$_2$N [2]. Therefore, this material-design criterion can be applied to the case in doped ternary materials. We have conducted a computational search for high-piezoelectric wurtzite materials by identifying materials with smaller $c/a$ values. It is theoretically proposed that the piezoelectricity of ZnO can be significantly enhanced by partial substitutions of Zn with Ca. Though the calculated value of $e_{33}$ of CaZn$_{0.5}$O is still smaller than that of ScAl$_2$N, we expect that CaZn$_{0.5}$O is at a definite advantage in material costs and natural abundance of constituent elements.

References:


EP01.03.20
Physical Reality of the Preisach Model for Organic Ferroelectrics

Tim Cornelissen¹, Indre Urbanaviciute¹, Xiao Meng², Rint Sijbesma² and Martijn Kemerink¹; ¹Linköping University, Linköping, Sweden; ²Eindhoven University of Technology, Eindhoven, Netherlands.

Since the seminal work by Ferenc Preisach in 1935, the so-called Preisach model, in which a real, non-ideal ferroic material is described as the sum of a distribution of ideal ‘hysteres’, has been a cornerstone in the fields of ferromagnetism and ferroelectricity. However, the physical reality of the model in ferroelectrics has been hard to establish, limiting its further applicability and utility. Here, we show how an experimental Preisach distribution-based analysis can quantify the energetic disorder and elucidate the concomitant dispersive polarization switching kinetics common for different classes of ferroelectrics.

We experimentally determine the Preisach (hysteron) distribution for two differently structured ferroelectric systems, the liquid crystalline benzenetricarboxamide (BTA) and the polycrystalline copolymer P(VDF-TrFE). For BTA a broad circular distribution is found, in contrast to the narrow elliptical distribution for P(VDF-TrFE). We explain how this broadening can be directly related to the materials’ morphology: in BTA the ferroelectric domains consist of strongly interacting columns, while in P(VDF-TrFE) consists of non-interacting crystallites. Our explanation is supported by simulations using a simple electrostatic model. The offered insight in the shape of the Preisach distribution is especially relevant for ferroelectric multi-bit data storage applications.

The model also provides an explanation for the dispersive switching kinetics observed in most ferroelectrics, and the underlying distribution in switching times. By measuring the switching kinetics of discrete parts of the Preisach plane, we can directly extract this distribution. The combination of the Preisach model, the thermally-activated nucleation-limited switching formalism and the adapted Kolmogorov–Avrami-Ishibashi theory provides a full and consistent description of the measured macroscopic switching kinetics in terms of device morphology and energetic disorder.

Our results reveal that the in principle mathematical construct of the Preisach model has a strong physical basis and is a powerful tool to explain polarization switching processes of different types of ferroelectrics.

EP01.03.21
First-Principles Calculations of Lattice Dynamics and Thermodynamic Properties of the New Pre-Perovskite PbTiO$_3$ Phase

Mengqian Zhou¹,², Yi Wang¹, Yanhua Ji¹, Long-Qing Chen¹,² and Ce-Wen Nan¹; ¹School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; ²Department of Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

Recently, the emergence of pre-perovskite PbTiO$_3$ nanowires has attracted increasing research interests. In this work, systematic first-principles calculations were performed to investigate the lattice dynamics and thermodynamic properties of the new pre-perovskite PbTiO$_3$ phase. The stability of pre-perovskite PbTiO$_3$ at finite-temperature was analyzed in terms of the lattice contribution, and its thermodynamic properties were obtained and compared with those of cubic and tetragonal PbTiO$_3$. The pressure-temperature phase diagram for these three types of PbTiO$_3$ was established, indicating that pre-perovskite PbTiO$_3$ can be stable under negative pressure. These theoretical insights are useful for understanding the origin of phase transitions among pre-perovskite, traditional cubic and tetragonal PbTiO$_3$ phases, hence providing meaningful guidance for future experimental study and potential applications of pre-perovskite PbTiO$_3$.

EP01.03.22
A Rhombohedral Ferroelectric Phase in Epitaxially-Strained Hf$_5$Zr$_9$O$_{28}$ Thin Films

Yingfen Wei¹, Pavan Nukala¹,³, Mart Salverda¹, Sylvia Matzé², Hongjian Zhao¹, Janno Momand⁴, Arnaud S. Everhardt¹, Graeme R. Blake¹, Philippe Lecoeur⁵, Bart J. Kooi¹, Jorge Iñiguez⁶, Brahima Dkhil⁷ and Beatriz Noheda⁸; ¹University of Groningen, Groningen, Netherlands; ²Center for Nanoscience and Nanotechnology, Université Paris-Saclay, Paris, France; ³Materials Research and Technology Department, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg; ⁴Laboratoire Structures, Propriétés et Modélisation des Solides, Université Paris-Saclay, Paris, France.

Our results reveal that the in principle mathematical construct of the Preisach model has a strong physical basis and is a powerful tool to explain polarization switching processes of different types of ferroelectrics.
After decades of searching for robust nanoscale ferroelectricity that could enable integration into the next generation memory and logic devices, hafnia-based thin films have appeared as the ultimate candidate because their ferroelectric (FE) polarization becomes more robust as the size is reduced. This exposes a new kind of ferroelectricity, whose mechanism still needs to be understood. Towards this end, thin films with increased crystal quality are needed. We report the epitaxial growth of HfO2/ZrO2 (HZO) thin films on (001)-oriented La0.6Sr0.4MnO3/SrTiO3 substrates. The films, which are under epitaxial compressive strain and are (111)-oriented, display large FE polarization values up to 34 μC/cm² and do not need wake-up cycling. Structural characterization reveals a rhombohedral phase, different from the commonly reported polar orthorhombic phase. This unexpected finding allows us to propose a compelling model for the formation of the FE phase. In addition, these results point towards nanoparticles of simple oxides as a vastly unexplored class of nanoscale ferroelectrics.

**EP01.03.23**

Mesoscopic Varistor Modelling Kyle Taylor and Erion Gjonaj; Institut für Theorie Elektromagnetischer Felder, Technische Universität Darmstadt, Darmstadt, Germany.

This newly developed modelling framework for the simulation of electric current flow in ZnO varistors is based on an equivalent circuit representation of the varistor microstructure where the grain boundaries are represented by nonlinear resistors in the circuit. The present approach extends on similar models introduced earlier by including the effect of mechanical stress on the grain boundary conductivity. This effect is based on the coupling between the semiconducting and the piezoelectric properties of ZnO. The stress-induced piezoelectric polarization modifies the interface charge at the grain boundaries. This changes the effective potential barrier and therefore leads to a stress induced modification of the current voltage characteristics of the grain boundary. The model used for the calculation of single grain boundary conductivities is based on the theory of Blatter et al. and Verghese et al. It includes a self-consistent solution for the interface charge and for the potential barrier of the boundary, taking into account the local stress in the grain. Using the above model, the grain boundary potential barriers are parametrized with respect to voltage and piezoelectric charge density. Such tabulated data can be easily incorporated in the modeling of larger varistor structures. 2D and 3D varistor models are constructed using appropriate Voronoi tessellations as well as measurement data obtained by EBSD scans. The mechanical stress distribution within the material is calculated by FEM. The electrical resistance of each grain boundary is then determined according to the local voltage and piezoelectric polarization charge. Finally, the electric current flow patterns within the microstructure and the corresponding current-voltage characteristic of the bulk material are obtained by solving the nonlinear circuit equations for each applied voltage and mechanical stress condition of the sample. The simulated characteristics reveal a significant sensitivity of the bulk electrical conductivity to mechanical stress. Furthermore, the simulations demonstrate the current concentration effect in the voltage breakdown region. Further topics of interest, which have been addressed by the modeling, include the influence of microstructural inhomogeneities, the investigation of the properties of purposely tailored microstructures (such as sandwiched polycrystalline layers) and the influence of sintering temperature on residual stresses and varistor characteristics.

**EP01.03.24**

Improvement in Magnetic Properties by Coating Surfactants on M-Type Strontium Hexaferrite Tai P. Poudel1, Deepa Guragain1, Jeetikanta Mohapatra2, Sunghyu Youn1, J. Ping Liu1 and Sanjay R Mishra1; 1Department of Physics and Material Science, University of Memphis, Memphis, Tennessee, United States; 2Department of Physics, The University of Texas at Arlington, Arlington, Texas, United States; 3Gunsan National University, Gunsan, Korea (the Republic of).

M-type SrFe2O4 were synthesized via auto consumption method and coating Polyvinylpyrrolidone (PVP) Polyethylene Glycol (PEG) and Cetyltrimethyl Ammonium Brome (CTAB) on crystals of hexaferrite. The effects of PVP, PEG and CTAB on the formation, structure, morphology, magnetic and dielectric properties of the SrFe2O4 nanoparticlewere studied. X-ray diffraction results show perfect match of phase of SrFe2O4. Morphological changes including grain and lattice parameter were seen increased with coating. With the coating of PVP, PEG and CTAB, powder particles growth can be seen in hexagonal plates. Increase in saturation magnetization, Ms, remanence magnetization,Mr, and coercivity, Hc, with different surfactant was observed. A slight increase in Curie temperature (765 K) is observed for samples coating with CTAB as compared to that of sample prepared in absence of coating. These results can be taken as coating surfactant like PVP, PEG and CTAB act as a crystallization agents, controlling the nucleation and growth of SrFe2O4 crystal. The study shows good impact on the scope of improving magnetic properties of ferrites without substitution of metal ions.

**EP01.03.25**

A Tunable Piezoelectric MEMS Sensor for the Detection of Weak Magnetic Signals Florian Niekiel1, Simon Fichtner2, Christine Kirchhof2, Dirk Meyners2, Eckhard Quandt2, Bernhard Wagner2 and Fabian Lofink1; 1Fraunhofer Institute for Silicontechnology (ISIT), Itzehoe, Germany; 2Christian-Albrechts-Universität zu Kiel, Kiel, Germany.

Piezoelectric MEMS devices are well established in the field of filters, e.g. RF filters for communication applications. The modal behavior and thus the filter characteristics are strongly affected by the in-plane and out-of-plane geometry and are therefore controlled by the design. A post-fabrication adjustment is difficult and commonly made with irreversible processes far away from application conditions, for example modifying the residual stress in the resonating structure by annealing processes. Here we present the study of a piezoelectric resonator, whose modal characteristics can be tuned using additional piezoelectric elements. This concept allows a flexible and reversible adjustment of the modal behavior in the application under operation conditions. The design is made of three parallelly-suspended cantilevers have been realized from a poly-Si layer using backside release. While the principle is generally applicable to achieve tunable piezoelectric MEMS filters, this study focuses on the use as magnetoelectric sensors for weak magnetic signals, e.g. for biomagnetic applications [1]. To achieve the sensitivity to a magnetic field, a magnetostrictive FeCoSiB layer is added on the unimorph structure. The piezoelectric and magnetostrictive layers build a magnetoelectric composite capable of converting a magnetic signal into an electrical signal via the mechanical coupling. The resonance of the cantilever structure is employed to enhance the mechanical response for certain frequencies and thus the electrical signal. The fabricated devices are used to study the fundamental relationship between sensitivity and stress in the resonator structure.

Several benefits of the presented tunable magnetoelectric sensor are anticipated. The frequency can be adjusted precisely to the magnetic signal in the measurement to get the highest benefit from the resonance effect. In addition, different measurements with varying signal frequencies can be addressed without having to change the sensor. Superimposed magnetic signals at different frequencies can be measured with a single sensor in a serial manner, due to the filter effect of the narrow-bandwidth resonance amplification.
Funding by the DFG via the Collaborative Research Center SFB 1261 is gratefully acknowledged.


EP01.03.26 A First-Principles Study of the LaAlO3/SrTiO3 (111) Interface Taewon Min, Jinho Byun and Jaeckwang Lee; Pusan National University, Busan, Korea (the Republic of).

The emergent discovery of two-dimensional electron gas (2DEG) at the LaAlO3/SrTiO3 (LAO/STO) heterostructure with n-type interface has attracted considerable attention over the past decade. Despite several mechanisms such as polar catastrophe, oxygen vacancy and cation intermixing have been suggested, the origin of 2DEG remains still unclear. Recently, unlike LAO/STO (001) interface, a wide 2DEG distribution have been reported at the LAO/STO (111) interface. According to the polar catastrophe, although the p-type 2DEG is expected at the LAO/STO (111) interface consisting of [Ti]+/[LaO3]- layers, the n-type 2DEG has been experimentally observed. Here, using a first-principles density functional theory calculations, we explore the origin of wide n-type 2DEG at LAO/STO (111) interface at the atomic scale. Compared with LAO/STO (001) interface, we find that the oxygen adsorption on the [Al]2+-terminated LAO (111) surface and following surface reconstruction play a key role in forming n-type 2DEG and the existence of critical thickness.

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (2018R1A2B6004394). This work also was supported by the MOTIE(Ministry of Trade, Industry & Energy (#10080643) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

EP01.03.27 Design and Fabrication of ZnO Nano-Architectures with High Piezoelectric Coefficient and Elastic Limit Seokiumg Yun1,4, Hoon Kim1, Dahye Shin1, Seongwoo Cho1, Changdeuck Bae1, Dongchan Jang2 and Seunghum Hong1; 1Department of Materials Science and Engineering, Korean Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 3Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); 4Memory Business, Samsung Electronics Co., Ltd., Hwaseong, Korea (the Republic of).

Piezoelectric ceramics are used for sensors and actuators as they have high piezoelectric coefficient. However, due to the brittle nature of ceramics coming from the fact that the size of flaw or crack determines the ultimate strength and elastic strain limit, it is still a challenge to use them for flexible or stretchable devices. In this study, we introduce ZnO truss nanostructure which shows high piezoelectric coefficient confirmed by local piezoresponse map and high elastic limit measured by nano-indentor. The photoresist SU8 was used for the template of ZnO truss structure via 3D photolithography. We used low temperature atomic layer deposition to coat the SU8 truss template with conformal ZnO thin film. The piezoelectric characteristics of the ZnO/SU8 composite truss were analyzed by Dual AC Resonance Tracking Piezoresponse Force Microscopy (DART-PFM) where the effective piezoresponse was 37.8 pm/V. This is almost three times larger than the piezoelectric coefficient reported for bulk ZnO (8–10 pm/V). The stress vs strain curve was measured by nano-indenter, and showed linear behavior up to ~4%, which is more than 10–20 times the strain limit of bulk ZnO. We expect that our novel ZnO truss nanostructure can serve as basic materials component for future haptic enhanced applications.

SESSION EP01.04: Growth of New Piezoelectric, Pyroelectric and Ferroelectric Optoelectronic Materials
Session Chairs: David Ginley and Darrell Schlom
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 103

8:15 AM EP01.04.01 Switchable and Rectifying Conductivity in Molecular Ferroelectrics Indre Urbanaviciute, Tim Cornelissen and Martin Kemereink; Linkoping University, Linkoping, Sweden.

The broken inversion symmetry in ferroelectric semiconductors causes the bulk photovoltaic effect. The same symmetry considerations predict a non-equivalence between electrical currents flowing parallel and anti-parallel to the polarization direction. While ferroelectrically-switchable current rectification in metal-ferroelectric-metal diodes has been observed due to interfacial phenomena like injection or tunneling barrier modulation, a coupling between bulk conductivity and polarization has not been observed. Here, we present a class of molecular ferroelectrics that show a polarization-dependent bulk conductivity.1

We have synthesized disc-like semiconducting organic molecules that are functionalized with strong dipolar side groups.2 These materials self-assemble into supramolecular polymers, which provides long-range polar order that supports collective ferroelectric behavior of the side groups, as well as charge transport through the stacked semiconducting cores.

We find that the ferroelectric polarization couples to the charge transport and leads to a bulk conductivity that is both switchable and rectifying. When sweeping the applied electric field, the conductivity is switched from a high to low state at the ferroelectric coercive field. Detailed analysis of the current-voltage curves shows that the current is a combination of Ohmic and space-charge-limited currents. This demonstrates that it truly is the bulk conductivity that is modulated by the ferroelectric polarization.

A simple quasi-1D hopping model is developed to investigate the effect of the asymmetric potential caused by the polarization. This model reproduces the experimental on/off ratio using reasonable parameters.

References:

8:30 AM EP01.04.02
**Photo-Induced Phenomena of Strongly Correlated YMnO$_3$ Ferroelectric Epitaxial Films**

Norifumi Fujimura, Takeshi Yoshimura, Takayuki Hasegawa and Masaaki Nakayama; Osaka Prefecture University, Osaka, Japan; University of Hyogo, Ako, Japan; Osaka City University, Osaka, Japan.

We have studied the photo-induced phenomena using strongly correlated YMnO$_3$ ferroelectric thin films. Unipolar material YMnO$_3$ is suitable for studying the effect of the ferroelectric polarization on the photo-induced current. The clear relationship between the direction of the polarization and the photo-induced current was recognized using (0001) YMnO$_3$ epitaxial films. The current switching corresponding to the polarization switching is also observed under the illumination of white light. To study the origin of the photo-induced current originated from the photo-induced carrier generation, the light energy dependence of the photo-induced current was investigated. The small peak at 1.75 eV and broad peak at around 2.5 eV are observed at room temperature. The peak at 1.75 eV corresponds to the optical absorption at 1.7 eV that generated by the electron transition between Mn 3d (xy,x$^2$- y$^2$)($e_g$ state)/O 2p hybridized band and upper Mn 3d (3z$^2$-r$^2$,$a_{1g}$ state) orbital [1]. The broad peak of photo-induced current corresponds to the broad photoluminescence excitation spectrum at around 2.5 eV, which is never observed in absorption measurement but reported as the hidden optical channel. After the introduction of the origin of photo-induced current of YMnO$_3$, it is discussed including associated with the carrier generation and the emission process, ultrafast dynamics of coherent optical phonon correlated with the antiferromagnetic transition in a hexagonal YMnO$_3$ epitaxial film is discussed.

The observations of the coherent optical phonon using a reflection-type pump-probe technique at various temperatures, excitation powers and energies were carried out. We detected an oscillatory structure with a frequency of ~5.1 THz, which is assigned to the coherent optical phonon with A1 symmetry, in a time-domain signal. It was found that the coherent optical phonon can be observed at temperatures from 10 K to room temperature, while the oscillation amplitude markedly decreases with an increase in temperature around ~70 K corresponding to the Néel temperature. The temperature dependence of the oscillation amplitude indicates that the coherent optical phonon is sensitive to the spin-lattice coupling connected with the antiferromagnetic transition [2].


**8:45 AM *EP01.04.03***

**Materials Design for the Bulk Photovoltaic Effect—Theoretical Limits and Novel Materials**


The bulk photovoltaic effect (BPVE) is the generation of photocurrents in the bulk of a single-phase material. It holds advantages over traditional photovoltaics based on p-n junctions, such as above-band gap photovoltages, and current generation in the bulk without the need for interface engineering. Despite numerous theoretical and experimental research efforts into the BPVE, there has been no systematic investigation into its maximum magnitude attainable in solid-state materials. In this talk, we present an upper bound on the dominant microscopic mechanism of BPVE: the shift current response. We show that this bound depends on the band gap, band width, and geometrical properties of the material in question. As a proof of principle, we perform first-principles calculations of the response tensors of a wide variety of materials, finding that the materials in our database do not yet saturate the upper bound. This suggests that new large BPVE materials will likely be discovered by future materials research guided by the factors mentioned in this work. These results imply that small band gap materials can potentially host large BPVE. As examples, we propose materials which are tuned across a band-gap-closing phase transition from a normal semiconductor into a topological insulating phase. This class includes some inorganic layered semiconductors, such as BiTeI, and inorganic halide perovskites, such as CsPbI$_3$. We show that this results in a dramatic enhancement of photocurrent as well as an abrupt transition in its direction. Using first-principles calculations, we show that this effect is robust across different materials systems as long as such a transition into a topologically insulating phase is present.

**9:15 AM *EP01.04.04***

**Band Gap Modulation and Interface Engineering in Solution Deposited BiFeO$_3$-CoO$_x$: Thin Films**

Mariona Coll, Pamela Machado, Mateusz Scigaj, Jaume Gazquez, Antonio Sanchez-Díaz, Ignasi Fina and Mariano Campoy-Quiles; ICMAB-CSIC, Bellaterra, Spain.

In this work we study the chemical substitution of the transition metal in BiFeO$_3$ by Co-ions to explore the potential to judiciously engineer the optical band gap and examine its impact on the ferroelectric properties and the photoresponse. Nonetheless, the stabilization of BiFeO$_3$:CoO$_x$(BFCC) phases shows a rather narrow growth window requiring high pressure synthetic conditions. Here by using first-principles calculations, we have been able to stabilize by epitaxial growth the perovskite BF phase modulating the band gap from 2.7 to 2.4 eV while preserving robust ferroelectricity (P$_r$ = 60 μC/cm$^2$). Photoreponse measurements performed at 520 nm and 1.5 W/cm$^2$ on 100 nm BFCC films show a clear enhancement of the current density compared to pristine BF films. Also, we observe that the magnitude of the current can be modulated by applying a voltage of a particular polarity and this effect is stronger in cobalt substituted films. Towards an all-oxide device, the use of selective layers and transparent conducting oxides are also assessed to further improve the incident photon to charge carrier efficiency of these devices. With this comprehensive study we demonstrate the complexity but also the richness of this system for future light harvesting applications.

**9:30 AM *EP01.04.05***

**Bulk Photovoltaic Effect as Quantum Mechanical Shift Current in Polar Semiconductors**

Masashi Kawasaki; 1, 2 Department of Applied Physics and Quantum Photon Electronics Center (QPEC), The University of Tokyo, Tokyo, Japan; 3RIKEN Center for Emergent Matter Science (CEMS), Wako, Japan.

We discuss a novel manifestation of quantum mechanical current flow in solids upon photoexcitation. From old days, bulk photovoltaic effect has been known to exist in non-centrosymmetric crystals such as poled ferroelectrics [1]. Naive explanation was that the drift current flows due to electric field uncompensated by insufficient formation of electric double layer on the surfaces of polar crystals. Now, it is proposed and confirmed that a quantum mechanical effect, described by the Berry’s connection of Floquet bands, drives photocurrent called “shift current” as a second order optical process [2, 3].

As a proof of principle, we perform first-principles calculations of the response tensors of a wide variety of materials, finding that the materials in our database do not yet saturate the upper bound. This suggests that new large BPVE materials will likely be discovered by future materials research guided by the factors mentioned in this work. These results imply that small band gap materials can potentially host large BPVE. As examples, we propose materials which are tuned across a band-gap-closing phase transition from a normal semiconductor into a topological insulating phase. This class includes some inorganic layered semiconductors, such as BiTeI, and inorganic halide perovskites, such as CsPbI$_3$. We show that this results in a dramatic enhancement of photocurrent as well as an abrupt transition in its direction. Using first-principles calculations, we show that this effect is robust across different materials systems as long as such a transition into a topologically insulating phase is present.

Layered van der Waals crystals like ferroelectric CunP2S6 (CIPS) provide a range of intriguing functional properties. They open a straightforward path to magnetization switching such coupling is termed as positive magnetoelctric (ME) effect.\(^\text{1}\) Craig J. Fennie proposed a theoretical scheme/criteria to design structures of spontaneous polarization and a net magnetization are mutually exclusive.\(^\text{2}\) In recent years, great attention has been paid to synthesize materials with simultaneous polarization and a net magnetization due to their constructive performance of these materials.

In the present work, we choose Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\) (BNT) as our ferroelectric matrix which is an excellent ferroelectric oxide with large remnant polarization looking for another strong ferroelectric oxide. Moreover, the most interesting feature observed here is the negative ME (N-ME) coupling shown by these samples. It is observed that there is a decrease of \(Tc\) ~330 °C. We substituted Ti with Fe ions systematically as \(x\) = 0, 0.005, 0.01, 0.02, 0.05, 0.1 and 0.2, using solid state reaction route. Interestingly, in this BNT based series, the solid solubility limit of Fe substitution in this BNT matrix could be increased up to 20%; giving us a broader range to test the hypothesis given by Craig J. Fennie. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. The research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy.

References:
\(^1\) Neumayer et al, "Giant negative electrostriction and dielectric tunability in a van der Waals layered ferroelectric", arXiv:1803.08142 (2018)
\(^2\) R. Nechache, C. Harnagea, S. Li, L. Cardenas, W. Huang, J. Chakrabarty, F. Rosei, Nature Photonics, 2015, 9, 61

11:15 AM EP01.04.08
Large Negative Magnetoelastic Effect in Fe Substituted Ferroelectric Bio\(_{2}\)Na\(_{2}\)TiO\(_{4}\) Ceramics—A Combined Experimental and Theoretical Study Mukesh Kumari1,2, Sushma Shantapuri1 and Ratnamala Chatterjee1; 1IIT Delhi, New Delhi, India; 2Physics, National University of Singapore, Singapore, Singapore.

In recent years, great attention has been paid to synthesize materials with simultaneous polarization and a net magnetization due to their constructive practical applications in spintronics and non-volatile memory.\(^\text{1}\) However, such materials are difficult to obtain as the conditions for observation of spontaneous polarization and a net magnetization are mutually exclusive.\(^\text{2}\) Craig J. Fennie proposed a theoretical scheme/criteria to design structures of perovskite oxides (ATiO\(_{3}\), A = Mn, Fe and Ni), such that a polar distortion at Ti-site (B-site of perovskite unit cell) can induce weak ferromagnetism and the direction of magnetization can be switched by application of electric field (known as magnetoelastic (ME) coupling).\(^\text{3}\) Following this scheme, in one of our earlier works,\(^\text{4}\) we have demonstrated experimentally that a partial substitution of Ti\(^+\) (B-site) with Fe\(^+\) in a pure ferroelectric system Ba\(_{2}\)Zn\(_{1-x}\)Fe\(_x\)O\(_{3}\) (BZFO) gives rise to a reasonably large ME coupling. In these samples, it was observed that the electrical polarization favors the magnetization switching such coupling is termed as positive magnetoelastic (P-ME) coupling. However, one of the major drawbacks in the BZFO series is that the solid solubility limit of Fe in the main matrix of BZT. Thus, In order to have a broader range to test the hypothesis given by Craig J. Fennie, we looked for another strong ferroelectric oxide.

In the present work, we choose Ba\(_2\)Na\(_2\)TiO\(_4\) (BNT) as our ferroelectric matrix which is an excellent ferroelectric oxide with large remnant polarization ~38 \(\mu\)C/cm\(^2\) (in comparison of BZT ~21 \(\mu\)C/cm\(^2\)) and high Curie temperature \((Tc)\) ~330 °C. We substituted Ti with Fe ions systematically as Ba\(_2\)Na\(_2\)Fe\(_x\)Ti\(_{3-x}\)O\(_{10}\) with \(x\) = 0, 0.005, 0.01, 0.02, 0.05, 0.1 and 0.2, using solid state reaction route. Interestingly, in this BNT based series, the solid solubility of Fe substitution in this BNT matrix could be increased up to 20%; giving us a broader range to test the hypothesis given by Craig J. Fennie. Moreover, the most interesting feature observed here is the negative ME (N-ME) coupling shown by these samples. It is observed that there is a decrease of ~19% (at 40 kOe) in magnetization in poled sample \((x = 0.05)\) in comparison to the unpoled one. To understand this N-ME effect, we have developed a Landau-Devonshire thermodynamic model and estimated theoretical value of ME coupling co.~430 kV/cm Oe. Our Temperature dependent dielectric studies reveal that there is a small down shift in ferroelectric Curie temperature with increasing \(x\). Ferroelectricity is still maintained in all the substituted samples.

References:

10:00 AM BREAK

10:30 AM EP01.04.06
Ferroelectric Inorganic Perovskite Oxides for Photovoltaic Applications Alessandro Quattropani1, Daniel Stoeffler2, Jean-Luc Reshpringer2, Guy Schmerber2, Silviu Colis3, Gilles Versini3, Mirela Rastel2, Bohdan Kundy2, Aziz Diniz2, Abdelilah Slaoi4 and Thomas Fix4; 1ICube CNRS-Univ Strasbourg, Strasbourg, France; 2IPCMS - Université de Strasbourg and CNRS, Strasbourg, France.
Hydrothermal Synthesis of Yb Doped Bismuth Ferrite Crystallites and Their Structural, Magnetic and Ferroelectric Characteristics

Multiferroic materials have attracted a great deal of attention because of their ferroelectric, ferromagnetic and ferroelastic properties in a single material. They enable to control electrical polarization under the application of magnetic field, or magnetization under the application of electric field. Due to its promising feature, they have gained a remarkable usage area in non-volatile information storage, spintronics, multiple state memories and sensors. Among multiferroics, BiFeO₃ (BFO) is one of the possible candidate for room temperature multiferroic materials. There are several methods to synthesize BFO varying from conventional solid state reaction to sol-gel technique.

In this study, one of the multiferroic material, BiFeO₃ (BFO) was investigated. It was hereby with this work proposed a hydrothermal method to synthesize BFO powders. Well-crystallized BFO and Yb-doped BFO (Biₓ₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋₅₋}_{(1,3)}

SESSION EP01.05: New Applications of Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Bor-Rong Chen and Shyam Dwaraknath
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 103

1:30 PM EP01.05.01
Preparation of κ-Al₂O₃-Type Ferroelectric Single Crystal and Single Domain Epitaxial Thin Film and Their Properties

Shintaro Yasui¹, Koki Tachiyama¹, Tsukasa Katayama¹, Takuro Dazai¹, Yosuke Hamasaki¹, Huan He², Hui Wang², Jiajing Yu² and Mitsuhiro Ichii²
1Tokyo Institute of Technology, Yokohama, Japan; 2The University of Tokyo, Tokyo, Japan; 3National Defense Academy, Yokosuka, Japan; 4Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

κ-Al₂O₃, same as ε-Fe₂O₃, GaFeO₃ structures, structured materials whose space group is Pna₂̅, are one of very attractive multiferroics because of coexistence of ferroelectric and ferrimagnetic properties at room temperature. Ferroelectric property of this material has been investigated using single crystal and epitaxial thin films. However, measurement of ferroelectricity is prevented by very large leakage current in GaFeO₃ single crystal. Moreover, this structured single crystal, except to GaFeO₃, is difficult to prepare due to metastable phase. On the other hand, the measurement of ferroelectric property was achieved by formation of high quality epitaxial thin film. However their measured polarization values were one order smaller than calculated values.
one[4]. We resulted that this issue was originated to three-fold structural variant which is formed on (111)SrTiO$_3$ single crystal. Therefore, we have tried to prepare GaFeO$_3$ single crystal and then prepare single crystal k- Al$_2$O$_3$ structured thin films on GaFeO$_3$ single crystal substrate. GaFeO$_3$ single crystal was prepared by floating zone method using 10 atom oxygen pressure. Then we cut and polished this single crystal for preparation of thin films using substrate, Sc$_0.5$Fe$_{1.5}$O$_3$ epitaxial thin films were fabricated on (001)GaFeO$_3$ single crystal by pulsed laser deposition method. Growth temperature and oxygen pressure for deposition condition were 800°C and 300 mTorr, respectively. Lase image of prepared GaFeO$_3$ single crystal measured along 001 zone axis is in good agreement with simulated one. From X-ray diffraction (XRD) 2θ-θ patterns of Sc$_0.5$Fe$_{1.5}$O$_3$ and (001)GaFeO$_3$ thin films and (001)GaFeO$_3$ single crystal substrate, k-Al$_2$O$_3$ type structured Sc$_0.5$Fe$_{1.5}$O$_3$ thin film was grown along 001 direction. XRD phi scan at (013)Sc$_0.5$Fe$_{1.5}$O$_3$ and (013)GaFeO$_3$ shows two-fold peaks at same phi degree. This result indicates that prepared Sc$_0.5$Fe$_{1.5}$O$_3$ thin films is single domain epitaxial thin films without structural variant. We will report ferroelectric, dielectric, leakage, magnetic properties of GaFeO$_3$ single crystal and Sc$_0.5$Fe$_{1.5}$O$_3$ single domain epitaxial thin film. [1]T. Arima et al., Phy. Rev. B 70, 064426 (2004). [2] M. Gich et al., Adv. Mater. 26, 4645 (2014). [3] T. Katayama et al., Adv. Funct. Mater. 28, 1704789 (2018). [4]D. Stoeffler, J. Phys.: Condens. Matter 24, 185502 (2012).

1:45 PM EP01.05.02 Tunable Dielectrics from First Principles—Effect of Chemistry and Epitaxial Strain Gerhard H. Olsen, Natalie M. Dawley, Darrell G. Schlom and Craig J. Fennie; Cornell University, Ithaca, New York, United States.

Progress in miniaturization of electronic devices, such as antennas and tunable filters, relies on continued development of thin film dielectric materials. Ruddlesden-Popper (RP) oxides based on strontium titanate (STO) have emerged as promising candidate materials, as they are highly tunable by electric fields and can be operated at +10 GHz frequencies with low dielectric losses. Such films can be grown on a range of substrates by molecular-beam epitaxy (MBE), but a remaining challenge is the trade-off between dielectric performance, improved by large epitaxial strains, and the maximum thickness that can be achieved before relaxation and high dislocation density of the film occurs. Here, we use first-principles calculations to investigate the effects of modifying the STO-based dielectrics with barium titanate (BTO). While BTO-based RPs cannot be synthesized with conventional methods, metastable RP phases with high Ba content can be grown using MBE. Our calculations show that even a small chemical modification both reduces the effective strain, allowing thicker coherent films to be grown, and at the same time enhances ferroelectricity to compensate for the reduced strain.

2:00 PM EP01.05.03 Two-Dimensional Materials for Electronic Applications: Design, Discovery, and Characterization John Brehm1, Marius Chyasnavichius2, Nina Bulke3, Sahine M. Neumayer4, Michael A. Sousner4, Michael McGuire5, Panchapakesan Ganesh6, Petro Maksymovych7 and Sokrates Pantelides7; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Air Force Research Laboratory, Dayton, Ohio, United States; 3Vanderbilt University, Nashville, Tennessee, United States.

Two-dimensional materials are of scientific and technological interest as they run the gamut of electronic classifications from metal, to semiconductor, to insulator while being able to be easily joined to other materials with controlled number of layers. Metal thiophosphates offer a rich class of 2D materials, comprising metal ions occupying octahedrally coordinated sites in the with [P$_5$S$_8$]$^{1+}$ triangular lattice, leading to a variety of magnetic, structurally correlated and polar ground states. Copper indium thiophosphate (CuInP$_2$S$_6$) is one such member of this family and has been noted for its ferrielectric characteristic. In this talk, we present the results of density functional theory calculations that explore the effect of strain on the structure and polarization of CuInP$_2$S$_6$. We show CuInP$_2$S$_6$ exhibits a negative longitudinal piezoelectric coefficient, and a strain-induced phase transition between two phases, differentiated by the relative displacement of Cu within the individual layers. The existence of two phases may also explain the experimentally observed inhomogeneity of piezoresponse observed experimentally. More generally, these calculations reveal the crucial role played by the van-der-Waals gap in defining their functional properties.

2:15 PM EP01.05.04 Voltage-tunable radio frequency (RF) electronics are critical for fifth-generation (5G) millimeter-wave telecommunications; applications include frequency-agile filters and tunable phase shifters. For the former, these materials allow handsets to communicate on many frequencies. For the latter, they enable phased-array antennas for beam-steering, which mitigates atmospheric attenuation and interference. State-of-the-art tunable materials are too lossy for these applications because the 5G network requires the use of high carrier frequencies to meet capacity demands. This problem requires new, highly-tunable, low-loss compounds that can support 5G.

Combinatorial methods provide an opportunity to rapidly screen many candidate materials, and develop better models of materials behavior as a function of composition, frequency, and applied DC voltage. These models inform the search for materials with optimal properties. The primary advantage of combinatorial experiments is that full materials systems are synthesized simultaneously, maintaining constant experimental conditions over the full sample space.

In this presentation, we will explain a novel approach to extract the frequency-dependent complex permittivity and voltage-tuning behavior of combinatorial thin-film composition spreads from DC – 110 GHz. We tested our approach on the well-studied Ba-doped SrTiO$_3$ (BSTO) system, emphasizing 5G frequency bands, and developed a unified model of the frequency dependence, voltage tunability and composition. Such models assist in the design of 5G RF electronics, and are related to thermodynamic quantities. This relationship points to a potential path connecting optimal RF performance to materials through first-principles theory.

2:30 PM *EP01.05.05 Coupling Between Ferroelectricity and Chemistry on Mesoscopic and Atomic Scales Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Ferroelectricity on the nanoscale has remained a subject of much fascination in condensed matter physics for the last several decades. It is well-recognized that stability of the ferroelectric state necessitates effective polarization screening, and hence screening mechanism and screening charge dynamics become strongly coupled to ferroelectric phase stability and domain behavior. Similarly, atomic scale defects can strongly affect polarization stability and affect wall pinning and nucleation and give rise to relaxor states. In this presentation, I will illustrate several recent results on ferroelectric and ferroic – chemical coupling on mesoscopic and atomic scales. In the nanoscale systems, the ferroelectric state is fundamentally inseparable from electrochemical state of the surface, leading to emergence of coupled electrochemical-ferroelectric states. These considerations further stimulate the development of the novel SPM modalities addressing time-dependent dynamics and chemical changes during SPM imaging, and studying in situ reactions from transformations from...
atomically-resolved data. I will further delineate the applications of in-situ SPM – time of flight secondary ion mass spectrometry (ToF SIMS) to map the changes in surface chemistry during tribological and local electrochemical experiments, including ferroelectric polarization switching and pressure-induced resistance changes in oxides. On the atomic scales, significant inroads in in-situ ferroelectric behaviors can be obtained from atomically-resolved studies of ferroelectric materials that allow direct visualization of materials structures and order parameter fields. These approaches further necessitate analysis and data mining of large volumes of information, and first examples of deep learning analysis on STEM data to infer local materials behavior and kinetics of point-defect reactions will be illustrated.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE, and was conducted at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division.

3:00 PM BREAK

4:00 PM *EP01.05.07
Regenerative Electroceramics for High Temperature Energy Converters
Anke Weidenkaff, Wenjie Xie and Xingxing Xiao; University of Stuttgart, Stuttgart, Germany.

Electroceramics are needed for diverse energy converters (1,2). The prerequisite for a durable active material is the constant regeneration of the structure under thermochemical and heating cooling cycles. Perovskite-type ceramics as well as their nanocomposites are prospective candidates for multifunctional high temperature energy converters. Their good performance relies on their flexible crystal structure being able to accommodate defects during thermal redox processes. The design of our materials is based on theoretical predictions and a deep knowledge on composition-structure-property relationship. The perovskite structure allows diverse substitution reactions to tune the band structure, charge carrier density and mobility as well as thermal and ionic transport. The electronic mobility can become high while the thermal conductivity can be low. Strongly correlated electronic systems are employed as additional design elements for a targeted materials design (3).

The resulting high temperature oxide materials as well as low temperature intermetallic (half-Heusler) and chalcogenite phases are characterized and tested in in-situ high temperature applications to improve the efficiency and energy density of energy conversion devices.


4:30 PM *EP01.05.08
Piezo-Phototronic Effect on Performance Enhancement of Anisotype and Isotype Heterojunction Photodiode
Zijian Pan, Wenbo Peng, Fangpei Li and Yongning He; School of Microelectronics, School of Electronic and Information Engineering, Xi’an Jiaotong University, Xi’an, China.

The piezo-phototronic effect has been confirmed as a promising methodology to optimize the performances of optoelectronic devices. However, not only positive effects but also negative effects may be produced in some types of photodiodes (PDs) by the piezo-phototronic effect, resulting in the restriction of the PDs’ photoreponse performance enhancement. In order to obtain as large photoreponse performance enhancement as possible, it is essential to investigate how the piezo-phototronic effect influences the photoreponse performance of PDs with different device configurations and structures. Here, we have thoroughly investigated the piezo-phototronic effect on the photoreponse performance enhancement of anisotype (p-Si/n-ZnO) and isotype (n-Si/n-ZnO) heterojunction PDs. The experimental results show that distinct photoreponse performance enhancement of the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs are both achieved by the piezo-phototronic effect. The photoresponsivity enhancement can reach maximized values of 151.06% and 54.95% for the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs, respectively, under -1.0% externally applied compressive strain condition and 6.00 × 10⁸ W 405 nm laser illumination, additionally indicating that the magnitude of the photoreponse performance improvement of the p-Si/n-ZnO heterojunction PD is much larger than that of the n-Si/n-ZnO heterojunction PD. The fundamental working mechanisms of how the piezo-phototronic effect influences the photoreponse performances of the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs are systematically investigated by carefully analyzing their different energy band diagrams under a series of externally applied compressive strain conditions, to explore the in-depth physics beneath the experimental phenomenon. Our proposed mechanisms together with the finite element analysis theoretical simulation results reveal that, two positive effects are introduced to and contribute to the photoreponse performance improvement of the p-Si/n-ZnO heterojunction PD, whereas one positive effect and two negative effect are introduced to the photoreponse performance improvement of the n-Si/n-ZnO heterojunction PD. These three effects compete with each other and finally lead to a weakened photoreponse performance improvement compared with the case of the p-Si/n-ZnO heterojunction PD.

This work not only presents in-depth understandings about the piezo-phototronic effect on the photoreponse performances of PDs with different device configurations and structures, but also provides methodology guidance to achieve optimized photoreponse performances of optoelectronic devices by the piezo-phototronic effect.

A Novel CMOS Compatible III-V Semiconductor Based Ferroelectric with Intriguing Properties

Simon Fichtner1,2, Fabian Lofink2 and Bernhard Wagner1,2; 1CAU Kiel, Institute for Material Science, Kiel, Germany; 2Fraunhofer Institute for Silicon Technology, Iitzehoe, Germany.

We regret that, due to ongoing patent applications, we are as of now still unable to discuss aspects that would reveal the composition of the new ferroelectric compound (such as its crystal structure) and the intended applications or related literature. We are however certain that we will be able to share all relevant information in the end of August the latest. For the same reasons, this work is still pending journal publication.

The drive towards miniaturization of piezoelectric sensors and actuators as well as the introduction of ferroelectric functionality into integrated circuit (IC) technology have led to substantial scientific and commercial interest in ferroelectric thin-films. Many of the more important ferroelectrics are perovskite oxides, with typical disadvantages such as low paraelectric transition temperatures, non-linear displacement or compatibility issues with complementary metal-oxide-semiconductor (CMOS) technology. Here, we report experimental results of a first material of what can be expected to be a new group of CMOS compatible ferroelectrics with remarkable properties: Solid-solutions based on a technologically significant subgroup of the III-V compound semiconductors.

Virtually leakage current free polarization hysteresis loops with large remnant values of up to 110 μC/cm² are obtained on polycrystalline thin-films grown by sputter-deposition. Unypcial for a polycrystalline ferroelectric, sharp switching events give rise to an almost perfectly square hysteresis. Systematic tuning of the coercitive fields from 1.8 MV/cm to 3.5 MV/cm was achieved by varying the composition of the solid solution and, independently, via permanent process induced lateral straining of the films. Both mechanisms, as the occurrence of ferroelectricity itself, can be related to a continuous distortion of the initial III-V crystal structure with increased alloying or strain. The inverse piezoelectric effect reveals highly linear strain regimes over a wide range from -0.3% to 0.4% - a direct result of the narrow polarization switching events. Moreover, polarization inversion appears to be complete, as direct and inverse piezoelectric coefficient measurements result in largely identical absolute coefficient values for both polarization states. Measurements of the direct piezoelectric effect after annealing at up to 600°C revealed only a slight decline of the piezoelectric performance without subsequent repolarization, therefore setting a high lower limit of 600°C for the paraelectric transition temperature of the material.

We are confident that these findings could make a valuable contribution towards a more extensive implementation of ferroelectric functionality in thin-film technology.

SESSION EP01.06: Characterization of Semiconducting Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Shyam Dwaraknath and Anke Weidenkaff

Wednesday Morning, November 28, 2018

8:00 AM EP01.06.01
Flexible and Controllable Piezo-Phototronic Pressure Mapping Sensor Matrix by Organic/Inorganic Hybrid LED Array
Rongrong Bao and Caofeng Pan; Chinese Academy of Sciences, Beijing, China.

Functional tactile sensing device is mandatory for next-generation robotics and human-machine interfaces since the emulation of touching requires large-scale pressure sensor arrays with high-spatial resolution, high-sensitivity, and fast-response[1]. Some tactile sensors fabricated with organic transistors or micro-structured rubber layer pressure sensor arrays have been reported[2]. While with a resolution at the order of millimeter, these devices have not yet met the requirements for artificial skins whose spatial resolution is near 50 μm. Our group have demonstrated pressure sensor array base on piezotronic and piezophototronic effect[3]. An ultra-high resolution of 2.7 μm was derived from piezo-phototronic pressure sensor array using ZnO nanowire (NW)/p-GaN LEDs array[4]. These devices provide stable, fast response, as well as parallel-reading detections of spatial pressure distributions. However, the lacking of flexibility with a rigid sapphire substrate prevents the NW-LEDs array device from applications as smart skin; and the pressure measuring range of the device is in a relatively high pressure region. Therefore, a flexible pressure mapping system with moderate spatial-resolution become necessary and may find numerous potential applications in human-machine interfaces.

Recently, we designed and fabricated a flexible LED array composed of PEDOT:PSS and patterned ZnO NWs with a spatial resolution of 7 μm for mapping of spatial pressure distributions by using the piezo-phototronic effect. These devices possess a wide range of pressure measurements from 40 MPa to 100 MPa depending on the growth conditions of ZnO NWs. Furthermore, a LED array composed of PEDOT:PSS and CdS nanorods had been demonstrated for mapping spatial pressure distributions. The emission intensity of which depends on the local strain owing to the piezo-phototronic effect. Therefore, pressure distribution is obtained by parallel-reading the illumination intensities of LED arrays based on electrofluorescence working mechanism. The spatial resolution is achieved as high as 1.5 μm. Flexible LED device array has been prepared by Cds nanorod array on Au/Cr/Kapton substrate. The flexibility and stability of these LED arrays mapping system was studied. The outstanding flexibility, high resolution and controllability of these pressure mapping sensors provide promising technologies for future applications in biological sciences, human-machine interfacing, smart sensor and processorsystems, and even defense technology.

Reference

8:15 AM EP01.06.02
Ferroic and Multiferroic Behavior in Fe Doped BaTiO3 Single Crystals

Peter Finkel1, Margo L. Staruch1 and Markys G. Cain2; 1NRL, Washington, District of Columbia, United States; 2Electrosciences Ltd, Surrey, United Kingdom.

Single crystals of BaTiO3 (BTO) that have been doped at the titanium site with Fe⁺ or Mn⁺ have previously been shown to demonstrate large and recoverable electrostrain of up to 0.8 % that is thought to be due to the alignment of defects (i.e. O²⁻ vacancies) with the crystallographic symmetry in the ferroelectric state when the samples are aged.[1,2] This results in a restoring force where the ferroelectric domains favour alignment with the defect dipoles, giving rise to a large reversible strain due to repeated non-180° domain rotation. There is also the possibility that the incorporation of a magnetic ion could give rise to a magnetic signature and even possibly multiferroic coupling in these doped samples, the possibility of which has not been previously
investigated. In this presentation, results from magnetic measurements and polarization measurements with bias magnetic fields will be discussed for a 0.5% Fe doped BTO crystal. Impact of repeated cycling at different electric fields and the recoverability of this large strain will also be presented.

8:30 AM EP01.06.03 Flexible Transparent Nonvolatile Transistor Based on Aluminum-Doped Zinc Oxide/ Lead Lanthanum Zirconate Titinate Heteroepitaxial Structure Meng-Fu Tsai1, Jie Jiang2 and Ying-Hao Chu1, 3, 4; 1Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 2Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Xiangtan, China; 3Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan; 4Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan.

With the rise of Internet of Things, flexible and transparent electronic devices are expected to fulfill rising technical requirements which silicon-based electronics cannot achieve. As known to everyone, the advancement of transistors is most close to the development of technology. However, the performance of present flexible and transparent transistors have been restricted due to the poor crystallinity. In order to make a high quality nonvolatile transistor with full transparency and lower energy consuming, here, we demonstrated a transparent ferroelectric field effect transistor (TrFET) on muscovite substrate. With a high quality aluminum-doped zinc oxide as active channel layer and high transparency lead lanthanum zirconate titinate as ferroelectric layer, this heteroepitaxy performs excellent electrical properties. Moreover, this flexible TrFET not only shows high transparency and high thermal stability, but also exhibits promising stability against to mechanical strain during a series of bending tests. Our study demonstrates an unusual concept to achieve flexible transparent nonvolatile transistor for development of next-generation smart devices.

8:45 AM EP01.06.04 Organic Ferroelectric Tunnel Junctions for Synaptic Computation Sayani Majumdar; Aalto University, Espoo, Finland.

The performance of current information processors are predominantly based on complementary metal-oxide-semiconductor (CMOS) transistors. However, CMOS scaling have started to face significant challenges and besides the physical limits, the conventional computing paradigm based on binary logic and Von Neumann architecture is becoming increasingly inefficient with onset of big data revolution and growing complexity of computation. Neuromorphic computing is the state-of-the-art research trend in the field of memory and logic devices where the goal is to build a versatile computer that is efficient in terms of energy and space, homogeneously scalable to large networks of neurons and synapses, and flexible enough to run complex behavioral models of the neocortex as well as networks inspired by neural architectures. Memristors, with their gradually modified conductivity level can mimic the biological synapses. Low energy consumption, ultrafast operation and small dimensions are the most essential requirements for a memristor to perform tasks similar to a synapse and become as efficient as human brain. A ferroelectric tunnel junction (FTJ), where gradual modulation of conductance can be achieved by controlled rotation of ferroelectric domains can act very efficiently as a synapse. Also the non-volatility of the stored information in the ferroelectric memories make them even more attractive as potential candidates for future neuromorphic computing building blocks. Here, we report on the performance of FTJs with a spin-coated organic ferroelectric (P(VDF-TrFE)) tunnel barrier. We have measured up to 10% tunneling electroresistance (TER) effect in these FTJs on a semiconducting Nb-doped STO bottom electrode at room temperature that persists until the ferroelectric Curie point of P(VDF-TrFE). Also these junctions show very clear and reproducible memristive behavior based on variable amplitude and duration of the applied voltage pulses, fast switching, long data retention of the high, low and different intermediate states, short and long-term potentiation (STP & LTP) and depression and spike-time-dependent-plasticity (STDP) which is extremely promising for neuromorphic applications. Our recent experiments suggest based on the morphology of the ferroelectric film and the top electrode material, the available number of computational states in these devices can be significantly modified that can bring advantages for the synaptic computational devices.

References:

9:00 AM EP01.06.05 Piezoelectric β-PVDF:Yb Composite with Photochromic Properties Pedro Perdigon Lagunes, Eduardo Malagon, Jimena de la Mora, Yessica P. Reyes-Castro, Octavio Estvez and Raul Herrera-Beccera; Universidad Nacional Autónoma de Mexico, Mexico City, Mexico.

Nowadays piezoelectric systems have been studied and used in interesting daily applications, such as smartphone cameras, accelerometers and microphones [1]. Another interesting area studied for piezoelectric materials is energy harvesting, as transducers capable of convert vibrations, electromagnetic waves or even wind/water flow into electric potential difference [2]; this might lead to improve our actual collection of renewable power sources, and will let us explore other energy solutions. Even though these materials are promising with their applications, there are some limitations such as energy dissipation through Joule heating [3]. In addition, the most common piezoelectric materials are based in ceramic materials, hence, they are susceptible to wear fatigue. An interesting option is to use instead piezoelectric polymers, these materials are flexible, fatigue resistant and biochemical resistant due to their chemical composition. One of the most renown materials of this type is PVDF (Poly vinylidene fluoride), a semi-crystalline fluoropolymer stable to an unexpected optical result was found; when β-PVDF:Yb is exposed to sunlight, it presents a photochromic response that correlates to the interaction electronic density of Yb3+ interacts with the polymer chains, a fixed order is promoted into the PVDF structure with a tendency of a b structure. In addition, β-PVDF is an excellent option to be used as piezoelectric material for renewable energies and sensors. In addition, this material, owing to its photochromic properties, might be used also as a wearable biosensor/actuator that tracks in real time changes on blood pressure. Nevertheless, the real challenge is to obtain a predominant β-PVDF phase; this is because PVDF, as a semi-crystalline polymer, still has an entropic tendency to rearrange its molecules in lower energy state. We solved this problem by doping the polymer with ytterbium ions (Yb3+) in different concentrations below 10% in weight. As the electronic density of Yb3+ interacts with the polymer chains, a fixed order is promoted into the PVDF structure with a tendency of a b structure. In addition, an unexpected optical result was found; when β-PVDF:Yb is exposed to sunlight, it presents a photochromic response that correlates to the interaction absorption frequencies of the Yb3+. Thus, we consider that a piezoelectric polymer with photochromic characteristics, is an interesting system to be further explored for technological applications in relevant fields.

References:

9:15 AM EP01.06.06
Electro-Chemo-Mechanical Actuator Operating at Room Temperature
Eran Mishuk, Evgeniy Makagon, Sidney Cohen, Ellen Wachtel and Igor Lubomirsky; Weizmann Inst of Science, Rehovot, Israel.

Chemical expansion of a solid refers to dimensional change due to change in stoichiometry. Dimensional change due to charged defects redistribution in an electric field has been termed the electro-chemo-mechanical (ECM) effect. Such instability is clearly deleterious for batteries or fuel cells, but, as recently suggested, has potential for use in actuation[1]. A typical ECM actuator scheme includes: electrode/WB/ferroelectric-electrolyte(SE)/WB2/electrode2, where WB denotes working-body solids with large chemical expansion coefficient. The main advantage of ECM is that it can deliver simultaneously large strain and large stress, which is difficult to achieve with other actuation mechanisms. We have constructed a room temperature ECM nanocrystalline membrane actuator (2nm diameter; ≈2µm thick) with Gd-doped ceria as SE. We tested two alternatives for WB’s: (1) metal/metal oxide or (2) ceria/metal nanocrystalline composite. Electrical and electromechanical measurements demonstrated that actuator response with metal/metal oxide WB is limited by the rate of oxygen diffusion from the solid electrolyte to the metal surface. Actuators with ceria/metal composite WB provide faster response time (~20sec) and larger vertical displacement (~3.5µm). Our findings suggest that ECM may become a viable actuation mechanism.


10:00 AM EP01.06.07
A Pathway Toward 100mV Switching of Ferroelectricity
Yen-Lin Huang1, Bhagwati Prasad1, Shang-Lin Hsu1, Etvonton Bonturin1, Yunlong Tang1, Arnold S. Everhardt1, Chia-Ching Lin2, Tanay Gosavi3, S Manjapatrun4, D Nikonov5, I Young6 and Ramamoorthy Ramesh7,8; 1University of California, Berkeley, Berkeley, California, United States; 2Educational Integrated Circuits and Components Research, Intel Corporation, Hillsboro, Oregon, United States; 3Department of Physics, University of California, Berkeley, Berkeley, California, United States.

The demand for ultra low-powered high-speed devices has pushed scientists and engineers to consider new approaches that involve many aspects, such as materials engineering, device architectures, power management, etc., for the next generation electronics. Ferroelectrics offer a promising route toward a nonvolatile and low power consumption per bit operation (~10 aJ/bit) if one can switch the ferroelectric polarization by 100 mV. Here we demonstrate a reliable pathway to achieve 100 mV switching by the heterostructure: SrRuO3/La-doped BiFeO3/SrRuO3, BiFeO3 exhibits a robust ferroelectricity at room temperature and possesses a large polarization ~ 80 µC/cm2, which can be a burden during switching. Substituting Bi with La enables BiFeO3 to be switched at a lower voltage due to the suppressing of rhombohedral distortion and resulting in a reduced polarization down to ~ 40 µC/cm2 and a lower Curie temperature as well. Moreover, in order to further reduce the coercive voltage, the thickness of the ferroelectric layer also needs to be scaled. However, thinner ferroelectric films generally face multiple issues such as leakage, and depolarization effect, which will lead to an unmeasurable or degraded ferroelectricity. A detailed chemical analysis revealed a limited interdiffusion, which limits the leakage current as well, at the interface between the metal and ferroelectric layer by cross-sectional TEM/EDX. We also explore several oxide metal electrode materials, such as SrRuO3, LaNiO3, and La0.8Sr0.2MnO3, to minimize the depolarization effect and the contact potential difference. By carefully controlling the interfaces, film growth, and La doping concentration, the coercive voltage of ~100 mV can be achieved in a 20 nm La0.8Sr0.2MnO3 film. Our results not only provide a profound understanding of low-voltage ferroelectric switching as well as pave the way to the low-power information storage/processing technology.

10:15 AM *EP01.06.08
Acoustically Driven Ferromagnetic Resonance Driven Excitation of Vacancy Centers
Sayeef Salahuddin; University of California, Berkeley, Berkeley, California, United States.

Sound waves flowing in a piezoelectric crystal could be exploited to excite a ferromagnetic resonance. Here we shall discuss our recent work that aims to exploit such ferromagnetic resonance as a way to couple to nearby defect centers. Specifically, we have studied the nitrogen vacancy centers in diamond. We find that it is indeed possible to couple to these NV centers efficiently, even at zero external magnetic field. These findings may allow drive defect centers purely electrically.

10:45 AM DISCUSSION TIME

11:00 AM EP01.06.10
Electrically Tuned Photoelectrochemical Properties of Ferroelectric PVDF/Cu/PVDF-NaNbO3 Photoanode
Simrit Singh1; 2 and Neeraj Khare; 2 Panjab University, Chandigarh, India, Ludhiana, India; 3Physics, Indian Institute of Technology Delhi, New Delhi, India.

In recent years, photo-electrochemical (PEC) water splitting with an aim to generate hydrogen (H2) as a clean and renewable fuel has been the subject of intense research interests [1]. Ferroelectric semiconductors have been demonstrated to exhibit enhanced PEC properties as these can be polarized with the application of an external electric field resulting in a built-in potential which helps in separating out the photogenerated charge carriers. In addition to this, by changing the polarization direction, the energy band alignment at the electrode/electrolyte interface can be modulated in a way that it can help in easy transfer of the charge carriers from electrode to electrolyte [2-4]. In this paper, we investigated the PEC properties of ferroelectric PVDF/Cu/PVDF-NaNbO3 PEC cell and demonstrated that PEC properties can be tuned with ferroelectric polarization and piezophototronic effect. Photocurrent density is enhanced from ~0.71 mA/cm2 to 1.97 mA/cm2 by changing the polarization direction. Furthermore, due to flexibility and piezoelectric properties of PVDF/Cu/PVDF-NaNbO3 PEC cell, a further ~26% enhancement in the photocurrent is obtained using the piezophototronic effect. A model depicting the modulation of band alignment between PVDF and NaNbO3 with electric field is proposed to explain the observed tuning of the PEC properties. Electrochemical impedance spectroscopy measurements supports the validity of the proposed model.

References:
S. Singh and N. Khare, Nano Energy 38, 335 (2017).

11:15 AM *EP01.06.11
PETMEM: Piezoelectronic Transduction Memory Device—A European Research Project Update
Markys G. Cain; Electrosences Ltd, Farnham, United Kingdom.

Computer clock speeds have not significantly increased since 2003, creating a challenge to invent a successor to CMOS technology able to resume the improvement in clock speed and power performance. The key requirements for a viable alternative are scalability to nanoscale dimensions - following
Moore’s Law - and simultaneous reduction of line voltage in order to limit switching power. Achieving these two aims for both transistors and memory allows clock speed to again increase with dimensional scaling, a result that would have great impact across the IT industry. PETMEM is a European partnership amongst Universities, Research Institutions, SMEs and a large company that will focus on the development of new materials and characterization tools to enable the fabrication of an entirely new low-voltage, memory element. This element makes use of internal transduction in which a voltage state external to the device is converted to an internal acoustic signal that drives an insulator-metal transition. Modelling based on the properties of known materials at device dimensions on the 15 nm scale predicts that this mechanism enables device operation at voltages an order of magnitude lower than CMOS technology (power is reduced two orders) while achieving 10Ghz operating speed. In this presentation the first two years results will be summarised with a focus on new piezoelectric and new piezoresistive materials development, and some performance properties of our first demonstrator device will be discussed.

11:45 AM EP01.06.12
Efficient Piezocatalytic Activity Driven by the Piezoelectric Effect of BaTiO3 Nanowires
Jiang Wu, Ni Qin and Dinghua Bao; Sun Yat-Sen University, Guangzhou, China.

Recently, a novel catalysis technology, which named piezocatalysis, has received significant attention due to independence of light irradiation. Here, we report the new advances in the piezocatalysis of BaTiO3 and further investigate the relationship between piezoelectric potential and piezocatalysis. In this work, we successfully synthesized BaTiO3 nanowires and nanoparticles by a two-step hydrothermal method. It was found that the BaTiO3 nanowires exhibit effectively enhanced piezocatalytic activity under ultrasonic vibration compared with the BaTiO3 nanoparticle. To explore the origin of the excellent piezocatalysis performance of BaTiO3 nanowires, the distribution of piezoelectric potential in these nanomaterials was simulated by the finite element method (FEM) with the aid of COMSOL multiphysics software package. On the basis of the piezoelectric potential analysis by FEM stimulation, the enhanced piezocatalytic activity of the BaTiO3 nanowires can be attributed to the larger piezoelectric potential along the polar axis. A relatively larger piezoelectric potential of the catalyst surface can induce a greater shift of conduction band and valence band, resulting in easier and faster immigration of the electrons and holes, during reacting with dissolved oxygen and hydroxyl to form superoxide radicals and hydroxyl radicals. Furthermore, we demonstrate that the intrinsic charge carriers (not piezoelectric charges) in piezoelectric crystals play the role of charge transfer in the catalysis process through regulating the concentration of charge carriers in catalyst. This study provides further understanding of piezocatalysis of piezoelectric nano-materials as well as insights on the relationship between piezoelectric potential and piezocatalysis.

SESSION EP01.07: Bulk Photovoltaic Materials
Session Chairs: Lauren Garten and Abdelilah Slaoui
Wednesday Afternoon, Wednesday, September 26, 2018
Hynes, Level 1, Room 103

1:30 PM EP01.07.01
Electric Field Manipulation of Ferroelectric Vortices—In Situ TEM
Christopher T. Nelson1, 2, 3, 4, Zijian Hong5, Cheng Zhang6, 7, Ajay Yadav8, Sujit Das9, Anoop R. Damodaran1, 2, Sheng-Lin Hu9, 1, James D. Clarkson1, 2, Miaofang Chi1, 2, Philip D. Rack2, 7, Long-Qing Chen8, 9, Lane W. Martin10 and Ramamoorthy Ramesh1, 2, 3, 4, 5, 6, 7, 8, 9, 10; 1Lawrence Berkeley National Laboratory, Oak Ridge, Tennessee, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3University of California Berkeley, Berkeley, California, United States; 4Pennsylvania State University, State College, Pennsylvania, United States; 5University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 6University of California Berkeley, Berkeley, California, United States; 7University of California Berkeley, Berkeley, California, United States; 8University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Arrays of ferroelectric vortices formed in ferroelectric / paraelectric thin film multilayers with a predominant Néel-type rotational character [1] and emergent chirality [2] are an enticing foray into topological complexity that is typically the purview of magnetic systems. The nanometer length scale and direct electric field manipulation makes ferroelectric polarization texture an attractive counterpart to spin systems wherever parity exists. Moreover, electric field control of vortex array blocks has been demonstrated by scanning surface probe [3] in geometries where the vortex structure is degenerate with classic a1/a2 domains [4]. In this work using in situ TEM we present the electric field response of these ferroelectric vortices length scales comonat with the vortex structure (nm). In geometries where the vortex structure is highly stable, applied electric fields induce vortex asymmetry within the PTO layer manifesting as shifts of the rotation centers. In this manner the vortex structure adapts to applied fields via short range small domain wall translations without need of nucleation events. In geometries degenerate with a1/a2 domains, deterministic switching between vortex and a1/a2 structures can be achieved as in bulk [3].

[5] Authors acknowledge support by the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract number DE-AC05-00OR22725

1:45 PM EP01.07.02
Electronic Conductivity of Charged Ferroelectric Nanodomains
Stuart R. Burns2, Ye Cao3, Alexander Tselev4, Rama K. Vasudevan5, Joshua Agar6, Lane W. Martin2, Mark Huijben6, Sergei V. Kalinin7, Nagarajan Valanoor8, Anna Morozovska6, Petko Maksymovych3; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2University of New South Wales, Sydney, New South Wales, Australia; 3The University of Texas at Dallas, Dallas, Texas, United States; 4University of Aveiro, Aveiro, Portugal; 5University of California, Berkeley, Berkeley, California, United States; 6University of Twente, Enschede, Netherlands; 7National Academy of Sciences, Kyiv, Ukraine.

Ferroelectric nanodomains are inevitably created upon polarization reversal. They provide a natural setting to explore conductive properties of ferroelectrics, because the repolarization nuclei are decorated by weakly charged domain walls, and because they can be created and subsequently tuned on demand by appropriately chosen electric field. As such, nanodomains are a model system to probe presently open questions surrounding domain wall conductance, such as pathways to increase conductance (through carrier density and possibly mobility), understanding the stability of conductive walls and the origin of the screening charge.

We have measured conductance of two different kinds of ferroelectric nanodomains, aiming to maximize polarization charge in the ferroelectric volume. In the first case, a radially symmetric electric field is applied to a ferroelectric with substantial component of in-plane polarization – in our case the 100-oriented film of BiFeO3. Such nanodomains are intentionally unstable but arguably achieve the largest possible polar discontinuity. Indeed, we observe...
near-record high local conductivity for ferroelectric as well as metastability in applied electric field, producing an electronic function of a volatile resistive switch. However, the net conductance is not metallic in this case. Phase-field modeling reveals localization of polarization charge to near-electrode region, effectively screening applied electric field. We anticipate that conductance will be dramatically enhanced in the ultrathin limit, where the volume of polar discontinuity becomes comparable to the overall film thickness. On the other hand, we have investigated the signatures of inclined domain walls in lead zirconate titanate at the instance of ferroelectric switching by microwave probe, which is sensitive to the bulk volume of the film. We have again observed the largest microwave conductance among accessible polarization configurations, as well as profound metastability of nandomains in a relatively broad range of applied fields. An inspection of the dielectric properties of domain walls at and above their depinning field was carried out to separate the contributions of domain wall motion from nanodomains hysteresis. This analysis provided further evidence for electronic (rather than dispersive) origin of microwave conductance for ferroelectric structures created by localized electric fields. Finally, we will comment on the stability of the charged configurations based on detailed analytical modeling of charged domain walls in various screening scenarios. Charged domain walls appear to be generally unstable for polarization exceeding ~10 microC/cm², even with efficient supply of the screening carriers. Support provided by the U.S. Department of Energy, Basic Energy Sciences, Materials Science and Technology Division. Microscopy experiments performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

**2:00 PM *EP01.07.03**

**Electrochemical Phenomena of Polarization Switching in Ferroelectrics**

Anton V. Ievlev, Sergei V. Kalinin and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Polarization switching in ferroelectric materials underpins a broad gamut of applications ranging from random access memory, tunneling barriers, data storage, and ferroelectric ceramics. Classically, the polarization switches due to a co-existence of energetically equivalent crystallographic states, that can be altered with an external electric field. To stabilize polarization, charge discontinuity at surfaces and interfaces requires compensation, or screening, to avoid long-range electrostatic fields that destabilize the ferroelectric phase. Most studies consider polarization screening to be chemically inert; leaving the composition of the ferroelectric intact. However, analysis of extreme ferroelectric phenomena suggests higher complexity. It is well known that multiple polarization switching cycles can accumulate damage at interfaces, dubbed “ferroelectric fatigue.” Typically, tens or hundreds of thousands switching events are required, and the exact mechanisms remain controversial. Furthermore, polarization-dependent photovoltaic effects in perovskites suggest that even under optimal screening conditions a considerable electric field remains in the material. Thus, switching is associated with high fields, which can chemically alter material composition.

Here we utilize multimodal approach combining time of flight secondary ion mass spectrometry (ToF-SIMS) with atomic force microscopy (AFM) to explore the structure property interplay of ferroelectrics during polarization switching in lead zirconate titanate (PZT, PbZr₀.₂Ti₀.₈O₃) thin films. Using this multimodal imaging platform, we demonstrated that chemical phenomena plays significant role in ferroelectric switching process. Specifically, we found that local ferroelectric switching by the AFM tip, significantly alters the chemical composition in the 3-nm-thick surface layer of the sample, forming reversible concentration wave, of Pb²⁺ ions. Furthermore, investigations of the polarization cycling in the PZT sample with copper electrodes, showed penetration of the copper cations into the structure of PZT. This explains ferroelectric fatigue phenomenon, leading to decrease in spontaneous polarization with sample cycling.

Altogether, explored chemical phenomena associated with ferroelectric switching will enhance fundamental understanding of ferroelectric phenomena and aid in the practical application of ferroelectrics in devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

**2:30 PM BREAK**

**3:30 PM *EP01.07.04**

**Reliability of PbZr₀.₅₂Ti₀.₄₈O₃ Thin Films for Actuators**

Susan E. Trolier-McKinstry, Wanlin Zhu, Kathleen Coleman, Betul Akkopru-Akgun, Michael Lanagan and Clive Randall; The Pennsylvania State University, University Park, Pennsylvania, United States.

Lead zirconate titanate (PbZr₀.₅₂Ti₀.₄₈O₃, or PZT) films are of interest for piezoelectric microelectromechanical systems as actuators, e.g. in inkjet printers, adjustable optics, micromirrors, and ultrasound transducer arrays. In many cases, these actuators are driven at higher electric fields than would be characteristic of bulk ceramic actuators. Thus, understanding the factors that control the electrical and mechanical reliability of these films under aggressive conditions for electric fields and strains is critical. To address this, acceptor (1-4% Mn) and donor (1-4%) doped PZT films were grown. Thermally stimulated depolarization current (TSDC) measurements in Mn doped PZT films showed one depolarization peak with an activation energy of 0.6-0.8 eV, associated with ionic space charge presumably due to ionic migration of oxygen vacancies. The magnitude of the depolarization current peak increases with increasing degradation times, suggesting the dissociation of defect dipoles during electrical degradation. A similar depolarization current peak attributed to existence of mobile oxygen vacancies was also observed for undoped and Nb doped PZT films; the magnitude of this peak increases on lowering Nb or PbO contents. An additional TSDC peak, associated with trapped charges was found in both Nb doped PZT films and undoped PZT films annealed under low PbO partial pressure. The trap depth is estimated to be 1.1±0.03 eV, which is attributed to trapped electronic charge carriers at reduced Ti on the B site. Electron energy loss spectroscopy studies of degraded Nb doped samples confirmed localized Ti reduction near the cathode. A model describing the failure mechanisms will be presented.

**4:00 PM EP01.07.05**

**Measurements of Polarization Switching Dynamics in the Tens of Picoseconds**

Aaron M. Hagerstrom¹, Eric Marks², Xiaohang Zhang², Christian J. Long¹, James C. Booth¹, Ichiro Takeachi¹ and Nathan D. Orloff¹; ¹National Institute of Standards and Technology, Boulder, Colorado, United States; ²University of Maryland, College Park, Maryland, United States.

Technological applications of ferroelectric materials often depend on their tuning under an applied electric field. In recent years, polarization switching processes have attracted interest for their role in transient negative capacitance, which could be used increase transistor energy efficiency. Switching processes also govern how quickly a microwave-frequency device based on ferroelectric materials can be reconfigured. Despite the technological motivations to study switching speed, high-frequency measurements remain difficult. In particular, separating the behavior of the measurement circuit from the behavior of the material under test is increasingly difficult with increasing frequency. Interpretation of measurements often requires complicated models of both the material and the measurement circuit. In this talk, we describe a new method for quantifying switching dynamics through nonlinear mixing products up to 40 GHz. From our measurement technique, we are able to empirically describe the dynamical switching behavior of the material under small signals in the tens of GHz without making any physical assumptions about the material itself. We apply this method to Ba₀.₅Sr₀.₅TiO₃ as a proof of concept, and show that our frequency-dependent results agree with a physical model derived from Landau-Ginzburg-Devonshire (LGD) theory.
4:15 PM EP01.07.06

Thermally Stable SrRuO4 Electrode for Ferroelectric BaTiO3 and Photocatalytic Rh: SrTiO3 films

Ryota Takahashi1,2 and Mikk Lippmaa1;1 Univ of Tokyo, Chiba, Japan; 2 JST PRESTO, Tokyo, Japan.

Sr:Ru:Otet is the n=1 member of the Srn+1RunO3n+1 Ruddlesden-Popper family and a well-known metallic oxide that becomes superconducting below 1.5 K. Since it is thermodynamically the most stable phase in this ruthenate family, it can be grown at very high temperatures compared to several other metallic oxides such as Fe3O4, SrRuO3, or (La,Sm)MnO3. Moreover, the oxygen pressure window is wider than for many other oxides, notably SrRuO3, that are commonly used as metallic electrodes in oxide device structures. We present the results of a study on the thermal stability of SrRuO4 thin film electrodes and demonstrate the usefulness of this electrode layer material for high-temperature growth of ferroelectric BaTiO3 films and photocatalytic Rh: SrTiO3 films.

The SrRuO4 electrode films were prepared on BHF-treated SrTiO3(001) substrates by pulsed laser deposition. Atomic force microscopy revealed atomically smooth surfaces for 20-nm-thick SrRuO4 films. To investigate the thermal stability, ferroelectric BaTiO3 thin films were deposited at 700-1000°C on the SrRuO4 electrode layer. Pyroelectric hysteresis loop measurements were used to verify that the BaTiO3 films grown on SrRuO4 electrodes were ferroelectric, implying that the SrRuO4 electrode layers were thermally stable even during high-temperature deposition at 1000°C in 100 mTorr of oxygen. The wide oxygen pressure window of SrRuO4 electrode was investigated by the deposition of Rh: SrTiO3 thin films for photoelectrochemical water splitting electrodes. At growth temperature of around 800°C in 10⁻¹⁰ Torr of oxygen, the SrRuO4 electrode formed an atomically sharp interface with the film even at high growth temperatures and low oxygen pressures, yielding atomically flat Rh: SrTiO3 photocathode films.


SECCION EP01.08: Poster Session II: Applications of Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Silyam Dwaraknath and Abdelilah Slaoui
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP01.08.01

Improve Energy Harvesting from Ocean Wave Energy by Using 3D Printed Devices with Aim of Frequency Modulation in Piezoelectric Based Wave Energy Harvesters and Scavengers

Sina Baghban Kordmahale; Electrical Engineering, Texas A&M University, College Station, Texas, United States.

There are various methods to harvest sustainable energy from various resources (1, 2). We have used piezoelectric Macro Composite Fibers (MFCs) combined with soft material and 3D printed solid parts to harvest energy from the sea and ocean waves. Durable, low cost, low maintenance, and efficient wave energy harvesters alongside the availability of powerful waves can provide a sustainable green energy source for various applications. The commercialized wave energy harvesters have problems like: expensive complicated elements, heavy structures, too much mechanical and moving parts which will increase the unit price, high deployment, and maintenance expenses. In the proposed design, the flexible MFCs are sandwiched between two 3D printed slabs with saw-tooth surfaces and are encapsulated in a soft elastomer block. Ecoflex 030 is chosen as the soft elastomer (3, 4). The soft material casting method has been used to form the encapsulation and shape the Ecoflex based slabs (5). The different 3D printed blocks, with various saw-toothing periods and amplitudes, were used in this experiment to prove the hypothesis of efficiency of proposed design. In total, four different combination of period and amplitude of saw-tooth used in this experiment and it is approved that the higher amplitude and shorter period of saw-tooth on the surface, will cause on higher energy harvesting. The fabricated samples, placed and tested in a wave flume tank horizontally and the open circuit voltage and power measurement have done on the samples. The designed structure can harvest remarkably more energy in comparison with formerly designed wave energy harvesters which were just based on the soft materials, MFCs and anchoring in some cases. So this improved design could increase the efficiency of piezoelectric based wave energy harvesters and also can be a mesoscale model for piezoelectric based smaller scavengers. While the same design can be used for silicon-based mems structures, still the same 3D printing, like the one in this article, can be more economical for small scavengers too.

References:
2) S. Mir Varzandeh, S Baghban Kordmahale, “TURNING WASTEWATER (GREYWATER) INTO ELECTRICAL ENERGY IN BUILDINGS.” SET2011, 10th International Conference on Sustainable Energy Technologies, Sep 2011

EP01.08.02

Stretchable, Transparent and Self-Healing Triboelectric Nanogenerators with Ionic Current Collector

Kaushik Parida and Pooi See Lee; Nanyang Technological University, Singapore, Singapore.

Triboelectric nanogenerators have emerged as a promising power source for portable and stretchable electronic devices. However most of the nanogenerators use metallic electrodes, thus the devices could not achieve high stretchability and transparency, simultaneously. This work demonstrates the use of an ionic conductor as the current collector in a triboelectric nanogenerator, resulting in a highly transparent, stretchable and self-healing device. The device has a transparency of 92% transmission, it can sustain a tensile strain up to 700%, and autonomously self-healable. The energy harvesting performance of ionic triboelectric nanogenerator is 12 times higher than that of the metallic based triboelectric nanogenerator. The resulting device demonstrates an extremely stretchable, highly transparent self-heal power source to be used as a power supplies for sensors, wearable electronics and soft robotics.

Reference
Electromechanical Properties of Flexible Piezoelectric Nanogenerator (PENG) Using Different Patterns of Vertically-Aligned BaTiO$_3$ Nanotubes

Camelle Kaye A. Aleman, James Albert B. Narvaez and Candy C. Mercado; University of the Philippines Diliman, Quezon City, Philippines.

With the advancement catered by the use of lead-free piezoelectric nanogenerators (PENGs) for flexible electronics in energy harvesting, the challenge is to design an efficient system which is high power-producing. For this study, structural engineering approach was implemented to improve the electromechanical response of PENGs. Effects of varying patterns of the one-dimensional, vertically-arrayed BaTiO$_3$ nanotubes used in PENG devices, theoretically balanced with concepts on pile patterning and geometries in building foundations, on their output power were observed. Different patterns of vertically-arrayed, tetragonal phase BaTiO$_3$ nanotubes were synthesized via in situ conversion of selectively-anodized TiO$_2$ nanotubes on Ti substrates using hydrothermal process. Selective anodization which established the patterning of the BaTiO$_3$ was achieved through photolithography using a negative photoresist dry mask. The patterns of two sets vary in the diameter (1 mm and 1.5 mm), and the arrangement (linear and staggered arrays) of the circles printed on the mask. The methodology produced highly crystalline BaTiO$_3$ nanotubes based on the obtained X-ray diffractogram and EDX analysis. SEM images showed that the synthesized nanotubes had an average length of 66 μm and inner diameter of 67 nm. In addition to this, the study established that selective anodization using photoresist dry film mask can be utilized in creating patterned BaTiO$_3$ without significant loss in accuracy of pattern. Using this material, PENG devices were fabricated. The PENGs comprised a sandwich structure of Ti- BaTiO$_3$ nanotube-graphite-Ti and were further made flexible by encapsulating the structure with polydimethylsiloxane. The cantilever-type PENG devices were subjected to repeated bending stresses using a rotating motor to determine the effect of different BaTiO$_3$ patterns on the output voltages of the devices under constant cyclical stress. It was observed that pile characteristics such as pile diameter, pile arrangement, and pile spacing which was brought about by the varied diameter and arrangement parameters, affect the output voltage and voltage behavior of the PENG devices. Decrease in both BaTiO$_3$ nanotube array spacing and pattern diameter, increases the lateral displacement of the piezoelectric material and decreases the pile stiffness, respectively; all conditions consequently leading to an increase in the output voltage of the device. It was observed that the voltage behavior is dependent on the pile-matrix-pile interaction which is affected largely by adjacent pile spacing. Furthermore, the piezoelectric test showed that the highest peak to peak output voltage generated by the unpoled devices reached up to 1.9 V using the pattern with linear arrays of smaller circle diameter. The research, overall, is majorly a proof of concept study wherein the aim was to see the effect of patterning the piezoelectric material on the output voltage values of the fabricated PENG devices.

Nobel Lead Free Relaxor Multiferroic for High Energy Storage Application

Mohan K. Bhattarai, Sita Dagu, Alvaro Instan and Ram Katiyar; Physics, University of Puerto Rico, Rio Piedras, San Juan, Puerto Rico, United States.

We synthesized modified Barium zirconate titanate electro ceramics by a conventional solid-state reaction method with stoichiometric formula Ba$_{1-2x}$La$_{2x/3}$Zr$_{0.30}$Ti$_{0.70-3y/4}$Fe$_2$O$_3$ (BLZTF), where $y = 0.01$ & $0.05 \leq x \leq 0.06$ & investigated its structural, microstructural, dielectric, electrical, ferroelectric and magnetic properties. X-ray diffractometry was used to investigate the phase purity and to derive the crystallographic parameters. A uniform distribution of grains on the surface of the sample was observed using electron micrographs (SEM) recorded on pellets. The stoichiometry of the chemical compositions was examined using energy dispersive x-ray (EDS) analysis method. We carried out dielectric measurements on Ag/PLZTS/Ag metal-ferroelectric-metal capacitors using impedance analyzer as a function of temperature (100-600 K) and frequency (10^2-10^6 Hz). We observed enhanced dielectric constant in doped BZT. The room temperature magnetic measurements (M-H) were obtained using a vibrating sample magnetometer. Additionally, we observed thin PE hysteresis loop, suggesting that synthesized materials is relaxor multiferroics and promising materials for high energy storage applications.

Foam-Type Piezoelectric Composite for Internal Cochlear Implant

Jeonjae Ryu, Jinwon Oh, Kwangsoo No, Seunghum Hong and Steve Park; KAIST, Daejeon, Korea (the Republic of).

A cochlear implant is a device for people with hearing loss caused by inner ear damages. Despite its great use to improve hearing, the microphone and other electronics of the cochlear implant, typically located outside the ear, are not aesthetically attractive. Therefore, many studies to insert a cochlear implant into the body have been conducted. In this study, we present a new approach for fabricating piezoelectric sensors that are attached on the cochlea. We made a foam-type piezoelectric composite not to interfere with the movement of auditory ossicles. Generally, to avoid the aggregation of piezoelectric particles in a polymer layer, MWCNT has been used, but it is being suspected for its toxicity. On the other hand, we coated biocompatible polydopamine on piezoelectric particles and then dispersed them in the PDMS layer. We calculated porosity of the composites and measured their stress-strain curves. We characterized the output performance as a function of the frequency of sound. We anticipate that the foam-type piezoelectric composite is promising as a sensor capable of detecting the sound pressure for cochlear implant.

Field and Frequency Dependence of Magnetodielectric Coupling in Ni/PZT/Ni Multiferroics

Fernando Aponte1, Roberto Masso1, Gopalan Srinivasan2 and R Palai1; 1University of Puerto Rico, San Juan, Puerto Rico, United States; 2Physics, Oakland University, Oakland, Michigan, United States.

Spin capacitors have the potential to store both the electronic charge and magnetic spin that can produce conventional electric current and spin polarized current. The time evolution of spin polarized electrons injected into the piezoelectric material can be used for accurate sensing of magnetoelectric fields. To further study the application of multiferroic spin capacitors for future use in memory applications, Ferromagnetic/Ferroelectric/ Ferromagnetic tri-layer artificial multiferroic structures in spin capacitor configuration were fabricated by sputtering ferromagnetic Nickel (Ni) electrodes on lead zirconate titanate (PZT). Magnetocapacitance, magnetooimpedance, and phase angle measurements were carried out by a wide range of frequencies (100 Hz – 5 MHz) and magnetic fields (0T – 2T) at room temperature. We also compared the magnetodielectric measurements of the Ni/PZT/Ni spin capacitor with Ni/PZT/Ag and Ag/PZT/Ag tri-layers structures and their behavior. Two PZT layer thickness were studied, including 200 μm and 1 mm PZT. Ni/PZT/Ni spin capacitor shows a significantly different behavior compared to conventional PZT capacitor with Ag electrode and mixed electrode capacitor with one ferromagnetic and one conventional electrode. The spin capacitor (Ni/PZT/Ni) with the 1 mm PZT layer show mayor resonance peaks at ~166 kHz and at ~890 kHz, where the first peak is not present in the other capacitor structures. Second level peaks are found at 231 kHz, 444 kHz, 2.03 MHz and at 3.2 MHz. This las peak in the spectrum is shared with the three structures. The second level peaks have and ~32% intensity compared to the major peaks at ~166 kHz and at ~890 kHz. There is a notable reduction on the intensity of the peaks when the ferromagnetic electrode is present, with the mayor difference between the conventional capacitor having a 83% higher intensity ($\epsilon=55586$) compared with the Ni/PZT/Ag capacitor ($\epsilon=10015$) and a 57% reduction between Ni/PZT/Ag and Ni/PZTNi. For the 200 μm sample, the three structures of capacitor share a very similar behavior, with a certain shift for the Ni/PZT/Ag capacitor, where Ni/PZT/Ni and the conventional capacitor share the resonance peak at ~260 kHz and Ni/PZT/Ag has a shift of 50 kHz.
towards higher frequencies (308 kHz). And similar to the 1 mm layer PZT samples, there is a reduction in dielectric peak permittivity, with the conventional capacitor being the highest and lowering with the presence of the ferromagnetic lanthanum oxide with a difference of 28% between the conventional capacitor and Ni/PZT/Ag, and a 33% difference in reduction between Ni/PZT/Ag and Ni/PZT/Ni. The Lorentz model was used to study the peaks behavior by fitting the equation into dielectric measurements per range of frequencies and obtaining information from selected peaks.

**EP01.08.07**

Ultrasfast Zero-Bias Photocurrent in GeSe Single Crystals—A Promising New Ferroelectric Photovoltaic Material Kateryna Kushnir1, Ying Qin2, Guangjiang Li1, Sehaattin Tongay3 and Lyubov V. Titova4; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States.

Solar cells based on bulk photovoltaic effect (BPVE) may provide an efficient alternative to traditional p-n junction-based ones [1,2]. The prevailing mechanism behind BPVE is a shift current, a zero-bias photocurrent that can occur in a non-centrosymmetric material as excitation of an electron from the valence to the conduction band, resulting in a coherent spatial shift of the electron charge density. Ferroelectric semiconductors have been predicted to exhibit significant shift currents, spurring the search for ferroelectric semiconductor candidates for BPVE with bandgaps in the visible range [1-3]. Theory predicts that monolayer group-IV monochalcogenides are multiferroic and capable of generating significant shift currents [3,4]. Previously, we have demonstrated ultrasfast shift current following above bandgap excitation of GeS nanosheets [5].

Here, we present the evidence of a shift current response in a single crystalline GeSe with μm thickness. While the stacking sequence of the layers in this van De Waals material results in inversion symmetry in the bulk, this symmetry is broken at the surface, and a spontaneous surface polarization can exist in the same armchair direction as in a monolayer GeSe [3,4,6]. We have detected the ultrafast shift currents in GeSe single crystalline flakes using terahertz (THz) emission spectroscopy [5]. Detecting free space propagating electromagnetic pulses emitted by the sample excited at normal incidence by the ~ 100 fs, 800 nm or 400 nm pulses allows contact-free, all-optical monitoring of the transient photocurrents that result in this emission. We find that photoexcited GeSe crystals emit nearly single-cycle THz pulses in response to either 800 nm (1.55 eV) or 400 nm (3.10 eV) excitation. Excitation fluence, orientation and polarization dependence of the THz emission confirms that shift currents flowing along one crystallographic direction, presumably determined by the spontaneous polarization of the surface layer, are responsible for the observed emission. Stronger THz emission in response to 400 nm excitation, compared to the equivalent fluence of 800 nm excitation, stems from stronger absorption of 400 nm light by GeSe, which leads to the higher excitation of a surface layer. Highly efficient shift current photoexcitation in GeSe and the optical absorption that covers the entire visible range suggests applications of these layered materials in third generation BPVE photovoltaics.

**References:**


**EP01.08.08**

Enhanced Photodetection of Au-g-C3N4/CdS/ZnO Based Flexible Heterojunction Device Utilizing Piezo-Phototronic Effect Sourabh Pal1, Sayan Bayan2 and Samit K. Ray2; 1Advanced Technology Development Centre, Indian Institute of Technology Kharagpur, Kharagpur, India; 2Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur, India.

Two dimensional (2D) materials and their derivatives have witnessed the scientific community owing to their promising application in photonic and optoelectronic devices. In recent times, 2D graphic carbon nitride (g-C3N4) has been found to be a potential material for various photophysical properties. This n-type semiconductor is characterized by interesting electronic structure originating from the lone pair of nitrogen and electron delocalization in which the band gap can be easily tuned. Nanosheets of g-C3N4 both in the pristine form and in heterojunction with other semiconductors are found to be promising for optoelectronic device applications. The fabrication of heterostructured devices through the integration of g-C3N4 with various promising materials offer the basis of futuristic flexible optoelectronic nanostructures. Amongst different basis semiconductor nanostructures, zinc oxide (ZnO) is a well studied material owing to its distinguished performance in the field of optoelectronics. Apart from the well known ultraviolet (UV) light emission properties, piezoelectric properties of ZnO are also fascinating due to its tremendous scope in the application of high performance photodetectors. Coupling the piezoelectric properties with the semiconductor properties under mechanical stimuli can definitely lead to the modified output of the host material through modification in the local interface and charge-carrier transport. Herein, we report on efficient and enhanced photodetector in ZnO based hybrid heterojunction with CdS and Au nanoparticle loaded g-C3N4 nanosheets under bending state. In the present investigation, the scheme of g-C3N4/CdS/ZnO based heterojunction has been adopted due to elevate charge carrier separation under visible light, which can be further enhanced (~18 times at 530 nm) by plasmonic effects with the exploitation of Au loaded g-C3N4 nanosheets. Strain induced piezoelectric potential development in ZnO has also been witnessed in the hybrid heterojunction and it has been found this piezo-potential can efficiently trigger the photodetector response (~102 times as compared to normal state) through the band alignment at the interface of the hybrid heterojunction.

**References:**


**EP01.08.09**

Large Local-Compressive Stress-Induced Improvements in Piezoelectric Characteristics of Lead Zirconate Titanate Thin Films on a Ni Nanodots-Array Chan Su Han, Ahra Cho, Da Bin Kim and Yong Soo Cho; Yonsei University, Seoul, Korea (the Republic of).

This manuscript introduces a nonconventional way to improve piezoelectric properties of PZT thin films substantially by forming Ni nanodots-array on a Si substrate with the assistance of uniform magnetic field upon deposition. The existence of Ni nanodots induces extrinsic compressive stress at the initial stage of film growth due to an enormous difference of ~94% in thermal expansion coefficient between the Ni and PZT film. The level of thermal mismatch is typically not allowable at the regular film interface. Specifically, heavily 12 mol% Nb-doping was selected for the sputtering process since the heavy doping has been recently reported to uniquely produce the in situ domain formation during deposition when combined exclusively with the Ir/TiW bottom electrode. Interestingly, the relatively high content of 12 mol% Nb is all dissolved into the perovskite structure without segregation. The final film/electrode structure corresponds to Pt/Nb-doped PZT/Ir/TiW/Ni nanodots/SiO2/Si. The role of an AlNiCo magnet used here provides uniform external magnetic field strength to facilitate consolidation of the Ni nanodots at high temperature. This nanodot approach induces local large compressive stress.
only around the region of Ni nanodots so that the film structure can be sustained. As a result of this unique local stress approach, a substantial enhancement of effective piezoelectric coefficient by ~33% is obtained from the changed crystal orientation and easier domain formation. The shift of polarization-electric field curve indicates the presence of internal field in the domain structure. This in situ process does not require the subsequent annealing and poling procedure, which have been commonly demanded for piezoelectric materials. So the adoption of Ni nanodots with the in situ processing creates very unique improvements.

EP01.08.10
ZnO-BaTiO3-Epoxy Multifunctional Electro-Active Thin Films—Enhancement in Electron Transport Regimes by Comparison of ZnO Nanowires and Nanoparticle Composites Walker Tuff1, Saqib Ahmed2 and Sankha Banerjee; 1; California State University, Fresno, Fresno, California, United States; 2Mechanical Engineering, Buffalo State College, Buffalo, New York, United States.

Piezoelectric and electro-active composites are investigated as new generation self-powered energy harvesting devices for a wide range of applications from the industrial to the medical field while maintaining high reliability, durability and sensitivity over wide range of frequencies. The electrical, dielectric and piezoelectric properties can be enhanced by embedding electro-active and conductive inclusions in the matrix material. The present work involves the fabrication of three-phase, multifunctional lead-free, BaTiO3-Epoxy-ZnO (nanowire) and BaTiO3-Epoxy-ZnO (nano-particle) composite and flexible thin films. The volume fraction of the BaTiO3 phase was held constant at 40%, while the volume fraction of the ZnO nanowire phase was varied from 1% to 10%. The work compares the role of ZnO nanowire and ZnO nano-particle inclusions distributed in an epoxy matrix to fabricate three-phase composites. The influences of several factors on the effective electromechanical properties of the composites are also analyzed. The dipoles of the electro-active phases were aligned using a plasma-microdischarge (Corona) poling technique. The piezoelectric strain coefficients, dielectric constant, dielectric loss tangent, capacitance, impedance, resistance, and conductance of the samples were measured and compared as a function of poling regime. The impedance and dielectric spectra of the composites were recorded over a frequency range of 20 Hz to 10 MHz. The fractured surface morphology and distribution of the phases were observed with the aid of Electron Dispersion Spectroscopy (EDS) and a Scanning Electron Microscope (SEM). The crystal structure of different phases in the composite were also characterized used Raman Spectroscopy.

EP01.08.11
Thickness Scaling of Ferroelectricity and Electrical Conductivity in Multiferroic BiFeO3 James Steffes1, Ramamoorthy Ramesh2 and Bryan D. Huey; 1; University of Connecticut, Storrs Mansfield, Connecticut, United States; 2University of California, Berkeley, California, United States.

Computed tomography atomic force microscopy (CT-AFM) is presented as a novel experimental modality for nanometer-scale measurements of the size-dependence of functional properties in the room temperature multiferroic BiFeO3. Intrinsic and extrinsic properties of ferroelectric thin films are known to have strong dependencies on electrical and mechanical boundary conditions, resulting in finite size effects in electronic and magnetic properties at length scales below several hundred nanometers. By combining recently-developed CT-AFM techniques with piezoresponse force microscopy (PFM) and conductive AFM (CAF), nanometer-scale three-dimensional imaging of ferroelectric domains and conductive defects at polarization discontinuities has been achieved in thin film BiFeO3. CT-AFM additionally provides a platform for quantifying the thickness dependence of the local spontaneous polarization, ferroelectric coercive field, and electrical conductivity in BiFeO3 across two decades of thickness. The thickness-resolved ferroelectric properties of BiFeO3 acquired with CT-AFM strongly correlate with both Landau-Ginzburg-Devonshire phenomenological theory and the semi-empirical Kay-Dunn scaling law for ferroelectric coercive fields, providing an unambiguous determination of a stable and switchable polar state in BiFeO3 at thicknesses below 5 nm. Complimentary tomographic PFM and CAFM data reveals the geometric dependence of polar discontinuities on the heterogeneous electrical conductivity of BiFeO3 as a function of film thickness, which shows strong agreement with the model of Schottky emission for bulk BiFeO3 as well as several electrically-conducting defect types in BiFeO3. Along with complementary transmission electron microscopy (TEM) analysis, this work provides new insights into the relationship between thickness and ferroelectric properties in heteroepitaxial multiferroics.

EP01.08.12

Ferroelectric perovskites such as barium titanate (BaTiO3) have had numerous applications in nonvolatile memories, transducers, micro sensors and capacitors because of their unique properties such as spontaneous polarization, piezoelectric and pyroelectric effects, as well as large dielectric constants. In order to design and optimize these devices, it is essential to obtain detailed, atomistic-scale insight of the BaTiO3 ferroelectric perovskite. Currently, there are three approaches to model the ferroelectric behavior of BaTiO3: Phenomenological, First-principles and Force field-based methods. Phenomenological models are not able to provide atomistic level description of the ferroelectric perovskites. First-principles methods such as the density functional theory (DFT) are considered as the most accurate models, however, because of heavy computational costs these methods can be only viable for relatively small systems and short time scales. Moreover, since the DFT models are mainly limited to zero Kelvin, most of ferroelectric properties of the perovskite materials such as hysteresis loop, sequential phase transitions and domain wall motions cannot be investigated using the first-principles methods. Force field based methods can provide the computational speed required to perform molecular dynamics (MD) simulations with system sizes and time scales sufficiently large to describe the full chemistry of the ferroelectric perovskites. ReaxFF reactive force fields first developed for hydrocarbons and later applied to different systems such as ceramics, metals and their oxides and provided precise results for those systems. We developed the first reactive force field for BaTiO3 systems which captures both chemical and electro-mechanical properties of the material. We performed realistic size molecular dynamics simulations to investigate the phase transition sequence, ferroelectric and thermal hysteresis loops for the BaTiO3 crystal structure. Furthermore, we investigated the effects of oxygen vacancies and different surface terminations on the material polarization.

EP01.08.13
Spiral Domain Walls in Ferroelectric PbTiO3 Thin Films Christopher T. Nelsen1, 2, 3, 3, 1, Zijian Hong1, Ayaj Yadav1, Sujit Das3, Anoop R. Damodaran1, Shang-Lin Hsu1, 1, Long-Qing Chen1, Lane W. Martin2 and Ramamoorthy Ramesh2, 2, 1; Lawrence Berkeley National Laboratory, Oak Ridge, Tennessee, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3University of California Berkeley, Berkeley, California, United States; 4Pennsylvania State University State College, Pennsylvania, United States.

Defects in the ferroelectric topology such as domain walls are dynamically controllable low-dimensional entities that can manifest local non-bulk properties such as a 2D electron gas [1, 2]. Domain walls try to adopt electrical neutrality, i.e. the Polarization has a constant flux (∇ P = 0), and those that violate this either compensate the bound charge or low energy configurations including geometries that ensure a price of high electrostatic energy. As a result, charged domain walls can exhibit significant property differences to the bulk[2], but are typically metastable or present in low remnant polarization systems with a sufficient screening charge density such as improper ferroelectrics. In ferromagnetic systems, where screening charges are unavailable,

**EP01.08.14**

**Studies on Magnetic and Electrical Properties of Gallium Ferrite Multiferroic Thin Film**

Sita Dungu1, Dhiren K. Pradhan2, Shalini Kumari3, Mohan K. Bhattacharja4, Alvaro Insta1 and Ram S. Katiyar1; 1Department of Physics, University of Puerto Rico, San Juan, Puerto Rico, United States; 2Geophysical Laboratory, Washington, District of Columbia, United States; 3Department of Physics, West Virginia University, Morgantown, West Virginia, United States.

Magnetoelectric materials might hold the future for the ultimate memory, spintronics, and other multifunctional devices as they exhibit simultaneous ferroelectric and ferromagnetic behaviors and permit control and switching of the magnetic order parameters via an electric field, and polarization with a magnetic field. Orthorhombic gallium Ferrite is a prominent multiferroic due to its piezoelectricity and ferrimagnetism coupled with magnetoelectric effects. Herein we studied the dielectric, ferroelectric and magnetic behavior of ~ 200nm highly oriented orthorhombic GaFeO3 thin film deposited on a SrRuO3 buffered SrTiO3 substrate by optimized Pulsed Laser Deposition method. SrRuO3 was deposited at an optimized temperature of 680°C under an oxygen pressure of 200 mTorr, with a laser energy density ~ 1.5 J/cm² and a frequency of 10 Hz. Subsequently, GaFeO3 was grown on the top of SrRuO3 at 725°C with oxygen pressure 300mT and energy density ~ 2 J/cm² at a frequency of 5 Hz. The film was then cooled at the rate of 2°C/min under the pressure of 200mT. The 0-20 large angle x-ray scans (10° to 90°) showed highly oriented film grown at (001) direction without any secondary peaks. Surface morphology was analyzed with AFM studies which showed the film is smooth, free of microcracks, pores or holes with average surface roughness around 2-3 nm. Temperature-dependent magnetization behavior was studied at both field-cooled and zero-field-cooled conditions in between 5- 395 K using several magnetic fields (such as 100 Oe, 500 Oe, and 1000 Oe) identify the Neel transition temperature T_N around 225 K. Ferroelectricity of GaFeO3 was demonstrated by polarization hysteresis and PFM measurement. The film exhibits the net switching polarization of ~12 μC/cm² with a maximum field of 700kV/cm. The single phase RT GFO shows multiferroic behavior with a magnetoelectric coupling which might be a potential candidate for spintronic and microelectronic applications.

**EP01.08.15**

**Influence of Metal Element Addition on Crystal Structure of AIN Piezoelectric Thin Film**

Masato Uehara, Sri Ayu Anggraini, Hiroshi Yamada and Morio Akiyama; National Institute of Advanced Industrial Science and Technology, Saga, Japan.

It is vital to adopt piezoelectric materials for microelectromechanical systems (MEMS), where aluminum nitride (AIN) has been regarded as an attractive candidate for featuring a sensor, an energy harvester and a bulk acoustic wave resonator. Akiyama et al. have dramatically improved by Sc-Addition but the Sc-AIN is expensive for industrial uses. We succeeded in improvement of the piezoelectric coefficient by simultaneous addition of Mg-Nb. The improvement is comparable to Sc-AIN. According to other paper, Mg-Hf, Mg-Zr, and Mg-Ti are also effective. The lattice constant ratio c/a of wurtzite decreases by addition of the effective elements.

In this paper, we have investigated the influence of various element addition on AIN crystal structure. With single addition of Mg and Ca, considerable decrease of crystallinity was confirmed. This would be caused by a problem of charge compensation. In case of Nb and Ti, the crystallinity decrease was smaller but the other phase formation was observed. In case of Sc, above phenomena were not observed until addition ratio of 0.5. The change in the a-axis is similar for each element additions and increases monotonically. On the other hand, the change of c-axis was different. By Sc addition, the c-axis increased to the addition ratio of 0.3 and decreased with addition of more. For the other elements, the c-axis increased until the addition ratio at which crystallinity decrease or other phase formation was observed. Particular, by Nb and Ti addition, the c-axis increase was large. These ion radii are not particularly large, but rather the Ti ionic radius is the smallest. The large increase of c-axis can not be explained by ion radius. The electronegativity of Nb and Ti is large compared with Mg, Ca, and Sc, and the fraction of ionic bonding would be larger than them. The fraction of covalent and ionic bonding would be related with the change of crystalline structure such as c:a ratio. We think that by addition of Sc and Mg the fraction of ionic bonding would increase and the crystalline would soften, leading to piezoelectric increase of AIN.

**EP01.08.16**

**Stroboscopic Materials Testing by Synchrotron X-Rays on the Sub-Nanosecond to Picoseconds Time Scale**

Klaus-Dieter Liss1,2,3; 1Guangdong Technion - Israel Institute of Technology, Shantou, China; 2Technion – Israel Institute of Technology, Haifa, Israel; 3MMM, University of Wollongong, Wollongong, New South Wales, Australia.

X-ray diffraction is a very common method to analyze strain fields and crystallographic phases in a wide range of materials, including functional materials such as multiferroics. The presentation resumes my work on stroboscopically time resolved synchrotron X-rays probing materials under periodic external stimulus. Ultrasonic strain fields can be evaluated as a function of oscillation period, in both low and high frequency cases, where additional diffraction phenomena take place. Switching of electric fields in ferroelectric material reveal phase transformation response. An overview on the technique, examples and future potential, particularly to ferro and piezoelectrics will be given.

**EP01.08.17**

**Ferroelectric Lead Free Na0.52K0.44Li0.04Nb0.84Ta0.10Sb0.06O3 Material—Giant Electromechanical Response with Intrinsic Polarization and Resistive Leakage Analyses**

Abid Hussain and Binay Kumar; Department of Physics and Astrophysics, University of Delhi, New Delhi, India.

Environment friendly lead free Na0.52K0.44Li0.04Nb0.84Ta0.10Sb0.06O3 (NKLNTS) ceramic was synthesized by solid state reaction method in search of a potential candidate to replace lead based ceramics such as PbZrO3-PbTiO3 (PZT), Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) etc., for various applications. The ceramic was calcined at temperature 850 °C and sintered at 1090 °C. The powder XRD pattern revealed the formation of pure perovskite phase having tetragonal symmetry with space group P4mm of the synthesized ceramic. The surface morphology of the ceramic was studied using Field Emission Scanning Electron Microscopy (FESEM) technique. The well defined grains with homogeneous microstructure were observed. The average grain size was found to be ~ 0.6 μm. A very large value of piezoelectric charge coefficient (d33 ~ 754 pm/V) was obtained for the synthesized ceramic which indicated its
potential for use in transducers and actuators. In dielectric measurements, a high value of ferroelectric to paraelectric phase transition temperature (310°C) and a high value of maximum dielectric permittivity (2110 at 1 kHz) and a very small value of dielectric loss (<0.6) were obtained which suggested the utility of NKLNTS ceramic in high temperature ferroelectric devices. Also, the degree of diffuseness (γ) was found to be 1.61 which confirmed a relaxor ferroelectric behavior in NKLNTS ceramic. P-E hysteresis loop was traced and the value of spontaneous polarization was found to be ~11µC/cm² at room temperature. The pyroelectric coefficient was obtained to be very high (p ~ 1870 µCm²°C⁻¹) for the present case indicating its applicability in pyroelectric detector applications including fire and burglar alarms, infrared imaging, etc. NKLNTS ceramic showed fatigue free behavior over 10⁷ switching cycles. Remanent hysteresis task was performed to determine the true-remanent (or intrinsic) polarization of NKLNTS ceramic by eliminating non-switchable components which showed that a major portion (83.10 %) of the remanent polarization (P_r) is switchable in the sample which makes NKLNTS ceramic a suitable material for memory switching devices applications. Time-Dependent Compensated (TDC) hysteresis task was carried out which revealed resistive leakage free nature of the ceramic. The performance of NKLNTS ceramic was found to be superior to many lead based piezoceramics and hence can effectively replace them for use in piezoelectric, pyroelectric and long duration ferroelectric applications.

EP01.08.18
Thermal-Induced Ferroelastic Domains in Barium Titanate Qianwei Huang¹, Zhibin Chen¹, Feifei Wang², Simon Ringer¹,², Haosu Luo³ and Xiaozhou Liao¹; ¹School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, New South Wales, Australia; ²Key Laboratory of Optoelectronic Material and Device, Department of Physics, Shanghai Normal University, Shanghai, China; ³Australian Centre for Microscopy and Microanalysis, The University of Sydney, Sydney, New South Wales, Australia; ³Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Ferroelectric materials have extensive applications in electric devices due to their unique properties. The ferroelectric/ferroelastic domain structures in ferroelectric materials can be manipulated via external stimuli including heat, electric bias and mechanical stress. Previous researches on how heat (or temperature) affects ferroelectric domain structures were normally carried out at temperatures close to phase transition points. Here we show that temperature variation far away from a phase transition point could have a significant effect on the ferroelectric/ferroelastic domain structure in ferroelectric materials. Our results indicate that thermal-induced degradation or thermal stability of ferroelectrics is not negligible. In our work, barium titanate (BaTiO₃) single crystals were slowly heated to several temperatures in the range of ~ 40 – 60°C (the Curie point is ~120°C) in the transmission electron microscope (TEM) and were kept at each temperature for detailed structural characterization. As the temperatures were far below the Curie point and higher than the ambient temperature, the BaTiO₃ remains as a stable tetragonal phase. It is surprising to see that nano-sized lamellae based domains appeared along the [110] direction within the initial domains at a small temperature range of ~ 50°C. The new domain structure disappeared above or below the temperature range and the phenomenon was repeatable. The orientation of the newly formed domain walls indicated that the new domains were 90° ferroelastic domains. The mechanism for the formation of the new domain structure will be discussed based on detailed TEM investigation results.

EP01.08.19
Visualization of Domain Structure and Switching Property of Hf₀.₅Zr₀.₅O₂ for the Ferroelectric Field Effect Transistors Hoon Kim¹, Soekjung Yun¹, Seongwoo Cho¹, Myungsoon Seo², Min-Ho Kang¹, Yang-Kyu Choi¹ and Seungbum Hong¹; ¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Department of Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ³Department of Nano-process, National NanoFab Center (NNFC), Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of). Zr-doped HfO₂ (HZO), a conventional gate dielectric material, has attracted much attention for displaying negative capacitance in Field Effect Transistors (FETs) and its potential application for next generation nonvolatile memory devices. Furthermore, compared to conventional ferroelectric materials, HZO is more suited to FET fabrication because of its higher scalability, thermal stability, and compatibility with Si processes. Despite the material’s potential, there is few research on its ferroelectric properties due to its limited window of allowable thickness at the nanoscale. Herein, we analyzed the ferroelectric properties and domain structures of HZO to understand the negative capacitance reported in HZO and mechanism behind ferroelectricity and related domain structure as well as its switching behavior at the nanoscale. First, in order to understand the switching characteristics of HZO thin films, we measured and analyzed the polarization versus electric field (PE) loops. Second, we investigated the domain structures of HZO using angle-resolved PFM, which entails using vertical and lateral PFM as well as the rotation angle of the sample to derive the sample’s complex polarization state. We envision that our results will elucidate the origin of negative capacitance in terms of the domain structure of HZO film and contribute to the development of ultralow power logic transistors and future nonvolatile memory devices.

EP01.08.20
Effects of Post Metal and Forming Gas Annealing on Characteristics of Ferroelectric FinFETs with HfZrO₂ Gate Dielectric Myungsoon Seo¹,², Min-Ho Kang¹, Wu-Kang Kim¹, Jae Hur¹, Soekjung Yun¹,², Hoon Kim¹, Seungbum Hong¹ and Yang-Kyu Choi¹; ¹School of Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Foundry Business, Samsung Electronics, Yongin, Korea (the Republic of); ³National Nanofab Center, Daejeon, Korea (the Republic of); ⁴Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ⁵Memory Business, Samsung Electronics, Hwasung, Korea (the Republic of).

Since excellent ferroelectric (FE) characteristics were demonstrated with a CMOS-process compatible thin hafnium-based material, FE field-effect-transistors (FETs) have attracted considerable attention as a promising candidate for next-generation nonvolatile memory, analog synaptic devices for neuromorphic systems, and steep slope devices called negative capacitance (NC) FETs, with low power consumption. Among various HfO₂ thin film dopant materials suitable for FE operation, such as Si, Zr, Y, and Al, Zr is well-known as showing stable characteristics thanks to having almost identical chemical properties with Hf. HfZrO₂ (HZO) films consist of tetragonal, orthorhombic, and monoclinic phases. The orthorhombic phase is known to be responsible for the ferroelectricity of the thin film. Annealing after FE deposition, for example post metal annealing (PMA) or forming gas annealing (FGA), leads to crystallization which is a key factor in the final ferroelectric characteristics of the HZO thin film. Even though the effects of PMA and FGA on metal-ferroelectric-metal (MFM) capacitors have been investigated by several research groups, there has been no report on metal-ferroelectric-insulator-silicon (MFSIS) structured FE FETs yet. In this work, the effects of PMA and FGA on characteristics of a highly-scaled FE FinFET with a 10 nm thick HZO film were carefully investigated. The effects of PMA at temperatures from 400 °C to 900 °C for 30 s were examined. An FGA split experiment was conducted with various temperatures and hydrogen (H₂) gas content ratios. Changes of orthorhombic phase peak were investigated by spectral measurements with the grazing incidence X-ray diffraction (GI-XRD), and changes in domain behavior were also investigated using piezoresponse force microscopy (PFM). MFM capacitors with a TiN top and a Ti bottom electrode exhibited different butterfly-like features in capacitance-voltage (C-V) characteristics and polarization-electric field (P-E) hysteresis loops by splitconditions. Finally, the electrical characteristics of the highly-scaled FE FinFETs were compared to those of the MFM capacitors for the first time under various conditions. The FE FinFETs were fabricated with a fin width of 50 nm, a fin height of 100 nm, and a gate length of 120 nm on bulk silicon wafers with gate last processes. The optimized PMA and FGA conditions determined in this experiment are expected to provide insights into the use of FE FETs as next-generation memory, synaptic devices for neuromorphic
Magnetoelectric (ME) multiferroic materials are promising materials for this novel multifunctional applications. BiFeO₃ (BFO), ferroelectric Tc ~ 830 °C and antiferromagnetic TN ~ 370 °C, is one of the rarest single-phase room temperature multiferroic materials with many interesting physical phenomena. However, high leakage current of BFO and weak magnetoelectric (ME) coupling are detrimental for applications. A strong ME coupling is an important requirement for practical applications. To enhance the ME coupling in BFO, we doped with GdMnO₃ (GMO), an oxide ferromagnetic. In this present work, we report synthesis and characterized BFOₓ-GMO (BFO-GM) solid solutions (0.0 ≤ x ≤ 0.2) by auto-combustion method. The materials have been systematically characterized and examined to study the possibility of the compositional driven structural phase transition and its correlation with the ME coupling. The structural, microstructural, Raman spectroscopy, dielectric, ferroelectric, magnetic, and magnetoelectric properties were studied as a function of field (magnetic and electric), frequency, and temperature. For quantitative understanding, various modified theoretical models (Maxwell-Wagner, universal power law, Debye, etc.) were used to model the data. We found that BFO with 10% GMO doping shows strong ME effect. Details of this study will be discussed in the presentation.

**EP01.08.21**

**Magnetoelectric Coupling in BiFeO₃-GdMnO₃ Multiferroics**

Roberto Maso1, Satya N. Tripathy2, Ricardo Martinez Valdés1, Dilip K. Pradhan1, Fernando Aponte1 and R Palai1; 1Univ of Puerto Rico, San Juan, Puerto Rico, United States; 2Physics, National Institute of Technology, Odisha, India.

**EP01.08.22**

**Easy Control of Ferroelectric Vortices Array by Sweeping Field**

Ye Ji, Lele Ma, Linjie Liu, Weijin Chen and Yue Zheng; State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, China.

Plenty of novel ferroelectric domain structures are pursued for over a decade due to both theoretical interest (topology phase transition, emergent phenomena, etc.) and practical use. Specifically, ferroelectric vortex with at least two-fold chirality and small size, is a competitive candidate for high capacity memory storage. Accordingly, manipulation of vortex chirality is of fundamental significance. Several proposed approaches have made notable progress by introducing local field with distinctive origins such as external inhomogeneous electric field and mechanical dislocation to break the circular symmetry of vortex (or discrete rotational symmetry for flux-closure structure). However, these approaches are either hard to perform or need a priori knowledge of imperfection which severely restrict the universality. In this paper, we generalize the symmetry broken idea to the sweeping direction in a time-dependent sweeping process, facilitating a simple yet robust vortex switching method conducted by phase field modeling. We firstly consider that a biased tip sweeps over a vortex where the electric field is no need to be stronger than that totally destroys the vortex. The sweeping process will produce a dominant dipole region (DDR) which serves as a new nucleus. Based on this mechanism, we propose a BaTiO3/SrTiO3 (BTO/STO) composite nanowire system for 1D memory architecture where each BTO block can form vortex thus carry information with STO block being the isolation zone. The vortex orientation can be tuned as well for multi-bit storage. The sweeping method is successfully employed into this system under varies conditions. Note that the coupling between adjacent BTO blocks is tuned by thickness of STO blocks. While strong coupling may cause crosstalk, it also provides a new controlling factor within the framework of sweeping method. We observe that vortex switching process is effectively reduced under temperature field. Since the DDR exhibits no preferential orientation under temperature field, the neighboring part of adjacent BTO block behind the sweeping field will induce a DDR with same orientation to reduce gradient energy, therefore determines the final chirality. We hope the sweeping method will promote the understanding of vortex switching and be beneficial to device development.

**EP01.08.23**

**Strain, Temperature and Electric-Field Effects on the Phase Transition and Piezoelectric Responses of KₓNaₓNbO₃ Thin Films**

Mengjun Zhou1,2, Jianjun Wang2, Long-Qing Chen1,2 and Ce-Ween Nan1; 1School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; 2Department of Material Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

KNbO₃-based solid solution system is environment-friendly with good electromechanical performance. This work established the misfit strain–strain and temperature–strain phase diagrams for KₓNaₓNbO₃ thin films and calculated the polarization switching, phase transition, and piezoelectric responses of KₓNaₓNbO₃ thin films under various strains, temperatures and electric fields. The results show that the piezoelectric coefficient d₃₃ can be enhanced near the phase boundaries. For the ferroelectric phase with nonzero out-of-plane polarization component, an optimal electric field is identified for maximizing d₃₃, which is desired in applications such as thin-film piezoelectric MEMS, transducers for ultrasound medical imaging and energy harvesting. The present results are expected to provide guidance for future experimental study of KₓNaₓNbO₃ thin films and the optimization of ferroelectric thin film-based devices.

**EP01.08.24**

**IR-Active Modes Detected by Tip-Enhanced Raman Spectroscopy in SrTiO3 Nanostructures—Field Gradient or Strain Gradient Contribution?**

Azza Hadi Youssef1, Chahinez Dab1, Jiawei Zhang1, Gitanjali Kolhatkar1, Alexandre Merlen2 and Andreas Ruediger1; 1Institut National de la Recherche Scientifique, Varennes, Quebec, Canada; 2IM2NP, UMR 7334 CNRS, Universities of Aix Marseille and Toulon, Toulon, France.

SrTiO₃ is an incipient ferroelectric perovskite, which has been extensively studied for its applications in electronics and electro-optic devices. When subjected to a biaxial strain, SrTiO₃ thin films show polar properties due to structural distortion. The structural distortion has a giant impact on the Raman modes, which correspond to the zone-center optical phonons symmetry, forbidden in bulk system. Raman spectroscopy of forbidden vibrational modes has been identified as a qualitative diagnostic tool for studying the strain effects and for providing vibrational spectroscopic information on the dynamic behavior of thin films. Tip-enhanced Raman spectroscopy (TERS), where the Raman and apertureless near-field scanning optical microscopy are combined with the contribution of a metallic tip, provides a comprehensive approach to those modes with improved sensitivity and spatial resolution.

In this work, we experimentally investigate strain-induced polarisation by monitoring vibrational Raman and IR-active modes in SrTiO₃ thin films (15 nm or less) deposited on platinized MgO (100) substrates by radio-frequency magnetron sputtering. In these films, the strain gradient is generated by the lattice-mismatch between the film and the substrate. We employ conventional Raman spectroscopy to investigate the effect of the interfacial strain gradient on the optical phonon modes of SrTiO₃ thin films. We detect first-order polar transverse optic T₁, T₂ and T₄ modes that indicate a lowering of the crystal symmetry for the SrTiO₃ and thus the appearance of spontaneous polarization generated in localized strained regions.

Second, to present an evidence of the existence of the nano-polar regions with respect to conventional Raman spectroscopy, (TERS) measurements were...
recorded on a SrTiO$_3$ thin film. The gold tip introduces an electric field gradient contribution to the signal amplification of the polar phonons and it images the surface of SrTiO$_3$ nanostructures based on the optical phonon mode response. Finally, we discuss the field gradient contribution to the significant signal enhancement as well as to the appearance of symmetry-forbidden IR-active modes and first-order Raman modes associated to the nano-polar regions induced by local structural distortions.

EP01.08.25

Nanoscale Linear Dielectric Constant Imaging Using $\partial C/\partial z$ -Mode Scanning Nonlinear Dielectric Microscopy

Yoshiomi Hiranaga and Yoshi Cho; Tohoku University, Sendai, Japan.

The continued miniaturization of electronic devices containing dielectric materials has increased the impact of nanoscale linear dielectric constant distributions on device characteristics [1]. As a result, more precise control of process damage is required to ensure the fabrication of reliable highly integrated devices, and the nanoscale analysis of dielectric constant has become important. Dielectric constant assessments over nanoscale regions require the measurement of capacitance with sufficiently high sensitivity. Various techniques for the measurement of local capacitance based on scanning probe microscopy (SPM) have been proposed to date, including scanning capacitance microscopy (SCM) [2], scanning microwave microscopy (SMM) [3], microwave impedance microscopy (MIM) [4] and scanning nonlinear dielectric microscopy (SNDM) [5]. SNDM is an especially useful technique as it is highly sensitive to variations in capacitance on the order of 10$^{-22}$ F$/\sqrt{Hz}$ [6]. As a result, SNDM can detect capacitance variations even when employing extremely sharp probe tips, and so is a very effective means of obtaining improved spatial resolution.

Conventional SNDM is typically used to determine nonlinear dielectric constant and to visualize dielectric (or electrical) anisotropy in ferroelectrics and semiconductors. In contrast, there have been only a few reports concerning linear dielectric constant imaging using SNDM [7-9]. Herein, we propose a novel method for linear dielectric constant imaging, termed $\partial C/\partial z$ -mode SNDM ($\partial C/\partial z$-SNDM), that substantially reduces the effects of stray capacitance and enables quantitative imaging with high spatial resolution. $\partial C/\partial z$-SNDM technique employs probe-height modulation to suppress disturbances originating from stray capacitance and to improve measurement stability. This method allows local dielectric constant distributions to be examined with extremely low noise levels (approximately 0.01 aF) by virtue of the highly sensitive probe. A cross-section of a multilayer oxide film was visualized using $\partial C/\partial z$-SNDM as a demonstration, and numerical simulations of the response signals were conducted. Moreover, the beneficial aspects of higher-harmonic response imaging are discussed herein, taking into account assessments of spatial resolution and quantitation.


EP01.08.26

Investigation of Piezoelectric Responses of BaTiO$_3$ Nanorod Bundle Arrays

Moon-hyeok Choi, Seon Min Jang, Sang-Mok Chang and Su Chul Yang; Department of Chemical Engineering, Dong-A University, Busan, Korea (the Republic of).

Low-dimensional piezoelectric nanostructures with nanoparticles, nanorods, thin films have been studied for potential applications of energy harvesters, self-powered sensors, and piezoelectric transistors. For a decade, one-dimensional (1D) nanostructures have been widely approached for miniaturization in piezoelectric field, however, there are still critical limitations of insufficient piezoelectricity and unstable standing on a conductive substrate.

In this study, lead-free BaTiO$_3$ nanorod bundle arrays (NBA) with highly piezoelectric properties were synthesized on conductive fluorine-doped tin oxide substrate via a two-step process consisting of TiO$_2$ epitaxial growth and BaTiO$_3$ conversion. First, in order to develop framework of NBA, effects of pH and Ti precursor on TiO$_2$ nanostructures were investigated with adjusting area density, aspect ratio and free standing. It is illustrated that area density was enlarged as an increase in Ti precursor concentration and increase in pH, respectively. Optimum TiO$_2$ NBA was found to exhibit single-rod diameter of 10 nm, bundle diameter of 100 nm, no-aggregation, and high area density over 60%. Next, M-shaped TiO$_2$ nanorod bundles were developed via chemical etching process to conduct complete perovskite BaTiO$_3$ conversion. During chemical etching, top surface was found to be more etched compared to side wall because of the higher surface energy of (001) with Z-axis than (110) with X and Y axis. As a result of XRD analysis, it is noted that the M-shaped nanostructure can offer large diffusion sites of Ba$_2^+$ ions determining perovskite phase. The effective BaTiO$_3$ conversion using M-shaped nanostructures was confirmed with volume expansion and ion mapping by SEM and STEM analysis, respectively. Finally, the final structure of perovskite BaTiO$_3$ NBA was found to exhibit a feasible piezoelectric response of 3.56 nm with a clear phase change of 180$^\circ$ from the single BaTiO$_3$ bundle, by point piezoelectric forced microscopy analysis. In conclusion, BaTiO$_3$ NBA with high piezoelectric properties could be a promising nanostucture for various nanoscale electronic devices.

EP01.08.27

Two-Dimensional Analysis of Nanoscale Contact Electrostatics in Hysteretic Materials—To Switch or Not to Switch, Part Trois

Sabine M. Neumayer, Sergei V. Kalinin, Nina Balke and Petro Maksymovych; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A major task for piezoresponce force microscopy (PFM) is to detect and quantify piezoelectric displacements near the present sensitivity limit of ∼ 1 pm/V. Measuring the relatively weak piezoresponse is needed to probe new candidate ultrathin ferroelectrics, such as HfO$_2$ thin films and quasi-2D layered ferroelectrics, while high sensitivity measurements are likewise beneficial to understand the performance of sensors, actuators, energy harvesters. The challenge of the measurement is primarily rooted in the contribution of electrostatic interaction, thermal expansion and other forces to the net measured signal, which may obscure or even disguise the detection of piezoelectric response.

Recently, we applied contact mode Kelvin probe force microscopy (cKPFM) to differentiate electrostatic and piezoelectric contributions in PFM measurements [1,2]. In this talk, we will present a new approach to visualize and analyze cKPFM measurements aimed at improving and eventually automating the relevant data analysis. The approach, which we refer to as the field-response function, treats applied fields during the measurement and the write cycle on equal footing, thereby mapping the measured probe displacement onto a 2D grid of applied potentials. Though relatively simple, the change of the representation brings in significant benefits: (1) the relevant information of the cKPFM measurement is captured as a single image, presenting regions of stable, unstable or metastable states; (2) ferroelectric switching and electrict-type behaviors are clearly differentiated; (3) the response function can in general be acquired with arbitrary sequence of applied fields, not necessarily sequential voltage cycling; (4) from the few representative cases, such
as pre-breakdown window of lead zirconate titinate, it is becoming progressively clear that a simple picture of additive piezoresponse and electrostrictivity is not generally valid in FPM, even for well established ferroelectrics (5) fitting the whole field-response function enables further elucidation toward and subsequent supervised and unsupervised classification of characteristic responses, which we will demonstrate using Gaussian process regression combined with multivariate clustering analysis. These developments enhance the ability of FPM to probe “difficult” ferroelectrics and advance cKPFM toward to analysis of defect chemistry and more generally hysteretic materials, such as electrets, electroresistive, phase change materials and mixed electron-ion conductors. This research was sponsored by the Division of Materials Sciences and Engineering, BES, US DOE. Experiments were conducted at the Center for Nanophase Materials Sciences, a DOE Office of Science User Facility.

References:

EP01.08.28
Carrier Concentration-Dependent Piezotronic and Piezo-Phototronic Effects in ZnO Thin-Film Transistor Zijian Pan, Wenbo Peng, Fangpei Li and Yongning He, Xi'an Jiaotong University, Xi'an, China.

The piezotronic and piezo-phototronic effects have been confirmed as promising methodologies to optimize the performances of electronic/optoelectronic devices. However, these strain-induced modulations (i.e., piezotronic and piezo-phototronic effects) are strongly dependent on the carrier concentration of the piezoelectric semiconductor. In this work, the carrier concentration dependence of both the piezotronic and piezo-phototronic effects are carefully and systematically investigated in ZnO thin-film transistors (TFTs) by varying manufacturing process and introducing 365 nm UV illumination to modulate the carrier concentration of ZnO film. The experimental results show that significant performance improvement can be obtained in the ZnO TFTs by the piezotronic and piezo-phototronic effects but strongly depend on the carrier concentration in the ZnO films: (1) For the moderate carrier concentration ZnO NW TFT, distinct performance improvement is achieved in the ZnO NW TFT by the piezotronic effect with a maximum enhancement of 48.89% in saturation field-effect mobility $\mu_{SF}$ observed. (2) Whereas, the photoresponse performance of the ZnO NW TFT to 365 nm UV illumination shows no modulation by the piezo-phototronic effect due to the screening effect that is dramatically strengthened/enhanced by the significant increase of the photogenerated carrier concentration. (3) For the ultra-low carrier concentration ZnO seed TFT, there is almost no change in performances of the ZnO seed TFT when introducing the piezotronic effect, which is because the ultra-low carrier concentration ZnO seed film exhibits “piezoelectric characteristic” much more than “semiconductor characteristic” and therefore its semiconductor characteristic is difficult to be modulated by the external compressive strain. (4) By introducing 365 nm UV illumination to the ZnO seed TFT, the photogenerated carrier concentration in ZnO seed film becomes moderate and therefore significant photoresponse improvement of the ZnO seed TFT is obtained by the piezo-phototronic effect with a maximum enhancement of 56.37% in photoresponsivity $R$ observed. In all, significant performances improvement can be obtained in the ZnO TFT by the piezotronic/piezo-phototronic effect only when the carrier concentration in the ZnO is moderate, while there is no obvious modulation in performances of the ZnO TFT when the carrier concentration is ultra-low or ultra-high. This study presents in-depth understanding about the carrier concentration dependence of the piezotronic and piezo-phototronic effects in ZnO TFT and also provides feasible, compatible and adjustable methodologies to enhance/optimize the performances of electronic/optoelectronic devices.

EP01.08.29
Water Actuation Through Nanomembranes Using Surface Acoustic Waves (SAW) Zamart Ramazanova1, Karbangali B. Tynyshtykbayev2 and Zinetula Z. Insepov3, 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan.

Nanofiltration technology for water desalination and other fluids purification from salts, germs, bacteria and viruses are based on the so called Nanopumping (NP) effect, when a fluid flow through nanomembranes and nanochannels is actuated using Surface Acoustic Waves (SAW) is presented. The paper considers processes of water nanofiltration through a carbon nanomembrane using ultrasonic waves, which generated surface acoustic waves (SAW) devices under different RF powers and frequencies. We considered droplet of water volume in the 2-20 $\mu$L range, and use SAW devices with different frequencies from 34 to 116 MHz. The effect of frequency on microfluidic performance, such as moving, atomization, and passage of nanodroplets has been studied using a video camera in a range of SAW power. This identified that SAW with higher resonant frequencies have increased power values for moving, atomization, and passage of droplets through nanopores. The device consisted of a Lithium niobate (LiNbO3) piezoelectric substrate and a carbon nanomembrane placed on the substrate. Such nanopumping devices will be of practical interest for the development of future energy sources, for fuel cells, hydrogen energy, pharmaceutical processes and nanomachine for medical robots, as well as for use in a wide variety of chemical, food and agricultural applications. It is demonstrated that the process of nanofiltration of water includes the processes of droplet moving, atomization and passage through nanoparticles and will be useful for future water desalination processes. The dependences of the travel time of droplet moving and atomization of water on the power, frequency and volume of the droplet were established. It is shown that with increasing of power and frequency of SAW, the filtration process proceeds rapidly and has a power-law character.

EP01.08.30
Pyroelectric Properties of BiFeO3 Thin Films Lei Zhang1, Olivier Paul1, Daniel Sando2, Gabe Velarde1, Shishir Pandya1, Nagarajan Valanoo2 and Lane W. Martin1, 2; 1Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia; 3Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Pyroelectric materials that exhibit changes of spontaneous polarization with temperature variation are of great interest for application such as thermal sensing and waste-heat energy harvesting. Owing to large electrical fields that can be applied at modest voltages and the possibility of direct integration on semiconductors, pyroelectric thin films, in particular, have received considerable attention recently. Scientific investigation of pyroelectric thin films has, however, traditionally been challenging due to possible convoluted pyroelectric responses with thermally-stimulated currents that prevent an accurate determination of the intrinsic pyroelectric properties. Recently developed electrothermal test platforms which are microfabricated for the thin-film geometry, however, now allows for the direct measurement of pyrocurrent and an accurate extraction of pyroelectric coefficient utilizing phase-sensitive local heating and thermometry [1].

In this work, we leverage such an experimental approach to understand the pyroelectric response of one of the most widely-studied ferroelectric materials recently – BiFeO3. In particular, we explore the evolution of pyroelectric response as a function of strain – probing the effects in rhombohedral- and tetragonal-like, as well as mixed-phase versions of BiFeO3 heterostructures – with an emphasis on understanding how temperature-driven competition of different structural ground states impacts pyroelectric response. Here we study BiFeO3 films grown on a range of substrates including DyScO3 (wherein small compressive strains produce strained versions of the parent rhombohedral structure) and LaAlO3 (where large compressive strains produce both single-phase tetragonal-like and mixed-phase structures which exhibit intimate mixtures of the two structural polymorphs depending on the film thickness) [2]. Of great interest is the fact that the relative fraction of the rhombohedral- and tetragonal-like phases is strongly temperature- and electrical-field-
dependent. As such, the interconversion of the two phases with temperature change implies the potential for large changes in the out-of-plane spontaneous polarization. In turn, pyroelectric and ferroelectric dielectric and magnetoelectric effects make possible by the use of our novel microfabricated electrothermal device structures. This approach will provide a complete picture of the electrothermal response of this interesting system.

Reference:

EP01.08.31
Room Temperature Ferroelectricity in Multiferroic Al$_x$Fe$_{2-x}$O$_3$ Epitaxial Thin Films
Badari Narayana A. Rao, Shintaro Yasui and Mitsuru Itoh; 1Tokyo Institute of Technology, Yokohama, Japan; 2Department of Chemistry, The University of Tokyo, Tokyo, Japan.

Single-phase multiferroic materials have attracted considerable attention among scientists, due to the strong drive in the industry towards device miniaturization, faster processing speed and addition of new functionalities. Currently, most of the discovered materials are multiferroic only at low temperatures, thereby hindering their induction into practical devices. $\alpha$-Al$_2$O$_3$-type Al$_x$Fe$_{2-x}$O$_3$ ($x$-AFO) oxides belong to a relatively new class of metastable multiferroic compounds (space group: Pmn2$_1$), which can be stabilized as thin films [1]. We have found that some compositions of $x$-AFO can exhibit both ferromagnetism and ferroelectricity at room temperature. The $x$-AFO system is attractive compared to other systems such as GaFeO$_3$ [2] since both Al and Fe are environment friendly, and abundantly available in the earth’s crust. Similar to GaFeO$_3$, the ferrimagnetic easy axis for $x$-AFO is observed along the a-axis and ferroelectricity along the c-axis [1]. Though epitaxial films of $x$-AFO have been grown earlier, only indirect evidences of room temperature ferroelectricity in $x$-AFO are available in literature till date [1,3]. Large leakage currents in these $x$-AFO films made it difficult to carry out ferroelectric and magnetoelectric measurements at room temperature. We have used pulsed laser deposition technique to successfully fabricate epitaxial thin films of $x$-AFO on Nb-doped SrTiO$_3$ (111) substrates. We were able to significantly reduce the leakage current for our films by careful tuning of deposition parameters, to attain films with very smooth surface and small grain size. Direct ferroelectric measurements could be carried out on the films at room temperature, showing good hysteresis loops for $x$-AFO ($x = 0.5 \pm 1.0$). While the ferroelectric characterization showed that the coercive electric field increases with increasing $x$, magnetic measurements showed that the coercive magnetic field decreases with increasing $x$. Furthermore, magnetocapacitance was observed at room temperature, thereby demonstrating their potential as a promising multiferroic material.

References

EP01.08.32
Yttrium Iron Garnet Waveguide for Forward Volume Spin Wave Interference
Taiichi Goto, Takuya Yoshimoto, Caroline A. Ross, Koki Sekiguchi, Alexander Granovsky, Yuichi Nakamura, Hironaga Uchida and Mitsuteru Inoue; 1Toyohashi University of Technology, Toyohashi, Japan; 2JST PRESTO, Kawaguchi, Japan; 3Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Yokohama National University, Yokohama, Japan; 5Lomonosov Moscow State University, Moscow, Russian Federation.

Yttrium iron garnets (YIG, Y$_2$Fe$_{12}$O$_{19}$) are well-known as an excellent material for spin wave (SW) waveguide because of its low magnetic damping constant. However, demonstrated functionalities of spin waves were limited because of the difficulty of fabrication and patterning of thin YIG films. In addition, the integration of SW-excitation antennas onto YIG waveguide is also important for device development.

In this study, ~50 nm thick single crystal YIG was grown on a 10 mm x 10 mm x 0.5 mm rare-earth substituted gadolinium gallium garnet (SGGG) substrate by pulsed laser deposition (PLD). The substrate was (111) oriented. The temperature of the substrate during growth was ~850°C under an oxygen pressure of 2.6 Pa. The base pressure was 2.0 x 10^-4 Pa. The grown YIG was characterized by 2g-w-x-ray diffraction. The x-ray was monochromated using two Ge(220) single crystals. The obtained diffraction pattern showed clear fringes, showing flat surface and the deposited thickness was ~50 nm. The reciprocal space map showed fully strained film state. The unit cell side length was 1.2476 nm. The magnetic properties were measured by vibrating-sample magnetometer, showing an in-plane coercivity of 0.37 Oe, an out-of-plane saturation magnetic field of 1.73 kOe, and a saturation magnetization of 1.80 kG (~143 emu/cc). The estimated magnetic anisotropy energy Ku was ~9.88 x 10^4 Goe. The strained lattice angle was 90.4°.

This YIG was patterned into 400 mm x 100 mm using phosphoric acid at 140°C, with the etching process being controlled using an oil bath. Its taper angle was 15° with respect to the in-plane direction. Osteo on this YIG waveguide, three coplanar waveguides were fabricated with ~50 nm distances and SW interference was demonstrated. A magnetic field of 2.80 kOe was applied perpendicular to the film. The phase of the SW was changed, and the synthesized SW based on interference was confirmed. These YIG was successfully patterned as SW waveguide and the uniformity of the quality single crystalline YIG was sufficiently high for showing SW interference. This was an important milestone of development of a SW integrated circuits.

In Situ Study of Inter-Ferroelectric Phase Transitions In Domain Engineered Ferroic Crystals
Markus G. Cain, Peter Fink, Margo L. Staruch, Paul Thompson and Didier Wermille; 1Electrosciences Ltd, Farnham, United Kingdom; 2U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 3XMAS CRG, ESRF, Grenoble, France.

It is well established that domain engineered ferroelectric single crystals deliver an order of magnitude improvement in piezoelectric properties compared to conventional PZT. The unusual electromechanical properties of these domain engineered single crystals of Pb$_2$Zn$_{1/3}$Nb$_{2/3}$O$_3$–Pb$_4$Ti$_3$O$_{12}$ (PZN-PT) and PbMg$_{1/3}$Nb$_{2/3}$O$_3$–PbTiO$_3$ (PMN-PT) have been demonstrated for the compositions poised at the ferroelectric rhombohedral (FR) side of the morphotropic phase boundary (MPB), with domain engineering regarded as one of the most significant breakthroughs in relaxor ferroelectrics for enhanced actuation performance. To exploit the extremely large actuation capabilities of these new single crystal piezoelectric materials, the stability of their crystallographic variants is critical as well as the ability of the material to respond quickly to changes in electrical or stress fields. The latter is determined through an understanding of the dynamical nature of the materials’ domain switching response. In this work, we explored this stability using in situ electric field synchrotron X-ray diffraction at the XMaS beamline (BM28), at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The electric field induced and mechanical stress induced ferroelectric-ferroelectric phase transitions were studied as a function of frequency, field and static stress in the relaxor ferroelectric system Pb(In$_{1/2}$Nb$_{1/2}$)$_2$O$_3$–Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_{12}$–PbTiO$_3$ (PIN-PMN-PT) (lead indium niobate – lead magnesium niobate – lead titanate) for compositions close to the morphotropic boundary. The novel in situ PE loop and strain measurement system was used on the XMaS facility, with strain measured using a strain gauge affixed to the side of the sample. The X-Ray data was collected in a synchronous manner to the application of electrical field.

Reference:
Preliminary results show that X-ray diffraction is in good agreement with macroscopic observations and phenomenological models confirming our proposed transformational pathway. Our data is taken using full 2D X-Ray images (Pilatus 2M camera) allowing us to very rapidly explore the nature of competing crystallographic transformations arising across quite a large reciprocal space. Finally, we performed glancing angle measurements that permit imaging of the crystallography just beneath the surface of the crystal face allowing calculation of strain transfer through heteroepitaxial interfaces in composite multiferroics. The phenomena presented in this work are envisioned to be universal in domain engineered ferroics enabling mechanical stress to be used for strain- and polarization-control of electromechanical energy conversion. The results shed more light on the nature of this reversible transformation between two ferroelectric phases, including the mechanism responsible for incredible lack of fatigue after millions of cycles, and advance towards the development of a wide range of ferroic and multiferroic devices.

**EP01.08.34**

**Structural Correlation of Ferroelectric Behavior in Mixed Hafnia-Zirconia High-k Dielectrics for FeRAM and NCFET Applications**

Vineetha Mukundan1, Karsten Beckmann1, Steven Consiglio2, Kandabara Tapily2, Robert Clark2, Gert Leusink2, Nathaniel Cady3 and Alain Diebold3; 1Colleges of Nanoscale Sciences and Engineering, SUNY Polytechnic Institute, Albany, New York, United States; 2TEL Technology Center, America, LLC, Albany, New York, United States.

The recent discovery of ferroelectric behavior in doped hafnia-based dielectrics, attributed to a non-centrosymmetric orthorhombic phase, has led to attractive applications such as negative differential capacitance field-effect-transistors (NCFET) and ferroelectric random access memory devices (FeRAM) [1]. Alloying with similar oxides like ZrO2, doping with specific elements such as Si, novel processing methods, encapsulation and annealing schemes are also some of the techniques that are being explored to target structural modifications and stabilization of the non-centrosymmetric phase. In this study, we utilized synchrotron-based x-ray diffraction in the grazing in plane geometry (GIIXRD) to determine the crystalline phases in hafnia-zirconia (HZO) compositional alloys deposited by atomic layer deposition (ALD). Here we compare and contrast the structural phases and ferroelectric properties of mechanically confined HZO films in metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) structures. Both MIM and MIS structures reveals a host of reflections due to non-monoclinic phases in the d-spacing region between 1.75Å to 3.25Å [2-4]. The non-monoclinic phases are believed to consist of distorted tetragonal and orthorhombic phases and a suppression of the monoclinic phase in MIM structures compared to the MIS structures was observed. We also report the structural changes with different Hf/Zr ratios (1:4, 4:1 and 1:1) and overall thickness of the HZO film (10nm, 7nm, 5nm, and 3nm). The correlation of the electrical properties with the structural analysis obtained by GIIXRD highlights the route to obtaining non-centrosymmetric orthorhombic phases which enable ferroelectricity [5,6]. Additionally, this work highlights the importance of understanding the effects of the underlying substrate (metal vs. Si) for different target applications.


**EP01.08.35**

**Second Harmonic Generation in Ferroelectric HfO2 Based Metasurfaces**

Fei Huang1, 2, 6, Jun Qin1, 2, Xinyue Li1, 4, Longjiang Deng1, 2, Huigao Duan1, Jialiang Xu3, 4 and Lei Bi1, 2; 1National Engineering Research Center of Electromagnetic Radiation Control Materials, Chengdu, China; 2University of Electronic Science and Technology of China, Chengdu, China; 3Tianjin University, Tianjin, China; 4Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China; 5State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, Hunan University, Changsha, China; 6Department of Electronic Engineering, Stanford University, Stanford, California, United States.

Hybrid nonlinear photonic structures, in which nonlinear optical materials such as ferroelectrics are incorporated in the near field of a nanophotonic structure, provide a new way to significantly boost the nonlinear photonic effects at the nanoscale. However, several challenges prevent on-chip integration of such hybrid nonlinear metasurface with standard CMOS fabrication technologies, such as material compatibility, scaling and operation wavelength range. Recently, ferroelectric HfO2 thin films have attracted great research interest. As a widely applied high-K oxide material for gate dielectrics, this material is compatible with CMOS technologies. Room temperature ferroelectric properties in such materials can maintain down to a film thickness of 3-5 nm, with similar remnant polarization compared to thicker films. These unique properties ignite great research interest on this material for microelectronic applications. However, to the best of our knowledge, there has been no report on using such materials for second harmonic generation applications.

Here, we demonstrate an on-chip hybrid nonlinear metasurface for second harmonic generation using nanometer thick ferroelectric yttrium doped HfO2 thin films. XRD, hysteresis loop and PFM are measured to verify its ferroelectricity. Optical constant characterizations of ferroelectric HfO2 indicate an wide optical band gap of 4.8 eV for Y:HfO2 thin films. Gold metasurfaces with different grating width ranging from 50 nm to 125 nm are fabricated by EBL. By incorporating a 24 nm thick ferroelectric Y:HfO2 thin film in a plasmonic metasurface nanocavity, we observed one order of magnitude enhancement of SHG compared to bare ferroelectric HfO2 thin films. Moreover, a 3 fold enhancement of SHG is observed in the hybrid metasurface compared to a control device using non-ferroelectric HfO2 showing almost identical linear optical properties, demonstrating a major contribution of SHG from ferroelectric Y:HfO2. We also demonstrated good scalability of such devices down to a Y:HfO2 thickness of 13 nm with another 2 fold enhancement of SHG. Using numerical simulations, we demonstrate an SHG coefficient $\chi^{2}$ of 5 pm/V of the polycrystalline Y:HfO2 thin films, which is comparable to 5%MgO:LiNbO3 (9.4 pm/V) epitaxial thick films and UV transparent materials such as BaB2O4 (4.4 pm/V). These findings demonstrate the promising potential of ferroelectric HfO2 for on-chip nonlinear photonic devices, which also provide a general way of high efficiency SHG using on-chip hybrid nonlinear metasurfaces.

**EP01.08.36**

**Towards Infinite Polarization Retention in Thin-Film Small-Molecular Organic Ferroelectrics**

Indre Urbanaviciute1, Subham Bhattacharjee2, Michal Biler1, Tim Cornelissen1, Mathieu Linares1, Rint Sijbesma3 and Martijn Kemink1; 1IFM, Linköping University, Linköping, Sweden; 2Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; 3Theoretical Chemistry and Biology, KTH Royal Institute of Technology, Stockholm, Sweden.

With increasing demand for cheap, lightweight and flexible electronics, a matching memory technology is required. Ferroelectricity-based memory devices assure non-volatility and low energy consumption, while organic materials, potentially used for this purpose, guarantee easy processability, low cost and advantageous physical properties including flexibility. It has been speculated that a recently discovered class of organic ferroelectric materials – columnar discotic liquid crystals – could offer an intriguing possibility to extend bit density limits of the conventional memory devices.
devices substantially, if these discrete ferroelectric columns were addressed individually. However, despite being very well established in the field of electro-optics, ferroelectric liquid crystals lacked interest from a memory device perspective due to modest remnant polarization and/or poor polarization retention.

Here, we demonstrate how simple structural modification of a prototypical supramolecular ferroelectric liquid-crystal benzene-1,3,5-trisamide (BTA) leads to significant improvements in the main ferroelectric properties and results in materials with extrapolated data retention time of more than 10 years in thin-film solution-processed capacitor devices. The BTA is a C3 symmetry molecule consisting of a π-stacking benzene core, to which three free-to-rotate dipolar amide groups (O=C-NH), having a dipole moment of 3 Debye each, and flexible solubilizing alkyl (-CH2-)n chains are attached. We show that all the core properties of the ferroelectric – remnant polarization, coercive field, polarization retention time and operation temperature range – increases continuously in BTAs with shortening of the alkyl chain length (from C18H37 to C6H13). The optimal hexyl-tailed BTA material demonstrates performance close to that of P(VDF-TrFE): remnant polarization of ~60 mC/m2, fast polarization switching, low fatigue and polarization retention of several months at room temperature. Furthermore, if linear tails are changed to branched (achiral ethylhexyl and heptylhexyl), effectively infinite data retention is achieved. The origin of these improvements is discussed in context of electrostatic and steric interactions, as well as inherent morphological layer properties, the latter being the dominant.

Easy-processability, room temperature operation, remnant polarization as high as 40 mC/m2, and polarization retention exceeding commercial requirements distinguish the BTA material from other small-molecular organic ferroelectrics and makes it a perspective choice for applications that require cheap, flexible and lightweight ferroelectrics. The study results, furthermore, bring more understanding into the field and propose guidelines for further advancement in molecular engineering.


**EP01.08.37**

**Synthesis, Microscopy and Spectroscopic Characterizations of Rare Earth- Doped BaTiO3 Nanocubes for Optical and Ferroelectric Applications**

**Benard Kavey**

1Science of Advanced Materials, Central Michigan University, Mount Pleasant, Michigan, United States; 2Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States.

Rare-earth doped BaTiO3 nanocubes have been synthesized using a highly versatile, energy-efficient solvothermal route at temperatures as low as 150 °C. Transmission electron microscopy images of the as-synthesized Ba0.6-Ln3+TiO3 (0.01 ≤ x ≤ 0.09; Ln = La3+, Ce3+, Nd3+) showed highly monodisperse and self-assembled nanocubes with a mean particle size of 20 ± 2 nm for all nominal dopant compositions. High resolution transmission electron microscopy was used to explore in detail the atomic planes, polarization direction, distribution of individual dipoles and the ferroelectric domains within a single nanocube. Also, piezoelectric force microscopy and lithography techniques were employed to further understand the ferroelectric behavior of the Ln-doped BaTiO3 nanocubes. It was determined that all Ln-doped BaTiO3 nanocrystals present a ferroelectric behavior at room temperature with maximum values of the permittivity around the Curie temperature. Dielectric spectroscopy measurements were performed by using vacuum sintered pellets of the as-synthesized nanocubes and measured at both the megahertz and terahertz electric field frequencies. We observed significantly higher dielectric constant values up to 6000 for lower dopant concentrations. An FTIR technique was employed to study the surface characteristics of the nanocubes and the nature of binding of the capping ligand molecules to the surface of the nanocrystals. It was determined that the oleic acid ligand used as a capping agent binds to the Ba ions in the Ln-doped BaTiO3 crystal structure via a bidentate coordination mechanism. The insulating properties of the Ln-doped BaTiO3 was further determined using diffuse reflectance spectroscopy and the Kubelka-Munk theory of reflectance. The band gaps of the as-synthesized nanocubes were determined for all different Ln dopants and various concentrations.

**EP01.08.38**

**Electrostatic Force Driven Oxide Heteroepitaxy for Interface Control**

**Mengjiao Wu, Ren Zhaohui and Han Gaorong:** Materials Science and Engineering, Zhejiang University, Hangzhou City, China.

Oxide heterostructure interfaces create a platform to induce intriguing electric and magnetic functionalities for possible future devices. A general approach to control growth and interface structure of oxide heterostructures will offer a great opportunity for understanding and manipulating the functionalities. Here we report that an electrostatic force, originating from a polar ferroelectric surface, can be used to drive oxide heteroepitaxy, giving rise to an atomically sharp and coherent interface by using a low-temperature solution method. These heterostructures adopt a fascinating selective growth, show a saturation thickness and the reconstructed interface with concentrated charges accumulation. The ferroelectric polarization screening, developing from a solid-liquid interface to the heterostructure interface, is decisive for the specific growth. At the interface a charge transfer and accumulation take place for electrical compensation. The facile approach present here can be extremely useful for controlling oxide heteroepitaxy and producing intriguing interface functionality via an electrostatic engineering.


**EP01.08.40**

**Imaging and Engineering the Dynamic Motion of Multiferroic Device Walls by an Electron Beam**

**Michele Conroy**

1Alan Harvey, 2Charlotte Cochrane, 3Kalani Moore, 4Roger Whatmore, 5Alexei Gruverman, 6Marty Gregg and 7Ursel Bangert; 1Bernal Institute, University of Limerick, Limerick, Ireland; 2Centre for Nanostructured Media, Queen’s University Belfast, Belfast, United Kingdom; 3Imperial College London, London, United Kingdom; 4University of Nebraska Lincoln, Lincoln, Nebraska, United States.
Recently there has been a dramatic increase of research activity in multiferroic materials.1-4 More specifically in charged domain walls (DWs) within these materials.5,6 These previously overlooked features are now seen as new form of two-dimensional (2D) material in their own right. With all the potential unique characteristics that make 2D materials such as graphene, DWs have become a new field of research. The main aspect that sets DWs apart from other 2Ds is the ability to create, destroy, and move by an external field or physical force. They’re dynamic nature immediately suggests a potential role for them as interconnects in completely new forms of agile or adaptive nanoscale circuitry. In this study we use the electric field applied by the scanning electron microscope (SEM) probe to study the motion of charged DWs in the improper ferroelectric material Cu3BiTl3Cl7. By changing the applied voltage, current and magnification we conducted a detailed quantification of the DW dynamics due to applied electric field. Focused ion beam (FIB) lamellas were prepared of these selected regions within the bulk crystal and the DWs in cross-section were analyzed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Weak beam dark field TEM and selected area diffraction analysis revealed there was distinct domains within the cross sections after the SEM probe DWs studies. This was not seen in lamellas formed from regions with low dose imaging pre FIB lamella formation. Suggesting that above a certain dose, and thus electric field new DWs are formed. Additionally the geometry of the DWs seen in cross section are significantly different depending on their freedom of movement seen in the SEM probe study. 1 Evans, D. M. et al. The nature of magnetoelectric coupling in Pb (Zr, Ti) O3–Pb (Fe, Ta) O3. Advanced Materials 27, 6068-6073 (2015). 2 Eerenstein, W., Mathur, N. D. & Scott, J. F. Multiferroic and magnetoelectric materials. Nature 442, 759, doi:10.1038/nature05023 (2006). 3 Ramesh, R. & Spaldin, N. A. in Nanoscience And Technology: A Collection of Reviews from Nature Journals 20-28 (World Scientific, 2010). 4 Spaldin, N. A. Multiferroics: from the cosmically large to the subatomically small. Nature Reviews. Materials 2, 17017 (2017). 5 Ma, J. et al. Controllable conductive readout in self-assembled, topologically confined ferroelectric domain walls. Nature Nanotechnology, doi:10.1038/s41565-018-0204-1 (2018). 6 Scott, J. F. et al. Superdomain dynamics in ferroelectric-ferroelastic films: Switching, jamming, and relaxation. Applied Physics Reviews 4, 041104 (2017). 7 McQuaid, R. G., Campbell, M. P., Whatmore, R. W., Kumar, A. & Gregg, J. M. Injection and controlled motion of conducting domain walls in improper ferroelectric Cu3Cl1 boracite. Nature communications 8, 15105 (2017).

SESSION EP01.09: Physics of Semiconducting Piezoelectric, Pyroelectric and Ferroelectric Materials
Session Chairs: Lauren Garten and Wilfrid Prellier
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 103

8:00 AM *EP01.09.01 Quantifying Voltage-Modulated Electromechanical Sensitivity and Hysteresis Measurements on the Nanoscale Liam Collins1, Aleksander Labuda1, Olga Ovchinnikova1 and Roger Proksch1; 1Asylum Research, Santa Barbara, California, United States; 2Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Since the very early days of atomic force microscopy (AFM), voltage modulation (VM) of AFM has been used to try to quantify a host of electronic, electrochemical and electromechanical functionalities across nanometer length scales. The critical importance of such information has resulted in the development of a plethora of VM-AFM techniques for exploration of either long or short-range forces. Of relevance for ferroelectrics, piezoresponse force microscopy (PFM) imaging and spectroscopies have effectively opened the door to the exploration of nanoscale ferroelectric properties. The rise of PFM, however, can also be associated with the emerging trend of claims of ferroelectricity in materials which were subsequently thought to be not ferroelectric.[1] even unlikely materials such as soda-lime glass. Furthermore, quantification of piezoelectric properties with PFM is notoriously difficult, and is known to be influenced by parasitic effects including factors such as long range electrostatic forces, tip-sample contact stiffness variations, cantilever frequency dependent dynamics. In this talk, we will explore the parasitic effects during normal PFM operation, including some recent results that:

Demonstrate that some hysteretic interactions surprisingly originate from common long-range dynamics. This hysteresis seems to be linked to sample surface water, suggesting that ionic dynamics in the surface water layer must be accounted for in nanoscale electromechanical measurements.

Demonstrate experimental approaches for using interferometric AFM[2] for quantifying both the inverse piezo sensitivity, d33 and hysteresis loops.

Since surface water is ubiquitous in ambient conditions for even mildly hydrophilic surfaces, these observations may explain the plethora unexpected hysteretic behavior discussed above. Finally, another significant result of the interferometric approach is that it allows putting quantitative limits on the electromechanical sensitivity. For example, we have demonstrated that [end] --> for soda-lime glass mentioned above, much smaller than that implied by conventional VM-AFM measurements.

References

8:30 AM EP01.09.02 Spin Mixing and Loss of Spin During Tunneling in Ferromagnet/Ferroelectric Junctions—Is a Strong Ferroelectric Polarization Desirable? Ibrahim B. Misirlidou1,2, Canhan B. Sen1, Wael B. Aldulaimi1 and Omid B. Moradi1; 1Sabanci University Nanotechnology Application Center, Sabanci University, Istanbul, Turkey; 2Integrated Manufacturing Technologies Research and Application Center, Sabanci University, Istanbul, Turkey; "Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey.

Electric field control of magnetization allows further miniaturization of integrated circuits relying on functional layers for binary bit processing and data storage as it eliminates the need for bulky sophisticated systems to induce magnetic fields. Tailoring magnetoelectric coupling inherent to the bulk of multiferroic thin films and piezoelectric strain control of spin orientation in magnetic layers have been two approaches standing out. One other phenomena, namely spin-dependent screening has been studied especially from the perspective of spin selective tunnel junctions. In this work, we analyze the spin-dependent screening of ferroelectric polarization in a film interfacin and electrodes with a magnetic structure using the continuity equations in continuum media. The effect of ferroelectric polarization on the ferromagnetism of the electrodes near the interfaces are discussed in the light of our results. The competition between the electrostatic screening and the mean-field exchange between spins in the ferromagnetic (FM) electrodes gives rise to a reduction in the net magnetic moment near the interface extending to a distance comparable to the Thomas-Fermi screening length. This apparent loss of magnetic order at the interface is due to spin mixing that is held partly responsible for reduction in the tunnel magnetoresistance (TMR) effect. In fact, even in an ideal system with no other effects to cause spin flips, our results imply that interface states can lead to great losses in spin polarization during tunneling.
Correlation Between the Structural, Ferroelectric, Piezoelectric and Dielectric Properties of Lead-Free BCT-BZT Piezoelectrics

We report the structural, ferroelectric, piezoelectric and dielectric properties correlation in lead-free Ca(Ta,Ga)Si2O7 (1-x)BaTiO3 (x; x = 0.55, 0.45) piezoelectric ceramics. These piezoelectrics were synthesized by conventional solid state reaction method and further analyzed using different characterization techniques such as x-ray diffraction (XRD), Raman spectroscopy, scanning electron microscope (SEM), polarization-electric field (P-E) loop, strain-electric field (S-E), etc. XRD analysis along with the Rietveld refinement shows that the 55BCT8 and 45BCT8 piezoelectrics possess both the tetragonal (T: space group P4mm) and orthorhombic (O: space group Amn2) crystal structure which is further confirmed from Raman spectroscopy analysis. Also, the structural phase transitions with temperature were studied in details from the temperature dependent Raman spectroscopy analysis. The scanning electron micrographs shows dense microstructure for both the piezoelectrics with larger grain size 7-10 µm for 45BCT8. Also, the elemental mapping analysis indicates the microstructural distribution of the constituent elements. The presence of P-E and S-E hysteresis loop confirms the ferroelectric and piezoelectric nature of these piezoelectrics. Further, the polarization current density-electric field curves show the presence of two sharp peaks in opposite directions which suggests the two stable states with opposite polarity. The higher values for maximum polarization (Pm = 22.47 µC/cm²), remnant polarization (Pr = 11.61 µC/cm²), coercive electric field (Ec = 4.77 kV/cm) and % Strain (Sm = 0.21) were observed for 55BCT8 while higher values of piezoelectric coefficients (d33 ~ 220 pC/N and d31 ~ 295 pm/V) and electrostrictive coefficient (Q33 ~ 0.0509 m4/C2; higher than the conventional lead based piezoelectrics (0.026 m4/C2) i.e. PbMgNbO3-PbTiO3) were observed for 45BCT8. Temperature dependent dielectric measurements at different frequencies show the phase coexistence (T + O) near room temperature (consistent with XRD and Raman spectra analyses); exhibiting O to T phase transition at 285 K and 298 K for both the 55BCT8 and 45BCT8, respectively. Moreover, the Curie temperature (Tc) ~ 410 K observed to be same for both the studied piezoelectrics. The observed trends in the ferroelectric, piezoelectric and dielectric properties can be explained in detail on the basis of structural phase contribution (55BCT8: 28% T + 72% O & 45BCT8: 41% T + 59% O) as analyzed from Rietveld fitted XRD pattern and Raman spectrum of 55BCT8 and 45BCT8. The observed properties shows that the environment friendly lead-free piezoelectrics in the present work are suitable for ferroelectric memory device, piezoelectric sensor, capacitor, etc. applications and can replace the toxic lead based piezoelectric ceramics (e.g. PbZn0.5Ti0.5O3, PbMgNbO3-PbTiO3, etc).

Stability, Transport and Electromechanical Properties of Ca1-xTal-xGa,xSi2O7 Piezoelectric Crystals at Elevated Temperatures

Application of piezoelectric materials at elevated temperatures faces many restrictions including thermally induced changes of the dielectric, piezoelectric and electromechanical properties, increased loss with temperature, and chemical instability (decomposition, oxidation). In this respect, piezoelectric crystals of the langasite (LGS, LaGa3SiO10) family are recognized as excellent candidates for high temperature applications as their piezoelectric activity is present up to temperatures above 1300 °C. CTGS (Ca1-xTal-xGa,xSi2O7) is a relatively new crystal of the langasite family which has a fully ordered structure with lower conductivity and loss than LGS.

This work focuses on detailed and thorough investigations of CTGS temperature behavior. In particular, the full set of dielectric, piezoelectric, and elastic constants are determined in the temperature range from 4.2 K to 900 °C. Further, the electromechanical loss is determined as a function of temperature and described in the framework of a model that includes several physical mechanisms. Moreover, investigations of atomic transport mechanisms in CTGS are carried out at temperatures up to 1300 °C and correlated with electromechanical properties. Finally, the evaluation of CTGS long-term stability at high temperatures is performed by examination of its electric conductivity and resonant properties. CTGS crystals used in this study are grown by the Czochralski technique by IKZ (Berlin, Germany), Fomos-Materials (Moscow, Russia) and SICCAS (Shanghai, China). The material constants are determined using two independent methods, namely resonant and ultrasonic pulse-echo. Additionally, piezoelectric coefficients are derived using laser Doppler vibrometry. The investigations of electromechanical loss are performed by means of impedance spectroscopy and a tone-burst excitation technique. The sample preparation process, measuring techniques and crystals cuts and geometries used for the investigations are described in [1, 2].

The analysis of ion transport mechanisms is performed in the temperature range of 1000-1300 °C by application of stable tracer isotope 18O and subsequent secondary ion mass spectrometry and provides oxygen self-diffusion coefficients of CTGS. These coefficients are found to be at least 3 orders of magnitude lower than those of LGS, confirming better high-temperature stability of CTGS.

Long-term measurements of CTGS conductivity and resonance frequency are performed in air during one year of uninterrupted thermal treatment at 1000 °C. The resonance frequency is found to change by about 0.4% during 8000 hours of heat treatment.


Physical Nature of Negative Capacitance Emerged in Ferroelectric-Gate FETs

Recently, the power consumption of integrated circuits has increased because the scaling of the operating voltage is limited. To solve this issue, it is necessary to overcome the limit of subthreshold swing of 60 mV/decade at 300 K. Negative capacitance FET (NCFET), in which gate dielectric is replaced with a ferroelectric material, is attracting much attention because of the capability of overcoming the limitation by using the NC effect of ferroelectric. A number of papers have demonstrated sub-60 mV/decade switching in ferroelectric-gate FETs. However, the physical nature of emerging the NC have not been clarified. To investigate the physical nature, we simulated the time-developed electrical behaviors, such as the voltage across the ferroelectric gate (Vf), surface potential of semiconductor (φS) and electric displacement of ferroelectric layer (Df), for the applied voltage (Vgs) in metal-ferroelectric-semiconductor capacitor (MFS) by using Landau-Khalatnikov equation which includes the dynamics of ferroelectric polarization switching. In this simulation, the ferroelectric properties similar to ferroelectric HfO2 films were used, because the HfO2 film is expected to be the most suitable for the ferroelectric-gate insulator in the NCFETs due to its compatibility with the complementary metal-oxide-semiconductor (CMOS) process and scaling.
ability. As the results, when $V_d$ is swept from negative to positive, the entire $V_d$ and the depolarization voltage from a semiconductor (p-type) due to the remanent polarization are simultaneously applied to the ferroelectric layer before polarization switching. Whereas, after polarization switching, $V_d$ divides into the ferroelectric layer and surface potential of semiconductor because of the formation of depletion layer at the semiconductor surface. Therefore, $V_d$ decreases with increasing $D_0$ ($\partial D_0/\partial V_d$) indicating that NC emerges. For this reason, transient NC in MFS capacitor is realized under the effect of the depolarization field from semiconductor due to the remanent polarization before polarization switching and the non-linear response of a semiconductor and a ferroelectric materials against external electric field after polarization switching. The subthreshold slope of $I_d$-$V_d$ characteristic is below 10 mV/decade due to the effect of the transient NC. The simulations were also performed by using the ferroelectric properties with different remanent polarization (P=$10$, $15$, $20$ $\mu$C/cm$^2$). As the results, NC is recognized regardless of the remanent polarization, as far as the carrier modulation at the semiconductor surface against the potential change is much faster than the ferroelectric switching speed.5

[Reference]
2) K. Takada et al., Meeting on ISAF-FMA-AMF-AMEC-PFM Joint Conference.p112 (2018)
3) K. Takada, Y. Yoshimura, N. Fujimura, Appl. Phys. Express, Submitted
4) K. Takada, Y. Yoshimura, N. Fujimura, Jpn. J. Appl. Phys, Submitted

9:30 AM EP01.09.06 Negative Piezoelectric Effect in the Organic Supramolecular Ferroelectric BTA Indre Urbanaviciute1, Xiao Meng1, Yingfen Wei2, Tim Cornelissen1, Rint Sijbesma2 and Martin Kemerink1; 1IFM, Linköping University, Linköping, Sweden; 2Faculty of Science and Engineering, University of Groningen, Groningen, Netherlands; 3Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands.

Due to their softness and flexibility, organic ferroelectrics may become relevant for a wide variety of applications like conformal and/or flexible sensors and actuators for which inorganic ferroelectrics are unsuitable. Yet, with the notable exception of the ferroelectric copolymer P(VDF-TrFE), the piezoelectric properties of organic ferroelectrics are only sparsely known and far from completely understood. The vast majority of piezoelectric materials demonstrate a positive piezoelectric effect. Even though it has been recently discussed that the negative piezoelectric coefficient could be theoretically found in certain ferroelectrics, in practice PVDF and its copolymers have remained the only ferroelectric materials showing this anomalous effect of longitudinal contraction with increasing applied field.5

Here, we investigate the piezoelectric activity in an archetypical class of organic ferroelectrics – small-molecular liquid-crystalline BTA (benzene-1,3,5-tricarboxamide).6 Interestingly, both the large- and small-signal piezoelectric responses, measured interferometrically on BTA solution-processed thin-film capacitors, reveal a pronounced negative piezoelectric effect with $d_{33}$ reaching values as high as ~20 pm/V. The measured ‘inverted’ piezoelectric butterfly hysteresis loops are of close-to-ideal form with a well-expressed negative slope.

The dipolar disc-like BTA molecules self-assemble in columns that further pack tightly in a hexagonal lattice. In real device conditions this interruption is interrupted by zones with higher disorder. Therefore, the negative $d_{33}$ in such structure can be explained by the so-called dimensional effect, which considers the ferroelectric layer as a set of rigid dipoles that are distributed in an easily deformable matrix. The dimensional effect is also considered to underly the negative electrostrictive and piezoelectric coefficients in P(VDF-TrFE). We show that in BTA the magnitude of $d_{33}$ decreases with increasing disorder and remnant polarization. Comparison of the piezoelectric response under large- and small-signal conditions further reveals that irreversible extrinsic polarization switching processes dominates the large-signal strain.

Studies on the ferroelectric liquid-crystal BTA enrich our general understanding about the negative piezoelectric effect in soft ferroelectrics and reveal the application potential of the material for cost-efficient flexible piezoelectric devices.


9:45 AM BREAK

10:15 AM *EP01.09.07 Strain and Size Effects on the Structure and Properties of Relaxor Ferroelectric Thin Films Jieun Kim1, Hiroaki Takenaka1, Yubo Qi2, Anoop R. Damodaran3, Abel Fernandez3, Ran Gao3, Shishir Pandya1, Margaret McCarver4, Andrew M. Rappe3 and Lane W. Martin1, 4; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Department of Physics, University of California, Berkeley, Berkeley, California, United States; 4Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 5Department of Physics, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

The large field-induced strains produced by single crystals of solid solutions between relaxors and ferroelectrics make them technologically important materials. Understanding and ultimately controlling these large effects requires intimate knowledge of how the local polar order and resulting small-sized domains separated by low-angle domain walls form and evolve under applied stimuli. Traditionally, the evolution of polar structures in relaxors with various thermodynamic forces including temperature, composition, electric field, and hydrostatic pressure has been studied in bulk single crystals. The instability under large, non-hydrostatic pressure (such as uni- or bi-axial strain) in bulk materials, however, has limited our understanding of how these polar entities evolve under driving forces that enhance long-range order. In addition, there is a lack of understanding of how relaxors behave in low dimensions (i.e., size effects). In this work, we use a combination of thin-film epaxy, X-ray diffuse scattering, dielectric and ferroelectric characterization, and molecular-dynamics simulations to investigate the evolution of and correlations between polar structures and properties in the prototypical relaxor ferroelectric 0.68$\beta$PbMg$\text{_{1/3}}$Nb$\text{_{2/3}}$O$\text{_{3}}$-0.32PbTiO$\text{_{3}}$. First, we investigated the effect of epitaxial strain to understand the relationship between structure and properties of relaxors under a driving force towards enhanced long-range order. Increasing the bi-axial, in-plane compressive strain (from -0.5 to -1.5%) drives an increase in the dielectric maximum temperature (from 150 to 210°C), intermediate temperature (from 230 to 320°C), and the Burns temperature (from 290 to 350°C). Diffuse-scattering experiments reveal marked strain-induced changes in the diffuse-scattering pattern, namely from a classical butterfly- to a disc-shaped pattern; which is attributed to polarization rotation and an increase of the correlation length of polar domains (from 8 to 25 nm). Molecular-dynamics simulations provide direct visualization of the domain structures and analysis of local dynamics reveals that such changes are due to the anomalous correlation behavior of unit cells with complex chemistries. Using the same thin-film platform, we further explored size effects in relaxor thin films. Here we demonstrate that reducing the size, contrary to popular belief, first enhances relaxor behavior until a threshold thickness below which the critical temperatures that characterize various relaxor phases (i.e., dynamic, static, and frozen) collapse together, indicating destabilization of the relaxor
state. Using temperature-dependent diffuse scattering and ferroelectric measurements, we demonstrate that the relaxor loses its defining characteristics below this threshold thickness. The mechanism for destabilization of realtor behavior below the critical thickness is discussed in terms of faster dynamics of polarization fluctuations in ultrathin relaxor films.

10:45 AM EP01.09.08 Surface Pyroelectricity in SrTiO3 Elena Meirzadeh1, Evgeniy Makagon1, Dennis V. Christensen2, David Ehre1, Meir Lahav1, Nini Pryds2 and Igor Lubomirsky3, 5; 1, 5Weizmann Inst of Science, Rehovot, Israel; 2Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark.

Single crystals of perovskite-structured SrTiO3 are used in a variety of applications ranging from catalysis to substrates for epitaxial thin film growth. Although SrTiO3 is paraelectric (space group Pm-3m), it is incipient ferroelectric. Surface structure of SrTiO3 changes under various conditions and has been thoroughly studied over the years both computationally and experimentally. It has been suggested that the crystal undergoes surface relaxation leading to the formation of a near-surface polar layer[1]. Improvements in current measurement equipment during the last decade have increased the sensitivity of pyroelectric measurement[2], allowing us to measure surface pyroelectricity from single crystals of SrTiO3. Our results provide a direct experimental proof for the presence of a near-surface polar layer in this material. We have found that annealing the crystals in the presence of TiO2 powder eliminates the surface pyroelectricity while chemical treatment with dilute nitric acid restores it.

One can expect that the existence of the surface pyroelectric layer might affect the structure and macroscopic properties of the functional materials for which SrTiO3 is used as a substrate.


11:00 AM EP01.09.09 Optimizing a Floating-Base Bipolar Heterojunction Phototransistor by Piezo-Phototronic Effect Fangpei Li, Zijian Pan, Wenbo Peng and Yongming He; Xian Jiaotong University, Xian, China.

Recently, extensive research works have demonstrated significant modulation on photoresponse performances by the piezo-phototronic effect in various optoelectronic devices. However, although piezo-charges of both positive and negative polarities always appear in pairs and in same amount simultaneously and equally, most research works till today only utilize piezo-charges of one polarity, either positive or negative, excluding the potential combined advantages of utilizing both positive and negative piezo-charges at the same time. In this work, a p-Si/n-ZnO/p-PEDOT:PSS bipolar heterojunction phototransistor is fabricated, and its strain-induced improvements in photoresponses are reported: the photoresponsivity is improved from 62.80 to 90.30 mA/W (with an improvement of almost 50%) and the specific detectivity is improved from 0.31×10⁹ to 0.42×10⁹ Jones (with an enhancement of about 35%). Experimental results also show interesting optimizing behaviors, of which the fundamental physics are thoroughly explained by carefully analyzing the strain-induced modulations in local energy band diagrams at p-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interfaces, respectively. For the first time, the piezo-phototronic effect has been validated in a ZnO-based bipolar heterojunction phototransistor, where the device structure of two back-to-back p-n heterojunctions possesses great potential capability to achieve low noise, large photoresponsivity and high speed qualities. More importantly, by successfully utilizing both positive and negative piezoelectric charges in one device, this work advances the practical applications of the piezo-phototronic effect in tri-/multi-layer device structures where excellent performances can be expected.

11:15 AM EP01.09.10 Tunable Electroresistance and Electro-Optic Effects of Transparent Molecular Ferroelectrics Shengjiang Ren; University at Buffalo, The State University of New York, Buffalo, New York, United States.

Recent progress in molecular ferroelectrics (MOFEs) has been overshadowed by the lack of high-quality thin films for device integration. We report a water-based air-processable technique to prepare large-area MOFE thin films, controlled by supersaturation growth at the liquid-air interface under a temperature gradient and external water partial pressure. We used this technique to fabricate Im2ClO4 thin films and found a large, tunable room-temperature electroresistance: a 20-fold resistance variation upon polarization switching. The as-grown films are transparent and consist of a bamboo-like structure of (2,-1,0) and (1,0,-2) structural variants of $d_{33} = 38.8$ pm/V. Polarization switching results in a change of the refractive index, $n$, of single domains, $\Delta n/n = 0.3$. The remarkable combination of these characteristics renders MOFEs a prime candidate material for new nanoelectronic devices. The information that we present in this work will open a new area of MOFE thin-film technologies.

11:30 AM EP01.09.11 Blowing Polar Skyrmion Bubbles in Oxide Superlattices Zijian Hong1, 3 and Long-Qing Chen1; 1The Pennsylvania State University, State College, Pennsylvania, United States; 3Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Particle-like topological structures such as skyrmions and vortices have garnered ever-increasing interests due to their rich physical insights and potential broad applications in spintronics. Here we discover the reversible switching between polar skyrmion bubbles and ordered vortex arrays in ferroelectric superlattices under an electric field, reminiscent of the Plateau-Raleigh instability in fluid mechanics. An electric field phase diagram is constructed, showing a wide stability window for the observed polar skyrmions. A ‘volcano’-like Pontryagin density distribution is formed, indicating the formation of a smooth circular skyrmion. The topological charge $Q$ at different applied field is calculated, verifying the field-driven topological transition between $Q=0$ and $Q=\pm 1$ states. This study is a demonstration for the computational design of field-induced topological phase transitions, giving promise for the design of next-generation nanoelectronic devices.

11:45 AM EP01.09.12 Inducing Magnetism in the Electron Gas at LaAlO3/GdTiO3/SrTiO3 Interfaces Nikita Lebedev1, 2; 1Kamerlingh Onnes Laboratory, Leiden University, Leiden, Netherlands; 2Physikalisches Institut (EP 3), Universität Würzburg, Würzburg, Germany; 3MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; 4School of Engineering and Technology, BML Munjal University (Hero Group), Gurugram, India.

At the interface between band insulators LaAlO3 (LAO) and SrTiO3 (STO) a two-dimensional electron gas (2DEG) can be formed. There are also indications that the Ti3+ ion can give rise to (spurious) magnetism. However, fabricating a homogeneous spin-polarized electron gas is still a challenge.
One strategy is to bring rare earth ions close to the interface. After inserting a 2-unit-cell layer of the band insulator EuTiO$_3$ (ETO) an anomalous Hall effect (AHE) was reported [1], as a signature for magnetism. In our work we inserted 2 unit cells of the Mott insulator GdTiO$_3$ (GTO) between LAO and STO. Note that the Eu-ion in ETO is divalent (like Sr), while the Gd-ion in GTO is trivalent (like La). Samples were prepared by Pulsed Laser Deposition. The temperature dependence of the sheet resistance shows that a 2DEG has formed. Gating the system at low temperatures with a negative voltage leads to a metal-insulator transition, with a Kondo like resistance minimum. For positive voltages, the system becomes increasingly metallic and shows an AHE as well as hysteretic behavior of Hall coefficient. It appears that magnetism is induced, but only at finite gate voltages.


SESSION EP01.10: Non-Conventional Applications of Polar Materials
Session Chairs: Jennifer Andrew and Thomas Fix
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 103

1:30 PM *EP01.10.01
Magnetoelectric Sensors—PicoTesla Magnetometers and Ultracompact Acoustically Actuated Antennas Nian Sun, Hwaider Lin and Neville Sun; ECE Department, Northeastern University, Boston, Massachusetts, United States.

Recent research have demonstrated strong magnetoelectric (ME) coupling realized through strain mediated interactions in layered magnetic and ferroelectric multiferroic heterostructures. Most ME effects have been demonstrated in a static or quasi-static process used in applications such as reconfigurable RF components and spintronics. However, utilizing the strong ME coupling effect dynamically at very high frequency (VHF) and ultra-high frequency (UHF) will allow for receiving and transmitting electromagnetic waves with devices on the micro-scale. Here we present the most recent progress on novel RF nanomechanical ME resonators with pico-Tesla sensitivity and a new antenna miniaturization mechanism to create acoustically actuated nanomechanical ME antennas. Modern compact antennas that rely on electromagnetic (EM) wave resonance typically have a size greater than λ/10, making it difficult to reach VHF and UHF. The large electromagnetic wavelength λE puts a constraint on miniaturizing antennas for wireless communication systems where ultra-compact antennas can help save space. This novel concept utilizes the acoustic wave resonance due to the ME affect instead of relying on the electromagnetic wave resonance to reduce the antenna size 1-2 orders of magnitude without any performance degradation.

2:00 PM *EP01.10.02
Functional Oxide Thin Films for Diverse Applications Wilfrid Prellier; CRISMAT Laboratory, Caen, France.

Transition metal oxides often having a perovskite structure form a wide and technologically important class of compounds. In these systems, ferroelectric, ferromagnetic, ferroelastic, or even orbital and charge orderings can develop and eventually coexist. These orderings can be tuned by external electric, magnetic, or stress field, and the cross-couplings between them enable important multifunctional properties, such as piezoelectricity, magneto-electricity, or magneto-elasticity. Here, I will illustrate the utilization of emerging materials prepared as thin films. By growing PrVO$_3$ thin films epitaxially on an SrTiO$_3$ substrate, I will show that the role of oxygen vacancies can be rationalized to introduce a chemical strain similar to the so-called mechanical strain (±2%), which in turns produce a nontrivial evolution of Neél temperature in a range of 30 K. The possible ferroelectricity will also been discussed.

Financial support from ANR, Labex, and Region Normandie (INCOX project) are acknowledged.

2:30 PM EP01.10.03
Structure-Function Relations in Mixed Phase BiFeO$_3$ via Phase Population Control—The Roles of Electric Field and Nanoscale Stress Aaron Nadeau$^{1, 2}$, David Edwards$^{3, 4}$, Sabine M. Neumayer$^{3, 5}$, Joseph Guy$^1$, Brian J. Rodriguez$^3$, Nazanin Bassiri-Gharb$^5$ and Amit Kumar$^1$; $^1$Queen's University Belfast, Belfast, United Kingdom; $^2$School of Chemistry, University of St Andrews, St Andrews, United Kingdom; $^3$School of Physics and Conway Institute, University College Dublin, Dublin, Ireland; $^4$Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^5$G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Mixed phase BiFeO$_3$ (BFO) films have recently attracted significant attention due to their advantageous functional properties which are often strongly related to the films’ microstructures. The crystallographically mixed phase microstructure is obtained through epitaxial growth on substrates with a large lattice mismatch with the BFO film. In such systems, monoclinic phases with alternating tetragonal- and rhombohedral-like structures (which we refer to as T- and R-phase for brevity) form spontaneously in order to accommodate the epitaxial strain. Despite the favourable properties of these films, significant challenges remain in understanding the precise nature of the interplay of structural transitions and ferroelectric switching and how this behaviour of phenomena influences the behaviour of mixed phase BFO.

Here we demonstrate deterministic nanoscale control of the R/T-phase population between ~100 % and ~30 % T-phase using electric field and nanoscale stress applied through an atomic force microscope (AFM) tip. To develop a truly holistic understanding of the phase population, we explore the effects of electric field and nanoscale stress on the electromechanical properties of the material using a variation of band excitation piezoresponse force microscopy. Simultaneously application of these external fields via the AFM tip results in enhancements in the electromechanical response which manifest in the form of peaks, or noses, in the piezoresponse loops at a single given polarity of applied electric field: when the AFM tip is biased positively relative to the bottom electrode, corresponding nominally to a downward polarisation. By collecting nanoscale electromechanical hysteresis loops and simultaneously monitoring the elastic behaviour during switching, we develop a comprehensive picture of the complex interplay of ferroelastic structural transitions and ferroelectric switching and its impact on the overall functional response. Such an understanding is a crucial step towards realising practical electronic devices, such as pressure sensors, incorporating this promising material.

2:45 PM BREAK

3:15 PM EP01.10.04
High-Field Nonlinear Dielectric and Piezoelectric Properties of Fe$_3$O$_4$ Doped PMA$_x$PZN-PZT Ceramics Huaizhang Zhang, Jie Shen, Quan Wei, Kunkun Han, Jing Zhou and Wen Chen; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials
High-power devices, such as ultrasonic motors, underwater acoustic transducers and piezoelectric transformers, require piezoelectric ceramics with low dielectric loss tan δ, high mechanical quality factor Qm (low mechanical loss), and simultaneously large piezoelectric constant d33 and electromechanical coupling factor k2. In our previous work, Fe3O4 doped Pb(Mn1/3Nb2/3)O3-Pb(Zn1/3Nb2/3)O3-Pb(Zr, Ti)O3 (PMnS-PZN-PZT) ceramics were found to possess a relatively high piezoelectric property and an extremely low dielectric loss [3], showing that the ceramics are promising for high-power applications. Nevertheless, the electric field-dependence of piezoelectric property and the origin of the low losses of Fe3O4 doped PMnS-PZN-PZT ceramics are still remained to be clarified.

In this study, electric field dependence of dielectric and piezoelectric properties in subswitching field range, and effect of temperature on high-field nonlinearity of dielectric property for Fe3O4 doped PMnS-PZN-PZT high-power piezoelectric ceramics are investigated. To characterize the domain wall motion, the electric field dependent dielectric and piezoelectric properties are discussed in terms of Rayleigh analysis [4-5]. Results show that with the increase of electric-field level, both the dielectric and piezoelectric properties deviate their low-field values and exhibit increase trends, due to the enhanced domain wall motion at high field. Rayleigh analysis reveals the contribution from lossless reversible domain wall motion to the high-field nonlinear dielectric and piezoelectric properties in Fe3O4 doped PMnS-PZN-PZT ceramics. This behavior is associated with the orderly distribution of defect pinning centers, and is thought to be responsible for the low losses of the ceramics. At elevated temperatures, the mobility of the oxygen vacancies increases, so that the distributions of the defect pinning centers are gradually randomized, which consequently lead to the enhancement of high-field nonlinearity.

References:

3:30 PM EP01.10.05
Ferroelectric Materials—A New Antimicrobial Class
Sandeep K. Shukla, Rahul Vaish and Satvasheel Powar; Indian Institute of Technology Mandi, Mandi, India.

Bacterial contamination is one of the major concerns around the world especially in developing countries where safe drinking water and bacterial diseases are still a primary risk. Current antibacterial substances suffer from their own limitations such as sustainability, resistance and cost. Herein, we propose a novel method for bacterial disinfection using ferroelectric materials. Ferroelectric materials like Ba0.5Ca0.5Ti0.5Zr0.5O3 (BCTZO), BaTiO3 possess remnant polarization on the surface as a result of aligned dipoles, attained through electric field poling. The effect of poling on the photocatalytic performance of ferroelectric materials has been investigated. The improved photocatalytic performance of poled samples attributed to the charge separation capability of poled samples. The antibacterial property of ferroelectric materials found to be surface selective as the positive side of ferroelectric materials electrostatically attracts negatively charged bacterial cells. The effect of photocatalysis on bacterial degradation studied further under UV irradiation. The antibacterial performance of poled ferroelectric material was tremendously improved in combination with UV irradiation. The complete bacterial eradication attained in less than 60 min of exposure when tested in combination. DCFDA assay study confirmed that the reactive oxygen species produced during electrolysis of water is one of the crucial factors for this remarkable photo-driven antibacterial performance. Poled ferroelectric materials exhibited excellent photocatalytic property for resazurin ink (Rz) and bacterial degradation. Interestingly, a synergistic effect observed against Rz ink and bacteria employing Ferro-photocatalysis and piezocatalysis. With these promising results, we believe, Ferrocailalys will open new ways for disinfection of drinking water, food products, and environmental pollutants.

3:45 PM EP01.10.06
Polymer-Based Efficient and Robust Piezoelectric Energy Harvesters
Deepa Singh1,2, Aditya Choudhary1 and Ashish Garg1; 1Department of Materials Science and Engineering, Indian Institute of Technology Kharagpur, Kharagpur, India; 2Department of Physics and Astronomy, Western University, London, Ontario, Canada.

Ferroelectric materials are the most sought out electronic materials because of their multifunctional applications in energy harvesting, sensing, memory and biomedical applications. Organic devices based on ferroelectricity are a promising approach towards the development of a low cost, low temperature, solution processed technology. Here, we demonstrate flexible devices with MgO-Poly(vinylidenefluoride-trifluoroethylene)(P(VDF-TrFE)) nanocomposites. P(VDF-TrFE) is known for its high remnant polarization, low switching time and highly insulating properties. Incorporation of a small amount of MgO leads to improved dielectric, ferroelectric and piezoelectric performance without affecting its other electrical properties such as leakage current and breakdown strength: two long-lasting problems with nanocomposites. MgO, a hygroscopic material, is considered to have inherent –OH bonds at its surface. These –OH bonds form hydrogen bonds with PVDF-TrFE as estimated by FTIR measurements. This interaction further improves electric fatigue and leakage current by reducing the gauche defects such as chain folding and kinks. PVDF-TrFE polymer can sustain larger strains compared to conventional inorganic materials due to their flexibility. This makes them more appropriate for harvesting energy from mechanical fluctuations. Flexible nanocomposite devices exhibit 50% improvement in piezoelectric properties. The piezoelectric coefficient (d33) value of ~65 pm/V was obtained for 2wt % MgO(P(VDF-TrFE) nanocomposites in contrast to pure P(VDF-TrFE) devices with d33 value of about ~40 pm/V. In addition, output voltage response increases two times with MgO nanoparticles as compared to pure P(VDF-TrFE) based devices. Bending test confirmed that d33 values remain unaffected even after 10000 bending cycles. This corroborates the beneficial role of MgO in sensing and memory applications.

SYMPOSIUM EP02

Materials for Manipulating and Controlling Magnetic Skyrmions
November 28 - November 30, 2018

Symposium Organizers
Skyrmion Dynamics—From Thermal Diffusion to Ultra-Fast Motion

Mathias Klaui
1, 2: 1Univ Mainz, Mainz, Germany; 2Materials Science in Mainz, Johannes Gutenberg University Mainz, Mainz, Germany.

The three key requirements for spintronics devices are: (i) stable spin structures for long term data retention; (ii) efficient spin manipulation for low power devices and (iii) ideally no susceptibility to stray fields as realized for antiferromagnets. We explore different materials classes to tackle these challenges and explore the science necessary for a disruptive new technology.

To obtain ultimate stability, topological spin structures that emerge due to the Dzyaloshinskii-Moriya interaction (DMI), such as chiral domain walls and skyrmions are used. These possess a high stability and are of key importance for magnetic memories and logic devices [1,2]. We have investigated in detail the dynamics of topological spin structures, such as chiral domain walls that we can move synchronously with field pulses [3]. We determine in tailored multilayers the DMI, which leads to perfectly chiral spin structures. For ultimately efficient spin manipulation, spin torques are maximized by using highly spin-polarized ferromagnetic materials [2] and using spin-orbit torques, we can efficiently manipulate magnetization [4-6].

We then combine materials with strong spin-orbit torques and strong DMI where novel topologically stabilized skyrmion spin structure emerge [5]. Using spin-orbit torques we demonstrate in optimized low pinning materials for the first time that we can move a train of skyrmions in a “racetrack”-type device reliably [5,6]. We find that skyrmions exhibit a skyrmion Hall effect leading to a component of the displacement perpendicular to the current flow [6]. We study the field - induced dynamics of skyrmions [7] and find that the trajectory of the skyrmion’s position is accurately described by our quasi particle equation of motion.

While thus highly reproducible driven skyrmion motion is possible, we have recently developed new ultra-low pinning multilayer stacks, which exhibit thermally activated dynamics of skyrmions [8]. Here the energy landscape is sufficiently flat so that we observe pure diffusive motion of skyrmion quasiparticles at room temperature [8]. Furthermore, in contrast to the analytical calculations, we find a strong temperature dependence of the diffusion and explain these observations based on thermally activated excitations. Finally we can employ skyrmion diffusion in a skyrmion reshuffler device enabling novel stochastic computing approaches [8].

References:

Real-Space Observation of Topological Spin Textures and Their Dynamics in Thin Chiral-Lattice Magnets

Xiuzhen Yu; RIKEN CEMS, Saitama, Japan.

The real-space spin textures have recently attracted enormous attention owing to their topological nature and emergent electromagnetic properties [1]. Here, I will present real-space observations of nanometer-scale topological spin textures and their lattice forms, such as meron-antimeron square lattice (sq.-ML), hexagonal skyrmion lattice (hex-SkL) and their structural transition from the sq.-ML into hex-SkL with finely tuning the magnetic field which is applied normally to a thin chiral-lattice magnet, Co$_8$Zn$_9$Mn$_3$. The topological phase transition between a hex-SkL phase and non-topological spin textures, helical or conical structure, have been demonstrated by means of the in-situ Lorentz transformation electron microscopy observations with current excitation [2] or quenching the thermal equilibrium SkL in thin helimagnets [3]. In addition, the skyrmion dynamics, such as the Brownian motion of skyrmion in a chiral-lattice insulator, the collective transformation of sparsely-populated skyrmions to microcrystals of skyrmions, and the current-driven skyrmion motion will be shown.

These works were done in collaborations with Profs. Yoshinori Tokura, Naoto Nagaosa, Masashi Kawasaki, Taka-hisa Arima, Maximam Mostovoy, Yusuke Tokanaga, Fumitaka Kagawa and Masahiko Morishizuki and Drs. Tasjirou Taguchi, Wataru Koshibae, Shinichiro Seki, Naoya Kanazawa, Tomoyuki Yokouchi, Daiuke Morikawa, Masao Nakamura, Kiyou Shibata, and Yoshih Kaneko.

References:
via a giant AHE for single crystals of Mn3Sn and Mn3Ge [7,8]. In general Mn-rich Heusler compounds with heavy transition metals such as Mn2RnSn can be designed with frustrated spins, large Berry curvature as a consequence of Weyl points close to the Fermi energy [6]: this has recently been proven to induce Weyl points in magnetic fields, which break time-reversal symmetry [3-5]. However, even antiferromagnetic Manganese-rich Heusler compounds applications that result from the large Berry phases that they exhibit: these lead to giant anomalous Hall effect (AHE), spin Hall effects (SHE) and tunable topological insulators, half metallic ferromagnets and non collinear topological spin structures [1]. The required band inversion has already been unambiguously identified by angle-resolved photoemission (ARPES) and transport [2]. Weyl and Dirac semimetals open up new research directions and applications that result from the large Berry phases that they exhibit: these lead to giant anomalous Hall effect (AHE), spin Hall effects (SHE) and topological spin structures. In the C1b Heusler compounds such as GPdB, the inclusion of rare earth atoms allows the use of magnetic exchange fields to induce Weyl points in magnetic fields, which break time-reversal symmetry [3-5]. However, even antiferromagnetic manganese-rich heusler compounds can be designed with frustrated spins, large Berry curvature as a consequence of Weyl points close to the Fermi energy [6]: this has recently been proven via a giant AHE for single crystals of Mn5Sn and Mn5Ge [7,8]. In general Mn-rich Heusler compounds with heavy transition metals such as Mn5RnSn show a large Dzyaloshinskii-Moriya interaction (DMI) and therefore non-collinear spin structures [9,10]. Skyrmions, topologically stable spin textures, are of great interest for new generations of spintronic devices. Depending on the crystal symmetries, two distinct types of swirling of the skyrmions, named Bloch and Neel types, have been observed experimentally. In a family of acentric tetragonal Heusler compounds with D4h crystal symmetry Skyrmions with a special type of spin-swirling, called antiskyrmions, can even be realized. The interplay between the anisotropic exchange and DMI modifies a helical magnetic phase that propagates in the tetragonal basal plane into antiskyrmions arranged on a hexagonal lattice. The flexibility of their manipulation in the present system is demonstrated by the achievement of antiskyrmions up to 400 K and their zero field metastable state at low temperatures [11]. The family of tetragonal Heusler materials including non-collinear spin structures and Skyrmions opens a new spintronics direction including the realization of skyrmionics.


4:00 PM EP02.02.02
Terbium, Europium and Thulium Iron Garnets as a Platform for Insulator Spintronics Ethan Rosenberg, Jackson A. Bauer, Lukas Beran, Can Onur Avci, Bingjian Song, Geoffrey Beach and Caroline A. Ross; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Rare earth (RE) garnets with formula RE Fe2-xGd2x/3O3 provide a rich class of ferrimagnetic insulators in which anisotropy, saturation magnetization and temperature compensation can be tuned by choice of rare earth, ratio of rare earth to iron, and oxygen off-stoichiometry. Here we describe the growth, magnetic and spintronic properties of epitaxial terbium iron garnet (TBIG) and europium iron garnet (EuIG) thin films with perpendicular magnetic anisotropy (PMA), in comparison to the better-studied thulium iron garnet (TmIG). Reciproc space mapping shows that all the films are lattice matched to gadolinium gallium garnet (GGG) or substituted GGG (SGGG) substrates without strain relaxation, even for films up to 56 nm thick. The PMA is governed by magnetoelastic anisotropy, and both EuIG and TbIG are under in-plane compression on GGG. EuIG exhibits PMA for both (111) and (100) GGG orientations whereas TbIG exhibits PMA for (111) but not (100) GGG, as expected from the sign of the magnetostriction coefficients. In contrast, TbIG on SGGG (111) is in tension and has an in-plane easy axis. Films grown at higher oxygen pressures have excess rare earth which is believed to replace Fe2+ on the octahedral sites, altering the sublattice magnetization. TbIG films have a compensation temperature of around 330K. The EuIG films have damping parameter of 0.025, whereas damping in TmIG is 0.016 and increases when a Pt overlayer is added. Polycrystalline EuIG was grown on a range of substrates and showed PMA when the thermal expansion mismatch led to in plane compression. Anomalous Hall effect (AHE) measurements of Pt/EuIG/GGG Hall cross show that the spin mixing conductance of Pt/EuIG is orientation-dependent, with values for (111) EuIG being an order of magnitude larger than those of (001) EuIG. AHE measurements of Pt/TbIG/GGG Hall crosses reveal a sign change in the AHE amplitude at the compensation point, analogous to all-metallic Pt/ferrimagnet systems, and indicating that the spin Hall magnetoresistance-induced AHE is dominated by the Fe sublattice rather than the net magnetization. Pt/TmIG/GGG showed a Dzyaloshinskii-Moriya interaction (DMI) field of ~50 Oe, sufficient to stabilize homochiral Neel-type domain walls in 5 nm thick TmIG. Moreover, magnetic imaging showed domain sizes of 10 – 20 nm. These results show that RE garnet/Pt heterostructures are excellent candidates for obtaining skyrmions and other chiral textures at room temperature.

4:15 PM EP02.02.03
Current-Driven Dynamics of Chiral Domain Walls in Thulium Iron Garnet/Platinum Bilayers Can Onur Avci, Ethan Rosenberg, Lucas M. Caresza, Lukas Beran, Felix Buettner, Caroline A. Ross and Geoffrey Beach; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Magnetic insulators (Mls), especially iron-based garnets, possess remarkable properties such as ultralow damping, long magnon decay lengths and high structural quality which can provide significant advantages for practical applications with respect to their metallic magnetic counterparts. Recently, robust perpendicular magnetic anisotropy is obtained in ferrimagnetic thin films of thulium, europium, and terbium iron garnet (TmIG, EuIG, and TbIG) grown on gadolinium gallium garnet (Gd3Ga5O12) substrates down to a thickness of 5.1 nm with saturation magnetization close to the bulk value [1,2]. By using the spin Hall effect in Pt we have demonstrated efficient spin current injection through the TmIG/Pt interface, which we quantified by the spin Hall magnetoresistance and harmonic Hall effect measurements [1-3]. This spin current is strong enough to realize deterministic spin-orbit torque-driven magnetization switching of TmIG (~10 nm)/Pt bilayer both with quasi-dc (5 ms) as well as pulsed currents down to 2 ns width [1,4]. The switching current density through Pt is found to be of the order of ~10^-7 A/cm~2 using dc (pulsed) current comparable to the reported values, e.g., for Pt/Co[5]. We then investigated the structure and current-driven dynamics of domain walls in TmIG/Pt bilayer. We found that, solely using electrical currents, domain walls can be efficiently.
moved indicating the presence of Neel-type domain wall texture in this system. Detailed analysis revealed that homochiral domain walls are stabilized by the Dzyaloshinskii-Moriya interaction occurring at the TmIG/Pt interface which produces an effective field of ~50 Oe. By using nanosecond-long pulses we determined the current-driven domain wall intrinsic velocities of the order of ~800 m/s per current densities as low as ~1.2x10^4 A/m^2, one of the highest reported in any ferromagnetic system thus far. In this presentation, along with the above findings, we will discuss the scanning transmission x-ray microscopy imaging of chiral textures in TmIG/Pt and the possibility of obtaining skyrmions in rare earth-based garnets at room temperature.


4:30 PM EP02.02.04 Rare Earth-Transition Metal Alloys as Promising Materials for Small Skyrmions and Ultrafast Chiral Spin Texture Dynamics Lucas M. Caretta¹, Maxwell Mann¹, Felix Buettner¹, Kohei Ueda¹, Bastian Pfau¹, Cristian Guenther¹, Piet Hessing², Alexandra Cherukova¹, Christoph Klose², M Schneider², D Engel², Colin Marcus², David Boni², Kai Bagchi³, Stefan Eisebitt² and Geoffrey Beach³; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Max-Born Institute, Berlin, Germany; ³DISY, Hamburg, Germany.

Spintronics is a research field geared towards understanding and controlling spins on the nanoscale, enabling next-generation data storage and manipulation. Ultimately, the technological and scientific challenge is to create ultrasmall solid-state magnetic bits (<10 nm) and to control their motion efficiently with ultrahigh velocities (>1 km/s). Inspired by materials used for hard disk drives, research so far has focused on ferromagnetic materials. However, these materials show fundamental limits for speed and size making applications unlikely. Ferromagnetic materials have large stray fields, causing ferromagnetic spin textures to repel each other over long distances. Stray field interactions also lead to a preferred demagnetization of the material, i.e., skyrmions are large (>100 nm) if they are not assisted by external fields or strong pinning. In addition, the velocity of magnetic solitons is fundamentally limited by the precessional dynamics underlying any coherent spin texture displacements, ultimately making motion inefficient. For skyrmions, the velocity is also limited by stripe-out instabilities and by topological damping. In both cases, the observed skyrmion velocities in ferromagnetic materials have always been lower than ~100 m/s. Moreover, ferromagnetic materials suffer from a large skyrmion Hall angle and from topological damping. These fundamental limitations of ferromagnets call for new materials systems.

Here, we demonstrate that compensated rare earth - transition metal ferrimagnets (FiM) are not affected by these limits. FiM, comprised of two antiferromagnetically coupled sublattices, have two compensation temperatures: the magnetization compensation temperature TM, defined by Ms(TM)=0, and the angular momentum compensation temperature TA with vanishing spin density S(TA)=0. Near TA, the spins align with the magnetic field without any precession and a driving force immediately leads to acceleration in the direction of force. Near TM, stray fields become negligible and spin textures are stabilized by the competition of local exchange, anisotropy, and Dzyaloshinskii-Moriya interaction (DMI). Thus, zero field skyrmions with less than 10 nm in diameter can be realized at room temperature and interactions skyrmions is completely suppressed. In other words, very efficient dynamics are expected to occur near TA and very small spin textures can be realized at TA. Using these concepts in ferrimagnetic Pt/GdCo/Ta films, we realize a record-fast current-driven domain wall velocity of 1.3 km/s and record small room-temperature stable ~10 nm diameter skyrmions near TA and TM, respectively. Moreover, TA and TM are engineered to be near each other and near room temperature for both fast dynamics and small textures. Compensated FiM are a promising spintronics candidate, as a range of easily accessible knobs, such as interfaces, annealing, sample temperature, and composition can control their properties.

4:45 PM EP02.02.05 Electrical-Field-Control of Ferromagnetism and Magnetic Skyrmions in 2D CrI3 Monolayers Pinghu Mo¹, Mengchao Shi¹, Jiwu Lu¹ and Jie Liu¹; ¹College of Electrical and Information Engineering, Hunan University, Changsha, China; ²Department of Electrical Engineering, University of Washington, Seattle, Washington, United States.

We report our recent research findings about the electrical-field-controllability of ferromagnetism and magnetic Skyrmions in two-dimensional chromium tri-iodide monolayers [1][2]. By combining the fully first-principles non-collinear self-consistent field density functional theory (DFT) with relativistic spin-orbital coupling effects and the Monte Carlo calculations, we show that, an externally-applied out-of-plane electrical field can significantly alter the spin configuration of a free-standing two-dimensional chromium tri-iodide (CrI3) ferromagnetic monolayer.

The electrical-field-dependent Dzyaloshinskii-Moriya interaction, magnetocryalline anisotropy, and magnetic exchange effects are quantitatively analyzed. It is shown that, by taking advantage of the counterbalancing effects of anisotropic symmetric exchange energy and antisymmetric exchange energy, the intrinsic ferromagnetism can be manipulated by externally applied out-of-plane electric fields. It is revealed that the out-of-plane electrical field could induce topologically-protected Neel-type Skyrmion ground state due to the breaking of inversion symmetry. By taking advantage of the above-mentioned properties, it is shown that 4-level data can be stored in a single monolayer-based spintronic device, which is of practical interests to realize the next-generation energy-efficient quaternary logic devices and multilevel memory devices.

Reference:

SESSION EP02.03: Nucleation and Stabilization of Magnetic Skyrmions Session Chairs: Karin Everschor-Sitte and Song Jin Thursday Morning, November 29, 2018 Hynes, Level 2, Room 204

8:00 AM *EP02.03.01 Electrical Writing, Processing and Deleting of Room-Temperature Ferrimagnetic Skyrmions Seonghoon Woo; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

In spintronics, magnetic skyrmions are one of the most promising candidate for the next-generation memory-type application due to their nanometer-size, topological stability and efficient current-driven motion. [1] Recent efforts have realized the room-temperature stabilization of magnetic skyrmions and their current pulse-induced dynamic behaviours on nanotracks in magnetic heterostructures. [2, 3] However, there still exist many practical limitations for

Reference:
the realization of fully functional skyrmionic devices. In this presentation, we show our recent experimental demonstrations of the electrical writing, processing and deleting of ferrimagnetic skyrmions observable static and dynamic soft X-ray microscopy.

We first demonstrate a new type of skyrmion, called ferrimagnetic skyrmion. Ferrromagnetic skyrmions show undesirable topological effect, the skyrmion Hall effect, which leads to their current-driven motion towards device edges, where skyrmions could easily be annihilated by topographic defects. In this work, we present the stabilization of antiferromagnetically exchange-coupled skyrmions – ferrimagnetic skyrmions - and their current-driven dynamics in GdFeCo films. We demonstrate that ferrimagnetic skyrmions can move at a velocity of ~50 m s⁻¹ with significantly reduced skyrmion Hall angle, ΔH_{Hall} < 20°, which highlights the possibility to build more reliable skyrmionic devices using ferrimagnetic materials. [4]

Using the same material, we then demonstrate the electrical writing and subsequent deleting of a single magnetic skyrmion at room temperature, which are essential prerequisites for device application but have remained elusive so far. We also present that the number of written and destroyed skyrmions can be controlled by modulating the strength of spin orbit torques. The stroboscopic pump-probe X-ray measurement serves as a key technique to reveal the deterministic and completely reproducible nature of the observation. Micromagnetic simulations reveal the microscopic origin behind the observed topological fluctuation with great qualitative and quantitative agreement. Our findings show that the deterministic field-free writing and deleting of magnetic skyrmions can be readily achieved using electrical methods, which leap over a crucial hurdle toward building a practical skyrmionic device. [5]

References.

8:30 AM EP02.03.02
Isolated Magnetic Skyrmions—From a Fundamental Understanding to the Observation of Ultrasmall Skyrmions at Room Temperature Felix Büttner1, Ivan Lemesl1, Lucas M. Caretta1, Maxwell Mann1, Kohei Ueda1, Bastian Pfaü1, Christian Günther1, Pier Hessing2, Alexandra Churikova2, M Schneider2, D Engel2, Christopher Klose2, Kai Bagschik2, Stefan Eisебitz3 and Geoffrey Beach1; 1Massachusetts Institute of Technology, Cambridge, United Kingdom; 2Max Born Institut, Berlin, Germany; 3Technische Universität Berlin, Berlin, Germany; 4DESY, Hamburg, Germany.

Skyrmions are the smallest non-trivial entities in magnetism with great potential for data storage applications. They were recently observed at room temperature in magnetic multilayer systems [1-4], most of them in materials with sizable Dzyaloshinskii-Moriya interaction (DMI). Despite this experimental breakthrough, our understanding of skyrmions is still limited because existing theories cannot analytically predict how the skyrmion energy changes as a function of its size. In particular, for many decades, the 6-fold integral of the stray field energies was considered unsolvable and the contributions of DMI and stray fields to stabilizing skyrmions could not be distinguished.

This problem has now been solved. In this talk, I will present a unified theory that analytically approximates the energy, including stray fields, of isolated skyrmions of all sizes with 1% precision [5]. I will show that there are indeed two types of skyrmions, 'stray field skyrmions' and 'DMI skyrmions', but in contrast to common belief it is not the domain wall angle (Neel or Bloch type) that distinguishes these two types. Surprisingly, the type of skyrmion is also not a material property: DMI and stray field skyrmions can even co-exist in the same material at the same field. This form of bi-stability opens a whole new area of potential skyrmion applications.

There is a strong desire to make room-temperature skyrmions small and to move them fast. However, all room temperature skyrmions observed so far are stray field skyrmions, and I will show that this fundamentally limits their stable size to much larger than 10 nm at room temperature. By contrast, DMI skyrmions can be smaller than 10 nm even at room temperature and zero applied field. All presently available data indicates that such skyrmions cannot exist in ferrimagnetic materials. Instead, ferrimagnets and antiferromagnets are the most promising materials for finding room-temperature DMI skyrmions. This theoretical prediction is confirmed by our first observation of sub-15 nm skyrmions in a ferrimagnetic material with strong DMI, where we also confirm that these skyrmions remain stable and retain their size at zero applied field.


8:45 AM EP02.03.03
Stability and Manipulation of Magnetic Skyrmions Giovanni Finocchio; University of Messina, Messina, Italy.

Magnetic skyrmions are topological protected solitons with a chirality that can be stabilized by the Dzyaloshinskii-Moriya interaction (DMI). Understanding the physical properties of magnetic skyrmions is important for fundamental research with the aim to develop new spintronic device paradigms where both logic and memory can be integrated at the same level or for unconventional computing. We have recently studied different mechanism of stabilization of skyrmions in confined devices, one of them needs a large DMI to introduce in the energy landscape an energetic minimum associated with a metastable skyrmion state and one that gives a skyrmion state which size depends on a trade off among magnetostatic, exchange and DMI energies. In this invited talk, we will show a universal model based on the micromagnetic formalism combining a proper ansatz and scaling relationships and a specific Q-d phase space (quality factor Q vs. reduced DMI d) that can be used to study skyrmion stability as a function of magnetic field and temperature[1]. We consider ultrathin, circular ferromagnetic magnetic dots. These results show that magnetic skyrmions with a small radius—compared to the dot radius—are always metastable, while large radius skyrmions form a stable ground state. The change of energy profile determines the weak (strong) size dependence of the metastable (stable) skyrmion as a function of temperature and/or field. We also show as this fundamental results can be used for specific application in a racetrack memory device where the skyrmions in the track are metastable and therefore small—giving a high storage density while are detected under a magnetic tunnel junction having a polarized layer with a magnetization pointing along the out-of-plane direction which generates a dipolar field parallel to the skyrmion core magnetization [1]. This field can modify the stability properties of the skyrmion in the region below the contact, moving it through the Q-d phase space. By shifting the skyrmions across the line of stability, their radius will expand significantly making it much easier to detect from the tunnel magnetoresistance signal. After leaving the detection regions, the skyrmions will return to their small size in the metastable region.

Finally, I will discuss the SHE-driven dynamics of a skyrmion in presence of an anisotropy gradient showing a scenario where the skyrmion is accelerated[2].

Magnetic skyrmions are topologically stable spin textures exhibiting quasi-particle like behavior and consequently can be directed with low electric currents. The controlled manipulation of magnetic skyrmions at room temperature in thin films is envisioned to enable skyrmion-based low-power information technologies, and consequently has engaged the interest of the scientific community in recent years [1]. Using trilayered heterostructures we have demonstrated how diverging electric charge currents combined with the spin Hall effect in a heavy metal layer can be used to generate and manipulate magnetic Néel skyrmions in an adjacent ferromagnetic layer [2,3]. Under application of homogeneous currents, the motion of magnetic skyrmions is experimentally shown to exhibit transverse motion relative to the current direction, i.e., the skyrmion Hall effect [4]. This effect arises due to the non-trivial topological charge of the skyrmions and is the analogue of the ordinary Hall effect for electrical charges in the presence of a magnetic field. With increasing current density, the skyrmion Hall angle first increases monotonically, which can be linked to the influence of pinning by defects, and then saturates, indicating the flow regime for motion has been reached. From an applications perspective, minimizing the skyrmion size is equally important to controlling the creation and motion of skyrmions. To this end, we have investigated inversion asymmetric [Pt/FM/X]Nmultilayers, where FM is a ferro- or ferrimagnet and X a transition or rare earth metal, which allows for various competing interactions to be tuned. Using magneto-optic Kerr imaging and Lorentz transmission electron microscopy, we show how the skyrmion size varies depending on the choice of metal X, the trilayer repetition number N, and the magnetic field.

Work at Argonne was supported by the Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division.


Skyrmions in UltraThin Films

Stephan von Malottki1, Pavel Bessarab2, Soumyajitoyi Haldar1, Anna Delin1-3 and Stefan Heinze1; 1Institute of Theoretical Physics and Astrophysics, University of Kiel, Kiel, Germany; 2Department of Applied Physics, School of Engineering Sciences, KTH Royal Institute of Technology, Kista, Sweden; 3Department of Physics and Astronomy, Materials Theory Division, Uppsala University, Uppsala, Sweden; 4School of Engineering and Natural Sciences, Science Institute, University of Iceland, Reykjavik, Iceland.

The thermal stability of magnetic skyrmions is a key issue for potential applications in spintronic devices. An Arrhenius law can be used to describe the skyrmion lifetime as a function of temperature, which requires knowledge of the energy barrier and the pre-exponential factor. While the energy barrier has already been addressed by several studies (e.g. [1]), the pre-exponential factor for the skyrmion collapse remains largely unexplored [2, 3]. Here, we obtain skyrmion lifetimes by calculating not only the energy barriers but also the pre-exponential factors for ultrathin films such as Pd/Fe bilayers on Ir(111) – a system which has been extensively studied from experiment [4]. We have developed an analytical topological soliton model containing expressions of the long range demagnetising and exchange curvature energies, two key ingredients to stabilize bubbles and skyrmions in ferromagnetic thin films. This allowed us to construct a skyrmion and bubbles phase diagram and explore quantitatively the possible transitions between them. The observed skyrmion-bubble transition present similarities with the liquid-gas transition, in particular a critical point is present above which the transformation between both spin textures becomes continuous. While distinct characteristics of skyrmions and bubbles remain, their common nature as topological solitons is emphasised.

Magnetic skyrmions in noncentrosymmetric chiral magnets form ordered lattices with a periodicity ranging from 3-100 nm. This lengthscale lends itself to soft x-ray scattering experiments owing to the large resonant scattering cross-section for 3d elements, the excellent reciprocal space resolution, as well as the tunable surface sensitivity. We will present an overview of the capabilities of resonant elastic x-ray scattering (REXS) for the study of magnetic skyrmions [1], highlighting the following effects:

1) Topology [2]: Using circularly polarized light, REXS is capable to accurately determine the topological winding number of a skyrmion. This topology determination principle is a general experimental strategy, applicable to a wide range of topologically ordered magnetic materials.

2) Microscopic skyrmion properties [3]: By exploiting the polarization dependence of REXS, the exact surface helicity angles of twisted skyrmions for both left- and right-handed chiral bulk Cu2OSeO3 was determined.

3) Full 3D spin structure of skyrmions [4]: Using polarization-dependent REXS we found a continuous transformation of the skyrmion tubes from pure Néel-twisting at the surface to pure Bloch-twisting in the bulk over a distance of several hundred nanometers.

4) Rotating lattices [5]: In a magnetic field gradient, skyrmions undergo rotation with well-defined dynamics. This provides an effective way of controlling skyrmions in racetrack memory schemes.

References

11:30 AM *EP02.03.08
Stabilizing Spin Spirals and Isolated Skyrmions at Low Magnetic Field Exploiting Vanishing Magnetic Anisotropy Marie Hervé1, Bertrand Dupé2, Rafael Lopes3, Marie Böttcher1, Maximilianio Martino1, Timofey Balashov1, Lukas Gerhard4, Jairo Sinova5 and Wulf Wulfhekel4, 4Physikalisches Institut, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; 2Institut für Physik, Johannes Gutenberg Universität Mainz, Mainz, Germany; 3Serviço de Nanotecnologia Laboratório de Nanoscopia, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte, Brazil; 5Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Skyrmions are topologically protected non-collinear magnetic structures. The non-collinear Dzyaloshinskii-Moriya interaction originating from spin-orbit coupling drives their formation. The Dzyaloshinskii-Moriya interaction is enhanced at surfaces and interfaces via the hybridization of the magnetic atoms with 5d elements. It competes with Heisenberg exchange and magnetic anisotropy favoring collinear states. Isolated skyrmions in ultra-thin films so far coupling drives their formation. The Dzyaloshinskii-Moriya interaction is enhanced at surfaces and interfaces via the hybridization of the magnetic atoms with 5d elements. It competes with Heisenberg exchange and magnetic anisotropy favoring collinear states.

Skyrmions Under the X-Rays

Christos Panagopoulos; Nanyang Technological University, Singapore, Singapore.

Multilayers of Fe/Fe(x)/Co(y)/Pt enable us tailor the magnetic interactions governing skyrmion (Sk) properties, thereby tuning their thermodynamic stability parameter by an order of magnitude. In particular, Sk’s exhibit a crossover between isolated (metastable) and disordered lattice configurations across samples, while their size and density can be tuned by factors of 2 and 10, respectively. To study magnetization dynamics, we determined the damping parameter characterizing the magnetization response, and identified a gyrotropic Sk excitation that persists over a wide range of temperatures and across varying sample compositions. To explore the interaction of skyrmions with electrical current we carried a detailed microscopic investigation, which allowed us identify magnetic structures forming via Sk-Sk interaction and their role in designing and interpreting electrical signatures in materials and devices hosting Sk’s.

2:00 PM EP02.04.02
Magnetic Imaging and Magnetotransport Measurements of Skyrmion Hosting Cubic B20 Fe1-xCoSi and Fe1-xCoGe Nanostructures Nitish Mathur1, Matthew J. Stolt1, Sebastien G. Schneider2, Kodai Nishiu3, Xiazhun Vu4, Bernd F. Rellingerhaus3, Yoshihori Tokura3 and Song Jin1; 1University of Wisconsin-Madison, Madison, Wisconsin, United States; 2IFW, Dresden, Germany; 3RIKEN Center for Emergent Matter Science (CEMS), Wako, Japan.

Magnetic skyrmions are topological spin textures that have shown promise due to their potential application in high density and energy efficient memory nanodevices. Stable skyrmion phase can exist in chiral helimagnets with the non-centrosymmetric cubic B20 crystal structure, such as Fe1-xCoSi and Fe1-xCoGe.
FeGe, that have antisymmetric spin exchange interaction known as the Dzyaloshinskii-Moriya interaction (DMI). Nanostructuring further enhances the stability regime of skyrmion phases in these materials to larger range of temperature and applied magnetic field. We have developed “bottom-up” chemical vapor deposition (CVD) synthetic techniques to synthesize single-crystal FeGe nanowires (NWs), and cobalt alloyed Fe1-xCoSi (x<0.5) NWs and Fe1-xCoGe (x<0.1) nanowires (NPLs). We have imaged the spin structures in these nanostructures with Lorentz transmission electron microscopy (LTEM) for Fe1-xCoSi NWs and more intensive TEM-based magnetic imaging technique known as off-axis electron holography (EH) for Fe1-xCoGe NPs. Further, the evolution of different spin structures under varying applied magnetic field below Tc could be electrically detected by the field-dependent magnetoresistance (MR) measurements which enable us to determine the critical fields for magnetic state transitions at different temperatures. For the Fe1-xCoGe NPLs, Hall measurements further revealed the topological Hall effect (THE) characteristics of skyrmion phases. The imaging and transport measurements were used in conjunction with one another to construct representative magnetic phase diagrams for the Fe1-xCoSi NWs and Fe1-xCoGe NPs respectively. These B20 materials can serve as nice model systems to study skyrmion physics and prototype devices by taking advantage of nanometer-sized magnetic skyrmion domains.

2:15 PM *EP02.04.03
Emergent Transport Effect in Chiral Spin Textures Yuriy Mokrousov1, 2, Fabian Lux3, Jan-Philipp Hanke1, 2, Matthias Redies1, Patrick Buhl1, Frank Freimuth1 and Stefan Bluegel1;
1Forschungszentrum Juelich, Juelich, Germany; 2University of Mainz, Institute of Physics, Mainz, Germany.

In the field of skyrmionics the progress in creation and manipulation of skyrmions with various size and charge has been truly remarkable. From the side of theory, in the past years various novel chiral particles such as chiral bobbers or hopfions have been predicted to exist under certain conditions. On the other hand, for experimental discovery and integration of these particles into future generation of devices their realizable detection by means of magnetotransport is imperative. Currently, this presents a significant problem, since our understanding of the transport properties of chiral spin textures is at a very preliminary level. In my talk I will review the recent progress in our understanding of the Hall effects and orbital magnetism exhibited by chiral particles of various nature. In particular, by starting from the adiabatic viewpoint that has been very successful in predicting various physical properties of chiral magnets such as topological Hall and topological spin Hall effects, we will arrive at and unravel the emergence of chiral and topological orbital magnetism in one- and two-dimensional spin systems. We will demonstrate that the emergent orbital magnetism has remarkable properties such as topological quantization, and its dynamics in skyrmionic systems can be used not only to detect the formation of skyrmions with different charge, but also to distinguish various types of dynamical “breathing” modes of skyrmion dynamics. Moreover, we will show that while beyond the adiabatic viewpoint the orbital magnetism of spin textures goes hand in hand with emergent Hall transport properties, remarkably, engineering the details of spin-orbit interaction and electronic structure in interfacial chiral systems allows for tuning the orbital and transport characteristics over orders of magnitude. We trace back such sensitivity of the emergent transport properties to the unique interplay of real-space and reciprocal-space topologies, and demonstrate that the Hall and orbital magnetization measurements can be used to categorize and uncover various topologically distinct phases of complex chiral magnets. This work was supported by Deutsche Forschungsgemeinschaft (projects MO 1731/5-1 and MO 1731/7-1) as well as by the DARPA TEE program through grant MIPR# HR0011831554 from DOD.

2:45 PM BREAK

3:15 PM *EP02.04.04
Detection and Manipulation of Magnetic Skyrmions in Metal Silicide and Germanide Nanostructures Song Jin; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Skyrmions, novel topologically stable spin vortices, hold promise for next-generation magnetic storage due to their nanoscale domains to enable high information storage density and their low threshold for current-driven motion to enable ultralow energy consumption. One-dimensional (1D) nanowires are ideal hosts for skyrmions since they not only serve as a natural platform for magnetic racetrack memory devices but also can stabilize skyrmions. We have developed synthetic methods for nanowires (and nanoplates) of non-centrosymmetric cubic B20 monosilicides (MnSi, FeSi, CoSi) and monogermanides (FeGe) and their alloys (such as Fe1-xCoSi and Fe1-xCoGe), many of which display exotic helimagnetic and skyrmion magnetic phases with domain sizes from 10 to 230 nm. Collaborating with several groups, we have used Lorentz TEM, off-axis electron holography (EH), magnetotransport measurements, and dynamic magnetic cantilever measurements to confirm that magnetic skyrmion phases are stable over a larger magnetic field-temperature range in these nanostructures compared to bulk crystals and thin films. Magnetoresistance (MR) measurements revealed the critical magnetic fields for the transitions between different magnetic spin structures at different temperatures. Topological Hall effect (THE) measurements of MnSi nanowires and Fe1-xCoGe (x<0.1) nanowires further confirmed the extended skyrmion stability. Particularly, FeGe nanowires and Fe1-xCoGe (x<0.1) nanowires can host skyrmions with stability up to about 280 K. We have further demonstrated the current-driven motion of skyrmions in this extended skyrmion phase region in MnSi nanowires. These results open up the exploration of nanowires as an attractive platform for investigating skyrmion physics in 1D systems and exploiting skyrmions in magnetic storage concepts.

3:45 PM *EP02.04.05
Various Topological Spin Textures and Emergent Phenomena in B20-Type Chiral Magnets Naoya Kanazawa; Department of Applied Physics, University of Tokyo, Tokyo, Japan.

Topological properties of skyrmions, such as topological Hall effect and current-driven skyrmion motion, stimulate researches on design of new topological spin textures in pursuit of further functionalities. Examples of those spin textures include biskyrmions, Néel-type skyrmions, and chiral soliton lattice. One guiding principle for creating such winding spin textures is utilizing antisymmetric spin exchange interaction, namely Dzyaloshinskii-Moriya (DM) interaction, allowed in crystals without local/global space inversion symmetry. We have realized various topological magnetic structures in a prototypical skyrmionic material, so-called B20-type compounds, by changing DM interaction, magnetic anisotropy and electronic structure, which are controlled by element substitution and device manufacturing. In this talk, we would like to show our recent results on formations of topological magnetic structures and consequent emergent phenomena in bulk and films of B20-type compounds [1-3].
DARPA MIPR# HR0011831554 for financial support.

Acknowledgments: EU grant MAGICSky No. FET-Open-665095, FLAG-ERA SoGraph (ANR-15-GRFL-0005), ANR grant TOPSky (ANR-17-CE24-0025) and to disruptive “beyond CMOS” technologies such as neuro-inspired architectures.

Up to recently, skyrmions were observed only at low temperature but an important effort of research has been recently devoted in several groups to stabilize small (< 100 nm) skyrmions above room temperature (RT) in magnetic multilayers through engineering of interfacial DMI [1].

Mokrousov; Forschungszentrum Jülich, Jülich, Germany.

Influence of Magnetic Field on Current Induced Skyrmion Motion in Multilayer Systems Katharina Zeissler1, Simone Finizio2, Joerg Raabe2, Thomas A. Moore1, Gavin Burnell1 and Christopher Marraro2,1; University of Leeds, Leeds, United Kingdom; 2Paul Scherrer Institut, Villigen, Switzerland.

This work was supported by the DARPA TEE program through grant MIPR# HR0011831554 from DOI.

Effect measurements [3], iii) the... thimel (RT) in magnetic multilayers through engineering of interfacial DMI [1].

In this presentation, I will present experimental imaging at RT on small skyrmions (30-80 nm) in several types of multilayers associating magnetic layers of Co and nonmagnetic layers of heavy metals (Pt, Ir, Ru etc…). First, the talk will be devoted to illustrate the wealth of skyrmions and describe some of our key recent results. We will discuss: i) the creation of skyrmions by current pulses and its mechanism (spin transfer torque vs thermal effects) [2], ii) the detection of skyrmions (one by one) by Anomalous Hall Effect measurements [3], iii) the current-induced motion of skyrmions, the influence of defects on velocity and Skyrmion Hall Angle [2]. Then, we will present some experimental results together with modelling on shaping skyrmions in 3D [4] by a control of the relative values of DMI and dipole interactions for a given number of layers experimentally revealed by x-ray magnetic scattering (XRMS) [5] and its impact on spin torque induced dynamics. These advances made in technologically relevant materials opens the way for the development of several concepts of skyrmion based devices going from race-track memory type to MRAM, from still highly silicon-compatible memories, such as multi-level MRAM or skyrmion racetrack memories to disruptive “beyond CMOS” technologies such as neuro-inspired architectures.

ACKNOWLEDGMENTS: EU grant MAGICSky No. FET-Open-665095, FLAG-ERA SoGraph (ANR-15-GRFL-0005), ANR grant TOPSky (ANR-17-CE24-0025) and DARPA MIPR# HR0011831554 for financial support.

Magnetic quasi-particles such as skyrmions are of importance for novel magnetic information storage designs. In ultrathin multilayer systems skyrmions are stabilised by the interfacial Dzyaloshinskii-Moriya interaction which is present at interfaces between ferromagnets and heavy metals [3]. The room temperature stability of skyrmions in these multilayers is a desirable property for technological applications (2-5). Active focal areas are electrical skyrmion detection and manipulation. In the experiment outlined here we stabilized skyrmions in a 2 μm wire of [Pt/CoB/Ir]. Short current pulses (10 ns) were used to move the skyrmions through the wire while a static out of plane magnetic field was applied. Scanning transmission microscopy images were taken after each current pulse. The velocity and Skyrmion Hall angle was evaluated and a field dependence on the Skyrmion Hall angle was observed.

This work was funded by Horizon 2020 MagicSky and has received funding from the EU H2020 research and innovation programme under grant agreement N 654360 having benefitted from the access provided by the Paul Scherrer Institut in Villigen within the framework of the NFFA Europe Transnational Access Activity.


9:45 AM *EP02.05.03*

**Skyrmions with Antiferromagnets** Oleg Tretiakov; Tohoku Univ, Sendai, Japan.

Skyrmions are topologically protected spin textures, which can be used in spintronic devices for information storage and processing. Ferromagnetic skyrmions attracted a lot of attention because they are small in size, better than domain walls at avoiding pinning sites, and can be moved very fast by electric current in ferromagnet/heavy-metal bilayers due to novel spin-orbit torques.

Meanwhile, the ferromagnetic skyrmions also have certain disadvantages to employ them in spintronic devices, such as the presence of stray fields and transverse to current dynamics. To avoid these unwanted effects, we propose a novel topological object: the antiferromagnetic skyrmion. This topological texture has no stray fields and its dynamics are faster compared to its ferromagnetic analogue. More importantly, I will show that due to unusual topology it experiences no skyrmion Hall effect, and thus is a better candidate for spintronic applications. Then I will discuss the lifetimes of both antiferromagnetic and ferromagnetic skyrmions at finite temperatures.

Lastly, I will talk about antiskyrmions -- unusual anisotropic topological objects, which were recently observed in systems with anisotropic Dzyaloshinskii-Moriya interaction. I will make predictions for the antiskyrmion existence and properties in antiferromagnets.

9:45 AM BREAK

10:15 AM *EP02.05.04*

**Skyrmion Dynamics, Nucleation and Stability in Ultrathin Metallic Heterostructures** Geoffrey Beach; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Magnetic skyrmions [1,2] are particle-like chiral spin textures that are topologically protected from being continuously ‘unwound’. Their topological nature gives rise to rich behaviors including ordered lattice formation, emergent electrodynamics and robust current-driven displacement by spin-orbit torque. This talk focuses on skyrmions in ultrathin ferromagnetic transition metal multilayers in which interfaces with heavy metals generate a strong Dzyaloshinskii-Moriya interaction (DMI) [3]. Inversion-asymmetric multilayer stacks such as [Pt/CoFeB/MgO]N have been shown to host room-temperature-stable skyrmions and skyrmion lattices, with sizes <50nm and current-driven velocities in excess of 100 m/s [4]. Here, we describe their current-driven creation and dynamics probed with x-ray microscopy, and their stability and materials-based design through an accurate fully-analytical model. Using time-resolved imaging, we demonstrate that in low-pinning CoFeB-based structures, current-induced shifting is repeatable over billions of cycles, and we reveal an analogue to the conventional Hall effect, in which the skyrmion trajectory depends on its topological charge much as a particle in a magnetic field is deflected due to its electric charge [5]. We then demonstrate deterministic current-induced skyrmion writing at sub-nanosecond timescales through the combined action of DMI and spin-orbit torque [6], and show that thermal excitation can drive morphological phase transitions between chiral phases in a controlled way [7]. Finally, we present an analytical framework [8] for computing the energy and structure of any skyrmion in any material, and apply the resulting design principles to experimentally realize room-temperature stable skyrmions with sizes approaching 10nm [9].


10:45 AM EP02.05.05

**Controlling the Dynamical Properties of Single Skyrmions in Magnetic Multilayers by Spin-Orbit Torques** Jan-Philipp Hanke1,2, Frank Freimuth2, Bertrand Dupé3, Stefan Bluegel4 and Yuriy Mozgousov2,4; *1 Institute of Physics, Johannes Gutenberg University Mainz, Mainz, Germany; 2Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich, Jülich, Germany.

Originating from the interplay of spin-orbit coupling and broken spatial inversion symmetry, the antisymmetric exchange interaction, also known as Dzyaloshinskii-Moriya interaction (DMI), attracts ever-growing attention as it mediates the formation of fascinating chiral spin textures that are perceived to be of great technological relevance, e.g., for future memory devices. Recently, the interfacial DMI was shown to be tunable in magnetic heterostructures of Co sandwiched between different heavy transition metals such as Pt and Ir, heralding bright prospects for the observation of small magnetic skyrmions at room temperature [1,2]. In this context, the phenomenon of current-induced spin-orbit torques (SOTs) can be envisaged to provide a particularly efficient means for controlling and manipulating the dynamical properties of such chiral nano-scale objects. Remarkably, electrically driven switching of the
magnetization due to SOTs in inversion-asymmetric crystals has been demonstrated in single ferromagnetic layers [3] and even in antiferromagnets [4].

Here, we apply a recently developed advanced Wannier interpolation for the Berry phase expressions of DMI and SOTs [5,6] to correlate the microscopic origin of these phenomena with the ab-initio electronic structure of the considered magnetic trilayers Ir(8 nm)/Co/Pt and Au(1 nm)/Co/Pt. Strikingly, we find that the DMI changes sign if we tune the chemical composition ratio in these heterostructures, which promotes the corresponding systems as promising candidates for detailed experimental studies of the antisymmetric exchange interaction. While the DMI is nearly isotropic with respect to the orientation of the ferromagnetic Co moments, the current-induced antidamping torques in clean Ir/Co/Pt reveal a particularly pronounced dependence on the magnetization direction according to our density functional theory calculations. Finally, we elucidate how the obtained anisotropy of fieldlike and antidamping SOTs imprints on the general control and manipulation of the dynamical properties of chiral nano-scale spin textures in Co-based trilayers, including in particular magnetic skyrmions and anti-skyrmions. Our ab-initio results pave the way towards a universal design principle for the skyrmion motion in magnetic multilayers.

This work was supported by the DARPA TEE program through grant MIPR# HR001831554 from DOI.


11:00 AM *EP02.05.06 Micromagnetic Simulations of Skyrmion Dynamics at Nonzero Temperature Jonathan Leliaert, DyNaMat Group, Ghent University, Gent, Belgium.

The dynamics of magnetic skyrmions at nonzero temperatures is governed by the complex interplay between driving forces, thermal fluctuations and material disorder. This interplay leads to rich behavior, e.g. creep, which needs to be fully understood before skyrmions can be reliably used in technological applications like the racetrack memory[1]. Because skyrmions do not always behave as rigid objects, micromagnetic simulations are indispensable to bridge theoretical models and experimental results. To this end, we developed an algorithm offering a twentyfold speedup without a loss of accuracy to perform simulations at nonzero temperatures [2], thus mitigating the problem that large numerical studies were practically infeasible due to the extremely small time steps required. First, a validation of this methodology is shown against theoretical results for skyrmion diffusion [3]. Next, we present a large scale study of the impact of temperature and disorder on the skyrmion motion and compare the results against experimental data of the velocity and skyrmion Hall angle as function of the driving force[4]. [1] A. Fert, et. al, Nat. Nanotech. 8, 152156 (2015) [2] J.Leliaert, et al., AIP Adv. 7, 125010 (2017) [3] J. Millat, et al., Phys. Rev. B 97, 214426 (2018) [4] K. Litzius, et al., (under review)

11:30 AM *EP02.05.07 Skyrmion Clustering, Creep and Depinning Charles Reichhardt: Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

We examine skyrmion depinning and sliding dynamics in systems with random and periodic pinning arrays. For finite temperature, we find a skyrmion creep regime where the motion is dominated by thermal jumps or avalanches. In this regime the average skyrmion velocity is finite but the skyrmion Hall angle is zero. At higher drives the skyrmion motion becomes continuous and the skyrmion Hall angle increases from zero to its intrinsic value. In general we find that the skyrmion Hall angle increases with increasing temperature at a fixed drive. We also find that for strong pinning, the moving phases are unstable against the formation of a clustered or segregated state where skyrmions attract one another due to the Magnus force. These results are in agreement with recent continuum based simulations which also show clustering of moving skyrmions when the quenched disorder is strong.

SESSION EP02.06: Emerging Topics in Magnetic Skyrmions
Session Chairs: Shinichiro Seki and Oleg Tretiakov
Friday Afternoon, November 30, 2018
Hynes, Level 2, Room 204

1:30 PM *EP02.06.01 Electric Excitation of Topological Defects in Mott Insulators Maxim Mostovoy: Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Topological nature of magnetic skyrmions recently observed in chiral magnets is a source of rich and interesting physics. Effective electromagnetic fields acting on electrons and magnons propagating through non-coplanar spin configurations result in unconventional spin, charge and heat transport. Skyrmion dynamics in magnetic conductors under applied electric currents can be used in new magnetic memory and data processing devices.

Mott insulators with competing Heisenberg exchange interactions form a new class of materials where topological magnetic defects, such as skyrmions, can exist in absence of inversion symmetry breaking [1-4]. Skyrmions in centrosymmetric materials have more degrees of freedom and show more complex dynamics than skyrmions in chiral magnets. In addition, the electric polarization induced by non-collinear spin textures couples topological magnetic defects to an applied electric field [5]. The magneto-electric coupling allows for an electric control of skyrmions in Mott insulators accompanied by low energy losses. In my talk I will discuss stability, dynamics and ferroelectric properties of skyrmions and merons in frustrated magnets. I will also discuss materials that can host these topological defects.

References:
Twisted Domain Walls in Perpendicularly Magnetized Multilayers

Ivan Lemesh and Geoffrey Beach; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Multilayer films with perpendicular magnetic anisotropy (PMA) are highly active media in modern magnetic technologies and research. Domain walls in such materials are usually treated either in 2D, similarly to homogeneous magnetic layers (via the so-called effective medium model, in which all the magnetic constants are effectively scaled), or as in multilayers, but with a trivial assumption of a fixed domain wall width Δ and angle ψ across the layers. However, recently it has been argued that the actual equilibrium configuration of the domain walls in multilayers is rather different. Both Δ and ψ, as revealed from the explicit multilayer simulations in these studies, vary from layer-to-layer, with the Néel-like caps of opposite chirality developing at the bottom and the top layers.

In this work, we rigorously prove that such a twist is indeed a ground state in PMA multilayers and find that it persists even for films with high Dzyaloshinsky-Moriya Interaction (DMI). The key aspect of our work is that it — for the first time — provides an accurate and complete calculation of the magnetostatic energy in multilayers, including the contributions that were inherently ignored in the well-known effective medium model.

By solving the exact magnetostatic integrals, we evaluate the total micromagnetic energy density of the domain walls in multilayers analytically and derive the equilibrium Δ and ψ in every magnetic layer. We find that the value DMI at which all the layers become Néel (threshold DMI) is underestimated by the earlier 2D model and provide the exact numerical relations for the new 3D model that contains the wall twist. We analyze the exact influence of this twist on the size of the domains and skyrmions and detect notable differences from the expressions provided by the 2D model. We also find that the extraction of DMI from the domain width measurements is highly inaccurate in the region of small and intermediate values of DMI, where the wall twist usually persists.

Finally, we identify the impact of the domain wall twist on the dynamics of skyrmions in multilayers under the influence of injected currents carrying the spin-orbit torque. We show that the skyrmion velocity and skyrmion hall angle derived from the exact multilayer theory can vary significantly compared with the predictions of the 2D model. We provide the numerical multilayer relations that are valid at low and intermediate values of current density (j). We also explore the high-j regime with the help of multilayer micromagnetic simulations and reveal new physical phenomena, such as the domain wall precession that result in the impeded skyrmion motion.

Our findings are confirmed with explicit multilayer micromagnetic simulations. The corresponding paper is under the preparation to be submitted to Physical Review Letters journal.

X-Ray Spectroscopy of Non-Trivial Spin Textures and Their Ultrafast Dynamics

Peter Fischer1, 2; 1Lawrence Berkeley National Lab, Berkeley, California, United States; 2Physics Department, University of California, Santa Cruz, Santa Cruz, California, United States.

Spin textures and their dynamics hold the key to understand and control the properties, behavior and functionalities of novel magnetic materials, which can impact the speed, size and energy efficiency of spin driven technologies. Advanced characterization tools that provide magnetic sensitivity to spin textures at high spatial resolution, ultimately at buried interfaces and in all three dimensions, and at high temporal resolution to capture the spin dynamics across scales, are therefore of large scientific interest.

Magnetic soft X-ray spectro-microscopies [1] provide unique characterization opportunities to study the statics and dynamics of spin textures [2,3] in magnetic materials combining X-ray magnetic circular dichroism (XMCD) as element specific, quantifiable magnetic contrast mechanism with spatial and temporal resolutions down to fundamental magnetic length and time scales.

Current developments of x-ray sources aim to increase dramatically the coherence of x-rays opening the path to new techniques, such as ptychography [4] or x-ray interferometry that will allow unprecedented studies of nanoscale heterogeneity, complexity, and fluctuations.

We will report a recent study of topological spin textures [5] that were imprinted from the vortex state in a 30nm thin permalloy (Py) nanodisk with diameters from 250-1000nm into a multilayer Ir/Co/Pt film with strong DMI. Using element-specific magnetic soft x-ray microscopy we were able to image the magnetic structure of the Py nanomagnets and the spin texture in the DMI film independently. We found a significant increase of the imprinted domain period (240nm) in the DMI film compared to the free film (80nm). Depending on the size of the nanodisks, we observed a change of the skyrmion diameter, and we found evidence for target Neel skyrmions due to an asymmetric expansion of the domain walls as a function of applied magnetic fields. Further, we will show results from a study at LCLS using x-ray photo correlation spectroscopy (XPCS) with a novel 2-pulse scheme that allowed us to discover an unexpected and drastic change of the correlation times in nanoscale spin fluctuations near phase boundaries, i.e., in the skyrmion phase, and near the boundary with the stripe phase of a multilayered Gd/Fe system [6].

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division Contract No. DE-AC02-05-CH1123 in the Non-Equilibrium Magnetic Materials Program (MSMAG).

References:
Its basic functioning does not require any knowledge of the reservoir topology or node weights for training purposes and can therefore utilize naturally existing networks formed by a wide variety of physical processes.

In this talk we will discuss how a random skyrmion “fabric” composed of skyrmion clusters embedded in a magnetic substrate can be effectively employed to implement a functional reservoir. This is achieved by leveraging the nonlinear resistive response of the individual skyrmions arising from their current dependent anisotropic magneto-resistance effect (AMR). Complex time-varying current signals injected via contacts into the magnetic substrate are shown to be modulated nonlinearly by the fabric’s AMR due to the current distribution following paths of least resistance as it traverses the geometry. By tracking resistances across multiple input and output contacts, we show how the instantaneous current distribution effectively carries temporally correlated information about the injected signal. This in turn allows us to numerically demonstrate simple pattern recognition. We argue that the fundamental ingredients for such a device to work are threefold: i) Concurrent probing of the magnetic state; ii) stable ground state when forcings are removed; iii) nonlinear response to input forcing. Whereas we demonstrate this by employing skyrmion fabrics, the basic ingredients should be general enough to spur the interest of the greater magnetism and magnetic materials community to explore novel reservoir computing systems.

3:45 PM DISCUSSION TIME

4:00 PM EP02.06.06
Non von Neumann Computing with Skyrmion Diode and Skyrmion Transistor
Linjie Liu, Weijin Chen, Ye Ji and Yue Zheng; State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, China.

Magnetic skyrmions are a class of topological defects with non-coplanar swirling spin structure. Recently, they attracted intensive attention for their non-trivial physical properties and potentials in high-density memory and new type spintronic devices. Importantly, latest studies indicate that devices based on skyrmions are particular suitable for so-called Non von Neumann devices, which combine the processing and memory units and avoid large communication cost between them. However, there are few concepts about new types of skyrmion devices until now. This work demonstrates new types of skyrmion devices, which are termed as skyrmion diode and skyrmion transistor. These devices are based on the interaction between terrace-like structures and skyrmions. Micromagnetic simulation indicates that terrace-like structures can effectively modulate the velocity of skyrmions (in both the directions and the speed), due to the potential energy changes of skyrmions. Further investigation shows that output characteristics of skyrmion diodes are tunable by changing the geometry. Moreover, as a type of basic devices, skyrmion diodes can be coupled with each other to form a new devices with more complex functions. Based on these ideas, we design a skyrmion transistor by coupling two skyrmion diodes. In the transistor, transport characteristics of skyrmions can be controlled by other skyrmions on the gate line. Our study for the first time proposes the concept about skyrmion diodes and their important implication on the design of complex skyrmion devices.

4:15 PM EP02.06.07
Controlling the Configuration of Magnetic Skyrmions Visualized by Full-Field Soft X-Ray Microscopy
Mi-Young Im1, Soong-Geun Je1, Jung-Il Hong1 and Anjan Soumyanarayanan3; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2DGIST, Daegu, Korea (the Republic of); 3Data Storage Institute, Singapore, Singapore.

Magnetic skyrmion is a spin structure stabilized by Dzyaloshinskii–Moriya interactions and/or dipolar interactions. Magnetic skyrmions have attracted enormous interests not only because of their fascinating topological character but also due to their potentials in a wealth of technological applications such as high efficient storage and computational devices. In the past couple of years, generating skyrmions at room temperature and realizing their movements have been main research directions and soft X-ray microscopy has been a vital role in such researches [1,2]. Another critical issue in the study of skyrmions has been to tune the topological properties of skyrmions and skyrmion configurations. In our works, we experimentally addressed the issue by direct observation of skyrmions and skyrmion configurations in Pt/Co/Fe/Ir and Pt/Co/Pt multilayered heterostructures utilizing a soft X-ray transmission microscope at Advanced Light Source (XM-1, BL6.1.2), enabling the direct observation of in-plane and out-of-plane magnetic components with a high spatial resolution down to 25 nm. We demonstrated that the properties of skyrmions such as size and density of skyrmions could be controlled by varying Co and Fe thicknesses in Pt/Co/Fe/Ir [3]. Through the work, a platform for investigating functional room temperature skyrmions for the development of skyrmion-based memory devices was established. In Pt/Co/Pt systems, the controllability of skyrmion configurations was investigated. We observed that skyrmion configuration significantly changes by injecting current pulses. Skyrmions could be either created or annihilated by the injected current pulse depending on the strength of applied magnetic field [4]. Our results suggest that the Joule heating plays a critical role in the formation and/or elimination of the bubbles and skyrmions. In the work, the schematic phase diagram for the creation and annihilation of bubbles is presented, suggesting an optimized scheme with the combination of magnetic field and electric current necessary to utilize skyrmions in the practical devices.

This work was supported by Leading Foreign Research Institute Recruitment Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (MEST) (2012K1A4A3053565) and by the DGIST R&D programme of the Ministry of Science, ICT and future Planning (18-IT-02). Work at the ALS was supported by the U.S. Department of Energy (DE-AC02-05CH11231).

References:

4:30 PM EP02.06.08
Chiral Domain Walls and Skyrmions in Co/Pd Exchange Coupled Multilayers—Statics and Dynamics
Shawn D. Polland1, Joseph Garlow2, Marco Beleggia3, Kaining Cai1, Yiming Zhu1,4, and Hyunsoo Yang1; 1Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore; 2Materials Science and Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; 3Center for Electron Nanoscopy, Technical University of Denmark, Kgs Lyngby, Denmark; 4Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York, United States.

Magnetic skyrmions in multilayer geometries have gained significant attention in recent years, as they provide the opportunity to simultaneously tune demagnetization, anisotropy, exchange, and interfacial Dzyaloshinskii-Moriya interaction (DMI) energies by varying layer thicknesses and compositions. We demonstrate the presence of zero field, room temperature Néel skyrmions in Co/Pd multilayers using Lorentz transmission electron microscopy (L-TEM), investigate their nucleation and annihilation processes [1]. We show this to be a consequence of the strong DMI associated with the Co/Pd multilayer geometry, confirmed with MOKE microscopy imaging of asymmetric bubble expansion. This structure differs from conventional multilayer geometries as, traditionally, a multilayer stack is composed of three different materials, HM1/FM/HM2, where HM1 and HM2 are heavy metals with...
varying signs of DMI, to prevent cancelation from top and bottom interfaces. Further, due to orbital hybridization of Pd with Co, the entire layer is exchange coupled. Using micromagnetic simulations, we show that this has important consequences in the domain wall structure and can play a role in the dynamics of magnetic skyrmions in magnetic multilayers.

We further extend previous studies using L-TEM to quantify the thickness-averaged domain wall deviation from pure Bloch or Néel states, which originates from the completion between demagnetization and DMI energies. This technique complements measurements such as X-ray resonant magnetic scattering [2] by providing nanoscale maps of the local domain structure. Further, it is sensitive to the magnetization of the entire multilayer stack, allowing for full determination of the averaged structure, unlike various surface sensitive techniques (i.e. photoemission electron microscopy or SEMPA) [3,4]. Using L-TEM, we determine the nature of the domain wall as a function of Co thickness and repetition number. This technique is extendable to other multilayer systems and could allow for the determination of a full magnetic phase diagram of systems with strong interfacial DMI.

Excitation-Induced Transition to Indirect Band Gaps in Monolayer TMDCs

Daniel Erben, Alexander Steinhoff, Gunnar Schönhoff, Tim O. Wehling, Christopher Gries and Frank Jahnke; Institute for Theoretical Physics, University of Bremen, Bremen, Germany; Bremen Center for Computational Materials Science, Bremen, Germany; MAPEX Center for Materials and Processes, Bremen, Germany.

Monolayers of transition metal dichalcogenides (TMDCs) exhibit an exceptionally strong Coulomb interaction between charge carriers due to their two-dimensional nature and weak dielectrical screening. Modifying the interaction via changing the dielectric environment or exciting charge carriers offers a possibility to control the interactions and as a consequence also the macroscopic optical properties. More generally, due to their many-body interactions, excited charge carriers directly influence the electronic and optical properties of monolayer TMDCs. This includes scenarios of electrical and optical excitation as well as charge carrier doping. In this talk the strong many-particle renormalizations caused by the Coulomb interaction of the excited carriers will be investigated for MX$_2$ with M = (Mo, W) and X = (S, Se).

To study the properties of these four TMDCs we solve the semiconductor Bloch equations on the full Brillouin zone using ab initio methods. To this end we construct the respective Hamiltonians for all the considered materials. To account for the electronic and optical properties of these materials, we perform computations over the full Brillouin zone, taking explicitly into account the many-body effects. In addition, we study the influence of an external electric field and the modification of the dielectric environment.

The central finding of our investigation is a relative shift between the K- and the neighboring Σ-valley in the conduction band induced by the many-body effects. All four TMDCs show a tendency to become more indirect as the Σ-valley shifts to energetically lower values than K. While monolayer TMDCs are usually celebrated for offering direct band gaps, we predict a transition from a direct to an indirect band gap for MoS$_2$ and WS$_2$. This transition is tunable up to 90 meV by varying the trion-phonon coupling as a function of temperature, electric field and substrate orientation. Our work provides a platform to realize unprecedented selective tunability of the quasiparticles in 2D semiconductors, driven by many body effects.

In this work, we present characterization of MoS$_2$-WS$_2$ lateral heterostructures based on morphology, electrical properties, photovoltaic properties, and nanoscale optical microscopy. These characterizations were performed using a variety of techniques. In particular, we used atomic force microscopy (AFM) for imaging, Scanning Kelvin Imaging for mapping the surface potential, Raman microscopy to map the optical properties, and tip-enhanced Raman and PL microscopy to map the surface potential with high spatial resolution.

A unique collection of characterization techniques were used to map the surface potential and capacitance change dramatically in a reversible manner when the heterostructures are illuminated by a laser, highlighting their photovoltaic properties. Raman and photoluminescence (PL) maps were recorded with 532 nm excitation, which enabled collection of Raman and PL bands from both materials simultaneously with reasonable separation. In addition, the tip-enhanced Raman and PL maps were collected across the interface, with sub-diffraction limited spatial resolution. In summary, a unique collection of characterization techniques were used based on AFM-Raman instrumentation to study morphological, electrical, photovoltaic properties, and chemical composition of MoS$_2$-WS$_2$ lateral heterostructures.
There is an ever-increasing need for portable and wearable electronics, because of the societal demand for active, efficient, and integrated devices. With the emerging Internet of Things, these devices require wireless communication devices that are lightweight and portable. Therefore, new fabrication techniques are needed to develop these unobtrusive wireless communication devices. Antennas for these novel devices are required to be conformal and compact, but retain good radio-frequency conductivity which is an essential property of antenna materials. Recently, nanomaterials such as graphene, carbon nanotubes, carbon onions and conductive polymers have come into play, but low conductivity is a limitation for their use. However, discovered in 2011, 2D titanium carbide MXene eliminates the problem of conductivity due to its metallic behavior. The conductivity of MXene Ti3C2 film reaches 10000 S/cm which makes it a promising candidate for portable wireless communication devices. Here we show a class of radio-frequency devices for wireless communication based on two-dimensional titanium carbide MXene prepared by a single step spray coating. We fabricated a transparent MXene antenna with less than 100 nm thickness with less than -10 dB reflection coefficient at a resonant frequency of 2.4 GHz. By increasing the antenna thickness to 8 μm, we achieved -70 dB of reflection coefficient. Additionally, we fabricated a 1-μm-thick MXene RFID tag in the 875 MHz band reaching a read range of 8 meters. Our findings show that two-dimensional MXenes operate below the skin depth of copper or other metals as well as give an opportunity to produce transparent antennas. Being the most conductive among the solution processed two-dimensional materials, as well as water dispersible, MXenes open new avenues for manufacturing various classes of radio-frequency devices. Using MXene as a conductor will thus be essential for the development of novel portable, flexible, and wearable electronic devices.

1. X. Huang et al., Graphene radio frequency and microwave passive components for low cost wearable electronics. 2D Mater., 3, 025021 (2016)
2. I. Puchades et al., Carbon Nanotube Thin-Film Antennas. ACS Appl. Mater. Interfaces, 8, 20986-92 (2016)
propylene carbonate upon sonication, producing thin flakes observable by transmission electron microscopy. The flakes with lateral sizes of 0.5-3 µm showed clear electron diffraction patterns which matched structurally to [Sr2N]+•e−, confirmed also by X-ray diffraction. From these results, we can conclude that the structure of [Sr2N]+•e− is retained after exfoliation.

In addition to comparing structural characteristics, it is also important to observe changes in the electronic properties. UV-Vis-NIR spectroscopy was performed on the exfoliated [Sr2N]+•e− sample to visualize band transitions occurring within the material. A Drude-Lorentz response typical of metals was observed with two peaks at 375 nm and 625 nm and a linear tail in the infrared region, which was attributed to reflection by the electron gas. The band structure confirms the metallicity of [Sr2N]+•e− since the electron gas band crosses the Fermi level, and the two peaks observed in the spectrum correlate to peaks in the joint density of states, which is an integration of the band transitions near the Fermi level. From these results, we can conclude that the electronic properties of [Sr2N]+•e− are also retained in the electrene form. Given the low workfunction for bulk [Sr2N]+•e−, the 2D form of this layered electride could act as a strong electron donor to other two-dimensional materials, defining a new kind of heterostructure not demonstrated previously.

Future work for electrene [Sr2N]+•e− will involve further quantifying the electron donation ability of this new 2D material.

10:30 AM EP03.01.09
Locally Controlled Cu-Ion Transport in Layered CuInP2S6
Sabine M. Neumayer1, Nina Balke1, John Brehm2, Michael A. Susner1, Brian J. Rodriguez3, Stephen Jesse1, Sergey V. Kalinin1, Sokrates Pantelides4, Michael McGuire1 and Petro Makysmovych1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Vanderbilt University, Nashville, Tennessee, United States; 3University College Dublin, Dublin, Ireland.

Van-der-Waals crystals of metal thiophosphates can be seen as derivatives of transition metal dichalcogenides where 1/3 of metal atoms is replaced with diphosphorous, thereby stabilizing the remaining 2/3 of metal ions in low oxidation states. As a result, thiophosphates develop a panoply of desired properties, such as magnetic, dipolar and correlated electron orderings, all of which are rare or non-existent in the dichalcogenide family. Thiophosphates therefore enable ultrathin magnetic, ferroelectric and Mott insulating materials, while also presenting new opportunities for multifunctional interfaces with electronic 2d materials. We recently established giant out-of-plane piezoelectric coefficients, ferroelectric switching, and dielectric tunability in copper indium thiophosphate (CuInP2S6) [1]. Here, we reveal that CIPS additionally exhibits ionic conductivity that enables localized extraction of Cu ions from the lattice above the Curie temperature upon application of electric fields via a conductive scanning-probe-microscopy tip. Surprisingly, the extraction is fully reversible, dependent on the polarity of the applied electric field. Cu crystalites of up to 90 nm in height can be formed and erased on the surface utilizing ion transport in a process that can be precisely controlled by the amplitude of the applied voltage, frequency, temperature, and position of the tip. The underlying resilience of CIPS to large-scale ionic displacements and Cu vacancies is further corroborated by density-functional-theory calculations. At room temperature, newly created vacancy-rich areas exhibit even higher electromechanical response than pristine CIPS areas, making it possible to tailor piezoelectric properties through ion transport. The tunable surface deformation provides interesting opportunities for applications as sensors and actuators, and control of van-der-Waals heterostructures.

Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. The experimental work was supported by the Division of Materials Sciences and Engineering, Basic Energy Sciences, Department of Energy.


10:45 AM EP03.01.10
Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging
Michael A. Susner1, Michael McGuire1 and Petro Makysmovych1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Air Force Research Laboratory, Dayton, Ohio, United States.

Recently, the family of van-der-Waals layered transition metal thiophosphates – exhibiting ferroelectric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown. Here we present the first atomically resolved imaging of CuInP2S6 – carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Se2− within the layer, which forces the surrounding displacing Cu+ ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of electronic imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with CuInP2S6 – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. More generally, non contact atomic force microscopy promises to resolve structural and defect properties of 2D materials particularly those with large band-gaps or isolated from electrical contacts. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.


11:00 AM EP03.01.11
Electric Field Effects on Few-Layer WS2/S6O: Investigated by Scanning Nonlinear Dielectric Microscopy
Kohei Yamase, Toshiaki Kato, Toshihiro Kaneko and Yasuo Choy; Tohoku University, Sendai, Japan.

Ultrathin transition metal dichalcogenides (TMDs) have recently been under intense research towards their electronic device applications. Some of TMDs such as MoS2 and WSe2 have band-gaps and retain semiconductor properties even if they are atomically thin. The application of TMDs to field-effect transistors (FETs) needs understanding how carrier type and carrier concentration are controlled with electric field effects in a nanoscale. Therefore, a tool for the nano-scale investigation of the electric field effects is important for boosting the studies in this field. Scanning nonlinear dielectric microscopy (SNDM) [1] is a scanning probe microscopy method, which can determine dominant carrier types and give information on carrier concentration...
out-of-plane polarizability of excitons and trions in monolayer WSe₂

Excitons in monolayer semiconductors such as MoS₂ are strongly confined in the plane layer with minimal freedom to orient themselves in the out-of-plane direction. Recent gated spectroscopy measurements have suggested that this may not be the case. However, there is a large discrepancy in the experimental and theoretical polarizability values. Here we investigate the out-of-plane polarizability of excitons in monolayer WSe₂ up to large electric fields of ~1.5 V/μm using double-gate photoluminescence spectroscopy and electroabsorption spectroscopy. The double gate configuration allows us to independently control the doping level and the vertical electric field while avoiding unintentional laser-induced photo-doping effects. We find that the photo-doping density increases linearly with vertical electric fields due to interfacial charge traps even when the sample is encapsulated in hexagonal boron nitride (hBN) crystals. We show that neutral excitons exhibit negligible Stark shift contrary to the earlier experimental observations. On the other hand, charged exciton energy was found to exhibit small but linear Stark shift suggesting the presence of permanent dipole moment.

Dynamics and Spin-Valley Locking Effects in Monolayer Transition Metal Dichalcogenides

Monolayer transition metal dichalcogenides have been the primary materials of interest in the field of valleytronics for their potential in information storage, yet the limiting factor has been achieving long valley coherence times. We explore the dynamics of four monolayer TMDCs (MoS₂, MoSe₂, WS₂, WSe₂) by describing electron-electron and electron-phonon interactions from first principles. We isolate the crucial impact of spin-orbit coupling on the valence band edge by over an order of magnitude, with a corresponding rise in hole mobility. This drastic change is attributed to spin-valley coupling. At temperatures of 50 K, we find valley coherence times on the order of 100 ps, with a maximum value of ~140 ps in WSe₂. Our results capture the entangled relationship between spin and valley degrees of freedom, which is critical for valleytronic applications. Further, our work points towards interesting quantum properties on-demand in transition metal dichalcogenides that could be leveraged via driving spin, valley and phonon degrees of freedom.

11:30 AM EP03.01.13
Dynamics and Spin-Valley Locking Effects in Monolayer Transition Metal Dichalcogenides
Chris Ciccarino1,2, Thomas Christensen1, Ravishankar Sundaraman1 and Prineha Narang1; 1John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 2Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; 3Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Monolayer transition metal dichalcogenides have been the primary materials of interest in the field of valleytronics for their potential in information storage, yet the limiting factor has been achieving long valley coherence times. We explore the dynamics of four monolayer TMDCs (MoS₂, MoSe₂, WS₂, WSe₂) by describing electron-electron and electron-phonon interactions from first principles. We isolate the crucial impact of spin-orbit coupling on the valence band edge by over an order of magnitude, with a corresponding rise in hole mobility. This drastic change is attributed to spin-valley coupling. At temperatures of 50 K, we find valley coherence times on the order of 100 ps, with a maximum value of ~140 ps in WSe₂. Our results capture the entangled relationship between spin and valley degrees of freedom, which is critical for valleytronic applications. Further, our work points towards interesting quantum properties on-demand in transition metal dichalcogenides that could be leveraged via driving spin, valley and phonon degrees of freedom.

1:30 PM EP03.02.01
Layer Resolved Splitting for Atomic Precision-Control of 2D Materials
Sanghoon Bae1, Jaewoo Shim1, Wei Kong1, Kuan Qiao1, Doyoon Lee1, Ruike Zhao1, Suresh Sundaram2, Xin Li3, Jagadeesh S. Moodera1, Xuanhe Zhao1, Chris Hinkle3, Abdallah Ougazzaden2 and Jeewhan Kim1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Georgia Institute of Technology, Metz, France; 3The University of Texas at Dallas, Dallas, Texas, United States.

Heterostructures formed by weak van der Waals interactions between 2D materials have revealed novel physics and device functionalities. However, it is challenging to precisely control the number of layers at wafer scale. The tape mechanical exfoliation method has been used as main method to obtain few monolayer 2D flakes from various bulk crystals, which allows stacking of multiple 2D materials. The method relies on trial-and-error based operation, which lead substantial time-consuming. In addition, the typical size of stacked heterostructures is only limited to hundreds of microns. An effort to avoid these issues focuses on direct growth of 2D materials on wafers. However, it has been noted that controlling nucleation of 2D layers via growth is even more challenging because of easy-additional nuclei formation on top of the initial nuclei. Accordingly, it has been required to develop alternative way. Here we report a layer-resolved splitting (LRS) for 2D materials that permits precise control of the number of layer of 2D materials. It produces multiple monolayers of wafer-scale 2D materials from one multilayer 2D material growth. We grow thick 2D materials, such as WS₂, hBN, WSe₂, and MoSe₂, and precisely split them into multiple monolayers. We study the underlying mechanics of LRS for the 2D material multilayers into many individual monolayers. The wafer-scale monolayer of transition metal dichalcogenides after LRS exhibits substantial photoluminescence enhancement uniformly across a 2-inch wafer which relates to indirect-to-direct band gap transition. Through this LRS approach, we successfully demonstrate van der
Waals heterostructures with single-atom resolution. We strongly believe LRS will open up new venue for 2D material research community.

1:45 PM EP03.02.02
Near-Field Coupled Two-Dimensional InSe Photodetector on Optical Fiber Zehua Jin, Fan Ye, Xiang Zhang, Shuai Jia, Liangliang Dong, Sidong Lei, Robert Vajtai, Jacob T. Robinson, Jun Lou and P. M. Ajayan; Rice University, Houston, Texas, United States.

Two-dimensional (2D) van der Waals layered materials possess unique advantages as integrable sensors, due to their thinness, flexibility and sensitivity. They can be seamlessly integrated onto surfaces with different geometries where detection of near-field signal is desired. In this study, we develop a device transfer technique to integrate 2D devices onto an arbitrary smooth surface. Such technique utilizes a sacrificial polymer under layer and achieves clean and non-destructive full device transfer. For demonstration, we transferred a complete 2D multilayer InSe photodetector onto a stripped optical fiber. Due to the extreme vicinity of the 2D photodetector with the fiber core, the device can efficiently couple with the evanescent-field and accurately detect information transmitted inside the optical fiber. In addition, these super thin flexible devices can be integrated onto the fibers themselves to non-invasively monitor the optical fiber performance. The demonstration of optically coupled, conformal 2D devices on substrates of different form factors can enable a variety of near-field optical and sensor applications.

2:00 PM EP03.02.03
Electrical and Magnetic Doping of Transition Metal Diselenides Layers Grown by van der Waals Epitaxy Matthieu Jamet, Céline Vergnaud, Minh-Tuan Dau, Alain Marty, Cyrille Beigne, Carlos J. Álvarez, Hanako Okuno, Maxime Gay, Olivier Renault, Gilles Renaud and Jean-François Jacquot; CEA Grenoble, Grenoble, France.

Top-down exfoliation from bulk transition metal dichalcogenides like MoS₂ usually leads to micron-sized flakes. We have recently developed an alternative growth method of two-dimensional transition metal diselenides (TMDs) from multilayers down to a single layer based on the Van der Waals (VdW) epitaxy. In the VdW epitaxy, the TMD is grown either on a passivated surface with a very low density of dangling bonds (it is then called quasi-VdW epitaxy) or on a layered VdW substrate. The basic concept of this growth method relies on the very weak interaction between the epilayer and the substrate in order to largely release the constraint of lattice matching. Therefore it leads to the formation of fully relaxed TMDs layers. Moreover, this technique allows for the growth of uniform layers over centimeter scale surfaces making it compatible with the development of a large scale 2D electronics substrate in order to largely release the constraint of lattice matching. Therefore it leads to the formation of fully relaxed TMDs layers. Moreover, this technique allows for the growth of uniform layers over centimeter scale surfaces making it compatible with the development of a large scale 2D electronics.

1:45 PM EP03.02.04
Alloying of Monolayer Transition-Metal Dichalcogenides—Role of Native Defects Hossein Taghinejad1, Ali A. Eftekhar1, P. M. Ajayan2, Evan J. Reed3 and Ali Adibi1; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Stanford, Palo Alto, California, United States; 3Rice University, Houston, Texas, United States.

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) are currently under widespread scrutiny for a diverse set of optoelectronic applications. At the monolayer limit, TMD crystals offer a direct optical bandgap, enabling the light emission within a large spectral range covering a large portion of the visible spectrum and the near infra-red regime. In this line, the synthesis of ternary alloys has served as a powerful technique for changing the optical/electrical bandgap of monolayer TMD crystals beyond what a binary compound (i.e., MX₂; M: transition metal and X: chalcogen) may offer. We have previously shown that “ternary” alloys can be produced via doping a “binary” MX₂ crystal by an isoelectronic element (e.g., X') to yield MoS₂X₂Sx₁. The approach has shown a great promise in the formation of ternary heterostructures with arbitrary shapes and dimensions [1, 2]. In this approach, the quality of the as-synthesized alloys depends on the fine details of the starting binary MX₂ crystal.

Here, we study the influence of native defects in starting MX₂ monolayers on the obtained properties of the MX₂X₃₋ₓSₓ alloys. For the demonstration purpose, we use monolayer MoSe₂ films as starting crystals in which replacing Se atoms by S atoms yields MoS₂SₓSe₂₋ₓ ternary compounds. Our results show that native point defects (primarily chalcogen vacancies) in the starting MoSe₂ lattice serve as atomic sites from which S atoms incorporate into the lattice of MoSe₂ and form the MoS₂Se2₋ₓ alloy. Thus, the abundance of the chalcogen vacancies in the starting MoSe₂ films promotes the alloying process and reduces the required temperature needed for this process. We believe that our findings shed light on the fundamental details of the alloying mechanism in 2D TMD crystals as well as opening a new avenue for synthesis of complex alloys via defect engineering.


2:15 PM EP03.02.05
Size-Dependent Properties of Solution Processed 2D Transition Metal Carbides (MXenes) Kathleen A. Malecký1, Chang Evelyn Ren1, Mengjiang Zhao1,2, Babak Anasori2 and Yury Gogotsi1; 1Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Two-dimensional (2D) transition metal carbides and/or carbonitrides (MXenes) have been developed as promising materials for a wide variety of applications due to their advantageous mechanical, electrochemical, electrical, and optical properties. MXenes exhibit a general formula of Mₓ₋ₓTx₀₋ₓ, where M represents a transition metal (Ti, Mo, Nb, V, Cr, etc.), X is either carbon and/or nitrogen, and Tₓ represents surface terminations. Along with the high electronic conductivities (8,000-10,000 S/cm), the materials are hydrophilic and can be synthesized in large quantities (~100 g per batch) and high concentrations (>50 mg/mL), making them fundamentally feasible for solution processing. However, the as-produced colloidal solutions contain flakes with widespread lateral sizes (ranging from 0.1 to ~5 µm), presenting a challenge for maintaining precise control over properties and performance.

Here, we will discuss recent progress on developing size selection methods to control and sort 2D MXene flake sizes after synthesis based on sonication and density gradient centrifugation, respectively. Furthermore, characterization of size-dependent properties will be discussed, including tuning the
conductivity of free-standing films, changes in optical absorption, and differences in electrochemical behaviors. This size selection methodology allows for control of a diverse family of materials, optimizing the performance in applications for MXenes beyond energy storage, including but not limited to, gas sensors, conductive inks, coatings, fibers, and electronic, optic and biomedical devices.

References

3:15 PM DISCUSSION TIME

EP03.02.07
Making the Colloidal 2D PbS Brighter

Liangfeng Sun1, Antara Antu2, Zhoufeng Jiang1, Shashini M. Premathilaka1, Yiteng Tang1, Jianjun Hu2 and Ajit Roy1; 1Bowling Green State University, Bowling Green, Ohio, United States; 2Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States.

Colloidal quasi-two-dimensional ( quasi-2D) nanoplatelets and nanosheets have attracted a broad interest due to the novel properties resulted from their anisotropic nanostructures. As an infrared material, quasi-2D PbS has its own unique properties due to its small energy gap, large exciton Bohr radius, and strong spin-orbit coupling. Since a larger nanosheet has more surface states, the photoluminescence quantum efficiency of nanosheets is low. To improve their optical properties, reducing the diameter of the nanosheets is one of the solutions since the number of surface trap states per sheet can be significantly reduced.

In our experiments, colloidal lead sulfide (PbS) nanoribbons are synthesized using organometallic precursors with chloroalkane co-solvents. The few-atom-thick nanoribbons have a typical width 20 nm and a length of more than 50 nm. In contrast to nanosheets, the nanoribbons are much brighter. At room temperatures, well-passivated nanoribbons have achieved a typical 30% photoluminescence quantum yield in the infrared spectrum. While the best one has reached 60% photoluminescence quantum yield, exceeding the well-developed colloidal lead chalcogenide quantum dots of the similar energy gap.

The highly bright nanoribbons are advantageous to explore the intrinsic novel properties of the PbS caused by the anisotropic confinement in the quasi-2D nanostructure including enhanced optical radiative recombination and slow Auger recombination as well as to find the applications in infrared photonic and optoelectronic devices.

References

3:45 PM DISCUSSION TIME

EP03.02.09
Low-Temperature Synthesis of Crystallized Molybdenum Disulfide Using Atomic Layer Deposition

Wonsik Ahn1, Taejin Park1,2, Hyangsook Lee1, Hoi Jo Kim1, Mirim Leem1 and Hyungsung Kim1; 1School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of); 2Department of Semiconductor and Display Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of); 3Semiconductor R&D Center, Samsung Electronics, Hwasong, Korea (the Republic of); 4Samsung Advanced Institute of Technology, Suwon, Korea (the Republic of).

To accelerate the commercialization of various innovative electronic and optical devices using molybdenum disulfide (MoS2), it is required to develop a large-scale deposition method of MoS2 with a high film quality and a low thermal budget. Among many deposition techniques, atomic layer deposition (ALD) is the most ideal approach due to its atomic-scale thickness controllability. Recently, several researchers have demonstrated initial feasibilities for the ALD of MoS2 using several Mo precursors, such as Mo(CO)6, Mo(NMe2)4, Mo(thd)3 and MoCl5 [1-6]. However, there are still many problems to be solved, such the requirement of high deposition temperature or high-temperature post-deposition annealing to improve film crystallinity. In addition, more in-depth understanding of the effects of various process parameters on the film growth and quality is required.

In this presentation, a few-layered MoS2 films were synthesized via ALD using MoCl5 and H2S precursors at temperatures less than 450 °C. Particularly, the effects of various process parameters, such as a substrate temperature, a MoCl5 canister temperature, and H2S flow rate on the MoS2 film characteristics were investigated. The nucleation density and final surface coverage of the MoS2 films were examined using scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. Raman and photoluminescence characteristics were also studied, and the electrical properties were evaluated by fabricating transistor devices.


4:00 PM EP03.02.10
Photo-Mediated Defect Passivation of MoS2 by Adsorption of Ambient Gas Molecules


Monolayers of transition metal dichalcogenides (TMD) are promising components for flexible optoelectronic devices due to their direct band gap and atomically thin nature. The photoluminescence (PL) from these materials is strongly dependent on mid-gap defects which serve as non-radiative recombination sites for excitons. Improving the PL is a key step towards realizing high efficiency optoelectronics such as solar cells and light emitting diodes. Here, we demonstrate up to a 200x increase in PL intensity by exposing MoS2 synthesized by chemical vapor deposition (CVD) to laser light in ambient. This spatially resolved passivation treatment is air and vacuum stable, which indicates strong bonding of moieties from ambient. Regions unexposed to laser light remain dark in fluorescence despite continuous impingement of ambient gas molecules. This suggests a large barrier towards adsorption and subsequent PL brightening. A wavelength dependent study confirms that the PL brightening is concomitant with excitation generation in the MoS2; laser light below the optical band gap of MoS2 fails to brighten the TMD. In contrast to previous laser modification studies that use mW's of laser
power, we highlight the photo-sensitive nature of the process by successfully brightening with a broadband white light source (< 10 mW). Cryogenic studies show that the treatment results in an increase of both the bound and neutral exciton intensities. Additionally, we measure higher absorption from the laser brightened MoS2 regions. We decouple changes in absorption from defect passivation by examining the degree of circularly polarized PL. This measurement, which is independent of excitation generation, confirms that the laser brightening reduces non-radiative recombination sites in the MoS2. We propose that isovalent O2 passivates sulfur vacancies in the CVD-grown MoS2 but requires photo-generated excitons to overcome the large adsorption barrier. This work represents an important step in understanding the passivation of CVD synthesized TMDs.

This research was performed while S.V.S and M.R.R held a National Research Council fellowship and H.-J.C. held an American Society for Engineering Education fellowship at NRL.

4:15 PM EP03.02.11

Ionic Solutions of Two-Dimensional Materials and Their Use as Reducing Agents Patrick L. Cullen; Department of Chemical Engineering, University College London, London, United Kingdom.

Exfoliating layered materials within liquids to create dispersions of nanosheets allows for a scalable method to both isolate and manipulate 2-dimensional materials. However, most methods for this so-called “liquid phase exfoliation” rely on aggressive chemical or physical processes to separate the layers, followed by ultracentrifugation to remove large aggregates, making the processes difficult to scale-up. Moreover, such routes typically result in metastable suspensions of fragmented, physically damaged, or chemically modified nanosheets. I will discuss recent work on the true, spontaneous dissolution of 2-dimensional materials from layered materials [1,2]. For the naturally uncharged layered materials, true dissolution into polar aprotic solvents is achieved by introducing charges onto the layers via intercalation of ions. This gentle process maintains the morphology of the starting material, is stable against reaggregation and can achieve solutions containing exclusively individualized, crystalline monolayers. The charge on the anionic nanosheets solutes is reversible, enables targeted deposition over large areas via electroplating and can initiate novel self-assembly upon drying. I will go on to present more recent work which takes advantage of the charge on the nanosheets for further processing. Specifically, a distribution of metal nanoparticles of optimal size and high uniformity has been achieved on 2-dimensional materials for the oxygen reduction reaction (ORR), resulting in a catalyst with remarkable stability.


4:30 PM EP03.02.12

Band Edge Tuning for Selective CO2 Reduction in MoS2-xSex Films Yi-Rung Liu1, 2, Wen-Hui Cheng1, Matthias H. Richter1, Joseph S. DuChene1, Cora Went1, Zakaria Al Balushi1, Deep M. Jarwala1, Li-Chyong Chen2 and Harry A. Atwater1; 1California Institute of Technology, Pasadena, California, United States; 2Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; 3Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Molybdenum disulfide (MoS2) and its related layered transition-metal dichalcogenides (TMDs) have attracted much attention as potential electrocatalysts for converting carbon dioxide to fuels due to their lower price compared with precious metals and their prominent catalytic features. MoS2 and MoSe2 have recently been shown to perform as excellent electrocatalysts in ionic-liquid-based systems for the CO2 reduction reaction (CO2RR)1,2. However, achieving selectivity in the CO2RR is challenging due to the numerous possible chemical reaction pathways and their very similar reduction potentials, often leading to a multitude of CO2RR products. Theoretical calculations3 indicate that the conduction band (CB) edge position of TMD materials can be tuned by adjusting the layer thickness (i.e. monolayer vs. bilayer), as well as by chemical alloying (e.g. MoSSe). The TMDs therefore offer a suitable material system for adjusting the CB edge of the catalyst relative to a given reduction potential for CO2RR. Herein, we report the thickness-controllable, large-area (~1 cm²) synthesis of MoS2-xSex thin-films for the CO2RR via metal–organic chemical vapor deposition (MOCVD) followed by a post-selenization process. The post-treatment enables the Se incorporation into the MoS2 films as well as tunability of the S/Se ratio in MoS2-xSex alloys. As a first step, we evaluated bulk crystals of MoS2, MoSSe, and MoSe2 for electrochemical CO2RR in aqueous K2CO3 solution (pH = 6.8) at -0.4 V vs. RHE. The results showed that both MoSSe and MoSe2 produce 4 times more CO and CH4 than MoS2. To further explore the effect of the CB edge position relative to the CO2RR, we examined the performance of thickness-controlled, MoS2-xSex electrodes incorporated on glassy carbon substrates for electrocatalysis. We found that the MoS2-xSex, (x=0.46) films own the highest faradaic efficiencies about 16.6%, which is much higher than MoS2 film. The CO2RR product analysis as a function of film composition will be discussed and compared to the relevant CO2RR reduction potentials.

SESSION EP03.03: Scalable Synthesis and Large Area Growth of 2D Materials II

Session Chairs: Feng Miao and Qing Hua Wang

8:00 AM EP03.03.01

Synthesis of Titanium Di- and Tri- Sulfides by Atomic Layer Deposition Saravanan Balai Basuvilangal, Marcel Verheijen, Wilhelmus (Erwin) Kessels and Aageh A. Bol; Eindhoven University of Technology, Eindhoven, Netherlands.

Recently, two-dimensional transition metal chalcogenides (TMC) such as MX2 and MX3 (M= Mo, W, Nb, Ti; X= S, Se, Te) have gained considerable attention due to their unique physical and chemical properties. Among these TMCs, titanium trisulfide (TiS3) has a unique semiconducting behaviour independent of its thickness with a direct band gap of ~1eV which could be ideal for future (opto) electronics applications4. On the other hand, titanium disulfide (TiS2) is a highly conductive semimetal which is suitable for energy storage5, photovoltaics6, and catalysis7 applications. Synthesising both TiS2 and TiS3 at low temperature in a controlled manner over a large area would be beneficial for the aforementioned applications. Atomic layer deposition (ALD) provides advantages such as precise thickness control, low temperature processing environment, uniformity over large area, and conformality over a 3D substrate. Therefore, ALD could be a valuable method to grow layered titanium sulfides for a wide range of applications compared to other deposition techniques.

In this work, TiS2 and TiS3 thin films were deposited by ALD using a metalorganic precursor and H2S at temperatures between 50 and 250°C. TiS2 growth was achieved by both thermal and plasma-enhanced atomic layer deposition (PE-ALD) processes, whereas TiS3 growth was only attained by PE-ALD
process where H2S plasma was used as the co-reactant. To the best of our knowledge, this is the first work to report on synthesising TiS2 by ALD. *In situ* spectroscopy ellipsometry was used to confirm the self-limiting ALD behaviour and also to measure the growth per cycle (GPC). For both TiS2 and TiS3 films, GPC between ~1.6 and 2.5 Å was achieved with both ALD processes in the studied temperature range. In case of PE-ALD process, TiS2 was only grown at lower temperature, whereas at higher temperature pyrolysis leads to formation of TiS3. The synthesis of both TiS2 and TiS3 was elucidated by Raman spectroscopy studies where vibrational modes identical to two-dimensional TiS2 and TiS3 structure were observed. X-ray photoelectron spectroscopy and Rutherford back scattering measurements indicated sulphur deficient TiS2 films, while for TiS3 excess sulphur content was detected. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed control over film morphology was achieved by varying the processing conditions. Four point probe measurements yielded low resistivity for TiS2 films in the order of $1 \times 10^{-4}$Ω-cm. To summarise, we show a novel low temperature process to synthesis both di- and tri- sulfides with precise thickness control over a large area.


8:15 AM EP03.03.02

Single-Step, Direct Silicon-Substrate Growth of Black Phosphorus with *In Situ* Sn Passivation

Nezhueyotl Izquierdo, Stephen Campbell and Sushil Kumar Pandey; University of Minnesota, Minneapolis, Minnesota, United States.

Over the past decade, the class of 2D materials has been mined for substances with unique properties to serve as the foundation for a potential post-silicon or silicon-plus era. The effects of scaling which demands a miniaturization of the device size in all three dimensions, has led research into single or few-layer thick materials. Black phosphorus (BP) is highly attractive since it contains a direct band gap ranging from 0.3 (bulk) to 1.7-2.0 eV (monolayer) allowing for the electrical properties of the material to be tailored to specific devices, such as optoelectronics and transistors, while retaining a high carrier mobility. Mono and few-layer films of BP are called phosphorene.

A synthesis method to grow large area phosphorene films under easily obtained conditions is required in order for commercialization. A reasonable first step would be the growth of black phosphorus thin films directly onto substrates. Here we present a single-step growth of black phosphorus thin film crystals directly on silicon using a self-contained short-way transport technique under relatively low-pressure conditions (<1.5 MPa). The synthesis proceeds with SnI4, Sn, and red phosphorus as the starting materials. The region of precursor concentrations and growth conditions required for thin film crystals are found to be substantially different from bulk crystal growth. Violet phosphorus has been suggested to be an important intermediate in the bulk growth process. We find that it is the preferred phosphorus phase at low SnI4 concentrations, while black phosphorus is the preferred phase at higher SnI4 concentrations. The effect of the starting molar ratio has been mapped to optimize direct growth of BP on silicon wafers. However, the successful direct growth of BP has also been achieved on silicon dioxide, silicon nitride, and sapphire wafers. The same phase forms on each substrate, however, silicon is found to produce slightly larger crystals. This may be due to the fact that the optimization was done on Si and suggests that substrate epitaxy is not a critical factor in growing BP thin films.

Raman spectroscopy of many of the BP deposits show no sign of degradation for A1g, B2g, and A2g phonon modes found at 360.5, 436.5, and 464 cm$^{-1}$, respectively. This is true up to several months of exposure to ambient conditions. Auger electron spectroscopy reveals an ultra-thin (~3 atoms) layer of Sn only grown at lower temperature, whereas at higher temperature pyrolysis leads to formation of TiS2. The synthesis of both TiS2 and TiS3 was elucidated by X-ray photoelectron spectroscopy and Rutherford back scattering measurements indicated sulphur deficient TiS2 films, while for TiS3 excess sulphur content was detected. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed control over film morphology was achieved by varying the processing conditions. Four point probe measurements yielded low resistivity for TiS2 films in the order of $1 \times 10^{-4}$Ω-cm. To summarise, we show a novel low temperature process to synthesis both di- and tri- sulfides with precise thickness control over a large area.


8:30 AM EP03.03.03

Chemically and Atomically Ordered states in 2D Crystal Alloys

Nasim Alem; Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Alloying and doping are considered versatile strategies for tuning charge and heat transport in nanostructures. Whether the resulting alloy structure is random or ordered can have a profound impact on the macroscale electronic, optoelectronic, vibrational, and transport properties of the material. In this talk, we present structural and chemical ordering as a mechanism to design anisotropy in the family of 2D transition metal dichalcogenides (TMDs) alloys. Leveraging recent advancements in atomic resolution scanning/transmission electron microscopy imaging and spectroscopy, we show the formation of chemically ordered states and vacancy/dopant coupling that leads to unusual relaxation effects around dopant-vacancy complexes leading to local strain and symmetry breaking around individual dopant sites. In addition, we will further uncover the defect structure, i.e. grain boundaries and anti-phase boundaries, and their stability and dynamics in monolayer TMD crystals and their alloys. This understanding can have a strong impact on the synthesis and functionality of novel nanostructure alloys and provides the key to properly design devices for heat dissipation applications, energy storage, electronics, optoelectronics, and thermoelectrics.

9:00 AM EP03.03.04

Building Atomically Thin Integrated Circuits

Jiwoong Park; University of Chicago, Chicago, Illinois, United States.

Manufacturing of paper, which started two thousand years ago, simplified all aspects of information technology: generation, processing, communication, delivery and storage. Similarly powerful changes have been seen in the past century through the development of integrated circuits based on silicon. In this talk, I will discuss how we can realize these integrated circuits thin and free-standing, just like paper, using two-dimensional materials and how they can impact the modern information technology.

In order to build these atomically thin circuits, we developed a series of chemistry-based approaches that are scalable and precise. They include wafer-scale synthesis of three atom thick semiconductors and heterojunctions (*Nature*, 2015; *Science* 2018), a wafer-scale patterning method for one-atom-thick lateral heterojunctions (*Nature*, 2012), and recently, atomically thin films and devices that are vertically stacked to form more complicated circuitry (*Nature*, 2017). Once realized, these atomically thin circuits will be foldable and actutable, which will further increase the device density and functionality. The fact that these circuits could be realized and function without any substrate will allow them to be used tether-free (or wirelessly) in environments not previously accessible to conventional circuits, such as water, air or in space.

9:30 AM BREAK

10:00 AM EP03.03.05
Epitaxial Growth and Properties of Transition Metal Dichalcogenide Monolayers, Alloys and Heterostructures by Gas Source CVD Joan M. Redwing, Xiaotian Zhang, Tanushree H. Choudhury and Mikhail Chubarov; The Pennsylvania State University, University Park, Pennsylvania, United States.

Monolayer transition metal dichalcogenides (TMDs, MoS2, WSe2, etc.) possess a range of intriguing optical and electronic properties including direct bandgap, large exciton binding energies, valley polarization, etc. Current research is typically carried out using flakes exfoliated from bulk crystals or monolayer domains grown by powder source chemical vapor deposition (CVD) which are challenging to scale to large area. Our research is aimed at the development of an epitaxial growth technology for layered dichalcogenides, similar to that which exists for III-V and other compound semiconductors, based on gas source CVD. This approach provides a high overpressure of chalcogen species needed to maintain stable growth at elevated temperature and excellent control of the precursor partial pressures to achieve monolayer growth over large area wafers.

Our initial studies focused on the epitaxial growth of binary TMD monolayers (MoS2, WS2, WSe2 and MoSe2) using metal hexacarbonyl and hydride chalcogen precursors on 2° sapphire substrates in a cold-wall CVD reactor. A multi-step precursor modulation growth method was developed to independently control nucleation density and the lateral growth rate of monolayer domains on the substrate. This approach also enables measurement of metal-species surface diffusivity and lateral growth rate as a function of growth conditions providing insight into the fundamental mechanisms of monolayer growth. Using this approach, uniform, coalesced monolayer and few-layer TMD films were obtained on 2° sapphire substrates at growth rates on the order of ~1 monolayer/hour. In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to the sapphire with narrow X-ray full-width-at-half-maximum indicating minimal rotational misorientation of domains within the basal plane. Post-growth transmission electron microscopy carried out on monolayers transferred from the sapphire demonstrates that the films consist of large single crystal regions with anti-phase grain boundaries that result from a merging of 0° and 180° oriented domains that form on sapphire. Growth of (Mo,W)S2 alloy mono- and few layers was also achieved over the entire composition range by controlling the inlet gas phase ratio of Mo and W hexacarbonyl precursors. Applications and challenges of this technique for the growth of vertical 2D heterostructures will also be discussed.

10:30 AM *EP03.03.06
Scalable Synthesis and Electrocatalytic Activities of 2D Sulfides and Tellurides Judy Cha1, 2, Yale Univ, New Haven, Connecticut, United States; 2Canadian Institute for Advanced Research, Toronto, Ontario, Canada.

The layer-dependent material properties and emergent electronic properties of van der Waals heterostructures make 2D materials attractive for a wide range of electronic and energy applications. However, the biggest hurdle for realizing these applications lies in the lack of scalable synthesis of 2D materials with precision control over crystallinity, doping, and other parameters that greatly influence their electrical properties. In this talk, I will discuss our efforts in scalable synthesis of sulfides, tellurides, and their heterostructures and the effects of strain on the crystalline quality and morphology of the synthesized thin films [1-4]. Based on these results, an alternative synthetic route is being explored for large-area synthesis. I will also discuss the electrocatalytic activities of MoS2 and WTe2 for hydrogen evolution reaction, paying particular attention to how electron injection and transport within the catalyst can be a rate limiting step [5], irrespective of thermodynamic energy considerations of hydrogen adsorption on the catalytic site. By performing the electrochemical hydrogen evolution reaction on nanodevices of isolated flakes and heterostructures, we showed that the presence of a Schottky barrier between a catalyst and an electrode can significantly inhibit the catalytic reactions. The nanodevice approach based on a single-crystalline flake enables us to measure interfacial effects accurately, which is challenging in complex nanostructured catalysts. Our finding is broadly applicable to other semiconducting catalysts or catalysts with low electrical conductivity.

11:00 AM *EP03.03.07
Liquid Exfoliation and Defect Engineering of Inorganic 2D Materials Claudia Backes; Applied Physical Chemistry, Heidelberg University, Heidelberg, Germany.

Liquid exfoliation has become an important production technique to give access to large quantities of two-dimensional nanosheets in colloidal dispersion.[1] Importantly, this is a highly versatile technique that can be applied to numerous layered materials beyond graphene such as transition metal dichalcogenides, III-VI semiconductors, black phosphorus, layered oxides to name just a few. These can be cast into films and composites and have proven useful in a number of application areas. Recent progress in size selection has enabled the production of high quality nanosheet dispersions with controlled thickness and lateral size.[2] This was made possible by spectroscopic size and thickness metrics that allow us to extract nanosheet lateral size, thickness and monolayer content from simple measurements such as extinction spectroscopy.[2,3,4] We now use this basic understanding to systematically compare a range of 2D materials with respect to exfoliation, size selection and size-dependent properties to identify unifying principles. In all cases, we investigate chemical degradation/oxidation via the characteristic optical fingerprints. In addition, we explore different ways for further functionalisation of TMD nanosheets by various methods. This includes noncovalent approaches, where we can track the functionalization in optical spectra due to the dielectric screening of the excitonic transitions. We also elaborated ways to chemically modify the basal plane [5,6] or edge sites [7] of TMDs. For example, we demonstrate that chemical functionalisation of vacancy defect sites can be used to protect otherwise instable materials from degradation while edge defects such as thiols can be converted to disulfides in redox reactions. These findings present an important step towards defect engineering in 2D materials.

11:30 AM EP03.03.08
Controllable Wafer-Scale Doping of Monolayer Semiconducting Transition Metal Dichalcogenides Hui Gao1, 2, Joonki Suh2, Michael Cao1, Kan-
Doping plays a crucial role for tuning the functionalities of semiconductors. The ability to control the charge carrier density and polarity as well as their optical properties is the fundamental to our current optoelectronic technology. Atomically thin transition metal dichalcogenides (TMDs) have been the material of focus in recent years due to their exceptional physical properties and great potential as the platform for next generation optoelectronic devices. 

Here we present an air stable and scalable doping method based on metal-organic chemical vapor deposition (MOCVD) where the charge carrier polarity (electrons or holes) and carrier densities can be precisely controlled. Using gas phase precursors, we achieved 2 cm by 2 cm scale (limited by the size of the furnace) growth of Nb-doped and Re-doped MoS$_2$ which are p-type and n-type semiconductors respectively, that is homogeneous over the entire substrate. The amounts of dopants of each polarity can be precisely tuned from sub 1% to 25%. The resulting film is stable in ambient up to months evident by the intact conductivity of the as fabricated FETs. Furthermore, the resulting p-type and n-type films can be further detached from the substrate and stacked together generating more functional devices in large scale.

11:45 AM EP03.03.09

**Single Atomic Vacancy Catalysis**

**Jieun Yang**, Viacheslav Manichev, Maureen Lagos, Yan Wang, Raymond Fullon, Leonard C. Feldman and Manish Chhowalla; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Single atom catalysts provide exceptional activity and turnover frequencies. However, single atom catalytic activity is often measured by dispersing atoms and nanoparticles on catalyst support. This makes it difficult to study the fundamental activity from a single atom in real electrochemical environments.

Here, we report catalytic activity from precise number of sulfur vacancies on two dimensional molybdenum disulfide grown by chemical vapor deposition. The vacancies were introduced by precisely varying the dose of helium ions in a helium ion microscope (HIM). We then counted the number of vacancies per cm$^2$ using high resolution scanning transmission electron microscope (STEM). The catalytic activity was measured using micro-electrochemical cells previously developed in our group [1]. The devices allow precise control of the area over which the catalytic properties are measured to ensure that activity is only coming from the sulfur vacancies. Our results show that the catalytic properties of the MoS$_2$ improves with the number of vacancies. More importantly, we demonstrate that it is possible to extract the activity from a single sulfur vacancy. We have found that at a vacancy concentration of 5.4 x 10$^{14}$cm$^{-2}$, the intrinsic turn over frequency (TOF) and Tafel slope of a single atomic vacancy is ~ 6 s$^{-1}$ and 38 mV/dec, respectively. The TOF is amongst highest reported and the Tafel slope approached that of platinum.


**SESSION EP03.04: Photonic Properties and Optoelectronic Devices I**

**Monday Afternoon, November 26, 2018**

**Hynes, Level 2, Room 210**

**1:30 PM *EP03.04.01**

**Layered Material Heterostructures for Photovoltaics and Photocatalysis**

**Harry A. Atwater**, California Institute of Technology, Pasadena, California, United States.

The strong absorption and visible spectrum energy bandgaps for the transition metal dichalcogenides (TMDs) of molybdenum and tungsten render them as attractive candidates for photovoltaics (PV) and optoelectronics. Further, the atomically thin nature is favorable for efficient separation and collection of photo-excited charge carriers. Thus if the three major optoelectronic criteria, i.e., i) sunlight absorption, ii carrier collection and iii) operating voltage can be addressed for TMD materials, they may be candidates for high efficiency photovoltaics and photocatalysis. We recently demonstrated near-unity broad-band absorption of above band-gap photons for <15 nm TMD layers, and have also achieved high external quantum efficiency in <10 nm thick active layer photovoltaic devices in a pn junction of WSe$_2$/MoS$_2$ with graphene contacts. To date, achievement of high open-circuit voltage (Voc) has remained an outstanding challenge for achieving high photovoltaic efficiency. We report here high open circuit voltages (Voc) in TMD absorbers based photovoltaic devices, achieved by tailoring the conduction and valence band-alignments between a single TMD absorber layer and carrier-selective contact layers for electron collection (titanium oxide) and hole collection (nicket oxide), respectively. The band alignments measured using X-ray photoelectron spectroscopy indicate the asymmetric and selective nature of the metal oxide carrier-selective contacts, and we observe open circuit voltages indicate the asymmetric and selective nature of the metal oxide carrier-selective contacts, and we observe open circuit voltages.
Exciton Manipulation for Valley/Spin Devices with 2D TMDCs

A. K. Geim, K. S. Novoselov

Exciton manipulation for valley/spin devices with 2D TMDCs.

**2:15 PM**

**EP03.04.03**

Exciton Manipulation for Valley/Spin Devices with 2D TMDCs Andras Kis; Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The band structure of transition metal dichalcogenides (TMDCs) with valence band edges at different locations in the momentum space could be harnessed to build devices with operation relying on the valley degree of freedom. To realize such valleytronic devices, it is necessary to control and manipulate the charge density in these valleys. In addition, the long lifetime of interlayer excitons in TMDC heterostructures and the associated long diffusion length offer new opportunities. In my talk, I will present our recent efforts in this direction. In the first part, I will present our direct measurements of the conduction band splitting in MoS2 quantum point contacts. In the second, I will present our recent results on the electrical manipulation of interlayer excitons in TMDC heterostructures.

**2:45 PM BREAK**

**3:15 PM**

**EP03.04.04**

Band-Bending Junctions—A New Concept for Carrier Transport in 2D Materials Joeson Wong1, Artur Duvoym1, Deep M. Jariwala1–2, Bolin Liao1–4, Eli Rotenberg1, Chris Jozwiak1, Aaron Bostwick1, Ahmed Zewail1 and Harry A. Atwater2, 1California Institute of Technology, Pasadena, California, United States; 2Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Mechanical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

Metal-semiconductor contacts are one of the most ubiquitous and fundamental types of junctions in all optoelectronic devices, usually associated with the formation of a Schottky barrier and a depletion region. In the limit that the metal-induced depletion region is larger than the thickness of the semiconductor, an effective doping of the semiconductor is obtained. Two-dimensional junctions such as MoS2 present an attractive platform to examine this proximity effect because of their naturally passivated surfaces and interlayer van der Waals interactions, allowing them to be placed on arbitrary substrates. We explore this substrate interaction through angle resolved photoemission spectroscopy measurements of few-nmn thick MoS2 on As, showing evidence for Fermi level shifts that are dependent on the thickness of MoS2. This effect suggests the possibility of creating novel homojunction devices through thickness variation, even in the absence of bandstructure renormalization. Here, for the first time to the best of our knowledge, we measure the spatiotemporal dynamics of such junctions with ultrafast scanning electron microscopy. We observe ultrafast anisotropic carrier transport in space and time. We further investigate the carrier dynamics in such a complex junction with laser-induced photocurrent mapping, which suggests counter-intuitive carrier dynamics. We conclude by analyzing and describing the time and length scales that are relevant for these junctions, which have far-reaching consequences for applications in atomically-thin semiconductor devices.

**3:30 PM**

**EP03.04.05**

Excitonic Electro-Optical Phenomena in van der Waals Heterostructures Goki Eda; National Univ of Singapope, Singapore, Singapore, Singapore.

Excitons in two-dimensional (2D) semiconductors possess giant oscillator strength and play a fundamental role in mediating the strong light-matter interaction. Among others, monolayer transition metal dichalcogenides exhibit strong excitonic absorption due to band nesting [1] and allow exploration of hybrid quasi-particle states such as plexcitons [2] through strong dipole-dipole coupling [3]. The first part of this talk will focus on our approaches to realizing electrical generation, manipulation, and detection of excitons and their complexes based on various van der Waal heterostructures. Specifically, I will discuss how MIS-type heterostructures allow electrically tunable excitonic electroluminescence and electro-optic upconversion in linear optics regime. We demonstrate that hexagonal boron nitride can serve as a unipolar tunnel barrier that allows hot carrier injection and energy harvesting [4]. The second part will discuss our recent discovery of a novel monolayer MoS2 growth mechanism based on vapor-liquid-solid conversion [5]. We show that alkali metal plays a key role in reducing the melting point of the precursors and triggering the vapor-liquid-solid mode, yielding epitaxial growth of monolayer nanoribbons.

Layered hexagonal boron nitride (hBN) is a wide band gap semiconductor (> 6 eV), which attracts a growing interest for its strong UV photoluminescence properties [1]. The optical properties of bulk hBN as well as BN layers are governed by strong excitonic effects. They have been studied recently, but experiments are difficult because of the necessity to work in the far UV range [2].

In this contribution, we present a detailed theoretical study of the first excitonic levels, and characterize their energies and shape by combining ab initio calculations (GW plus Bethe-Salpeter equation) and a simple tight-binding model (as put forward by Wannier long time ago) [3].

In case of the monolayer, we analyse the first five excitons of single layer hBN, corresponding to the first three bright peaks and two dark states. Strong deviations from the usual hydrogenic model are evidenced due to both lattice effects and the 2D nature of the screening which can be approximated by a potential of the Keldysh type. Moreover, the analysis of the excitonic dispersion at finite $q$ is also discussed. Then the effects of the number of layers on quasiparticle energies, absorption spectra and excitonic states is presented, placing particular focus on the Davydov splitting of the lowest bound excitons. We show that for $N > 2$ (N being the number of layers), one can distinguish between surface excitons mostly localized on the outer layers, and inner excitons, which leads to an asymmetry in the energy separation between split excitonic states. In particular, the bound surface excitons lie lower in energy than their inner counterparts. Additionally, this enables us to show how the layer thickness affects the shape of the absorption spectrum [4].

As hosts for tightly-bound electron-hole pairs carrying quantized angular momentum, atomically-thin direct-gap semiconductors of transition metal dichalcogenides provide an appealing platform for studying exciton physics and for optically addressing the valley degree of freedom. In ultra-high quality WSe$_2$ monolayers, the photoluminescence (PL) emission peaks are sharp and can arise from excited exciton states at high energies and multi-particle bound states at low energies. We observe PL of the 1s, 2s, 3s and 4s Rydberg series [1]. Interestingly the 2s exciton exhibits much better valley polarization and coherence than the 1s exciton [2]. We also observe PL emission from correlated quantum states involving three, four and five particles [3]. Through a set of control experiments including charge doping, thermal activation, and magnetic-field tuning, we determine that the biexciton consists of a bright exciton and a dark exciton, while the exciton-trion is composed of a bright trion and a dark exciton, and that both of them are intervalley entities. Such unique spin-valley configuration gives rise to emissions with large, negative valley polarizations in contrast to that of the well-known two-particle excitons. We also observe PL emission from correlated quantum states involving three, four and five particles [3]. The energy splitting of the biexciton and exciton-trion complexes is larger than that of the 2s exciton [2].

**References**


Strong Coulomb interactions in single-layer transition metal dichalcogenides (TMDs) result in the emergence of strongly bound excitons, trions and biexcitons. These excitonic complexes possess the valley degree of freedom, which can be exploited for quantum optoelectronics. However, in contrast to the good understanding of the exciton and trion properties, the binding energy of the biexciton remains elusive, with theoretical calculations and experimental studies reporting discrepant results. In this work, we resolve the conflict by employing low-temperature photoluminescence spectroscopy to identify the biexciton state in BN encapsulated single-layer WSe$_2$. The biexciton state only exists in charge neutral WSe$_2$, which is realized through the control of efficient electrostatic gating. In the lightly electron-doped WSe$_2$, one free electron binds to a biexciton and forms the trion-exciton complex. Improved understanding of the biexciton and trion-exciton complexes paves the way for exploiting the many-body physics in TMDs for novel optoelectronics applications.
SiO$_2$ Substrates  Omke Wi and Young Jae Song; Sungkyunkwan University, Suwon, Korea (the Republic of).

The environmental stability of the large-sized and single-crystalline antimony flakes was systematically investigated with temperature and time dependence at the fixed humidity. The antimony flakes used in this work were grown by chemical vapor deposition (CVD) directly on SiO$_2$ substrates, where antimonene layers are stacked up to 100 nm thick with typical area of ~100 mm$^2$. As antimony oxide (Sb$_2$O$_3$) has clear fingerprint prints of Ramon peaks, comparing with those in antimonene, spatial and spectral variations in Raman measurements had been traced for the samples stored in ambient conditions even up to 3 months to confirm the environmental stability of the single-crystalline antimony flakes without severe oxidation, where no significant shift nor oxidation signature in Raman bands could be observed. Further investigations for the oxidation condition of antimony, therefore, has been performed with different heating temperatures at the fixed ambient humidity of ~42%, where spatial distributions, spectral signatures and stoichiometric information of the oxidized antimony flakes were quantitatively measured and analyzed by optical microscopy (OM), Raman spectroscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy. The single-crystalline antimony flakes are still chemically robust without any oxidation below 250 °C, while the $A_h$ peak of antimony oxide in Raman spectroscopy comes out above the temperature. And at 350 °C, the surface of the antimony flake will be almost fully oxidized within 10 minutes. Therefore, the successful CVD growth of large-sized and single-crystalline antimony flakes and the characteristics of their environmental stability in this work might motivate further studies on the electrical and chemical properties of antimonene as another alternatives for future applications.

EP03.05.02  Effect of Doping on Few Layer Pristine Black Phosphorus  Seunghun Han$^2$, Ho Won Jang$^2$ and Chul-Ho Lee$^1$; $^1$KU-KIST Graduate School of Converging Science and Technology, Korea University, Seongbuk-gu, Korea; $^2$Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, Korea (the Republic of).

The elemental two dimensional material, Black phosphorus (BP), exhibits layer-dependent tunable optical and electronic characteristics. [1] BP is known for its widely tunable and thickness dependent band gap which makes it a choice of material for various applications. [2] Each application demands an operational band gap and a material with a wide band gap range will suit the purpose. [3] There are no simple and reliable technique to control the thickness of BP without introducing defects or in-gap states. This study demonstrates two ways of doping BP to tune the band gap by defect doping and by chemical doping. [4-6] Doping, a non destructive method, was used to efficiently modulate the carrier concentration by extracting or injecting carriers into few layer pristine BP enabling a convenient pathway to control its optical and electronic properties. Here, we study the effects of the doping by engineering the defects and tuning the in-gap states introduced during the process. This opens up opportunities to expand the potential applications of few layer pristine BP. Effect of doping on few layer pristine Black phosphorus.


EP03.05.03 Superior Visible Light Photocatalytic and Gas Sensing Performance of Metallic Ag and MoS$_2$ Loaded Graphitic Carbon Nitride Vijay Kumar$^1$, Ritu Malik$^2$ and S.P. Nehra$^3$; $^1$University of California, Berkeley, Berkeley, California, United States; $^2$Technical Faculty, Institute of Material Science, University of Kiel, Kiel, Germany; $^3$University of California, Santa Barbara, Santa Barbara, California, United States.

Two-dimensional (2-D) materials are emerging as new class of multifunctional materials with an extensive range of promising attributes for futuristic energy and environmental applications. In this work, we report the synthesis of ordered mesoporous Ag-MoS$_2$/g-CN nanohybrid by using a facile nanocasting method using cubic mesoporous silica (KIT-6) as hard template. With its 3D mesoporous architecture, the Ag-MoS$_2$/g-CN nanohybrid revealed outstanding visible-light photocatalytic performance, high stability and reusability towards Rhodamine B (RHB) dye which could be due to the improved charge separation properties of photo-induced e-•h$^+$ pairs. The remarkably high degradation efficiency (~98.9%) results from the combined effect generated from the catalytically active Ag and MoS$_2$ nanoparticles loaded in cubic mesoporous g-CN and intrinsic 3D ordered mesoporous morphology of the nanohybrid. In addition to the degradation performance, the Ag-MoS$_2$/g-CN nanohybrid also possesses an excellent volatile organic compounds (VOCs) sensing performance with significantly higher sensitivity, selectivity and short response/ recovery towards n-butanol at lower working temperatures. This study demonstrates a simple and scalable approach to design and develop next generation of 3D layered ordered mesoporous materials for multifunctional applications.

EP03.05.04 Anomalous Pressure Characters of Defects in Hexagonal Boron Nitride Flakes  Baoquan Sun; Institute of Semiconductors, Chinese Academy of Sciences, Beijng, China.

The research on hexagonal boron nitride (hBN) has been intensified recently due to its application as a promising system of single photon emitters. As yet its single photon origin remains under debate even though a lot of experiments and theoretical calculations have been done. We have measured the pressure-dependent photoluminescence (PL) spectra of hBN flakes at low temperature by using diamond anvil cell (DAC) device. It is found that the absolute values of pressure coefficients of discrete PL emission lines are all below 15 meV/GPa which is much lower than 36 meV/GPa, the pressure-dependent photoluminescence (PL) spectra of hBN flakes at low temperature by using diamond anvil cell (DAC) device. It is found that the absolute values of pressure coefficients of discrete PL emission lines are all below 15 meV/GPa which is much lower than 36 meV/GPa, the pressure-dependent red-shift rate of hBN bandgap. These PL emission lines are originated from the atom-like localized defect levels confined within the band gap of hBN flakes. Interestingly, the experimental results of pressure-dependent PL emission lines present three different types of pressure response, corresponding to red-shift (negative pressure coefficient) and blue-shift (positive pressure coefficient), or even a sign change from negative to positive. Density functional theory calculations indicate that there is a competitive relation between the intralayer and interlayer interaction contributions, which leads to the different pressure-dependent behaviors of the PL-peak shift.

EP03.05.05 Atomically Thin Heterojunction Catalysts for Efficient Photoelectrochemical Hydrogen Production  Jae Yoon Lee$^1$, Sungwoo Kang$^2$, Donghun Lee$^1$, Seokhoon Choi$^1$, Sooho Choi$^1$, Soo Min Kim$^1$, Seung Hoon Yang$^1$, Yoon Seok Kim$^1$, Ki Chang Kwon$^2$, Haeli Park$^1$, Woong Huh$^1$, Hee Seong Kang$^1$, Insoo Kim$^1$, Jin Young Cho$^1$, Young Ho Song$^1$, Jong Seob Kim$^1$, Youngil Yoo$^1$, Sang Hyun Kang$^1$, Qinke Wu and Young Jae Song; Sungkyunkwan University, Suwon, Korea (the Republic of).

Anomalous pressure characters of defects in hexagonal boron nitride flakes  Baoquan Sun; Institute of Semiconductors, Chinese Academy of Sciences, Beijng, China.

The research on hexagonal boron nitride (hBN) has been intensified recently due to its application as a promising system of single photon emitters. As yet its single photon origin remains under debate even though a lot of experiments and theoretical calculations have been done. We have measured the pressure-dependent photoluminescence (PL) spectra of hBN flakes at low temperature by using diamond anvil cell (DAC) device. It is found that the absolute values of pressure coefficients of discrete PL emission lines are all below 15 meV/GPa which is much lower than 36 meV/GPa, the pressure-induced red-shift rate of hBN bandgap. These PL emission lines are originated from the atom-like localized defect levels confined within the band gap of hBN flakes. Interestingly, the experimental results of pressure-dependent PL emission lines present three different types of pressure response, corresponding to red-shift (negative pressure coefficient) and blue-shift (positive pressure coefficient), or even a sign change from negative to positive. Density functional theory calculations indicate that there is a competitive relation between the intralayer and interlayer interaction contributions, which leads to the different pressure-dependent behaviors of the PL-peak shift.
Catalysts that can reduce a kinetic overpotential, a potential barrier for charge transfer from a solid-state electrode to a liquid-phase electrolyte, are necessary for the realization of efficient photoelectrochemical (PEC) hydrogen generation. Recently, atomic layered transition metal dichalcogenides (TMDCs) such as MoS2 have emerged as a promising candidate for non-precious and earth-abundant catalysts. Considerable research efforts have been devoted to identifying the active sites such as atomic edges and vacancies in those layered materials and activating (or maximizing) such catalytic sites for efficient hydrogen evolution reaction (HER). In addition to the optimization of catalytic active sites, the photo-excited charges must be efficiently separated and transported from the photocathode to the electrolyte for further enhancement on the PEC performances. To achieve such a goal, many previous studies have attempted to utilize the heterojunctions that form the cascade alignment between the band edge of a semiconductor and the hydrogen reduction potential. In this respect, the capability to build atomically thin heterojunctions with the designed energy alignment using various TMDCs with different band edges and work functions offers unexplored opportunities in optimizing the interfacial kinetics of photoelectrolysis. Nevertheless, it is difficult to exactly correlate PEC performance with the specific properties of the heterostructures and to study the corresponding HER mechanism due to ensemble averaging effects of various active sites. Here, we propose a novel strategy to reduce an overpotential by employing the atomically thin TMDC heterojunction as a HER catalyst. To prove our hypothesis, we newly develop the spatially-resolved PEC characterization platform using scanning photocurrent microscopy combined with a standard electrochemical measurement, allowing not only to visualize the enhanced PEC activity of the heterojunction catalyst but also to solely reveal their effects on HER without ensemble averaging effects of other extrinsic factors. Through the spatially-defined characterization under global illumination, we further confirm that the overpotential and charge transfer resistance at the interface can be significantly reduced by the atomically thin heterojunction catalyst. Our demonstration offers unprecedented opportunities not only to investigate the fundamental HER mechanism correlating with the tailored properties of a catalyst, but also to design highly efficient PEC cells.

EP03.05.06
Fast, Self-Driven, Air-Stable and Broadband Photodetector Based on Vertically Aligned PtSe2/GaAs Heterojunction Zeng Longhui; The Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Two-dimensional (2D) layered transition metal dichalcogenides (TMDS) are favorable for use in electronic and optoelectronic device application due to their excellent electrical and optical properties. Platinum diselenide (PtSe2), is exciting and interesting a Group-10 transition metal dichalcogenide (TMD), which has unique electronic properties such as high carrier mobility, tunable bandgap, stability, and flexibility. Particularly, PtSe2 exhibits widely tunable bandgaps transition from monolayer (1.2 eV) to semimetal at bulk with zero bandgap. In this work, we demonstrate high-performance photodetector based on vertically aligned PtSe2-GaAs heterojunction, which exhibits a broadband sensitivity from deep ultraviolet to near-infrared light, with peak sensitivity from 650 to 810 nm, is reported. The response speed of t½/t∞ is in the range of μs, which represents the best result achieved for Group-10 TMDs based optoelectronic device thus far. According to first-principle density functional theory, the broad photosensitivity ranging from visible to near-infrared region is associated with the semiconducting characteristics of PtSe2 which has interstitial Se atoms within the PtSe2 layers. It is also revealed that our heterojunction photodetector does not exhibit performance degradation after six weeks in air.

EP03.05.07
Nitrogen-Doped Graphene Electrode for Lowering Contact Resistance of MoS2: Dong-jae Seo1, Yong Duck Kim2, Jaejun Lee1, Dukwan Na3, Jaeheun Yoo1, Takashi Taniguchi2, James Hone3, Keunsoo Kim1 and Heonjun Choi1; 1Department of Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of); 2Department of Physics, Kyung Hee University, Seoul, Korea (the Republic of); 3National Institute for Materials Science (NIMS), Sengen, Japan; 4Department of Mechanical Engineering, Columbia University, New York, United States; 5Department of Physics, Sejong University, Seoul, Korea (the Republic of).

Semiconducting two-dimensional transition metal dichalcogenide(TMDC) with wide visible range bandgaps of about 1-2 eV has been extensively studied for potential applications in electronics, optoelectronics, a memory device, and sensor. Furthermore, the combination of spin valley and valley degrees of freedom in semiconductor TMDC creates the possibility of manipulating them for future applications in spintronics and valleytronics devices. However, there are still challenges such as air stable and thermally stable Ohmic contacts with an order of magnitude lower contact resistance. To date, large gate doping is required for graphene contact and 1T-phase of TMDC is considered to be unstable in phase at cryogenic temperature. Here, we demonstrate low resistance Ohmic contact to single layer molybdenum disulfide (MoS2) using highly n-type graphene, nitrogen-doped graphene, which has a work function similar to the electron affinity of single-layer MoS2. FETs fabricated on hexagonal boron nitride (hBN) encapsulated MoS2 has n-type behavior with an on/off ratio of about ~10⁶ and a field-effect mobility of 65 cm²/Vs at room temperature. The Vth of the transistors fabricated on pristine MoS2 flakes falls in the negative regime (~7 to 5 V) with an average on/off current ratio of ~10⁻⁶. Transfer characteristics (IDS versus VGS) for different source-drain voltages VSD (10-50 mV) recorded in 2-point configuration shows pronounced increase of IDS at positive VGS due to the formation of an n-type channel. By decreasing the temperature of MoS2 transistor can be left-shifted from the more n-type behavior of nitrogen-doped graphene to enhancement mode with the dominance of the pyridinic-N configuration in N-doped graphene. This work demonstrates the Vth tuning of the MoS2 transistor and the newly developed contact engineering approach is applicable to a wide range of TMDC, compatible with conventional semiconductor processes. Also, this is expected to be a good electrode material for observing the band split in the conduction band of MoS2 for future application in spintronics and valleytronics.

EP03.05.08
Controllable Water Vapor Assisted Chemical Vapor Transport Synthesis of WS2-MoS2 Heterostructures Yuzhou Zhao and Song Jin; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Two-dimensional transition metal dichalcogenides (MX2) have attracted considerable research interests in their electro-optical properties and potential application of high-performance and flexible electronic-photonic devices. Although 2D MX2 can be directly grown on various substrates by vapor deposition synthesis, such synthesis can often be unreliable and recently people realize water vapor or uncontrolled environmental humidity can play important roles in the growth of MX2, regardless if metal chlorides, metal oxides, or MX2 bulk powder precursors are used. It was found that water vapor can work as a transport agent that react with bulk transition-metal dichalcogenide at high temperature and form volatile metal oxyhydroxide species (MO2(OH)x) and hydrogen chalcogenides (HxM) that dramatically increase the effective vapor pressure. Here we report the controllable synthesis of WS2, MoS2 and their heterostructures using water-assisted chemical vapor transport (CVT). The amount of water vapor can be tunably controlled by utilizing the thermal decomposition of calcium sulfate dihydrate (CaSO4·2H2O), which as a solid state source of water vapor not only provides much lower vapor pressure baseline than liquid water, thus guarantees a wider tunable range, but can also be easily integrate into a chemical vapor deposition system without changing the setup. This allows precisely control of the nucleation and growth on the substrate, leading to the lateral epitaxial growth on the edge of transition-metal dichalcogenide and more reproducible growth of large area heterostructures. Raman spectral mappings confirm the heterostructure and electrical transport measurements revealed the p-type transport behavior for WS2 and the n-type transport behavior for MoS2. Our research provides chemical insight into the growth mechanism of transition-metal dichalcogenide and it can potentially be a general approach to controllable grow other metal chalcogenides.

EP03.05.09
Large-Area CVD Growth of Uniform Multilayer h-BN as an Excellent Template for 2D Materials Yuki Uchida1, Sho Nakandakari1, Kenji

Two-dimensional (2D) layered transition metal dichalcogenides (MX2) have attracted considerable research interests in their electro-optical properties and potential application of high-performance and flexible electronic-photonic devices. Although 2D MX2 can be directly grown on various substrates by vapor deposition synthesis, such synthesis can often be unreliable and recently people realize water vapor or uncontrolled environmental humidity can play important roles in the growth of MX2, regardless if metal chlorides, metal oxides, or MX2 bulk powder precursors are used. It was found that water vapor can work as a transport agent that react with bulk transition-metal dichalcogenide at high temperature and form volatile metal oxyhydroxide species (MO2(OH)x) and hydrogen chalcogenides (HxM) that dramatically increase the effective vapor pressure. Here we report the controllable synthesis of WS2, MoS2 and their heterostructures using water-assisted chemical vapor transport (CVT). The amount of water vapor can be tunably controlled by utilizing the thermal decomposition of calcium sulfate dihydrate (CaSO4·2H2O), which as a solid state source of water vapor not only provides much lower vapor pressure baseline than liquid water, thus guarantees a wider tunable range, but can also be easily integrate into a chemical vapor deposition system without changing the setup. This allows precisely control of the nucleation and growth on the substrate, leading to the lateral epitaxial growth on the edge of transition-metal dichalcogenide and more reproducible growth of large area heterostructures. Raman spectral mappings confirm the heterostructure and electrical transport measurements revealed the p-type transport behavior for WS2 and the n-type transport behavior for MoS2. Our research provides chemical insight into the growth mechanism of transition-metal dichalcogenide and it can potentially be a general approach to controllable grow other metal chalcogenides.
Multilayer hexagonal boron nitride (h-BN) has been widely recognized as an ideal insulator to bring out the intrinsic properties of 2D materials [1,2]. Catalytic chemical vapor deposition (CVD) method is capable to produce large-area h-BN films suitable for practical applications [3-5]. However, Cu foils/films mainly give monolayer h-BN, which is not thick enough to screen out influences from substrate surface [3,4]. Recently, CVD growth of multilayer h-BN film was reported by using Fe foil, in which dissolution and segregation processes occur during the CVD due to relatively high B and N solubilities in Fe, but the multilayer h-BN film lacks uniformity [5].

Here, we demonstrate the successful synthesis of large-area, uniform multilayer h-BN on Ni-Fe alloy by suppressing the grain boundaries and tuning the solubilities of B and N [6]. To compare the crystallinity of Fe and Ni-Fe alloy catalysts, we measured their electron back-scatter diffraction (EBSD) after h-BN growth. Although Fe has polycrystalline structure with different crystal planes, Ni-Fe alloy is highly crystallized with a low density of grain boundaries. Moreover, the multilayer h-BN film transferred from Ni-Fe alloy to SiO$_2$/Si substrate shows a uniform optical contrast, while the one transferred from Fe indicates a large variation of thickness. Raman $E_{2g}$ intensity collected from the h-BN film produced on Ni-Fe alloy is highly uniform, supporting the high uniformity of the h-BN thickness. To demonstrate the performance of our multilayer h-BN as a substrate for 2D materials, we have investigated the optical properties of WS$_2$ grown on the multilayer h-BN [6]. Intriguingly, we observed an intense and narrow PL peak from the WS$_2$ grown on h-BN as compared with that on SiO$_2$/Si. The minimum PL line width of WS$_2$/h-BN (24 meV) is much narrower than that observed on SiO$_2$ substrate (67 meV) and is almost comparable to that of WS$_2$ on mechanically exfoliated h-BN (26 meV) [2]. This result demonstrates that our h-BN is effective as a substrate for 2D materials. Therefore, our CVD-grown multilayer h-BN is expected to offer an ideal platform for 2D materials, greatly contributing to their practical applications.


EP03.05.10
Hydride-Free Metal-Organic Vapour Phase Epitaxy of Coalesced 2D WS$_2$ Layers on Sapphire

Annika Grundmann1, Michael Heuken2, 1, Holger Kalisch3 and Andrei Vescan1; 1Compound Semiconductor Technology, RWTH Aachen University, Aachen, Germany; 2AIXTRON SE, Herzogenrath, Germany.

The 2D transition metal dichalcogenide (TMDC) WS$_2$ has attracted great interest due to its unique properties and prospects for future electronics. However, compared to MoS$_2$, the development of a reproducible and scalable deposition process for 2D WS$_2$ has not advanced very far yet. Here, we report on the systematic investigation of 2D WS$_2$ growth on sapphire (0001) substrates using a hydride-free metalorganic vapour phase epitaxy (MOVPE) process in a commercial AIXTRON planetary hot-wall reactor in 10 × 2" configuration. Tungsten hexacarbonyl (WCO, 99.9%) and di-tert-butyl sulfide (DTBS, 99.9999%) are used as MO sources. MO precursors allow a high-purity material synthesis as well as fine-tuning the H$_2$ partial pressure which is crucial for controlling nucleation, lateral growth and unwanted C deposition. Sapphire substrates enable a 3-on-2 superstructure of WS$_2$ and hence a clearly defined crystal alignment and orientation. All samples are characterized using Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and optical in-situ and ex-situ reflectometry.

MOVPE processes are started with a substrate prebake step at 1050 °C for 15 min in H$_2$. Our previous work on 2D MoS$_2$ has shown that such a step prior to growth can reduce the nucleation density and strongly inhibit the formation of a parasitic carbonaceous film directly on the sapphire surface. On the prebaked substrate, WS$_2$ is deposited at 30 hPa total pressure in N$_2$ atmosphere. Comparably to MoS$_2$, the suitable growth temperatures for WS$_2$ lie between 750 °C and 845 ºC (845 ºC chosen as optimum here). However, temperatures lead to an increasing parasitic C deposition, while lower temperatures result in a rapid decrease of the WS$_2$ domain size. Because nucleation and growth of TMDC are mainly controlled by the metal species, the influence of the WCO flow on lateral growth was investigated. Increasing the WCO flow during the stacking of layers.

EP03.05.11
Microscopic Description of Localized Quantum-Dot-Like States in Molybdenum Disulfide Nanostructures

Michael Lorke, Christian Carmesin, Matthias Florian, Daniel Erben, Tim O. Wehling and Frank Jahne; University of Bremen, Bremen, Germany.

Atomically thin two-dimensional semiconductors have emerged as an interesting class of material systems, both for applications and fundamental studies. For opto-electronic applications like displays, light sources, and photovoltaics, transition-metal-dichalcogenides (TMDS) are an appealing system, as they combine great mechanical strength with high carrier mobility and an direct optical band gap. In this rapidly developing field, attention has recently shifted towards the realization of nanostructures.

The generation of localized state, either induced via defects or via systematic confinement engineering, opens the possibility to deterministically generate single-photons or, more generally, provide sources of quantum light. For this purpose, flakes of TMDS have been placed on nanowires, over gold edges and over etched holes to form single-photons emitters. We focus on a different platform, which consists of TMDS nano-bubbles that develop if air is enclosed during the stacking of layers.

The physics governing all of these examples has predominantly been discussed in terms of strain engineering. Due to the high bending rigidity, strain induces large variation of the band gap that can lead to a transition from a direct to an indirect band gap. Another, much less discussed, mechanism is the change of the dielectric environment which also induces strong bandgap variations.

We report on results of atomistic tight-binding calculations of different sizes and height-to-diameter ratios of these nanostructures and demonstrate that the
formation of confined quantum-dot-like single-particle states is caused by an interplay of strain and dielectric screening. We show that the strain pockets are caused by a crumpling of the material due to its high bending rigidity and discuss the implications of the underlying physics to other TMD-based nanostructures.

EP03.05.12
**Nonequilibrium Doping, Conversion and Formation of Lateral Heterostructures**

Masoud Mahjouri-Samani¹, Andrew Lupini², Alexander Puretzky³ and David B. Geohegan³; ¹Auburn University, Auburn, Alabama, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Controlled doping and formation of heterostructures in bulk semiconductors have been the key processes in controlling the transport characteristics of electronic devices. Developing similar processes are essential in order to unleash the full potential of the emerging atomically-thin two-dimensional (2D) semiconductors.

In this work, we demonstrate a nonequilibrium process that allows controlled doping of 2D materials from few atoms to the full conversion state. In contrast to the near-equilibrium growth processes, CVD, where the control of flux, activation energy, diffusion, and reaction time are challenging, the digital delivery and tunable kinetic energy of atoms in the laser ablation process can be a powerful tool to overcome these barriers. Formation and digital delivery of atoms in the pulsed laser ablation allows us to precisely tune the doping concentration while the kinetic energy helps us to overcome the potential barriers. We show that by coupling this nonequilibrium technique with conventional lithography and patterning processes, selective conversion and formation of patterned arrays of lateral heterojunctions between monolayer 2D semiconductors, e.g., MoSe₂/MoS₂, can be obtained. For example, the e-beam lithography and deposition processes are used to mask monolayer MoSe₂ crystals with desired patterns where the exposed regions are selectively converted to MoS₂ by pulsed laser generated sulfur atoms. This approach provides a unique capability for controllable and selective doping and conversion of crystals in predefined locations. The doping concentration and heterojunctions are studied by Raman and photoluminescence spectroscopy, atomic-resolution scanning transmission electron microscopy (STEM). This nonequilibrium process appears to be a powerful technique that could be extended to form other metallic, insulating, and semiconducting regions within 2D materials required for ultrathin electronics.

Biography
Dr. Mahjouri-Samani is Assistant Professor of Electrical & Computer Engineering at Auburn University (AU). His research interest is focused on developing laser-based approaches for synthesis, processing, and in-situ/real-time characterization of emerging low-dimensional materials and devices.

EP03.05.13
**Molecular Mechanics of MoS₂ Monolayer with Point Defect and Grain Boundary**

GangSeob Jung and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Molybdenum disulfide (MoS₂) monolayer is a two-dimensional (2D) material, which is expected to provide the next generation of electronic devices together with graphene and other 2D materials. Due to its significance for future electronics applications, gaining a deep insight of the fundamental mechanisms upon MoS₂ failure is crucial to prevent mechanical failure towards reliable applications. Here, we report atomic simulations to investigate how the mechanical properties are affected by various point defects and grain boundary. The mechanical properties (elasticity and strengths) of three different point vacancies (S₁, S₂, Mo) and three different point substitutions (MoS, MoS₂, Mo₂S₂) are systematically investigated from the defect ratios 0 to 30%. Also, the bi-crystals with different tilt angles (0–60°) are generated from our newly developed algorithm, where the defect shapes show good agreement with those from the previous experiments. The strengths of the bi-crystals reveal novel mechanistic insight into MoS₂ with various defects and grain boundary.

EP03.05.14
**Metallic Atomic-Glue for Clean Interface in van der Waals Heterostructures**

Doyoon Lee, Sanghoon Bae and Jeehwan Kim; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

2D material-based heterostructures have been intensively studied because of their unique device functionalities and novel physics. However, it is extremely challenging to have clean interface in the large area 2D heterostructures because a transfer method always accompanies residue issue on top of the 2D materials, which degrades the performance of the 2D heterostructures. For example, the most common approach for transfer of the 2D material at large scale is based on a polymer supporting layer such as poly(methyl methacrylate). It always remains the polymer residue on the 2D materials and wet-processing during the transfer is unavoidable, which can have extra molecular contamination involved at interface of 2D heterostructures during stacking. Accordingly, it has been required to develop an alternative way to produce extremely clean interface in 2D heterostructures

Here, we report that atomically smooth metal glue for 2D heterostructures. We studied the underlying mechanisms to find a suitable material for 2D materials transfer. It was important to investigate and simulate the interfacial toughness at each interface and the internal stress in the material to induce driving force for exfoliation and transfer. Based on our experience, nickel is the best material which satisfies the crucial criteria for atomically smooth glue for 2D material stacking. Removing metal has been extensively studied and we could find the best way to get rid of the nickel glue from the 2D materials. In addition, this approach does not accompany wet-process during transfer and stacking, which preserves the cleanliness at interface uniformly across wafer.

We also confirmed that this discovery substantially improved uniformity in terms of electrical and optical properties of a wafer-scale heterostructure compared to one of 2D heterostructures made by wet-process. We believe this finding will lead a new opportunity for 2D material research since it can preserve ultra clean interface at 2D heterostructures at wafer-scale.

EP03.05.15
**Intrinsic Mobilities of Charge Carriers in Two-Dimensional Metal Dichalcogenides**

Yuanvye Liu and Long Cheng; The University of Texas at Austin, Austin, Texas, United States.

Although two-dimensional metal dichalcogenides (MX₂) have showed great potential for electronics and optoelectronics, they are limited by a low carrier mobility, which has been recognized as one of the major challenges impeding their further developments, and urges efforts to understand the mobility-limiting factors as well as discovery of higher-mobility alternatives.

Here using the density functional perturbation theory, Wannier interpolation of the electron-phonon matrix, as well as analytical derivations, we reveal the underlying physical factors that govern the electron and hole mobility in MX₂. Moreover, we derive a simple descriptor that can be used for rapidly screening the 2D MX₂ database for high-mobility semiconductor candidates. [1]

[1] Long Cheng, Yuanvye Liu, submitted

EP03.05.16
**Superhydrophobic 2D MoS₂-Based Multifunctional Sponge for Spontaneous Detection and Absorption of Spilled Oil**

Tae-Jun Ko, Jae-Hoon Hwang,
Oil spill pollution in marine environment is a major threat to the ecosystem, thus invokes immediate yet viable solutions. Amongst various technologies developed for oil-water separation, directly applying sorbent materials of high porosity to spilled oil presents advantages of low cost and operational simplicity. Efficient sorbent materials should combine high hydrophobicity and high porosity for simultaneous water repulsion and oil absorption, which has generally been achieved by their complicated surface modification. In this study, we report two-dimensional (2D) molybdenum disulfide (MoS2) coated polydimethylsiloxane (PDMS) sponge and demonstrate their high proficiency in rapid and spontaneous oil-water separation and spilled oil detection. This novel sorbent material realized by the simple template-assisted fabrication of sponges and the dip-coating of 2D MoS2 layers benefits from followings; 1) hydrophobic and semiconducting 2D MoS2 layers for water repulsion and oil detection, respectively, and 2) intrinsic porosity in the sponge for oil absorption. The MoS2-PDMS sponge presents the water contact angle of > 152° demonstrating excellent superhydrophobicity as well as achieving high oil absorption (> 100 wt%) for various tested oils including vegetable oil and fuel waste such as standard bilge mix (SBM). Also, the material can be recycled for > 10 times upon repetitive absorption/squeezing maintaining the excellent oil absorption capacity, enabled by its intrinsically excellent elasticity. The versatility of this sorbent material has been further extended for the spontaneous detection and identification of oils containing electrically conducting components, e.g., crude oil and SBM.

EP03.05.17
Rhological Characteristics of 2D Titanium Carbide (MXene) Dispersions—A Guide for Processing MXenes
Akuzum Bilgen1, 2, Kathleen A. Malecki1, Babak Anasori1, Pavel Lelyukh1, Nicolas Alvarez1, Emin C. Kumbur2 and Yury Gogotsi1; 1Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 2Mechanical Engineering and Mechanics, Drexel University, Philadelphia, Pennsylvania, United States; 3Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States.

In recent years, 2D transition metal carbides, also known as MXenes, have attracted much attention and found applications in many different areas due to their unique physical structure and properties [1]. High electronic conductivity, good chemical and structural stability, and high surface area of MXenes allowed them to find applications ranging from energy storage to medicine to optoelectronics [1-2]. However, in spite of a clay-like behavior, not much is known about the rheological response of MXenes in solution. Understanding the rheological properties of two-dimensional (2D) materials such as MXenes in suspension is critical in the development of solution processing and manufacturing techniques. In this study [3], some of our most recent work on investigating the rheological response of single- and multi-layer TiC2 MXenes in aqueous environments will be presented. Viscosity and viscoelastic properties of these solutions at various loadings will be combined with “processability charts” to understand the suitability of different MXene morphologies for various fabrication techniques.

References

EP03.05.18
Optical Behavior of Bioinspired Encapsulated Black Phosphorous
Stephen F. Bartolucci and Joshua A. Maurer; U.S. Army ARDEC, Watervliet, New York, United States.

Phosphorene is a promising semiconducting nanomaterial for electronic and optoelectronic applications. It exhibits tunable photoluminescence in the infrared, based on the number of phosphorene layers. However, phosphorene rapidly degrades in the presence of water and oxygen, which significantly limits its viability for real-world applications. In this work, we have developed a biomimetic strategy for encapsulation of phosphorene for degradation stabilization. To control oxygen diffusion, which results in degradation, phosphorene has been encapsulated in self-assembled natural and synthetic lipid bilayers. The kinetics of degradation have been examined by measuring changes in lipid bilayer vesicle size using dynamic light scattering, fluorescence, coupled quartz crystal microbalance analysis, and scanning probe microscopy. Additionally, the tunability of this biomimetic protective layer has been examined using vesicles composed of different lipid compositions and photo-crosslinkable lipids.

EP03.05.19
Mechanisms of Nitridation of MXene Carbides
Patrick Urbanowski1; 1Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Chemical and Biomolecular Engineering, School of Engineering and Applied Sciences, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

MXenes are a growing family of 2D transition metal carbides and nitrides, including 2D Ti2C, Ti3C2, Mo2TiC2 and W1.33C. In recent years, since the discovery of Ti3N4, this family grew to include nitrides. 2D transition metal nitrides have attracted attention due to their potential applications in plasmonics and energy storage, due to their higher values of electrical conductivity. Although most MXene carbides are synthesized by the selective etching of bulk MAX phase precursors, new routes have been investigated for the synthesis of MXene nitrides. Recently reported 2D Mo3N and V3N/VN can be synthesized using one of several new routes, nitridation. With this technique, MXene carbides are used as precursors that are transformed into 2D metal nitrides via treatment under ammonia at elevated temperatures. While this procedure yields materials with higher electrical conductivities than their precursors with new potential applications, the mechanism of this transformation and the products that are formed are not well understood. In this study, we present the nitridation of MXene carbides using a multiphase fluid flow exfoliation method for producing 2D h-BN nano sheets using a multiphase flow of 2D layered materials suspended in a high pressure gas undergoing expansion. The expanded gas-solid mixture is sprayed in a suitable
solvent, where a significant portion (up to 10%) of the initial hexagonal boron nitride (h-BN) material is found to be exfoliated with a mean thickness of 4.2 nm. Moreover, 33% of the exfoliated h-BN were found to be 10 layers or less thick, while retaining a flake length of 276 nm and a concentration of 0.22 mg/mL in Isopropyl Alcohol (IPA) after mild centrifugation. Shear-induced exfoliation occurs due to the high velocities that expanding and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate ($\gamma > 10^5$ s$^{-1}$) experienced by the bulk h-BN particles. Decoupling of exfoliation step from liquid suspension step leads to a very stable suspension of h-BN nano sheets in IPA for a long time (6 months). The CFE method has significant advantages over current 2D material exfoliation methods, such as chemical intercalation and exfoliation, as well as liquid phase shear exfoliation, with the most obvious benefit being the fast, continuous nature of the process. Other advantages include environmentally friendly processing, reduced occurrence of defects and versatility to be applied to any 2D layered material using gaseous medium. Scaling this process to industrial production has a strong possibility of reducing the cost of creating 2D nanomaterials.

To demonstrate the utility of our ultrafast CFE method, we considered improving the barrier property of polyethylene terephthalate (PET) by reinforcing it with exfoliated h-BN nano sheets. PET is commonly used for food and beverage packaging where the simultaneous requirements of high optical transparency and limiting oxygen transport have proven to be a technical challenge. The PET films remained transparent (>90%) when 0.017 and 0.15 vol% of CFE-BN were added. Addition of 0.15 vol% CFE-BN resulted in an improvement of the modulus of PET by 21%. Also this resulted in the dropping of oxygen permeation rate (OPR) of the PET film by 26%.

EP03.05.21
Electrochemical Exfoliation of Black Phosphorus
Alexandra Burger, Gonzalo Abellán, Frank Hauke and Andreas Hirsch; Universität Erlangen-Nürnberg, Erlangen, Germany.

Black phosphorus (BP) has recently attracted great attention due to its tunable, layer-dependent bandgap, high carrier mobility, good current on/off ratio, as well as unique in-plane anisotropy, which renders the material attractive for nanoelectronic, thermoelectric and photonic devices.[1,2] This major challenge for a successful application lies in the fabrication of few- or single layer nanosheets of BP. Several methods have been developed, while chemical and liquid exfoliation of the bulk crystals figure amongst the most prominent ones.[3,4] However, large-scale exfoliation leading to uniform and stable dispersions in high yield remains a challenge.

Herein, we present the electrochemical exfoliation of BP, which has already been successfully employed for graphene and other 2D materials, yielding nanosheets in good quality and high yield. Importantly, this technique is not limited to aqueous systems[5] but has also been reported for various organic solvents and ionic liquids, which have an outstanding protective effect on BP.[6] We present a screening of different electrolytes and anodic/cathodic conditions for the exfoliation process. Finally, Raman spectroscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) have been applied to characterize the material, confirming the formation of BP nanosheets of good quality and in high yields.


EP03.05.23
CVD Growth and Characterization of Two-Dimensional MoO2 Nanoplatelets
Natalia Vorobeva1, Alexey Lipatov1, Dmitry Muratov1, 2 and Alexander Sintskii2, 3; 1University of Lincoln-Nebraska, Lincoln, Nebraska, United States; 2National University of Science and Technology “MISIS”, Moscow, Russian Federation; 3University Center for Materials and Nanoscience, Lincoln, Nebraska, United States.

Ultrathin and two-dimensional materials have an enormous potential for device applications because they offer very diverse electronic properties and are generally compatible with planar fabrication technologies. We report on the chemical vapor deposition synthesis of MoO2 nanoplatelets by sublimation of MoO3 and its reduction in a hydrogen atmosphere at 750 °C. When grown on Si/SiO2 substrates, the platelets primarily assume a rhomboidal shape and have thicknesses ranging from several to tens of nm. The morphology of MoO2 crystals was found to depend on the chemical nature of substrates. MoO2 platelets on Si/SiO2 were characterized by a number of microscopic and spectroscopic techniques, and the electrical measurements revealed the metallic nature of their conductivity averaging at about 2300 S/cm. Raman spectroscopy of MoO2 platelets on graphene indicates their strong hole injection property. Small thickness, planar morphology, high chemical stability and metallic conductivity of ultrathin MoO2 platelets make them potentially interesting for integration with other two-dimensional materials in a variety of electronic structures and devices.

EP03.05.24
Zero-Valent Cu and Sn Intercalation into GeS Nanoribbons—Tailoring Ultrafast Photocative Response
Guanjiang Li1, Mengjing Wang2, Katerina Kushnir3, Kristie Koski3 and Lyubov V. Titova1; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2Chemistry, Brown University, Providence, Rhode Island, United States; 3Chemistry, University of California Davis, Davis, California, United States.

GeS belongs to a class of 2D group-IV monochalcogenides with a layered structure similar to that of black phosphorus. It has been theoretically predicted to combine robust room temperature ferroelectricity, high carrier mobility, and large excitonic effects [1-5]. We have recently demonstrated that photoexcitation of GeS nanoribbons results in an ultrafast shift current, suggesting possible applications in solar energy conversion devices based on the bulk photovoltaic effect [6]. Theory also predicts that extraordinary anisotropie electronic and optical properties of GeS can be engineered by strain and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate ($\gamma > 10^5$ s$^{-1}$) experienced by the bulk h-BN particles. Decoupling of exfoliation step from liquid suspension step leads to a very stable suspension of h-BN nano sheets in IPA for a long time (6 months). The CFE method has significant advantages over current 2D material exfoliation methods, such as chemical intercalation and exfoliation, as well as liquid phase shear exfoliation, with the most obvious benefit being the fast, continuous nature of the process. Other advantages include environmentally friendly processing, reduced occurrence of defects and versatility to be applied to any 2D layered material using gaseous medium. Scaling this process to industrial production has a strong possibility of reducing the cost of creating 2D nanomaterials.

To demonstrate the utility of our ultrafast CFE method, we considered improving the barrier property of polyethylene terephthalate (PET) by reinforcing it with exfoliated h-BN nano sheets. PET is commonly used for food and beverage packaging where the simultaneous requirements of high optical transparency and limiting oxygen transport have proven to be a technical challenge. The PET films remained transparent (>90%) when 0.017 and 0.15 vol% of CFE-BN were added. Addition of 0.15 vol% CFE-BN resulted in an improvement of the modulus of PET by 21%. Also this resulted in the dropping of oxygen permeation rate (OPR) of the PET film by 26%.

Extensive reports have shown band-gap tuning in transition metal dichalcogenides (TMDs), from indirect band gap in the bulk material to a direct gap in single layer due to the absence of interlayer coupling. This unique property stems from the modified electronic states. The phonic properties are extremely critical in optimizing and understanding such electronic and optoelectronic behaviors. Several physical phenomena such as layered effect, quantum confinement effect, inhomogeneous heating effect, doping effect and disorder induce effect have strong influence on the phonon lineshape of TMDs. Using WS$_2$ as a prototype, we employ analytical studies to elucidate on how each of these process affect the phonon modes and provide a systematic route on how to clearly delineate these effects in the phonon lineshapes of TMDs.

EP03.05.25


Enhanced junction reliability and long-term stability with TMDs-based FET are attracting attention in two-dimensional (2D) nano-scale electronic devices. We investigate heterostructures of compositionally and electronically different 2D atomic layers of TMDs to improve contact properties of 2D metal-semiconductor heterojunction. Through interfacial doping with niobium atoms, we engineered composition of transition region between semiconducting WS$_2$ atomic layer channels and metallic NbSe$_2$ contact layers. This van der Waals junction with W$_x$Nb$_{1-x}$Se$_2$ mixed transition regions considerably lower the potential barrier of the heterojunction and enhancing the performance of the corresponding 2D TMDs-based FET devices. Also, it has atomically sharp semiconductor heterojunction.

EP03.05.26

Two-Dimensional Atomic-Layered FET Utilizing Metallic-Semiconducting TMDs Heterostructure Deok Min Seo, Yoon Jun Kim and Myoung Gwan Hahn; Materials Science and Engineering, Inha University, Incheon, Korea (the Republic of).

Two-Dimensional Atomic-Layered FET Utilizing Metallic-Semiconducting TMDs Heterostructure Deok Min Seo, Yoon Jun Kim and Myoung Gwan Hahn; Materials Science and Engineering, Inha University, Incheon, Korea (the Republic of).

AA′-Stacked Trilayer Hexagonal Boron Nitride for Proton Exchange Membrane Fuel Cells Seong In Youn$^1$, Dong-Jun Seo$^2$, Kwangwoo Kim$^3$, Tae-Young Kim$^4$ and Hyeon Suk Shin$^5$; 1Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2Buam Fuel Cell Center, Buam, Korea (the Republic of).

Hexagonal boron nitride (h-BN) and graphene have emerged as promising materials for proton exchange membranes because of their high proton conductivity and chemical stability. However, the defects and grain boundaries generated during the growth and transfer of two-dimensional materials limit their practical applicability. Here, we report the fabrication of membrane electrode assemblies using large-area single-oriented AA′-stacked trilayer h-BN (3L-BN), which exhibits very few defects during the growth and transfer, as a proton exchange membrane for use in fuel cell systems. The fuel cell based on AA′-stacked 3L-BN showed a H$_2$ permeation current density as low as 2.69 mA cm$^{-2}$ and an open circuit voltage (OCV) as high as 0.958 V; this performance is much superior to those for cells based on Nafion (3.7 mA cm$^{-2}$ and 0.942 V, respectively) and single-layer h-BN (10.08 mA cm$^{-2}$ and 0.894 V, respectively). Furthermore, the fuel cell with the AA′-stacked 3L-BN membrane almost maintained its original performance (OCV, maximum power density, and H$_2$ permeation current density) even after 100 h of an accelerated stress test at 30% RH and 90 °C, while the fuel cells with the Nafion and single-layer h-BN membranes exhibited severely deteriorated performances. The stability of the cell based on the AA′-stacked 3L-BN membrane was better because the membrane prevented gas crossover and suppressed the generation of reactive radicals during cell operation.

EP03.05.27

Controlled and Tunable Light Emission of Heat Treated Black Phosphorus—Towards Optoelectronic Devices Sarah A. Alodan$^1$, Justin M. Gorham$^1$, Frank DeRic$^2$ and Mohammed Amer$^1$; 1King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia; 2Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Layered black phosphorus (BP) has shown exceptional optical properties due to its layer-dependent band gap, which ranges from 0.3 to 1.7 eV for bulk to monolayer, respectively. However, instability of black phosphorus nanosheets can be a major hurdle in controlling this light emission and requires various passivation methods. Moreover, the tunability of the emitted light can only be controlled by changing the nanosheet thickness, which in turns changes the band gap energy. Here, we show for the first time a well-controlled tunable light emission from heat treated black phosphorous nanosheets. We show tunable wideband photoluminescence (PL) between 590nm to 720nm, with a tunability resolution of 5nm. This tunable PL is found to be anisotropic and can last for at least 10 days when nanosheets are properly stored. The origin of this light emission is found to be the formation of stable suboxides on the surface of black phosphorus, as confirmed with i-XPS measurements. Our findings unlock doors for optoelectronic applications of layered black phosphorus nanosheets.

EP03.05.28

Spectral Light Absorption and Plasmon Resonance in Monolayer MoS$_2$ with Vertically Standing Nanoflakes Bok Ki Min$^1$, Van-Tam Nguyen$^{1,2}$, Seong Jun Kim$^3$, Youn Sik Yi$^4$ and Choon-Gi Choi$^{1,2}$; 1Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); 2University of Science and Technology, Daejeon, Korea (the Republic of).

Molybdenum disulfides (MoS$_2$), is composed of one layer of Mo atom covalently bonded with two S atoms on either side, has attracted much interest for the optoelectronic applications due to its significantly high photon absorption and electron-hole pair creation at even room temperature resulting from the strong interaction with the incident light. However, the absolute light absorption and the spectral selectivity of a monolayer MoS$_2$ are limited by its atomically thin layers and the electronic band gap, respectively. Recently, several methods, including the plasmonic surface and 3D nanostructure with the high surface area, have been developed with the aim to increase the light-matter interaction for light absorption enhancement and broad detection ranges.
Especially, the desirable dispersion relation of a monolayer MoS₂ allows readily controlling their plasmon resonance wavelength ranges than metals. According to the Drude model, a plasmon resonance within selective wavelength ranges can be observed by controlling the doping concentration in the semiconductors. Generally, the doping concentration should be larger than $10^{17} \text{cm}^{-3}$ for observing the plasmonic peaks in the NIR and visible regions. Thus, developing the 3D plasmonic surface of a monolayer MoS₂ can be one of the crucial methods to effectively promote the detection ability of photodetectors by amplifying photoelectric gain and extending the detection range.

In this study, the spectral light absorption and plasmon resonance induced by the charged exciton (named as trion) in a monolayer MoS₂ with highly doped vertical nanoflakes are explored. First, we successfully synthesize the monolayer MoS₂ with vertically standing nanoflakes using one-step chemical vapor deposition (CVD) process. The size and density of the nanoflakes can be controlled by the CVD condition such as the Mo source/target substrate distance and the growth time. From the photoluminescence (PL) analysis, a higher contribution of the charged exciton in the nanoflake regions than the lateral MoS₂ layer is observed, which evidence that the structural defects from the edges of nanoflakes induce the excess charge carriers. Furthermore, the electron concentration of the nanoflakes can be tuned from $10^{19}$ to $10^{21} \text{cm}^{-3}$ by the oxygen chemical bonding. The absorption peak in the range of 800-1000 nm is observed that is evidence of the presence of the plasmon resonance in a monolayer MoS₂ with highly doped vertical nanoflakes. This result is consistent with the theoretical estimates of plasmonic peaks as a function of doping concentration. Finally, we demonstrate the enhancement of photodetection ability regarding broadening detection ranges toward NIR as well as the visible regions in a monolayer MoS₂ with vertical nanoflakes compared with a monolayer MoS₂.

**EP03.05.30**

**Cellulose Acetate-Assisted Clean Transfer of Transition Metal Dichalcogenides Grown by Chemical Vapor Deposition**

Tianyi Zhang¹, Kazunori Fujisawa², Tomotakah Granzier-Nakajima³, Fu Zhang¹, Zhong Lin², Nestor Perea-Lopez², Ana Laura Elias³, Yin-Ting Yeh² and Mauricio Terrones¹,²,³; ¹Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ²Department of Physics and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, Pennsylvania, United States; ³Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States.

The implementation of chemical vapor deposition (CVD)-grown two-dimensional (2D) transition metal dichalcogenides (TMDs) into practical applications largely relies on a robust and efficient transfer of TMDs onto target substrates. However, conventional transfer approaches such as the poly(methyl methacrylate) (PMMA)-based wet-transfer technique, suffer from surface contamination from polymer residues and structural damages induced by high-temperature etching process. In this work, using cellulose acetate (CA) as an alternative protection layer, we developed a facile CA-transfer technique for CVD-grown TMDs which can address the issues above. The structural and optical properties of the transferred TMD materials are well-preserved in the CA-transferred samples. Atomic force microscopy (AFM) in combination with scanning transmission electron microscopy (STEM) characterizations reveal largely improved micro- and nano-scale cleanliness and no observable wrinkles and/or cracks in TMDs transferred with CA-assisted method. The surface cleanliness and morphology improvement can be attributed to the low adhesion energy between CA and TMDs, as well as the usage of room-temperature etching process. Furthermore, we also demonstrated the capability of CA-transfer to be integrated with a deterministic transfer system for transferring flakes to selected locations on the substrate despite the substrate fragility. The CA-transfer technique developed in this work can be used as a clean and low-cost alternative to the PMMA-transfer method, thus paving the way to the high-resolution nanometer-scale characterizations and the implementations of novel applications of CVD-grown TMDs.

**EP03.05.31**

**Investigation on Growth Mechanism of Multilayer Hexagonal Boron Nitride on Ni(111)**

Kyung Yeol Ma and Hyeon Suk Shin; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Hexagonal boron nitride (h-BN) have received considerable attention as promising materials for two-dimensional dielectric material, along with graphene and other such materials. Recently, large-area, high-quality h-BN films have been fabricated by chemical vapor deposition (CVD) method. Especially, to control the number of layer, significant progress in understanding of the underlying growth mechanism of graphene has been achieved by many researchers. However, the growth control of h-BN is currently limited owing to the lack of understanding the growth mechanism. Herein, we present growth of multilayer h-BN by high-temperature and low-pressure CVD on the single crystal Ni(111) with an ammonia borane as a precursor. We found that an ammonia borane decomposes into B and N atoms and the only B atoms react with the Ni(111) to form a nickel boride structure on the Ni surface prior to growth of h-BN. Microscopic characterizations reveal that the nickel boride is epitaxially formed on surface of Ni(111) and subsequently, multilayer h-BN with AA’ stacking order was grown on the nickel boride surface. This work will provide to expansion of controlled growth of h-BN.

**EP03.05.32**

**Simulating Raman Spectra of Sputtering Deposited Polycrystalline MoS₂ Films by Phonon Confinement Model**

Seiya Ishihara¹,², Yusuke Hibino¹,², Yuya Oyanagi¹, Naomi Sawamoto¹, Takumi Ohashi³, Kentarou Matsuura³, Hitoshi Wakabayashi³ and Atsushi Ogura¹; ¹Meiji University, Kawasaki-shi, Japan; ²Research Fellow of the Japan Society for the Promotion of Science, Chiyoda-ku, Japan; ³Tokyo Institute of Technology, Yokohama-shi, Japan.

Molybdenum disulfide (MoS₂) has remarkable properties and is expected to be promising for next generation device applications. Fabrication of MoS₂ films with RF magnetron sputtering has various advantages, such as large area uniformity and reduction of carrier concentration. However, morphological properties of sputtered polycrystalline MoS₂ films are quite different from the single-crystal MoS₂ fabricated with mechanical exfoliation and chemical vapor deposition. For example, its grain size is greatly reduced due to fundamental problems of deposition environment, such as sulfur-deficient ambient originated from using Mo:S=1:2 target and high deposition rate. Moreover, such growth conditions produce vertically oriented MoS₂ grains in a thick region. Due to the morphological properties, Raman spectra of the sputtered MoS₂ films show unique behavior. In the case of single-crystal MoS₂, it is well known that frequency difference between $E_{2g}$ and $A_{1g}$ Raman modes (Doo) decreases with decreasing layer number. However, sputtered MoS₂ show a reverse trend. In addition, $E_{2g}$ and $A_{1g}$ Raman modes show shifting towards lower wavenumber in a thick region ($> 20$ nm). In order to reveal the origin of the unique phenomena and investigate the film characteristics, such as grain size, residual stress, and crystal orientation, we utilized thermal and strain influence introduced phonon confinement model (PCM) and simulated Raman spectra of horizontally and vertically oriented polycrystalline sputtered MoS₂ films. From the results of PCM simulation, the grain size of sputtered MoS₂ film deposited at 250°C was estimated to be 10 nm. The residual stress value increase with increasing film thickness, which was caused by crystal orientation transition and the difference of the linear expansion coefficient between a- and c-axis.

This work was partly supported by JSPS KAKENHI Grant Number 16H11377 and JST CREST JPUMCR16F4.

**EP03.05.33**

**Wettability of MoS₂ Thin Films Supported on Transparent Quartz Substrates**

Buddhi Singh¹, Subhasis Ghosh¹ and D. Kabiraj²; ¹Jawaharlal Nehru University, New Delhi, India; ²Inter-University Accelerator Centre, New Delhi, India.

We fabricated MoS₂ thin films on transparent quartz substrates by chemical vapor deposition method. The quality of MoS₂ thin films has been characterized by x-ray photoelectron spectroscopy, Raman spectroscopy, and transmission electron microscopy. The water contact angle ($θ_w$) measurement
sh ed a light on the MoS₂-water interaction which will be crucial for the development of future MoS₂-based applications. The θ₀w increased with increasing number of MoS₂ layers. The θ₀w of the bare quartz substrate is ~57.3° and coating of MoS₂ layers results θ₀w as 85.9° ± 0.3°, 88.2° ± 0.3°, 90° ± 0.3°, and 95° ± 0.3° for 3 nm, 5 nm, 9 nm, and 16 nm, respectively. An increase in θ₀ of MoS₂ by almost 50 % from the bare quartz substrate indicates that MoS₂ can efficiently screen the van der Waals (vdW) interaction of the underlying substrate with water. The observed advancing and receding θ₀w are 95.8° and 39.40°, respectively indicates a significant contact angle hysteresis of 42°. This represents an adhesion between water and MoS₂ layer. The kinetics of wetting and spreading of a water molecule on bulk MoS₂ has been discussed via a single exponential behavior i.e. \cosθ₀(τ) = \cosθ₀(0) + \beta(1 - \exp(-τ/τ₀))

by considering intrinsic defects as a surfactant. Here, β is a dimensionless parameter depends on the initial and final θ₀, and τ is the time scale of water molecule transfer from the drop to the solid-liquid interface. We obtain c=0.88, which is little smaller than the single exponential case (c=1) indicates a slower approach to final θ₀. Neuman’s equation of state theory is used to determine the surface free energy of MoS₂ layer and is estimated to be about 39 mJ/m².

EP03.05.34
Raman Scattering Modulated by Excitonic Effects in Monolayer MoS₂
Yuanxi Wang1, Bruno R. Carvalho2 and Vincent Crespi1; 1The Pennsylvania State University, State College, Pennsylvania, United States; 2Universidade Federal do Rio Grande do Norte, Natal, Brazil.

The resonance Raman spectra of monolayer MoS₂ contains a rich variety of frequency-dependent features. Strong excitonic effects present in this 2D semiconductor call for further scrutiny on its Raman intensities. We present a first-principles computational framework to calculate resonance Raman intensities (beyond the Placzek approximation) based on perturbation theory, where the Bethe-Salpeter equation (BSE) is only solved once statically, offering a clear advantage compared with finite differences methods where the BSE is solved twice for each Raman mode. Comparisons with experimental Raman spectra for monolayer MoS₂ using more than 50 laser excitation lines are discussed.

EP03.05.35
Roll-to-Roll Production of Layer-Controlled Molybdenum Disulfide—A Platform for 2D Semiconductor-Based Industrial Applications Yi Rang Lim1, 2, Wooseok Song1, Sung Myung1, Ki-Seok An1, Sun Sook Lee2 and Jongsun Lim1; 1Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Yonsei University, Seoul, Korea (the Republic of).

Molybdenum disulfide (MoS₂) opens up new possibilities for 2D electronic devices in terms of applications for low standby and low operating power electronics coupled with further miniaturization beyond Moore’s Law. Unfortunately, previous synthetic approaches appear to be technically hampered for practical applications due to their inability to obtain large-area and continuous MoS₂ layers. Here, a facile methodology for the large-scale production of layer-controlled MoS₂ layers on an inexpensive substrate involving a simple coating of single source precursor with subsequent roll-to-roll-based thermal decomposition was developed. The resulting 50 cm-long MoS₂ layers synthesized on Ni foils possessed excellent long-range uniformity and optimum stoichiometry. Moreover, this methodology was promising because it enables simple control of the number of MoS₂ layers by simply adjusting the concentration of (NH₄)₂MoS₂. For actual industrial applications, not only a method for large-scale production but also an efficient transfer method following the synthesis to locate the sample onto diverse substrates is a prerequisite. We thus transferred layer-controlled MoS₂ onto PET films using our custom-made roll-to-roll transfer machine. Based on these results, it is envisaged that the cost-effective methodology will trigger actual industrial applications, as well as novel research related to 2D semiconductor-based multifaceted applications.

EP03.05.36
Plasma-Assisted Fabrication and Gate-Tunable Transport Properties of ‘In-Depth’ Doped MoS₂ Vertical Homoostructure Xiao-Mei Zhang; Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Two-dimensional (2D) atomic layered crystals are believed to be the most promising candidates for optoelectronic applications, due to their unique properties such as their optimum thickness scalability, superior intrinsic strain limit and near ideal transparency. Large-bandgap transition metal dichalcogenides (TMDs) (for example, MoS₂ and WSe₂) offer experimental mobility approaching single-crystal silicon thin-film transistors (TFTs), with two orders of magnitude thinner profile and high scalability (up to 20-30%L). More importantly, the broad spectrum which MoS₂ can absorb light from near-infrared spectral region (350-950 nm) is higher than GaAs and SiL. Although the layered transition metal dichalcogenides (LTMDs) exhibit very strong light-matter interactions and very high light absorption coefficients, atomically thin p-n junctions from van der waals-bonded TMDs layers with superior photovoltaic (PV) performance have not been demonstrated. The junctions exhibit both rectifying electrical characteristics and PV response, but the maximum achievable photovoltage is limited by the smallest band offsets for electrons and for holes. For example, in the case of MoS₂/WSe₂, the band offset for electrons is approximately 0.7 eV.[1]

In this work, I present the characterization of a MoS₂ vertical homoostructure in the intermediate thickness regime (~15nm) between the monolayer and the bulk. The MoS₂ vertical homoostructure is fabricated via an ‘In-Depth’ doping process by plasma surface treatment. To generate a p-n homojunction in multilayer (ML)-MoS₂, an effective doping depth control is a challenging due to their atomistically thin dimensions. Compared to surface functionalization and substitutional CVD doping, plasma treatment emerges as the most effective doping technique for layered MoS₂ due to a wide range of doping that can be achieved with good control and selectivity. Fluorine (F)- and oxygen (O) atoms are the critical dopants responsible for the p-doping in MoS₂ due to their inability to obtain large-area and continuous MoS₂ layers. Here, β is a dimensionless parameter depends on the initial and final θ₀ and τ is the time scale of water molecule transfer from the drop to the solid-liquid interface. We obtain c=0.88, which is little smaller than the single exponential case (c=1) indicates a slower approach to final θ₀. Neuman’s equation of state theory is used to determine the surface free energy of MoS₂ layer and is estimated to be about 39 mJ/m².

Acknowledgement:
This work was supported by JST in Japan, Research and Education Consortium for Innovation of Advanced Integrated Science (CIAIS).

References:

EP03.05.37
Fabrication of WS₂ Film by DC Bias Applied High-Temperature Sputtering Yuuya Oyanagi1, Seiya Ishihara1, 2, Yusuke Hibino1, 2, Naomi Sawamoto1, Takumi Ohashi1, Kentarou Matsuura1, Hitoshi Wakabayashi1 and Atsushi Ogura1; 1Meiji University, Kawasaki, Japan; 2Research Fellow of the Japan Society for the Promotion of Science, Chiyoda, Japan; 3Tokyo Institute of Technology, Yokohama, Japan.

Tungsten disulfide (WS₂), a two-dimensional layered material, has attracted attention due to its unique properties such as the band structure change from an indirect transition type of 1.35 eV in bulk to a direct transition type of 1.79 eV in a single layer, and no dangling bond on the surface. Because of these...
favorable physical, chemical, and optical properties, researchers have been developing channel materials and various sensors. We have been fabricating WS$_2$ and other TMD thin films with sputtering deposition. In order to fabricate film with high quality, the substrate is heated to a high temperature. However, S atoms tend to desorb from the film at high substrate temperature. In this research, positive DC bias was applied for the purpose of suppressing desorption of S atoms in the sputtering process even with high substrate temperature. WS$_2$ thin films were prepared by RF magnetron sputtering. The deposition was carried out on SiO$_2$ substrate using WS$_2$ target. As sputtering conditions, the sputtering time was 46.7 s, the RF power was 100 W, the substrate temperature was 250 °C, and the Ar flow rate was 7.6 sccm. The bias voltage was varied from 0 to +60 V. The prepared samples were evaluated for chemical bonding state by X-ray photoelectron spectroscopy. The formation of the bond between W and S was confirmed from the peak positions of W 4f and S 2p spectra. The composition ratio of W and S was calculated using the peak area ratio. As a result, the W/S ratio increased as the bias voltage increased positively, and the desired value of 2.0 was achieved with a bias voltage of +40 V. From this result it is suggested that the positive bias voltage effectively attracts S$^2$-.

This work was partly supported by JSPS KAKENHI Grant Number 16H1377 and JST CREST JPMJCR16F4.

EP03.05.38
Growth of NbS$_2$/NbSe$_2$ Monolayer Superconductor Heterostructures and Alloys

Kwang Hyun Park$^1$, Hyo Jung Kim$^2$, Sun-gyu Park$^1$, Gaetanee Jin$^{1,3}$, Jun Sung Kim$^{1,3}$, Tae-Hwan Kim$^2$ and Moon-Ho Jo$^{1,3}$, 1Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang, Korea (the Republic of); 2Department of Physics, Pohang University of Science and Technology, Pohang, Korea (the Republic of); 3Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Atomic monolayer (ML) NbS$_2$ and NbSe$_2$ crystals provide interesting platforms to explore electronic phase transitions at the atomic thickness limit. Here, we report controlled growth of ML heterostructures, composed of NbS$_2$ and NbSe$_2$, via sequential chemical vapor deposition. We have achieved two kinds of heterostructures, such as lateral epitaxial NbS$_2$/NbSe$_2$MLs and ML alloys, with growth kinetics controls. Initial observations of superconducting transitions at the ML interfaces, probed by scanning tunneling microscopy, are discussed around the critical roles of point and extended defects on coupled transitions.

EP03.05.39
Selective Deposition of van der Waals Semiconductor Monolayers in Wafer-Scales

Gangtae Jin$^{1,3}$, Chang-Soo Lee$^{1,3}$, Juho Kim$^{1,3}$ and Moon-Ho Jo$^{1,3}$, 1Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Korea (the Republic of); 2Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang, Korea (the Republic of).

Spontaneously area-selective deposition of van der Waals (vdW) semiconductor monolayers in large scales, i.e., transition-metal dichalcogenides (TMDCs) in wafer-scales, can provide a new 2D device platforms without conventional lithography for various applications. In fact, such self-assembled 2D structures may establish “clean” atomically thin crystals, free of defects and impurities from lithography and lift-off fabrication processes. In this work, we utilize a cost-effective spin-on polymer mask, which can be easily patternable and removable in large scales, as an inhibitor layer during crystallization of various TMDC monolayers. Thereby selective deposition of MoS$_2$ monolayers in wafer-scales is achieved by metal-organic chemical vapor deposition. We discuss the critical roles of such inhibitor layers within the framework of nucleation kinetics in vdW epitaxy.

EP03.05.40
High Performance Indium Selenide Field-Effect Transistor with Tunneling Barrier Enabled by Atomic-Scale Surface Oxidation

Yi-Hsun Chen$^1$, Han-Ting Liao$^2$, Shih-Wei Huang$^1$, Chih-Yi Cheng$^1$, Wei-Liang Bai$^2$, Raman Sanka$^2$, Fang-Cheng Chou$^2$, Kenji Watanabe$^2$, Takashi Taniguchi$^3$, Chun-Wei Chen$^2$ and Wei-Hua Wang$^1$, 1Academia Sinica, Taipei, Taiwan; 2National Taiwan University, Taipei, Taiwan; 3National Institute for Materials Science, Tsukuba, Japan.

Two-dimensional (2D) semiconductors have emerged as a promising channel material for next-generation electronics due to the ultrathin channel and the lack of short channel effect [1,2]. 2D-semiconductor-based field-effect transistors (FETs) incorporated with layered insulators for enabling low contact resistance has been reported [3]. However, a feasible method to grow large-area, high-quality tunneling barrier has not been realized. We demonstrate highly controlled surface oxidation in layered indium selenide (InSe) FETs to achieve enhanced transport properties. By utilizing the inherent layered structure of 2D materials, the surface oxidation can be controlled with atomic-scale precision as indicated by transmission electron microscopy. The characteristics of the oxide layer is further examined by a combination of Raman spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy. The InSe FETs with oxide tunneling barrier exhibit distinct transport properties, including a field-effect mobility of 1240 cm$^2$/Vs, ohmic contact at low temperature, low trap state density, and a contact barrier of 13 meV. With the ultrathin oxide barrier, we successfully achieve the suppression of the Fermi-level pinning effect, which severely limits the tunability of the electrical transport properties. Consequently, the contact barrier of the InSe FETs can be effectively modified by using contact metals with different work functions. The realization of high-performance InSe FETs with low contact barrier via oxide tunneling barrier shows promising results in utilizing 2D semiconductor materials for practical applications.

References

EP03.05.41
Hybrid Black Phosphorus/Zero-Dimensional Quantum Dot Phototransistors—Tunable Photodoping and Enhanced Photoresponsivity

A-Young Lee, Hyun-So Ra, Min-Hye Jeong and Jong-Soo Lee; DGIST, Daegu, Korea (the Republic of).

Recently, black phosphorus (BP) with direct band gap exhibited excellent potential for optoelectronic applications because of its high charge carrier mobility and low dark current as well as the variable band gap of 0.3–1.5 eV depending on the number of layers. However, few-layer BP-based phototransistors (photo-FETs) have been limited in sensitivity and wavelength selectivity. To overcome the drawback of these photo-FETs, we studied hybrid photo-FETs combined with the novel properties of the two materials between the channel and sensitizer layers. By combining a strong absorbance of a quantum dot (QD) layer and a two-dimensional layer material with high carrier mobility, the hybrid photo-FETs are expected to produce high-performance photodetectors that can effectively control the responsivity, detectivity, and response time. In this study, we demonstrate that the photogenerated carriers formed from QD sensitizer layers migrate to the BP transport layer with high charge mobility and not only improve the photodetector performance but also enhance the photodoping effect of the BP transport layer with an ambipolar characteristic by electrons transferred from n-type CdSe QDs or holes injected from p-type PbS QDs. The responsivity and detectivity of hybrid BP/0D photo-FETs exhibit $1.16 \times 10^4$ AW$^{-1}$ and $7.53 \times 10^3$ Jones for the BP/CdSe QD photo-FET and $5.36 \times 10^4$ AW$^{-1}$ and $1.89 \times 10^3$ Jones for the BP/PbS QD photo-FET, respectively. The photocurrent rise
Methods for synthesizing nanosheet materials are divided into two types, the top-down method and the bottom-up method. In the top-down method, the ultrasonic exfoliation method is known as a common process which is simple and highly productive process, but it is hard to synthesize few-layered solid solutions such as Mo(S,Se)₂; because a bulk solid-solution is required as a starting material. On the other hand, as a representative of the bottom-up method, the chemical vapor deposition method is widely known for the synthesis of nanosheets with high quality and large area, but its drawbacks include low yield, poor productivity, and a vacuum process entailing high process costs. Thus, each recent technology entails trade-offs between quality, productivity and cost. Therefore, this study proposes a synthesis method of metal chalcogenide solid solutions with high productivity under supercritical reductive conditions. Moreover, this process realizes synthesizing Mo(S,Se)₂ and (Mo,W)S₂ nanosheets from MoO₃, WO₃, pure sulfur, selenium and non-toxic solvents at 400°C for a shorter time than 60 min. XRD patterns and Raman spectrum for Mo(S,Se)₂ and (Mo,W)S₂ were consistent with previous reports. The peak shift was observed by Se or W being incorporated in MoS₂. TEM images revealed that Mo(S,Se)₂ and (Mo,W)S₂ have edge-rich structures composed of nanosheets for both samples. The formation of this nanosheet structure should be caused by high affinity between supercritical fluid and the surface of TMDs nanosheets. The XPS analyses showed the almost stoichiometric composition (Metals : Chalcogens ≈ 1 : 2) among the both samples. The hexavalent Mo and W derived from MoO₃ and WO₃ were not detected, whereas only tetravalent Mo and W were detected; thus, we concluded that the reduction process had completely progressed. Furthermore, STEM images at an atomic level showed that elements were solid-dissolved without segregation.

We achieved the synthesis of Mo(S,Se)₂ and (Mo,W)S₂ using less-toxic starting materials for a short time. This synthesis process combining environmental adaptability and easiness can be also be applied for synthesis of various other kinds of two-dimensional metal chalcogenides.

**EP03.05.42**

**Synthesis of Mo(S,Se)₂ and (Mo,W)S₂ Nanosheets from Metal-Oxide and Pure-Chalcogen Precursors In Supercritical Fluids**

Yuta Nakayasu, Hiroki Kobayashi and Ibaru Honma; Tohoku University, Sendai, Japan.

Few layer black phosphorus (BP) has attracted tremendous interest in optoelectronic applications due to their optical and excellent semiconducting properties. It has a thickness-dependent bandgap of 0.3 eV for bulk to ~2 eV for single layer, high hole mobility of ~1000 cm²V⁻¹s⁻¹ and high on-off ratio up to 10⁵. Under air ambient condition, the surface of black phosphorus is rapidly degraded by forming phosphorus oxide. In our study, we demonstrate that 1, 2-ethanediethiol (EDT) treatment effectively reduces oxygen atoms weakly adsorbed on the BP surface. The oxygen reduction mechanism on the degraded BP by EDT treatment is analyzed by utilizing density functional theory (DFT) calculations, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Also, the reduction of surface oxides by EDT treatment results in the recovery of the electrical properties. Furthermore, we show that BP field-effect transistors (FET) are preserved against humidity in air for more than one week using hexagonal boron nitride as a passivation layer. The results suggest that the EDT treatment to degraded BP FET presents a potential for practical semiconductor device applications, such as logic gates, photodiodes, and solar cells.

**EP03.05.43**

**Recovering Effect on Oxygen-Degraded Black Phosphorus by 1,2-ethanediethiol Surface Treatment**

Dohyun Kwak, Hyun-Soo Ra, Min-Hye Jeong, A-Young Lee and Jong-Soo Lee; DGIST, Daegu, Korea (the Republic of).

Two-dimensional layered black phosphorus has shown great potential for next-generation electronics with tunable band gap and high carrier mobility. For the electronic applications, the thickness modulation of a BP flake is an essential due to its thickness-dependent electronic properties. However, controlling the precise thickness of few-layer BP is a challenge for the high-performance device applications. In this study, we demonstrate that thermal treatment under ambient condition precisely controls the thickness of BP flake. The thermal etching method utilizes the chemical reactivity of BP surface with oxygen and water molecules by the repeating formation and evaporation of phosphoric acid during thermal annealing. The thermally etched BP FETs show a high hole mobility of ~576 cm²V⁻¹s⁻¹ and a high on-off ratio of ~10⁵. In spite of the thermal treatment under air ambient condition, the BP FETs showed long-term stability without significant degradation for one month resulting from the conservation of phosphorus layered structure under phosphorus oxide layers.

**EP03.05.44**

**Thickness-Controlled Black Phosphorus with Enhanced FET Stability Under Ambient Condition**

Min-Hye Jeong, Dohyun Kwak, Hyun-Soo Ra, A-Young Lee and Jong-Soo Lee; Daegu Gyeongbuk Institute of Science and Technology, Daegu, Korea (the Republic of).

The interfaces between magnetic nanoparticles(NPs) and atomic layer material(ALM) are receiving attention in developing high-density magnetic memory devices because of the finding of the ALM-induced perpendicular magnetic anisotropy [1, 2] and the template effect of ALM nanomesh(NM), which is a kind of moiré structures, for the ordered growth of metal nanoparticles [3]. In this study, we report a successful growth of monodisperse FePt NPs on hexagonal boron nitride(h-BN) NM. The h-BN NM was grown on a Ru(0001) thin film on sapphire c-plane by means of chemical vapor deposition. FePt was deposited on the surface of h-BN NM by means of RF magnetron sputtering at room temperature. Through the scanning tunneling microscopy measurements, we found that FePt deposited on h-BN NM/Ru(0001) forms monodisperse disk-like NPs with a diameter of 3 nm which corresponds to the periodicity of h-BN NM. In contrast to Fe which has been reported to aggregate into large NPs on AL NM [3], this study demonstrated that small monodisperse FePt NPs can be grown by utilizing h-BN NM as a template. In the conference, we are going to discuss the magnetic properties of the FePt NPs and the effect of thermal annealing.

References:

Fully-printable devices have attracted much interest in the field of large-scale printable electronics. Apart from high-performance inks for conductive patterns, a dielectric component is also very important in electronics, for example, in capacitors and electroluminescent devices. The current printable dielectric inks most commonly utilise barium titanate (BaTiO3) as the main filler material, having the drawbacks of high cost, thick printed layer and demanding curing process. Here, we employed solution processed hexagonal boron nitride (h-BN), as a filler material incorporated into a commonly used polymer binder matrix, with enhanced dielectric properties, enabling a cost effective, single-pass printable, pin-hole free dielectric ink.

We exfoliate the h-BN directly into the solvent and polymer binder matrix by ultrasonication for 12 hours followed by centrifuge. This 'one-pot' process introduces exfoliated h-BN flakes directly into the ink system and does not require any additional chemical surfactant or post processing. A stable h-BN ink system is formulated by an optimised proportion of the h-BN filler material, polyurethane (PU) polymer binder and butyl cellosolve (BC) solvent. The ink shows excellent printability on polymer substrates (e.g. PET) with 15mPa.s viscosity at 10 s⁻¹ shear rate under 25°C, and is suitable for coating and printing. The deposited film has a high transparency with ~ 85% transmittance. Measurement on printed parallel-plate capacitor arrays with our inks containing 0.6wt% h-BN show a two-fold increase in relative permittivity (εr) over pristine PU. An average areal capacitance 336pF/cm² is achieved by averaging an array of capacitor samples with an electrode-overlap area of 20-50mm². We then incorporate our printed capacitors to construct a simple 4-bit dynamic random-access memory (DRAM), demonstrating the viability of our ink for printable electronics.

MoS2 FETs with Doped HfO2 Ferroelectric/Dielectric Gate Stack

Atomristors—2D Non-Volatile Memory and Switches

We have observed non-volatile resistance switching (NVRS) memory effect in semiconducting or insulating atomic sheets in a standard vertical device configuration. In this work, we demonstrate NC-MoS2 FETs by incorporating a ferroelectric doped HfO2 (Al:HfO2 or Si: HfO2 ) in the FET gate stack. Standard HfO2 has monoclinic crystal structure which can be transformed into orthorhombic phase by temperature, pressure, or doping. The electrical properties of the doped HfO2 thin-films can be tuned from dielectric to ferroelectric and even antiferroelectric by changing dopant type (Zr, Al, Si, Gd, Y, etc.), dopant fraction and/or capping layer. The ferroelectric nature of typical doped HfO2 thin film can be confirmed by the polarization measurement. Here, Si:Hf composition is kept fixed by controlling the 3DMAS/TEMAH pulses during the ALD. We observe steep SS in FETs when used these FE in the gate stack with carefully matched FE/DE bilayer. The NC-MoS2 FET built on a typical FE/DE bilayer showed a significant enhancement of the SS to 57 mV/dec at room temperature, compared with SSS = 67 mV/dec for the MoS2 FET with only HfO2 as a gate dielectric.

Neuristors from Solution-Processed 2D Materials

Non-linear dynamical systems such as neuristors embody essential complexity in spike-timing behavior for hardware implementation of neuromorphic computing architectures. In order to experimentally realize a neuristor, the constituent materials need to possess attributes that enable concurrent functionality as a distributed energy source, an energy storage element, and an active channel. Towards this end, two-dimensional (2D) materials such as MoS2, show promise for neuristors since they have demonstrated bipolar resistive switching at low fields, gate-tunable learning response, heterosynaptic plasticity in memtransistors, and multi-bit memory. Furthermore, solution-processed 2D material thin films possess versatile chemical tailoring, compositional tunability, and compatibility with flexible substrates for large-area printed electronics. In this talk, solution-processed thin-film MoS2 memristors are shown to possess all-or-nothing spiking behavior in a geometry that is amenable to in situ optical, Raman, and photoluminescence microscopy. Furthermore, in situ thermal imaging reveals three kinds of switching behaviors (i.e., soft switching with negative differential negative resistance, hard switching with thermal runaway, and irreversible switching) that are correlated with distinct features of filaments and dendrites. This resistive switching is found to be a generalized phenomenon across a wide range of 2D materials such as MoS2, WS2, ReS2, and InSe films since the morphology of composite thin-films with large curvature flakes plays a dominant role in field-emission transport between neighboring flakes. The net result is that curvature-induced large local fields achieve resistive switching at low electric fields (~4 kV cm⁻¹) due to electrical discharge. Overall, this work utilizes temperature as a new state-variable, which can be exploited for a range of applications including higher-order memristors, neuristors, random number generators, and chaotic circuits. In particular, the circuit modeling neuristors based on solution-processed MoS2 thin-films are used to realize Pearson-Anson oscillators with qualitative features similar to the Hodgkin-Huxley axon model.

Atomristors—2D Non-Volatile Memory and Switches

We have observed non-volatile resistance switching (NVRS) memory effect in semiconducting or insulating atomic sheets in a standard vertical device configuration. Results suggest a rich multi-physics effect persistent in both poly- and single-crystalline monolayer and few-layer sheets. NVRS is observed in several TMDs including MoS2, MoSe2, WSe2, and WS2 and also in h-BN. This alludes to a universal memory effect in non-metallic 2D materials. Our findings overturn the contemporary thinking that non-volatile memory is not scalable below a few nanometers. Emerging concepts in non-volatile flexible memory fabrics, zero static power radio-frequency switches, and brain-inspired (neuromorphic) computing could benefit substantially from the pervasive NVRS effect in atomic sheets. Experimentally results for FE switching have been achieved at operating frequencies beyond 50GHz with the potential for
Fundamental Properties and Device Prospectives of Emerging Two-Dimensional Materials

Han Wang; Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States.

In this talk, I will discuss our recent work in studying the electronic, optical and ferromagnetic properties of emerging two-dimensional materials, and in developing them for novel electronic and photonic device applications. The first part of the talk will focus on discussing the basic properties of emerging 2D materials such as black phosphorus and its applications in mid-infrared optoelectronics. Our recent research on the phonon-spin and phonon-electron coupling in ferromagnetic monolayer materials will also be presented. In the second part of the talk, I will discuss our work on the origami and kirigami of 2D materials and the development of substrate-free foldable and adaptive membrane electronics based on these materials. A unique method for the deterministic folding of 2D materials and their heterostructures will be discussed. Reconfigurable electronic devices and circuits realized through the patterned folding of 2D material heterostructures will be reported. I will conclude with remarks on promising future research directions of two-dimensional electronic and photonic devices, and how the newly developed 2D material origami and kirigami techniques may enable adaptive reconfigurable electronics and advanced sensor technologies.

Synaptic Barristor Based on Phase-Engineered Two-Dimensional Heterostructures

Woong Huh1, Seonghoon Jang1, Jae Yoon Lee1, Donghun Lee1, Jung Min Lee2, Hong-Gyu Park2, Jong Chan Kim1, Hu Young Jeong4, Gunuk Wang1 and Chul-Ho Lee2; 1KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, Korea (the Republic of); 2Department of Physics, Korea University, Seoul, Korea (the Republic of); 3School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 4UNIST Central Research Facilities, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Heterostructures built from various two-dimensional (2D) layered materials, including semimetallic graphene, semiconducting transition metal dichalcogenides, and insulating hexagonal boron nitride, are emerging material platforms for low-power and high-performance electronic devices because of their high-quality heterointerfaces with atomic precision as well as the exceptional properties from their atomically thin constituent materials. In addition, the competitive ability to electrostatically control the energy barrier (or band alignment) at the van der Waals (vdW) interfaces allows us to rationally design 2D functional heterostructures by band-structure engineering for a variety of gate-tunable electronic devices. Particularly, a vertical triode with a gate-controlled Schottky barrier, so-called the ‘barristor’, has been proposed as a new switching device with potential advantages in scaling and integrating highly-networked device functionality. Such unique capabilities of 2D heterostructured devices can also offer unexplored opportunities for realizing an energy-efficient artificial synapse with high controllability. Nevertheless, the artificial synapse based on 2D heterostructures has rarely been realized elsewhere, but only bulk form of the diode was developed at that time. [Yan, R. et al., Nano Lett. 2015, 15 (9), 5791] The point is that gate-tunable p-n heterojunction and band-to-band tunneling are the key to operate as TFET.

Here, we demonstrated black phosphorus–tin diselenide (BP-SnSe2) heterostructure tunneling field-effect transistors operating as both Esaki diode mode with negative differential resistance (NDR) region and backer diode mode at negative and positive gate bias, respectively. By introducing relatively high carrier concentration even in few-layer form of SnSe2 sheets, only BP channel was able to be modulated by global electrostatic gating, making the device fabrication and operation much simpler. Gate-tunable 2 staggered band alignment at the heterojunction was demonstrated by scanning photocurrent microscopy (SPCM). Temperature-dependent NDR behavior was unlikely with a conventional tunneling diode, but it was successfully explained by series resistance and thermal assisted tunneling mechanism. Also, the backward rectification behavior followed the thermionic emission theory, which confirmed that the another potential barrier had been created at the heterojunction due to the negative bias electrostatic gating. Besides, we pointed out that deposition conditions of the Al2O3 passivation on the device were important to observe these effects.
Two-dimensional (2D) layered materials have been actively explored for electronic device applications because of their ability to form van der Waals heterostructures with unique electronic properties. Vertical integration of atomically thin 2D materials can enable the design of three-dimensional (3D) circuit which is a promising pathway to continuously increase device density. In this study, we vertically stack 2D materials, such as graphene, MoS2 and black phosphorus (BP) to build transistors, heterostructure p-n diodes and 3D logic circuits. The vertical transistors built from MoS2 or BP semiconductor exhibit a good on-off ratio of up to 105 and high current density of ~200 A cm−2 at a very small VOCs of 50 mV. The graphene/BP/MoS2 vertical heterostructure p-n diodes show a high gate-tunable rectification ratio of 106. Finally, we have demonstrated a 3D CMOS inverter by vertical integration of graphene, BP (p-channel), graphene, MoS2 (n-channel) and a 50-nm-thick gold film in sequence. The ability to vertically stack 2D layered materials by van der Waals interactions offers an alternative way to design future 3D integrated circuits.

Vertically Stacked van der Waals Heterostructures of 2D Layered Materials for Electronic Devices and 3D Logic Circuits

Jinshui Miao1, Zhihao Xu1, Haschuan Wai1 and Chuan Wang1; 1Electrical and Systems Engineering, Washington University in St. Louis, St. Louis, Missouri, United States; 2Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Michigan State University, East Lansing, Michigan, United States.

As the dimensions of semiconducting channels in field effect transistors (FETs) decrease, the contact resistance of metal-semiconductor interface at the source and drain electrodes dominates the performance. Two dimensional (2D) transitional metal dichalcogenides (TMD) such as molybdenum disulphide (MoS2) have been demonstrated to be excellent semi-conductors for ultra-thin FETs. However, unusually high contact resistance has been observed across the metal-2D TMD interface. Recent studies have shown that van der Waals (vdW) contacts formed by graphene on 2D TMDs provide lowest contact resistance. However, vDW contacts between evaporated three-dimensional metal and 2D TMDs have yet to be demonstrated. Here, we report the realization of ultra-clean vDW contacts between indium metal electrodes and thin MoS2. Using scanning transmission electron microscopy (STEM) imaging, we show that the indium-MoS2 interface is atomically sharp with no detectable chemical interaction between the metal and 2D TMD, suggesting van-der-Waals-type bonding between the metal and MoS2. We show that the contact resistance of indium electrodes is ~ 800 Ω-μm – amongst the lowest observed for metal electrodes on MoS2 and is translated into high performance FETs with mobility in excess of 100 cm2-V-s−1. We also demonstrate low contact resistance of 220 Ω-μm on NbS2 and near ideal band offsets, indicative of defect free interfaces, in WS2 and WSe2 contacted with indium.

Rewritable Floating Gates in Two-Dimensional Electronics by Tunnelling Triboelectrification

Tae Yun Kim1, Seongsu Kim2, Christian Falconi1 and Sang-Woo Kim1; 1 Electronic Engineering, University of Tor Vergata, Rome, Italy; 2 Advanced Material Science & Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Gates can electrostatically control charges inside two-dimensional materials. However, integrating independent gates typically requires depositing and patterning suitable insulators and conductors. Moreover, after manufacturing, gates are unchangeable. Here we introduce tunnelling triboelectrification for localizing electric charges in very close proximity of two-dimensional materials. As representative materials, we use chemical vapour deposition graphene deposited on a SiO2/Si substrate. The triboelectric charges, generated by friction with a Pt-coated atomic force microscope tip and injected through defects, are trapped at the air-SiO2 interface underneath graphene and act as ghost floating gates. Tunnelling triboelectrification uniquely permits to create, modify and destroy p and n regions at will with the spatial resolution of atomic force microscopes. As a proof of concept, we draw rewritable p/n- and p/p+ junctions with resolutions as small as 200 nm. Our results open the way to time-variant two-dimensional electronics where conductors, p and n regions can be defined on demand.
IAEs in 2D interlayer. Here, we report a new type of 2D electrode with van der Waals layered structure with 2D electron gas at intralayer space. The experimental and theoretical investigation on the electrical and ferromagnetic properties of 2D van der Waals [YCl]2+2e- and [LaCl]2+2e- electrides will be discussed. Our findings provide an important insight into the design strategy of new 2D electrides with magnetism based on the IAEs.

1:45 PM EP03.07.02

Strain-Induced Villari and Nagaoka-Honda Effects in a Two-Dimensional Ferromagnetic Chromium Tri-Iodide Monolayer

Mengchao Shi1, Pinghui Mo2, Jiuw Lu1 and Jie Lii3; 1College of Electrical and Information Engineering, Hunan University, Changsha, China; 2Department of Electrical Engineering, University of Washington, Seattle, Washington, United States.

We report our recent research findings on the impacts of strain on the emerging two-dimensional ferromagnetic chromium tri-iodide monolayer [1]. By combining first-principles density functional theory and Metropolis Monte Carlo methods, the strain-dependent magnetocrystalline anisotropy energy, Heisenberg isotropic symmetric exchange effects, anisotropic symmetric exchange effects, magnetic moment, and Curie temperature are quantitatively analyzed.

The Villari effect, i.e. the inverse magnetostriective effect, and the Nagaoka-Honda effect, i.e. the inverse Barret effect are unresponsive. It is shown that, though a small strain exhibits small impacts on the Curie temperature, it can noticeably influence the hysteresis curve shape and significantly alter the coercive magnetic field. This offers one of the possible explanations of the large variation of coercive magnetic field measured on the strain-proxexfoliated CrI3 monolayers [2]. This also indicates the importance to push strain to reduce device-to-device variation of magnetic properties in the monolayer-based spintronics memory and logic devices. It is revealed that strain can induce changes on a series of key magnetic properties (e.g., the strain-induced magnetization direction flip, the strain-induced ferromagnetic/antiferro- magnetic transition, the strain-induced change of magnetic coercivity, etc.). The strain-induced properties unreported here are of practical interests to implement next-generation monolayer-based devices and sensors.

Reference:

2:00 PM EP03.07.03

In Situ Substitutional Doping of Monolayer MoS2—The Significance of Substrates

Kehao Zhang1, Brian Bersch1, Nicholas Borys2, Ke Xu3, Simin Feng4, Jaydeep D. Joshi5, Rafik Addou6, Chexi Zhang7, Ke Wang8, Robert Wallace9, Kyeongjae Cho5, Patrick Vora10, Mauricio Terrones1, Susan Fullerton-Shew1, Feliciano Schuck2, and Joshua Robison1; 1The University of Pennsylvania State University, University Park, Pennsylvania, United States; 2Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 4George Mason University, Fairfax, Virginia, United States; 5The University of Texas at Dallas, Richardson, Texas, United States.

Doping, as a fundamental technique to functionalize conventional semiconductors, holds unique promise to tune the properties of 2D materials. However, due to the ultra-low thickness and simple structure of 2D materials, the chemical environment (i.e. substrates) may drastically modify the properties of synthetic 2D materials, leading disagreements between the experiments and simulations. Indeed, realizing the in-situ substitutional doping of monolayer MoS2, by chemical vapor deposition necessitates the in-depth understanding of the substrates’ properties. Here, we present successful in-situ doping studies achieved by fine-tuning the substrate properties. First, the substrate surface ineffectiveness directly impacts on the doping efficacy of manganese (Mn). Substitutional Mn doping of monolayer MoS2 can only be achieved on 2D substrates such as graphene due to the presence of polarized dangling bonds on the surface. On 3D substrates such as graphene and SiO2, Mn is adsorbed by the surface dangling bond instead of being bonded in the MoS2 lattice (Nano Lett., 2015, 15 (10) 6586-6591). Second, the substrate surface termination guides the film/substrate charge transfer and limits carrier density tunability by foreign dopants. Aluminum terminated sapphire (c-sapphire) surface exhibits strong electron doping to the synthetic MoS2 monolayers, leading the 100X higher electron concentration in MoS2 than its counterpart grown on oxygen terminated sapphire (r-sapphire) surface, evident by field effect transistor characterization. Meanwhile, the reduced electron doping and the interaction between Mn and surface oxygen on r-sapphire results in 100X enhancement of photoluminescence (PL) intensity and carrier lifetime (~ 1 ns) (Sci. Rep., 7 (1), 16938). Utilizing r-sapphire, nearly degenerately n-doped MoS2 is realized by 1 at% Re substitutional doping, evident by various electronic measurements including conductive atomic force microscopy, scanning tunneling microscopy and FETs, agreeing well with density function theory (DFT) calculations. In contrast, 1 at% Re doping is unable to effectively tune the electron doping from the strong electron doping from Al terminated substrate. Surprisingly, X-ray photoelectron spectroscopy (XPS) and low temperature PL indicates that Re doping is also able to reduce the density of sulfur vacancies by 25% (Adv. Funct. Mater., 2018, 28, 1706950), demonstrating the possibility of multifunctional doping of 2D materials.

2:15 PM EP03.07.04

Rational Design of 2D Magnetic Materials

Nathan Frey, Hemant Kumar, Liang Dong and Vivek Shenoy; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Recent experimental success in the realization of twodimensional magnetism has invigorated the search for low-dimensional material systems with tunable magnetic anisotropy that exhibit intrinsic long-range ferromagnetic order. Using a crystal field theory model and first-principles simulations, we demonstrate intrinsic ferromagnetism, high magnetic moments, high Curie temperatures, and intrinsic semiconducting and half-metallic transport behavior in nitride and ordered double-transition-metal MXenes. We report that modifying the surface termination and transition metal in monolayer Mn3N2, nitride MXenes gives rise to a rich diversity of noncollinear spin structures and finely tunable magnetocrystalline anisotropy. We predict that manipulating the strength of the spin-orbit interaction and electron localization via the chemical degrees of freedom can induce sufficient anisotropy to counteract thermal fluctuations that suppress long-range magnetic order. Ti3N2 and Mn3N2 MXenes have continuous O(3) and O(2) spin symmetries, respectively, that may be broken by an applied field, while Cr2N2O and Mn2N2O are intrinsic Ising ferromagnets with out-of-plane easy axes and magnetic anisotropy energies up to 63*105 eV/atom. These systems also exhibit both gapped and gapless Dirac points near the Fermi level. Our work suggests that nitride MXenes offer a promising avenue for achieving both practical spintronic devices and investigating fundamental spin processes in two-dimensional materials.

2:45 PM EP03.07.05

Hematene—A New Non-van-der Waals 2D Material

Aravind P. Balan1, Sruhti Radhakrishnan1, Cristiano F. Woelfler1, Shyam K. Sinha2, L. Z. Deng3, Carlos de los Reyes1, B. Mannmadha Rao4, Maggie Paulose5, Ram Neupane6, Robert Vajtai7, Ching-Wu Chu7, Gelu Costin6, Douglas S. Galvao1, Angel A. Martí3, 8, Peter A. van Aken8, Oomman K. Varghese7, Chandra S. Tiwary3, M R. Anantharaman9 and P. M. Ajayan3; 1Applied Physics Department, University of Campinas, Campinas, Brazil; 2Departamento de Física, Universidade Federal do Paraná, Curitiba, Brazil; 3Department of Electrical and Information Engineering, Hunan University, Changsha, China; 4George Mason University, Fairfax, Virginia, United States; 5The University of Texas at Dallas, Richardson, Texas, United States.
University, Houston, Texas, United States; 3Max Planck Institute for Solid State Research, Stuttgart, Germany; 4Department of Chemistry, Rice University, Houston, Texas, United States; 5Department of Earth Science, Rice University, Houston, Texas, United States; 6Department of Physics, University of Houston, Houston, Texas, United States; 7Texas Center for Superconductivity, University of Houston, Houston, Texas, United States; 8Department of Physics, Cochin University of Science and Technology, Cochin, India.

With the discovery of graphene, there is a renewed interest in two-dimensional (2D) nanostructures due to their unique physical and chemical properties, as well as their potential applications in different fields ranging from electronics to biomedical ones. Many inorganic (IGAs) structures similar to graphene have been synthesized and are being exploited for novel applications. Many of these structures are van der Waals 2D solids, and it is possible that these solids are not stable after 200 ps (picoseconds) and [001] oriented plane is the most stable one [1].


3:00 PM BREAK

3:30 PM EP03.07.06
Ferromagnetic Quasi-Atomic Electrons in Two-Dimensional Interlayer Space of Digadolinium Carbide Electride Seungyong Lee1, Jae-Yeol Hwang1, Jongho Park1, Chandani N. Nandadasa2, Seong-Gon Kim2 and Sung Wng Kim1; 1Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of k); 2Department of Physics & Astronomy and Center for Computational Sciences, Mississippi State University, Mississippi, United States.

Electride is a generalized form of interstitial anionic electrons (IAEs) confined in the positively charged cavities as found in many compounds and elements. Depending on the size and geometry of cavities, IAEs show different degrees of localization, exhibiting various exotic properties. The most strongly localized IAEs are theoretically conceptualized as quasi-atoms in elemental electrides under high pressure. However, there is an experimental evidence for quasi-atomic IAEs has yet been discovered in practical electrides. Furthermore, as the pressurized potassium can be stabilized by ferromagnetic ordering, a quasi-atomic IAE, which is the simplest magnetic system with a distinct magnetic moment, can behave as a ferromagnetic atom, but no ferromagnetic electride originating from quasi-atomic IAEs has been realized. In this talk, present the IAEs in layered [Gd2C]2+:2e− as atoms of ferromagnetic elements in two-dimensional interlayer space. We verified that the inherent quasi-atomic IAEs have their own magnetic moments of ~0.5 Bohr magneton per one IAE, which are critical for the ferromagnetism in [Gd2C]2+:2e−. It was found that the ferromagnetic IAEs facilitate the exchange interactions between not only intralayer gadolinium atoms but also interlayer gadolinium atoms across IAEs, forming ferromagnetic Gd-IDAE-Gd layer separated by non-magnetic carbon atomic layer, which exhibits a characteristic anisotropy in magnetoresistance analogous to those of typical ferromagnetic/non-magnetic layered systems. The substitution of paramagnetic chlorine atoms for IAEs proves the existence of ferromagnetic quasi-atomic IAEs from a clear transition to non-electride antiferromagnetic Gd3C3I caused by attenuating all interatomic exchange interactions of IAEs with gadoliniums, which are consistent with theoretical calculations. These results confirm that strongly localized quasi-atomic IAE at two-dimensional interlayer space acts itself as a single ferromagnetic element and triggers a spin alignment in antiferromagnetic [Gd2C]2− lattice framework. These results present a broad opportunity to tailor intriguing ferromagnetism originated from quasi-atomic interstitial electrons in low-dimensional materials.

Reference

3:45 PM EP03.07.07
Strong Phonon-Spin and Phonon-Electron Coupling in Monolayer Ferromagnetic CrBr3 Jiangbin Wu1, Miaolong Lin2, Amber McCreary3, Zhonghao Du1, Angela Hight Walker1, PingHeng Tan2 and Han Wang1; 1University of Southern California, Los Angeles, California, United States; 2Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China; 3National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The bulk chromic halides (CrCl3, CrBr3, and CrI3) have long been known as ferromagnetic materials with layered van der Waals structure. Recently, the monolayer CrI3 has been isolated and confirmed to be two-dimensional (2D) ferromagnet. Those 2D magnets offer an exciting platform for studying the interplay between the light and magnetic ordering. Here, we present the Raman spectroscopy study of monolayer CrBr3 from the chromic halides family, which also possesses ferromagnetic properties in its monolayer form. The phonon modes are identified by combining the polarized Raman spectroscopy and density functional perturbation theory (DFPT). The Raman frequencies show an abnormal redshift below the Curie temperature (CT) due to strong spin-phonon interaction. The CT of monolayer CrBr3 is measured to be at 20 K, which is about 15 K lower than that in its bulk form. Moreover, the resonance Raman spectroscopy measurement is used to reveal the mechanism of vibronic (phonon-electron) coupling in the monolayer CrBr3. The E2g mode at 150 cm−1 plays a key role in the Jahn–Teller distortion with the parity-forbidden d-d transition (4T2), which is confirmed by DFPT calculations. This study paves the way to understand the magneto-optical interaction in the 2D transition metal halides.

4:00 PM EP03.07.08
Electric Field Dependence of Dzyaloshinskii-Moriya Interaction in Two-Dimensional Ferromagnets Takashi Koretsune; Tohoku University, Sendai, Japan.

Recent experimental observations of ferromagnetism in two-dimensional van der Waals crystals open new possibilities in the applications of atomic layer materials. One characteristic feature in atomic layer films is the controllability of the electronic structures through the gate voltage or the electric field. In this study, we discuss the electric field dependence of the electronic structure in a two-dimensional ferromagnet, Cr3Ge2Te6, from first-principles calculations. Using the spin-current method[1], we evaluate the Dzyaloshinskii-Moriya interaction induced by the electric field. The results indicate the possibility of controlling the magnetic behavior by the electric field.

Fe₃GeTe₂ is one of the most promising candidates for two-dimensional (2D) ferromagnetic material based spin devices due to its high Curie temperature \( T_c = 220 \text{ K at bulk state} \). Long-range ferromagnetism in mechanically exfoliated Fe₃GeTe₂ flakes, which has a van der Waals layered structure, were investigated with varying thickness from bulk to a few layers. The Fe₃GeTe₂ crystal was synthesized with Fe deficiencies \( (x \approx 0.3) \) which yield significant variations in magnetic properties. The thickness dependence of the Curie temperature and magnetic coercivity were studied by observing the thickness dependent magnetic hysteresis loops using magneto optical Kerr effect (MOKE) and anomalous Hall effect measurements. Compared to Fe₃GeTe₂ with no Fe deficiencies, the Fe deficient Fe₃-xGeTe₂ shows much smaller coercivity, i.e. it is a magnetically softer material, at all thicknesses. Since soft ferromagnetism is advantageous for certain spin device applications such as current induced magnetic switching, Fe₃-xGeTe₂ is a 2D ferromagnetic material with high potential for spintronic applications.

Since the exfoliation of graphene, the magnetic orderings in two-dimensional (2D) materials have been intensively searched for the great potentials in nanostructured spintronics or valleytronics applications. However, the magnetism in 2D materials is once considered prohibited by Mermin-Wagner restriction and therefore the introduction of 2D magnetism may require external modulations, such as external electric field, defects, adatoms, and carrier doping. By density functional theory based first-principles calculations, we have predicted that substitutional doping of Co atoms at the edge of the most stable configuration of zigzag WSe₂ nanoribbons can induce long-range ferromagnetic ordering and robust half-metallicity that enables spin-selected doping. By density functional theory based first-principles calculations, we have predicted that substitutional doping of Co atoms at the edge of the most stable configuration of zigzag WSe₂ nanoribbons can induce long-range ferromagnetic ordering and robust half-metallicity that enables spin-selected transport along the nanoribbon edges. The half-metallicity was also found quite robust against large size, low doing density, and large tensile strain. The 2D extended materials with intrinsic magnetic ordering is more advantageous for practical spintronics or valleytronics applications due to their facile fabrication and good controllability. Recently in experiments, various 2D ferromagnets, such as CrI₃, have been synthesized, breaking the Mermin-Wagner restriction by realizing strong magnetocrystalline anisotropy in 2D structures. These results have attracted considerable attention in searching more ideal ferromagnetic 2D materials with high stability, robust long-range ordering, high Curie temperature \( T_c \), and possible tuning of magnetism. Through first-principles investigation, we have investigated a series of transition metal thiophosphate TMPS₄ monolayers and predicted their stable long-range ferromagnetic orderings with room-temperature \( T_c \). Integrated with 2D transition metal dichalcogenides (TMDCs) as heterostructures, they allow spin-valley coupled carrier injection from TMPS₄ into TMDCs.

References
(2) Unpublished results

Ferromagnetism Created from 2D Heterostructures Cheng Gong1, Peiyao Zhang2, Tenzin Norden2, Zhen Guo1, Apoorva Chaturvedi2, Yuan Wang1, Hao Zeng1, Hua Zhang2, Athos Petrou2 and Xiang Zhang1; 1University of California, Berkeley, Berkeley, California, United States; 2University at Buffalo, The State University of New York, Buffalo, New York, United States; 4Nanyang Technological University, Singapore, Singapore.

Intrinsic long-range ferromagnetic order has recently been discovered in two-dimensional (2D) atomic crystals. However, the prospect of 2D magnets remains largely hindered by the scarcity of 2D ferromagnets with limited diversity in magnetic attributes. In this context, creative ways to bring forth ferromagnetism from non-magnetic 2D materials are attractive and profitable for both fundamental physics and device applications. In this talk, I will show you the possibility of such creation based on our magneto-optical study of 2D heterostructures and discuss the underlying material physics. Our work paves the new path to harvest 2D ferromagnetism.

Surface Acoustic Wave Enhanced Photodetection of the Black Phosphorus-MoS₂ p-n Diode Enxiu Wu, Yuan Xie, Jing Liu and Daihua Zhang; Tianjin University, Tianjin, China.

We developed a new way to enhance the photoresponsivity of a van der Waals heterojunction p-n diode using surface acoustic waves (SAWs). The diode was constructed on top of a piezoelectric LiNbO₃ substrate and composed of p-type black phosphorus (BP) and n-type molybdenum disulfide (MoS₂) flakes that partly overlapped with each other. This layout facilitated the applied SAWs to rapidly drive carriers out of the depletion region. In this structural design, SAWs promoted the separation of photogenerated carriers, and thus greatly increased the photocurrent. The measured photocurrent for the device with SAWs was about 10³ times higher than that of the device without SAWs. The device using SAWs showed a photoresponsivity as high as 2.17 A/W at the wavelength of 532 nm.

This excellent performance was attributed to the SAWs suppressing electron–hole recombination in the device under light illumination. When light is incident on the surface of the material, the SAW piezoelectric field confines the photogenerated electrons and holes within the maxima and minima of the potentials in the conduction and valence bands, respectively. The potential along the confinement direction \( z \)-direction enables electrons and holes to rapidly shift their mean position and separates them spatially, which increasing carrier lifetime and lowering their recombination rate. Moreover, the BP and MoS₂ flakes form a V-shaped configuration that provides two misaligned paths that aid electrons and holes to rapidly drift into neutral regions. Our device exhibits promise as a high-performance photodetector and reveals new possibilities for acoustic devices in optoelectronics.
We investigate and compare changes in the optical response of 2H-MoTe2 and 2H-Mo1-xWxTe2 alloys as they undergo phase transition between semiconductor-to-semimetal phases in an all vdW device structure using an hBN gate dielectric and graphene contacts. Transition metal dichalcogenides (TMDs), such as Mo1-xWxTe2, exhibit a wide range of electronic properties (semiconducting, semimetal and metallic phases) with unique polymorphs that depend on atomic stacking and coordination. Phase modulation in TMDs is of interest for applications in electronics and optoelectronics. However, reversible tunability between such phases is challenging. This is largely due to a combination of significant differences in the free energy between TMD polymorphs and phase transition kinetic barriers. Phase modulation in MoTe2 has, however, gained recent interest due to the low barrier for transition (~40 meV) between its semiconducting and semimetal phases when compared to other TMDs. Evidently, dynamic control between the thermodynamically favorable semiconducting 2H phase and the metastable semimetal 1T' phase in MoTe2 is achieved with a variety of external stimuli, including strain, temperature and electrostatic doping. In the latter case, theory predicts that this phase transition occurs when the charge density exceeds ~10^{14} cm^{-2}, which has been experimentally verified in monolayer MoTe2 using ionic gating. However, reversible switching between these phases with a solid-state electrolyte gate still remains elusive. To circumvent the charge density requirements, theory predicts that the barrier for phase transition can be reduced in MoTe2 when alloyed with tungsten. Evidence of this was demonstrated by Zhang et al. (arXiv:1709.03835), where an all solid-state resistive random-access memory device fabricated with Mo1-xWxTe2 showed reversible switching between high and low resistance states. In addition to changes in conductivity, another feature of the phase transition in MoTe2 includes in-plane structural changes that should give rise to district optical anisotropic responses in monolayers. However, changes in the optical response in MoTe2 and Mo1-xWxTe2 alloys as they undergo phase transition remains highly unexplored.

In this study, both exfoliated and grown 2H-Mo1-xWxTe2 monolayers with x=0 and x=0.09 are explored. The optical response of the vdW stack are investigated using angle- and polarization-dependent reflection measurements as a function of gate voltage. Initial results showed changes in optical response of the vdW stack between (1.1–1.4) μm with applied gate voltage in alloys with x=0.09. Furthermore, polarization- and temperature-dependent Raman measurements are also performed to map out structural changes in Mo1-xWxTe2 as a function of applied gate voltage. These results will provide new insight into the optical response of these materials to enable new avenues for application in low-voltage and ultrafast modulators and other nanophotonic devices.
Laminar MoS₂ membranes are one of the two-dimensional (2D) materials showing outstanding practical applications in energy conversion/storage, as sensors, and as nanofluidic devices. Especially in water purification technologies, MoS₂ membranes forming abundant nanocapillaries from layered stacks of MoS₂ nanosheets demonstrate excellent ionic rejection with high water permeation rates, as well as long-term stability with no significant swelling when exposed to aqueous/organic solvents. Here, we demonstrate the dye functionalised MoS₂ laminar membrane (MoS₂/SY), under the influence of an applied electric potential, performed the ion transport through membrane as ionic sieving and size effect, which was found to decrease by about a factor of 5 in cations mobility at 3 μm thick compared to pristine exfoliated MoS₂ membrane as well as providing high stability in a range of pH conditions. Hydrated and non-hydrated cations were also performed with MoS₂/SY membranes, demonstrating that higher electric charge density affect predominantly toward inorganic cations of the comparable organic cation radii. We expect dye functionalized laminar MoS₂ membrane as performed ionic sieving with charge selectivity using chemically modified nanocapillary channels will be further utilized as electro-dialysis for water filtration technologies.

EP03.08.06
Exfoliation of Centimeter-Sized MoS₂ on Gold Substrate Facilitated by Strong Physisorption
Matěj Velecký1-3, Gavin E. Donnelly2, Héctor D. Abravanel and Fumin Huang1; 1Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States; 2School of Mathematics and Physics, Queen's University Belfast, Belfast, United Kingdom.

The conflict between the material quality and production scalability is one of the major challenges for future applications of two-dimensional (2D) materials. The typical size of monolayer transition metal dichalcogenides (TMDCs), such as MoS₂, achieved by mechanical exfoliation (which yields the highest quality materials) is currently limited to ca. 100 μm on insulating substrates. Recently, direct exfoliation or synthesis of TMDCs on metallic substrates of much larger dimensions has increasingly gained attention with a focus on potential applications in optoelectronics and catalysis. Herein, we report mechanical exfoliation of centimeter-sized monolayer MoS₂ on gold substrates, facilitated by strong physisorption between the two materials. The surface contamination and roughness of the Au substrates were found to be the key parameters for successful high-yield exfoliation. Microscopic and spectroscopic characterization of the MoS₂/Au heterostructures confirmed the existence of a strong van der Waals interaction (physisorption) between the two materials, resulting in a significant charge transfer without compromising the structural integrity of the monolayer MoS₂. Furthermore, electrochemical characterization revealed an efficient modulation of the monolayer MoS₂ density of electronic states by the underlying Au. This simple and reproducible exfoliation technique is a useful practical guide for the production of TMDCs, enabling studies of fundamental phenomena at the atomically-flat semiconductor-metal interface. It is likely that these findings will be applied in research areas such as electrode modification, photo voltaics, and photocatalysis.


EP03.08.07
Van der Waals Epitaxial Growth of 2D Metallic Vanadium Diselenide Single Crystals and Its Heterostructures
Zhepeng Zhang; Peking University, Beijing, China.

Two-dimensional (2D) metallic transition metal dichalcogenides (MTMDs) have recently emerged as a new class of materials for the engineering of novel electronic phases, 2D superconductors, magnets, as well as novel electronic applications. However, the mechanical exfoliation route is predominantly used to obtain such metallic 2D flakes, the batch production remains challenging. Herein, we report the van der Waals epitaxial growth of monocrystalline, 1T-phase, few-layer metallic VSe₂ nanosheets on an atomically flat mica substrate via a “one-step” chemical vapor deposition (CVD) method. The thickness of the VSe₂ nanosheets is precisely tuned from several nanometers to several tens nanometers. More significantly, the 2D VSe₂ single crystals are found to present excellent metallic feature, as evidenced by an extra-high electrical conductivity of up to 10⁶ S m⁻¹, 1-4 orders of magnitude higher than that of various conductive 2D materials. The thickness-dependent CDW phase transitions are also examined through low-temperature transport measurements, which reveal that the synthesized 2D metallic 1T-VSe₂ nanosheets should serve as good research platforms for the detecting novel many-body states. The heterostructures of VSe₂ and semiconducting TMDs also demonstrated in this work. The present results open a new path for the synthesis and property investigations of nanoscale-thickness 2D MTMDs crystals and their heterostructures.

EP03.08.08
Defects-Engineered WS₅ Exploration by KPFM—A Direct Insight into Band Structure
Xinyuan Wang; National University of Singapore, Singapore, Singapore.

Defects involved in the two-dimensional (2D) materials such as monolayer WS₂ during the chemical vapor deposition (CVD) process is always an inevitable and critical problem. Here, we report a simple and straightforward approach using Kelvin probe force microscopy (KPFM) to reveal the intrinsic structural defects distribution in monolayer WS₂. By combining the KPFM surface potential, conductivity, Raman and PL mapping, we found a vigorous correlation among them, which are consistent with our DFT estimation and STEM results. This KPFM potential image contains rich information of material band structure, which brings us a new perspective to explore material physical properties and may stand as a new reference of the band structure change in near future research.

EP03.08.09
Extrinsic P-Type Doping of Few Layered WS₂ Films with Niobium by Pulsed Laser Deposition
Urmilaben P. Rathod, Justin Egede, Andrey Voeyodin and Nigel Shepherd; Materials Science and Engineering, University of North Texas, Denton, Texas, United States.

The ability to control dopant profiles in the WS₂ and other transition metal dichalcogenide films is essential for creating p-n junctions, and applications in a wide range of electronic and optical devices including but not limited to transistors, photodiodes, and light emitting diodes. We report successful Nb doping of few layered 2H WS₂ films grown by pulsed laser deposition, by controlling the Nb content of the ablation targets. The undoped controls were n-type, exhibited a Hall mobility of 0.4 cm²/V.s, and characterized by a Fermi level at 1.41 eV from the valence band edge. The latter was determined using ultraviolet photoelectron spectroscopy. Films doped at 0.5 and 1.1 atomic percentages niobium were p-type, and characterized by Fermi levels at 0.31 eV and 0.18 eV from the valence band edge. With increased Nb doping, the hole concentrations increased from 2.7x10¹⁰ to 8.6x10¹⁵ cm⁻³, while the mobility decreased from 7.2 to 2.6 cm²/V.s, presumably due to increased ionized impurity scattering. X-ray photoelectron spectroscopy indicates that Nb substitutes on W lattice sites. The approach demonstrates the potential of PLD for targeted doping of transition metal dichalcogenides.

EP03.08.10
Towards Large-Scale, Low-Temperature van der Waals Epitaxy of 2D Materials Using Atomic Layer Deposition
Miika Mattinen, Georgi Popov, Juni Hämäläinen, Peter King, Mikko Ritiala and Markku Leskelä; Department of Chemistry, University of Helsinki, Helsinki, Finland.
Van der Waals (vdW) epitaxy is a special case of epitaxy, which may occur when a film/substrate interface consists of inert surfaces without dangling bonds – as is the case with 2D materials. In contrast to conventional epitaxy, an indispensable tool for high-quality film growth, in vdW epitaxy the absence of covalent bonding between the film and the substrate allows for epitaxial growth even in case of large lattice mismatch or different crystal structure.[1,2] Thus, vdW epitaxy offers unprecedented possibilities to grow high-quality 2D materials as well as 2D/2D and 2D/3D heterostructures.

Atomic layer deposition (ALD) is a gas-phase thin film deposition technique based on sequential surface-reactions of alternately pulsed precursors. ALD enables facile and accurate control and uniformity of film thickness on wafer scale and complex 3D structures. Nevertheless, ALD also has certain challenges in the deposition of 2D materials stemming from the typically low reactivity of precursors on 2D surfaces: the growth rates may be low, films may become rough, and the grain size may be small due to large nucleation density and low deposition temperatures. These challenges, perhaps excluding the growth rate, may be overcome using suitable vdW epitaxy substrates.

We present results on ALD of various 2D materials, including semiconductors SnS2,[3] ReS2,[4] and PbI2[5] on commonly used vdW epitaxy substrates, sapphire and muscovite mica. In contrast to most previous reports on vdW epitaxy based on CVD or MBE, the depositions are performed both at relatively low temperatures from 75 to 400 °C and in modest, mbar-level vacuum conditions. The epitaxial relations are studied by out-of-plane and in-plane X-ray diffraction. Different tested materials and substrates show varying degrees of registration to the substrate as well as different numbers of domains. In some cases, epitaxy is enabled or improved by mild post-deposition annealing. In general, we find muscovite mica more effective than sapphire in enabling low-temperature vdW epitaxy of large-scale 2D films by ALD with possible applications in (opto)electronics, photovoltaics, and catalysis, for example.

**EP03.08.11**

**Human-Eye-Inspired Soft OptoElectronic Device Using MoS2-Graphene Curved Image Sensor Array**

Changsoo Choi1, 2, Minsung Kim1, 2 and Dae-Hyeong Kim1, 2; 1School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of); 2Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul, Korea (the Republic of).

Soft bioelectronic devices provide new opportunities for next-generation implantable devices due to their large to minimal immune responses and tissue damage. However, a soft form of the optoelectronic device for optical sensing and retinal stimulation has not been developed yet mainly because of the rigidity and bulkiness of conventional imaging modules. In this study, we describe a human-eye-inspired soft opto-electronic device using a high-density curved image sensor (CurvIS) array that leverages the atomically thin MoS2-graphene heterostructure and strain-releasing device designs. Unique advantages of the soft omnidirectional CurvIS array include the high-density array design, small optical aberration, and simplified optical. High photosensitivity and infrared blindness are important benefits of the MoS2-graphene-based ultrathin imager, and the CurvIS array successfully acquires pixilated optical signals. It is the first attempt to achieve high-quality imaging using the ultrathin MoS2-based opto-electronic device in a hemispherically curved format with the single-lens optics. We corroborate the validity of the proposed soft materials and device designs through theoretical analysis based on mechanics and optics. The ultrathin CurvIS array is applied to the human-eye-inspired soft implantable optoelectronic device that can detect optical signals and apply programmed electrical stimulation to optic nerves with minimum mechanical side effects. The proposed human-eye-inspired soft optoelectronic device is a step forward to the next-generation soft bioelectronics and the soft imaging elements of the retinal prosthesis.

**Reference**


**EP03.08.12**

**ARPES Study of MoS2 Monolayer on Graphite—Electronic Band Structure and Charge Dynamics of a Model 2D Van der Waals Heterostructure Interface**

Fabio Bussolotti1, Hidroyo Kawai2 and Kuan Eng Johon Goh1, 2; 1Institute of Material Research and Engineering, Singapore, Singapore; 2National University of Singapore, Singapore, Singapore.

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) layers are currently being investigated intensely in anticipation that they may play a major role in future optoelectronic technology, their importance being mainly motivated by the wide range of band gap tunability, formation of strongly bounded excitons, and spin-valley coupling phenomena in the monolayer (ML) form [1]. Combining TMDC MLs with other 2D layers to form van der Waals heterostructures represents a promising strategy to further extend the span of control of the electronic and optical properties of TMDC layers [2] as charge redistribution and structural changes can generally occur within the neighboring layers, depending on their relative orientation and separation [3]. Understanding the impact of interlayer interactions and structural defects on the electronic properties in TMDC-based van der Waals heterostructures is therefore a critical first step towards asserting their advantage for optoelectronic devices. Here we report the electronic band dispersion of MoS2 single crystal ML on highly ordered pyrolytic graphite substrate (HOPG) [4], a model system for the study of 2D Van der Waals heterostructure interface, as investigated by angular resolved photoemission spectroscopy (ARPES). The role of the MoS2-substrate interaction in determining the valence band dispersion of the MoS2 layer has been investigated with the support of dedicated band structure calculations. The complex interplay of wave function spatial extension, substrate-layer interaction and interfacial defects in determining the quasiparticle dynamics in the MoS2 layer will be discussed and clarified via detailed ARPES lineshape analysis. We discuss the relevance of our results for charge-transport in single layer devices as well as for the control of valley polarization in TMDC-based van der Waals heterostructures.

**References**


**EP03.08.13**

**Reduction of Fermi Level Pinning at Cu-BP Interface by Passivating Atoms on the Surface of Cu(111)**

Pengfei Ou and Jun Song; Department of Mining and Materials Engineering, McGill University, Montreal, Quebec, Canada.

Black phosphorus (BP) is a semiconducting material with a direct bandgap of ~2.0 eV in its monolayer and has attention in the application of field effect transistors (FETs). It is known that BP has an n-type contact with Cu which is a high work function metal, representing the strong Fermi level pinning (FLP) at Cu-BP interface. However, such FLP may hinder the achievement of high performance of field effect devices. In this regard, it is crucial to understand the FLP which occurs at metal-semiconductor interface. So, the possibility to reduce the FLP at Cu-BP interface by passivating the Cu(111) surface was examined using first-principles calculations in this study. The passivation by chlorine, sulfur, fluorine, nitrogen, and hydrogen atoms has been
Silicene, a two-dimensional (2D) silicon nanosheet, has gained immense interest due to potential applications, better compatibility, and expected integration with current silicon (Si) technology. Inspired by graphene, researchers have proposed that a 2D layered silicon nanosheet, Silicene, with a honeycomb lattice and van der Waals (vdW) interlayer interactions will be a perfect alternative to silicon as an anode material. This work explores the effects of silicene sheet size on its optoelectronic properties using time-dependent density functional theory (TDDFT). Four structures of hydrogen-terminated Silicene (Si13H22, Si19H30, Si54H74, and Si104H134) are considered with 13, 19, 54 and 104 Si atoms, respectively. Calculations were carried with hybrid density functional B3LYP functional and 6-31G basis set in Gaussian 16 package. The size of the sheet plays a significant role in changing its optoelectronic properties. It is observed that the structures have size tunable spectral response in the IV spectrum. The sheets showed a relatively smaller physical deformation compared to equivalent sized 2D Germanium sheets, noticeable on the largest structure considered in this work. As the number of atoms increases, from Si13H22 to Si104H134, the excitation energy decreases substantially by 29%. The absorption spectrum from the TDDFT calculations shows that the optical absorption moves towards the visible range of light, with increase in size. It is observed that the absorption is higher in the large structures. IR spectra calculations of various bond vibration show a good match with reported experimental results.

**EP03.08.14**

**TDDFT Studies on Sheet Size-Dependency of Optoelectronic Properties of 2D Silicon Mo Rajvan Alam1, Ganesh Subramanian Alwarappan1, Aashka Bhandari1, Walid M. Hassan2, Mohamed F. Shibli3, Sunil Patel2, Reza Nekovei1 and Amrit Vernal1; 1Texas A&M University Kingsville, Kingsville, Texas, United States; 2Physical Chemistry, Qatar University, Doha, Qatar; 3Qatar University, Doha, Qatar; 4Indian Institute of Science Education and Research Mohali, Mohali, India, United States.**

Considered. The calculated results illustrate that the passivated atoms can prevent the direct contact between BP and Cu(111), thus reducing FLP at Cu-BP interface. In particular, significant reduction in FLP can be achieved by chlorine- and sulfur-passivation. Furthermore, chlorine- and sulfur-passivated Cu(111) can form ohmic contact with BP, indicating almost zero Schottky barrier height (SBH). Our results suggest an effective surface passivation route towards the control of SBH for the BP-Cu system.

**EP03.08.15**

**2D Materials as Active Tunable Elements for Flat Optics Ozgur Burak Aslan1, Yifei Yu2, Linyou Cao3, 4 and Mark L. Brongersma1; 1Materials Science and Engineering, Stanford University, Stanford, California, United States; 2Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; 3Physics, North Carolina State University, Raleigh, North Carolina, United States.**

The ability to tune the optical spectra of atomically thin (2D) semiconducting transition metal dichalcogenides (TMDCs) is valuable for optoelectronic applications [1]. Strain tuning has been repeatedly employed to engineer the excitonic emission and absorption of monolayer (1L) TMDCs [2-10]. Various ways of applying strain have been demonstrated and strain engineering has been established as an external control of 2D materials. Even though strain can significantly alter the optical properties, the strain-dependent dielectric functions of 1Ls, the relevant property for an optical element, has not yet been reported. Moreover, repeatability of strain over many cycles is needed for active optical elements [5,8]. In this study, we investigate the strain-dependent optical properties of suspended monolayers. We exert air pressure on the 1Ls and achieve large tensile strain [2]. This way, as the TMDCs are impermeable to air [11], we realize reversible tuning of the optical spectra and thus the dielectric functions of 2D materials. We demonstrate redshifts of 100s of meV in the excitonic features which dominate the optical spectra of 1Ls. Due to the spectrally narrow excitonic features, we observe that the reflection spectra of the 1Ls are strongly dependent on strain and the wavelength of interest. In this manner, we pave the way to the use of 2D materials as active tunable elements for flat optics.

**EP03.08.16**

**Large-Area Deposition of High Quality MoS2 Films for the Applications of High Mobility Field Effect Transistors Kwang Hoon Jung1, 2, Sun Jin Yun1, 2, Yongsek Choi1, Jung Ho Cho1, Jung Wook Lim1, 2, Hyun-Jun Chai1, 2, Dae-Hyoug Cho1, Yong-Duck Chung1 and Gayoung Kim1, 2; 1Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); 2Korea University of Science and Technology, Daejeon, Korea (the Republic of); 3SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Korea (the Republic of).**

Recently, due to their remarkable electronic and optical properties, two dimensional (2D) transition metal dichalcogenides (TMDCs) have received much attention. Among 2D-TMDCs, molybdenum disulfide (MoS2) has been the most widely investigated. The monolayer MoS2 has a direct bandgap (1.8 eV) while the bulk MoS2 has an indirect bandgap energy of 1.2 eV. Monolayer MoS2 flakes had been first obtained by a mechanical exfoliation method. Although this exfoliation method has the potential to obtain high quality single crystalline MoS2 flakes, it is very unsuitable for large scale production and large area applications. On the other hand, large area methods of growing 2D-TMDCs thin films such as chemical vapor deposition (CVD) techniques require a high temperature and produce randomly distributed MoS2 islands on the substrate. Therefore, a new fabrication method to provide a high quality and wafer-scale uniformity is required for high quality and other 2D-semiconductors.

In typical CVD methods, S-vapor evaporated in the form of large S-molecules participates in the deposition of sulfides, and a high substrate temperature is required to obtain the high film quality. Contrarily, in the present work, we demonstrated a new method to obtain high quality MoS2 films on large wafer-scale substrates at a relatively low substrate temperature. We could produce small S-molecules by thermally cracking the evaporated large S-molecules. The S-molecules cracked in the high temperature cracking zone actively react with Mo precursor film to form MoS2 on the substrate. Very thin Mo precursor films were deposited on SiO2/Si substrates using an e-beam evaporator at room temperature. In the sulfuration chamber equipped with the S-cracker, the Mo films reacted with small S-molecules and formed high quality MoS2 films on wafer-scale large substrates which temperature was maintained at 570 °C or lower. The surface morphology and roughness of Mo and MoS2 films were characterized by atomic force microscopy and Raman spectroscopy was also carried out to determine the crystalline quality and uniformity of MoS2 films. The high resolution TEM images showed that the MoS2 film was successfully formed on SiO2 and the 6 nm-thick film was composed of well aligned 8-10 layers of MoS2. We also fabricated a field effect transistor with the MoS2 channel layer formed at 570 °C by the process proposed in this work. The MoS2 FETs using 6.1...
Selective Growth of Ultrathin HfS2 Layers on Hexagonal Boron Nitride for Highly Sensitive Photodetectors Dengeui Wang1,2, Xing Wang Zhang1,2, Junhua Meng1,2, Zhigang Yin1,2 and Jingbi You1,2; 1Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China; 2College of Materials Science and Opto-electronic Technology, University of Chinese Academy of Sciences, Beijing, China.

Hafnium disulfide (HfS2) has attracted significant interest because of the predicted excellent electronic properties superior to group VIB transition metal dichalcogenides. For instance, the room-temperature acoustic-photon-limited mobility of HfS2 was calculated to be above 1800 cm2V-1s-1, which is much higher than that of widely studied MoS2 (340 cm2V-1s-1). These extraordinary properties make HfS2 attractive for applications in logic and optoelectronic devices. On the other hand, hexagonal boron nitride (h-BN) has a wide band gap, making it an ideal dielectric substrate for optoelectronic applications of other 2D materials. Recent reports reveal that heterostructures vertically aligned by two 2D materials exhibit novel properties, offering a promising approach to design and fabricate novel electronic devices. Thus, searching for a suitable 2D material as substrate to achieve high-quality 2D HfS2 is highly desirable.

Herein, for the first time we report the synthesis of high-quality HfS2 on h-BN transferred on SiO2/Si by chemical vapor deposition. It is found that the HfS2 layers are selectively grown on h-BN rather than on SiO2/Si. Density functional theory calculations are performed to help understand the mechanism of selective growth of HfS2. Furthermore, the photodetectors based on the HfS2/h-BN heterostructures exhibit excellent visible-light sensing performance, such as a high on/off ratio of more than 106, an ultrafast response rate of about 200 μs, a high responsivity of 26.5 mA W-1 and a competitive detectiveivity exceeding 3×1011 Jones, superior to the vast majority of the reported 2D materials based photodetectors. These results indicate that HfS2/h-BN heterostructures, as well as the selective direct growth of HfS2, are very promising for future applications in high performance nano-optoelectronics.

Stabilizing Phosphorene via Hexagonal Boron Nitride Passivation Natechanok Yutthasaksunthorn, Sanjay Behura and Vikas Berry; University of Illinois, Chicago, Chicago, Illinois, United States.

Layered crystals have revolutionized the field of nanoelectronics and optoelectronics due to their potential to be exfoliated (mechanically or chemically) into atomically-thin two-dimensional (2D) sheets (for example, graphene from graphite). Several 2D crystals and their complex van der Waals heterostructures are recently realized via micromechanical cleavage (peeling) technique. Phosphorene, a two-atom thick 2D material has found significant attention because of its unique physical properties including: sizable band gap (0.3-1.2 eV), in-plane anisotropy, and high charge carrier mobility. Further, the 2D phosphorene layers can be easily exfoliated from the bulk 3D black phosphorous crystals and can also be transferred onto any arbitrary substrates. However, the wide applications of photo-induced doping in nanomaterials are severely constrained by the low doping concentration and poor stability that can be reached. Here, we propose a novel photo-induced doping mechanism based on external photoelectric effect of metal coating on TMDs to significantly enhance the achievable doping concentration and stability. We demonstrate this photo-induced doping effect on Au coated MoS2 field effect transistors (FETs) annealed in the gas mixture of argon (Ar) and oxygen (O2) (V:V = 98:2). Under ultra-violet (UV) light illumination, the modified MoS2 achieves degenerated n-type doping density of 1014 cm-2 rapidly according to the experimentally observed >104 times incensement in the channel mobility. The doping level persists after the removal of UV illumination with non-obervable decrease over 1 day in vacuum (less than 23% over 7 days under ambient environment). In addition, we have applied the same approach to another two TMDs: ReS2 and MoSe2, both exhibit similar photo-induced doping effects. The achieved stable and high concentration doping on the annealed Au/MoS2 (M is Mo or Re, and X is S or Se) FETs by convenient UV treatment enables various photoelectronic applications such as photo-switch, photo-memory and photonic neuromorphic devices.
such as MoS₂, or MoSe₂ are n-type, while few materials, such as phosphorene, which suffers from rapid oxidation, are p-type. We tested the synthesized material. This is critical to fabricate devices such as p-n junctions and heterojunctions, since most of the recently discovered and studied layered materials overpotential to reach -10 mA/cm² is reduced by 210 mV, and the Tafel slope is reduced from 122 to 49 mV per decade (mV/dec) compared to undoped WS₂ nanotubes.

EP03.08.21
Rapid Flame Doping of Co to WS₂ for Efficient Hydrogen Evolution Xiniang Shi, Jens K Norskov and Xiaolin Zheng; Stanford University, Stanford, California, United States.

Transition metal sulfides have been widely studied as electrocatalysts for the hydrogen evolution reaction (HER). Though elemental dopant is an effective way to enhance sulfide activity for HER, most studies have only focused on the effect of doping sulfide edge sites. Few studies have investigated the effect of doping the basal plane or the effect of doping concentration on basal plane activity. Probing the dopant concentration dependence of HER activity is challenging due to experimental difficulties in controlling dopant incorporation. Here, we overcome this challenge by first synthesizing doped transition metal oxides and then sulfurizing the oxides to sulfides, yielding core/shell Co-doped WS₂/W₁₈O₄₉ nanotubes with a tunable amount of Co. Our combined density functional theory (DFT) calculations and experiments demonstrate that the HER activity of basal plane WS₂ changes non-monotonically with the concentration of Co due to local changes in the binding energy of H and formation energy of S-vacancies. At an optimal Co doping concentration, the overpotential to reach ~10 mA/cm² is reduced by 210 mV, and the Tafel slope is reduced from 122 to 49 mV per decade (mV/dec) compared to undoped WS₂ nanotubes.

EP03.08.22
High Yield Bottom-Up Synthesis of Layered Metal Sulfides and Phosphides Using Chemical Vapor Deposition and Top-Down Exfoliation of Monolayers Gilbert D. Nessing, Eti Teblum, Anat Itzhak, Yulia Kostikov and Tarik Aziz; Bar Ilan University, Ramat Gan, Israel.

Since the excitement about graphene winning the 2010 Nobel Prize, there has been extensive research in the synthesis of other non-carbon few/monolayers exhibiting a variety of bandgaps and semiconducting properties (e.g., n or p type). The main approaches to deposit few/monolayers on a substrate are: (a) bottom-up synthesis from precursors using chemical vapor deposition (CVD) or (b) top-down exfoliation (liquid or mechanical) of bulk layered material. Here we show a combined bottom-up and top-down approach where (a) we synthesize in one step high yields of bulk layered materials by annealing a metal in the presence of a gas precursor (sulfur or phosphorous) and (b) we exfoliate and dropcast few/monolayers on a substrate from a sonicated mixture of our material in a chosen solvent. It is important to note that, besides the structure being 2D layered, the properties of the nanomaterials synthesized slightly differ from the materials with the same stoichiometry synthesized using conventional chemical methods. We synthesized CuS₂ and characterized it using multiple spectroscopy, X-ray, techniques, and electrical AFM. We found that is a highly doped, p-type material. This is critical to fabricate devices such as p-n junctions and heterojunctions, since most of the recently discovered and studied layered materials such as MoS₂, or MoSe₂ are n-type, while few materials, such as phosphorene, which suffers from rapid oxidation, are p-type. We tested the synthesized CuS₂ as an electrode for Li-ion battery. These results were recently published in Chemistry of Materials (Vol. 30, 2379–2388, 2018).

Using the same approach, we synthesized high yields of bulk layered silver sulfide (Ag₂S), which exhibits very high performance for hydrogen evolution reaction (HER) and copper phosphide (Cu₃P), which shows a promising application in supercapacitors. We will also discuss progress in the synthesis of other metal sulfides and phosphides and enhancements of this process using custom-made mini-reactors. In this talk, we will discuss the synthesis, the extensive characterizations, the applications tested, and the promise of this technique for the fabrication of bulk materials for energy application and of p-n heterojunctions based on monolayers for future electronic devices.

EP03.08.23
Real-Time Observation of MoS₂ Crystal Growth in the Presence of Other Metals Neha P. Kondekar, Matthew G. Boebinger and Matthew McDowell; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

MoS₂ is a layered transition metal dichalcogenide (TMDC) with crystallographic anisotropy featuring chemically active edge sites and relatively inert basal sites. Few-layered MoS₂ materials have chemical and electronic properties that can be tuned based on crystallographic orientation, making it attractive for (electro)catalytic applications for the hydrogen evolution reaction (HER) and for hydrodesulfurization (HDS). Doping MoS₂ crystals with transition metals has been shown to improve the HER and HDS activity due to the decoration of Mo edge sites with metals atoms. While the effect of additions of metal atoms to the MoS₂ lattice on physicochemical properties has been investigated, there is a lack of understanding of how the addition of other transition metals influences the synthesis and fabrication process of MoS₂ from the precursor stage. For the development of more efficient catalyst materials, improved knowledge of catalyst synthesis is essential to enable engineering of structure and properties. In this study, we use in situ transmission electron microscopy (TEM) to investigate the growth of MoS₂ crystals with and without the addition of a Ni metal film. Thermolysis of ammonium thiomolybdate is used to grow crystalline MoS₂ within the TEM. The pure MoS₂ precursor forms a polycrystalline film with predominantly small, vertically-oriented grains of MoS₂ at 400°C, with the grains growing until 700°C and transitioning to (100) or horizontal grains above 800°C. Using a similar thermolysis process in the presence of Ni, a polycrystalline film with a mixture of horizontal and vertical MoS₂ grains already form by 400°C and further heating causes the growth of large-area and horizontal single crystals with an average grain size of ~70 nm. Thermogravimetric experiments also suggest differences in the crystalization kinetics of MoS₂ upon addition of Ni. Finally, x-ray photoelectron spectroscopy (XPS) experiments are used as a complementary technique to probe the chemical interaction of metal films with edge sites and basal planes after synthesis. These findings have important implications for the synthesis of MoS₂-based catalysts, which is necessary for engineering catalytic materials with improved activity.

EP03.08.24
Synthesis of Large-Size Single-Crystal Hexagonal Boron Nitride Domains with Controlled Orientation on Epitaxial Nickel Thin Film Junhua Meng¹,², Ye Wang¹,², Menglei Gao³, Likan Cheng² and Xing Wang Zhang¹,²; ¹Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China; ²College of Materials Science and Opto-electronic Technology, University of Chinese Academy of Sciences, Beijing, China.

Atomically thin materials have attracted significant attention in recent years because of their unique structures and properties. Among the family of two-dimensional (2D) materials, hexagonal boron nitride (h-BN), an isomorph of graphene, has been intensively investigated as dielectric or substrate layers for other 2D materials due to its outstanding properties such as ultra-smooth surface, low density of dangling bonds/trapped charges, wide band gap, high thermal conductivity, and low dielectric constant. For electronic applications, high quality and large-area h-BN layers with few defects is strongly desirable. Thus far, many efforts have been devoted to synthesize large-size h-BN domains by optimizing the growth parameters or pretreating the substrate surface. However, the lateral size of single-crystal h-BN domains is still rather small, and further enlarging the domain size remains a challenge. In this work, we demonstrated the growth of millimeter-size single-crystal h-BN domains on the epitaxial Ni (111) substrate by ion beam sputtering deposition. Under the optimized growth conditions, the single-crystal h-BN domains up to 0.6 mm in edge length were obtained, the largest reported to date. The formation of large-size h-BN domains is mainly due to the reduced grain boundaries and the improved crystallinity of underlying Ni.
films. The conductive atomic force microscopy indicates that the merged h-BN layer exhibits quite uniform and excellent dielectric behavior. Furthermore, it was found that the in-plane orientation of the Ni thin film play an important role in the oriented configuration of the h-BN domains. Due to the stitching of the Ni(111) film deposited on the six-fold symmetrical sapphire substrate, the h-BN domains on Ni/sapphire show two antiparallel orientations. By using the three-fold symmetrical MgO(111) substrate, a perfect epitaxial Ni(111) film with only one in-plane orientation were demonstrated, and thus the h-BN domains with unique orientation were also successfully synthesized. This work provides an effective approach for synthesizing large-scale high-quality h-BN layers for electronic applications.

**EP03.08.25**

**Fully Printed Flexible and Transparent MoS2 Phototransistors with Organic Electrodes and Dielectric**

Seojun Chung1, 2, Jawook Ha1, Tae-Young Kim1, Hoichang Yang1, Yongtaek Hong2 and Takhee Lee1; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Electrical and computer engineering, Seoul National University, Seoul, Korea (the Republic of); 3Physics and astronomy, Seoul National University, Seoul, Korea (the Republic of); 4Chemical engineering, Inha University, Incheon, Korea (the Republic of).

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have gained considerable attention as an emerging semiconductor due to their promising atomically thin film characteristics with good field-effect mobility and tunable band gap energy. However, their electronic applications have been generally realized with conventional inorganic electrodes and dielectrics implemented using conventional photolithography or transferring processes that are not compatible with large-area and flexible device applications. [1] Specifically, unnecessary procedures, such as a photoresist deposition or ultraviolet exposure, can degrade the electrical characteristics of TMDs channel layers. Recently, the use of graphene electrodes or hexagonal boron nitride dielectric layers to introduce dangling bond free interfaces on TMDs has been suggested. [2] However, these layers require complicated and time-consuming etching and transferring processes with additional supporting layers. To facilitate the advantages of 2D TMDs in practical applications, strategies for realizing flexible and transparent 2D electronics using low-temperature, large-area, and low-cost processes should be developed. Motivated by this challenge, we report fully printed transparent chemical vapor deposition (CVD)-synthesized monolayer molybdenum disulfide (MoS2) phototransistor arrays on flexible polymer substrates. [3] All the electronic components, including dielectric and electrodes, were directly deposited with mechanically tolerant organic materials by inkjet-printing onto transferred monolayer MoS2, and their annealing temperature of <180 °C allows the direct fabrication on commercial flexible substrates without additional assisted-structures. By integrating the soft organic components with ultrathin MoS2, the fully printed MoS2 phototransistors exhibit excellent transparency and mechanically stable operation under tensile stress. Furthermore, by conducting the carefully optimized printing processes, the fabricated fully printed phototransistors exhibited comparable photocharacteristics, including photoresponsivity and external quantum efficiency (EQE), to those of previously reported phototransistors with inorganic components fabricated by conventional photolithographic processes on rigid SiO2/Si substrates.


**EP03.08.26**

**Centimeter-Scale Periodically Corrugated Few Layer MoS2 with Tensile Stretch-Driven Tunable Multifunctionalities**

Emmanuel F. Okogbue1, 2, Jung Han Kim3, Jung-Tae Kim4, Hee-Suk Chung3, Adithi Krishnaprasad5, Jean Calderon Flores4, 6, Shradhha Nebate4, Md Golam Kaum4, Jong Bae Park2, Sei-Jin Lee7, Kalpathy Sundaram3, Lei Zhai4, 5, Tania Roy1, 2, 5 and Yeonwoong Jung1, 2, 5; 1Electrical and Computer Engineering, University of Central Florida, Orlando, Florida, United States; 2Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States; 3Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States; 5Analytical Research Division, Korea Basic Science Institute, Jeonju, Korea (the Republic of); 6Chemistry, University of Central Florida, Orlando, Florida, United States; 7Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States.

Two-dimensional (2D) transition metal dichalcogenide (TMD) layers exhibit superior optical, electrical, and structural properties unattainable in any traditional materials. Many of these properties are known to be controllable via external mechanical inputs, benefitting from their extremely small thickness coupled with large in-plane strain limits. However, the realization of such mechanically-driven tunability often demands highly complicated engineering of 2D TMD layer structures, which is difficult to achieve on a large wafer-scale in a controlled manner. In this work, we report chemically grown centimeter-scale corrugated 2D molybdenum disulfide (MoS2) layers with tailored dimensions and study their strain-tunable multi-functionalities. For the purpose of structural engineering of 2D MoS2 layers, we developed a water-assisted method to transfer them from the growth substrates onto the large area (~2cm2) pre-strained three-dimensionally patterned elastomeric substrate. The transferred and integrated 2D layers maintain precisely defined and corrugated structures preserving their intrinsic material characteristics while exhibiting the excellent controllability of in-plane strain. We identified the well-retained electrical conductivity of these large-area corrugated 2D MoS2 layers even upon significant (> 30 %) tensile stretch. In addition, these corrugated MoS2 layers present periodically tunable photoresponsivity, optical absorbance and surface wettability which are concurrently actualized upon mechanical stretching. These novel three-dimensionally structured 2D materials are believed to offer exciting opportunities for large-scale, mechanically deformable devices of various form factors.

**EP03.08.27**

**Thermal Edge Reconstruction and Size Control of Nanopores in Transition Metal Dichalcogenides**

Kevin Bogart1, 2, Tao Liu2, Massimo Spina2, Chris Boothroyd1, Martial Duchamp1, Silvia Gradecak1 and Slaven Garaj1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2National University of Singapore, Singapore, Singapore; 3Nanyang Technological University, Singapore, Singapore; 4Nanyang Technological University, Singapore, Singapore.

Atomically thin nanoporous membranes are versatile structures with applications in energy, sensing, and filtration platforms including reverse electrodialysis, DNA sequencing, and reverse osmosis. The functionality of these devices is derived from the chemistry and geometry of the nanopore edge. Current methods for nanopore formation and processing include electron beam drilling, electrochemical reaction, and oxidative annealing. Since one of these methods offers a set of trade-offs, no universal method exists to precisely control both pore nucleation (e.g. number and location) as well as functionality (e.g. size, shape, and edge chemistry). Here we report vacuum annealing as a route toward reproducible engineering nanopore edge in two-dimensional (2D) transition metal dichalcogenides (TMDs) with tunable pore sizes, shapes, and edge chemistries.

In order to study nanopore growth kinetics and edge reconstruction in 2D TMDs, nanopores were introduced and annealed in situ in an aberration-corrected scanning transmission electron microscope. We find that nanopore edges become more ordered at higher annealing temperatures, favoring metal-terminated edges along the zigzag orientation. Further, we observe that nanopore area increases quadratically with time with an Arrhenius temperature-dependent rate corresponding to an activation energy of approximately 0.6 eV for pore growth in a MoS2 model system. Our findings are guided and corroborated by Monte Carlo simulations comparing the relative effects of time, temperature, and pore size on growth rate. The implementation of these findings in the fabrication of nanopore devices will aid in the rational design of targeted geometries and chemistries of nanopore edges to optimize device performance.
EP03.08.28
Free-Standing Bialkali Photocathodes Using Atomically Thin Substrates for Accelerator Technology
Hisho Yamaguchi1, Fangze Liu1, Jeffrey DeFazio2, Mengjia Gaowei1, Claudia W. Narvaez Villarrubia1, Junqi Xie1, John Sinzheimer1, Derek Strom1, Vitaly Pavlenko1, Kevin Jensen1, John Smalley1, Aditya D. Mohite1 and Nathan Moody1; 1Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2Photonis USA

Synthesis of Tunable 2D TMDs and Their Applications in Opto-Electronics and Rechargeable Batteries

8:30 AM

EP03.09.01
From 3D Ferrocrystals to 2D Layers—Layered Structures from Modulated Elemental Precursors
Fabian Göhler1, Erik Hadland2, Danielle Hamann2, Niels Rösch1, Constance Schmidt1, Dietrich R. Zahn1, Florian Speck1, David C. Johnson2 and Thomas Seyller1; 1Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany; 2Department of Chemistry, University of Oregon, Eugene, Oregon, United States.

A lot of recent research efforts have been devoted to the creation of stacks of single sheets of 2D materials, due to their enticing possibilities in designing new materials. However, large scale production of such structures still poses a significant experimental challenge. The Modulated Elemental Reactants (MER) technique is a promising candidate for the synthesis of a variety of new heterostructures, as it allows independent control of constituents and layering sequence. MER uses a two-step process, where first an amorphous precursor mimicking the appearance of the target material is deposited on a substrate, which then self-assembles upon annealing at relatively low temperatures. Three-dimensional [MX1+δ]m[TX2]n layered structures grown with MER are generally referred to as ferrocrystals. They consist of nanocrystalline layers that show rotational disorder along the crystal's c-axis. Their unique structure leads to emerging properties which make them interesting for fundamental materials science research as well as potential applications.

This contribution will give an overview over recent results obtained from surface science techniques on various ferrocrystalline compounds. For example, X-ray photoelectron spectroscopy (XPS) is a powerful tool to investigate electronic interactions as well as structural modulations within and between the single layers, such as interlayer charge transfer in [SnSe1+δ]m[TiSe2]2, polytypism of MoSe2 layers, and antiphase boundary formation in rocksalt-like BiSe.

Furthermore, we will present the synthesis and characterization of new van-der-Waals heterostructures consisting of monolayer MoSe2 grown by MER on epitaxial graphene on SiC(0001), thus pushing the MER synthesis towards the 2D limit. Similar to 3D ferrocrystals, these two-dimensional structures show nanocrystalline domains and rotational disorder. This fundamental study may provide the base of expanding this concept to create more sophisticated heterostructures and devices by combining large-area epitaxial graphene grown on SiC(0001) with products of the MER synthesis.

8:15 AM EP03.09.02
Compression Induced Modification of Boron Nitride Layers—A Conductive Two-Dimensional BN Compound
Ana Paula M. Barboza1, Matheus Matos1, Helio Chacham1, Ronaldo Batista1, Alan Oliveira1, Mario Mazzoni2 and Bernardo Neves1; 1Universidade Federal de Ouro Preto, Ouro Preto, Brazil; 2Universidade Federal de Minas Gerais, Belo Horizonte, Brazil.

The ability of creating new materials with improved properties upon transformation processes applied to conventional materials is the keystone of materials science. Here, hexagonal boron nitride (h-BN), a large bandgap insulator, is transformed into a conductive two-dimensional (2D) material – bontril – that is stable at ambient conditions [1]. We report on the compression-induced modification of few-layered h-BN into such a conductive boron nitride 2D material via scanning probe microscopy (SPM) experiments. The full phenomenology of bontril's electronic properties is consistent with a proposed ab initio model of a hydroxylated, two-dimensional sp2-bonded BN material. In our calculations, pressure-induced sp2-sp3-ve-hybridization between the two uppermost BN layers in the presence of hydroxyl chemical groups lead to formation of this new material. Both experiments and theory indicate that bontril is a conductive magnetic material with a large work function. Finally, the present work may also mark the consolidation of a new strategy in the discovery of exclusively man-made materials via SPM nanomanipulation, resulting in the rise of unprecedented novel 2D materials with yet undescribed properties.

Reference:

8:30 AM EP03.09.03
Synthesis of Tunable 2D TMDs and Their Applications in Opto-Electronics and Rechargeable Batteries
Wonbong Choi; University of North Texas, Denton, Texas, United States.
Recent advances in atomically thin two-dimensional transition metal dichalcogenides (2D TMDs) have led to a variety of promising technologies for nanoelectronics, photonics, sensing, energy storage, and opto-electronics, to name a few. The TMDs are finding niche applications for next-generation electronics and optoelectronics devices relying on ultrathin atomics in thicknesses [1]. Albeit several challenges in developing scalable and defect-free TMDs on desired substrates, new growth techniques compatible with traditional and unconventional substrates have been developed to meet the ever-increasing demand of high quality and controllability for practical applications. This talk will present two important subjects; (1) Synthesis of large scale 2D TMDs and their bandgap engineering for opto-electronics applications - especially our recent development of uniform and scalable single-layer TMDs by CVD method followed by a laser thinning process. Excitons’ behavior based on composition and layer dependent photoluminescence analysis will be highlighted [2-4]. (2) 2D MoS2 protective layer for Li-metal anodes in Li-S batteries - we observe stable Li electrodeposition and the suppression of dendrite nucleation sites from the 2D MoS2 coated Li-metal. The deposition and dissolution process of a symmetric MoS2 coated Li-metal cell operates at a current density of 10 mA cm\(^{-2}\) with low voltage hysteresis, and a three-fold improvement in cycle-life than using bare Li-metal. In a Li-S full cell configuration, we obtain a specific energy density of \(\sim 600\) Wh kg\(^{-1}\) and a Coulombic efficiency of \(\sim 98\%\) for over 1200 cycles at 0.5 C. Our approach can lead to the realization of high energy density and safe Li-metal based batteries [5]. The large-scale synthesis of 2D TMDs and their tunable optical properties and atomic layer passivation of 2D MoS2 on Li-metal could empower a great deal of flexibility in designing atomically thin optoelectronic devices and Li-metal batteries.

References
2. Synthesis of uniform single layer WS\(_2\) for tunable photocataluminescence, Juhong Park, MinSu Kim, Eunho Cha, Jeongyong Kim & Wonbong Choi, Scientific Reports, 7, 16121 DOI:10.1038/s41598-017-16251-2 (2017).

8:45 AM *EP03.09.04
Novel Air-Stable Ultrahigh-Mobility Semiconducting 2D BOX Hailin Peng; Peking University, Beijing, China.

Identifying new 2D materials with both high carrier mobility and large electronic bandgap is a pivotal goal of fundamental research since the ultrathin limit cannot be reached for traditional semiconductors such as Si and GaAs. However, to date, air-stable ultrathin semiconducting materials with superior performances remain elusive. Here our recent studies on the controlled synthesis of high-mobility semiconducting 2D crystals such as layered bismuth oxchalcogenides (BOX, Bi\(_2\)O\(_x\)X; X = S, Se, Te), as well as their electronic and optoelectronic properties will be discussed. We report on chemical vapor deposition (CVD) growth of large-area layered Bi\(_2\)O\(_2\)Se single crystals with the thickness down to monolayer, exhibiting excellent air-stability, low electron effective mass of \(\sim 0.14\) m\(_e\), and tunable bandgap values of \(\sim 0.8\) eV. 2D BOX crystals can be fabricated into high-performance field-effect transistors and NIR photodetectors, in which pronounced quantum oscillations were also observed.

9:15 AM *EP03.09.05
Point Defects in Transition Metal Dichalcogenides Abhay N. Pasupathy; Columbia University, Ithaca, New York, United States.

Two dimensional (2D) transition-metal dichalcogenide (TMD) based semiconductors have generated intense recent interest due to their novel optical and electronic properties, and potential for applications. In this work, we characterize the atomic and electronic nature of intrinsic point defects found in single crystals of these materials synthesized by two different methods - chemical vapor transport and self-flux growth. Using a combination of scanning tunneling microscopy (STM) and scanning transmission electron microscopy (STEM), we show that the two major intrinsic defects in these materials are metal vacancies and chalcogen antisites. We show that by control of the synthetic conditions, we can reduce the defect concentration from above 10\(^{13}\)cm\(^{-2}\) to below 10\(^{11}\)cm\(^{-2}\). Because these point defects act as centers for non-radiative recombination of excitons, this improvement in material quality leads to a hundred-fold increase in the radiative recombination efficiency.

9:45 AM BREAK

10:15 AM *EP03.09.06
Controlling and Tailoring the Electronic Properties of Chemically Reactive 2D Materials Mark C. Hersam; Northwestern University, Evanston, Illinois, United States.

Following the success of ambient-stable two-dimensional (2D) materials such as graphene and hexagonal boron nitride (hBN), new classes of chemically reactive layered solids are being explored since their unique electronic and optical properties hold significant promise for improved device performance [1]. For example, chemically reactive 2D semiconductors such as phosphorus (BP) and indium selenide (InSe) have shown significantly enhanced field-effect mobilities under controlled conditions that minimize ambient degradation [2]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [3], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [4,5]. Even the nominally ambient-stable transition metal dichalcogenides (e.g., MoS\(_2\)) are susceptible to chemically driven phase transformations under relatively benign conditions [6]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required. This talk will thus explore recent efforts to control and tailor the electronic properties of chemically reactive 2D materials. In particular, covalent organic functionalization of black phosphorus minimizes ambient degradation, provides charge transfer doping, and enhances field-effect transistor mobility and on/off ratio [7]. In contrast, noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral organic-borophene heterostructures [8]. Even in the absence of chemical reactants, field-driven bond breaking in polycrystalline MoS\(_2\) enables reconfiguration of doping profiles and novel device functionality such as hybrid memristor and transistor responses [9], which can be exploited in neuromorphic memtransistors [10]. Emerging efforts with additional chemically reactive 2D materials (e.g., InSe) will also be discussed.

References
resulted in p-type, while TeCl₄-assisted growth led to n-type behavior, as determined from the FET transport measurement on thick (over ≈ 50 nm) in 2H phase. For the semiconducting 2H phase, a choice of particular CVT transport agent dictated its intrinsic conductivity: iodine-assisted growth stabilize 2H phase or semimetallic 1T’ phase. A particular crystal structure was controlled by the growth temperature as well as by the post-growth. exfoliated layers were evaluated by TEM, SEM/EDS/EBSD, XRD, XPS, SIMS and Raman measurements. The CVT growth conditions were optimized to Ar ions is performed to induce S removal. X-ray Photoemission Spectroscopy measurements and Rutherford Backscattering Spectrometry showed that S and useful methods to adapt the MoS₂ properties for future applications.

MoTe₂ exists in two thermodynamically stable crystal forms: semiconducting 2H phase at ambient conditions, and semimetallic 1T’ phase at elevated temperatures. Reversibility of the 2H↔1T’ phase transition can be controlled by temperature or, as theoretically predicted, by other external stimuli [1], which makes this material attractive for advanced 2D electronics.

For this work, we have grown MoTe₂ single crystals by chemical vapor transport (CVT). Structural properties and composition of bulk MoTe₂ crystals and exfoliated layers were evaluated by TEM, SEM/EDS/EBSD, XRD, XPS, SIMS and Raman measurements. The CVT growth conditions were optimized to stabilize 2H phase or semimetallic 1T’ phase. A particular crystal structure was controlled by the growth temperature as well as by the post-growth annealing: 1T’ phase was stabilized by quenching at ≈ 900 °C processing temperature, while the growth/annealing temperature below ≈ 800 °C resulted in 2H phase. For the semiconducting 2H phase, a choice of particular CVT transport agent dictated its intrinsic conductivity: iodine-assisted growth resulted in p-type, while TeCl₄-assisted growth led to n-type behavior, as determined from the FET transport measurement on thick (over ≈ 50 nm) MoTe₂ layers. A conductivity type was additionally tuned by scaling down the FET channel thickness: for TeCl₄-assisted growth, the polarity was switching sign from n-type for thick to p-type for thin (below ≈15 nm) layers, with an ambipolar behavior for the intermediate, 15 nm to 50 nm, thickness range. On the contrary, for the iodine-assisted CVT growth, p-type polarity remained unaffected by reducing the MoTe₂ layer thickness in the ≈ 50 nm to ≈ 5 nm range.

The talk will conclude by comparing 2H↔1T’ phase transition in bulk MoTe₂ induced by the growth/annealing temperature, with the electric-field-induced reversible phase change during formation of conducting filaments in 2H-MoTe₂ memristive devices [2].

References:

SESSION EP03.10: Mechanical Properties, Chemical and Biological Applications of 2D Materials
Session Chairs: Deep Jariwala and Feng Miao
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 210
Biexciton Engineering in MoSe$_2$

Yuerui Lu; Research School of Engineering, College of Engineering and Computer Science, Australian National University, Canberra, Australian Capital Territory, Australia.

Biexcitons have been of keen interest for both fundamental studies of the remarkable many-body interactions and investigations of novel device applications, such as quantum logic gates, biexciton lasing devices, entangled photon sources, etc. [1] Recently, tightly bound biexcitons have been observed in monolayer TMDs, such as WSe$_2$, MoSe$_2$ and W$_5$. These biexcitons in monolayer TMDs show an ultra-large binding energy in the range of 50−70 meV, which is more than 1 order of magnitude higher than the values found in III−V quasi-2D quantum wells [2]. This strong binding necessitates the complete understanding of the structures of these biexcitons and their dynamics in 2D materials as well as characterization of their properties and full investigation of their potential functionalities. Hence, it is necessary to demonstrate a system that exhibits these biexcitons with high binding energy to make their study possible. Here we have successfully used PL spectroscopy to study biexcitons in free standing monolayer MoSe$_2$. We observed tightly bound biexcitons with a binding energy of ∼60 meV in atomically thin MoSe$_2$ [3]. The measured binding energy matches well with the theoretically predicted value of the excited state biexcitons in MoSe$_2$. We further probed the formation dynamics of these biexcitons and found that the density of biexcitons increases with increasing density of negative trions and decreases with increasing density of excitons. This finding suggests that the biexcitons observed here are excited state biexcitons instead of ground state biexcitons. More importantly, we successfully triggered the emission of excited state biexcitons at room temperature in a freestanding bilayer MoSe$_2$ by modulating three independent parameters: (1) dielectric screening, (2) density of trions, and (3) excitation power. The implications of the tightly bound biexcitons at room temperature in 2D materials are far reaching. It provides a room-temperature 2D platform to explore fundamental many-body interactions, which provides a route for quantum logical devices and entangled photon sources operating at room temperature.

References

may also perfectly transfer the synthesized wafer-scale films onto any arbitrary substrates without compromising the quality and surface smoothness. With the unique synthetic and transfer capabilities, we have systematically studied the electronic, optical, and catalytic properties of 2D TMD materials, and developed a variety of novel devices.

4:00 PM EP03.10.05
Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites
Qing Tu1, 2, Ioannis Spanopoulos1, Poya Yasaei1, Shaqiang Hao1, Costas Stoumpos3, Christopher Wolverton1, Mercouri G. Kanatzidis1, Gajendra Shekhawat1 and Vinayak P. Dravid1; 1Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 2NUANCE Center, Northwestern University, Evanston, Illinois, United States; 3Northwestern University, Evanston, Illinois, United States.

Two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) are new members of the 2D materials family with wide tunability, highly dynamic structural features and excellent physical properties. The mechanical properties of such functional materials are both fundamentally and practically important to achieve both high performance and mechanically stable (flexible) devices. Here we report for the first time both the in-plane and out-of-plane mechanical properties of 2D lead iodide perovskites. We measured the out-of-plane mechanical properties of a series of 2D layered lead iodide HOIPs as a function of structural sub-units (e.g., variation of the length of the organic spacer molecules -R and the number of inorganic layer -n) by nanoindentation. We found 2D HOIPs have much lower elastic moduli and hardness than 3D HOIPs, and larger n number and shorter R result in stiffer material. Furthermore, by AFM-based nanoindentation of suspended 2D HOIP membranes, we measured the in-plane Young’s modulus and breaking strength of ultrathin 2D HOIP membranes and their dependence on the membrane thickness. The in-plane Young’s modulus of 2D HOIPs are smaller than that of conventional covalently bonded 2D materials. Both the Young’s modulus and breaking strength first decrease and then plateau as the thickness increases from monolayer to 4 layers due to interlayer slippage during deformation. Our results show that ultrathin 2D HOIPs exhibit outstanding breaking strength/Young’s Modulus ratio compared to many other widely used engineering materials and polymeric flexible substrates, which renders them suitable for application into flexible electronic devices. We compared our findings with other 2D materials and shed light on routes to further tune the mechanical properties of 2D layered HOIPs.

References

4:15 PM EP03.10.06
Exciton Transport in Strained Monolayer WSe2
Darwin F. Cordovilla Leon1, Zidong Li2 and Parag Deotare2, 1; 1Applied Physics Program, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Electrical Engineering and Computer Science, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

A number of devices exploiting the remarkable optoelectronic properties of monolayer Transition Metal Di-chalcogenides (TMDs) have been demonstrated in recent years [1–3]. Most of these devices rely exclusively on the transport of unbound electrons or holes. However, purely excitonic devices leverage the high tunability of TMDs’ band structure and their large binding energies [4] to control the motion of excitons in room-temperature applications. Here, we experimentally demonstrate a visualization of exciton transport in a non-uniformly strained WSe2 monolayer. The strain modulates the monolayer’s direct band gap giving rise to a built-in excitonic potential that results in the funneling of excitons in the direction of the strain gradient.

Our device consists of 400nm diameter, 300nm tall SiO2 pillars on a Si substrate. The WSe2 monolayer is deposited onto one of the pillars using a dry transfer technique [5]. We performed the optical characterization of the strain field by measuring the photoluminescence (PL) emission of the monolayer across the strained region and tracking the shift in the spectra with respect to an unstrained point. In addition, by scanning an avalanche photodiode detector across the PL beam we obtained a map of the time-dependent exciton density as a function of position [6]. This technique reveals essential excitonic transport parameters such as diffusivity and mobility. Our measurements indicate two regimes of diffusive transport [7]: a short, super-diffusive regime characterized by a time-varying diffusivity ranging between 1.6–1.9cm2/s, and a sub-diffusive regime with a time-varying diffusivity ranging between 0.5–1.5cm2/s. Similarly, our measurements indicate that the excitons drift in the direction of the strain gradient in two steps: a fast drift with an approximate strain mobility of 11.4cm2/s, and a slow drift with a strain mobility of 5.3cm2/s. These results will prove to be vital in the design of next-generation excitonic devices.


4:30 PM EP03.10.07
Application of MXenes in Single-Molecule Biophysics
Mehran Mafiabavi1, Armin VahidMohammadi1, Majid Beidaghi2 and Meni Wanunu2; 1Department of Bioengineering, Northeastern University, Boston, Massachusetts, United States; 2Department of Physics, Northeastern University, Boston, Massachusetts, United States; 3Auburn University, Auburn, Alabama, United States.

Since the emergence of nanoprobes as promising biosensors for single-molecule detection, two classes of them have been developed: solid-state and biological (mostly protein-based). Solid-state nanoprobes have drawn attention during the past few years since they provide a more physically robust framework for hosting a nanopore, and further allow experiments under experimental conditions in which lipid membranes or protein channels may not be chemically compatible with. The quest to find an atomically thin membrane that can provide superior spatial resolution along with high mechanical...
stability has introduced two-dimensional (2D) materials such as Graphene, MoS₂, WS₂, and BN as second generation solid-state nanopores.

MXenes are an emerging family of 2D transition metal carbides and nitrides with a general formula of Mn+1XnTx (i.e. Ti₃C₂Tx), where M is a transition metal, X represents carbon or nitrogen (n=1, 2, and 3), and T indicates different functional groups (O, OH, F) present on surface of MXenes. MXenes are produced by selective removal of A layer atoms from a group of layered ternary carbides and nitrides called MAX phases. Since their discovery in 2011, MXenes have been vastly studied for a variety of applications including energy storage and sensors, however, their applications in single molecule sensing and biophysics has remained unexplored. Herein, we investigate the application of a freestanding thin membrane of MXenes, in biomolecules detection and characterization. After fabrication of sub -10 nm diameter pore on the ultrathin MXene membranes, and immersion of the membrane in two buffer baths such that the pore is a sole liquid junction between the two chambers, application of a small voltage across the membrane results in an electric field that threads polymers such as DNA through the nanopore. This results in a transient drop in the ion current, which is used to probe electrically and/or optically structural features in the polymer.

Our preliminary data shows that MXenes provide high mechanical robustness, long-time stability, and low-noise ionic currents through the pore for single molecule detection. With more than 20 different MXenes synthesized, each having different properties, and their facile tunability, this study provides the basis knowledge for application of MXenes as potential materials for second-generation solid-state nanopores.


4:45 PM EP03.10.08 Direct Observation of Atomic Healing in Two-Dimensional Semiconductors Shrawan Roy¹, Wooseon Choi¹, Sera Jeon², Do-Hwan Kim², Hyun Kim³, Seokjoon Yun¹, Yongjun Lee¹, Jaeckwang Lee², Young-Min Kim¹,² and Jeongyong Kim³;¹ Sungkyunkwan University, Suwon, Korea (the Republic of);² Department of Physics, Pusan National University, Busan, Korea (the Republic of);³ CINAP, Institute for Basic Science, Suwon, Korea (the Republic of).

Monolayer transition metal dichalcogenides (1L-TMDs) are promising two-dimensional semiconductors with direct bandgap that ranges the energy of visible and infrared light, suitable for atomically thin nanophotonic device applications. However the very low quantum yields of intrinsic 1L-TMDs is a major drawback for practical use. There have been extensive studies that were able to induce significant increase of light emission of 1L-TMDs, among which chemical treatment using bis(trifluoromethane) sulfonimide TFSI have been shown to be surprisingly effective giving rise to a few order of magnitude increase of photoluminescence. While the healing of sulfur vacancies of 1L-MoS₂ were pointed out as the origin of increased quantum yield, the mechanism of healing the defects is in veil, and hindering practical use of this technique. Here we provide direct observation of atomic healing of 1L-TMDs caused by TFSI treatment. We performed the optical characterization and STEM imaging on the same samples of CVD-grown 1L-MoS₂ and 1L-WS₂ before and after TFSI treatment and found that most (~90%) of sulfur vacancies observed in pristine 1L-MoS₂ were fully repaired with TFSI treatment. Such greatly reduced density of sulfur vacancies were not observed when other chemical treatment that caused moderate increase of PL was used, which indicates that sulfur atoms dissociated from TFSI molecules have filled in vacancies of pristine 1L-MoS₂. The direct filling of sulfur atoms was found to be energetically stable by density functional theory calculation. Our observation unveils the intriguing healing process of lattice defects of 1L-TMDs and suggests that 1L-TMDs can be made completely defect-free, widening and prompting the practical uses of 1L-TMDs in nanophotonic applications. This work was in part supported by the National Research Foundation of Korea (NRF) grants funded by the Korean government (NRF-2018R1D1A1B07042917).

EP03.11.01 Supramolecular Approach to 2D Heterostructures and to the Non-Covalent Functionalization of 2D Materials Manjodh Kaur¹, Navin K. Singh², Aritra Sarkar², Subi J. George³ and Chintamani Nagesa R. Rao³;¹ Sheikh Saqr Laboratory (SSL), International Centre for Materials Science (ICMS), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India;² New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India;³ New Chemistry Unit and International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

Synthesis of 2D heterostructures by van der Waals vertical stacking to modulate their properties has gained interest over the past few years. van der Waals stabilization is an efficient synthetic strategy to obtain 2D heterostructures, although precise sequence and composition of the components still remains a challenge. A new synthetic strategy of covalent cross linking of different 2D materials has been extensively explored by Rao et al.[1]. This novel class of covalently cross-linked 2D materials are different from van der Waals heterostructures and show exciting properties. Although, cross-linked heterostructures show superior properties, further advancement to obtain the heterostructures of higher complexity with multiple components and precise sequences is appealing to explore novel applications. Therefore, for the first time successfully, supramolecular non-covalent synthetic strategy has been utilised to obtain reversible non-covalent heterostructure assemblies with self-organising components.[ii] Wherein, Kumar et al reported the novel, stable and reversible multi-component heterostructures of graphene : BN and MoS₂ : graphene. The 2D-materials have been covalently functionalized by organic coupling reactions between surface functional groups and organic molecules. Thereafter, the covalently functionalized 2D sheets have been noncovalently attached in the presence of cucurbit[8]uril to obtain supramolecular heterostructures. The work has been extended to synthesise supramolecular heterostructures of MoS₂ : g-C₃N₄ and MoS₂ : BC-N. The supramolecular heterostructures have been investigated for their potential application in visible-light assisted photo and electrochemical H₂ evolution studies. These results for H₂ evolution were found to be in good agreement with current literature reports and these results will be presented.[iii] In order to tailor the electronic properties of 2D materials like MoS₂, which unlike graphene cannot be functionalized by π-π stacking or CT interactions, new strategy for non-covalent functionalization of MoS₂ with organic chromophores based on host-guest ternary complexation has been achieved.[iv] This strategy can be utilised to tune the electronic properties of other 2D materials.

Two-dimensional (2D) semiconductors are finding a renewed interest in recent years, due to their combination of physical properties, e.g., mobility, fluorescence and spin selectivity, with a potential implementation in new and emerging opto-electronic and spin-electronic devices. The current work discusses structural properties and various magneto-optical phenomena, found in three different 2D systems: The transition metal phosphorous trichalcogenides, indium sulfide and magnetically doped colloidal nanoplatelets. The magneto-optical properties are investigated by following optical polarization in the presence of an external magnetic field, as various temperatures, as well as implementing the use of optically detected magnetic resonance spectroscopy.

The transition metal phosphorous trichalcogenides resemble the most common layered dichalcogenides, but one-third of the metals are replaced with a P-P pair; hence, the chemical formula is written as M$_2$(P-P)$_3$X$_2$ or M$_3$P$_3$X$_6$. The dilution of metal site by non-magnetic atoms, endows a column like arrangement of the remaining metals, leading to a special magnetic properties, from a full antiferromagnetic Neel, through antiferromagnetic zigzag to ferromagnetic character. The various arrangements can be tuned by variation of the metal cations (among the first row of transitions metal atoms). The work focuses on the influence of the created magnetism on the magneto-optical properties of the M$_3$P$_3$X$_6$ semiconductors. The indium sulfide (In$_2$S$_3$) nanoplatelets crystallize in a few different morphological shapes, hexagon, dodecagon and truncated triangular structures, and are associated either with different crystallographic phases.

Transition metal dopant embedded in colloidal semiconductor nanoplatelets (NPLs) exhibit special magnetic properties, resemble the bulk diluted magnetic semiconductors. However, the NPLs confined thickness induces an extremely intense spin-exchange interaction between the resident photo-excited carriers and the guest magnetic spins. Such an interaction leads to a giant magnetization and g-factor, and consequently endows the materials with special magneto-optical properties. The work emphasizes the investigation of the spin-exchange interaction while varying the magnetic dopants, by following variation in the magneto-optical properties, when detecting either an ensemble of NPLs or a focus on a single platelet.**

** Magnetically doped NPLs project was carried out in collaboration with Prof. Volkan Hilmi Demir and his groups from Nanyang Technological University – NTU Singapore 639798, Singapore and from Bilkent University, Ankara 06800, Turkey.

---

## EP03.11.02

**Magneto-Optical Properties of Two-Dimensional Semiconductors—Transition Metal Phosphorous Trichalcogenides, Indium Sulfide and Magnetically Doped Colloidal Nanoplatelets**

Efrat Lifshitz, Adam K. Budnik, Faris Horani, Rotem Strassberg, Yehal Barak and Joanna Dehnel; Technion–Israel Institute of Technology, Haifa, Israel.

Two-dimensional (2D) semiconductors are finding a renewed interest in recent years, due to their combination of physical properties, e.g., mobility, fluorescence and spin selectivity, with a potential implementation in new and emerging opto-electronic and spin-electronic devices. The current work discusses structural properties and various magneto-optical phenomena, found in three different 2D systems: The transition metal phosphorous trichalcogenides, indium sulfide and magnetically doped colloidal nanoplatelets. The magneto-optical properties are investigated by following optical polarization in the presence of an external magnetic field, as various temperatures, as well as implementing the use of optically detected magnetic resonance spectroscopy.

The transition metal phosphorous trichalcogenides resemble the most common layered dichalcogenides, but one-third of the metals are replaced with a P-P pair; hence, the chemical formula is written as M$_2$(P-P)$_3$X$_2$ or M$_3$P$_3$X$_6$. The dilution of metal site by non-magnetic atoms, endows a column like arrangement of the remaining metals, leading to a special magnetic properties, from a full antiferromagnetic Neel, through antiferromagnetic zigzag to ferromagnetic character. The various arrangements can be tuned by variation of the metal cations (among the first row of transitions metal atoms). The work focuses on the influence of the created magnetism on the magneto-optical properties of the M$_3$P$_3$X$_6$ semiconductors. The indium sulfide (In$_2$S$_3$) nanoplatelets crystallize in a few different morphological shapes, hexagon, dodecagon and truncated triangular structures, and are associated either with different crystallographic phases.

Transition metal dopant embedded in colloidal semiconductor nanoplatelets (NPLs) exhibit special magnetic properties, resemble the bulk diluted magnetic semiconductors. However, the NPLs confined thickness induces an extremely intense spin-exchange interaction between the resident photo-excited carriers and the guest magnetic spins. Such an interaction leads to a giant magnetization and g-factor, and consequently endows the materials with special magneto-optical properties. The work emphasizes the investigation of the spin-exchange interaction while varying the magnetic dopants, by following variation in the magneto-optical properties, when detecting either an ensemble of NPLs or a focus on a single platelet. **

** Magnetically doped NPLs project was carried out in collaboration with Prof. Volkan Hilmi Demir and his groups from Nanyang Technological University – NTU Singapore 639798, Singapore and from Bilkent University, Ankara 06800, Turkey.

---

## EP03.11.03

**Magneto-Transport Properties of the MoTe$_2$ Layers Grown by Molecular Beam Epitaxy**

Marta Gryglas-Borysiewicz, Zuzanna W. Ogorzalek, Adam Kwiatkowski, Janusz Sadowski, Krzysztof Kormor, Magdalena Grzeszczyk, Dariusz Wasik, Rafal Bozek, Johannes Binder, Rafal Mirek and Wojciech Pacuski; Faculty of Physics, University of Warsaw, Warsaw, Poland; MAX-IV Laboratory, Lund University, Lund, Sweden; Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

The transition metal dichalcogenides are promising materials due to their unusual magnetic, optical and electrical properties. As it has been recently shown, Weyl semimetal including MoTe$_2$ can exhibit carrier mobility of 4000 cm$^2$/Vs and giant magneto-resistance (MR) of 16 000% in a magnetic field of 14 T at 1.8 K [1]. Most of the transport results of the MoTe$_2$, a relatively unexplored transitional metal dichalcogenide, are obtained on mechanically exfoliated samples and concern only most of temperature dependence of resistance [2–3]. Nowadays, there is a substantial progress in obtaining MoTe$_2$ by thin-film epitaxy or deposition [4–8]. In this paper, we present the studies of the MoTe$_2$ layers grown by molecular beam epitaxy (MBE). As it is well known the substrate is of critical importance for the electronic properties of the thin 2D layer. We have studied the role of the substrate using many different substrates: Al$_2$O$_3$, GaAs [100], silicon and GaAs [111B] with and without ZnTe buffer. An appropriate choice of growth temperature allows us to switch between 2H and 1T’ polytypes. It also influences the sample morphology, changing it from regular plane to nanodendrites. Magneto-transport properties of the layers will be presented and the impact of substrate will be discussed.

---

## EP03.11.04

**Synthesis and Processing of PbI$_2$ 2D Crystals for Applications in Opto-Electronics**

Anna Sinhu and Jamie Warner; University of Oxford, Oxford, United Kingdom.

Two-dimensional materials have attracted tremendous interest amongst the scientific community. Their ultrathin dimension makes them a desirable candidate for applications in electronics as well as their ability to form van der Waals heterostructures with other 2D materials opens the possibility to engineer novel properties and devices. Developments in this area of research requires study of broad range of 2D materials, including but not limited to graphene and transition metal dichalcogenides (TMDs). In this talk, I will present recent studies on the lesser studied material lead iodide (PbI$_2$).

PbI$_2$ is a luminescent, layered and 2.4eV direct band gap material and one of the very important materials for fabricating highly efficient solar cells. In this talk, I will present our recent results on mechanical exfoliation and chemical exfoliation of PbI$_2$ crystals in various solvents with studies on structure and layers using different microscopy techniques and device measurements. Comparisons will be made to monolayer graphene and other well known TMD materials. These results help shed light on how PbI$_2$ can be integrated with other molecular monolayers for expanding the application in opto-electronics.

---

## EP03.11.05

**Mechanical and Electrical Properties of Ti$_3$C$_2$Tx MXene**

Alexey Lipatov, Mohamed Alhabeb, Haidong Lu, Maria Lukatskaya, Alexei Gruverman, Yury Gogotsi and Alexander Sinitskii; University of Nebraska–Lincoln, Lincoln, Nebraska, United States; Drexel University, Philadelphia, Pennsylvania, United States.

Two-dimensional (2D) transition metal carbides and nitrides, known as MXenes, are a large class of materials that are finding numerous applications ranging from energy storage and electromagnetic interference shielding to water purification and antibacterial coatings. Yet, despite more than 20 different MXenes that have been synthesized, the mechanical properties of a MXene monolayer have not been experimentally studied. Here, we measured the elastic properties of monolayers and bilayers of the most important MXene material to date, Ti$_3$C$_2$Tx (T stands for surface termination). We developed a method for preparing well-strained membranes of Ti$_3$C$_2$Tx monolayers and bilayers, and performed their nanoindentation with the tip of an atomic force microscope to record the force-displacement curves. The effective Young’s modulus of a single layer of Ti$_3$C$_2$Tx was found to be 0.33 ± 0.03 TPa, which is the highest among the reported values for any solution-processed 2D material, including graphene oxide. This work opens the pathway to study the
mechanical properties of monolayers of other MXenes and extends the already broad range of MXenes’ applications to structural composites, protective coatings, nanoelectronics, and membranes that require materials with exceptional mechanical properties. Electronic properties of individual MXene flakes, which are important for understanding the potential of these materials, also remain largely unexplored. We report a modified synthetic method for producing high-quality Ti3C2Tx flakes. We fabricated field-effect transistors (FETs) based on monolayer Ti3C2Tx flakes and measured their electronic properties. Individual Ti3C2Tx flakes exhibit a high conductivity of 46000 ± 100 S/cm and field-effect electron mobility of 2.6 ± 0.7 cm²/Vs. We found that the resistivity of individual flakes is only one order of magnitude higher than the resistivity of multilayer Ti3C2Tx films, which indicates a surprisingly good electron transport through the surface terminations of different flakes, unlike in many other 2D materials. Finally, we used the fabricated FETs to investigate the environmental stability and kinetics of oxidation of Ti3C2Tx flakes in humid air. The high-quality Ti3C2Tx flakes are reasonably stable and remain highly conductive even after their exposure to air for more than 24 h. We demonstrate that after the initial exponential decay the conductivity of Ti3C2Tx flakes linearly decreases with time, which is consistent with their edge oxidation.

**EP03.11.06**

Transition Metal Chalcogenides as Active Phase-Change Materials for Infrared Photonics

Yifei Li1, Akshay Singh1, Ichiro Takeuchi2, Ju Li3 and Rafael Jaramillo1; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2University of Maryland, College Park, Maryland, United States.

Transition metal di-chalcogenides (TMDs) form in 2H (trigonal prismatic) and 1T' (distorted octahedral) polymorphs. For transition metals from the VIB and IBV columns, the 2H phase is semiconducting and the 1T' phase is a narrow-gap semiconductor or semi-metal. Switching between the 2H and 1T' phases could be the basis for useful phase-change technology, and the structural distortion between the phases – a martensitic translation of a single plane of chalcogen atoms in a van der Waals material – suggest that phase-change behavior could be relatively immune to fatigue. We will present our work towards designing phase-change TMDs for application to infrared photonics. Our density functional theory (DFT) calculations predict that the refractive index contrast between the 2H and 1T' phases is large and useful in the near-infrared (NIR) wavelength range 1 – 1.5 mm that is relevant to telecommunications. We study the (Mo,Co,Mo)(S,Se)2 valley system to optimize the energy and accelerate the kinetics of switching. Our DFT calculations predict that the 2H – 1T' transition occurs near 50 at. % Cr or Ti. To experimentally access this range of materials we use combinatorial metal sputtering, followed by sulfurization/selenization using H2S and H2Se gas, to make composition-graded TMD films across 2” wafers. We use Raman and X-ray diffraction mapping to distinguish the phase transition boundary and confirm our DFT calculations, and we use ellipsometry to measure the complex refractive index in the NIR. Our work helps build the foundation for rational design of thin film TMD phase-change materials that can be switched optically, electrically, and mechanically.

**EP03.11.07**

Solution-Processable 1T' WSe2 Nanosheets for Electrocatalytic Hydrogen Reduction

Maria S. Sokolikova, Peter C. Sherrell, Pawel Palczynski and Cecilia Mattevi; Imperial College London, London, United Kingdom.

Transition metal dichalcogenide (TMD) monolayers are three-atom thick and can exist in many different polymorphs where metal atom coordination changes from trigonal prismatic (1H phase) to octahedral and distorted octahedral (1T and 1T' phases). These crystal types demonstrate distinct electronic properties varying in a wide range from semiconducting to metallic to topological insulators. WSe2 monolayers synthesised via physical deposition techniques or wet chemical approaches acquire the thermodynamically favourable semiconducting 1H phase that can be then converted into the 1T (1T') as a result of either an electron transfer or applied mechanical strain. However, small energy difference between 1H and 1T' phase suggests that the metastable 1T' phase can be directly obtained under certain reaction conditions. Up until now the 1T' WSe2 has nearly not been synthesized and it has been predicted to be a quantum spin Hall insulator in monolayer limit. We report on direct solution phase synthesis of the 1T' WSe2 nanosheets from tungsten carbonyl precursor in a coordinating solvent. WSe2 forms well-defined flower-like nanostructures with atomically thin petals reaching 50 nm in lateral size. The 1T' phase can be converted into the semiconducting 1H phase upon thermal annealing at 400 °C preserving the starting flower-like morphology. The phase conversion was confirmed by high-resolution X-ray diffraction mapping to distinguish the phase transition boundary and confirm our DFT calculations, and we use ellipsometry to measure the complex refractive index in the NIR. Our work helps build the foundation for rational design of thin film TMD phase-change materials that can be switched optically, electrically, and mechanically.

**EP03.11.08**

Multidirection Piezoelectricity in Mono- and Multilayered Hexagonal α-In2Se3

Fei Xue1,2, Junwei Zhang3, Weijin Hu4, Wei-Ting Hsu5, Ali Han6, Sui-Fung Leung7, Jing-Kai Huang8, Yi Wan9, Shuhai Liu10, Junli Zhang11, J-Hau He12, Wen-Hao Chang13, Zhong Lin Wang14, Xixiang Zhang15 and Lain-Jong Li16; Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 1Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China; 2Shenyang National Laboratory for Materials Science, Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), Shenyang, China; 3Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan; 4Computer, Electrical, and Mathematical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 5School of Advanced Materials and Nanotechnology, Xidian University, Xi’an, China.

Piezoelectric materials have been widely used for sensors, actuators, and electronics, and energy conversion. Two-dimensional (2D) ultrathin semiconductors, such as monolayer h-BN and MoS2 with their atom-level geometry, are currently emerging as new and attractive members of the piezoelectric family. However, their piezoelectric polarization is commonly limited to the in-plane direction of odd-number ultrathin layers, largely restricting their application in integrated nanoelectromechanical systems. Recently, theoretical calculations have predicted the existence of out-of-plane and in-plane piezoelectricity in monolayer α-In2Se3. Here, we experimentally report the existence of out-of-plane and in-plane piezoelectricity in monolayer to bulk α-In2Se3, attributed to their noncentrosymmetry originating from the hexagonal stacking. Specifically, the corresponding d33 piezoelectric coefficient of α-In2Se3 increases from 0.34 pm/V (monolayer) to 5.6 pm/V (bulk) without any odd-even effect. In addition, we also demonstrate a type of α-In2Se3-based flexible piezoelectric nanogenerator as an energy-harvesting cell and electronic skin. The out-of-plane and in-plane piezoelectricity in α-In2Se3 flakes offers an opportunity to enable both directional and nondirectional piezoelectric devices to be applicable for self-powered systems and adaptive and strain tunable electronics/optoelectronics.
Rapid, Light-Induced Degradation of Molybdenum Disulfide in Water 
Lu Zhi, Adam Tetreault and Michael A. Pope; University of Waterloo, Waterloo, Ontario, Canada.

Single or few-layer molybdenum disulfide (MoS2) has demonstrated significant promise in a wide variety of applications including solar cells, transistors, supercapacitors, batteries and as photo/electrocatalysts. Chemical exfoliation of MoS2 by the traditional n-butyllithium route remains one of most common and efficient exfoliation methods which provides relatively high yields of single layers. However, it also results in the partial conversion of the MoS2 from the initially semiconducting 2H polymorph to the 1T polymorph which is a metastable metallic phase. Due to its metallic properties, 1T-MoS2 is the preferred polymorph when used, for example, as an electrocatalyst for the hydrogen evolution reaction (HER), in photoelectrochemical (PEC) water splitting and as electrodes for batteries and supercapacitors. Due to its technological promise, the air and water stability of 1T- and 2H-MoS2 single layers have drawn considerable attention. Herein, we report the discovery of a photo-induced degradation mechanism that can cause the rapid oxidation of MoS2 in water. Ambient light and pH are found to play a significant role in rate of oxidation of a 1T polymorph-dominated aqueous dispersion. Under certain conditions, only one week is necessary to cause the near complete conversion of the MoS2 into oxidation products and one month to convert an initially dark dispersion to transparent. The time evolution of the chemical and structural changes within the material and dispersion are monitored by a variety of advanced techniques such as Raman spectroscopy, Fourier transform infrared spectroscopy, UV/vis spectroscopy, atomic force microscopy and zeta-potential analysis. From these results, we discuss the nature of the decomposition product and the mechanism of the light-induced degradation. We probe conditions under which degradation is slow enough that the material remains stable and discuss the most suitable analytical techniques for detecting decomposition. We believe that the findings from this study will be of great value to those using MoS2 monolayers in various applications, where the stability of the active material is of paramount importance.

Large Area Growth of 2D- MoTe2 Niraj Bhatteri1,2, Rajendra P. Dula1, Andrew Forbes1,2, Ian L. Pegg1,2 and John Philip1,2; 1Department of Physics, The Catholic University of America, Washington, District of Columbia, United States; 2Vitreous State Laboratory, Washington, District of Columbia, United States.

Epitaxial single crystal thin films are very interesting which has drawn great scientific attention in recent time. Such thin films lack grain boundaries because of which they exhibit unique electric and transport properties leading a broad way for large scale applications in nanoelectronics, optoelectronics. Thin films over very large areas can be grown with controlled thicknesses, which paves the door for fabricating large-scale novel devices using MoTe2. We have grown 2D-MoTe2 thin film on Si/SiO2 substrate by chemical vapor deposition. We will present the growth, structural and transport studies of these films. These films exhibit semimetallic behavior and has unsaturated quadratic magnetoresistance. Hall resistivity measurements confirm the majority charge carriers are holes and using single band model, the concentration of holes is 6×1021 cm⁻³ at 10 K and increases with the increase in temperature.

Influence of Local Spatial Parameters of Transition Metal Dichalcogenides on Cellular Adhesion
Anthony Palumbo, Robert Chang and Eui-Hyeok Yang; Stevens Institute of Technology, Hoboken, New Jersey, United States.

Transition metal dichalcogenides (TMDs) are two-dimensional semiconductor analogues to graphene that have been widely explored for biomedical applications. However, cell-substrate interactions of TMDs are not well reported in literature, and TMD-incorporated cell culture platforms require further study to illuminate the influence of TMDs on the adhesive interactions of biological cells and the subsequent integration of these nanomaterials for potential biological applications involving biotic/abiotic interfaces.

We have explored cell-substrate interactions in which the influence of TMD geometric features on the resulting cellular morphology and proliferation is characterized quantitatively, offering insight into manipulating the adhesion of cells on TMD surfaces. We utilized WS2 and MoS2 on cytotoxic and cytocompatible substrates as cell culture platforms, and probed cell-substrate interactions via metrology and analysis of cellular morphometric features (i.e., cell area and eccentricity). Further, we performed analyses relating the influence of local TMD spatial parameters to the resulting cellular morphology, which provides a greater understanding on the causal relationship between TMD surfaces and cell attachment.

Our results show that TMD surfaces in arbitrary order can be used to enhance cell adhesion on substrates that are inerly undesirable to cell attachment, rendering otherwise cytotoxic substrates that are useful as 2D cell culture platforms. We also plotted and determined the significant correlation between TMD geometric variables and the resulting morphometric features of adherent cells, demonstrating that increased TMD island count and size parameters correlated to significantly larger and more elongated cells. These results indicate that by tailoring the geometric parameters of TMDs to a size scale comparable to the adhered cells, one can further guide the desirable adhesion of cells on diverse substrates (even those inherently adverse or cytotoxic to cells), which ultimately influences cellular survival, proliferation, differentiation and migration; coupled with TMD’s unique electronic and chemical properties, these findings can be further explored and applied in fields that utilize biotic/abiotic interfaces including biosensing, pharmacological testing, and organ printing.

Basal Plane Functionalization of Group VI Layered Transition Metal Dichalcogenides
Ali Jawaid and Richard Vaia; Air Force Research Laboratory, Wright, Ohio, United States.

Integration of Group VI 2H-MX2 Transition Metal Dichalcogenides (M = Mo, W; X = S, Se Te) into technologies ranging from chemical sensors to thermal-optical coatings and structural nanocomposites require direct chemical modification of the chalcogenide basal surface. Defect termination with elemental chalcogenide or organic ligands with terminal chalcogenides are routine, however the electronic structure of Group VI Transition Metal Dichalcogenides (TMDs) leads to an inert basal surface. Hybridization strategies therefore rely on extreme reduction processes to drive a transformation from the inert 2H to the reactive 1T phase. However, conversion back to the 2H phase is incomplete, resulting in heterogeneous materials. Here in, we demonstrate an alternative method for direct hybridization of Group VI 2H-MX2 TMDs via alkyl organometallic chemistry. Using the recently development redox exfoliation method, single to few layer TMDs are stabilized in a range of polar organic solvents that are compatible with organometallic chemistries. X-ray Absorption spectroscopy demonstrate strong chalcogen-ligand interaction while X-ray diffraction resolve an expanded interlayer gallery consistent with short-chain organics. The functionalized Group VI 2H-MX2 can be transferred to polar solvents (THF, CH3Cl, C2H5Cl), and show enhanced stability from oxidation and degradation. Finally, the organometallic chemistry is tolerant to –ene and –yne, facilitating post-functionalization modification via click chemistry, such as thiol-ene and thiol-yne conjugation. Tuning the optical, electrical and mechanical properties of MoX2 and NbX2 through integration into composites via surface functionalization is demonstrated.
Synergy of Redox Exfoliation and Mechanical Forces for Large Scale Exfoliation of Layered Transition Metal Dichalcogenides (Group IV – VII) by Ali Jawad, Allyson Ritter and Richard Vajta; Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States.

Transition Metal Dichalcogenides (TMDs) have attracted considerable attention due to their extensive property suite, which compliments many other low dimensional nanomaterials (e.g. graphene, BN, aluminosilicates, phosphenes, etc.). However, energy intensive sonication, aggressive chemistries, and a small choice of stabilizing solvents limit scalable exfoliation strategies, and thus access to large quantities of well-defined layers. Mechanically, exfoliation of low-dimensional nanoparticles from a large crystalline particle has two crucial steps: favorable modification of the nanoparticle surface, and subsequent nanoparticle separation to expose new surfaces. Therefore, the rate and efficiency of exfoliation is optimal for a combination of mechanical forces and surface chemistry; that is either alone is insufficient. Here in, we demonstrate that high-speed shear mixing rather than aggressive sonication balances the rate of chemical processes with nanoparticle separation for TMD exfoliation by the redox method. Chemically, this strategy generates in-situ polyoxometalates, which stabilize single-to-few layer Group IV – VII TMD sheets via coloumbic repulsion. Introduction of shear mixing during the formation of the polyoxometalates, rather than during the initial oxidation step or after the termination of chemical processing, significantly increases single layer exfoliation yields (> 10%) while drastically reducing reaction times (~ 24 hrs). Stable dispersions of Group IV – VII TMD TMDs in polar organic solvents (acetone, acetone, alcohols) at high concentration (10% w/w) are demonstrated for use in numerous bulk technologies, such as thermal/optical coatings, structural nanocomposites, and inks for flexible electronics.

EP03.11.14
CVD Growth of Monolayer MoS2 on Sapphire Substrates by Using MoO3 Thin Films as a Precursor for Co-Evaporation Sajeevi S. Withanage and Saiful Khondaker; University of Central Florida, Orlando, Florida, United States.

Molybdenum disulfide (MoS2) is an atomically thin semiconductor with direct bandgap in single layer (SL) which shows a great potential to wide range of applications in modern 2D electronics and optoelectronics. CVD based co-evaporation of molybdenum (Mo) and sulfur (S) precursors is becoming prevalent for the synthesis of SL MoS2; since conventional exfoliation methods cannot produce large scale samples for scalable device fabrication. For certain optoelectronic applications, choice of transparent growth substrate is critical as it can avoid transfer methods that involve chemicals which can degrade optical and electrical quality of grown SL crystals. Sapphire being an excellent candidate to serve this purpose has the additional benefit of good control over the crystal orientation of MoS2; hence the successful growth of large area MoS2 films on sapphire substrates is critical for scalable device fabrication. Here, we demonstrated that thin film based technique also produce MoS2 crystals with high reproducibility on sapphire without any special substrate treatments and we also studied the effects of parameters such as MoO3 film thickness and S concentration on the crystal growth. These crystals are as large as 25µm confirmed to be in the high quality SL MoS2 by atomic force microscopy measured thickness of 0.65 nm, 18.5 cm-1 gap between A1g and E2g peaks of the Raman single spectrum and very high photoluminescence (PL) response at 1.95eV. High optical quality of these crystals attests to their applications in next generation optoelectronic devices.

EP03.11.15
Elucidation of the Growth Mechanism of MoS2 During the CVD Process Sajeevi S. Withanage, Mike Lopez, Wasee Sameen, Vanessa Charles and Saiful Khondaker; University of Central Florida, Orlando, Florida, United States.

Chemical vapor deposition (CVD) based co-evaporation is a well-established method for the single crystal growth of transition metal dichalcogenides (TMDs) including molybdenum disulfide (MoS2) with excellent electrical and optical properties, still reproducibility of the results has been a challenge since the growth is very sensitive to small perturbations of the growth conditions. Poor understanding in the growth mechanism of this single crystal growth makes it even harder to control growth parameters for reproducible growth. Atomic scale control of the precursors in the vapor phase is the key for such growth. We found this is very hard to achieve with the solid precursors and other limited resources such as lacking independent temperature control of precursors, changes and turbulence of the flow due to internal and external conditions, etc. We evidenced that majority of the growth results in intermediate sub-oxidized MoSx (Sx/sub-2) crystals rather than single crystal MoS2 on the substrate due to these less optimized conditions, especially excess molybdenum environment. Characterization of these microcrystals by Raman spectroscopy showed that they are a combination of MoO3 and MoS2. We were able to successfully sulfurize and recrystallize them into MoS2 single crystals which are confirmed by Raman spectroscopy, photoluminescence spectroscopy and atomic force microscopy. We present systematic experimental results for MoSx formation and resulfurization process elucidating the growth mechanism of this CVD process. This study shows that MoSx formed at the intermediate state can be useful toward reproducible growth of MoS2.

EP03.11.16
CVD Growth of Monolayer MoS2 by Using MoO3 Thin Films as a Precursor for Co-Evaporation Sajeevi S. Withanage1, Mike Lopez1, Hirokjyoti Kalita1, Hee-Suk Chung1, Tania Roy1, Yeonwoong Jung1 and Saiful Khondaker1; 1University of Central Florida, Orlando, Florida, United States; 2Korea Basic Science Institute, Jeonju, Korea (the Republic of).

Transition metal dichalcogenides (TMDs) including molybdenum disulfide (MoS2) is a new class of 2D materials which has a wide range of applications due to their unique optical and electronic properties. Weak inter-layer Van der Waal bonding, direct band gap in single layer, photo conductivity, high sensitivity and high mobility of these materials has promising applications in next generation electronics and optoelectronics. Significant amount of research has been done over the years to synthesize high quality large area monolayers of MoS2; a solid method for large area single crystal growth with good reproducibility is yet to be achieved. We report novel method for chemical vapor deposition (CVD) based growth of monolayer MoS2; by using thermally evaporated thin films of molybdenum trioxide (MoO3) as the molybdenum (Mo) source for co-evaporation. Compared to the commonly used MoO3 powder, thin films give much precise control over the amount of MoO3 and uniform evaporation rate of these films creates a stable vapor pressure at the growth phase hence facilitate much uniform, clean single crystal growth reproducibly. These high quality monolayer crystals are as large as 95µm and were characterized by Raman spectroscopy, photoluminescence spectroscopy, atomic force microscopy and transmission electron microscopy. The bottom gated field effect transistors (FETs) fabricated on as grown single crystals shows a type transistor behavior with a good on/off ratio of 104 and mobilities up to 4.5 cm2/Vs under ambient conditions approving the ability of these materials in future semiconductor electronics.

EP03.11.17
Low Temperature Photodetector Based on GQDs/MoS2 with Laser Tunable Responsivity Minook Min1, Gustavo A. Saenz1 and Anupama Kaul1, 2, 3; 1Department of Materials Science and Engineering, University of North Texas, Denton, Texas, United States; 2Electrical Engineering, University of North Texas, Denton, Texas, United States; 3PACCAR Technology Institute, University of North Texas, Denton, Texas, United States.
Transition metal dichalcogenides (TMDs), which are semiconductors of the type MX2, where M is a transition metal atom such as Mo or W and X is a chalcogen atom such as S or Se are available as building blocks for novel optoelectronic and photonic devices. Among the various TMDs materials, Molybdenum disulfide (MoS2) a representative n-type semiconductor, possesses a band gap ranging from an indirect bandgap (1.2 eV) in bulk form to a direct bandgap (1.8 eV) in the monolayer which enables its applications in photo-electronics such as photocatalyst and phototransistors devices. Monolayer MoS2 demonstrated mobility of ~0.1-10 cm2V-1s-1 and on/off ratios of 106 at room temperature. The reported monolayer MoS2 photodetectors have obtained a responsivity of 880 AW-1 at a wavelength of 561 nm and a photo-response in the 400-680 nm range. Also, a hybrid 2D materials and quantum dots phototransistor has been reported to show very high gain and optical sensitivity determined by the property of the quantum dots. Here we present a quantum dots/MoS2 photodetector consisting of graphene quantum dots and multilayer MoS2 sheets. Graphene quantum dots and MoS2 hybrid films are characterized by Raman/PL spectroscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). We measured electrical property of GQDs/MoS2 devices under varied light range at low temperature. Our results suggest that the MoS2 and graphene quantum dots hybrid structure can be promising as efficient photo-detecting devices and optoelectronic circuits.

EP03.11.18
Scalable Single Step Route to Produce 2D-MoS2 Composites Rebecca F. Albers1, Elson Longo1 and Edson R. Leite1, 2; 1Chemistry Department, Federal University of São Carlos, São Carlos, Brazil; 2Brazilian Nanotechnology National Laboratory, Brazilian Center for Research in Energy and Materials, Campinas, Brazil.

Two-dimensional (2D) materials have attracted much attention from the scientific community due to their unique properties, such as optical, magnetic and mechanical. For example, due to its high Young’s modulus (~270 GPa), 2D-MoS2 is highlighted as a great candidate for nanofiller in polymeric composites. However, although 2D composite materials can be applied in many fields, the quality and the yield of their fabrication process are a constant concern. MoS2 is the most studied transition metal dichalcogenide in the world and many techniques have been developed to obtain this material, such as chemical vapor deposition and mechanical exfoliation. Recently, liquid exfoliation using ultrasonication has been used to obtain MoS2 sheets and functionalized MoS2 sheets in a single step. The exfoliation in the presence of the polymer polybutadiene (PB) increases the yield of the process, since the PB bonds in the edge of the MoS2 sheets stabilize the 2D structure during the exfoliation. Accordingly, in this study we provide some fundamental insights into MoS2 exfoliation process and yield increasing. For this, 2D-MoS2 materials were prepared by exfoliation under ultrasonication by using a bath and a tip, with three different molar mass of PB (5k (PB5k), 200k (PB200k) and 200k-300k (PB300k)) and two different solvents to disperse the polymers (toluene and tetrahydrofuran). When the exfoliation was performed by using PB5k, MoS2 sheets with very similar quality were obtained, inasmuch as Raman spectroscopy showed a frequency difference between A1g and E2g bands around 25 cm-1 (value for bulk MoS2 is 26.3 cm-1), regardless of the solvent used. On the other hand, when the exfoliation was performed by using PBS, better results are obtained when no solvent was used to disperse the polymer, since this polymer is liquid at room temperature (i.e., its role occurs without the need of a new medium). Moreover, characterizations of the 2D-MoS2 materials by X-ray and electron diffraction showed a higher degree of exfoliation in the presence of the polymer than in its absence. Besides, although the nature of the used solvents to disperse the polymer did not influence the quality of the sheets, the yield of the process was quite enhanced when toluene was used (11.26 % for the exfoliation when PB200k was used). This methodology provides a promising avenue toward the producing 2D-MoS2 composites with high degree of exfoliation and yield.

We thank FAPESP (CDMF, proc. 2013/07296-2) for the financial support; FAPESP (2016/14493-7) for the scholarship; CNPq and CAPES.


EP03.11.19
Scalable and Highly Crystalline Chemical Vapor Deposition of Atomically Thin TMDs Using a Combinatorial Metal Foil-Gas Precursor Method Paolo P. Ferrari1, Apratim Khandelwal2, Mohammad A. Hossain1 and Arend Van Der Zande1; 1Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Transition metal dichalcogenides (TMDs), a branch of the family of 2D materials, offer a wide range of electronic properties that rival or complement those of traditional materials such as silicon and III-V semiconductors. However, growing high-quality monolayers of these materials in a robust, reliable, and scalable way remains a challenge. The majority of studies utilize solid precursors, which is an easy, but unreliable and nonuniform growth method. Two methods which have particular promise are to use metal-organic chemical vapor deposition or solid metal foils with sulfur powder. Using metal-organic chemical vapor deposition to grow 2D monolayers leads to large area and uniform films [1,2], but it proves to be a difficult method to optimize and, typically, it yields domain sizes in the sub-micron range. A more recent method uses foil in combination with soda-lime glass and sulfur powder to achieve large crystal grain size over large areas [3], however, it is subject to the same issues associated with the use of solid precursors. Here, we report a new method that combines the two disparate methods of MOCVD and foil growth with the goal of achieving high quality, large area, and highly uniform monolayers of different TMDs. In the new method, metal foil is used as a source of the metallic precursor of the TMD, including molybdenum and tungsten, and a gas for the chalcogenide component, including hydrogen sulfide H2S or selenide H2Se. The feasibility of the proposed method is demonstrated by growing monolayer MoS2 and WSe2 in the form of individual crystals with grain sizes up to 100 µm as well as continuous films. Using PL and Raman spectroscopy, the as grown WSe2 crystals display 1.62 eV bandgap and FWHM of 60 meV, while the intensity ratio between the photoluminescence and E2g Raman peak is typically 25, indicating quality comparable to the solid precursor and MOCVD growth methods. The influence of growth time and temperature, the presence of salt or soda-lime glass, and flow rate of different gases on the number of layers, domain size and areal coverage are investigated to elucidate the optimal conditions of growth. This robust method is a robust and versatile growth technique that competes with the quality obtained through MOCVD while being much more scalable than solid precursors.


EP03.11.20
Surface Functionalization and Property Correlations of MXenes Gregory Nehrer1, 2, James Hecker1, 2, David Lioi1, 2, Andrew Sharratt1, 2, Faisal Mehmood4, Dhiraj Nepal3, Ruth Pachter3, Richard Vaia2 and W. J. Kennedy2; 1Universal Technology Corporation, Beavercreek, Ohio, United States; 2Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States; 3UES, Inc., Beavercreek, Ohio, United States.

MXenes are a new class of 2-D layered compounds that show promise as a highly-tunable material for next generation composites. In the last decade it has been demonstrated that these ceramic-derived materials can be easily processed into inks, aerosols, paints, and thin films via solution methods not available
to many other 2-D layered materials. Furthermore, they are inherently hydrophilic which is favorable for chemical functionalization. Prior work has demonstrated favorable applications in energy storage and electromagnetic shielding. However, a fundamental understanding of the intrinsic properties of MXenes is lacking, and methods for surface functionalization are needed.

To the purpose of developing tailored MXene bulk films for aerospace applications, we present fundamental electronic, chemical, and structural studies of individual MXene flakes utilizing experimental and theoretical methods. We have size-selected ultrathin sheets and verified their thickness using AFM and TEM and developed anaerobic protocols to surface functionalize individual particles using chemistries of catechols and silanes. Additionally, we confirmed modifications to the crystal lattice and local functional groups using XPS and Raman spectroscopies, as well as used EELS and ultralast transparent optical spectroscopy to extract microscopic electronic properties which were corroborated by theoretical calculations.

EP03.11.21
Understanding and Tuning Electronic Band-Offsets in Mixed-Dimensional van-der-Waals Heterostructures

computational analysis of the sulfurization process for molybdenum trioxide, through interactions with sulfur, still remains poorly understood and insufficiently investigated. Ab initio calculations and molecular dynamics simulations of the reaction of sulfur allotropes (S2-8) with molybdenum trioxide (MoO3) have been used to elucidate the mechanism of sulfurization pathway. These simulations show that the sulfurization process takes place through the formation of molybdenum oxysulfide rings, which can decompose into more sulfurized molybdenum species, oxysulfur molecules and/or smaller sulfur allotropes. As the sulfur allotrope is in a nanoscale sulfur distribution in a vapor phase, our approach can be adjusted to maximize the efficiency of the powder vaporization process.

Effect of Oxidation on the Raman and Photoluminescence Properties of Unpassivated and Novel-Passivated Layered GaTe

Large-area, high-quality two-dimensional molybdenum disulfide crystals have commonly been grown through powder vaporization because of its simplicity and cost-effectiveness. However, the sulfurization process for molybdenum trioxide, through interactions with sulfur, still remains poorly understood and insufficiently investigated. Ab initio calculations and molecular dynamics simulations of the reaction of sulfur allotropes (S2-8) with molybdenum trioxide and experimentally proposed molybdenum oxysulfide intermediates (MoO2S, MoO2S2) have been used to elucidate the mechanistic steps in the sulfurization pathway. These simulations show that the sulfurization process takes place through the formation of molybdenum oxysulfide rings, which can decompose into more sulfurized molybdenum species, oxysulfur molecules and/or smaller sulfur allotropes. As the sulfur allotrope is in a nanoscale sulfur distribution in a vapor phase, our approach can be adjusted to maximize the efficiency of the powder vaporization process.

EP03.11.23
Effect of Oxidation on the Raman and Photoluminescence Properties of Unpassivated and Novel-Passivated Layered GaTe

Emerging two-dimensional gallium chalcogenides, such as gallium telluride (GaTe), are considered promising layered semiconducting materials that can serve as vital building blocks in the field of nanoelectronics, optoelectronics and quantum photonics. Studies on the physical behaviors of layered GaTe are at early stages of fundamental research, and thus, are of significant interest from the scientific and technological point of view. However, oxidation-induced electronic, structural and optical changes observed in ambient-exposed gallium chalcogenides need to be further investigated and addressed. Herein, we report on the thickness-dependent effect of air and oxygen exposure on the Raman and photoluminescence (PL) properties of GaTe flakes, with thicknesses spanning in the range of a few layers to 65 nm. We have developed a novel chemical passivation that results in complete encapsulation of the as-exfoliated GaTe flakes in ultrathin siliconesquioxane (HSQ) film. A combination of correlation and comparison of Raman and PL studies reveal that the HSQ-capped GaTe flakes are effectively protected from oxidation in air ambient over the studied-period of 7 months, and thus, preserving their structural and optical characteristics. This contrasts with the behavior of uncapped GaTe, where we observe a significant reduction of the GaTe-related PL (~100×) and Raman (~4×) peak intensities. Furthermore, the time-evolution of the Raman spectra of uncapped GaTe is accompanied with the appearance of two new prominent broad peaks, at ~130 cm⁻¹ and ~146 cm⁻¹, which are associated to photo-induced effects, such as oxidation and amorphization, in GaTe. The oxidation of the uncapped GaTe is consistent with our Auger spectroscopy findings. Moreover, our surface-passivation has a dual role. Along with effectively protecting the flakes, it offers the capability to simplify the integration process of fabricating GaTe-based nanodevices, given HSQ is the most commonly used resist for electron beam lithography. Our holistic approach can help further explore and reveal the physical properties of few-layer GaTe, towards the practical realization of nanophotonic devices with structural, and photoluminescence stability.

EP03.11.24
Polarity Governs Atomic Interaction Through Two-Dimensional Materials

Emerging two-dimensional gallium chalcogenides, such as gallium telluride (GaTe), are considered promising layered semiconducting materials that can serve as vital building blocks in the field of nanoelectronics, optoelectronics and quantum photonics. Studies on the physical behaviors of layered GaTe are at early stages of fundamental research, and thus, are of significant interest from the scientific and technological point of view. However, oxidation-induced electronic, structural and optical changes observed in ambient-exposed gallium chalcogenides need to be further investigated and addressed. Herein, we report on the thickness-dependent effect of air and oxygen exposure on the Raman and photoluminescence (PL) properties of GaTe flakes, with thicknesses spanning in the range of a few layers to 65 nm. We have developed a novel chemical passivation that results in complete encapsulation of the as-exfoliated GaTe flakes in ultrathin siliconesquioxane (HSQ) film. A combination of correlation and comparison of Raman and PL studies reveal that the HSQ-capped GaTe flakes are effectively protected from oxidation in air ambient over the studied-period of 7 months, and thus, preserving their structural and optical characteristics. This contrasts with the behavior of uncapped GaTe, where we observe a significant reduction of the GaTe-related PL (~100×) and Raman (~4×) peak intensities. Furthermore, the time-evolution of the Raman spectra of uncapped GaTe is accompanied with the appearance of two new prominent broad peaks, at ~130 cm⁻¹ and ~146 cm⁻¹, which are associated to photo-induced effects, such as oxidation and amorphization, in GaTe. The oxidation of the uncapped GaTe is consistent with our Auger spectroscopy findings. Moreover, our surface-passivation has a dual role. Along with effectively protecting the flakes, it offers the capability to simplify the integration process of fabricating GaTe-based nanodevices, given HSQ is the most commonly used resist for electron beam lithography. Our holistic approach can help further explore and reveal the physical properties of few-layer GaTe, towards the practical realization of nanophotonic devices with structural, and photoluminescence stability.

EP03.11.25
Polarity Governs Atomic Interaction Through Two-Dimensional Materials

Emerging two-dimensional gallium chalcogenides, such as gallium telluride (GaTe), are considered promising layered semiconducting materials that can serve as vital building blocks in the field of nanoelectronics, optoelectronics and quantum photonics. Studies on the physical behaviors of layered GaTe are at early stages of fundamental research, and thus, are of significant interest from the scientific and technological point of view. However, oxidation-induced electronic, structural and optical changes observed in ambient-exposed gallium chalcogenides need to be further investigated and addressed. Herein, we report on the thickness-dependent effect of air and oxygen exposure on the Raman and photoluminescence (PL) properties of GaTe flakes, with thicknesses spanning in the range of a few layers to 65 nm. We have developed a novel chemical passivation that results in complete encapsulation of the as-exfoliated GaTe flakes in ultrathin siliconesquioxane (HSQ) film. A combination of correlation and comparison of Raman and PL studies reveal that the HSQ-capped GaTe flakes are effectively protected from oxidation in air ambient over the studied-period of 7 months, and thus, preserving their structural and optical characteristics. This contrasts with the behavior of uncapped GaTe, where we observe a significant reduction of the GaTe-related PL (~100×) and Raman (~4×) peak intensities. Furthermore, the time-evolution of the Raman spectra of uncapped GaTe is accompanied with the appearance of two new prominent broad peaks, at ~130 cm⁻¹ and ~146 cm⁻¹, which are associated to photo-induced effects, such as oxidation and amorphization, in GaTe. The oxidation of the uncapped GaTe is consistent with our Auger spectroscopy findings. Moreover, our surface-passivation has a dual role. Along with effectively protecting the flakes, it offers the capability to simplify the integration process of fabricating GaTe-based nanodevices, given HSQ is the most commonly used resist for electron beam lithography. Our holistic approach can help further explore and reveal the physical properties of few-layer GaTe, towards the practical realization of nanophotonic devices with structural, and photoluminescence stability.
obtained epitaxially aligned single-crystalline GaAs, GaN, and LiF through monolayer (1ML), bilayer (2ML), and trilayer (3ML) graphene, respectively. More interestingly, we discovered that such field penetration is substantially attenuated through hexagonal boron nitride (hBN) that contains polarity in its bonding. Thus, van der Waals epitaxy seeded from hBN and remote epitaxy seeded from graphene occur simultaneously when we perform epitaxy of GaN through 1ML hBN. Through 3ML hBN, complete transition from remote epitaxy to van der Waals epitaxy occurs. The excellent consistency between the theoretical and experimental findings unequivocally confirms that the ionic character of atomic bonding determines remote atomic interaction through 2D materials. Our work demonstrates that 2D materials can be sensitively probed at atomic scale by performing epitaxy through them. This transparency highly depends on the nature of substrate materials, while it can also be tuned by modulating the thickness and bonding chemistry of the 2D materials.

EP03.11.25
The Role of Oxygen as a Growth Catalyst in the Formation of MoS2 by CVD
Seong Soon Jo and Rafael Jaramillo; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

MoS2 transition metal chalcogenide (TMD) thin films are often made using MoO3 as a precursor. Directly converting metallic Mo to MoS2 would hold advantages for certain studies such as research on metal alloy TMDs, and for processes such as vacuum deposition in an oxygen-free environment. Recent work shows that although the thermodynamics of MoS2 formation in sulfur-rich environments may be favorable, the outcome is highly dependent on the chemical pathway taken and in particular on the oxidation state of the Mo precursor [1,2].

Here we report a study of the role of oxygen as a catalyst for the sulfurization of metal Mo thin films in chemical vapor deposition (CVD). We study the formation of MoS2 at high temperature from Mo and MoO3 films in the presence of S and H2S vapor and with different trace levels of oxygen. By systematically varying the reduction potential of the CVD furnace environment we demonstrate the essential role of oxygen in catalyzing MoS2 formation at relatively low temperature. Our results help to interpret the sizable literature on the growth of MoS2 thin films by CVD, and provide useful guidance for developing processes to make wafer-scale MoS2 films for applications ranging from photonics to catalysis.


EP03.11.26
Cleaning, Passivating and Doping Monolayer MoS2 by Laser Irradiation
Rahul Ban1, Victor Carozo2, Yuanxi Wang3, Ahmad E. Islam4, Nestor Perea-Lopez2, Kazumori Fujisawa2, Vincent Crespi3, Mauricio Terrones2 and Benji Maruyama1; 1Air Force Research Laboratory, WPAFB, Ohio, United States; 2The Pennsylvania State University, State College, Pennsylvania, United States.

Lattice defects such as chalcogen vacancies drastically affect the optoelectronic properties of monolayer transition metal dichalcogenides (TMDs) grown by chemical vapor deposition (CVD). They can be passivated through charge-transfer doping by laser irradiation in air. Here we perform a systematic in situ study to elucidate the passivation mechanism upon laser irradiation and show how to controllably n-dope monolayer MoS2. By combining resonance Raman and photoluminescence (PL) spectroscopy we show that an increase in defect density correlates with a red-shifted PL emission and hence an increase in electron density. Density Functional Theory (DFT) calculations identify chalcogen vacancies to be facilitators (not the source) of n-doping, and population of mid-gap levels upon doping lowers the activation barrier for O2 adsorption from 0.3 to 0.03 eV. Laser irradiation aids in the oxygen-passivation of chalcogen vacancies, manifested by an increase in PL intensity and blueshifted emission, and this blueshift is determined by the laser power density. The passivation occurs on two timescales, with the removal of surface adsorbrates first, followed by oxygen adsorption at the sulfur vacancy sites. Our systematic study provides valuable insights into the defect passivation process, and also demonstrates a practical way to modulate the carrier concentration of monolayer MoS2.

EP03.11.27
MXene Nanosheets—Electrochemical Etching, Oxidation Impediment and Morphology Alteration
Smit Alkesh Shah1, Wannmi Sun1, Touseef Habib1, Miladin Radovic2, Jodie L. Lutkenhaus1,2 and Micah Green1,2; 1Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas, United States; 2Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

MXenes are a relatively new class of nanosheets, and they have gained significant interest due to their unique chemical, dielectric and transport properties. Since their discovery in 2011, they have shown promise in a wide range of applications such as electromagnetic shielding, supercapacitors, batteries and water desalination. Typically, MXenes are made from layered carbides and/or nitrides called MAX phases, by selectively etching the A layer using hydrofluoric acid. Here, we successfully demonstrate the electrochemical etching of Al from porous Ti2AlC electrodes in dilute hydrochloric acid (no F ions) to form a Ti2CTx MXene layer on Ti2AlC. These MXenes possess chloride terminal groups, along with the common ones, such as –O and –OH. However, electrochemical etching can result in subsequent over-etching of parent MAX phases to carbide-derived carbon (CDC). We propose a core–shell model to explain electrochemical etching of Ti2AlC to Ti2CTx and CDC. The proposed model suggests that a careful balance in etching parameters is needed to produce MXenes while avoiding over etching. Our electrochemical approach expands the possible range of both etching techniques and resulting MXene compositions. We also demonstrate that colloidal MXene nanosheets encapsulated within spray-dried droplets can be scrolled, bent, and folded into 3D crumpled structures by capillary forces during drying. This morphological change was observed to be reversible upon rehydration. Finally, Ti2CTx MXenes are prone to oxidation, which causes them to chemically degrade to TiO2 over time and become impractical for desired applications. This makes processing of Ti2CTx MXenes difficult. We demonstrate that processing Ti2CTx MXenes in organic solvents and polymer composites leads to lower TiO2 content and higher conductivity compared to Ti2CTx MXenes processed in water. We monitored the oxidation content by measuring the conductivity of the processed films.

EP03.11.28
Ultraslimly-Exfoliated Layer-Controlled Black Phosphorus Nanosheets for Gas Sensing Applications
Ying-Hao Pai, Wang Wei Chien and Chun-Hua Chen; National Chiao Tung University, Hsin-Chu, Taiwan.

Atomically thin black phosphorus (BP), a new family member of the two-dimensional (2D) material, has attracted great attention in these years due to its exceptional electrical, mechanical, and surface properties offering great potential in a variety of applications. However, synthesis, dimensional control, particularly the thickness, and even the preservation of BP remain the challenges since the BP is extremely sensitive to humidity, which would lead to
serious structure damage. In this work, extremely-high-energy ultrasonic exfoliation was performed not only for effectively obtaining mass-produced dimension controlled BP nanosheets, but for greatly reducing the risk of overexposure to the aqueous solvents. A series of BP nanosheets with various dimensions were successfully obtained and subsequently applied as single-nanocrystal and nanoassembled chemical sensors for evaluating their sensing performance.

EP03.11.30
Understanding the Role of the Contact-Material Interface in a MoS2 Chemical Gas Sensor Using Directly Grown Graphene-MoS2 Lateral Heterostructures

Donna Deng1, Shruti Subramanian1, Kehao Zhang1, Keith Perkins1, Ke Xu2, Jun Li1, Randall M. Feenstra1, Susan Fullerton-Shirey1 and Joshua Robinson1

As the synthesis and material properties of 2D materials is better understood, new fronts of potential applications are opened, such as chemical and biochemical sensing. 2D materials offer many advantages in this field, including physical flexibility and large surface-to-volume ratio. While the mechanisms and factors affecting nanorods and nanotubes using conventional 3D materials have been well studied, such details in 2D transition metal dichalcogenide based sensors are not fully understood. In this work, we look at the role of the electronic contact in the sensing capabilities of directly synthesized MoS2 sensors for trimethylamine (TEA). Comparing MoS2 sensors with conventional metal contacts to graphene contacts, we find the band structure and corresponding charge transfer at the contact-channel interface plays a large role in the sensing characteristic of such devices. Devices with Ti/Au-MoS2 contacts, experimentally shown to have Schottky barriers with approximately twice the height of barriers across epitaxial graphene (EG)–MoS2 contacts, exhibit up to 5 orders of magnitude higher sensing amplitude (defined as a fractional change in the device conductance, $\Delta G/G_0$) compared to devices using EG contacts. In addition, effects of controlled defects, such as substitutional doping and plasma induced defects, on the MoS2 channel is studied. By incorporating 2 atomic % of Nb, for example, the TEA sensitivity threshold is reduced by more than an order of magnitude.

EP03.11.31
Electronic Structure and Strain Engineering of Layered Group IV Monochalcogenides

Baiyu Zhang and Xiaofeng Qian
Texas A&M University, College Station, Texas, United States.

Group IV monochalcogenides (MX, M=Ge or Sn, X=S or Se) have attracted a lot of attention very recently as MX are isoelectronic to black phosphorus. Monolayer black phosphorus, namely phosphorene holds high carrier mobility, optical absorbance, negative Poisson’s ratio (NPR), and a semiconducting gap. Monolayer group IV monochalcogenides MX exhibit large piezoelectricity, ferroelectricity, and degenerate structural ground state due to their noncentrosymmetric characteristics, and ultrathin MX have been successfully synthesized. Here we report a first-principles theoretical study of their negative Poisson’s ratio and electronic properties of group IV monochalcogenides with increasing strain and thickness. Our results show that, as number of layers increases, both direct and indirect band gaps decrease. Unlike MoS2, whose band gap transits from indirect to direct when thickness reduces down to monolayer, all four MX remain as indirect-gap semiconductors from monolayer to bulk phase. Furthermore, similar to few-layer black phosphorus, electronic structures, particularly band gaps, of MX can be tuned by strain along either armchair or zigzag direction. Different from auxetic black phosphorus, bulk MX possesses nearly zero Poisson’s ratio along the plane normal direction when elastic strain is applied in the zigzag or armchair direction. The present results shed light on the possibility of van der Waals and elastic strain engineering of group IV monochalcogenides for applications in optoelectronics and functional devices.

EP03.11.32
Raman Analysis of Liquid-Exfoliated Layered Nanomaterials

Matthew Large1, Aline Amorim-Graf2, Sean P. Ogilvie2, Alice King and Alan Dalton2
Physics and Astronomy, University of Sussex, Brighton, United Kingdom.

Raman analysis is a powerful technique for investigating the atomistic structure of materials by probing the vibrational behaviour of covalent bonds. In the field of nanomaterials science, Raman is frequently used to demonstrate quality of nanomaterials prepared through bulk techniques (plasma synthesis, liquid exfoliation). In many cases metrics based on peak ratios, positions and separations have been presented that allow properties such as layer number, defect density and lateral size to be determined from a range of nanomaterials. Single spot spectra at low magnification are often taken and stated to be “representative” of a sample, and used alongside metrics to describe population averages. We ask the question, can this approach ever be representative? It is intuitive that the interaction cross-sections of thicker particles are necessarily higher than thinner ones, and likewise for particles with a greater lateral size; therefore large particulates with high-layer number are likely to dominate spectra collected when a wide distribution of particles are present in the interaction volume of the excitation source. On the other end of the scale, if the platelets are very large, the number of particles in the spot is no longer statistically representative of the sample, except in the limiting case of macroscopic CVD-produced materials.

We propose that the solution to this measurement problem is the use of Raman mapping at high magnification, and statistical analysis of the pixel-by-pixel spectra to build a truly representative picture of the particle distribution in the sample. We demonstrate the approach using three layered materials commonly discussed in the literature, prepared by standard liquid-phase exfoliation processes; molybdenum disulfide (MoS2), graphene, and hexagonal boron nitride (h-BN).

EP03.11.33
Structural Characterization of Defects in Hexagonal Boron Nitride Using Scanning Probe Spectroscopy

Daichi Kozawa1, Ananth Govind Rajan1, Volodymyr Koman1, Kevin Silmore1, Pingwei Liu1, Albert T. Liu2, Daniel Blankschtein3 and Michael Strano2

Lattice defects formed in 2D hexagonal boron nitride (h-BN) have emerged as unique nanopores. Their most useful property is photoluminescence (PL) from the defects in the form of single-photon emission even at room temperature. Even though the defects exhibit PL at multiple wavelengths in a visible range, which vary from defect to defect, the static characterization and analysis have been limited attention. To systematically characterize individual defects of h-BN, we develop scanning probe spectroscopy system combined with an atomic force microscope and a time-correlated single photon counting module. This system allows us to automatically measure thousands of PL spectra at each point, and correlate with PL lifetime, PL excitation, and thickness from individual defects. The statistical analysis of these collected data provides us insight into physical and chemical properties of nanoscale defects in h-BN and potential for ultrasensitive sensing and quantum photonics.

EP03.11.34
Raman Enhancement of Blood Constituent Proteins Using Graphene

Shengxi Huang1, Rishikesh Pandey2, Ishan Barman3, Jing Kong1 and Mildred S.
Texas A&M University, College Station, Texas, United States.

Raman spectroscopy has drawn considerable attention in biomedical sensing due to the promise of label-free, multiplexed and objective analysis along with the ability to gain molecular insights into complex biological samples. However, its true potential is yet to be realized due to the intrinsically weak Raman signal. Here, we report a simple, inexpensive and reproducible signal enhancement strategy featuring graphene as a substrate. Taking key blood constituent proteins as representative examples, we show that Raman spectra acquired from biomacromolecules can be reproducibly enhanced when these molecules are placed in contact with graphene. In particular, we demonstrate that hemoglobin and albumin display significant, but different, enhancement with the enhancement factor depending on the Raman modes, excitation wavelengths and analyte concentrations. This technique offers a new strategy for label-free biosensing owing to the molecular fingerprinting capability, signal reliability, and simplicity of the enhancement method.

**EP03.11.35**

A Comparison of Isotope-Enriched Bulk Hexagonal Boron Nitride Crystal Grown from Nickel- and Iron-Based Solutions  
Jiahun Li, Lianjie Xue, Bin Liu and James H. Edgar; Kansas State University-Chemical Engineering, Manhattan, Kansas, United States.

The growth of 10B and 11B isotope-enriched hexagonal boron nitride (hBN) single crystals from molten metal solutions was carried out through a combined experimental and theoretical approach. Using elemental 10B or 11B and nitrogen as the source, the hBN crystal size and quality obtained in molten iron (Fe), iron and chromium (Cr), and mixed Ni-Cr solutions were compared. In this work, the Fe-based solvent is shown to provide a less expensive growth environment than the more established nickel and chromium solvent.

hBN crystals were grown at 1,550 °C and atmospheric pressure, under continuously flowing nitrogen, in pure iron, 50 wt% Ni and 50 wt% Cr, and 80 wt % Fe and 20 wt% Cr. For the crystals grown using a pure Fe solvent, the lateral hBN crystal size and thickness were 0.5 mm and 30 microns, respectively. The predominant crystal domain shapes were equilateral triangles, with edge lengths up to 200 microns. This solvent produced the smallest crystals, presumably due to multiple nucleation sites due to the high solubility of nitrogen in Fe. The crystals grown from the Ni-Cr solution produced larger crystals sheets, up to 2.0 mm laterally and 80-100 microns thick. The surfaces were covered in parallel steps, suggesting the hBN grains had similar orientations. Some metallic inclusions were seen in the hBN produced from the Ni-Cr solvent. The domain shapes were equilateral triangles, truncated triangles, and hexagons. The hBN grown from 80 wt % Fe and 20 wt% Cr solvent had a similar lateral size and thickness with less surface steps, compared to crystal grown from Ni-Cr. Within the sheet were large individual grains, with lateral dimensions up to 400 microns. The main shape of domains were equilateral triangle and parallelogram. The crystals were colorless and free from any inclusions. A critical requirement for successful hBN crystal growth is that solvent and boron nitrogen effectively. DFT was applied to determine the solubility of the nitrogen and boron in bulk Fe, a 50 at% Fe- 50 at % Cr mixture, and a 50 at% Ni-50 at% Cr mixture. At 1,550 °C, the calculated order of nitrogen solubility was: Fe>Fe-Cr>Ni-Cr. For boron, the order was: Fe-Cr>Cr-Ni-Cr. Thus, both Fe and Fe-Cr were predicted to be good solvents for hBN crystal growth. The DFT calculations and experimental results are consistent.

**EP03.11.36**

Molybdenum Vanadium Carbide—A New Tailorable Double-Transition Metal MXene for Electrochemical Applications  
David Pinto1, Babak Anasseri2, Hemesh Avireddy2, Juan R. Morante2, William Porzio3 and Yuriy Gogotsi1; 1Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 2Catalonia Institute for Energy Research, Sant Adrià de Besòs, Spain; 3Faculty of Physics, University of Barcelona, Barcelona, Spain; 4Istituto per lo Studio delle Macromolecole, Milan, Italy.

MXenes are a large family of 2D materials made by selective etching of the aluminum layers from Mn+1AlCn MAX phases into open-structures with single layers of Mn-Cn. These new highly-conductive materials present a remarkable capacitance (1500 F/cm²) in H2SO4. In 2015, the MXene family was extended to include double-transition metal (M) MXenes by introducing two different M types in separate atomic layers of a MXene single-flake, such as Mo5TiC3. The latter phase has already found use as electrode material in supercapacitor and battery-type devices. More than two dozen different compositions of the ordered double-M MXenes were predicted theoretically. Here, we present the synthesis and characterization of Mo5V4-xC3 MAX, and its resulting Mo5V4-xC3 MXene. Unlike Mo2TiC3, this phase is less ordered than previously reported double-M phases. Besides this, without having a dramatic change in its crystallographic structure, Mo5V4-xC3 can be produced with various ratios of Mo and V. This tailoring modifies the electronic and electrochemical properties, and surface terminations, making Mo5V4-xC3 a promising candidate for various applications. For example, in aqueous supercapacitors (1 M H2SO4), Mo5V4-xC3 has demonstrated one of the largest positive electrochemical window so far (up to 0.6 V vs. RHE, 0.75 V voltage window) with capacitance of 850 F/Cm². And, because of this, Mo5V4-xC3, positive electrode, can be coupled with TiC3, negative electrode, in a first full-MXene supercapacitor device producing 150 F/cm² device capacitance with a 1 V window. Besides the application in energy storage, Mo5V4-xC3 may be a promising electrocatalyst for hydrogen generation in water splitting devices.

**EP03.11.37**

Surfactant-Mediated Direct Patterned Growth of Atomically Thin Monolayers of Transition Metal Dichalcogenides  
Xufan Li1, Ethan L. Kahn2, Xiahao Sang3, Akina Oyede4, Kazunori Fujisawa2, Tianyi Zhang2, Raymond R. Unocic3, Kai Xiao3, Gugang Chen1, Mauricio Terrones2 and Avetik Harutyunyan1, 2; 1Honda Research Institute USA Inc., Columbus, Ohio, United States; 2Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, United States; 3Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

To realize tremendous potential of two-dimensional (2D) monolayers of transition metal dichalcogenides (TMDs) requires high quality crystals with controllable morphologies and sizes, supported by various substrates, which in turn assumes deep understanding of the growth mechanisms. Moreover, these monolayers are particularly sensitive to surface contaminants associated with lithographical processes to create desired geometries. Here, we show that during the chemical vapor deposition growth of MoS2 monolayer single crystals from MoO3 and NaBr powder precursors, the presence of halide alters island growth (3D) mode of MoS2 to layer-by-layer growth (2D) mode. We found that alkali metal halide salt additive behaves as a surfactant in the growth of the TMD monolayers by chemical passivation of the edges that facilitates the strain and thereby kinetically suppresses 3D islanding growth. This insight enables us to enhance the growth of MoS2 monolayers on various substrates by preliminarily depositing a salt layer. Such a surfactant-mediated growth can also be applied to other 2D TMDs (e.g., WS2, MoSe2). Moreover, using various patterns of pre-deposited salt, we demonstrate direct growth of high quality MoS2 monolayers with corresponding patterns, which can be used for patterned 2D electronic devices. Our results open a perspective for direct patterned fabrication of pristine MoS2 monolayers on various substrates without lithography or transferring.

**EP03.11.38**

Substantial Impact of Charge on Electrochemical Reactions of Two-Dimensional Materials  
Junjian Shi, Donghoon Kim and Yuanyue Liu; The University of Texas at Austin, Austin, Texas, United States.
Two-dimensional (2D) materials have attracted great interest in catalyzing electrochemical reactions such as water splitting, oxygen reduction, and carbon dioxide reduction. Quantum mechanical simulations have been extensively employed to study the catalytic mechanisms. However, these calculations typically assume that the catalyst has a zero/constant charge for computational simplicity, while in reality, the catalyst usually has a varying charge as the reaction proceeds due to the match between its Fermi level and the applied electrode potential. These contradictions urge an evaluation of the charge effects.

Here using grand canonical density functional theory calculations, we show that the charge on 2D materials can have a much stronger impact on the electrochemical reaction than the charge on 3D metals, which arises from the unique electronic properties of 2D materials. Our work calls for reconsideration of some of the previously suggested electrocatalytic mechanisms of 2D materials by incorporating the charge effects. [1]


EP03.11.39
High-Performance, Flexible, Inkjet Printed Heterostructure Photodetector for Biosensing Applications
Ridwan Fayaz Hossain and Anupama Kaul;
University of North Texas, Denton, Texas, United States.

Age-related macular degeneration (AMD), a retinal degenerative disease that results in a continuous degeneration of photoreceptors in the retina which eventually leads to complete blindness [1]. One approach to combat AMD is through the use of artificially implantable photodetectors that are physically placed on the retina. The photodetector pixels allow the implantable photodetectors to be in intimate contact to retinal pigment epithelium. Interestingly, 2D materials such as photosensitive and semiconducting molybdenum disulfide (MoS₂) and electrically conducting graphene have recently received tremendous promise due to their unique photonic and optoelectronic properties and their potential in various types of micro and nano devices [2,3]. In this study, we have tested the biocompatibility of various 2D materials, such as graphene and MoS₂, in several organic solvents. A highly biocompatible photodetector on a flexible polyimide substrate was designed, fabricated using inkjet printing to form photosensitive pixels and tested as a function of photo intensity and strain.

Inkjet printed graphene and MoS₂ inks were characterized using techniques such as Raman Spectroscopy, PL, SEM and AFM. The inkjet printed 2D heterostructure devices were photoresponsive to broad-band incoming radiation in the visible regime, and the photocurrent scaled proportionally with the incident light intensity, exhibiting a photoresponsivity \( R \approx 0.30 \text{ A/W} \). This is \( 10^4 \) times higher compared to prior reports, and detectivity \( D \) was calculated to be \( 3.6 \times 10^{10} \text{ Jones} \) at room temperature. The strain-dependent measurements of photocurrent with bending showed a photocurrent of \( \approx 1.16 \mu\text{A} \) with strain levels for curvature up to \( \approx 0.262 \text{ cm}^{-1} \), indicating the feasibility of such devices for large format arrays printed on flexible substrate, unlike conventional Si implantable detectors that are rigid and nonconformable.

In conclusion, the inkjet printed, biocompatible 2D hetero-junction photodetector formed on flexible and conformable substrates was successfully shown to be photoresponsive to a wide range of light intensities and strain levels, making it a promising prospect for in vivo bio-sensing applications for AMD.

References:


EP03.11.40
Two-Dimensional Topological Conduction in SnTe Thin Films
Stephen D. Albright1, Ke Zou2, F. J. Walker3 and Charles H. Ahn1; 1Department of Physics, Center for Research on Interface Structures and Phenomena, Yale University, New Haven, Connecticut, United States; 2Department of Physics & Astronomy, Stewart Blusson Quantum Matter Institute, The University of British Columbia, Vancouver, British Columbia, Canada; 3Department of Applied Physics, Center for Research on Interface Structures and Phenomena, Yale University, New Haven, Connecticut, United States.

The recently developed ability to manipulate one-dimensional edge states in conventional topological insulators (TIs) by selectively breaking time-reversal symmetry is a promising step towards developing TI-based devices. The same control of topological states is also possible in topological crystalline insulators (TCIs), such as SnTe, by selectively breaking crystalline symmetry. Large area quasi-two-dimensional TCI films have been difficult to achieve, however, making control of topological states challenging. This work presents structural and transport characterization of high quality ultrathin SnTe films grown by molecular beam epitaxy on single crystal SrTiO₃. Films thin enough to achieve edge state control are continuous and single domain in nature, and transport measurements show two-dimensional topological conduction through the protected SnTe/SrTiO₃ interface. Analysis of quantum effects observed in magnetotransport reveals the nature of topological states in the SnTe films, presenting a path to manipulating these states in devices.

EP03.11.41
Defect-Assisted Heteroepitaxial Growth of Monolayer Tungsten Diselenide Films with Preferential Orientation on Hexagonal Boron Nitride
Xiaotian Zhang1, Fu Zhang1,2, Yuanxi Wang1,2, Daniel Schulman1, Tianyi Zhang1,2, Anushka Bansal1, Nasim Alem1,3, Saptarshi Das4, Stephen D. Albright1, Ke Zou2, F. J. Walker3 and Charles H. Ahn1; 1Department of Physics, Center for Research on Interface Structures and Phenomena, Yale University, New Haven, Connecticut, United States; 2Center for Two Dimensional and Layered Materials, The Pennsylvania State University, University Park, Pennsylvania, United States; 3Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania, United States; 4Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania, United States; 5Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, United States.

The rapid development of device technologies based on 2D transition metal dichalcogenides (TMDs) causes increasing demand for synthesis of high quality large area monolayer and few layer films. Our previous work demonstrated epitaxial growth of large area monolayer WS₂ films on c-plane sapphire using gas source chemical vapor deposition (CVD). However, the optical and electrical properties of coalesced monolayer films grown on sapphire are negatively impacted by the existence of anti-phase boundaries (APBs) resulting from a merging of an equal mixture of 0° and 180° orientated domains as well as non-uniformities arising from steps and charge-induced doping associated with the sapphire surface. Prior studies using powder source CVD demonstrated a preferred domain orientation for MoS₂ grown on hBN and first-principle calculations suggest this phenomenon originates from single atom vacancies on the hBN surface that act as nucleation sites. In this study, we further investigate the mechanism of defect-assisted domain alignment of 2D TMDs on hBN and demonstrate the growth of fully-coalesced WS₂ films on hBN with a reduced density of APBs and improved optical and electrical properties compared to films grown on sapphire.

WS₂ monolayer films were grown by gas source CVD at 800°C using W(CO)₆, and H₂S in a H₂ carrier gas employing a multi-step process to separately control nucleation density and lateral growth and coalescence of domains. Single crystal hBN flakes exfoliated from bulk crystals and transferred onto c-
plane sapphire were used as substrates. He plasma treatment and NH3 annealing were used to modify the surface defect density of hBN. Detailed studies of WSe2 deposition on hBN as a function of growth conditions and substrate pre-treatment confirm that domain nucleation is controlled by the surface defect density rather than the precursor concentration. Over 85% of WSe2 domains have consistent orientation via the defect-assisted growth. Through careful control of nucleation and extended lateral growth time, fully coalesced WSe2 monolayer films on hBN were produced for subsequent characterization. High resolution scanning transmission electron microscopy (S/TEM) analysis demonstrates the absence of APBs in coalesced regions formed by the merging of ¢0 oriented domains. The resulting Moï re pattern formed by the WSe2 on hBN indicates an epitaxial relationship of 3+3 WSe2 on 4+4 hBN. Temperature-dependent photoluminescence measurements show sharp and enhanced exciton and trion emission peaks, with no defect-related bound exciton emission from monolayer WSe2/hBN down to 80K. Backgated FET devices fabricated on WSe2/hBN films transferred to SiO2/Si substrates show an order of magnitude increase in room temperature carrier mobility (~5 cm2/V-s) compared to similar devices fabricated using monolayer WSe2 films transferred from sapphire. The results demonstrate the potential of hBN as a substrate for epitaxial growth of high quality monolayer TMD films.

EP03.11.42
Multifunctional In Situ Doping of Monolayer MoS2 for Electronic and Sensing Applications Kehao Zhang, Donna D. Deng, Shruti Subramanian and Joshua Robinson; The Pennsylvania State University, University Park, Pennsylvania, United States.

Substitutional doping has been demonstrated as an efficient way to tune the electronic and optoelectronic properties of 2D materials.1,2 Beyond the singular functionalization of 2D materials, multifunctional doping of 2D materials provides opportunities to realize great potentials to 2D materials by one dopant, which can be highly compatible to advanced technologies.3 Here, we report the multifunctional doping of monolayer MoS2; for electronic and chemical sensing applications. Niobium doped MoS2 with various doping concentration (0.5 at%–57 at%) is synthesized by metal organic chemical vapor deposition on c-plane sapphire. The Fermi level is tuned from 2.0 eV above valence band maxima (VBM) to 0.3 eV below VBM (degenerate doping) as doping concentration increases. Interestingly, this Fermi level tuning exhibits a significant shift from theoretical prediction. Evident from x-ray photoelectron spectroscopy and conductive atomic force microscopy, 0.5 at% can only slightly reduce the electron concentration in monolayer MoS2. –5 at% Nb concentration is needed to push the Fermi level to 0.2 eV above valence band maxima (p-doped) and >20 at% Nb doped MoS2 is degenerately p-doped, while <1 at% Nb for degenerate p-doping in theory. This unusual phenomenon is attributed to the strong electron doping from the sapphire substrate.4 Tunable Nb doping realizes multifunctionality of MoS2. 5 at% Nb doped MoS2 exhibits ~15× higher sensitivity (signal/noise ratio) to tetraethylammonium (TEA, a nerve agent) with <10ppb detection limit due to the enhanced conductivity and p-type conductance. Meanwhile, degenerate p-doped MoS2 provides an Ohmic contact between metals (Pt/Ir etc.) and both 2D (MoS2) and 3D (GaN) semiconductors, which may play an important role in contacting semiconductors. This work presents a promising route to cultivate the multifunctionality of doped 2D materials, enabling novel design of multifunctional electronic and sensing devices.

Reference

EP03.11.43
Composition-Tunable Synthesis of Large-Scale Mo1–xWxS2 Alloys with Enhanced Photoluminescence Juhong Park1, Min Su Kim2, Bumsu Park2, Sang Ho Oh3, Shrawan Roy3, Jeongyong Kim2 and Wonbong Choi1; 1University of North Texas, Denton, Texas, United States; 2Sungkyunkwan University, Suwon, Korea (the Republic of).

Alloying two-dimensional transition metal dichalcogenides (2D TMDs) is a promising avenue for band gap engineering. In addition, developing a scalable synthesis process and studying contributions of exciton complexes to the PL emission are essential for the practical application of these alloys with tunable band gaps in optoelectronic devices. Here, we report the synthesis of optically uniform single-layer Mo1–xWxS2 alloys by a two-step CVD method followed by a laser thinning process and investigations on their excitonic behavior with compositional changes. The amount of W content (x) in the Mo1–xWxS2 alloy is systematically controlled by the co-sputtering technique, and the post-laser process allows layer-by-layer thinning of the as-synthesized few-layer Mo1–xWxS2 alloys down to a single-layer. Photoluminescence (PL) and Raman mapping analyses suggest that the laser-thinning of the Mo1–xWxS2 alloys is a self-limiting process caused via heat dissipation to the substrate, resulting in spatially uniform single-layer Mo1–xWxS2 alloy films. As W content (x) increases, the single-layer alloys reveal controlled optical band gaps ranging from 1.871 to 1.971 eV. Furthermore, we found that the number of excessive charge carriers decreases as x increases, resulting in the change in the predominant component of the PL emission from trions for single-layer MoS2 to neutral excitons for single-layer WS2. Our findings present a promising path for the fabrication of large-scale single-layer 2D TMDs alloys and the design of versatile optoelectronic devices.

EP03.11.44
Superconductor-to-Insulator Quantum Phase Transition in Single Crystal LiMoS2 Nanosheets Ivan Verzhbitskiy1, Damien Voiry2, Manish Chhowalla3 and Goski Eda1; 1National University of Singapore, Singapore, Singapore; 2University of Montpellier, Montpellier, France; 3Rutgers, The State University of New Jersey, New Brunswick, New Jersey, United States.

Superconducting van der Waals ultrathin crystals have recently emerged as an excellent platform for studying the role of disorder and quantum fluctuations in reduced dimensions. Here we report our observation of two types of QPT in phase-engineered nanosheets of LiMoS2 having different contents of superconducting T’ phase and non-superconducting 2H phase. Our scaling analysis reveals that the as-synthesized samples with a predominantly T’ phase exhibit the ordinary QPT from superconducting to insulating state whereas the samples with a higher content of 2H phase display QPT with signatures of Griffiths phase evidenced by the diverging critical exponent. Our observations suggest that phase engineering allow formation of quenched disorder with a length scale suitable for the formation of rare superconducting puddles that lock the global superconducting phase above the mean upper critical field.
Large Enhancement of WS2 Photoluminescence in Two-Dimensional Perovskite—Transition Metal Dichalcogenide Heterostructure

Qin Yang1, Jean-Christophe Blancou2, Joeson Wong3, Yi-Rung Lin4, Hsinhan Tsai5, Wanyi Nie5, Deep M. Jarwala5, Aditya D. Mohite2 and Harry A. Atwater1; 1California Institute of Technology, Pasadena, California, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Rice University, Houston, Texas, United States; 4Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Heterostructures constructed from two-dimensional (2D) van der Waals materials such as transition metal dichalcogenides (TMD), graphene, and boron nitride, have sparked wide interest in both device physics and materials science. Apart from these inorganic 2D materials, two-dimensional organic-inorganic hybrid lead halide perovskites (2D PVSKs) have recently emerged as promising materials for solar cells, with power conversion efficiencies over 12% and stability over 2000 hours, compared to 10 hours for traditional 3D PVSKs. 2D PVSKs also show higher photoluminescence quantum yield (~26%) than their 3D counterparts (~1%), suggesting their intrinsic optoelectronic quality may be much higher.

Fundamental photophysics of 2D PVSK materials can be further explored upon making their electronically active heterostructures with other van der Waals semiconductors. In this study we explore these heterostructures with semiconducting double layers of transition metal dichalcogenides built via exfoliation and dry viscoelastic stamping. We observed 116-fold enhancement in indirect transition occurring at 681-706 nm (1.76-1.82 eV) and 277-fold enhancement in trion emission peak at 658-666 nm (1.86-1.88 eV) of WS2 photoluminescence in double layer WS2 on (BA)2(MA)3Pb4I13 2D-PVSK heterostructure. We have also observed ~60meV blue shift in indirect transition (from 1.76eV to 1.82eV) in heterostructure comparing to bare WS2. The larger enhancement of photoluminescence intensity of trion emission in comparison to indirect transition and blueshift of indirect transition indicate increased carrier concentration in WS2 in heterostructure, due to either charge transfer from or defect passivation by 2D PVSK. Emission enhancement in WS2 by 2D PVSK shows promising features of the heterostructure, and may provoke further studies of Van der Waals heterostructures to understand fundamental photophysics of charge separation and novel, long lived excited states.

Reference

8:45 AM EP03.12.03
Manipulating 2D Materials with Light—From Crystalization to Enabling Flexible Electronic Devices
Nicholas Glavin1, Rafael Vita2, Richard H. Kim1, Michael Beebe1, Kimberly Gliice1, Rahul Rao1, Benji Maruyama1 and Christopher Muratore2; 1Air Force Research Laboratory, Dayton, Ohio, United States; 2University of Dayton, Dayton, Ohio, United States.

Altering local properties (< 10 micron length scale) of 2D materials with light has the potential to enable new and exciting devices that were previously very difficult to make. Moreover, by precisely controlling the transient temperature within the material through light-matter interactions, the manipulation and transformation can be done directly on flexible substrates. In this talk, we discuss manipulating amorphous and polycrystalline 2D materials to create and improve 2D crystal quality, control local chemistry, and to demonstrate device performance on flexible substrates. Experiments reveal the successful phase transformation of amorphous transition metal dichalcogenides (TMD) including MoS2 and WSe2 deposited on stretchable polymer substrates to their crystalline van der Waals layered structures. Detailed kinetic studies of crystal formation were accomplished via high throughput in-situ Raman spectroscopy at different surface temperatures and environmental conditions. With this technique, heterostructures were formed incorporating multiple TMD layers that were annealed simultaneously, and insights into the role of surface diffusion and activation energy for crystalization will be discussed. Laser writing within MoS2 exhibits controllable local heating and transformation to form various oxide phases with altering electronic properties. Additionally, large area, wafer-scale crystallization of stretchable 2D photodetectors with the use of a broadband pulsed lamp source demonstrate the feasibility of laser transformation as a means to create unique device constructs.

9:00 AM EP03.12.04
2D Perovskite for Optoelectronics
Hsinhan Tsai1,2, Reza Asadpour3, Jean-Christophe Blancou1, Jackie Evert1, P. M. Ajayan2, M. Ashraf Alam1, Mercouri G. Kanatzidis4, Aditya D. Mohite1 and Wanyi Nie5; 1Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2Materials Science and Nanoeengineering Department, Rice University, Houston, Texas, United States; 3School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, United States; 4Fonctions Optiques pour les Technologies de l’Information, Rennes, France; 5Department of Chemistry, Northwestern University, Evanston, Indiana, United States.

Hybrid (inorganic-organic) perovskites have demonstrated an extraordinary potential for clean sustainable energy technologies and low-cost optoelectronic devices such as solar cells; light emitting diodes, detectors, sensors, ionic conductors etc. In spite of the unprecedented progress in the past six years, one of the key challenges that exists in the field today is the large degree of processing dependent variability in the structural and physical properties. This has limited the access to the intrinsic properties of hybrid perovskites and led to multiple interpretations of
Raman microscopy proved to be an extremely useful technique for characterization of 2D materials such as graphene, transition metal dichalcogenides (TMDs), black phosphorous, etc. Unfortunately, natural spatial resolution of confocal Raman microscopy, which is limited by the wavelength of the laser used (400-800 nm), is not sufficient for mapping heterogeneities and defects in these materials with characteristic dimensions of few – to few tens of nanometers.

Tip Enhanced Raman Spectroscopy (TERS) provides dramatically improved spatial resolution of Raman maps, down to few nanometers, and in addition provides dramatic enhancement of the Raman signal. Since TERS is a relatively new technique, peculiarities of the near-field Raman response of many 2D materials still remain to be discovered and explained.

We report an interesting observation we made during TERS imaging of thin (10-60 nm) flakes of MoO3 exfoliated to different metallic surfaces (Au, Cr, Al). Despite the fact that normal Raman spectra of this material feature at least 12 well distinguishable peaks within 100-1100 cm⁻¹ range, only one peak at 995 cm⁻¹ corresponding to out-of-plane Mo-O vibration was strongly enhanced in TERS spectra of MoO3 crystals. It should be expected and actually has been observed in TERS spectra of 2D semiconductors that out-of-plane modes get preferential enhancement, but the degree to which it happens in MoO3 is outstanding. Such mode selectivity in TERS spectra of 2D materials may be useful for mode assignment in case there are multiple possibilities for a
Exciton-Photon and Exciton-Photon Coupling Dynamics in Self-Assembled Hybrid Perovskite Quantum Wells

Limeng Ni1, Uyen Huynh1, Alexandre Cheminal1, Tudor H. Thomas1, Ravichandran Shivanna1, Ture F. Hinrichsen2, Shahab Ahmad2, Aditya Sadihanala2, Shuai Zhang3, Kenichi Yamashita1 and Akshay Rao1; 1Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 2Institute for Manufacturing - Department of Engineering, University of Cambridge, Cambridge, United Kingdom; 3Faculty of Electrical Engineering and Electronics, Kyoto Institute of Technology, Kyoto, Japan.

Limen Ni, Uyen Huynh, Alexandre Cheminal, Tudor H. Thomas, Ravichandran Shivanna, Aditya Sadihanala, Ture Hinrichsen, Akshay Rao Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom
Email: ln295@cam.ac.uk

Self-assembled hybrid perovskite quantum wells have attracted attention due to their tunable emission properties, ease of fabrication and device integration. However, the dynamics of excitons in these materials, especially how they couple to phonons remains an open question. Here, we investigate two widely
used materials, namely butylammonium lead iodide (CH₃(CH₂)₃NH₃)₂PbI₄ and hexylammonium lead iodide (CH₃(CH₂)₅NH₃)₂PbI₄, both of which exhibit broadband photoluminescence since tails at room temperature. We performed femtosecond vibrational spectroscopy to obtain a real-time picture of the exciton phonon interaction and directly identified the vibrational modes that couple to excitons. We show that the choice of the organic cation controls which vibrational modes the exciton couples to. In butylammonium lead iodide, excitons dominantly couple to a 100 cm⁻¹ phonon mode, whereas in hexylammonium lead iodide, excitons interact with phonons with frequencies of 88 cm⁻¹ and 137 cm⁻¹. Using the determined optical phonon energies, we analyzed PL broadening mechanisms. At low temperatures (<100 K), the broadening is due to acoustic phonon scattering, whereas at high temperatures, LO phonon-exciton coupling is the dominant mechanism. Our results help explain the broad photoluminescence lineshape observed in hybrid perovskite quantum wells and provide insights into the mechanism of exciton-phonon coupling in these materials. Strong exciton-phonon coupling in 2D perovskites can be a benefit, for instance, it can accelerate polariton relaxation and realize polariton lasing with very low threshold. It could also provide interesting opportunities for the development of broadband, short-pulsed lasers.

I will also show our recent results on exciton-phonon coupling and polaritons in monolayer perovskite crystals in high-Q microcavities. We found out that the coupling strength and the Rabi splitting energy are affected by quantum well thickness.

11:45 AM EP03.12.11
Direct Correlation of Defects with Photoluminescence and Electrical Conductivity in Monolayer Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMDs) are promising candidates for emerging applications such as transparent and flexible optoelectronics and electronics. Understanding the impact of defects on material properties, such as luminescence efficiency and charge carrier mobility, is essential for the advancement of these materials. However, it is challenging to observe discrete defects in monolayer TMDs at the nanometer-scale and to directly correlate defects with material properties. This is due to a lack of techniques capable of facile observation of defects in monolayers. Here, we demonstrate the ability to observe electronically active defects in monolayer TMDs using conductive atomic force microscopy (AFM) in ambient conditions, and we correlate defect density with local optoelectronic and electronic properties. We briefly discuss our AFM-based sample preparation technique which creates clean, homogenous samples that enable us to investigate the intrinsic optical and electronic properties. We find that CVD-grown WS₂ samples have up to an order of magnitude variation in defect density within a single triangular grain. We also find that the photoluminescence (PL) intensity is inversely proportional to defect density. We develop a model assuming non-radiative recombination occurs when excitons collide with defects, and we find good agreement between the model and experiments. To investigate electronic properties, we use kelvin probe force microscopy to obtain spatial maps of electrostatic potential in operating TMD transistors. The local potential gradient is proportional to the local resistivity, which allows us to observe variations in resistivity across the channel. We find that regions with low PL intensities exhibit large potential gradients. This suggests that the defects responsible for decreased PL intensity are also responsible for decreased electrical conductivity. In summary, we use a combination of conductive AFM, PL measurements, and kelvin probe force microscopy to understand the impact of defects on optoelectronic and electronic properties in monolayer TMDs. Our work demonstrates a simple and general methodology for correlating defects with various material properties in two-dimensional materials, which is essential for optimizing material and device performance.

SESSION EP03.13: Electronic Properties, Processes and Devices III
Session Chairs: Deep Jariwala and Hui Zhao
Thursday Afternoon, November 29, 2018
Hynes, Level 2, Room 210

1:30 PM EP03.13.01
High Surface Area BN Coated Graphene Aerogel for Sensitive and Selective Gas Sensing
Hu Long1, 2, Sally DeMaio-Turner1, 2, Aiming Yan1, 2, Hossain M. Fahad1, HongMei Xu1, Wu Shi1, 2, Thang Pham1, 2, Zhen Yuan3, Ali Javey3, Marcus A. Worsley4 and Alex Zettl1, 2; 1Department of Physics, University of California, Berkeley, Berkeley, California, United States; 3Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, Berkeley, California, United States; 5Lawrence Livermore National Laboratory, Livermore, California, United States.

Two dimensional layered materials, such as graphene, and transition metal dichalcogenides (TMD) have great potential for gas sensing applications due to its high surface to volume ratio. Ultrasensitive chemical detection using single-layer graphene and single- and few-layer MoS₂ have been reported. Unfortunately, graphene based sensors without proper surface modification suffer from lack of selectivity; TMD sensors show good selectivity but not long term stability. Recently, hexagonal boron nitride (h-BN) nanomaterials, eg. nanosheets and nanotubes, have been predicted to be an effective material for reversible gas adsorption with high selectivity once charged. By modifying the charge state of the BN nanomaterials, adsorption and desorption of gas on BN can be controlled. This makes the whole process controllable and suitable for gas sensing. However, despite the encouraging theoretical discovery, sensing with h-BN is difficult to realize experimentally due to its electric insulating nature with large band gap (around 5.8 eV). In this research, we report on the controlled synthesis of high surface area h-BN coated graphene aerogel and its application for selective gas sensing. Hybrid BN/graphene aerogel is synthesized using graphene aerogel as a template and boric acid and ammonia as boron and nitrogen source, respectively. A thin layer of BN can be uniformly coated on graphene aerogel while maintaining the macro- and nanoscale morphologies and mechanical properties of the aerogel. With thin BN and graphene combination, charge transfer between BN and graphene can be greatly improved compared to bare h-BN alone. Sub ppm level detection limit for NH₃ is shown, while negligible cross sensitivity to ppm of NO₂, 2000 ppm CO₂ and 50000 ppm hydrogen. The low detection limit, high selectivity and high stability makes the sensor suitable for practical sensing application.

1:45 PM EP03.13.02
Integer and Fractional Quantum Hall Effect in Various Few-Layer Black Phosphorus Transistors
Jeanie Lai; The Ohio State University, Columbus, Ohio, United States.

Since its isolation in 2014, few-layer black phosphorus (BP) has been under intensive research efforts, due to its many interesting material properties such as the combination of high mobility and sizable band gap, in-plane anisotropy and band structure modulation by electric field or strain. Many of the predicted properties can only be revealed in high mobility samples, in which the intrinsic phenomena are not obscured by impurities, and which are essential for further applications in any quantum device structures. Here I will present our recent works on ultra-high quality few-layer BP transistors, including the creation of double quantum wells, Landau level gaps in samples with demonstrated strong in-plane anisotropy, high quality integer quantum Hall effect and the first observation of fractional quantum Hall effect in BP. These results pave the way to the study of even more fragile fractional
quantum Hall states or more complicated quantum structures in BP.

2:15 PM EP03.13.03
Black Phosphorus and Its Analogue—Electrical Transport and Device Applications
Lihong Bao1, Guocai Wang2, Tengfei Pei1, Shixuan Du1, Sokrates T. Pantelides2 and Hong-Jun Gao1; 1Institute of Physics, Chinese Academy of Sciences, Beijing, China; 2Vanderbilt University, Nashville, Tennessee, United States.

As a young member in the family of two-dimensional materials, black phosphorus (BP) has attracted great attention due to its high hole mobility, and a sizable and tunable bandgap, meeting the basic requirements for logic circuits application. To realize a complementary logic operation, it needs to control the conduction type in BP FETs, i.e., the dominant carrier types, holes (P-type) or electrons (N-type). Absence of reliable substitutional doping techniques makes this task a great challenge, however. In this talk, I will demonstrate that capping the thin BP film with a cross-linked poly-methyl-methacrylate (PMMA) layer can modify the conductivity type of BP by a surface charge transfer process, converting the BP layer from p-type to n-type. Combining BP films capped by cross-linked PMMA to a standard BP, a family of planar devices can be created, including BP gated diodes (rectification ratio >10^5), BP barriers (on/off ratio >10^7), and BP logic inverter (gain ~0.75), which are capable of performing current rectification, switching, and signal inversion operations. Furthermore, the conversion of a bidirectional rectifier to a polarity-controllable transistor in black phosphorus (BP) by dual gate modulation can be realized. Employing cross-linked PMMA as a top gate and combining it together with the global back gate of the SiO_2 substrate, well-defined unipolar transport (n- or p-type) in BP could be get accessed. Inspired by the discovery of black phosphorus as channel material in FETs, the orthorhombic ones, such as GeS, GeSe, SnS, and SnSe, have attracted growing interest. I’ll also demonstrate ultrathin SnSe single crystals have been epitaxially grown on molten polydimethylsiloxane (PDMS) by the chemical vapor deposition (CVD) method. TEM characterization of octagonal SnSe nanosheets reveals a good crystalline nature and preferred crystalline orientations along the edges of the nanosheets. Thickness-dependent Ramans spectroscopy measurements result in a red shift of the A_{2g} mode and blue shift of the B_{1g} and A_{1g} modes, even when the thickness is over 10 nm, which is never observed in hexagonal Van der Waals structures. The octagonal SnSe nanosheets show an electrical anisotropic characteristic. Finally, the thermopower of SnSe nanosheets can be electrostatically tuned, and, when sweeping the gate voltage from -40 V to 40 V at 120 K, the thermopower can be tuned from 54 to 866 mVK^{-1}, indicating the unique advantage of gate modulation compared to chemical doping in thermoelectric applications.

References:

2:30 PM BREAK

3:00 PM *EP03.13.04
MBE-Grown Transition-Metal Dichalcogenide Ultrathin Films and Heterostructures—Superconductivity, Ferromagnetism and Interface Transport Phenomena
Masaki Nakano1 and Yoshihiro Iwasa1, 2; 1University of Tokyo, Tokyo, Japan; 2CEMS, RIKEN, Wako, Japan.

Transition-metal dichalcogenide (TMDC) has become an invaluable material platform for condensed matter research owing to its intriguing properties and functionalities emerging at monolayer limit. There, conventional mechanical exfoliation plays an central role for sample fabrication, while bottom-up synthesis by molecular-beam epitaxy (MBE) has expanded a lineup of materials under investigation even to hardly cleavable compounds, providing a promising route to further exploration of novel quantum phenomena emerging at monolayer limit including heterostructures. However, those MBE-based approaches have been mostly focused on spectroscopic studies using conducting graphene substrates, whereas transport studied has been less performed despite its essential importance due to difficulties in growing high quality TMDC thin films on insulating substrates.

We have recently established a versatile route to layer-by-layer epitaxial growth of millimeter-scale single-crystalline TMDC thin films on insulating sapphire substrates by MBE [1], opening the door for exploration of transport properties of various TMDCs and their heterostructures at nanometer scale. In this presentation, we will introduce our growth recipe in detail, together with an interesting aspect of van der Waals epitaxy that is missing in conventional epitaxy with strong substrate-film interaction. We will also present our recent achievements in transport studies including realization of spin-momentum locked ‘island superconductivity’ in millimeter-scale ultrathin films based on group-V TMDCs that are suitable for further investigation of 2D superconductivity, observation of emergent ferromagnetism with anomalous Hall effect in strongly-correlated TMDCs that are missing in their bulk counterparts, as well as development of monolayer van der Waals heterostructures exhibiting intriguing interface transport phenomena in combination with a variety of TMDC thin films.


3:30 PM EP03.13.05
Large Magnetoresistance in a Topological Insulator/Magnetic Insulator vdW Heterostructure
Yingjie Zhang1, 9, Joseph Sklenar1, 9, Matthias Jungfleisch1, Youngseok Kim2, Yiran Xiao1, Gregory MacDougall1, 9, Matthew Gilbert4, Axel Hoffmann5, Peter Schiffer1 and Nadya Mason1, 5; 1Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 9Department of Physics, University of Delaware, Newark, Delaware, United States; 2Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 3Department of Electrical Engineering, Stanford University, Stanford, California, United States; 4Department of Applied Physics, Yale University, New Haven, Connecticut, United States; 5Materials Sciences Division, Argonne National Laboratory, Lemont, Illinois, United States; 9Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 1Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 3Department of Electrical Engineering, Stanford University, Stanford, California, United States; 4Department of Applied Physics, Yale University, New Haven, Connecticut, United States; 5Materials Sciences Division, Argonne National Laboratory, Lemont, Illinois, United States; 9Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Layered topological insulators (TIs), such as Bi_2Se_3 and Bi_2Te_3, host spin-momentum locked surface states that are inherently susceptible to magnetic proximity modulations, which can be utilized for nano-electronic, spintronic, and quantum computing applications. Here we present a strategy to fabricate TI-magnetic insulator (MI) heterostructures with high-quality interfaces, and experimentally measure the magnetoresistance (MR) at various temperatures. We observe rich hysteretic MR features including sharp MR switching and large, broad MR bumps (a few percent in magnitude), which we attribute to domain wall switching and out-of-plane anisotropic MR in the surface state, respectively. The out-of-plane magnetic anisotropy leads to band gap opening in the TI surface state, confirmed by an analytical diffusive transport model. These results provide both fundamental insights into the mechanism of magnetic proximity and spin exchange interactions in layered heterostructures, and a route towards energy efficient spintronic device applications.
We demonstrate direct writing of self-aligned 18 nm electrical circuitry with a scanning light probe on a two-dimensional (2D) van der Waals (vdW) semiconductor at the time scale of a minute. Light illumination over Au-electrode patterns on n-type MoTe₂ 2D channels locally convert them into p-type ones by creating adatom-vacancy clusters as electron acceptors in the host lattice. We provide direct evidence of such a microscopic doping mechanism by atomic scale imaging and spectroscopy. This real-time writing process is precisely controllable within a minute, in that diffusive doping profiles can be controlled at the sub-micrometer scale, and doping concentrations are tunable to vary the channel sheet resistance over four orders of magnitude. As such, we assembled both n- and p-doped channels within the same atomic planes to fabricate 2D device arrays of n-p-n (p-n-p) bipolar junction transistor (BiT) amplifiers and radial p-n photovoltaic cells in high performances. This doping method can be potentially used to fabricate designer 2D circuits based on atomically thin vdW semiconductors in arbitrary shapes.

The crystal orientation of an exfoliated black phosphorous flake is determined by purely electrical means. A sequence of three resistance measurements on the sub-micron level. Our results imply that the variation in the bandgap induced by dielectric disorder can be over 100 meV in monolayer WS₂ and WSe₂ samples that have not been encapsulated in hexagonal boron nitride (h-BN), but are supported on typical substrates like SiO₂. This variation decreases to the order of 10 meV upon h-BN encapsulation. While there is widespread interest to improve the underlying microscopic picture has not been fully explored. From our study, we suggest dielectric disorder as a mechanism likely to play a significant role.


**EP03.13.08**

The Influence of Dielectric Disorder on the Electronic Properties of Two-Dimensional Materials

**Archana Raja, Lutz Waldecker, Tony F. Hinez, and Alexey Chernikov**

The remarkably strong and environmentally sensitive Coulomb interaction at the atomically thin limit allows for modification of the quasiparticle bandgap and exciton binding energy of two-dimensional (2D) materials through modification of the dielectric environment. The change in the non-local or distance-dependent dielectric screening strongly modulates the free-carrier bandgap energy and excited exciton states compared to the ground state exciton transition. By probing the inhomogeneous linewidth broadening of the excited exciton transition using optical spectroscopy, we have identified dielectric disorder as a significant source of electronic disorder at the 2D limit.

We infer that within the diffraction-limited, sub-micron area of study there exists a spatially disordered dielectric environment. This in turn leads to spatially inhomogeneous quasiparticle bandgaps on the sub-micron level. Our results imply that the variation in the bandgap induced by dielectric disorder can be over 100 meV in monolayer WS₂ and WSe₂ samples that have not been encapsulated in hexagonal boron nitride (h-BN), but are supported on typical substrates like SiO₂. This variation decreases to the order of 10 meV upon h-BN encapsulation. While there is widespread interest to improve the optical and electronic properties of atomically thin materials by substrate surface passivation or encapsulation in a wide bandgap insulator like h-BN, the underlying microscopic picture has not been fully explored. From our study, we suggest dielectric disorder as a mechanism likely to play a significant role.


**EP03.13.09**

Electrical Determination of Crystal Orientation in Anisotropic 2D Materials—5-Point van der Pauw Method Demonstrated on Black Phosphorus

**Lintao Peng, Spencer Wells, Christopher Ryder, Mark C. Hersam, and Matthew Grayson**

The crystal orientation of an exfoliated black phosphorus flake is determined by purely electrical means. A sequence of three resistance measurements on an arbitrarily shaped flake with five contacts determines the three independent components of the anisotropic in-plane resistivity tensor, thereby revealing the crystal axes, with the help of simple geometric transformations including conformal mapping. The crystallographic orientation deduced from this all-electrical conformal five-contact method is confirmed with polarized Raman spectroscopy. The resistivity anisotropy ratio is observed to decrease linearly with increasing temperature T and carrier density reaching a maximum ratio of 3.0 at low temperatures and densities, while mobility indicates impurity scattering at low T and acoustic phonon scattering at high T. In addition, we examine the disorder-related transient conductivity, and observe that the commonly observed hysteresis in both electrical and photoluminescence studies of 2D materials can be characterized as a heavy-tail transient response to a step-function excitation. Dispersive diffusion equations successfully fit the transients in both the pristine and highly disordered sample limits, and a microscopic model for the response is provided, based on the continuous-time random walk model. Finally, we observe for the first time a generalized scaling behavior for the gated conductivity of 2D materials with disorder strength.

*PHYS. REV. LETT. 120, 086801 (2018).*
Two dimensional (2D) materials belong to a large family of anisotropic compounds which have strong, covalent bonds within a layer while between layers there are only weak van der Waals interactions that can be overcome, obtaining molecularly thin sheets. Such a dimensionality reduction has a profound impact on properties, that vary strongly with the number of atomic layers. From the moment of graphite exfoliation into an atomically thin monolayer, known today as graphene [1], two dimensional materials have been of main interest for a variety of electronic applications.

Whereas graphene applications in electronics has thus far been hindered by its non-existent band gap, layered semiconductors are studied as potential candidates for future devices. Many Transition Metal Dichalcogenides (TMDs) including MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$ have been thoroughly investigated, however in order to meet rising demands new families of 2D semiconductors are studied. One family of such is the transition metal phosphides, denoted MPS$_x$, for $x$=3 or 4; for example bulk crystals of CrP$_3$ - chromium thiophosphate – which has been examined in the past for applications in lithium batteries. Nowadays, this compound has once again gained scientific interest due to its optical anisotropic properties and the possibility to obtain and study its few- and monolayer systems [2].

In this research, bulk crystals of CrP$_3$ were obtained by vapor transport synthesis (furnace method), followed by structure and composition confirmation via different techniques, for example Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM/EDX), Powder X-Ray Diffraction (PXRD) and Raman spectroscopy. Optical properties, such as band gap and optical transitions were investigated by Solid State UV-VIS Spectroscopy, PhotoAcoustic Spectroscopy (PAS) [3] and Modulated Spectroscopy (MS) [3]. Then, bulk crystals of chromium thiophosphate (CrP$_3$) were exfoliated in liquid by ultrasounds to obtain few layers systems and photoconductivity measurements were used to ascertain photoactive properties, both of re-stacked films and bulk crystals.

Acknowledgments:
This work was supported by the European Comission via the Marie-Sklodowska Curie action Phonsi (H2020-MSCA-ITN-642656)
This work was performed within the grant of the National Science Centre Poland (OPUS 11 no. 2016/21/B/ST3/00482).
S.J.Z. also acknowledges the support within the ETIUDA 5 grant from National Science Center Poland (no. 2017/24/T/ST3/00257).

References:

EP03.14.06
Defect Mediated Growth of Transition Metal Dichalcogenides on Epitaxial Graphene

Layered 2D materials have garnered huge interest due to their inherent chemical, optical and electronic properties. In addition to the individual material property the weak inter-layer bonding, characteristic of 2D materials, allows for variable stacking of a combination of these materials; forming heterostructures. These heterostructures can provide pathways to develop all 2D electronics or enhancing the novel properties of the resultant stack. Current research using transferred exfoliated flakes has demonstrated the rich landscape of possible properties and applications of these heterostructures. However, to study these heterostructures without the hindrance of transfer process contaminants, bottom-up growth techniques which can provide pristine interfaces are needed. To understand and control the bottom-up assembly process, it is imperative to investigate the impact of defects on the growth of other 2D materials. The defects can act as nucleation sites, which in turn can be used to control the density and the domain size of the growing 2D films.

In this work we investigate the effect of defects in epitaxial graphene on the growth of transition metal dichalcogenides like WS$_2$. Epitaxial graphene was grown on on-axis 6H (0001) SiC substrate. The defect density of epitaxial graphene was controlled by exposing it to a helium plasma for different durations. The pristine and plasma treated graphene was exposed to a H$_2$S environment and subsequently to a WS$_2$ growth environment. The H$_2$S treatment and WS$_2$ growth was carried out at 50 Torr at temperatures ranging between 700-1000°C. The H$_2$S and W(CO)$_6$ precursor flow rate was maintained at 400 sccm and 5.7×10$^{-4}$ sccm, respectively. The results show that the defect generation, and subsequent sulfur incorporation was higher when the buffer layer was present between the SiC substrate and the graphene layers. The higher defect generation is attributed to the distortion in the bonds of the top graphene layer when the interfacial layer is partially bonded to SiC. In addition, the duration of plasma treatment directly controls the nucleation density of WS$_2$ domains, which is a crucial factor for controlling the domain size. Another key observation was that the plasma treatment modified the WS$_2$ nucleation sites from step edges to terraces. This impact on the nucleation site was, however, temperature dependent. Additional details about the role of the buffer layer, the interaction of the defects with the precursors and the impact on the nucleation site and density will also be presented.

EP03.14.02
Indium and Indium Alloys as Ultra-Clean Contacts for 2D Materials

Two dimensional (2D) transitional metal dichalcogenides (TMD) such as molybdenum disulfide (MoS$_2$) have been demonstrated to be excellent semiconductors for ultra-thin FETs. However, the main challenging for improving the performance is the contact resistance for all 2D materials. The direct deposition of metals can introduce substantial damage to ultra-thin TMD materials, which leads to high contact resistance. Studies have shown that creation of van der Waals contacts by dry transfer (graphene, hBN, metal) method reduces damage to the TMDs. Here, we report the realization of ultra-clean van der Waals contact between Indium and 2D materials. From scanning transmission electron microscopy images, we can see the interface is atomically sharp with no detectable chemical interaction. This ultra-clean van der Waals contact can also be translated to good device performance for 2D materials such as MoS$_2$, WS$_2$, WSe$_2$, and NbSe$_2$. Because Indium is a soft metal, we demonstrate that alloys of Pd, Pt, and other metals can be formed to vary the work function so that both hole and electron injection can be facilitated. We have measured the work function of the alloys using Kelvin force microscopy and correlated them with band offsets in WS$_2$ devices.
Using Hexagonal Boron Nitride and Its Composites to Reduce Friction on Steel

Alexander I. Marsden1, Martin King2, Mark A. Bissett3 and Ian A. Kimloch4; 1Materials, University of Manchester, Manchester, United Kingdom; 2Renold Power Transmission Ltd, Manchester, United Kingdom.

Reducing friction and wear is essential in industrial sliding applications. Layered materials like graphite and boron nitride are extremely effective as solid lubricants and have been extensively applied. More recently, exploiting these layered materials yields 2D materials that have surfaces with very low coefficients of friction. These materials show promise for reducing friction in nano- and micro-electromechanical systems. However, they could also benefit larger scale applications, and exploiting the thinnest and low friction properties of 2D materials requires further development.

Here we study the deposition of hexagonal boron nitride (hBN) onto steel using chemical vapour deposition from the solid precursor ammonia borane. We find that hBN forms nanostructured, multilayer films when using higher precursor temperatures. These films yield a lower coefficient of friction on the surface under lubrication than those with no coating. We also investigate the effect of pre-plating the surface with copper and nickel, as these are more well-defined hBN growth surfaces.

We also study composites made from the electrodeposition of hBN with nickel. These composites are examined using atomic force microscopy to understand how the surface wears under repeated sliding. The hBN incorporates into the nickel film, again reducing the surface coefficient of friction. These techniques could help guide industrialscaleable coating techniques to help reduce friction in sliding applications.


Ultrasonic and VOC-Selective Metallic Ti3C2Tx MXene Gas Sensors

Hyunsang-Kyung Kah1, Seon Joon Kim1,2, Yury Gogotsi2 and Hee-Tae Jung1; 1Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejon., Korea (the Republic of); 2A.J. Drexel Nanomaterials Institute, Philadelphia, Pennsylvania, United States; 3National Nanofab Center, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Developing highly sensitive solid-state chemical sensors for detecting biological, environmental and chemical agents is a very important issue. To obtain very high sensitivity, two factors are simultaneously required: (i) low electrical noise, which can be derived from high conductivity, and (ii) strong signal, originating from abundant analyte adsorption sites. However, as the introduction of reactive sites on the surface significantly degrades the electrical conductivity, these two factors are always in a trade-off relation. Thus, none of the previous sensor materials were able to simultaneously satisfy the two characteristics.

Here, we demonstrate state-of-the-art metallic Ti3C2Tx MXene gas sensors by employing a vacuum filtration method. The abundant surface functionalities and high conductivity of Ti3C2Tx enable the Ti3C2Tx sensor to overcome previous trade-off limitations, substantially outperforming typical two-dimensional (2D) material gas sensors in two important aspects. First, it has a very high sensitivity and shows a limit of detection (LOD) of 50~100 parts per billion (ppb) at room temperature, which is one of the lowest LOD ever reported. Second, the extremely low noise of metallic Ti3C2Tx yields a signal-to-noise ratio (SNR) that is two orders of magnitude higher than that of other 2D materials. In addition, we have observed that Ti3C2Tx sensors have higher selectivity toward VOC gases over acidic gases, which is a rare property. In-situ X-ray diffraction (XRD) measurements were used to verify that the intercalation of gas molecules into Ti3C2Tx layers plays a fundamental role in detecting gas molecules. The interlayer swelling induced by the intercalation of gas molecules can explain not only Ti3C2Tx sensors’ selectivity, but also their universal positive response for various gas molecules. It is noteworthy that more than 30 MXenes are now accessible, and we expect that this study will open the door for a large family of MXene sensors.

Chemical and Atomic Structure of Doped Transition Metal Dichalgonide Monolayers

Greg Stone and Daniel Kaplan; Precision Armaments Intelligent Sensors Division, US Army RDECOM-ARDEC, Picatinny Arsenal, New Jersey, United States.

Substitutional doping of the transition metal atoms in transition metal dichalcogenides monolayers offers an attractive route to modify the electronic and optical properties of these materials, as well as, introduce new properties. For example, the inherent p- or n-type nature of 2D crystals can be changed via doping. Furthermore, theoretical models indicate that the crystal structure may support a variety of possible defect dopant complexes, each of which modify the material properties differently. Currently, little is known about the distribution and defect structure of dopants in synthesized materials. In this work, V and Mn doped MoS2 monolayers are grown by chemical vapor deposition on gold foils. Using atomic resolution scanning transmission electron microscopy and x-ray photoelectron spectroscopy we report on the chemical and atomic structure of the V and Mn defect clusters.

Branching Ratio of Photothermal to Photoelectric Transduction in Suspended PtSe2

Hamza Z. Gul1,2; Wonkil S. Kong1,2, Hojyon Yi1,2, Byungwook Ahn1,2 and Seong Chu Lim1,2; 1SungKyunKwan University, Suwon-si, Korea (the Republic of); 2Center for Integrated Nanostructure Physics, Institute for Basic Science, Suwon, Korea (the Republic of).

In this study, the light interaction with PtSe2 is studied. The optically excited carriers in PtSe2 dissipate their energy as the heat to the lattice vibrations or electrical current to the electrons. In order to assess how the incident light energy is divided into the heat and the electrical current, PtSe2 is partially suspended on SiN substrate to eliminate the heat conduction from PtSe2 to the substrate. A focused laser illuminates the partially suspended PtSe2.

Studying the power-current relation using the power law we observe at low laser power the mechanism of photocurrent due to photoelectric effect. However as the laser power is increased, heat is generated in the sample due to photothermal effect, the photothermal effect results in a change in the coefficient of the power-current relation. Further analysis of the photocurrent as a function of laser power and electrical input will enable us to understand the contribution of photovoltaic and photothermal effect in our devices. Temperature dependent measurements allow us to estimate the rise of temperature in our sample at various laser power which show that at high laser power the temperature of the sample can increase to as much as 10K. The possibility of these mechanism coexisting at the same time or one being dominant over the other is being investigated. Understanding the interaction between the two processes will allow for more efficient device structure and performance from a highly promising material.

Novel Valleytronics in Bulk IV-VI Monochalcogenides

Shuren Lin1,2 and Jie Yao1,2; 1University of California, Berkeley, Berkeley, California, United
Valleytronics provide an additional degree of freedom in optoelectronic devices by having multiple non-equivalent “valleys” in the reciprocal k-space bandstructure of a valleytronnic material. Such valleys obey certain selection rules and can be selectively polarized by optical means. Until recently, research in valleytronics has mostly been conducted using two-dimensional transition metal dichalcogenides. However, such systems can only be probed at low dimensions and/or with the application of certain experimental conditions, such as cryogenic temperatures and/or strong electric or magnetic field. This inevitably poses a plethora of practical challenges that create a high barrier in advancing technology towards practical applications.

In our recent work, we show experimental evidences of the valley effect in a bulk, ambient, and bias-free model system of Tin(II) sulphide (SnS). We elucidate the direct access and identification of different sets of valleys, based primarily on the selectivity in absorption and emission of linearly polarized light, and demonstrate strong optical dichroic anisotropy of up to 600% and nominal polarization degrees of up to 96% for the two valleys with band-gap values 1.28 and 1.48 eV, respectively; the ease of valley selection further manifested in their non-degenerate nature. Such discovery enables a new platform for better access and control of valley polarization.

There are two non-degenerate local band gaps along two high symmetry axes, ΓY and ΓX, in the orthogonal crystal structure of SnS (and most IV-VI monochalcogenides). By looking at the compositions of the conduction and valence bands, we obtained the point groups that describe the k points along ΓY and ΓX, and the IrRs of the respective bands and show, via the electric dipole approximation, that the transitions at ΓY and ΓX will only occur with excitation using y and x-polarized light respectively. This forms the basis for valley selectivity.

Experimentally, we demonstrate that Tauc plots of absorption measurement results give band-gap values of 1.48 and 1.28 eV, clearly distinguishing the two sets of valleys. We also see that SnS is able to maintain a more than 200% for a range of more than 0.2 eV, and also possesses a maximum of more than 600%.

The polarization dependence of two PL peaks at 817 and 995 nm, respectively, is clearly observed; under parallel polarization, the 817 nm peak maximizes at the polarization that minimizes the 995 nm peak, and vice versa, demonstrating a 90° phase shift between the peaks and hence the orthogonality in polarization selectivity of the two sets of valleys responsible for such PL emissions.

**EP03.14.10**

Highly Efficient Solid-State Photoluminescence from Graphene Quantum Dots Incorporate ...nt Technology, Daejeon, Korea (the Republic of); 3Department of Convergence IT Device and Material Engineering, Korea Polytechnic University, Siheung, Korea (the Republic of).

Emerging graphene quantum dots (GQDs) have attracted great attention due to their excellent resistance to photobleaching and tunable band gap, making them promising candidates for future light-emitting devices. However, in the solid-state, n-interaction-induced aggregation-caused quenching (ACQ) of photoluminescence (PL) in GQDs makes realization of high performance device challenging. Here we propose application of GQD incorporated boron oxynitride (GQD@BNO), fabricated by a simple microwave-assisted method, on alternating-current powder electroluminescent device (ACPEL) as an active material. The BNO, comprising an interfacial, zone-joining boric oxide and tubrostratic boron nitrde, is an ideal matrix material for incorporating GQDs for three reasons: i) the presence of abundant surface oxygen functional groups facilitates intermolecular interaction with GQDs, ii) the relatively high refractive index (1.6-1.8) can enhance PL quantum yields (PL-QY’s), iii) the creation of a localized dielectric environment is advantageous for high-field induced electrical exicitation of GQDs. With these advantages, blue-luminescent GQDs were successfully incorporated into a BNO matrix via intermolecular hydrogen bonding to form GQD@BNO, which showed 8-fold enhanced PL-QY compared to that of the same amount of GQDs in water. The PL-QY enhancement results from the increase in the spontaneous emission rate of GQDs due to the surrounding BNO matrix, which provides a high refractive index environment and fluorescence energy transfer from the larger gap BNO donor to the smaller gap GQD acceptor. In addition, the size effect of GQD@BNO and the GQD loading ratio in BNO on the photo-physical properties shed light on the in-depth carrier dynamics of GQD in a BNO matrix. The robust solid-state PL properties made the GQD@BNO an ideal active material for ACPEL devices, whose lumiance exceeded 283 cd m⁻² for the first time. This successful demonstration shows great potential of GQDs in the field of low cost, eco-friendly EL devices.

**EP03.14.11**

Electro-Mechanical Anisotropy of Phosphorene Kuo Ming Hu; University of South Carolina, Columbia, South Carolina, United States.

Highly asymmetric photocurrent in few-layer WSe₂ transistor achieved by selective dielectric deposition and molecular doping Seungpil Ko; Jungho Na1, 2, Young-Sun Moon2, Zhesiclung Ute1, Rachana Acharya1, Hagen Klauck1, Gyu-tae Kim2, Marko Burghard1 and Klaus Kern1; 1Max

Diverse Thermal Response of 2D Materials to Mechanical Strain Mine Hye; University of South Carolina, Columbia, South Carolina, United States.

Manipulation of thermal transport is in increasing demand as heat transfer plays a critical role in a wide range of practical applications, such as efficient heat dissipation in nanoelectronics and heat conduction hindering in solid-state thermoelectrics. It is well established that the thermal transport in semiconductors and insulators (phonons) can be effectively modulated by structure engineering such as external mechanical strain or materials processing. While three-dimensional bulk solid materials usually exhibit decreased lattice thermal conductivity upon mechanical stretching and enhanced thermal transport by compression, the thermal response of two-dimensional (2D) materials to mechanical strain is not that simple. Generally speaking, perfectly planar atomically-thin materials with graphene as representative have reduced thermal transport ability when tensile strain is applied. In contrast, some 2D materials with intrinsic buckled structure will possess enhanced thermal conductivity when being stretched. However, many exceptions exist in other 2D materials. For example, by performing comparative study of thermal transport in two-dimensional group III-nitrides (h-BN, h-AIN, h-GaN) and graphene, we found that the thermal conductivity of all three monolayer group III-nitrides is tremendously enhanced, especially for h-AIN and h-GaN (up to one order of magnitude). By deeply analyzing the orbital projected electronic structure, we establish a microscopic picture of the lone-pair electrons driving strong phonon anharmonicity in group III nitrides. We also found that the lone-pair electrons do not necessarily lead to enhanced thermal conductivity in strained penta-like 2D materials, which suggests the complexity of thermal response of 2D materials to mechanical strain. Our findings offer perspectives of modulating thermal transport properties of broad 2D materials for applications such as thermoelectrics, thermal circuits, and nanoelectronics.
Planck Institute for Solid State Research, Stuttgart, Germany; 2Korea University, Seoul, Korea (the Republic of); 3Sungkyunkwan University, Suwon, Korea (the Republic of).

Besides of graphene, two-dimensional (2D) van der Waals (vdW) layered materials have been intensively studied over the last eight years especially in the field of electronic and optoelectronic devices. Even though many interesting next-generation device physics such as spin transport, charge density wave, and topological insulator have been revealed in various 2D vdW materials, conventional device configurations like field-effect transistor, Schottky, and p-n diode implemented with the 2D vdW materials have also drawn researchers’ attention due to its similarity to the modern electronic and optoelectronic applications. Particularly, the Schottky and p-n junction based devices are essential elements of energy harvesting applications such as photovoltaic solar cell. In this sense, various surface doping methods have been used to tune the electronic and optoelectronic properties of the WSe2 sheets, but combination effects associated with different surface dopants and its detailed studies are still lacking.

Here, we have demonstrated a Schottky junction-based photovoltaic few-layer WSe2 device with an Al2O3 dielectric deposition near source electrode and a molecular doping (NDF-9) near drain electrode selectively. Scanning photocurrent microscopy (SPCM) with a 514-nm laser wavelength confirmed that a highly asymmetric photocurrent generation was occurred in the device, locally only at the WSe2/source electrode contact. Based on the SPCM and photoresponse results with various bias conditions from the devices, it was revealed that this asymmetric photocurrent was strong and its generation mechanism was originated from the enhanced Schottky junction at the WSe2/source electrode by the proper Al2O3 dielectric deposition and chemical doping. A peak photo-responsivity of ~20 mA W\(^{-1}\) as a photodetector and a peak external quantum efficiency of ~0.2 % as a photovoltaic power generator have been extracted. It is believed that our devices can pave the way for developing a van der Waals two-dimensional material-based Schottky junction solar cell.

**EP03.14.14**

**Origin of Trion Fluorescence at WS\(_2\): Monolayer Edges**

Zhenling Hu1, Junpeng Lu4, Xinyun Wang1, Jin Feng Long1, Qi Zhang1, Zehua Hu1,2, Junyong Wang1,2, Yanpeng Liu1,2, Wei Liu4, Chong haur Sow1,2, Antonio H. Castro Neto1,2 and Alexandra Carvalho2; 1Department of Physics, National University of Singapore, Singapore; Singapore; 2NUS Center for Advanced 2D Materials, Singapore, Singapore; 3Department of chemistry, National University of Singapore, Singapore; Singapore; 4Department of Physics, Southeast University, Nanjing, China.

For the frequently observed edge enhancement and spatial nonuniformities of photoluminescence (PL) of WS\(_2\) monolayer, even though tremendous effort has been put into, the fundamental physics behind remain elusive. Herein, we report that due to the chemisorption of oxygen atoms at the WS\(_2\) edges, and the much higher electronegativity of oxygen compared to that of sulfur and tungsten atoms, electrons accumulate at the edges, leads to the n-doping behavior and higher electron concentrations near the edges than that at the interior region, giving rise to the strong trion fluorescence. Using the first-principle calculations, it is proved that the edge exhibits n-doping semiconducting behavior instead of metallic behavior after oxygen adsorption at the edge.

**EP03.14.15**

**InSe Performance as a FET Sensor Device**

Badreyya A. AlShehhi and Irfan Saadat; Electrical and Computer Engineering Department, Khalifa University of Science, Technology and Research / Masdar Institute, Abu Dhabi, United Arab Emirates.

Indium Selenide (InSe) has attracted significant attention due to large tunability in the band gap, high carrier mobility and unique anisotropic optical properties compared to other two-dimensional (2D) graphene, based systems for chemical and gas sensing applications in the hostile environments. The expanded research requires integrating the chemical and gas sensing capability with optical sensing function. Therefore, in this work, we report the integration and characterization of this material as field-effect transistor (FET) device and as an optical sensor. High-quality InSe thin flakes were prepared using the Scotch-tape-based mechanical exfoliation method and then transferred to a cleaned 300 nm thermally grown SiO\(_2\) wafer. The InSe thin flakes were identified via color contrast by optical microscopy and Atomic Force Microscope (AFM). A direct laser writer was used for patterning while the deposition of electrodes (5 nm Cr /50 nm Au) was done by thermal evaporation. Results indicate that the measured output characteristics (I\(_{ds}\) vs V\(_{ds}\)) of the device exhibits ohmic behavior. Different current amplitudes have been observed with different flake thickness, which indicates the thickness modulated conduction path. Also within a fixed thickness, the channel current modulation can go up to more than 2% with increasing the gate voltage by 0.5 V (by accessing the substrate as a gate). In additional, the optical spectrometer studies shows that few layer of InSe flakes can absorb the light throughout the visible range. Conductivity assessment of InSe flakes and more gate modulation analysis will be reported in the conference.

**EP03.14.16**

**Study of Optical and Magnetic Properties of Transition Metal Doped MoS\(_2\): for Optoelectronic and Spintronic Applications**

Rosy Rahman, Amita Pathak and Tapan K. Nath; Indian Institute of Technology Kharagpur, Kharagpur, India.

The optical properties of MoS\(_2\) have been found to be vary with size and different doping concentration of transition metal (TM) ions as reported from first-principle calculations. The tuning of band gap in the optical range facilitates its application in optoelectronic devices. We have synthesized 2H phase pure MoS\(_2\) and Mo\(_2\)S\(_2\) with different Mn\(^{2+}\) and Co\(^{2+}\) doping (2%, 4%, 6% at. wt.) concentration using facile hydrothermal process. From the XRD analysis the highest intensity (002) peak at 14.2\(^\circ\) confirms the signature of formation of 2H MoS\(_2\) phase. The detailed morphological information of the as-synthesized Mn\(^{2+}\) and Co\(^{2+}\) doped MoS\(_2\), revealed by SEM and TEM technique provides the average length of the nanoflakes are of ~ 68 nm and width ~ 8 nm range. A single distinct peak at ~400 nm and two typical characteristic absorption peaks of undoped, Mn\(^{2+}\) and Co\(^{2+}\) doped MoS\(_2\) are clearly observed in the region of 600 - 690 nm. This corresponds to the A1 and B1 direct excitonic transitions of the MoS\(_2\) originated from the energy split of valence-band and spin-orbit coupling. The most interesting result which is seen from individual Tauc’s plot of undoped MoS\(_2\) and doped MoS\(_2\) is the red shift of peaks and decrease in band gap with increasing Mn\(^{2+}\) and Co\(^{2+}\) doping concentration. The maximum red shift obtained from undoped to 6% Mn\(^{2+}\) is ~ 30 nm with band gap variation of 0.4 eV. This indicates that the incorporation of TM ions lift the valence band edge causing decrease in band gap of 1T and 2H phases. It is confirmed from Raman spectroscopy having peak at 335 cm\(^{-1}\) along with characteristic peaks at 282, 379, 404, 452 cm\(^{-1}\) corresponds to the E\(_{1g}\), E\(_{2g}\), A\(_{1g}\) and A\(_{2g}\) phonon modes. MoS\(_2\) doped with different percentages of Mn\(^{2+}\) and Co\(^{2+}\) ions exhibits efficient fluorescence response although the fluorescence intensity gets quenched with increase in doping percentages due to incorporation of metal ions. Our results on MoS\(_2\), Mn\(^{2+}\) and Co\(^{2+}\) doped MoS\(_2\) nanoparticles can be used as better fluorescence probe as well as optoelectronic device applications in future. In addition we have also carried out magnetic (EPR, PPMS) measurements of the Mn\(^{2+}\) and Co\(^{2+}\) doped MoS\(_2\) samples from which we conclude the enhancement of temperature and structure dependent ferromagnetic signal with increasing doping concentration up to certain level (~ 6 at%). Such type of temperature, structural along with doping dependent variation of ferromagnetic moment in 2D transition metal dichalcogenides can offer a promising application in future spintronic device applications.

**EP03.14.17**

**Nonlinear Optical Spectroscopy of Two-Dimensional WSe\(_2\) Nanoflakes**

Sergey Lavrov, Arsenii M. Buriakov, Elena D. Mishina, Kirill Brekhov, Nikita Ilyin, Anastasia Sheskakova and Artur Avdzhian; RTU-MIREA, Moscow, Russian Federation.
Two-dimensional semiconductor graphene-like materials are currently extremely developing materials. This is primarily due to their unique properties, which make it possible to create on their basis a large number of effective devices of nano- and optoelectronics. A separate promising niche for the use of these materials is the creation of valleytronics devices on their basis. These materials are ideal candidates for studying the mechanisms of valleytronics and methods of its application. The charge carriers in these materials can be localized in two symmetric band valleys. However, optical absorption, carrier mobility, effective mass and other parameters of these materials directly depend on selected valley. Thus, valley selection may be accomplished by changing the parameters of the optical radiation excitation. This feature of these materials was the subject of presented work.

In this work we study two-dimensional flakes of transition-metal dichalcogenides - WSe₂. Flakes were obtained using a standard method of mechanical exfoliation on a Si/SiO₂ substrate, which ensured their uniformity and defectiveness. The substrate thickness was chosen on the basis of optimal conditions for the generation and detection of nonlinear optical processes in monolayer WSe₂ flakes.

To study the optical properties, a pump-probe technique combined with optical spectroscopy was used. Chosen technique allowed a complex analysis of the monomaterials to be studied with high spatial resolution (400 nm) and at low temperature (4K). Thus, characteristic relaxation times of these structures were established. An analysis of the valley lifetimes direct measurement in single-WSe₂ layer using circularly polarized light was made.

The second optical harmonic generation dependence on the excited radiation energy and its power and the temperature of the WSe₂ flakes are identified experimentally.

The work was supported by Ministry of Education and Science of Russian Federation (State task no. 3.7335.2017/9.10 and grant No. 14.Z50.31.0034).

EP03.14.18
Solving Mysteries in Contact Scaling for 2D FETs
Zhiliui Cheng¹, Hattan Abuzaid¹, Shreya Singh², Yifei Yu², Linyou Cao² and Aaron D. Franklin³-⁴. ¹Department of Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; ²Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; ³Department of Chemistry, Duke University, Durham, North Carolina, United States.

Atomically thin 2D crystals are promising channel materials for extremely scaled field-effect transistors (FETs). However, the challenge of contacting 2D materials, especially at the scaled contact lengths (L_c < 50 nm) required for future technologies, constitutes a major roadblock for realizing their full potential. Two mysteries have emerged from studying contact length scaling behavior in 2D FETs: the impact of 2D material thickness and contact gating.

It is unclear how the thickness of 2D materials impacts the transfer length (length over which the majority of carriers are injected at the metal-semiconductor contact). There are many incongruent claims around this mystery, from both experimental and theoretical studies. For example, some theoretical studies claim the transfer length is ~1 nm for monolayer MoS₂ FETs, whereas some experimental studies demonstrate a transfer length ranging from 30 nm to 100 nm. The second mystery is the influence of contact gating on contact scaling. Most 2D FETs demonstrated thus far use a back-gate configuration, which allows for electrostatic modulation of the metal-2D as the channel is gated, creating a contact-gating effect. Contact gating could induce stronger carrier injection, but conclusive evidence for its actual impact on the transfer length remains unknown. Unraveling these two mysteries is pivotal in order to understand how carriers are transported in scaled metal-2D contacts.

In order to investigate these mysteries, we fabricated 2D devices having identical channel length, but with different contact lengths (from 15 nm to 100 nm). The channel material is CVD-grown MoS₂ with the thickness ranging from 1 to 4 layers, allowing us to study the effects of 2D crystal thickness based on monolayer increments. For this range of MoS₂ thicknesses, we compared the devices in top and bottom gate configurations, to understand the impacts of contact gating on the transfer length and the contact scaling behavior. Furthermore, we benchmarked the contact scaling behavior of these various 2D FET configurations against the theoretical and experimental observations in the literature, providing a holistic picture of carrier transport at these metal-2D interfaces.

EP03.14.19
Understanding Interlayer Coupling in TMD-hBN Heterostructure by Raman Spectroscopy
Li Ding¹, M. Shoufie Ukhtry¹, Mikhail Chubarov¹, Tanushree H. Choudhury¹, Fu Zhang¹, Rui Yang,² Jonathan Fan¹, Mauricio Terrones¹, Joan M. Redwing¹, Feng Yang¹, Mingda Li⁶, Riichiro Saito¹ and Shengxi Huang¹. ¹The Pennsylvania State University, State College, Pennsylvania, United States; ²Stanford University, Stanford, California, United States; ³Tsinghua University, Beijing, China; ⁴Tohoku University, Sendai, Japan; ⁵Shenyang National Laboratory for Materials Science, Shenyang, China; ⁶Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In two-dimensional van der Waals heterostructures, interactions between atomic layers dramatically change the vibrational properties of the hybrid system and demonstrate several interesting phenomena, which are present in individual 2D materials. In this work, we have investigated the vibrational properties of the heterostructure between transition metal dichalcogenide (TMD) and hexagonal boron nitride (hBN) on gold film at low and high frequency ranges by Raman spectroscopy. Nineteen Raman modes have been observed from the sample, including a new interlayer coupling mode at 28.8 cm⁻¹. Compared to reported experimental results of WS₂ on Si/SiO₂ substrates, the Raman spectrum for WS₂ on hBN/Au emerges a blue shift of about 8 cm⁻¹. Furthermore, a remarkable enhancement of Raman intensity can be obtained when tuning hBN thickness in the heterostructure. Through systematic first-principles calculations, numerical simulations and analytical calculations, we find that the 28.8 cm⁻¹ mode originates from the shearing motion between monolayer TMD and hBN layers. In addition, the gold substrate and hBN layers form an optical cavity and the cavity interference effect enhances the obtained Raman intensity. Our research demonstrates novel vibrational modes of two-dimensional van der Waals heterostructure as an effective tool to characterize a variety of such van der Waals heterostructure and reveals a new method to enhance the Raman response of two dimensional materials.

EP03.14.20
Realization of 2D Quasicrystals Through Liquid Exfoliation Approach
Thakur P. Yadav¹, Cristianos F. Woelkner²-³, Shyam K. Sinha², Tiva Sharifi³, Amey Apte², Nilay Makhopadhyay², Onkar N. Srivastava¹, Robert Vajtai⁵, Douglas S. Galvao¹, Chandra S. Tiwary⁵ and P. M. Ajayan⁵. ¹University of Campinas, Campinas, Brazil; ²Departamento de Física, Universidade Federal do Paraná, Curitiba, Brazil; ³Department of Physics, University of Houston, Houston, Texas, United States; ⁴Department of Physics, Institute of Science Banaras Hindu University, Varanasi, India; ⁵Materials Science and Engineering, Rice University, Houston, Texas, United States; ⁶Department of Metallurgical Engineering, Indian Institute of Technology, Varanasi, India; ⁷Materials Science and Engineering, Indian Institute of Technology, Gandhinagar, India.

The realization of quasicrystals has attracted considerable attention due to their unusual structures and properties. The concept of quasicrystals in the atomic thin materials is even more appealing due to the in-plane covalent bonds and weak interlayer interactions. Here, it is demonstrated that 2D quasicrystals can be created/isolated from bulk phases because of long-range interlayer ordered aperiodic arrangements [1]. An ultrasonication-assisted exfoliation of poly-grained icosahedral Al–Pd–Mn quasicrystals at room temperature shows the formation of a large area of mono- and few layers in threefold quasi-crystalline plane. The formation of these layers from random grain orientation consistently indicates that the threefold plane is most stable in comparison to the twofold and fivefold planes in quasicrystalline clusters. The above experimental observations are further supported by theoretical simulations. The mono- and few-layered aperiodic planes render plentiful active sites for the catalysis of hydrogen evolution reaction. In order to
understand the origin of structural stability of 3D metallic Al, Pd, and Mn atomic arrangement into 2D ones we carried out ab initio (DFT level, full structural (NMAXEELS) calculations). The structural models consisted of 2D layers initially in a threefold crystallographically icosahedral symmetry. These structures constitute the first demonstration of quasi-crystalline monolayer ordering in a free-standing thin layer without requiring the support of periodic or aperiodic substrate.


EP03.14.21 Equilibrium and Non-Equilibrium Free Carrier Dynamics in Two-Dimensional Ti3C2Tx MXenes—THz Spectroscopy Study
Lyubov V. Titova1, Guangjiang Li1, Kateryna Kushnir1, Yongchang Dong2, Sergii Chertopalov1, Apparao Rao2, Vadym Mochalin1 and Ramakrishna Podila1; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2Physics and Astronomy, Clemson University, Clemson, South Carolina, United States; 3Chemistry, Missouri University of Science and Technology, Rolla, Missouri, United States.

MXenes is an emerging class of two-dimensional transition metal carbides, nitrides and carbonitrides which exhibit large conductivity, ultrahigh volumetric capacitance, high threshold for light-induced damage and nonlinear optical transmittance, which have been suggested as candidates for energy storage, optical modulation and THz detection, among other applications [1]. Successful implementation of photonic and optoelectronic devises based on MXenes such as Ti3C2Tx requires knowledge of intrinsic carrier mobility in these materials as well as of the effects of photoexcitation on conductivity and ultrafast nonequilibrium dynamics of charge carriers. We report on equilibrium and non-equilibrium free carrier dynamics of Ti3C2Tx investigated by THz spectroscopic studies [2]. We have studied intrinsic THz conductivity as well as photoinduced changes in conductivity of a 16 nm-thick film of Ti3C2Tx nanoplates. We find that a high, ~2×10^10 cm^3/s intrinsic charge carrier density and relatively high (~34 cm^2/Vs) mobility of carriers within individual nanoplates results in an exceptionally large, ~46 000 cm^2 absorption in the THz range, in agreement with prior theoretical predictions [3]. We also demonstrate that Ti3C2Tx conductivity and THz transmission can be manipulated by photoexcitation, as absorption of near-infrared, 800 nm pulses suppresses the conductivity for hundreds of picoseconds. Experimental observation of the control over THz transmission and conductivity by photoexcitation suggests the promise for application of 2D MXenes in THz modulation devices and variable electromagnetic shielding.


Evgeny Iakovlev, Petr Zhilyaev and Iskander Akhatov; Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

A two-dimensional (2D) material placed on an atomically flat substrate can lead to the formation of surface nanobubbles trapping different types of substances. In this paper graphene nanobubbles of the radius of 7-34nm with argon atoms inside are studied using molecular dynamics (MD). All modeled graphene nanobubbles except for the smallest ones exhibit an universal shape, i.e. a constant ratio of a bubble height to its footprint radius, which is in an agreement with experimental studies and their interpretation using the elastic theory of membranes. MD simulations reveal that argon does exist in a solid close-packed phase, although the internal pressure in the nanobubble is not sufficiently high for the ordinary crystallization that would occur in a bulk system. The smallest graphene bubbles with a radius of 7nm exhibit an unusual “pancake” shape. Previously, nanobubbles with a similar pancake shape were experimentally observed in completely different systems at the interface between water and a hydrophobic surface.

Leily Majidi, Poya Yasaee and Amin Salehi-Khojin; University of Illinois at Chicago, Chicago, Illinois, United States.

Energy has been one of the most challenging issues during the past decades. The necessity of research in overcoming current energy challenges is crucial because of various reasons such as: limited sources of fossil fuels and carbon emission which leads to global warming and pollution. Electrochemistry is one of the most promising technologies towards environment-friendly and sustainable energy systems. However, it has advanced much more slowly over the last two decades than many companion fields. Fundamental physical parameters such as catalysts’ activity and electronic properties are now hindering major developments in electrochemistry and electrocatalysis. Therefore, new generation of materials are necessary for future applications. In this study, we report on synthesis and characterization of 2D transition metal dichalcogenide (TMD) materials based on group V and VI of transition metals and their sulfides, selenides and tellurides. These materials demonstrate excellent catalytic performance and much higher activity in oxygen reduction and evolution reactions in an aprotic medium with Li salts compared to the reported catalysts. We believe these materials can be utilized as new generation of electrocatalysts for the future developments in catalysis and energy storage systems.

EP03.14.24 Graphene-Based Heterojunction and Its Photoelectric Conversion from Visible to Short-Wave Infrared Light
Xinming Li1,2,3, Hongwei Zhu2, Jian-Bin Xu1, Renzhi Ma1 and Takayoshi Sasaki1; 1International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan; 2School of Materials Science and Engineering, Tsinghua University, Beijing, China; 3Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

In the last few decades, the advances and breakthroughs in graphene and related two-dimensional (2D) materials have been witnessed both scientific fundamentals and potential applications. Graphene’s unique electronic and optical properties have made it an attractive material for developing optoelectronic devices, such as solar cells and photodetectors.[1]

In this talk, I will introduce the graphene-semiconductor heterojunction and its photoelectric conversion from visible light to short-wave infrared (SWIR) light. The graphene can form a Schottky junction with Si, wherein the graphene can function as the transparent electrode and carrier transport layer. In this Schottky junction, Si can absorb the sunlight and contribute photo-generated carriers, so that this heterojunction can be used as a solar cell and a photodiode. [2-3] This solar cell is considered to be a promising demonstration and the power conversion efficiency is raised to 15.6% with electrical and optical improvement.[4-5] Furthermore, this graphene-based heterojunction can be utilized for the photodetectors from visible to SWIR light through
Recent progress reveals the significance of metal dopants in transition-metal dichalcogenides (TMD) on reductive catalysis such as hydrogen evolution reaction. As the concentration of dopant increases, separately-distributed metal dopants tend to form energetically favored clustered structure. Higher concentration of dopant leads to phase separation and structural instability, demolishing the positive doping effect. As a result, the ideal performance of metal-doped TMD catalysts requires certain optimized doping concentration. In this work, we first realize controllable doping of various types of TMDs with desired concentration via a facile sulfurization process on homogenously mixed chloride precursors. The atomic structure of a series of doped TMDs was then unraveled by Raman and TEM techniques. Their catalytic performance was evaluated and the correspondence between atomic configuration, structural stability and catalytic activity was built to elucidate how doping booms the catalysis using TMDs to the greatest extent.

**Networks of Graphene Nanoribbons and Nanosheets Formed in Metals by the Electrocharging Assisted Process**

Lourdes G. Salamanca-Riba1, Xiaoxiao Ge1, Christopher Klingshirn1, Manfred Wuttig1, Oded Rabin1, Karen Gaskell1, Daniel Cole2 and Christopher M. Shumeyko2; 1University of Maryland, College Park, Maryland, United States; 2U.S. Army Research Laboratory, Aberdeen, Maryland, United States.

The incorporation of carbon nanostructures, such as graphene and carbon nanotubes, in the lattice of metals is desirable to take advantage of the superior mechanical and electrical properties of these graphitic nanostructures and the high density of electrons in metals. There have been numerous attempts to create composites of metals, such as copper or aluminum, with carbon nanostructures. These methods frequently require several steps and in aluminum produce the undesirable compound Al4C3. We use electrocharging assisted process which consist of the application of a high DC current to a mixture of liquid metal and carbon particles to incorporate carbon in the metal in a stable form. This method creates graphene nanoribbons and nanosheets in the metal lattice which form epitaxial nanostructures and grows to form a stable structure. The graphene structures bond with atoms in the metal lattice to form the composite very stable. We present a detailed investigation of the process and the effect on the properties of the composites. Raman spectra and mapping indicate that the carbon in the composite has sp2 character. Also, TEM imaging shows that the carbon forms graphene nanoribbons that extend along crystaline directions of the metal lattice. The improvement in electrical and thermal properties as well as the increase in tensile strength are due to the formation of the graphene nanoribbons.

This work is based upon work supported by the U. S. Department of Energy under Award No. DE-EE0008313. Dr. David Forrest is the Project Technology Manager and Debbie Schultheis is the Project Officer/Manager.

**High Performance Graphene Photodetector with van der Waals Heterostructure Through Tuning Carrier Tunneling**

Youngrae Kim and Woo Jong Yu; Sungkyunkwan University, Suwon, Korea (the Republic of).

In the present decade, graphene, which is one of the large number of possible two-dimensional (2D) materials, is considered as a remarkable material for photonics and optoelectrics due to its specific properties such as gapless band structure which enables to modulate optical properties, ultra-fast carrier mobility which makes a fast modulation, a wide absorption range from ultra-violet (UV) to far-infrared (FIR), transparency and flexibility. However, a weak absorption properties and small built-in potential in a monolayer of carbon atoms have limited the properties such as an external quantum efficiency (EQE) range of ~0.1 - 1 %. Also, existing graphene-based photodetector with the lateral structure which has a photo response near graphene-metal junction is not an ideal for the harvesting efficient photons. To increase optoelectronic properties in graphene, large number of devices integrating with 2D transition metal dichalcogenides (TMDs) materials and Quantum dots (QDs) materials which have high absorption properties were developed recently. However, integration with these materials limits the absorption range due to their own bandgap even graphene has advantages in large absorption range. Here, we developed large absorption range to infra-red (IR) range graphene photodetector with metal/insulator/graphene heterostructure by controlling the Schottky barrier. The absorption range can be controlled by utilize with different materials by controlling Schottky barrier. In visible range, we used Au/h-BN/graphene heterostructure which the existence of the h-BN tunneling layer makes extremely low dark current ~10^-13 A. As the result, our photodetector has the high IPH/IPD over ~20 contrast to reported lateral graphene photodetector which has under 5. Finally, we also show the possibility of the IR photodetector from Ni/NiO/graphene heterostructure.

**Torsional Instability in the Single-Chain Limit of a Transition Metal Trichalcogenide**

Thang Pham1, Sehoon Oh1, Patrick Stetz1, Seita Onishi1, Christian Kisielowski2, Marvin Cohen1 and Alex Zettl1; 1University of California, Berkeley, Berkeley, California, United States; 2Molecular Foundry, Berkeley, California, United States.

The scientific bounty resulting from the successful isolation of few-to-single layers of two-dimensional van der Waals materials suggests that related new physics resides in the few-to-single chain limit of one-dimensional van der Waals materials. In my talk, I will present our recent effort in the synthesis of the quasi-one-dimensional transition metal trichalcogenide NbS2 in the few chain limit, including the realization of isolated single chains. The chains are encapsulated in protective boron nitride or carbon nanotube sheaths to prevent oxidation and to facilitate characterization. Transmission electron microscopy reveals static and dynamic structural torsional waves not found in bulk NbS2 crystals. Electronic structure calculations indicate that charge transfer drives the torsional wave instability. Very little covalent bonding is found between the chains and the nanotube sheet, leading to relatively
unhindered longitudinal and torsional dynamics for the encapsulated chains.

**EP03.14.29**

**Fabrication of Size-Controllable Graphene Quantum Dot Array Embedded in Hexagonal Boron Nitride**

Zehua Huang, Qi Han and Jun Wang; School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

Zero bandgap materials are suitable candidates for the preparation of broad-band photodetectors. As a novel three-dimensional Dirac semimetal, Cd$_3$As$_2$ has shown many outstanding features such as linear dispersion, ultrahigh carrier mobility and zero bandgap. Cd$_3$As$_2$ nanosheet has higher light absorption rate compared to the monolayer graphene. Here we report a kind of Cd$_3$As$_2$ nanosheet and perovskite quantum dots FaPbBr$_3$($\text{CH(NH}_2\text{)PbBr}_3$) hybrid photodetector from visible to near infrared. After coating the perovskite QDs, the current responsivity increases more than 30 times. At room temperature, the pure Cd$_3$As$_2$ nanosheet has a responsivity of 62.8 mA/W at 780 nm under 1mV bias voltage, and the current response rate reaches 1.89 A/W after coating the FaPbBr$_3$ QDs. The Cd$_3$As$_2$ nanosheet and FaPbBr$_3$ QDs hybrid photodetector exhibits broadband responses from 405nm to 780nm at room temperature. Our work shows that coating perovskite QDs can significantly improve the performance of broadband photodetectors based on 3D semimetal Cd$_3$As$_2$.

**EP03.14.30**

**Black Phosphorus—An Exciting Material for Electronics and Optoelectronics**

Sumeet Walia, Taimur Ahmed and Sruthi Kuriakose; RMIT University, Melbourne, Victoria, Australia.

Black-phosphorus (BP) has emerged as a material of interest owing to its high carrier mobility and the presence of an intrinsic direct bandgap. Its thickness-dependent energy gap and highly anisotropic properties make it an important material to investigate amongst the family of two-dimensional (2D) materials. Few-layer BP has been a focus of several studies and is promising for applications in electronics, optoelectronics, energy storage, gas sensing, catalysis and chemical/biosensing. However, the ambient instability of BP remains the biggest hurdle in its progress. The fact that the material has to be stored and handled in an inert environment renders it to be unfavourable for practical implementation. To date, the solution to avoid degradation has been capping BP to minimize its interaction with the ambient environment. Here, we present a systematic investigation of the origins of oxidative degradation in few-layer black phosphorus (BP). Subsequently, we also propose an ionic liquid based approach to prevent ambient degradation of BP.

First, we conducted an in-depth investigation into the origins of degradation revealing that oxidation due to light causes degradation whereas humidity on its own does not cause any material and acts merely as a facilitator of photo-oxidation [1].

Subsequently, we have designed a new chemical sequestration strategy which will enable the handling and operating of BP in standard laboratory environments.

Finally, we designed an approach that allows this sensitive material to remain stable without requiring its isolation from the ambient environment [3]. We employ imidazolium-based ionic liquids (ILs) as quenchers of damaging oxidative species on the BP surface. This chemical sequestration strategy allows BP to remain stable for over thirteen weeks, while retaining its key electronic characteristics.

Besides, fundamental studies on the degradation of BP, we have also explored plasma thinning and defect engineering of BP layers.

References:


**EP03.14.31**

**Fabrication of Size-Controllable Graphene Quantum Dot Array Embedded in Hexagonal Boron Nitride**

Gwangwoo Kim$^1$, Kostya Novoselov$^2$, Byeon-Hyeok Sohn$^3$ and Hyeon Suk Shin$^2$; $^1$Ulsan National Institute of Science & Technology, Ulsan, Korea (the Republic of); $^2$School of Physics & Astronomy, University of Manchester, Manchester, United Kingdom; $^3$Seoul National University, Seoul, Korea (the Republic of).

Graphene quantum dots (GQDs) have received tremendous attention because their band gap can be controlled. Although many approaches have been developed to fabricate GQDs, they are time-consuming and costly, and furthermore, precise control over the morphology and size distribution of GQDs remains challenging. Here, we demonstrate spatially controlled conversion of hexagonal boron nitride (h-BN) to graphene on an array of Pt nanoparticles (NPs) to realize an array of uniform GQDs embedded in an h-BN sheet. A uniform Pt NP array was formed on a SiO$_2$/Si substrate with the aid of self-patterning diblock copolymer micelles, and the h-BN sheet was transferred on the Pt NPs array by the conversion of h-BN on Pt to GQDs. The size of the obtained GQDs corresponded with the sizes of the Pt NPs due to the selective conversion of h-BN on top of Pt NPs. Uniform and precisely controlled size of the GQDs ranging from 7 to 13 nm was achieved. Finally, we demonstrate electron transport by the size-controlled GQDs isolated by insulating h-BN like a Coulomb blockade, indicating that the splitting energy of the GQD is 80–160 meV, compatible with its dimension.

**EP03.14.32**

**Manufacture of Two-Dimensional Electrodes by Transition Metal Ditellurides Which Have High Electric Conductivity and Transparent Properties**

Taewon Yuk, Gyutae Jeon, Hakyu Kim, Byeonguk Min and Sukjun Kim; Korea University of Technology and Education, Cheonan, Korea (the Republic of).

Many two-dimensional materials show high electrical conductivity similar to Graphene. Especially, some of transition metal ditellurides has electrical conductivity as high as pure metals. Also, they can be transparent once they are in the form of a thin layer. Fortunately, they can be easily fabricated in the form of thin layer that consists of a few numbers of atomic layers. We attempt to fabricate thin films of nickel ditelluride in two ways (Intemmetallic Target, Co-sputtering). Both of fabricated thin film crystal structure is Ni$_2$Te$_2$, Melonite, 98-004-3293. Our results prove that nickel ditelluride are one of promising candidates for transparent electrodes (existing electrode/200 μm/cm, 80%). First, 2 inch-compound targets were prepared by fabricating the intermetallic followed by SPS. Thin film (thickness 9nm) was deposited by Radio frequency sputtering (PVD) using the Intemmetallic Target. Second, thin film (11nm) was deposited by co-sputtering a Ni and a Te target at Ni:Te=3:7. For two methods, we controlled sputtering power and deposition time and substrate heating conditions to maximize their electrical conductivity. Through TEM analysis proved that more grains with c-axis. Therefore, by after annealing and chemical exfoliation, Nickel ditellurides thin film grain size can be growth coarse and make more thin layer.

**EP03.14.33**

**A Solution-Processed Bi$_2$S$_3$ Photo-Sensing Film with High On-Off Ratio to Mitigate a Trade-Off Between Morphology and Electronic Properties**

Ryosuke Nishikubo$^1$ and Akinori Sacki$^{1,2}$; $^1$Osaka University, Osaka, Japan; $^2$JST-PRESTO, Tokyo, Japan.

Metal chalcogenides (MCs) with two-dimensional (2D) atomic layers have evolved as premier materials for functional devices, including WS$_2$-based field-
effect transistors, Bi$_2$Te$_3$-based topological insulators, and Bi$_2$Se$_3$-based thermoelectric converters. Despite being highly studied, MCs continue to be predominantly synthesized via solid-state reactions at high temperature (>1000 °C) or liquid-phase reactions, which afford microcrystal powders detrimental to low-cost processing of devices over large areas.

Bismuth sulfide (Bi$_2$S$_3$) is an attractive 2D-layered, visible light-absorbing semiconductor composed of non-toxic, abundant elements. However, improving the quality of a Bi$_2$S$_3$ thin film for device applications while maintaining its intrinsic electronic properties is a challenge, as conventional film fabrication processes require a trade-off due to the uncontrolled nucleation and growth steps. Herein, we report a novel procedure for Bi$_2$S$_3$ film formation involving spin-coating of a precursor solution of bismuth salt and sulfur-source organic molecule followed by crystallization under diluted H$_2$S gas. This two-step process produced a large-grained (<400 nm), smooth (surface roughness = 1.7 nm), and highly pure Bi$_2$S$_3$ film with a layer-stacked structure on a substrate. Most importantly, the thin film exhibited excellent photo-sensing performance as a phototransistor with improved photoconductance and on-off ratio compared to those prepared by conventional methods. The obtained high on-off ratio is a result of high photoconductance and low dark-current, supported by high crystallinity, morphology and purity. Our approach provides a versatile route for the development of metal sulfide semiconductors for optoelectronic devices.

**EP03.14.34**

**Green Integration of Layer-by-Layer 2D TMD Films on Arbitrary Substrates by Water-Assisted Layer Separation** Jung Han Kim$^1$, Tae-Jun Ko$^2$, Emmanuel E. Okogbue$^{3,4}$, Sang Sub Han$^2$, Mashiyat S. Shawkat$^2$, Kyu Hwan Oh$^1$, Hee-Suk Chung$^3$ and Yeonwoong Jung$^{1,2,4}$; 1Electrical and Computer Engineering, University of Central Florida, Orlando, Florida, United States; 2NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States; 3Nanotechnology Program, University of Central Florida, Orlando, Florida, United States; 4Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Two-dimensional (2D) transition metal dichalcogenides (TMDs) exhibit unusually superior and tunable electrical, optical, and chemical properties unattainable in conventional inorganic thin films. The intrinsically layered van der Waals (vdW) crystallinity of 2D TMDs coupled with their extremely small thickness suggest that such property advantages can be further promoted by integrating them onto the substrates of novel functionalities and unconventional geometries. A prerequisite for the full exploration of such unprecedented opportunities is to precisely transfer larger-energy-scale 2D TMDs onto targeted functional substrates without compromising their intrinsic material quality as-grown. Herein, we present a water-assisted “green” approach to efficiently separate, transfer, and integrate 2D TMD layers onto virtually arbitrary substrates without using additional chemicals. We demonstrate the successful integration of 2D TMDs onto a variety of unconventional substrates including paper, wood, and plastics as well as their layer-by-layer integration with controlled morphology. The success of this facile 2D layer integration is attributed to the surface energy imbalance in between as-grown 2D TMDs and their growth substrates (i.e., silicon dioxide (SiO$_2$)), which efficiently facilitates the penetration of water underneath the grown 2D layers. We further extend this novel 2D layer integration approach to develop large-scale 2D/2D heterostructures as well as 2D flexible photodetectors, which confirms its versatility for a wide range of device applications.

**EP03.14.35**

**Centimeter-Scale Three Dimensionally-Ordered 2D MoS$_2$ Vertical Layers Integrated on Flexible Elastomeric Substrates** Md Ashrafal Islam$^{1,2}$, Jung Han Kim$^1$, Tae-Jun Ko$^1$, Shraddha Nehate$^2$, Md Golam Kaim$^1$, Kalpathy Sundaram$^2$, Minjee Ko$^2$, Chang-Hee Cho$^2$, Hee-Suk Chung$^3$ and Yeonwoong Jung$^{1,2,4}$; 1Nanotechnology Program, University of Central Florida, Orlando, Florida, United States; 2Department of Electrical and Computer Engineering, University of Central Florida, Orlando, Florida, United States; 3Department of Emerging Materials Science, DGIST, Daegu, Korea (the Democratic People's Republic of); 4Analytical Research Division, Korea Basic Science Institute, Jeonju, Korea (the Democratic People's Republic of); 5Department of Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States; 6Department of Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States; 7Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

The intrinsically anisotropic layered structure of two-dimensional (2D) transition metal dichalcogenides (2D TMDs) enables a variety of intriguing material properties which strongly depend on the physical orientation of constituent 2D layers. For instance, 2D TMDs with vertically-aligned 2D layers exhibit numerous dangling bonds on their 2D layer edge sites, offering tremendous opportunities for a wide range of applications which demand high physical/chemical surface reactivity. Moreover, such property advantages can be further promoted as far as 2D TMDs with controlled layer orientation can be integrated onto the unconventional substrates of tailored geometry and functionality while their structural integrity is well retained. Herein, we report large-area (>2 cm$^2$) three-dimensionally (3D) structured 2D MoS$_2$ layers with vertically-aligned layers integrated on mechanically flexible elastomeric substrates. We synthesized 2D MoS$_2$ with vertically-aligned layers on silicon dioxide/silicon (SiO$_2$/Si) 3D pillars-patterned substrates. The 3D-ordered vertical 2D MoS$_2$ layers were subsequently transferred and integrated onto flexible polydimethylsiloxane (PDMS) substrates, enabled by the water-assisted layer transfer method developed in our group. The structural integrity of the vertical 2D MoS$_2$ layers was characterized by extensive spectroscopy and microscopy before and after the transfer and was confirmed to well retain. We demonstrated mechanically flexible humidity sensors based on the 3D-ordered 2D vertical MoS$_2$ layers and identified their superior sensitivity, which is attributed to the combined effect of increased surface area and enhanced 2D edge density.

**EP03.14.36**

**Scalable Synthesis of Crystalline vdw MOF Nanosheets with Large Aspect-Ratio Through Ultimate Control Over Hydrogen Bond Formation and Reaction Rates** Yuxia Shen$^1$, Bohan Shan$^2$, Hui Cai$^1$, Ying Qin$^1$, Ashutosh Agarwal$^2$, Bin Chen$^1$, Lei Li$^1$, Houlong Zhuang$^1$, Bin Mu$^1$ and Seliaatin Tongay$^1$; 1Arizona State University, Tempe, Arizona, United States; 2Arizona State University, Tempe, Arizona, United States.

Large scale synthesis of van der Waals (vdW) metal organic framework (MOF) nanosheets with controlled crystallinity and interlayer coupling strength has been one of the bottlenecks in the development of 2D materials. This has limited not only our visibility to their fundamental properties, but also the industrial daily life applications. Here, we demonstrate scalable synthesis of mBDC (m=Zn and Cu) 2D MOFs at large scales through a bi-phase method. By replacing water molecules in the reaction with pyridine, hydrogen bonding at metal cluster sites and between the layers is largely eliminated. This sustains vdw MOFs growth and prohibits tightly coupled MOF structures. By adding controlled amount of TEA and formic acid in the reaction solution, we are able to regulate the proton concentration and reaction rates, which allowed us to control the nucleation density, growth speed, crystallinity, and material thickness, to achieve highly crystalline vdw MOF nanosheets with extraordinarily high aspect ratio. Described synthesis route can be easily scaled up for large-scale production in either crystal powder or depositing onto various substrates. Benefiting from its large lateral size, vdw nature, and high crystallinity, we are able to perform AFM, KPFM, and Raman measurements to establish their fundamental properties as novel material characterization tools, allowing a new perspective on the structural identification via lattice vibration, as well as the very first insight on their thickness-dependent properties. This work provides a scalable synthesis method for production of high quality 2D MOF nanosheets, and structural and physical insight into the material properties for the first time.

**EP03.14.37**

**Sodium Chloride Induced Heterogeneities in Epitaxial MoS$_2$** Kehao Zhang$^1$, Brian M. Bersch$^1$, Fu Zhang$^1$, Natalie Briggs$^1$, Ke Xu$^1$, Ke Wang$^1$, Mikhail Chubarov$^1$, Joan M. Redwing$^2$, Susan Fullerton-Shirey$^2$, Mauricio Terrones$^1$ and Joshua Robinson$^1$; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2University of Central Florida, Orlando, Florida, United States.

Sodium chloride induced intrinsic heterogeneities in the epitaxial growth of MoS$_2$ film onto a silicon substrate at high temperature (>1000 °C) or liquid-phase reactions, which afford microcrystal powders detrimental to low-cost processing of devices over large areas.
The realization of wafer-scale transition metal dichalcogenide monolayer films\(^1\) and the successful exploration of 2D TMDs library\(^2\) are two major milestones in the recent efforts on the synthesis of 2D materials. Interestingly, NaCl is used in both cases to reduce the nucleation density and melting points of oxides. However, the presence of alkali metals is detrimental in conventional silicon-based semiconductors due to high rates of ion diffusion through the bulk, leading to degradation in device performance and reliability. In 2D materials, like traditional dopants such as tinium and niobium, alkali metals, such as potassium K\(^+\), results in degenerate doping of MoS\(_2\). Therefore, it is critical to comprehensively evaluate the impacts of NaCl on the properties of synthetic 2D materials. In this work, we elucidate NaCl-induced heterogeneities in synthesis, photonic response and electrical performance of MoS\(_2\) films, and demonstrate that salt-assisted synthesis of epitaxial MoS\(_2\) monolayers degrades electrical device performance. First, we develop the NaCl-free large area (2+2 cm\(^2\)) epitaxy of MoS\(_2\) evident from in-plane X-ray diffraction (XRD) and utilize it to compare to the growth with NaCl. Atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman, and photoluminescence (PL) indicate that growth of monolayer films without NaCl are crystalline and uniform across a wide range. Substrates without island growth, while two distinct growth modes (island and layer-by-layer) and rates are identified when NaCl is utilized. The heterogeneous growth kinetics due to NaCl leads to photonic heterogeneities related to non-uniform monolayer strain. Moreover, utilizing NaCl introduces a 1.5x decrease in mobility, 2x increase in subthreshold slope, and 100x reduction in on/off ratio due to electronic trap states. Finally, comparison of transport properties between devices fabricated using as-grown and transferred films reveals that interface coupling (charge transfer, trap states) can dominate the device performance, indicating the importance of substrate engineering to realize the high performance, synthetic 2D based devices.

Reference


EP03.14.38

Unveiling Growth Mechanisms in 2D/2D Layer-By-Layer Horizontal Epitaxy to 2D/3D Vertical Cross-Over in van der Waals Heterostructures

Nitin Choudhary\(^1\), Tae-Jun Ko\(^1\), Jung Han Kim\(^1\), Md Asriful Islam\(^1\), Hye Min Oh\(^1\), Kevin Coffey\(^1\), YounJoon Jung\(^1\) and Yeonwoong Jung\(^2\); \(^1\)University of Central Florida, Orlando, Florida, United States; \(^2\)Korea Basic Science Institute, Jeonju, Korea (the Republic of); \(^3\)Seoul National University, Seoul, Korea (the Republic of).

2D van der Waals (vdW) heterostructures composed of chemically distinct transition metal dichalcogenides (TMDs) exhibit exotic functionalities, projecting enormous opportunities for next generation semiconductor heterojunction devices. Despite the recent advances in developing 2D vdW heterostructures of various geometry and component, their fundamental growth principle, i.e. how 2D layers of one kind grow on top of the other, has not been fully clarified. In this work, we investigate the fundamental parameters that dictate the growth characteristics of 2D/2D heterostructures composed of vertically-stacked 2D MoS\(_2\)/W\(_{\text{S}}\). By employing tungsten trioxide (WO\(_3\)) nanowires as growth templates which enable the atomistic inspection of 2D/2D interfaces upon transmission electron microscopy (TEM), we observed a unique growth transition in these materials; i.e., 2D/2D layer-by-layer horizontal epitaxy to 2D/3D crossover akin to the Stranski-Krastanov (SK) growth of vertical layers. We further identified that this growth mode transition is driven by increasing the thickness of the seed metal films converted to 2D TMD layers. Molecular dynamics (MD) simulation confirmsthe formation of the internal strain that facilitates the 2D layer growth. The morphological characteristics of resulting 2D/2D heterostructures. Our finding is insightful for better understanding the growth principles behind generic 2D vdW heterostructures, thus pave ways for their utilization towards emerging 2D heterojunction devices.

EP03.14.39

Thermoelectric Properties of CVT-Grown Lithium-Intercalated Molybdenum Disulfide (Li\(\text{MoS}_2\))

Hong Kuan Ng\(^1\), Anas I. Abutaha\(^2\), Yi Liu\(^1\), Ivan Verzhbitskiy\(^3\), Goki Eda\(^4\) and Kedar Hippalgaonkar\(^5\); \(^1\)National University of Singapore, Singapore, Singapore; \(^2\)IMRE, A*STAR, Singapore, Singapore.

Thermoelectricity, based on the Seebeck effect, is an alternative for power generation and refrigeration due to its ability to directly convert thermal into electrical energy. Here, we study thermoelectric properties of exfoliated Li\(\text{MoS}_2\) grown using Chemical Vapour Transport (CVT), where a mixture of 1T’ and 2H phases coexist in a single sample due to the 2H to 1T’ phase transition induced by Lithium (Li) intercalation. We show that as-fabricated Li\(\text{MoS}_2\) devices are p-type in nature with high electrical conductivity due to its metallic 1T’ phase, and that in-situ thermal annealing of Li\(\text{MoS}_2\) in vacuum induces a p-type to n-type transition as a result of delithiation. A peak power factor of 18 uW/mK\(^2\) is observed in an effective medium of Li\(\text{MoS}_2\) with reasonable electrical conductivity is maintained by the metallic 1T’ phase and the Seebeck coefficient is controlled by the semiconducting 2H phase. By refining the thermal annealing temperature and annealing time that controls de-lithiation of LixMoS\(_2\), we hypothesize that a higher power factor can be achieved, showing an additional knob to tune energy dependent scattering in these novel materials.

EP03.14.40

Highly Enhanced Photoresponsivity of Monolayer WS\(_2\) Photodetector with Nitrogen-Doped Graphene Quantum Dots

Duc Anh Nguyen\(^1\), Hye Min Oh\(^1\), Ngoc Thanh Duong\(^1\), Seungho Bang\(^2,3\), Seok Jun Yoon\(^1,2\) and Mun Seok Jeong\(^1,2\); \(^1\)Department of Energy Science, Sungkyunkwan University, Suwon 16419, Korea (the Republic of); \(^2\)Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 16419, Korea (the Republic of).

Monolayer (ML) transition metal dichalcogenides (TMDs) such as tungsten diselenide (WSe\(_2\)) are particularly interesting in the field of nanoscale optoelectronic devices because of its direct band gap, high carrier mobility and high ON/OFF ratio. However, atomically thin material layers have limited ability to absorb and emit radiation because of their low cross-sectional area. To enhance the photoresponsiveness of ML WSe\(_2\), a strong light absorbing material such as PbS quantum dots (QDs) or organolead halide perovskite were introduced. However, these materials are toxic and unstable under ambient condition because of the presence of Pb compounds or organic materials. Therefore, it is a huge challenge for finding a low cost, non-toxic and stable material to create a hybrid structure with ML WSe\(_2\) to improve its optoelectronic performance.

In this work, we report a facile method for fabricating a hybrid structure that consists of ML WSe\(_2\) covered with Nitrogen-doped graphene quantum dots (ML WSe\(_2\)/N-QGQDs). The PL intensity of ML WSe\(_2\) is enhanced drastically because of the reduction of the positive trion and enhancement of the neutral exciton formations through electron transfer from N-QGQDs. The improved photoresponsivity in ML WSe\(_2\)/N-QGQDs photodetector is attributed to strong light absorption and charge transfer from N-QGQDs to ML WSe\(_2\). The photogating effect also plays a key role in the improvement of hybrid photodetector performance. Notably, this hybrid photodetector exhibits good stability under ambient condition.
2-dimensional (2D) material field effect transistors (FETs) are promising devices to overcome the problems of conventional devices with their new attractive electrical properties. Since 2D material FETs have very similar structures to Junctionless transistors (JLTs) with no junctions requiring heavily-doped silicon as a channel, the analysis of the conduction mechanism of 2D material FETs based on the conduction mechanism of JLTs is considered as an effective method. JLTs are a special type of FETs that operate in accumulation mode using bulk conduction mechanism instead of conventional inversion mode.

Prior studies show that, in a 2D material FETs with a multi-layered channel, the conduction path is formed on the surface of the channel material if the electrodes are fabricated on the surface of the channel. In this study, multi-layered 2D material FETs with edge-contacted channel using molybdenum disulfide (MoS2) were fabricated to investigate the effect of bulk conduction. The changes of transfer characteristics with the electrodes structure of FETs were observed, which can be explained by carriers directly injected at the interface between electrodes and edges of the channel. For the further analysis, mobility degradation factors using transconductance ($g_m$) and Low Frequency Noise (LFN) of FETs were evaluated. FETs with electrodes on the edge of the channel show less decrease of $g_m$ curve than the ones with electrodes on the surface of the channel. The change of the current fluctuation was observed in case of edge contacted FETs, attributed to the contribution of bulk conduction.

These results indicate the reduction of surface roughness scattering from the bulk conduction mechanism in multi-layered structures. An enhancement of bulk conduction was also observed in FETs with electrodes on the edge of the channel in LFN Characteristics. Our study suggests an effective method to analyse the mobility degradation factors depending on conduction path in multi-layered channel regime.

**EP03.14.43**

*Excitonic Energy Transfer in van der Waals Heterostructure of 2D Hybrid Perovskite and Monolayer WS2* Qi Zhang, Eric Linardy and Goki Eda; NUS, Singapore, Singapore.

Two-dimensional (2D) organic-inorganic hybrid perovskite is a re-emerging material with strongly excitonic absorption and luminescence properties that are attractive for optoelectronics. Similar to other excitonic 2D semiconductors, the excitons in 2D perovskite nanosheets are expected to exhibit near-field coupling with nearby excitonic systems. Here we report on an experimental observation of excitonic energy transfer in van der Waals heterostructures consisting of 2D hybrid perovskite ([C6H5C2H4NH3]2 PbI4) and monolayer WS2. We prepared the heterostructure using the dry-transfer technique with the WS2 layer encapsulating the perovskite sheet to protect it from degradation. Photoluminescence excitation spectroscopy with WS2 exciton emission in the detection channel reveals a distinct ground exciton absorption feature of perovskite, evidencing energy transfer from perovskite to WS2. At the resonance peak of perovskite, the emission from WS2 was enhanced by a factor of 2–5. This observation suggests that the energy transfer occurs not only from the top-most layer but also from the lower layers of perovskite. We further discuss the emergence of a peculiar sub-gap low energy emission peak which may be attributed to the interfacial hybridization between WS2 and the organic moiety of perovskite.

**EP03.14.44**

*Simultaneous Synthesis and Integration of Ultrathin Electronic Components for Beyond Silicon Circuits* Qi Zhang and Liying Jiao; Chemistry, Tsinghua University, Beijing, China.

When the silicon metal-oxide-semiconductor field effect transistor (MOSFET) was first introduced in integrated circuits, it shows strong scalability and the complexity of circuits increases exponentially in the past several decades according to the Moore’s law. However, as the characteristic dimension of MOSFET reaches the thermal and quantum limit, scaling down the device from lateral and vertical directions becomes increasingly difficult and costly. Driven by the urgent demand for continuously shrinking the size of transistors, great efforts have been made on exploring low dimensional electronic materials, such as nanowires, carbon nanotubes (CNTs) and two-dimensional (2D) materials as building blocks for constructing smaller devices during the past two decades. Although electronic devices based on individual nanomaterials have exhibited high performance, there is still a huge gap towards integrating these single devices into practical circuits that can compete with state-of-the-art silicon chips. Here we present an alternative device manufacturing strategy in which the ultrathin electronic components in the active layer are chemically synthesized and integrated simultaneously in a single step and each component is connected via covalent bonds instead of physical interfaces. As a proof of the concept, we synthesized arrays of logic devices and radio frequency devices through the phase-patterned growth of ultrathin atomic layers. The obtained circuits composed of semiconducting phase as channels and metallic phase as contacts and interconnects were ready to work after the synthesis process and exhibited high performance. Moreover, we successfully constructed multilayered devices with vertical interconnections to show the potential of our strategy on fabricating three-dimensional (3D) integrated circuits (IC) with ultimate circuit densities in vertical space. This approach makes the design and optimization of electronic devices much more flexible and preserves the intrinsic performance of the materials to the largest extent and therefore, provides a new technology for manufacturing high performance integrated circuits beyond silicon.

**EP03.14.45**

*Visualizing and Understanding the Microstructure of Transition Metal Dichalcogenide Monolayers* Xiaomin Xu1, Thorsten Schultz1, 2, Ziyu Qin1, 4, Benedikt Haas1, 2, Nikolai Severin1, 2, 3, Jan N. Kirkchof6, Andreas Optitz2, 3, Christoph T. Koch1, 2, Kirill Bolotin5, Jürgen P. Rabie1, 2, Goki Eda1 and Norbert Koch1, 2, 3, 4; 1Department of Physics, Humboldt-Universität zu Berlin, Berlin, Germany; 2Integrative Research Institute for the Sciences (IRIS Adlershof), Berlin, Germany; 3Department of Physics, National University of Singapore, Singapore, Singapore; 4State Key Laboratory of Materials Processing and Die Mould Technology, Huazhong University of Science and Technology, Wuhan, China; 5Department of Physics, Freie Universität Berlin, Berlin, Germany; 6Helmholtz-Zentrum für Materialien und Energie GmbH, Berlin, Germany.

Probing the microstructure of transition metal dichalcogenide (TMDC) monolayers is of paramount importance to understand the optical and electrical properties, and to facilitate a controllable application in optoelectronic devices [1]. Industry-scale fabrication on TMDC monolayers seems within reach due to the rapid development of chemical vapor deposition (CVD) [2], yet visualization of spatial structure variations in nondestructive and high-throughput manner remains challenging [3,4].

Here we report how grain boundaries, strain fields, and grain orientation can be identified unambiguously with combined lateral force microscopy (LFM) and transverse shear microscopy (TSM) for CVD-grown tungsten disulfide (WSe2) monolayers. In LFM images, sharp line-shape contrasts appear and persist after sample transfer, and their locations coincide with regions having photoluminescence (PL) intensity fluctuation, corresponding to inherent structural defects, i.e. grain boundaries. Differently, diffuse-shape contrasts disappearing after sample transfer solely arise from changes of the friction coefficient under strain. TSM is demonstrated to be superior in identifying grain orientation since the shear stress signal varies with respect to the scan vector due to the elastic anisotropy of the crystalline sample. Further, angle-dependent TSM measurements enable us to acquire the fourth-order elastic constants of monolayer WSe2 experimentally.
Our study exemplifies a rapid and non-destructive approach to visualize the microstructure of TMDC monolayers, insights into their elastic properties, thus providing an accessible tool to support the development of advanced two-dimensional optoelectronic devices.

References


EP03.14.46
Temperature-Dependent Electrical Properties of Piezoelectric Monolayered MoS₂

Abstract:

Monolayered molybdenum disulfide (MoS₂) is one of the most promising materials for next-generation electronic/optoelectronic devices because of its prominent piezoelectric property that can modulate Schottky barrier height and control transport behaviors without applying any external gate bias. Although temperature dependency of current transport in monolayered MoS₂ has been predicted in a theoretical study based on 2D thermionic equation, experimental result about temperature dependences of piezoelectric/piezophotoelectric effect in monolayered MoS₂ has not been reported yet. Several researchers have studied piezoelectric properties of monolayered MoS₂ only at room temperature. Here, we focused on temperature dependence of the piezoelectric effect in CVD grown monolayered MoS₂. In this study, transport behaviors of monolayered MoS₂ on polyethylene terephthalate (PET) as a flexible substrate under strain from 0 to 0.3 % in generally accepted operating temperature region from 273 K to 333 K were examined. Thermocouple was used to directly measure the temperature of such MoS₂. We observed that strain-generated piezoelectric charges in our MoS₂ affected the transport behavior by modulating SBH at the interface between electrodes and MoS₂. In addition, we found that the current and SBH had different tendencies depending on sample temperature. A dominant effect of the current behavior with the strain used in our monolayered MoS₂ depending on sample temperature was also determined by measuring photocurrent under the strain. The piezoelectric effect was found to be dramatically increased when sample temperature was decreased from 320 K to 270 K.

EP03.14.48
Growth of WS₂ Nanocrystals and Nanosheets by a New Lithium Intercalation Method for Multifunctional Device Application

Abstract:

Transitionnal metal dichalcogenides (TMDC) such as WS₂ has drawn immense attention recently owing to their thickness dependend band gap energy which is missing among other two-dimensional materials like graphene or carbon nitride. However, widespread application of semiconducting WS₂ is hampered by their low yield production methods. Among the two-dimensional (2D) TMDC, WS₂ is very reluctant to undergo liquid exfoliation than other. So, it is a new challenge to synthesize mono or few layer WS₂ flakes or nanocrystals of controlled size in large scale and simple way. WS₂ shows similar kind of band gap modulation like MoS₂ with the layer number attractive for opto-electronic device application. Here, we have synthesized bi-to-few layers WS₂ in solution from bulk WS₂ by Li-ion intercalation technique using lithium halide. In brief, WS₂ bulk powders and LiX (anhydrous) were mixed in hexane. The mixture was sonicated for 50 minutes in an ultrasonic bath sonicator. The black mixture was washed several times with N, N-Dimethylformamide (DMF) to remove unreacted lithium halides and further sonicated for 15 minutes to obtain yellowish green solution. In addition, WS₂ nanocrystals of different sizes have been synthesized by sonication induced fragmentation method. The structural and morphological properties of the as synthesized WS₂ nanocrystals were investigated by different spectroscopic and microscopic techniques such as TEM, AFM, RAMAN, XRD, XPS. We have observed that the photoluminescent property of the nanocrystals changes dramatically compared to the 2D flakes of WS₂. We have employed ZnO as n-type and WS₂ nanocrystals of 2-3 nm as p-type to fabricate heterojunction light emitting diode. The fabricated device shows a broad band emission from 400 to 700 nm at 0.9 mA. In addition, charge storage ability of WS₂ nanocrystals is investigated by integrating flexible solid state symmetric supercapacitor using acetylene black as a conducting filler and PVA-H₃PO₄ mixture as gel electrolyte. The fabricated supercapacitor shows 28 mF/cm² areal capacitance at a current density of 0.1 mA/cm². This result paves the way to fabricate future optoelectronic devices.

EP03.14.49
Phase Transition of T-phase WS₂ Derived by Adsorption of ORR Intermediates and Its Applications as Carbon-Free Cathode for Li-Air Batteries

Abstract:

T-phase tungsten disulfide (T-WS₂) is firstly suggested as a potential candidate for carbon-free cathode of Li-air batteries (LABs) to replace conventional carbon-based materials. Using density functional theory calculations, it was revealed that the electron transfer caused by the adsorption of oxygen reduction reaction (ORR) intermediates (i.e. Li₂O₂ and Li₂O₃) enhances the W – W clustering due to the electronic instability induced by additional charge, and it causes a phase transition to the new phases of T-WS₂ (named as DT-WS₂ and ZT-WS₂). Moreover, in terms of electrochemical performances, DT-WS₂ and ZT-WS₂ have a small discharge overpotential of 0.84 V and 0.91 V, respectively. For this reason, DT-WS₂ and ZT-WS₂ are predicted to have comparable electrochemical performance with well-known carbon-based cathodes. In addition, it is found that the adsorptions of intermediates induce the semiconductor to metal transition in DT-WS₂ and the increase of carrier concentration in ZT-WS₂, resulting in high electrochemical performance. It is therefore confirmed that DT-WS₂ and ZT-WS₂ are strong candidates as a carbon-free cathode based on two-dimensional materials for LABs.

EP03.14.50
Electronic Structure of a Zigzag Shaped Ternary Chalcogenide HfGeTe₄ Monolayer

Abstract:


Temperature-Dependent Electrical Properties of Piezoelectric Monolayered MoS₂

Abstract:

Monolayered molybdenum disulfide (MoS₂) is one of the most promising materials for next-generation electronic/optoelectronic devices because of its prominent piezoelectric property that can modulate Schottky barrier height and control transport behaviors without applying any external gate bias. Although temperature dependency of current transport in monolayered MoS₂ has been predicted in a theoretical study based on 2D thermionic equation, experimental result about temperature dependences of piezoelectric/piezophotoelectric effect in monolayered MoS₂ has not been reported yet. Several researchers have studied piezoelectric properties of monolayered MoS₂ only at room temperature. Here, we focused on temperature dependence of the piezoelectric effect in CVD grown monolayered MoS₂. In this study, transport behaviors of monolayered MoS₂ on polyethylene terephthalate (PET) as a flexible substrate under strain from 0 to 0.3 % in generally accepted operating temperature region from 273 K to 333 K were examined. Thermocouple was used to directly measure the temperature of such MoS₂. We observed that strain-generated piezoelectric charges in our MoS₂ affected the transport behavior by modulating SBH at the interface between electrodes and MoS₂. In addition, we found that the current and SBH had different tendencies depending on sample temperature. A dominant effect of the current behavior with the strain used in our monolayered MoS₂ depending on sample temperature was also determined by measuring photocurrent under the strain. The piezoelectric effect was found to be dramatically increased when sample temperature was decreased from 320 K to 270 K.

EP03.14.48
Growth of WS₂ Nanocrystals and Nanosheets by a New Lithium Intercalation Method for Multifunctional Device Application

Abstract:

Monolayered molybdenum disulfide (MoS₂) is one of the most promising materials for next-generation electronic(optoelectronic devices) because of its prominent piezoelectric property that can modulate Schottky barrier height and control transport behaviors without applying any external gate bias. Although temperature dependency of current transport in monolayered MoS₂ has been predicted in a theoretical study based on 2D thermionic equation, experimental result about temperature dependences of piezoelectric/piezophotoelectric effect in monolayered MoS₂ has not been reported yet. Several researchers have studied piezoelectric properties of monolayered MoS₂ only at room temperature. Here, we focused on temperature dependence of the piezoelectric effect in CVD grown monolayered MoS₂. In this study, transport behaviors of monolayered MoS₂ on polyethylene terephthalate (PET) as a flexible substrate under strain from 0 to 0.3 % in generally accepted operating temperature region from 273 K to 333 K were examined. Thermocouple was used to directly measure the temperature of such MoS₂. We observed that strain-generated piezoelectric charges in our MoS₂ affected the transport behavior by modulating SBH at the interface between electrodes and MoS₂. In addition, we found that the current and SBH had different tendencies depending on sample temperature. A dominant effect of the current behavior with the strain used in our monolayered MoS₂ depending on sample temperature was also determined by measuring photocurrent under the strain. The piezoelectric effect was found to be dramatically increased when sample temperature was decreased from 320 K to 270 K.
Two-dimensional materials having a van der Waals (vdW) gap have attracted considerable attention for future electronics and optoelectronics applications because of their ultimate thickness limit. One of the most intriguing properties of standard transition metal dichalcogenides (TMDs) is that they show a direct optical transition as a monolayer, while they possess an indirect band gap in the bulk counterpart. Even though they possess interesting properties, materials exploration of TMDs is limited to the composition of MX$_2$, where M is a transition metal and X represents a chalcogen element. In this study, we propose HfGeTe$_4$ as a new ternary transition metal dichalcogenide [1]. It was reported that bulk HfGeTe$_4$ was a layered structure having a zigzag vdw gap, which is a striking difference from a standard flat vdw gap. Therefore, it is expected that such the zigzag shape allows a higher cohesive energy between layers. The total energies were calculated by a density functional theory (DFT) code CASTEP as a function of inter-layer distances, and it was found that HfGeTe$_4$ has the highest cohesive energy than other typical TMDs like MoS$_2$ or MoTe$_2$. This would enable the stronger adhesion with metal or insulator layers that has advantage for industry. The band structures were calculated for bulk and monolayer HfGeTe$_4$ using a screened exchange (sx) hybrid functional. The bulk has a band gap of about 0.67 eV and a transition occurs from the $\Gamma$ point in the valence band maximum (VBM) to the $\Gamma$ point in the conduction band minimum (CBM), indicating an indirect semiconductor. On the other hand, the direct transition is realized at the $\Gamma$ point in ML with a band gap of 1.3 eV. Furthermore, it was also found that models more than 2ML show the indirect transition, demonstrating the same trend with TMDs. The band gap decreases with increasing number of layers toward the bulk limit. Based on the current study, the materials exploration of layered chalcogenides will dramatically extend from binary to ternary systems that may lead to the discovery of novel materials for future electronics applications.

However, traditional metal precursors like halides, oxides, and thiometallates implicate several disadvantages such as low solubility and volatility and the function modulation of BP. The heterojunction. Optoelectronic experiments on Esaki diode and Esaki diodes (peak to value current ratio ~ 4.4), backward-rectifying diodes and non-rectifying devices as a consequence of band-structure alignment at the heterojunction. Based on the findings, we have chosen BP/ReS2; van der Waals heterostructures due to following reasons: (i) In addition to opposite polarity of majority charge carriers i.e. p-type BP and n-type ReS2; BP/ReS2 forms type-II broken-gap alignment at the heterojunction and (ii) BP flakes show substantial dependence of work function on their respective thickness. In the Phosphorene (BP)/Rhenium disulfide (ReS2) heterojunction, we exploit BP work function tunability with varying flake thickness to demonstrate that BP-based broken-gap heterojunction could display diverse current-transport such as gate tunable rectifying p-n junction diodes (current rectification ~ 10^6), Esaki diodes (peak to value current ratio ~ 4.4), backward-rectifying diodes and non-rectifying devices as a consequence of band-structure alignment at the heterojunction. Optoelectronic experiments on BP diode and p-n junction diode clearly reveal that diversity of current-transport derives from the work function modulation of BP. The p'-n-p junction made of thick-BP/ReS2/thin-BP functions as multi-value inverters, and shows the behavior of bipolar junction transistor (BJT) with common-emitter current gain up to 50. Such tunability could be beneficial in the development of compact electronic circuits with devices of multifunctionality reducing the need of multiple materials. Current-transport tunability due to ΦBP modulation and p'-'n-p BJT with high gain, which benefits from the high hole-mobility of BP, demonstrates the high potential for a new class of scalable and multifunctional devices.

Tunable Current-Transport in Phosphorene Based Broken-Gap Heterojunction

At the few-atom-thick limit, transition metal dichalcogenides (TMDs) exhibit a host of attractive electronic, optical, and mechanical properties [1]. The possibility to pattern these properties may have a great impact on applied [2] and fundamental research [3]. In this work, we report on the effects of ionic hydrogen irradiation in multi-layer (number of layers greater than 10) TMDs. We found that production and accumulation of molecular hydrogen just one or few monolayers beneath the flake top surface are induced by proton irradiation. Molecular H2 therein produced coalesces to form bubbles, which lead to the localized swelling of prevalently one X-M-X plane. This results eventually in the formation of spherical domes on the basal plane of bulk WS2, WSe2, WTe2, MoS2, MoSe2, flakes. The domes contain highly-pressurized hydrogen (at around 10 atm), are prevalently one monolayer thin and are robust against aging and mechanical stress. Due to their single-layer peel, they emit light efficiently, also well above room temperature, display circular dichroism and feature second harmonic generation signal. The TMD membrane, which forms the domes, is subjected to both in-plane high biaxial-tensile strain (up to ~5% at the summit of the dome) and out-of-plane uniaxial compressive strain (up to about -1.6% at the summit of the dome). Finite-element calculations show that both tensile and compressive strains vary over the dome surface. More precisely, the absolute values of all the strain components decrease moving from the center to the edge of the domes. These results enable the unprecedented observation on a single dome of a direct-to-indirect band gap transition, due to the crossing of the Γ-K (indirect) and K-K (direct) optical transitions, as already predicted by theoretical calculations [4]. Furthermore, by means of electron-beam lithographic processing, all these features can be made spatially scalable [5]. Indeed, the domes can be produced with the desired density, well-ordered positions and size tunable from the nanometer to the micrometer scale, thus providing a template for the manageable and durable mechanical and electronic restructuring of two-dimensional materials.

An Efficient Approach to Atomic-Scaled 2D Chalcogenide Based Materials from a New Class of Single-Source Precursors

Heterometallic structures containing metal 4+ ions are interesting molecules for the creation of (multi)functional 2D materials such as high quality graphene-like 2D MX2 (M = transition metal, X= S, Se) structures, given their unique physical properties for optical, optoelectronic and electronic devices. However, traditional metal precursors like halides, oxides, and thionometallates implicate several disadvantages such as low solubility and volatility and the use of hazardous reactants such as H2S. Therefore, in this study, a novel class of [M4+(SE(N(Me)ESi)] single-source precursors was designed for a variety of tetravalent transition metal including tungsten(V), molybdenum(V), titanium(IV) and vanadium(IV). These complexes were formed by simple synthetic protocols and characterized by a combination of spectroscopic techniques, single crystal x-ray analysis and TG-DTA experiments. For instance, the controlled decomposition of the well-characterized [W(Se(N(Me)ESi]) complex during chemical vapor deposition (CVD) experiments resulted in the formation of highly crystalline 2D layered WS2 thin films without the necessity for further purification steps. As-prepared films were subjected to atomic scale imaging and x-ray analysis to confirm the synthesis of phase-pure MX2 materials. Dianionic, tridentate chelating pincer type XN2-ligands (X= S, Se) have thus opened up a new field of precursor engineering and allow an efficient approach towards the synthesis of scalable van der Waals heterostructured materials such as 2D transition metal dichalcogenides that are expected to play an important role for future energy applications.
Developing cost-effective high-performance catalysts for the hydrogen evolution reaction (HER) stands as a key issue for the utilization of hydrogen as a major energy carrier. While Pt may provide the best HER catalysis performance, it is too expensive and rare to be useful for massive production of hydrogen.

Here I will show our work on engineering two-dimensional transition metal chalcogenide materials to have even better HER catalysis performance than Pt. This includes the discovery of new fundamental understanding on the HER catalysis and optimization of numerous aspects of the catalysts. We rationally design the composition and structure as well as the materials following the guidance of the new understanding, and eventually develop HER catalysts with better than that of Pt.

**EP03.14.59**
Tailoring Material Properties of Nanostructured WS\textsubscript{2} During Plasma-Enhanced Atomic Layer Deposition for Enhanced Electrochemical Performance
Shashank Balasubramaniam\textsuperscript{1}, Longfei Wu\textsuperscript{2}, Vincent Vandalon\textsuperscript{1}, Marcel Verheijen\textsuperscript{1,3}, Wilhelmus (Erwin) Kessels\textsuperscript{1}, Jan Philipp Hofmann\textsuperscript{1} and Ageeth A. Bol\textsuperscript{1}; \textsuperscript{1}Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; \textsuperscript{2}Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; \textsuperscript{3}Phillips Innovation Laboratories, Eindhoven, Netherlands.

Non-noble metal catalysts such as transition metal dichalcogenides (TMDs) are being studied as alternatives to Pt for sustainable production of \textit{H}_2 through the electrochemical hydrogen evolution reaction (HER). Layered TMDs like WS\textsubscript{2} are promising candidates for HER catalysts when engineered into nanostructures with exposed reactive edge sites. In this work, we demonstrate a novel and highly reproducible approach based on plasma-enhanced atomic layer deposition (PEALD) to maximize the density of such reactive edge sites.

PEALD is a cyclic deposition technique based on sequential use of self-limiting precursor and plasma-activated co-reactant steps. Controlling the various parameters during the plasma exposure step of PEALD allows tailoring of material properties (morphology, composition etc.) which can significantly influence the HER performance. Sub-nanometer thickness control and low processing temperatures are some of the other key merits of PEALD.

In our work, two types of nanostructured WS\textsubscript{2} with distinct material properties were synthesized at a low temperature of 300 °C by using two different plasmas as co-reactant during PEALD. Transmission electron microscopy (TEM) studies revealed that the application of a H\textsubscript{2}S+Ar plasma resulted in the growth of WS\textsubscript{2} ‘nanosheets’ while the addition of H\textsubscript{2} to the plasma i.e. H\textsubscript{2}S+H\textsubscript{2} resulted in the growth of WS\textsubscript{2} ‘fins’, for the same tungsten precursor. The WS\textsubscript{2} nanosheets comprised of closely packed sheets with their edges predominantly terminating on the top surface, while the WS\textsubscript{2} fins comprised of high surface area open structures that tapered out on the top surface. Rutherford backscattering spectroscopy (RBS) studies indicated excess S content for the WS\textsubscript{2} nanosheets with a S:W ratio of 2.2, while a S deficiency was observed for the WS\textsubscript{2} fins with a S:W ratio of 1.9. Moreover, in line with TEM studies, X-ray diffraction (XRD) studies showed differences in preferential orientation of the crystals for WS\textsubscript{2} nanosheets and WS\textsubscript{2} fins.

The HER performance of WS\textsubscript{2} nanosheets was significantly better than of WS\textsubscript{2} fins when comparing the overpotential required to reach a current density of 10 mA/cm\textsuperscript{2}. A relatively lower overpotential of ~390 mV was sufficient for the nanosheets while a significantly higher overpotential of ~460 mV was required for the fins. In line with the HER results, copper underpotential depositions on the respective nanostructures revealed a higher number (3x) of reactive edge sites for the WS\textsubscript{2} nanosheets when compared with the WS\textsubscript{2} fins. To further enhance the HER performance, the catalytically superior WS\textsubscript{2} nanosheets were grown on top of the high surface-area WS\textsubscript{2} fins. This WS\textsubscript{2} layered stack (nanosheets on fins) showcased the best HER performance in our work (overpotential of ~365 mV). To summarize, we demonstrate how PEALD can be used as a new approach to nanoeengineer and enhance the HER performance of WS\textsubscript{2} by maximizing the density of reactive edge sites at low processing temperature (300 °C).

**EP03.14.60**
High-Throughput Identification and Characterization of Two-Dimensional Materials Using Density Functional Theory
Karnal Choudhary; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

We introduce a simple criterion to identify two-dimensional (2D) materials based on the comparison between experimental lattice constants and lattice constants mainly obtained from Materials-Project (MP) density functional theory (DFT) calculation repository. Specifically, if the relative difference between the two lattice constants for a specific material is greater than or equal to 5%, we predict them to be good candidates for 2D materials. We have predicted at least 1356 such 2D materials. In addition to structural and energetics, we compute electronic bandstructures with/without spin-orbit coupling, optoelectronic properties, dimension dependent elastic properties, topological invariant properties, thermolectric and phonon properties. The data is publicly available at the website http://www.ctems.nist.gov/~knc6/JVASP.html.

**EP03.14.61**
Revealing Strain-Induced Effects in Ultrathin Heterostructures at the Nanoscale
Ghazi Sarwat Syed and Harish Bhaskaran; University of Oxford, Oxfordshire, United Kingdom.

Atomic thick two-dimensional materials are being increasingly studied, particularly for flexible and wearable technologies because of their inherent thickness and flexibility. One aspect where our understanding is still limited is on the effect of mechanical strain, not on individual sheets of materials, but when stacked together as heterostructures in devices. In this talk, I will demonstrate the use of Kelvin probe microscopy in capturing the influence of uniaxial tensile strain on the band-structures of graphene and WS\textsubscript{2} (mono- and multilayered) based heterostructures at high resolution: a major advance in strain characterization tools through enabling a single-shot capture of strain defined changes in a heterogeneous system at the nanoscale, overcoming the limitations (materials, resolution, and substrate effects) of existing techniques such as optical spectroscopy. I will show that the strain-enhanced charge transfer with the substrate plays a dominant role, causing the heterostructures to behave differently from two-dimensional materials in their isolated forms.

**EP03.14.62**
Spectroscopic Appearance of Topological Nature in Two Weyl Semimetals
Chun-Liang Lin\textsuperscript{1}, Ryuichi Arafune\textsuperscript{1}, Emi Minamitani\textsuperscript{1}, Maki Kawai\textsuperscript{1} and Noriaki Takagi\textsuperscript{2}; \textsuperscript{1}Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan; \textsuperscript{2}MANA, National Institute for Materials Science, Tsukuba, Japan; \textsuperscript{1}Department of Materials Engineering, The University of Tokyo, Tokyo, Japan; \textsuperscript{2}Institute for Molecular Science, Okazaki, Japan; \textsuperscript{1}Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan.

Topology in abstract mathematics has revolutionized our conventional understanding of solid state physics, resulting in the emergence of exotic quantum phases such as topological insulators (TIs). Recently the realization of the Weyl semimetals (WSMs) leads us to uncover the topological properties of materials beyond TIs. WSMs have gathered a deal of great attention because the quasiparticles in WSMs behave as Weyl fermions, massless chiral fermions long sought in particle physics. WSMs are classified into two types, Type I and II, according to the topology of the Weyl point, where the electron and hole pockets touch each other. In our experiment, the electronic structures of two transition metal dichalcogenides (TMD) type-II WSMs were studied
by quasiparticle interference with scanning tunneling microscopy (STM). The results have shown the evidence that both Td phase Tungsten Ditelluride (WTe2) and Molybdenum Ditelluride (MoTe2) are type-II WSM, agreeing with the prior theoretical predictions. Also, the difference in the topological nature (i.e. the positions of the Weyl points and the Fermi arc surface states) between two type-II Weyl semimetals is clearly revealed.  

1) C.-L. Lin et al. ACS Nano 11 11459 (2017)  

EP03.14.63
Preparation of Oxygen-Enriched Silicon-Oxy-Carboide/Carbon (O-SiOxCy/C) Lamellas via Carbothermal Conversion of 2D Siloxene Sheets and Their Use as a High-Performance Electrode for Supercapacitors Parthiban Pazhamalai, Karthikeyan Krishnamoorthy, Surjit Sahoo, Vimal Kumar Marippan and Sang-Jae Kim; Nano Materials and System Lab., Department of Mechatronics Engineering, Jeju National University, Jeju, Korea (the Republic of).

The development of silicon (Si) based electrode materials for supercapacitors (SCs) are rapidly increasing in recent years due to ease of tailoring the energy/power metrics of the SCs via controlling the nanostructures and their composition. Herein, we have demonstrated a novel carbothermal reaction route for the preparation of oxygen-enriched silicon-oxy-carboide/carbon (O-SiOxCy/C) lamellas (using 2D siloxene sheets and alginate as Si-O and C source). Physico-chemical characterizations such as X-ray photoelectron spectroscopy, Fourier-transformed infra-red spectroscopy, and laser Raman analysis revealed the formation of O-SiOxCy/C powders via carbothermal reaction. The high-resolution transmission electron micrographs and elemental mapping analysis revealed the formation of lamella-like structures with homogenously distributed of Si, O and C atoms in the O-SiOxCy/C lamellas. The fabricated SiOxCy/C-based symmetric supercapacitors (SSCs) using 1 M TEABF4 electrolyte operates over a wide potential window (3.0 V), delivered a high specific device capacitance (16.71 F g−1), and holds high energy density (20.89 Wh Kg−1), high power density (15,000 W Kg−1), low-equivalent series resistance (compared to other O-SiOxCy/C based SSCs) with excellent cyclic stability and superior rate capability. Further the experimental results demonstrating a novel preparation method involving the carbothermal transformation of 2D siloxene sheets into O-SiOxCy/C lamella and their excellent supercapacitive properties which will create new-horizons on the development of next-generation supercapacitor devices.

ACKNOWLEDGMENTS: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2016R1A2B2013831 and 2018R1A4A1025998).

EP03.14.64
Resonant Bonding Driven Giant Phonon Anharmonicity and Low Thermal Conductivity of Phosphorene Guangzhao Qin and Ming Hu; University of South Carolina, COLUMBIA, South Carolina, United States.

Two-dimensional (2D) phosphorene, which possesses fascinating physical and chemical properties distinctively different from other 2D materials, calls for fundamental understanding of thermal transport properties for its rapidly growing applications in nano-/opto-electronics and thermoelectrics. However, even the basic phonon property, for example, the exact value of the lattice thermal conductivity (κ) of phosphorene reported in literature, can differ unacceptably by one order of magnitude. More importantly, the fundamental physics underlying its unique properties such as strong phonon anharmonicity and unusual anisotropy remains largely unknown. In this paper, based on the analysis of electronic structure and lattice dynamics from first-principles, we report that the giant phonon anharmonicity in phosphorene is associated with the soft transverse optical (TO) phonon modes and arises from the long-ranged interactions driven by the orbital gated resonant bonding. We also provide a microscopic picture connecting the anisotropic and low κ of phosphorene to the giant directional phonon anharmonicity and long-ranged interactions, which are further traced back to the asymmetric resonant orbital occupations of electrons and characteristics of the hing-like structure. The unambiguously low κ of phosphorene obtained consistently by three independent ab initio methods confirms the phonon anharmonicity to the large extent and is expected to end the confusing huge deviations in previous studies. This work further pinpoints the necessity of including van der Waals interactions to accurately describe the interatomic interactions in phosphorene. To the best of our knowledge, it is for the first time proposed in 2D material that resonant bonding leads to low thermal conductivity, despite that it was originally found in 3D thermoelectric and phase change materials. Our study offers new insights into phonon transport from the view of orbital states, which would be of great significance to the design of emerging phosphorene based nano-devices.

EP03.14.65
Anomalously Temperature-Dependent Thermal Conductivity of Monolayer GaN with Large Deviations from the Traditional 1/T Law Guangzhao Qin and Ming Hu; University of South Carolina, COLUMBIA, South Carolina, United States.

Efficient heat dissipation, which is featured by high thermal conductivity, is one of the crucial issues for the reliability and stability of nanodevices. However, due to the generally fast 1/T decrease of thermal conductivity with temperature increase, the efficiency of heat dissipation quickly drops down at an elevated temperature caused by the increase of work load in electronic devices. To this end, pursuing semiconductor materials that possess large thermal conductivity at high temperature, i.e., slower decrease of thermal conductivity with temperature increase than the traditional 1/T relation, is extremely important to the development of disruptive nanoelectronics. Recently, monolayer gallium nitride (GaN) with a planar honeycomb structure emerges as a promising new two-dimensional material with great potential for applications in nano- and optoelectronics. Here, we report that, despite the commonly established 1/T relation of thermal conductivity in plenty of materials, monolayer GaN exhibits anomalous behavior that the thermal conductivity almost decreases linearly over a wide temperature range above 300 K, deviating largely from the traditional κ ∼ 1/T law. The thermal conductivity at high temperature is much larger than the expected thermal conductivity that follows the general κ ∼ 1/T trend, which would be beneficial for applications of monolayer GaN in nano- and optoelectronics in terms of efficient heat dissipation. We perform detailed analysis on the mechanisms underlying the anomalously temperature-dependent thermal conductivity of monolayer GaN in the framework of Boltzmann transport theory and further get insight from the view of electronic structure. Beyond that, we also propose two required conditions for materials that would exhibit similar anomalous temperature dependence of thermal conductivity: large difference in atom mass (huge phonon band gap) and electronegativity (LO-TO splitting due to strong polarization of bond). Our study offers fundamental understanding of phonon transport in monolayer GaN, and the insight gained from this study is of great significance for the design and search of materials superior for applications in nano- and optoelectronics in terms of high-performance thermal management.

EP03.14.66
Strain Engineering Valleytronic Materials to Preserve State Coherence Nina Leclere1,2, Jonah Haber1,2 and Jeffrey B. Neaton1,3; 1Cornell University, Ithaca, New York, United States; 2Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Department of Physics, University of California, Berkeley, California, United States.

Recent developments in valleytronic devices demonstrate that exceptional 2D transition metal dichalcogenides (TMDs) possess degenerate energy levels at
Density functional theory (DFT) is employed to compute the electronic structure of the 2D MoS2 material as the system evolves with strain. In synthesis over large-areas, as well as its electronic tunability, which is possible through intercalation of atomic species such as H, O, F, and Li to the widespread adoption of these materials in opto-electronic, catalytic, and device studies. However, methods offering explicit control over the Natalia Drichko, David H. Gracias, Mingwei Chen and Thomas J. Kempa; Johns Hopkins University, Baltimore, Maryland, United States.

The emergence of 2D materials has led to increased attention on correlating the structural, optical, and optoelectronic properties of atomically thin transition metal chalcogenides like MoS2. We demonstrate the tunability of the photoluminescence (PL) properties of bulk MoS2 via implantation of Nb ions. Raman spectroscopy is used to confirm the p-type doping. The PL intensity of MoS2 is drastically enhanced by the adsorption of p-type dopants. X-ray photoelectron spectroscopy (XPS) is used to study the change of MoS2 structure after annealing in oxygen. We also demonstrate a stronger PL enhancement through defect engineering and oxygen bonding realized by oxygen anneal. Our results provide a new route for modulating the optical properties of two-dimensional semiconductors. The strong and stable PL from defects sites of MoS2 may have promising applications in optoelectronic devices.

SESSION EP03.15: Novel Heterostructure Devices—Fabrication and Properties
Session Chairs: Feng Miao and Xiaofeng Qian
Friday Morning, November 30, 2018 Hynes, Level 2, Room 210

8:00 AM EP03.15.01
Low Dimensional Material Hybrid Structure for Optoelectronics Application Hyun-Soo Ra, A-Young Lee, Dohyun Kwak, Min-Hye Jeong and Jong-Soo Lee; Energy Science and Engineering, DGIST, Dalsunggun, Korea (the Republic of).

The low dimensional materials (0D-2D) are candidate to optoelectronics application with high performance. It has unique functionality, such as mechanically flexible characteristic and transparency, for new paradigm functional device research. Among the low dimensional materials, TMDCs family and black phosphorus among 2D materials have advantages of best charge mobility and good absorption properties, also. Recently, 2D stack n-p heterojunction and lateral p-n homo-junction for photovoltaic device application was emerging research field. Additionally, 0D materials have that of best luminescence and absorption properties due to especially high volume to surface ratio, but poor electrical properties due to the long organic ligand chain to prevent quantum confinement effect from coupling with around quantum dots.

Here, we introduce each 2D-0D materials hybrid structure with ligand engineering and device with mix advantage of each low dimensional materials. Through phototransistor measurement, we demonstrated overwhelm responsivity (A/W) of >10^5 A/W and Detectivity (J) of >10^10. Based on the results, we proved mechanism of charge transfer and photo-doping (n-type and p-type) effect in hybrid system. Also, we introduce structure of 2D-2D p-n hetero-junction and 2D p-n lateral homo-junction for photovoltaic application. In the case of 2D-2D heterojunction, the solar cell characteristic is dominated. In the other case, diode-like phototransistor as the new paradigm device is introduced.

8:15 AM EP03.15.02
Dimension and Morphology Control in Transition Metal Dichalcogenide Crystals Through Prescribed Substrate Interactions Tomojit Chowdhury, Natalia Drichko, David H. Gracias, Mingwei Chen and Thomas J. Kempa; Johns Hopkins University, Baltimore, Maryland, United States.

Chemical vapor transport is an extensively used method for synthesis of bulk and 2D transition metal dichalcogenides (TMD) and it has fueled the widespread adoption of these materials in opto-electronic, catalytic, and device studies. However, methods offering explicit control over the dimensionality, morphology, and crystalline phase of TMDs are rare. In this work, we demonstrate that prescribed substrate interactions can control the dimensionality and morphology of MoS2 crystals from the nano- to micron-scale. Si substrates bearing phosphide moieties were prepared in a high vacuum chemical vapor deposition reactor. MoS2 synthesis was carried out on these substrates using standard protocols. At low surface phosphide concentrations, 2D MoS2 crystals exhibit periodic serrated edges. At high surface phosphide concentrations, MoS2 crystals form high aspect ratio (~200 nm wide and 10 µm long) quasi-1D filaments. Detailed kinetic studies and surface energy calculations indicate that the chemical nature of the underlying Si–phosphide substrate surface is instrumental in transforming growth of MoS2 from conventional 2D triangular to quasi-1D crystal morphologies. A significant blue shift of the photoluminescence of these quasi-1D TMDs is observed at room temperature and ambient pressure. These new materials underscore the importance of rational synthesis in elaborating materials with unique and prescribed properties.

8:30 AM EP03.15.03
Two-Dimensional Monoelemental Materials via Confinement Hetroepitaxy Natalie Briggs1, 2, Brian M. Bersh1, Ana De La Fuente Duran1, 2, Yuanxi Wang2, Angping Li2, Carolina Navarro2 and Joshua Robinson1, 2; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2D Crystal Consortium Materials Innovation Platform, University Park, Pennsylvania, United States; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Epitaxial graphene grown on silicon carbide has played a key role in the field of 2-dimensional materials research to date, owing in part to its relative ease of synthesis over large-areas, as well as its electronic tunability, which is possible through intercalation of atomic species such as H, O, F, and Li to the
epitaxial graphene (EG)/silicon carbide interface. But while the primary focus of EG intercalation studies has historically been the controlled doping of EG layers, resulting intercalant layers alone are also of great interest, due to potential for phenomena such as superconductivity in the ultra-thin, ordered, intercalant layers. Here we discuss the realization of atomically-thin materials in EG/SiC systems through an intercalation-based process termed confinement heteroepitaxy.

To realize graphene/intercalant/SiC heterostructures via confinement heteroepitaxy (CHet), synthesized EG layers are first plasma treated. Plasma treatments serve to increase defect density in the layers, which can promote the process of intercalation. Following this treatment, samples of plasma-treated EG/SiC are placed over elemental or compound precursors and heated in an argon atmosphere in a tube furnace from 600-1100°C. Cross-sectional transmission electron microscopy (STEM) allows for direct imaging of the graphene/intercalant/SiC heterostructures. Additionally, x-ray photoelectron spectroscopy indicates a change in the carbon bonding environment of the EG/SiC following the CHet, suggesting the presence of intercalant layers at the EG/SiC interface.

To-date, gallium, indium, and tin have each been realized at the EG/SiC interface via CHet, where STEM shows predominant formation tri-layer gallium, bi-layer indium, and mono- to bi-layer tin between SiC and EG. The observed thicknesses are consistent first principles calculations of structural energetics performed for a range of chemical potentials. First-principles calculations also indicate covalency between SiC and the first intercalant layer of Ga, and decreasing covalency between each subsequent Ga layers. Further investigation of graphene/Ga/SiC structures has shown a superconducting gap at roughly 2.9K via scanning tunneling microscopy. Transport measurements of the structures have suggested superconducting gaps at higher temperatures, which could be due to differing phases or chemistries of the Ga intercalant. Ongoing work aims to investigate possible superconductivity in intercalated In and Sn, as well as the impact of plasma chemistry and intercalation temperature on superconducting Tc.

8:45 AM *EP03.15.04
2D Materials—Scalable Approaches and Novel Devices Towards Step Changes in the Aerospace Industry Jesse Tice; NG NEXT, Northrop Grumman, Redondo Beach, California, United States.

NG Next, the Basic Research center of Northrop Grumman, located in Manhattan Beach, CA has had steady focus on 2D materials synthesis, stacked heterostructure properties, and device-scale first demonstrations. As an early adopter of new nanotechnologies, the aerospace industry has seen rapid uptake of in manufacturing and production on both CNTs and graphene. Here, we look to what is beyond graphene and can potentially offer discriminating heterostructure properties, and device-scale first demonstrations. As an early adopter of new nanotechnologies, the aerospace industry has seen rapid uptake of in manufacturing and production on both CNTs and graphene. Here, we look to what is beyond graphene and can potentially offer discriminating technologies, or step changes in the industry. An overview of the center’s 2D material activities internally and collaboratively will be discussed.

Several topics will be covered in this presentation including wafer-scale synthesis of black arsenic-phosphorus (b-AsP) alloys via MBE that offer platforms for future optoelectronic research [1], our collaborative work on atomically thin memristive devices[2-3], and recent progress on magneto-optical characterization.

[1] In Review

9:15 AM EP03.15.05
Controlled Synthesis of In-Plane Few-Layer 2H-1T′ MoTe2 Junctions for High-Performance 2D Electronics Youngdong Yoo1, Zachary P. DeGregorio1, Yang Su1, Steven J. Koester2 and James E. Johns3; 1Ajou University, Suwon, Korea (the Republic of), 2University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have attracted much attention due to their emergent electronic and optical properties. Formation of in-plane junctions of the 2D TMDs could build in new functionalities that are practically useful, leading to new applications such as high-performance electronics and flexible optoelectronics. Here we report on the fabrication of in-plane 2H-1T′ MoTe2 junctions by flux-controlled phase-engineering of few-layer MoTe2 from Mo nanoislands. By changing Te atomic flux, we control the phase of few-layer MoTe2. Few-layer 2H MoTe2 is obtained with high Te flux, while few-layer 1T′ MoTe2 is formed with low Te flux. With medium flux, we synthesize few-layer in-plane 2H-1T′ MoTe2 junctions. As-synthesized MoTe2 is characterized by Raman spectroscopy and X-ray photoelectron spectroscopy. Kelvin probe force microscopy and Raman mapping confirm that in-plane 2H-1T′ MoTe2 junctions possess abrupt interfaces between 2H and 1T′ MoTe2 domains. In addition, we fabricate few-layer 2H-1T′ MoTe2 patterns using the phase-selective synthetic strategy. Our flux-controlled phase engineering method could be utilized for the large-scale controlled fabrication of 2D metal-semiconductor junctions for high-performance 2D electronics.

9:30 AM BREAK

10:00 AM *EP03.15.06
Atomic Reconstruction at van der Waals Interface in Twisted 2D Materials Philip Kim; Harvard University, Cambridge, Massachusetts, United States.

Control of the interlayer twist in the vdW interface has been widely used to engineer an artificial 2-dimensional (2D) electronic systems by the formation of a moiré superlattice. Many exotic physical phenomena occur associated with the incommensurability of the moiré superstructures; the fractal energy spectrum of Hofstadter butterfly and recently discovered Mott insulating and unconventional superconducting behavior of the ‘magic’ twist angle bilayer graphene have demonstrated the wealth of the nontrivial topology of electronic band structures. However, the atomic scale microstructures and electronic structures of vdW interfaces have been understood in the frame of rigid rotational moiré structures without atomic scale relaxation. In this presentation, we will discuss the engineered atomic scale reconstruction at twisted vdW interface. We find that the vdW interaction energy that favors interlayer commensurability competes against the intralayer elastic lattice distortion to form a quasi-periodic domain structure, inducing profound changes in electronic structure. Particularly, we show quantitative analysis of the engineered atomic-scale reconstruction completely controlled by the twist angle between two graphene layers and anomalous electron transport occurring in the network of topologically protected propagation modes along the domain boundaries. Interfaces between vdW materials are a crucial material platform for realization of novel quantum electronics. Our discoveries of atomic scale reconstruction at vdW interfaces will provide a new route to engineer the 2D materials for exceptional functionalities.

10:30 AM EP03.15.07

Transition metal dichalcogenides (TMDs) have attracted immense attention in recent times owing to their unique structure and layer dependent properties and have shown great promises in the field of electronics, optoelectronics and energy conversion.1-2 Heterostructures of TMDs have emerged as a
fascinating platform to explore both fundamental and device applications. However, controlled synthesis of layered 2D heterostructures still remains a challenge. Here we report a novel approach towards the synthesis of WO3/WSe2 heterostructures through electrophoretic deposition (EPD) onto a conducting substrate. A large area uniform coating on to a conducting substrate can be obtained using EPD with minimal restriction on the shape and size of the substrate. We found that these heterostructures can provide electrocatalytic sites with superior electrochemical activity towards Hydrogen Evolution Reaction (HER). We attribute this exceptional catalytic activity to various parameters such as (i) higher electronic conductivity, (ii) higher proton diffusion coefficient of tungsten partial oxides, (iii) induced defects in the lattice during EPD and also to (iv) the hydrogen spill over mechanism exhibited by the hybrid catalyst. These factors synergistically contribute in achieving enhanced catalytic activity for HER. The deposited heterostructure offers a high exchange current density of 75.85 µA cm⁻², lower onset potential of 83 mV and very low Tafel slope of 47 mV decade⁻¹, which makes it a highly promising candidate for electrocatalytic HER.

References:

10:45 AM EP03.15.08
Synthesis of 2D Metal Carbides and Nitrides (MXenes) and Their Applications Babak Anasori, Kathleen A. Maleski, Patrick Urbankowski, Christine B. Hatter, Tyler Mathis, Kanit Hantanasirisakul, Arianna S. Levitt and Yury Gogotsi; Department of MSE and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States.

MXenes are a large family of 2D transition metal carbides and nitrides, such as Ti₃C₂, Ti₃C₂Tₓ, NbC, TaC, Mo₂C, Mo₃Ticl₂, and W₁₃C. A MXene single flake can be composed of 2, 3, or 4 atomic layers, each layer built of a transition metal interleaved with layers of carbon or nitrogen, with a total flake thickness of ~1 nm. Additionally, significant control over physical and electrochemical properties can be achieved with the possibility of having more than two transition metals in the in-plane and out-of-plane ordered forms. Because of the wet etching synthesis methods, all of the MXenes reported to date have surface functionalities, such as hydroxyl, fluorine, and oxygen, which add hydrophilicity to their surfaces. Free-standing films of MXenes, made from their colloidal solutions, have a high metallic conductivity (e.g., 10,000 S/cm for Ti₃C₂ films), enabling their use in a diverse set of applications. In this talk, an overview of conditions used to synthesize MXenes from their bulk precursors and delaminate to single-layer flakes will be presented. In addition, MXene flake assembly into transparent as well as thick films, fibers, composites, and devices and their energy storage, sensor, and catalysis applications will be discussed. At the end, a general summary and outlook for the future research on 2D MXenes will also be presented.

11:15 AM EP03.15.09
Controlled Electron Beam Induced Doping in van der Waals Heterostructures Wu Shi¹,², Salman Kahrn³, Lili Jiang³, Sheng-yu Wang⁴, Hsin-Zon Tsai¹, Dillon Wong⁴,⁵, Takashi Taniguchi⁶, Kenji Watanabe⁶, Feng Wang⁴,², Michael Crommie¹,² and Alex Zettl¹,²; ¹Lawrence Berkeley National Laboratory, Berkeley, California, United States; ©Department of Physics, UC Berkeley, Berkeley, California, United States; ³Princeton University, Princeton, New Jersey, United States; ²National Institute for Materials Science, Tsukuba, Japan.

Spatial control of charge density in electronic devices is an essential tool to explore exotic physics and enable new device applications. Traditionally, this has been achieved using conventional lithographic techniques that define gated regions or the use of molecular self-assembles on surfaces to spatially modulate charge transfer. These techniques suffer problems such as limited spatial re-writability and lack of feasible topological designs due to technical limitations of the developing process. Recent work has demonstrated an alternative way to induce nanoscale rewritable doping patterns in vdW heterostructures without introducing impurities by optical illumination or applying an STM tip voltage pulse. In this work we further develop this simple but efficient local patterning technique by utilizing electron beam induced doping. With this new doping scheme, we realize precise tunability of carrier density as well as patterning of doping profiles with nanoscale spatial resolution while preserving the high quality of the vdW heterostructure device. Our results demonstrate distinct advantages over conventional local gates, making it an ideal approach to study a variety of superlattice physics in van der Waals heterostructures and to create on-demand circuits for device applications.

11:30 AM EP03.15.10
Low-Temperature Epitaxy of SnS on MoS₂ for 2D-2D p-n Junctions Jack N. Olding, Alex Henning, Michael J. Moody, Jason Dong, Emily Weiss and Lincoln J. Lauhon; Northwestern University, Evanston, Illinois, United States.

The stability of two-dimensional (2D) materials down to the monolayer limit, and the weak van der Waals bonding between monolayers, enables fabrication of heterostructures beyond the constraints of conventional heteroepitaxy. Though many novel heterostructures have been created by mechanical exfoliation and stacking, the ability to directly grow 2D chalcogenide heterostructures over large areas would create new opportunities for large-scale integration. Here, p-type tin sulfide (SnS) is grown on n-type molybdenum disulfide (MoS₂) in an atomic layer deposition (ALD) reactor at low temperatures (180 °C) to form vertical p-n 2D-2D heterojunctions. X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) establish an axiotaxial relationship between the two crystals, with two preferred orientations rotated about the [001] axis normal to the (001) planes. The influence of precursor dose and purge times on lateral and vertical growth rates suggests that the growth is not strictly self-limiting, and is best described as pulsed chemical vapor deposition (CVD). Substrate preparations including annealing and exposure to a plasma indicate that rapid and reproducible nucleation is promoted by defects while preserving axiotaxial alignment. Kelvin probe force microscopy was used to establish a built-in potential as high as 0.9 eV, which is significantly larger than those previously measured in transition metal dichalcogenide heterojunctions (~0.2 eV). The photoresponse of heterojunctions was probed by photoconductive atomic force microscopy to further explore the potential for photodetection and photovoltic applications. This demonstration of direct growth at low temperatures is greatly enabling for fabrication (e.g. selected area growth of heterostructures using patterned resists) and characterization (e.g. fundamental studies of thickness dependent photophysics and device performance).

11:45 AM EP03.15.11

Two-dimensional (2D) materials have attracted tremendous attention since the advance of graphene. The field now has extended far beyond graphene with new exfoliation of the 2D family such as h-BN, transition metal dichalcogenides (TMDs), black phosphorus, etc. Assemblies of 2D materials into van der Waals heterostructures further exhibit many interesting properties in both fundamental research and practical applications. Herein, we report monolayer metal-organic frameworks (MOFs) as new 2D building blocks that can be assembled into van der Waals heterostructures with other 2D materials such as TMDS while at the same time maintain the versatility of MOFs. We develop a synthetic route based on liquid-liquid interface chemistry to produce several types of monolayer MOFs with high quality over an inch-scale. The growth mechanism has been characterized and studied through in situ optical measurements. The potentials of 2D MOFs are first demonstrated by generating van der Waals heterostructures with monolayer MoS₂ (ML-MoS₂) grown by metal-organic vapor deposition (MOVD). The resulting heterostructures can be laser patterned to selectively remove the 2D MOFs. Moreover, the 2D
MOFs and TMDs are assembled into vertical superlattices with controlled d-spacing and composition via a layer-by-layer vacuum stacking technique. The employment of versatile monolayer MOFs enables the incorporation of functional molecular moieties into two-dimensional electronic circuits. As a proof-of-concept device, we successfully demonstrate a photo-switchable tunneling junction by attaching photo-responsive ligands onto MOF layers in a MOF/MoS₂ heterostructure. These materials show promising applications in multifunctional 2D electronic devices.

The controlled growth of the conducting and semiconducting two-dimensional (2D) materials beyond graphene, represented by the transition metal dichalcogenides (TMDs), as well as the topological insulator Bi₂Se₃, is the necessary path towards the realization of their application prospects. The control of the thickness, in other word, the layer number of the 2D materials is one of the most important criteria, as their properties vary significantly with respect to the layer numbers. Ideally, the scheme of van der Waals epitaxy determines that the bottom-up synthesis of the 2D compounds should follow a layer-by-layer scenario, as strain does not accumulate in the direction normal to the layers, thanks to the van der Waals gap between the layers. However, in reality, layer-by-layer growth is rarely completely achieved. Multilayer growth still dominates the experimental observation in the laboratories. In addition, an island morphology is often observed, which strongly indicates a "wrong" stacking sequence in contrast to the more stable structure of mineral crystals. In this work, we developed multiscale simulation tools to investigate the morphology of island growth driven by combinations of screw dislocations, in order to shed light on the identification of the cause of such multilayer growth. With the phase-field model, we are able to reproduce all the spiral growth patterns previously reported in the experimental literature, and identify the morphology of the underneath driving defects, which cannot be easily revealed by experiments. More importantly, we discovered a type of defect that caused uncontrolled multilayer growth via a pair of screw dislocations, but the resulting domain showed no spiral lines, with the aforementioned "wrong" stacking sequence. This type of defect consists of a pair of opposite screw dislocations, which constitute a short step edge. The screw dislocations can be embedded in the substrate. They can also be generated within the film during epitaxy. The in-film step edges are generated from a linear accumulation of metal vacancies, via a lift-up mechanism due to the imbalanced growth rate of the adjacent edges. This mechanism was experimentally confirmed by us in the molecular beam epitaxy of Bi₂Se₃. In an atomistic perspective, we used first-principles calculation to show why this mechanism is likely to happen in the layered chalcogenides. We show that the lift-up mechanism is initiated by the dimerization of chalcogen elements, therefore it is expected to be transferable to other layered chalcogenides beyond the TMDs. Based on the mechanistic analysis, we are able to provide guidance for a better layer number control: targeted to avoid the growth scheme, experimental parameters should be tuned to prevent the generation of the initial defects. This work was supported by ASCENT, one of six centers in JUMP, a Semiconductor Research Corporation program sponsored by DARPA.

SESSION EP03.16: Computational Design and Modelling of 2D Materials

1:30 PM EP03.16.01 Dislocation Driven Spiral and Non-Spiral Growth of the Layered Chalcogenides—Morphology, Mechanism and Mitigation Yifan Nie¹, Adam Barton¹, Rafik Addou¹, Sarah Eichfeld², Joshua Robinson², Luigi Colombo³, Robert Wallace¹, Chris Hinkle¹ and Kyeongjae Cho¹; ¹The University of Texas at Dallas, Richardson, Texas, United States; ²The Pennsylvania State University, University Park, Pennsylvania, United States; ³Texas Instruments, Dallas, Texas, United States; ⁴Kookmin University, Seoul, Korea (the Republic of).

1:45 PM EP03.16.02 Data-Driven Discovery of New Two- and One-Dimensional Materials and Heterostructures Gowoon Cheon¹, Karel-Alexander N. Duerloo², Austin Sendke³, Chase Porter³, Yuan Chen³ and Evan J. Reed³; ¹Stanford University, Stanford, California, United States; ²Boston Consulting Group, Amsterdam, Netherlands.

2:00 PM EP03.16.03 Exploring and Understanding Quantum Nonlinear Optical Effect in 2D Materials Hua Wang and Xiaofeng Qian; Texas A&M University, College Station, Texas, United States.

Recent experiments demonstrated that 2D materials not only exhibit strong linear excitonic behavior upon photoexcitation, but also have strong nonlinear optical (NLO) responses. The latter could be useful for many technologically important applications. Here we will present our first-principles theoretical development and understandings of giant NLO responses in a number of 2D materials including group IV monochalcogenides and transition metal dichalcogenides, and demonstrate that 2D materials provide perfect solid-state platform for exploring nonlinear nanooptics. We will also present very recent work on other 2D NLO properties and discuss the relationship between the NLO responses and topological nature. Our present findings open up new avenues for ultrathin nonlinear optoelectronics. References: 1) Giant Optical Second Harmonic Generation in Two-Dimensional Multiferroics. Nano Letters 17, 5027-5034 (2017). 2) Two-dimensional multiferroics in monolayer group IV monochalcogenides. 2D Materials 4, 015042 (2017). 3) Quantum Nonlinear Optical Responses in 2D Materials. to be submitted (2018).

2:15 PM EP03.16.04 Controlled Growth Mechanism of Bilayer TMD Homo- and Hetero-Structures—A Multiscale Simulation Approach Kamalika Ghatak and Dibakar Datta; New Jersey Institute of Technology, Newark, New Jersey, United States.

After the discovery of Graphene in 2004, the research based on possible findings of other 2D structures are at peak due to the absence of band gap in
Among the new generation 2D materials, TMDs are one of the rising stars due to its wide variety of electrical and mechanical properties in between the semiconductor and metal. Moreover, the bilayers of 2D materials are receiving more limelight due to its unique properties such as layer-dependent tunable optoelectronic and mechanical behavior. These bilayers are attached to each other by weak van der Waals force and the control over the experimental growth technique is required in order to synthesize desired stacked products. Among several existing growth techniques, epitaxial growth mechanism is the most preferred one due to its technological advantages such as reduction of defect density (e.g., tilt grain boundaries), consistency in the overall growth, final products with sharper interfaces. Computational analysis involving Density Functional Theory (DFT) and Molecular Dynamics (MD) simulation is necessary to gain deeper insight into the post-growth analysis. We, therefore, considered different bilayers such as, WS2-WS2, WS2-MoS2, MoS2-MoS2, and MoS2–Graphene and compared their properties (electronic and physical). We considered both the chalcogen and metal terminated edge as the initial TMD structure to grow and we have also considered the length effect and the orientation effect of the second layer towards the formation energy of the overall structure. We find that the growth temperature plays a crucial role in governing the growth mechanism. The difference of formation energies of different TMD leads to the reaction rate difference and the growth temperature of TMD layers. For example, we find that formation energies of MoS2 and WS2 are 2.48 and 2.70 eV respectively and hence growth temperature of the WS2 (~ 800-1050) are higher than MoS2 (~ 600-850). At the controlled growth temperature, for chalcogen termination, one-step growth mechanism is preferable where the second layer starts from the center (core) and grows outwards (edge). On the contrary, for the metal terminated edge, two-step growth is preferred where the second layer starts from the edge and grows inwards (core). Our results conclude that the evolution of various TMD homo/hetero-structures originates from the competition between the adsorption, desorption, and the diffusion of metal (Mo, W) and chalcogen (S, Se) atoms under various growth temperatures. Our computational work provides a more in-depth understanding and guidelines of design and fabrication of TMD heterostructures.

2:30 PM EP03.16.05
The Kinetics of Two-Dimensional Materials’ Growth Feng Ding1,2; 1Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2Center for Multidimensional Carbon Materials, Institute for Basic Science, Ulsan, Korea (the Republic of).

After the discovery of graphene, research of two-dimensional (2D) materials attracted great attention. Until now, there are hundreds of 2D materials have been discovered and predicted but only very few of them, such as graphene, h-BN and MoS2, could be synthesized in large area and high quality. To achieve the industrial synthesis of various 2D materials in large area and high quality, understanding the kinetics of their growth is of crucial importance. In compare with the 3D crystals, 2D materials own their unique properties, such as the ultra-high flexibility and the strong edge-substrate interaction. Our research team has used various theoretical approaches, such as ab initio calculation, molecular dynamic (MD) simulation, kinetic Monte Carlo (KMC) simulation and phase field theory (PFT) simulation, to explore the kinetics of 2D materials' growth. Our studies have revealed a few key characteristics of 2D materials growth: (i) the growth and etching of an edge of a 2D material is reversible and the rate of the growth or etching is determined by the structure of the edge and a one-dimensional (1D) nucleation process; (ii) The shape of a 2D materials during growth or etching is determined by its symmetry, the interaction with the substrate and can be precisely described by the kinetic Wulff construction; (iii) By considering the structures of various edges of a 2D materials, our theoretical calculation can precisely predict the environment dependent edge structure and the shape evolution during a 2D material’s growth and etching. Our theoretical study has revealed that the key element of synthesizing 2D materials in large area and high quality is the selection of proper substrate.

2:45 PM EP03.16.06
Kinetics of Structural Phase Changes in Two-Dimensional MoS2; Aditi Krishnapriyan1, Qian Yang1, Yao Zhou2, Ekin D. Cubuk2 and Evan J. Reed1; 1Stanford University, Cupertino, California, United States; 2Google Brain, Mountain View, California, United States.

Predictive capabilities for kinetic processes in materials are in their infancy, but kinetics are critical for a spectrum of energy applications ranging from phase change materials, catalysis, materials synthesis, and combustion. The structural phase transition between the metallic 1T or 1T' and semiconducting 2H structures in two-dimensional transition metal dichalcogenide materials is important to understand for synthesis and may provide exciting new opportunities for energy-efficient electronic and optical devices. However, very little is known about the mechanisms and kinetics of these phase changes or how to engineer the kinetics. We propose a novel electronic structure based method to determine the nucleation kinetics and timescales of this phase change. Furthermore, we discuss the curious fact that the interface energies between phases for this challenging problem are mathematically ill-defined. We also point to strategies on the engineering of kinetics in these phase change materials that take into account nucleation barriers and nucleation time.

3:00 PM BREAK

SESSION EP03.17: Infrared and Thermal Properties of 2D Materials
Session Chair: Rui He
Friday Afternoon, November 30, 2018
Hynes, Level 2, Room 210

3:30 PM EP03.17.01

Achieving ultra-low thermal conductivity in solid-state materials is a grand challenge in nanotechnology, with applications in thermoelectric energy conversion and phase change memory. While a large majority of the best thermal insulators have low densities, there is a need to engineer materials that have excellent heat insulation properties while still being dense and mechanically stable. Van der Waals (vdW) materials offer a unique opportunity to achieve this goal, as heat conduction in the cross-plane direction is impeded by weak phonon transmittance at the interfaces. To do this, it is important to first understand the various factors that govern thermal transport at 2D material interfaces. This includes examining the role of phonon mismatch, which determines how the thermal boundary resistance (TBR) at “mismatched” interfaces between different 2D layers compares to that at “matched” interfaces between similar 2D layers. Furthermore, it is crucial to investigate the impact of interlayer coupling on phonon transmission and TBR at vdW interfaces.

To address these questions, here we study thermal transport in multilayer graphene/MoS2 (G/M) heterostructures. These samples are assembled layer-by-layer starting from large-area synthesized monolayers of each material using a residue-free transfer process [1,2]. We measure the cross-plane thermal resistance across various stacks of these layers (for example, G, G/G, G/M/G, G/M/M/G, and so on, sandwiched between Al metal and SiO2) using time-domain thermoreflectance (TDTR), an ultrafast optical pump-probe technique. Using a novel scanning approach, we produce quantitative maps of thermal resistance, connecting local variations in TBR with the underlying 2D-layer stacking sequence. The measured stack thermal resistance increases from ~10
to ~100 m²KGW⁻¹ as the number of inserted 2D layers is increased from 0 (direct Al to SiO₂ contact) to 4 (G/M/M/G stack). Importantly, we find that the thermal resistance at mismatched G/M interfaces is significantly higher than the matched G/G and M/M interfaces, pointing towards the important role of phonon mode overlap. In addition, we show that the strength of interlayer coupling has a strong influence on the cross-plane thermal resistance, which we tune via high-temperature vacuum annealing and monitoring using photoluminescence and Raman spectroscopy. Overall, our results show that heterogeneous stacking of atomically-thin layers has the potential to create “synthetic” solids with effective thermal conductivities falling below ~0.1 Wm⁻¹K⁻¹, approaching some of the lowest measured to date for dense solids.


3:45 PM EP03.17.02
Layer-by-Layer Temperature Probing Across 2D van der Waals Heterostructures
Sam Vaziri¹, Eilam Yalon¹, Miguel Muñoz Rojo¹, Saurabh V. Suryavanshi¹, Connor McClellan¹, Connor S. Bailey¹, Alex J. Gabourse¹, Victoria Chen², Sanchit Deshmukh¹, Kirby K. Smith¹ and Eric Pop¹,²,³
¹Electrical Engineering, Stanford University, Stanford, California, United States; ²Material Science and Engineering, Stanford University, Stanford, California, United States; ³Precourt Institute for Energy, Stanford University, Stanford, California, United States.

Van der Waals (vdW) heterostructures obtained by stacking different two-dimensional (2D) materials are known to exhibit tunable electronic and photonic properties [1]. However, their thermal properties have been relatively unexplored, whether such vdW interfaces could be tuned for thermoelectric applications [2] or could pose heat dissipation bottlenecks for 2D electronics [3]. In this work, we investigate cross-plane heat transport in layered vdW heterostructures by probing the temperature of individual 2D monolayers. We combine Raman thermometry and scanning thermal microscopy (SThM) to achieve monolayer cross-plane and ~50 nm in-plane temperature measurement resolution. vdW heterostructures are fabricated with a novel transfer process, achieving polycrystalline-free interfaces. The heterostructures consist of monolayers of MoS₂ and/or WSe₂ with graphene (Gr) on top as a transparent heater, all on SiO₂ substrates. We heat the graphene top layer electrically and probe the temperature of each 2D material in the heterostructure by its unique Raman signal. By measuring the temperature of each layer in the vdW stack, we can extract the thermal boundary conductance (TBCs) of all interfaces. As a result, we report here for the first time the TBCs at 2D/2D monolayer interfaces including Gr/WSe₂, Gr/MoS₂ and MoS₂/WSe₂ with values of 5±3 MWm⁻²K⁻¹, 11±3 MWm⁻²K⁻¹ and 9±3 MWm⁻²K⁻¹, respectively. However, measured 2D/3D interfaces exhibit somewhat higher TBCs of 15±4 MWm⁻²K⁻¹, 22±4 MWm⁻²K⁻¹ and 27±5 MWm⁻²K⁻¹ for WSe₂/SiO₂, MoS₂/SiO₂, and Gr/SiO₂, respectively. These interfaces correspond to an equivalent Kapitza thermal resistance ranging from 30 nm of SiO₂ (Gr/WSe₂ interface, lowest) to 200 nm of SiO₂ (Gr/WSe₂ interface, highest). The measured interface TBC trends can be explained by Landauer’s formalism, as a product of phonon density states overlap (modes) and area-mass mismatch (transmission) of the two materials forming the interface. These results are essential for understanding and tuning heat dissipation in 2D materials and their applications. In addition, the material-specific Raman thermometry measurement provides unprecedented (i.e. single-layer) temperature resolution, in the atomic scale limit.


4:00 PM EP03.17.03
Stacking-Dependent Interlayer Phonon Modes in 3R- and 2H-MoS₂
Eui He¹, Jeremiah van Baren², Gaihua Ye¹, Zhipeng Ye¹, Pouyan Rezaie¹ and Chun Hung Lui¹,²
¹Texas Tech University, Lubbock, Texas, United States; ²University of California, Riverside, Riverside, California, United States.

MoS₂ exhibits several stacking orders (polymorphs) with considerably different properties. The common 2H stacking order displays non-centrosymmetric crystalline structure for odd layer numbers, but centrosymmetry for even layer numbers. In contrast, 3R-MoS₂ is non-centrosymmetric for all layer numbers, and thus retains those properties that require a lack of inversion symmetry, such as the valley-selective optical rules. There is strong incentive to fully understand 2D materials of different stacking orders, as it may open the door to novel material and device applications. We study the interlayer phonon modes of the 3R- and 2H-MoS₂ polypeptides by ultralow-frequency Raman spectroscopy. In the spectral range of 5-60 cm⁻¹, we observe the Raman features of interlayer phonon modes, including the interlayer shear (S) and breathing (B) modes, which correspond to the lateral and vertical displacement of the atomic layers, respectively. The most intensive B modes have similar layer-thickness dependence for both 3R- and 2H-MoS₂. However, the most intensive S modes display opposite layer-dependent behavior for the two polytypes. Our experimental results are consistent with the predictions based on the linear chain model. In particular, the highest-intensity B mode corresponds to the lowest-band vibration for both polytypes, but the highest-intensity S mode corresponds to the lowest- and highest-frequency branches for 3R and 2H polytypes, respectively. Our results reveal a close relationship between the crystal structure and the Raman activity of interlayer modes in 2D materials, and provide insight into the materials’ optical and vibrational properties.

4:15 PM DISCUSSION TIME

4:30 PM EP03.17.05
Artificially Stacked van der Waals Heterostructures for Enhancing and Broadening Resonant Second Harmonic Generation
Chinh Tam Le¹, Yong Soo Kim¹ and Joon Jung²
¹Physics, University of Ulsan, Ulsan, Korea (the Republic of); ²Physics, Sogang University, Seoul, Korea (the Republic of).

Noncentrosymmetric transitional metal dichalcogenides (TMDs) and their vertical heterostructures (HSs) provide an ideal platform for studying atomic-scale nonlinear optics, especially second harmonic generation (SHG). TMD monolayers with different bandgaps can be artificially stacked not only to enhance the SHG efficiency but also to broaden the spectral range for the excitation resonance. We produced well-aligned homo-bilayer, hetero-bilayer, and hetero-trilayer structures, comprised of monolayers of MoS₂ and its alloy MoS₂-Se₂(1-x), and studied their broadband SHG properties. Photoluminescence analysis on all the vertically stacked HSs showed clear A- and B-excitonic transitions from each constituent layer, thereby confirming the excellent optical quality of the HSs. Especially, wavelength-dependent SHG measurements on the hetero-trilayer yielded strong SHG response over the spectral range of 550 nm to 780 nm. Our proof-of-concept study indicates that the spectral range for efficient SHG can be engineered by controlling the Se concentration in the MoS₂-Se₂(1-x) layers in the well-aligned HS systems, tuning the spin-orbit-split A- and B-excitons as well as the bandgap of each constituting layer. The strengthening and widening effects of SHG are interpreted as the superposition of resonant SHG across the A- and B-exciton levels from the constituent layers. Our results demonstrate the feasibility of artificial strong second-order nonlinear optical materials working over a broad spectral range by combining MoS₂ with different MoS₂-Se₂(1-x) alloys.

4:45 PM EP03.17.06
Exciton-Phonon Interaction and Upconversion Spectroscopy in Monolayer MoS₂
Shivangi Shree¹, Bo Han¹, Marco Manca¹, Emmanuel Courtade¹, Cedric Robert¹, Thierry Amand¹, Xavier Marie¹, Takashi Tanguichi², Kenji Watanabe², Marina Semina³, Leonid Golub³, Mikhail Glazov³ and Bernhard...
Transition metal dichalcogenides (TMDs) are ideal for exploring fundamental physics and applied optics as they are semiconductors with a direct bandgap in the monolayer (ML) limit. Encapsulation in hexagonal BN results in narrow optical emission linewidth, which allows investigating crucial details of the exciton spectra.

First, in MoSe2 MLs reduced emission linewidth at T=4K of about 1.5 meV enables us to observe unusual high-energy tails in absorption and emission for the neutral A-exciton. We show experimentally and theoretically that the exciton-acoustic phonon interaction in MoSe2 MLs is responsible for the asymmetric lineshape at the high-energy side both in emission and absorption [1]. We develop an analytical theory using the deformation potential due to longitudinal acoustic phonons that explains the origin of the observed asymmetric broadening. We show that this interaction in ML TMDs is much stronger compared to III – V nano-structures. The strong exciton-phonon interaction also results in prominent resonant Raman features in the photoluminescence (PL) excitation experiments.

Second, we show that resonant excitation of the neutral A-exciton transition results in emission of the B-exciton 200 meV above the excitation laser energy. When generated efficiently through resonant excitation, exciton densities become high enough for exciton scattering to occur, which can lead to the disappearance (annihilation) of one exciton as the second exciton absorbs its energy and occupies a high-energy state (upconversion).

In this work we show experimentally and theoretically that these Auger-type exciton-exciton interactions are qualitatively different in TMD MLs as compared to conventional semiconductors. In our theory we go beyond the usual analysis of the four-body interaction (2 electrons, 2 holes) within a two-band approach (conduction and valence band) and show that due to the particular conduction band energy spacing and strong exciton binding energy in MoSe2 but also MoS2, WSe2, and MoTe2 monolayers exciton upconversion is an efficient, resonant process [2].

Circularly polarized light (CPL) exhibits enantioselective interaction with chiral molecules, providing a pathway toward all-optical chiral resolution. Compared to existing chemical schemes like chiral chromatography, this all-optical approach could be rapid, economical, and readily adaptable to a wide variety of chiral molecules. CPL alone has been shown to achieve enantiomeric excesses only up to 2% while maintaining yield higher than 40%; however, high index dielectric nanoparticles can increase separation efficiencies. Such nanoparticles support both electric and magnetic Mie resonances, which locally increase the electromagnetic density of chirality, C, as well as the rate of differential absorption between enantiomers, g. Here, we investigate Si metasurfaces for all-optical chiral resolution. We consider a metasurface consisting of nanoscale cylinders and optimize C and g by varying the cylinder aspect ratio. First, using finite-difference time domain simulations, we simulate a square array of Si cylinders that are 100 nm high with a lattice parameter of 1000 nm. As we vary the radius of the disk from 170 to 360 nm, the electric dipolar mode redshifts relative to the magnetic mode, providing the opportunity to independently tune the phase of the electric and magnetic dipoles. Accordingly, we can achieve both electric and magnetic field enhancement as well as perfectly circular near-fields (a phase lag of π/2 between electric and magnetic field), the ideal condition for enantioselective light absorption. Using this method, we demonstrate that a disk with radius 280 nm gives a 4-fold average enhancement in enantioselective absorption (g) at λ = 1550 ± 50 nm. The enhancement occurs over the entire cylindrical surface and local enhancements up to 11x in g and 130x in C are also observed. Using the molecule camphor as an example, we show how this enhancement can give rise to 20% separation efficiencies with 40% yield over a large volume region. Moving to experiment, we fabricate metasurfaces using electron-beam lithography and disperse the chiral molecule helicene-diketopyrrolopyrrole in the near-field. This molecule shows strong, circularly dependent absorption at 592 nm and photoluminescence at 610 nm. We show how photoluminescence of this molecule tracks with our calculated enhancements in g. Our results pave the way for full chiral resolution based on absorption dependent photionization or photolysis.

8:45 AM EP04.01.03 Enhanced Directional Emission of Incoherent Radiation from All-Dielectric Vogel Spiral Arrays Sean Gorski1, Ran Zhang1, Abdullk Gok1, Alan Lene2, Madis Raukas1 and Luca Dal Negro1, 2; 1 Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; 2 CTO Materials, OSRAM Opto Semiconductors, Beverly, Massachusetts, United States; 3 Materials Science and Engineering, Boston University, Boston, Massachusetts, United States.

The development of scattering arrays of dielectric nanoparticles that can efficiently and directionally extract partially coherent radiation from high refractive index active materials poses significant challenges to traditional photonic approaches. In particular, the directional extraction of incoherent Lambertian radiation from dielectric interfaces, which is important to emerging lighting device applications, has not been systematically addressed so far. In our talk we experimentally address this relevant technological and scientific problem under realistic testing conditions by systematically studying directional emission enhancement from aperiodic arrays of dielectric nanorods atop light emitting LED materials. We prepared luminous materials with their surfaces functionalized by using transparent oxide nanorods arranged in the isotropically scattering golden angle Vogel spiral geometry and experimentally quantified the enhanced light extraction and directionality via Fourier-space photoluminescence imaging and microscopy. A variety of patterns were fabricated with varying nanopillar diameter and mean particle separations. The samples were excited with a 405 nm pump laser and directional emission was experimentally demonstrated comparing Fourier-space images of patterned and unpatterned regions of the samples. A total extraction enhancement of up to x2 times can be obtained with an angular directionality of ±30°. Our data have been compared with both numerical (FDTD) and analytical modeling of kinematic light scattering for incoherent radiation. Finally, based on our efficient analytical model we will also discuss general engineering design rules that enable directional extraction and enhancement using aperiodic scattering arrays with isotropic scattering.

9:00 AM EP04.01.04 All-Dielectric Materials Integration for Planar-Lens-Based Optical Beam Steering Josue J. Lopez1, Scott Skirlo1, Dave Khara2, Jamison Sloan1, Samuel Kim1, Sarur Baramhavar2, Jeffrey Herd3, Paul Juodvalkis3, Marin Soljacic1 and Cheryl Sorace-Agaskar1; 1 Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2 Lincoln Laboratory, Lexington, Massachusetts, United States.

Light Detection and Ranging (LIDAR) has attracted significant interest for autonomous navigation, imaging, and sensing. In particular, there is demand for compact, non-mechanically steered components with low size, weight, and power consumption requirements. Current leading LIDAR solutions use one-dimensional (1D) or two-dimensional (2D) phased-array antennas to steer a coherent beam bi-directionally. Interestingly, the RF Radar literature contains lens-based beam steering solutions (e.g. Rotman lenses) that overcome major challenges found in phased arrays. Their photonic analogs have not yet been investigated and are a viable solution for optical beam steering. Herein, we demonstrate the first planar-lens-based beam steering device that functions at λ = 1550 ± 50 nm and is fabricated with all-dielectric materials. The planar lens is fabricated with 25 nm of amorphous silicon on top of 195 nm of silicon nitride that allows for the design of a lens with a wide view in-plane of the lens. A grating made with the same dielectric stack allows for out-of-plane coupling in the far-field. We demonstrate this 2D beam steering through theory, simulations, and experimentally fabricated photonic components. The total angular range of this lens-based approach is an azimuthal range of φ = 41.0° and polar range of θ = 12.0°. In addition, we suggest new lens of-plane coupling in the far-field. We demonstrate this 2D beam steering through theory, simulations, and experimentally fabricated photonic components. A variety of patterns were fabricated with varying nanopillar diameter and mean particle separations. The samples were excited with a 405 nm pump laser and directional emission was experimentally demonstrated comparing Fourier-space images of patterned and unpatterned regions of the samples. A total extraction enhancement of up to x2 times can be obtained with an angular directionality of ±30°. Our data have been compared with both numerical (FDTD) and analytical modeling of kinematic light scattering for incoherent radiation. Finally, based on our efficient analytical model we will also discuss general engineering design rules that enable directional extraction and enhancement using aperiodic scattering arrays with isotropic scattering.

9:15 AM EP04.01.05 Digital Metasurfaces with Graphene Humeyra Caglayan, Mohsin Habib and Alireza Rashed; Tampere University of Technology, Tampere, Finland.

We have investigated graphene-gold metasurfaces to enhance light-graphene interaction in the MIR region and additionally, we demonstrate a new class of electrically controlled digital metadevices. In the first part, we will experimentally demonstrate that it is possible to increase and tune the optical transmission response of a graphene-based device substantially by applying less gate voltage compared to the back-gating methods via ionic liquid gating and nanoplasmonic antennas in the same device. Designing and utilizing V-shaped plasmonic structures enabled us to increase the interaction between the graphene layer and the incident field in the mid-infrared wavelengths. In this work, we have decided to use V-shaped plasmonic antennas. Among many candidates of plasmonic structures, V-shaped plasmonic nanoantennas have also proven useful in many applications including energy localization in nanosystems, unidirectional side scattering, and even sub-wavelength scale devices that can create abrupt phase changes and allows complete beam shaping. By using an ionic gating scheme, we are able to induce high electric fields near graphene to efficiently tune graphene’s Fermi level and control its carrier concentration, therefore shifting the transmission response of nanoantennas and the response of the device. In the second part, we will focus on the effect of the graphene supercapacitor. Graphene supercapacitor has been studied by different research groups for promising capacitor properties. In this work, we focused on its tuning effect. To understand the effect of the separation between graphene capacitor and metamaterial arrays on the performance of our metadevice, we measured near-field transmission spectrum in the forward direction at various separation values while sweeping the bias voltage between ±1.5 V. The fabricated active metadevices enable efficient control of both amplitude (< 50 dB) and phase (> 90°) of electromagnetic waves. In this hybrid system, graphene operates as a tunable Drude metal that controls the radiation of the passive metamaterials.
Furthermore, by integrating individually addressable arrays of meta-devices, we demonstrate a new class of spatially varying digital metasurfaces where the local dielectric constant can be reconfigured with applied bias voltages.

9:30 AM EP04.01.06
Active Infrared Niobium and Aluminum Oxide Plasmonic Metasurfaces Richard M. Osgood1, Lalitha Parameswaran2, Mordechai Rothschild2, Alkim Akyurtlu1, Yassine Air-El-Aoual1, Michael Okamoto1, Steven Koor1, Jimmy Xu1, Sergey Dichur1, Do-Joong Lee4 and Jin Ho Kim1; 1.U.S. Army NSRDEC, Natick, Massachusetts, United States; 2/MIT Lincoln Laboratory, Lexington, Massachusetts, United States; University of Massachusetts Lowell, Lowell, Massachusetts, United States; 3Division of Engineering Physics, Brown University, Providence, Rhode Island, United States; 4MIT ISN, Cambridge, Massachusetts, United States.

Rectification of GHz signals by diodes coupled to a surface of light-intensifying antennas has demonstrated optical-to-electrical (d.e.) power conversion efficiencies near 80%, an impressive achievement potentially useful for direct power beaming to charge batteries. In the infrared (IR) and visible, rectification occurs via quantum tunneling and/or hot-electron transport coupled to optically rectifying antennas, but IR rectennas are very challenging to investigate. Novel device concepts, including new metasurfaces, materials, and nanofabrication, must be employed. Because rectennas have absorption tuned by metamaterial dimensions, instead of by a band gap, they capable of light-harvesting and detecting broadband IR.

We designed microantenna arrays, consisting of plasmonic stripes that produce metamaterial and plasmonic resonances with near-perfect absorption [2], with teeth that induce a net asymmetric electric field driving electrons into the ground plane. The microrectenna is formed by these field-intensifying teeth and a vertical Metal-Insulator-Metal (MIM) diode (the metal-NbOx-Nb). The barrier layer NbOx, with thicknesses 5 – 30 nm, was ALD-deposited on Nb. Au stripes and symmetry-breaking stripe-teeth arrays were patterned atop the NbOx/Nb base layer with Ti and other adhesion layers. Ti adhesion layers did not provide sufficient asymmetry for rectifying diodes. Pt without an adhesion layer resulted in significantly asymmetric I-V curves as reported earlier [3], but required advanced patterning techniques since features are very small (hundreds of nm) and standard litho techniques don’t work well without good adhesion layers. We explore both front-side physical etching and forming the microrectenna arrays upside down on a Si handle wafer. In the latter case, IR illumination would pass through the wafer, shifting resonances such as the stripe arrays, making data analysis more challenging and requiring multiple excitation wavelengths. Nevertheless, we obtained good agreement between calculated and observed antenna resonances, large MIM diode asymmetry well-described by our advanced model of MIM diode conduction and rectification [4]. The short-wave IR reflectivity, polarized along the teeth, exhibits multiple peaks, whose positions depend on the separation between the teeth. Au stripes were also fabricated directly on the substrate using unique, "single-shot" electron-beam patterning. We also analyze Al/AlOx/Au microrectenna arrays and compare the resulting I-V curves under laser illumination with simulations. We compare the NbOx-based diodes, coupled to the Pt microantenna array, under SWIR illumination with the model, and predict the rectified signal, measured using a lock-in amplifier.


9:45 AM EP04.01.07
Amplitude and Phase Modulation of Femtosecond Pulses Using Silicon Metasurfaces Wenqi Zhu1,2, Shawn Divitt1,2, Cheng Zhang1,2, Henri Leze1 and Amit Agrawal1,2; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2University of Maryland, College Park, Maryland, United States.

Ultrafast optical science and technology depend on optical pulse shaping, which compliments pulse generation and characterization methods. Example applications for pulse shaping include pulse compression, dispersion compensation for fiber optic communications, coherent laser control of quantum mechanical processes, and spectrally selective nonlinear microscopy. Fourier-transform pulse shaping has emerged as the most successful and widely adopted technique, in which shaping is achieved by parallel modulation of spatially separated frequencies without requiring an ultrafast modulator. Here, we offer the first experimental demonstration of femtosecond pulse shaping using a centimeter-scale silicon metasurface acting as both amplitude and phase modulation mask. The deep-subwavelength silicon nanostructures, positioned with nanometer precision, provide accurate amplitude and phase modulations to each frequency component. Masks of this type offer a lower cost, larger size, higher resolution, high diffraction efficiency, high damage threshold method for controlling ultrafast pulses.

The experimental implementation is based on a Fourier-transform pulse shaping apparatus. A femtosecond optical pulse from a Ti:Sapphire oscillator covering the spectral range from 725 nm to 925 nm is angularly dispersed by the first grating and then focused by an off-axis parabolic mirror. A dielectric metasurface mask positioned at its focal plane can introduce amplitude and phase modulation to each spectral component. Our metasurface masks are composed of an array of polycrystalline silicon pillars resting on a fused-silica substrate. The rectangular pillars that form the metasurface are placed in a two-dimensional array. Each column of pillars along the y-axis introduces a designed phase to a narrow spectral range around a target wavelength. The cross-section of each pillar is chosen via an optimization algorithm to achieve the designed spectral phase shift while maintaining a large transmittance. The pillars provide a phase depth of 2π radians such that phase wrapping is necessary to impart the given phase function. As an example, we design a metasurface which imparts a pure quadratic phase (as a function of frequency). This design would generate enough dispersion to stretch a pulse from 15 fs to 40 fs. The measured spectral phase, group delay, and pulse shape applied by a representative, fabricated device match well with expected values. We have also achieved independent amplitude (through polarization) and phase shaping, as well as dynamic control, using metasurfaces.

In summary, we have designed, fabricated and tested an optical pulse shaper that uses a metasurface for spectral and amplitude phase modulation. The high precision with which metasurfaces can control polarization, amplitude, and phase point toward new, previously unrealizable applications in optical pulse shaping.

10:00 AM BREAK

10:30 AM EP04.01.08
Hybridization of Localised Surface Phonon Polaritons via Symmetry Breaking in Dolmen Nanostructures Swathi Iyer G.R.1, Chase T. Ellis1, Alexander J. Giles1, Dmitry N. Chigrin2, Michael Meeker1, Joshua D. Caldwell4 and Joseph Tischler1; 1Naval Research Laboratory, Washington, District of Columbia, United States; 2Institute of Physics (IA), RWTH , Aachen, Germany; 3CNST NanoFab, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 4Mechanical Engineering , Vanderbilt University, Nashville, Tennessee, United States.

Phonon-mediated subdiffractional confinement of light, combined with low optical losses has made polar-dielectrics such as SiC attractive for Infrared (IR) nanophotonic applications. By utilizing a nano-dolmen architecture, we experimentally and theoretically demonstrate hybridization between localized,
Indium Tin Oxide (ITO) has been demonstrated to have a tunable ENZ condition in near-infrared spectral range. Using co-deposited RF magnetron functionality for a broad range of IR-based applications including surface enhanced sensing and detection; thermal imaging and nanophotonic circuitry.

Current OLED displays rely on a circularly polarised (CP) filter to enhance contrast by trapping ambient light inside the display. However, this means that 50% of the randomly polarised light emitted from each OLED pixel never leaves the screen, halving display efficiency and operational lifetime. One way to overcome this is to create CP light emitting OLEDs (CP-OLEDs). A potential route to fabricate such devices is to induce chirality in a normally achiral electroluminescent polymer by blending it with a chiral small molecule. Our approach uses polyfluorene copolymers blended with an intrinsically chiral helicene dopant, which allows for CP-dependent applications while retaining much of the performance properties of the original polymer. Previously circularly polarised polymer emission has been achieved via thick cholesteric stacks of liquid crystalline polymers, where linearly polarised light becomes circularly polarised. To date, people have focused on the high film thickness regime to investigate the cholesteric stacking inside the active layer and the properties of the liquid crystal structure. Here, for the first time, we show that it is possible via film thickness to control the competitive effect between cholesteric packing and local chiral emission, the latter originating from an induced asymmetry in the polymer electronic and magnetic transition dipole moments. Remarkably, we observe handedness inversion in a system containing only one sign of chiral dopant. We compare how the chemical structure of the non-chiral polymer and post-deposition thermal processing impacts the chiroptical response of the resulting thin films and OLED devices in an effort to provide a set of design rules for future high-performance CP-OLEDs. We demonstrate a liquid-crystalline light emitting polymer with a record high induced circular dichroism. The circularly polarised photoluminescence and electroluminescence both show thickness-dependent CP emission and handedness inversion. In our system, the energy level alignment between dopant and host polymer ensures no charge trapping effects. As a result, the CP-OLED shows minimal change in the device performance compared to the original undoped OLED in terms of turn-on voltage and brightness. This provides new design rules for creating efficient circularly polarised light emitting diodes with high brightness and a high electroluminescent dissymmetry.

Photonic Band Structure Engineering in Strongly Absorbing Materials for Narrow-Band Optoelectronics. Arlene Chiu, Botong Qui, Ebuka S. Arinze, Yida Lin, Minda Wagenmaker, Andrew Rauch and Susanna M. Thon; 1Electrical and Computer Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 2Mechanical Engineering, The University of Alabama, Tuscaloosa, Alabama, United States.

Inorganic materials with finite absorption bandwidths could find uses in many optoelectronic applications such as wavelength-selective photodetection, optical imaging, target recognition, chemical detection and solar energy harvesting. They would be of particular interest for multijunction photovoltaics to facilitate current-matching between different cells, by, for example, enabling one of the cells to absorb only in the infrared while maintaining transparency in the visible regime. However, in contrast to molecular materials that exhibit finite absorption bandwidths in the ultraviolet or visible wavelength ranges, inorganic semiconductors typically strongly absorb at all energies larger than their bandgaps.

Here, we introduce a new set of materials based on photonic band structure engineering in strongly absorbing media to demonstrate inorganic semiconductors with finite absorption bandwidths. Photonic crystals (PCs), materials with periodic variations in their refractive indices, are used to manipulate light flow in a wide range of dielectric structures; however, the extent to which features such as photonic bandgaps can be supported in absorbing materials is still an open question. We studied this question in order to use PCs to artificially induce spectral transparency windows in the visible range in infrared-responsive materials.

To study the effect of absorption on photonic band structure in periodically structured materials, we used the finite-difference time-domain method to simulate the well-studied 2D GaAs slab PC structure, which consists of a triangular lattice of air pillars in a semiconductor membrane, as a test-case. We gradually increased the value of the imaginary part of the refractive index while keeping the real part of the refractive index constant in our hypothetical material to study how adding absorption affects the band structure. We quantified how, as absorption in the medium increases, the number of photonic band decreases, the magnitude of the remaining bands and contrast in the photonic bandgap diminishes. However, the band structure is partially preserved even in the high-absorption case, with the low frequency photonic bands and associated bandgaps retaining approximately 40% of their magnitude when compared to the non-absorbing case.

Experimentally, we demonstrated spectral tuning via photonic band structure engineering in a strongly absorbing infrared-responsive thin film composed of PbS colloidal quantum dots (CQDs). Using nanosphere lithography to create the PC structure, our photonic material had both twice the transmittance at 400 nm and twice the absorption at 960 nm compared to a planar CQD film. Employing photonic engineering to tune the spectral responsivity in strongly absorbing media, as demonstrated in this study, could provide a viable pathway for optoelectronic applications requiring finite absorption bandwidths.

Novel Tunable ENZ Media in the Near- to Mid-Infrared Range. Wesley Britton, Ran Zhang and Luca Dal Negro; 1Division of Materials Science and Engineering, Boston University, Brookline, Massachusetts, United States; 2Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States.

Dramatic advancements in areas such as electrical modulation, signal processing, and nonlinear frequency conversion have revitalized initiatives to develop more efficient nonlinear optical materials. In response, epsilon near zero (ENZ) media have emerged as a promising novel platform for nonlinear optical enhancement. However, ENZ materials operating in the near- and mid-infrared spectral ranges rely on metallic components with narrow wavelength tunability and high extinction losses. Likewise, they may require nano-manufacturing in three dimensions, which can severely limit device implementations and increase manufacturing costs. Heavily doped semiconductors are a common alternative. In particular, the transparent conductive oxide, Indium Tin Oxide (ITO) has been demonstrated to have a tunable ENZ condition in near-infrared spectral range. Using co-deposited RF magnetron
sputtering, we have developed an alternative material to ITO thin films, Indium Silicon Oxide (ISO). Upon post-deposition annealing this thin film material is found to extend the tunable ENZ condition into the mid-infrared with lower extinction losses. Moreover, the material is fully Si compatible, and has excellent surface smoothness properties that promised ease of scalability and device nanofabrication. We perform TEM and XRD measurements in order to correlate the structural and optical properties of this new material. In addition, we measure this material’s optical bandgaps and resistivity to determine and modulate charge carrier concentration. Our work significantly diversifies and expands the reach of ENZ medium and nonlinear optical materials in the infrared spectral range.

**11:45 AM EP04.01.13**

**Engineered Epsilon-Near-Zero Optical Nonlinearity of Al-Doped Zinc Oxide Thin Films Grown by Atomic Layer Deposition**

Subhajit Bej, Sudip Gurung and Howard Lee; Baylor University, Waco, Texas, United States.

Unusually large nonlinear optical properties of conducting oxide and metallic nitride materials in their epsilon-near-zero (ENZ) region (i.e. the region where the real part of their dielectric permittivity approaches zero), have been reported recently [1-4]. Processes involving nonlinear frequency conversion can be benefited from these ENZ regions due to relaxed phase-matching criteria. Moreover, nonlinear optical processes which do not require phase-matching, such as nonlinear refraction and nonlinear absorption, can also be largely enhanced in the ENZ region. This giant enhancement can be attributed to the hot free-carrier dynamics resulting from ultrafast laser assisted heating. Since the response time of such nonlinear processes can be ~100 fs, these ENZ materials could open distinct functionalities to the path to revolutionary nanoscale nonlinear optics and ultrafast on-chip optical applications.

In this work, we report an efficient method to engineer the nonlinear refraction coefficients ($n_2$) and the nonlinear absorption coefficients ($\beta_2$) of Al-doped zinc oxide (AZO) ENZ thin films. The AZO films with ENZ wavelengths ranging between 1500-1650 nm are synthesized on fused silica substrates by the atomic layer deposition (ALD) technique [5]. The properties of the ALD AZO films such as film thicknesses and ENZ wavelengths can be precisely controlled by changing the deposition conditions (e.g., number of deposition cycles and doping level of Al). Nonlinear optical properties of the fabricated films are measured using Z-scan technique using an ultrafast laser peaked at wavelength $\lambda_p$=1550 nm. Measured $n_2$ and $\beta_2$ values of the films are evaluated upon fitting the experimental closed-aperture and open-aperture data respectively. We also observed that the nonlinear refraction and the nonlinear absorption strengths can be engineered by controlling the ZnO to Al dopant layer ratios in the deposited AZO films even if they have similar thicknesses. The tunability of the ENZ nonlinearity can be attributed to the efficient control of free-carrier densities. Also, we experimentally demonstrate enhancement of the effective nonlinear properties of the films due to excitation of ENZ modes at oblique incidence while illuminating with TM polarized light. Measured values as large as $n_2=10^{-18}$ cm/Watt and $\beta_2=10^{-9}$ cm/Watt are obtained with a 216 nm thick ALD-fabricated AZO film for TM polarized light incidence at 60°. The results of this work provide an understanding about engineering nonlinear optical properties of AZO ENZ materials for nanophotonic applications.


This work is supported in part by the YFA Program from DARPA (grant number N66001-17-1-4047).
For what applications are plasmonic materials better than all-dielectric materials, and vice versa? Or 2D materials versus their bulk counterparts? How does the requisite bandwidth affect materials selection? Known material-based fundamental limits to optical response work at one of two extremes — a single frequency, or all-frequency sum rules — with no incorporation of bandwidth and no useful quantitative measure for all-dielectric approaches. Here, we use the complex-analytic properties of certain optical-response functions in conjunction with novel energy-conservation constraints to derive fundamental limits to near-field optical response for any material, over any bandwidth. We show that certain canonical geometries can approach the bounds at specific frequencies, while at many others there is significant opportunity for structured materials to surpass them by orders of magnitude. We map out a frequency-bandwidth phase space in which we identify optimal materials among plasmonic, all-dielectric, and 2D-material candidates and we put forward a quantitative material figure of merit to stimulate new-materials discovery.

2:15 PM EP04.02.03
A Comparative Study of Materials for Refractory Plasmonic Applications
Peter K. Petrov1, Matthew P. Wells1, Ryan Bower1, Rebecca Kilmurray1, Bin Zou1, Andrei Mihal1, Neil Alford1, Rupert F. Oulton1, Lesley Cohen1, Stefan A. Maier1 and Anatoly Zayats2; 1Imperial College London, London, United Kingdom; 2King's College London, London, United Kingdom.

Materials such as W, TiN, and SrRuO3 (SRO) have been suggested as promising alternatives to Au and Ag in plasmonic applications owing to their refractory properties. However, investigation of the reproducibility of the optical properties after thermal cycling at high operational temperatures is so far lacking. Here, thin films of W, Mo, Ti, TiN, TiON, Ag, Au, and SrRuO3 are investigated to assess their viability for robust refractory plasmonic applications. Films ranging in thickness from 50 - 180 nm are deposited on MgO and Si substrates by RF magnetron sputtering and, in the case of SrRuO3, pulsed laser deposition, prior to characterisation by means of AFM, XRD, spectroscopic ellipsometry, and DC resistivity. Measurements are conducted before and after annealing in air at temperatures ranging from 300 - 1000°C for one hour, to establish the maximum cycling temperature and potential longevity at temperature for each material. It is found that SrRuO3 retains metallic behaviour after annealing at 800°C, however, importantly, the optical properties of TiN and TiON are degraded as a result of oxidation. Nevertheless, both TiN and TiON may be better suited than Au or SRO for high temperature applications operating under vacuum conditions.

2:30 PM EP04.02.04
Synthesis of Transition Metal Dichalcogenide Thin Films as Very High Refractive Index Materials for Photonics
Christopher T. Chen1, Jacopo Pedroni2, Ashley Gaulding1, Christoph Kastl1, Tevye R. Kuykendall1, Francesca Maria Toma1, Adam Schwartzberg1 and Shaul Aloni1; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Università degli Studi di Milano-Bicocca, Milano, Italy.

New materials for conventional photonic index are predicated on high refractive index contrast for enabling high performance. Fabrication of nonphotonic devices also relies on the ease of pattern formation through lithographic templating and/or etching. Layered transition metal dichalcogenides are an area of intensive focus due to their emergent properties at the monolayer limit. Bulk transition metal dichalcogenides possess very high refractive index. One convenient synthetic route for large area coverage of transition metal dichalcogenides is the deposition of transition metal oxides, e.g. MoO3 and WO3, and subsequent conversion into transition metal dichalcogenides at elevated temperatures in the presence of reactive chalcogenide species.

In this presentation, we demonstrate a scalable method for producing high refractive index WS2 layers by sulfidation of WO3 synthesized via atomic layer deposition (ALD). High index of refraction is achievable through multiple synthetic procedures. With careful control of synthesis conditions, we can produce high refractive index WS2 thin films and conformal coatings by short high temperature (800°C) or prolonged moderate temperature (650°C) annealing in hydrogen sulfide. Although this process yields highly polycrystalline films with grain sizes on the order of 10 nm or less, the optical constants are in agreement with those reported for single crystal bulk 3R-WS2. The conformal nanocrystalline thin films demonstrate a surprisingly high index of refraction (n > 3.9), and structural fidelity compatible with lithographically defined features down to ~10 nm. Subsequently, we demonstrate three photonic structures - first, a two-dimensional hole array made possible by patterning and etching an ALD WO3 thin film before conversion, second, an analogue of the 2D hole array first patterned into fused silica before conformal coating and conversion, and third, a three-dimensional inverse opal photonic crystal made by conformal coating of a self-assembled polystyrene bead template. These results can be trivially extended to other transition metal dichalcogenides, thus opening new opportunities for photonic devices based on high refractive index materials.

2:45 PM EP04.02.05
Heteroepitaxy of Titanium Nitride for Plasmonic Applications
Amber N. Reed1, Hadley A. Smith1, 2, Zachary J. Biegler1, 2, Rachel L. Adams1, 2, Madelyn J. Hill1, Krishnamurthy Mahalingam1, Kurt Eynk1, Brandon M. Howe1 and Augustine Urbas1; 1Air Force Research Laboratory, WPAFB, Ohio, United States; 2University of Dayton, Dayton, Ohio, United States.

High temperature stability, chemical stability, low surface energy and mechanical robustness, combined with a zero-crossover wavelength in the visible region make titanium nitride (TiN) a promising plasmonics material. In this work we demonstrate the heteroepitaxial growth of TiN on (0001)-Al2O3, (001) MgO, (001) - LiNbO3 substrates using controllably-unbalanced reactive magnetron sputtering. Additionally, we discuss the relationship between TiN crystalline quality and optical properties. Coupled x-ray diffraction (XRD) of our TiN show high quality epitaxial growth on all three substrates, however, further structural characterization reveals differences in crystal defects, strain and surface morphology based on substrate crystal structure and lattice mismatch. Pendellosung fringes on the (111)-TiN diffraction peak for the coupled XRD of TiN on c-plane sapphire and LiNbO3 indicate uniform d-spacing and a pristine interface. Pole figure XRD show 6-fold symmetry for the TiN grown on sapphire, indicating the presence of stacking faults. These domains, which are further evident in atomic force microscopy (AFM) of the TiN surface, are attributed to different stacking within the TiN domains. XRD of the TiN on MgO show Pendellosung fringes on the (001)-TiN diffraction peak. Cross-hatching features similar to those on the bare MgO substrate seen in the AFM of the TiN surface. Variable angle spectroscopic ellipsometry (VASE) shows that TiN behaves metallic on all substrates with a zero crossover wavelength between 470 nm and 490 nm. Differences in the real (ε1) and imaginary (ε2) permittivity for TiN on the different substrates are also seen in the VASE measurements. From the ellipsometry measurements we calculate aquality factor (QLSPR = - ε2/ε1) of 3.34, 3.9 and 4.2 for TiN on LiNbO3, MgO and Al2O3 respectively, for a wavelength of 1550 nm. The differences in ε1 and ε2 become more pronounced at longer wavelengths.

3:00 PM BREAK

3:30 PM *EP04.02.06
New Materials for Photonics Beyond Noble Metals
Marina S. Leite; University of Maryland, College Park, Maryland, United States.

Steel is an alloy primarily formed by iron, carbon, and chromium that have transformed our society. Today, it is implemented in applications spanning from building construction to surgical tools. This disruptive material results from alloying, which provides superior mechanical properties. In analogy to steel, we propose the alloying of metals (Ag, Au, Cu, Al), which can enable the development of optical materials with unprecedented permittivity values, not found in its pure counterparts. Our paradigm overcomes the limitation imposed by the pre-defined permittivity of metals [1]. We demonstrate he unique
near- and far-field optical properties of these alloys for energy harvesting devices [2], and how they are correlated with the alloys band structure [3]. Further, we show perfect absorbers using Al-Cu semiconductor with near-unity (> 99%) and omnidirectional absorption in the visible and NIR range of the spectrum, formed by a simple dual-layer thin film stack [4]. Beyond coin-age metals, we introduce the use of earth-abundant materials for the realization of devices with on-demand response, including reconfigurability and transient behavior.


4:00 PM EP04.02.07
Tunable Fano-Resonance Alloy Metasurfaces Hauhua Li and Ji Zhou; Tsinghua University, Beijing, China.

Fano resonances are made of asymmetry components, which are either of different sizes or various shapes. In optical range, these kinds of nanostructure have strict requirements both for the design and the fabrication of each unit cell. Here, we put forward an alloy-made metasurface, which is composed of two kind of unit cells with different ingredients. In such a case, the properties of each counterpart can be adjusted gradually by changing the ratio of the alloy, which gives us a way to shift the phase of the metasurface, inducing the shift of asymmetry.

4:15 PM EP04.02.08
Single Crystal and Bicrystal Metal Growth on Amorphous Insulating Substrates Jonathan Fan and Lucia Gan; Electrical Engineering, Stanford University, Palo Alto, California, United States.

Metallic structures on insulators are essential components in advanced electronic and nano-optical systems. Their electronic and optical properties are closely tied to their crystal quality, due to the strong dependence of carrier transport and band structure on defects and grain boundaries. Here we report a general method for creating patterned single crystal metal microstructures on amorphous insulating substrates, using liquid phase epitaxy. In this process, the patterned metal microstructures are encapsulated in an insulating crucible, together with a small seed of a differing material. The system is heated to temperatures above the metal melting point, followed by cooling and metal crystallization. During the heating process, the metal and seed form a high melting point solid solution, which directs epitaxial metal growth. High yield of single crystal metal with different sizes is confirmed with electron backscatter diffraction images, after removing the insulating crucible. Unexpectedly, the metal microstructures crystallize with the direction normal to the plane of the film. This platform can readily extend to the growth of bi-crystals, by specifying two seed structures at each end of the metal stripe, thereby enabling the detailed study of single grain boundaries in microscale devices. This platform technology will enable the large scale integration of high performance plasmonic and electronic nanosystems.

4:30 PM EP04.02.09
3D Printed Metamaterials for High-Frequency Applications Aydin Sadeqi, Hojatollah Rezaei Nejad and Sameer Sonkusale; Tufts University, Medford, Massachusetts, United States.

We present a facile, low-cost and cleanroom-free technique for the fabrication of metamaterials using computer-aided 3D printing, metal deposition and wet etching. This hybrid approach enables realization of complex 2D and 3D geometries, which require multiple steps in conventional lithography. As an example we show innovative Mushroom-type metamaterials which consist of metamaterial unit cells standing on a thin pedestal. Such metamaterials are first designed in 3D CAD software (SolidWorks) and the entire 3D structure is first printed using a stereolithography (SLA) based printer (Formlabs Incorporated, Somerville, MA, USA). The printed device is then washed with Isopropyl alcohol (IPA) and distilled water. Then the device is fully cured with Form cure (by Formlabs). We use two approaches for metal deposition of the metal resonators on the top surface of 3D printed design. In our first approach, we stamp the top surface of the mushroom-type printed device with silver paste (AG-510 Silver conductive ink, Applied Ink Solutions; Westborough, MA, USA). We measure the transmission spectrum of the device with continuous wave THz spectrometer (Topoint Photonics, Munich, Germany). Unit cells show disk geometry with 250μm and periodicity of 1mm and the height of the pedestals are 8nm. The silver sputtered metamaterial shows resonant frequency at 222GHz matching with the simulation results. In our second approach, we sputter the printed device with 100nm of gold by NSC-3000 Magnetron sputter tool. Then we use gold etchant type TFA (TRANSENE Company, Incorporated; Danvers, MA, USA) to etch away gold from the whole device except the top surface of the disk resonators. Plasma treatment was used before etching so that the gold etchant would flow easily in between the pedestals of the mushroom-type metamaterials. The gold sputtered metamaterial shows a resonant frequency in 248GHz matching with the simulation results. We also characterized variability in fabrication by measuring the surface area of disks. The variability ranges from 235μm to 270μm showing a Gaussian distribution centered at 250μm. The coated areas by stamping method show high variability in the coated surface area with similar Gaussian distribution. We also extended our fabrication method for different types of metamaterials to show its versatility. As a second design we also implemented split ring resonator (SRR) geometry in a mushroom-type structure. The transmission spectrum of SRR shows a resonant frequency at 55.8GHz matching with the simulation result. In summary, our hybrid approach combining 3D printing, metal deposition and wet etching enables low cost realization of complex 3D metamaterials with unique electromagnetic functionalities.

4:45 PM EP04.02.10

Conductive transition metal nitrides (TMNs) have recently been suggested as viable alternatives to the noble metals gold and silver for plasmonic applications. Ceramic TMNs offer increased thermal stability [1] whilst also providing broad spectral tunability and CMOS compatibility. One such material, niobium nitride (NbN), has previously been suggested as a possible candidate for plasmonic devices at visible and near ultraviolet wavelengths, despite increased electronic losses [2].

We present an experimental investigation of the growth mechanism and optical properties of reactively sputtered NbN thin films grown at a range of deposition temperatures. Thin films of NbN have been demonstrated to display tunable double epsilon-near-zero behaviour, the mechanism of which will be discussed. Furthermore, in order to assess the viability of TMNs for inclusion within future plasmonic and optoelectronic devices it is essential to understand their optical properties and thermal stability when patterned on the nanoscale. We present an investigation of the plasmonic performance of NbN nanoparticles and nanodisc arrays fabricated by colloidal lithography and e-beam lithography.
An Actively Controlled Terahertz Metamaterial Based on Digital Microfluidics

Peiyi Song1, Leimeng Sun1, Kai Luo2, Kai Zhang1, Fangjing Hu1 and Liangcheng Tu1; 1MOE Key Laboratory of Fundamental Physical Quantities Measurement, Huazhong University of Science and Technology, Wuhan, China; 2School of Electronic Information and Communications, Huazhong University of Science and Technology, Wuhan, China.

Terahertz metamaterials (MMs) have shown their powerful capabilities in manipulating THz waves. By tailoring the unit cell’s properties and optimizing their arrangements, different functionalities such as filtering, absorption, focusing, and anomalous reflection of THz waves have been achieved. In the approaching to multi-functional THz MMs, reconfiguration at the unit cell level is of important. As one type of reconfigurable MMs, digital and programmable metamaterials have been experimentally validated in the microwave range, but not yet available in the THz regime. Therefore, finding the tuning mechanism at the unit cell level to achieve at least a 180° phase difference (for 1-bit) is the key for THz digital and programmable metamaterials. Once the digital states have been realized and controlled in a programmable manner, THz digital and programmable MMs can be realized.

Digital microfluidics has been developed recently based upon the manipulation of microdroplets. The size, spacing and flowing speed of microdroplets can be precisely controlled. Microdroplets in variety of materials, such as water, oil and liquid metal, can be generated and manipulated. More importantly, digital microfluidics possesses the capability to determine the locations of microdroplet within a small region of the device. This technique gives us an idea to design a very specific microfluidics device that integrates with carefully patterned microchannels to form an array of MM unit cells for THz manipulation. Channel in each unit cell then can be actively filled or unfilled by liquid material to obtain two digital states with a 180° phase difference, representing a reconfigurable operation of a 1-bit MMs unit cell.

In this paper, the idea of creating THz digital metamaterials using digital microfluidics technologies is investigated. A reflective-type 1-bit THz digital metamaterial based on a digital microfluidic system is designed for proof-of-concept purpose. A T-junction microfluidic setup is used to generate liquid metal microdroplets “train”. Next, the microdroplets train is delivered to the THz MM area with 9×9 subarrays, where each subarray contains 3×3 unit cells. By determining the size of each droplet and the spacing between them, each subarray can be set to be filled or unfilled with liquid metal for two digital states. It is worth noting that, the patterns of microdroplets train can be quickly and precisely created and modified by adjusting the pressures over the T-junction. Numerical simulation results show a ~180° phase difference for the two digital states within a 67% bandwidth. Radar cross-section (RCS) reduction is also demonstrated by optimizing the coding sequence of the microfluidic-based THz digital MM, giving a minimum 20 dB RCS reduction in the ±45° phi cuts. Methods and materials used in fabricating the THz microfluidics chip are discussed in the last part.

Development of Graphene Combined Terahertz Metamaterials for Biomolecule-Specific Sensing

Minah Seo1, Sang-Hun Lee1, Jong-Ho Choe2 and Chulki Kim1; Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Korea University, Seoul, Korea (the Republic of).

Various optical technologies for discrimination of biochemical molecules have been actively studied and steadily developed for medical diagnosis, pharmacuetics, mutagenesis, phylogenetics, and so on. In particular, terahertz (THz) electromagnetic waves have shown substantial promise for such applications since intrinsic vibrational, rotational, inter-molecular, and intra-molecular modes of many small molecules exist at broad THz frequency regime. Despite of such availability, it has been quite limited to obtain a reasonable signal from diluted molecule samples directly, since absorption cross section of the molecule is too small at THz frequency range. To increase sensing efficiency and absorption cross section of such target molecules, various types of nano metamaterial structure based sensing platform have been introduced [1, 2, 3]. Here, we performed THz time-domain spectroscopy (THz-TDS) using nanoscale metamaterial based sensing chips for discrimination and detection of small molecules including various types of nucleotides. This enables us to detect even very small quantities of sugar molecules sensitively and even selectively. Moreover, several extremely pathogenic types of viruses were also discriminated in terms of the THz optical characteristics [4]. Finally, by combining of high quality factor of resonance structure and suspended graphene mono layer can provide unprecedentedly increased sensitivity in sensing of such small biomolecules even with enormous size ratio between THz wavelength and DNA nucleotide. Our suggested THz transmission model modified by THz field enhancement at nano-slot resonances and molecular plate capacitor model show an excellent fitting curve to the measured THz transmission changes in terms of used DNA quantity. With this report, THz spectroscopy research can go beyond the absorption cross-section limit with enormously enhanced sensitivity. Two new major areas of research might emerge with our study:

1) Ultrasensitive label-free type sensing of biomolecules even in aqueous state
2) Contact-free investigation of electro-optic characteristics for suspended 2D materials

Acknowledgements
This research was supported by the Global Frontier Program CAMM-2016M1A6B3936653, and KIST intramural grants (2E28280 and 2V05880).
Metal-semiconductor metamaterials make it possible to enhance the light-matter interaction, due to resonant absorption and scattering of light by plasmon excitations in a system of metallic nanoparticles embedded into a semiconductor medium. The condition of such a resonance is \( \text{Re}(\epsilon_m + 2\epsilon_s) = 0 \), where \( \epsilon_m \) and \( \epsilon_s \) are the permittivities of the semiconductor and metal components of the metamaterial, respectively. The goal of this work was to develop and investigate new metamaterials based on the AlGaAs semiconductor matrix containing random or periodic systems of metallic AsSb nanoinclusions.

The 1 μm thick AlGaAs films were grown by molecular beam epitaxy at low temperature (200°C) on semi-insulating GaAs substrates with (001) orientation. The concentration of the Al was 30%. The low growth temperature provided incorporation of the excess As into the epilayer in the form of antisite defects As\(_{\text{Ga}}\), with concentration of 1%. During the grown process, AlGaAs epilayer was additionally doped with isovalent Sb impurity. The samples were subjected to annealing at temperatures of 400–700°C, which provided self-organization of the metallic AsSb nanoinclusions in the bulk of the AlGaAs epilayer. The volume fraction of the nanoinclusions was 0.17%. This value was determined by transmission electron microscopy and via measuring the concentration of arsenic antisite defects in the as-grown sample. Periodically arranged systems of layers of AsSb nanoinclusions were formed via periodic δ-doping of AlGaAs epilayer with Sb. The distance between δ-layers was 100 nm while their number was 12 and 24. The post-growth annealing at temperatures of 400–700°C provided formation of the periodic systems of layers of AsSb nanoparticles near the δ-layers of Sb.

The experimental study of AsSb-AlGaAs random system for various post-growth annealing temperatures was carried out by the investigation of optical extinction coefficient spectra. We observed significant absorption and scattering of light in the random system of plasmonic AsSb nanoinclusions in the transparency window of the AlGaAs matrix. However, the plasmon resonance peak corresponds to the energy within the fundamental absorption band of AlGaAs.

Investigation of the periodic system of AsSb-AlGaAs layers was carried out by optical reflection spectroscopy for light incidence angles up to 85° for s- and p-polarizations. In optical reflection spectra we observed resonant reflection peaks, accompanied by satellite oscillations. The magnitudes of the resonant peaks increased with the increase of average size of AsSb nanoinclusions and reached 19% and 31% for the 12 and 24 AsSb-AlGaAs periods, respectively. Resonance wavelengths corresponded to the expected values in accordance with the Bragg law. We relate these significant reflection magnitudes to the high dielectric contrast between the AsSb nanoinclusion layers and surrounding semiconductor medium, which is caused by the proximity of the plasmon and Bragg resonances.

**EP04.03.05**

**Switching the Extrinsic Chirality in Achiral Metasurfaces Using Magnetic Fields** 
Lei Bi\(^1\), Jun Qiao\(^2\), Tongtong Kang\(^1\), Huili Wang\(^2\), Bo Peng\(^1\)

Chiral plasmonic nanostructures have attracted great research interest due to their strong light-matter interaction in the subwavelength scale, leading to strong chiral optical response potentially applicable for enantiomer sensing, imaging or data communication. Active tuning the chiral optical response of chiral plasmonic devices can be realized by modulating the plasmonic modes at the nanoscale. Several methods have been proposed to effectively switch the optical chirality of such devices, including using phase change materials\(^{[1]}\), DNA origami\(^{[2]}\), mechanical deformation\(^{[3]}\) and magneto-optical effects\(^{[4]}\).

However, to achieve efficient chirality control is still a challenge. Here, we demonstrate switching of the extrinsic chirality of an achiral plasmonic metasurface at glancing incidence angles by using low magnetic oxide thin films. Upon switching the applied magnetic field direction, the metasurface shows sign reversal of the far field optical chirality in a wavelength range of 900 to 1100 nm. The device is composed of a thin film stack of perforated Au/Cu/YIG/YIG/SiO\(_2\)/TiN multilayers fabricated by sputtering and pulsed laser deposition (PLD). The periodic nanohole structure is fabricated by polystyrene (PS) sphere self-assembly in large areas. We experimentally demonstrate the circular dichroism (CD) of 0.15 rad induced by extrinsic chirality at an incident angle of 65°. Under an applied magnetic field of -3500 Oe to +3500 Oe out-of-plane, the far field CD can be switched with a dynamic range of -0.1 to 0.32 rad. Modal simulation also revealed a significant superchiral field modulation in the near field, which is about one-order of magnitude higher compared to previous work of magnetic chiral nanostructures. The effective modulation of optical chirality in our devices is due to a much higher field intensity enhancement in low loss magneto-optical oxide thin films. Our device provides a new method to realize efficient tuning of chiral metasurfaces using applied magnetic fields.

**EP04.03.06**

**Active Beam Scanning via Ge\(_2\)Sb\(_2\)Te\(_5\): Phase-Change Metasurface Employing Mie-Resonance**
Ali Forouzmand and Hossein Mosallaei;
Northeastern University, Boston, Massachusetts, United States.

Nonuniform graded-pattern metasurfaces as flat and compact realizations of conventional bulky optical elements have attracted immense interest with the opportunity of miniaturization and highly-densed integration in photonic/optical devices. So far, lack of reconfigurability and real-time phase/amplitude modulation has been a tremendous challenge that prevents realization of active spatial light modulation and dynamic beam steering. To surmount this obstacle, metasurfaces hybridized with functional materials can offer an ideal platform to create ultracompact modulators which enable a strong light-matter interaction and allow for introducing dynamic spatially-varying optical properties. Although various kinds of dynamic controllable paradigms have been introduced, they suffer from low reflection efficiency and limited phase shift due to high dissipative loss, short interaction length, and ineffective physical mechanism (e.g., hybridization with plasmonic nanoantennas with single on-resonance operation).

In order to attain highly efficient tunable optical design with simultaneous high reflection level and wide phase shift, a non-volatile optically controllable metasurface consisted of geometrically-fixed chalcogenide nanobars is theoretically investigated where the refractive index of each nanobar can be effectively tuned under assumption of multi-level partial crystallization and structural amorphous-to-crystalline transition. This can be accomplished through careful selection of a state-of-art tunable phase-change material (PCM) coupled with a unique physical mechanism. We utilize a recently emerged PCM called Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) with a strong resonant bonding, large bandgap, and low carrier concentration leading to large index contrast between amorphous and crystalline states (\(\Delta n=1.8\)) and low optical loss (\(\Delta \kappa=0.4\)) compared to the classical GST alloys. In addition, the GST nanobars as all-dielectric building blocks can support both the magnetic and electric resonances whose spectral positions and strength can be governed by varying the crystallization level. This gives us the possibility to take into account the contribution of both supported Mie-type dipolar modes and operate at the middle of them (off-resonance operation). By preventing from the concurrence of high field confinement and large extinction coefficient inside the PCM integrated element (known as the origin of an inevitable efficiency degradation), significantly large phase modulation of 270° is achieved while the reflection efficiency is not only high but also exhibits minimal changes between 0.6 and 0.8 for all the intermediate crystallization states. As a potential application, we leverage from phased-array concept and progressive phase-delay of nanoantennas in an array to achieve continuous steering ability when each GST nanobar is individually crystallized.

**EP04.03.07**

**Dielectric Metasurface Based Coherent Exciton-Photon Coupling with MoS\(_2\): Yoonsik Yi\(^2\), Van-Tam Nguyen\(^1\), Bok Ki Min\(^1\) and Choon-Gi Choi\(^1\)**

1. Graphene Research Lab, Emerging Devices Research Group, Electronics and Telecommunications Research Institute (ETRI), Daejeon, Korea (the Republic of); 2School of ETRI (ICT-Advanced Device Technology), University of Science and Technology (UST), Daejeon, Korea (the Republic of).

Chiral plasmonic devices can be realized by modulating the plasmonic modes at the nanoscale. Several methods have been proposed to effectively switch the optical chirality of such devices, including using phase change materials\(^{[1]}\), DNA origami\(^{[2]}\), mechanical deformation\(^{[3]}\) and magneto-optical effects\(^{[4]}\). In order to attain highly efficient tunable optical design with simultaneous high reflection level and wide phase shift, a non-volatile optically controllable metasurface consisted of geometrically-fixed chalcogenide nanobars is theoretically investigated where the refractive index of each nanobar can be effectively tuned under assumption of multi-level partial crystallization and structural amorphous-to-crystalline transition. This can be accomplished through careful selection of a state-of-art tunable phase-change material (PCM) coupled with a unique physical mechanism. We utilize a recently emerged PCM called Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) with a strong resonant bonding, large bandgap, and low carrier concentration leading to large index contrast between amorphous and crystalline states (\(\Delta n=1.8\)) and low optical loss (\(\Delta \kappa=0.4\)) compared to the classical GST alloys. In addition, the GST nanobars as all-dielectric building blocks can support both the magnetic and electric resonances whose spectral positions and strength can be governed by varying the crystallization level. This gives us the possibility to take into account the contribution of both supported Mie-type dipolar modes and operate at the middle of them (off-resonance operation). By preventing from the concurrence of high field confinement and large extinction coefficient inside the PCM integrated element (known as the origin of an inevitable efficiency degradation), significantly large phase modulation of 270° is achieved while the reflection efficiency is not only high but also exhibits minimal changes between 0.6 and 0.8 for all the intermediate crystallization states. As a potential application, we leverage from phased-array concept and progressive phase-delay of nanoantennas in an array to achieve continuous steering ability when each GST nanobar is individually crystallized.
Optical metasurface is an artificial optical interface capable of controlling the flow of light by bending, scattering, absorbing or filtering electromagnetic waves [1]. Metasurface is usually composed of periodic metallic components for their sub-wavelength scale response, but high refractive index based dielectric metasurface using Mie scattering is also desirable to integrate with dielectric circuit as well as the view of optic loss [2]. On the other hand, two-dimensional (2D) transition-metal dichalcogenides have emerged as a new class of active medium with atomic layer thickness [3]. 2D exciton-polaritonic state can play an important role in many optical properties such as enhancing emitting, lasing and modulating of light. However, light coupling such a dielectric metasurface with 2D material is still in lack of work. Here we report such a system in consisting of MoS2 and dielectric metasurface to engineer light-matter coupling. The MoS2 sample was grown by chemical vapor deposition (CVD) method. The nature of MoS2 was confirmed by both of AFM and Raman characterization, where by the thickness of typical ~5nm. The multi-layer MoS2 exhibit exciton emission centering at 1.95 eV, with narrow line width of 60 meV. Dielectric metasurface was precisely designed by amorphous silicon nanoblock in order to have first-order Mie scattering corresponds to the magnetic dipole in a range of MoS2 exciton emission. To enter the magnetic mode induced strong coupling regime, we investigate scattering spectra with various coupling strength by detuning its quality factor and distance of each layer. The spectral evolution of the composite system shows a spectral mode splitting phenomenon to depend on the energy detuning based on Si-nanoblock geometry. To understand the strong coupling effect properly, coupled mode theory is utilized, which can describe splitting energy of the coupled system. Calculated spectrum corresponding the 72meV (Si-nanoblock width=150nm, height=150nm, thickness =100nm) splitting energy shows the strong coupling condition above the vacuum Rabi splitting criterion. This strong coupled state of the composite system occurs when the energy exchanges between the MoS2 and Si-nanoblock is faster than their individual energy dissipation rate. As a result, we have systematically studied the geometry dependence of coupled state, demonstrating the validity of strong coupled state of the composite system. The occurrence and utilization of the strong coupling condition can be tailored by proper structural design and its related harmonic mode condition. These results could provide important clues to integrate 2D material on a chip level circuit, and also quantum optics devices.

**Acknowledgment:** This work is financially supported by The Hong Kong Ph.D. Fellowship Scheme supported by the Hong Kong RGC.

**References**


**EP04.03.08 Light Trapping in Perovskite Solar Cells with Non-Resonant Metasurfaces**

Mohammad I. Hossain1, Nivedita Yumnam2, Md Waysheh Qarony3, Veit Wagner4, Dietmar Knipp1 and Yuen H. Tsang1; 1Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong; 2Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Non-resonant metasurfaces were investigated as potential light trapping structures in perovskite thin film solar cells. The short-circuit current and energy conversion efficiency of thin-film single and tandem solar cells can be improved by light trapping while lowering the material consumption. Light trapping is commonly achieved by texturing the solar cells or at least texturing the contacts of solar cells. In the first part of the study periodically arranged metal oxide nanowire arrays were realized by electrodeposition. The zinc oxide nanowires were prepared by templated growth through a mask of photoresist. The subwavelength large zinc oxide nanowires can be used to texturing building blocks in controlling the phase of the incident light. In a second part of the study, optical simulations were used to design non-resonant metasurfaces with optical properties comparable to commonly used light trapping structures like pyramids or inverted pyramids. A comparison of the metasurfaces with the pyramid textured perovskite solar cells, exhibiting almost identical quantum efficiencies and short circuit currents. For thick perovskite solar cells, the incoupling of light in the solar cell is improved, and the short-circuit current and energy conversion efficiency is increased by approx. 15%. For thin perovskite solar cells the incident light is diffracted and scattered, and gain in the short-circuit current and energy conversion efficiency of 20-30% is observed. Guidelines for the design of the non-resonant metal oxide metasurfaces will be provided.

**EP04.03.09 Characterizing Optical Effects of Metasurfaces Using Photoelastic Modulators—Advantages and Limitations**

Ioan-Augustin Chioar1, Richard M. Rowan-Robinson1, Paolo Vavassori2 and Vassilios Kapaklis1; 1Physics and Astronomy, Uppsala University, Uppsala, Sweden; 2CIC nanoGUNE, San Sebastian, Spain; 3Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

Metasurfaces are nanostructured interfaces designed to induce abrupt changes to light wavefronts and polarization by means of arrays of sub-wavelength scatterers acting as optical antennas [1]. This tailoring largely depends on the size and shape of the scatterers, as well as on the choice of material, all of which can be designed to a high degree using modern fabrication techniques. Such flat metasurfaces offer a vast and exciting playground for both fundamental studies related to light-matter interaction at the nanoscale, as well as technological opportunities for designing a new generation of flat optical components.

Given the large freedom in design, appropriate characterization methods and tools need to be developed, thus enabling access to various optical parameters for such metasurfaces. Photoelastic modulators (PEM) are typically employed to quantify optical effects, such as linear and circular dichroism/birefringence. However, we have observed that conventional PEM-based methodology is quite challenging for determining such quantities [2] can be affected by artifacts and spurious effects, particularly when dealing with anisotropic and chiral metasurface architectures. We will present and discuss advantages, limitations, and different analysis methods that can still facilitate access to certain properties of such metasurfaces using PEM-based characterization techniques.

**References**


**EP04.03.10 Toroidal Resonances in Graphene-Based Planar Core-Shell Terahertz Metasurfaces**

Nazmin Akter, Mustafa Karabiýik, Fahmida Alam and Nezih Paşa; Electrical and Computer Engineering, Florida International University, Miami, Florida, United States.

Toroidal multipoles are one of the fundamental excitations which are considered as the third family of electromagnetic multipoles in addition to the electrical and magnetic multipoles. These multipoles have recently become an attractive area in metamaterials research. However, detection of this type of resonant moments is highly challenging since they do not efficiently couple to the free space. The toroidal dipole resonance possesses magnetic moments that are aligned head-to-tail and form a dynamic vortex in the shape of a torus' surface due to induced currents. Existence of toroidal multipolar modes in
planar 2D structures has received growing attention recently due to their easy fabrication and characterization. Devices based on toroidal modes have recently been used in practical applications such as biological sensing and microwave antennas. Resonant modes in complex structures such as core-shell structures can be explained by hybridization of elementary plasmons supported by nanostructures of elementary geometries. In such cases, the electromagnetic interaction between the elementary plasmons leads to mixing, splitting, and shifts of the plasmon energies of the entire structure. However, these changes have not been investigated for toroidal modes yet.

THz wavelengths have several advantages that could promote their use as sensing and imaging tool. THz radiation can penetrate non-metallic materials such as fabric, leather, plastic which makes it useful in security screening for concealed weapons. The THz frequencies correspond to energy levels of molecular rotations and vibrations of DNA and proteins as well as explosives, and these may provide characteristic fingerprints to differentiate biological tissues in a region of the spectrum not previously explored for medical use or detect and identify trace amount of explosives. Graphene with its exquisite material, electronic and optical properties, particularly with its potentially very high carrier mobility is an excellent material for THz applications.

In this paper, we report on a theoretical and experimental investigation of the hybridized toroidal plasmonic modes in metasurfaces composed of graphene core-shell resonators with different configurations. Spectral characteristics of the metasurfaces with core-only, shell-only and core-shell designs with various geometrical variations have been investigated using a finite-difference-time-domain (FDTD) tool. Selected structures have been fabricated using PDMS-based graphene transfer method and standard microfabrication tools and techniques on a high-resistivity Silicon substrate. Transmission spectra of these fabricated metasurfaces have been measured using backward wave oscillator (BWO) and THz time-domain spectroscopy (TDS) systems. We discuss the hybridization of the toroidal modes in core-shell resonators due to the coupling of the fields on individual core and shell components and their dependence on geometrical parameters.

EP04.03.11
System Level Considerations for Tunable Metasurface Designs
Artur R. Davoyan and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Optical phased arrays are important ingredients for beam forming in sensing, imaging and ranging applications. Electrically tunable metasurfaces comprised of elements where phase and/or amplitude may be addressed individually offer a highly integrated and versatile platform for beam shaping. However, addressing electrically a large number of metasurface elements may seem a substantial practical limitation. Here, we report a novel architecture of control for phased array antennas and metasurfaces. In contrast to previous schemes utilized for beam forming in phased array antennas and metasurfaces, our design involves a reduced number of control elements, is efficient and compact. A typical metasurface employed for beam forming contains periodic arrays of emitters and/or scatters, each having its own phase and amplitude. Coherent superposition of the fields scattered by each of the emitters forms a narrow beam, direction of which may be controlled by an applied voltage. However, current architectures assume individual control (e.g., by an applied voltage) of each of the scatter. While for a small number of elements this architecture works well, with increase of the number of array elements the control becomes complex and power inefficient. For instance, a square array with N elements on the side would require N2 of control voltages. Hence, for large aperture arrays, e.g., with 1000 elements on the side – that are operated at optical frequencies, 106 control elements are needed.

In contrast here we propose a different control scheme. Beam forming relies on a fundamental relation of independent phase progression along two orthogonal directions (e.g., x and y) and a constant phase gradient along these directions. It is this superposition of phase gradients along orthogonal planes that allows us to implement a perimeter control architecture. Control signals are applied along the orthogonal axes on the perimeter of the array superimpose at any given element inside the array. For the case of a linear voltage phase relation this voltage superposition directly corresponds to phase superposition. Such a control scheme in contrast to a previously mentioned one requires only 2N controls. We note that our architecture may also utilize nonlinear gradients and phase relations with a proper design. Our approach is generalizable to different frequency domains, including optics, infrared, terahertz, microwave and RF, as well as acoustics.

EP04.03.12
Anapoles in Disk Nanoantennas Fabricated from III-V Nanowires for Enhancement Second Harmonic Generation
Maria Timofeeva1, Lukas Lang1, Claude Renaut1, Flavia Timpu1, Igor Shtrom2, Alexei Bouravlev2, George Cirlin3 and Rachel Grange1; 1ETH Zurich, Zurich, Switzerland; 2Saint-Petersburg National Research Academic University of the Russian Academy of Sciences, Saint Petersburg, Russian Federation; 3ITMO University, Saint Petersburg, Russian Federation.

Nonlinear optics is a fast-developing research field with a high potential of applications with new types of metamaterials, nanoantennas, lasers and versatile photonic devices. Nanophotonics is usually associated with metallic nanostructures and nanoparticles due to their optoelectronic and plasmonic properties. Despite successful applications of such kind of structures, it is well known that plasmonics suffer from ohmic losses, heating and incompatibility with standard CMOS technology. However, recent research follows a new route of light manipulation at the nanoscale by employing optically induced Mie resonances in dielectric and semiconductor materials with high refractive indexes, for example silicon or germanium, as an alternative to metallic nanostructures to overcome these issues. In our work, we utilized the electromagnetic properties of III-V semiconductor nanowires to design building blocks for nonlinear all-dielectric metamaterials and devices. We developed a new concept of fabrication standing disk nanoantennas by slicing epitaxially grown nanowires with focused ion beam milling. This method allows us to create nanodisk configurations on any substrate and it significantly expands the possible applications of III-V disk nanoantennas.

In the fabricated standing disks from GaAs/AlGaAs nanowires, we studied nonradiating current distributions, called anapoles modes. The nonradiating current distributions have two essential features that make them very promising structures for photonic devices: first, lack of energy losses and second invisibility to the propagating electromagnetic field. We demonstrated in III-V standing disk nanoantennas the suppression of the far field radiation and strong electromagnetic field confinement inside the disk structure that lead to the strong enhancement of the second harmonic generation. We experimentally shown the drop in the linear scattering in the region of 800-900 nm and simultaneous enhancement around 5000 of the second harmonic generation from these disks in comparison with a layer of AlGaAs. For the theoretical analysis we developed a full model that allows us to calculate linear scattering, second harmonic generation and perform the multipole expansion of the electromagnetic field inside studied disks. Using this multipole expansion in both spherical and Cartesian coordinates, we confirm that the demonstrated nonradiating configurations are anapoles.

In the future, we believe that this approach of nanowires slicing can form a new branch of nanotechnology to fabricate different chains of disk and rod nanoantennas on different substrates. Such type of chains could become a core element for lasers and sensors with low power consumption based on lossless nonlinear photonic components supporting anapoles and compatible with CMOS technologies.

EP04.03.13
Following Polaritonic Chemistry with Photo- Switchable Molecules Using Optical Nanoantennas in the Strong Coupling Regime
Esteban Pedreauza Villalmanzo1, Valeria Suavedra1, Evgeniya Smetanina1, Mehdi Keshavarz Hedaya1, Mohsh Abdestayl Mahmoud Abedaliz8, Timur Shega1, Joakim Andreas1, Mady Elbuhri1 and Alexandre Dmitriev1; 1Department of Physics, University of Gothenburg, Gothenburg, Sweden; 2Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Chemical Physics, Gothenburg, Sweden; 3Department of Micro and Nanotechnology,
Optical resonant molecular systems often display what is called a strong coupling to the nanoplastic systems. This is primarily explored for the nanophotonic active control and in the studies of quantum optics [2]. At the same time, the strong coupling of the molecular resonances to the nanoplasmonic resonances has not been addressed to follow the light-induced molecular processes. Here we combine an exemplary molecular photo-switch, from spiropyran to photochromic family, with anisotropic nanoplasmonic antennas to earn the monitoring tool for the light-activated processes using molecular and nanoplasmonic resonances strong coupling regime [3]. We follow the reversible photo-isomerization of the spiropyran photoswitch from the spiro form to the merocyanine form by tuning in the nanoplasmon antenna to the excitonic state of the merocyanine form (at 570 nm), prompting the formation of a hybrid excitation-plasmonic state. Our anisotropic nanoantenna provides two polarization-dependent spectrally separated resonances in the visible region, allowing for separate monitoring of the plasmon-exciton strong coupling and the conventional enhanced optical near-field refractive index sensing. This system uncovers a new modality in polaritonic chemistry and optical label-free monitoring of the photo-activated processes and can find applications in photocatalysis, biosensing and in hybrid molecular-nanoantenna actively modulated systems.


EP04.03.14

Multiresonant Composite Optical Nanoantennas

Junyeob Song and Wei Zhou; Virginia Tech, Blacksburg, Virginia, United States.

Optical nanoantennas can concentrate light and enhance light-matter interactions in subwavelength domain, which is useful for photodetection, light emission, optical biosensing, and spectroscopy. However, conventional optical nanoantennas operating at a single wavelength band are not suitable for multiband applications. Here, we propose and exploit an out-of-plane plasmonic engineering strategy to design and create composite optical nanoantennas that can support multiple nanolocalized modes at different resonant wavelengths. These multiresonant composite nanoantennas are composed of vertically stacked building blocks of metal-insulator-metal loop nanoantennas. Studies of multiresonant composite nanoantennas demonstrate that the number of supported modes depends on the number of vertically stacked building blocks and the resonant wavelengths of individual modes are tunable by controlling the out-of-plane geometries of their building blocks. In addition, numerical studies show that the resonant wavelengths of individual modes in composite nanoantennas can deviate from the optical response of building blocks due to hybridization of magnetic modes in neighboring building blocks. Using Au nanoplate arrays as deposition masks to fabricate arrays of multilayered composite nanoantennas, we experimentally demonstrate their multiresonant optical properties in good agreement with theory predictions. These studies show that out-of-plane engineered multiresonant composite nanoantennas can provide new opportunities for fundamental nanophotonics research and practical applications involving optical multiband operations, such as multiphoton processes, broadband solar energy conversion, and wavelength-multiplexed optical system.

EP04.03.15

2D Surfaces as a Handle to Engineer 3D Photonic Nanostructures

Sadan Fu1, Xiaoxiong Wang1, Haoze Wang2, Jing Kong3 and Jifeng Liu1; Dartmouth College, Hanover, New Hampshire, United States; 2Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Two-dimensional (2D) materials, such as graphene and hexagonal Boron Nitride (h-BN), have been attracting the eyes from the materials research society, especially for their photonic and electronic applications. In addition to their own 2D material functionality, in recent years 2D materials are also being investigated as a template to engineer the growth of 3D photonic structures and devices. Here, we show that the drastic change in surface energy on single-layer 2D materials can be effectively applied to engineer self-assembled 3D photonic nanostructures, including Sn-SnO core-shell nanoneedles and Sn nanodot arrays. The wetting angle analysis reveals that the 2D layer, though only with atomic-scale thickness, can already modify the surface properties of the 3D nanostructures. Furthermore, for example, the single-layer graphene (SLG) lattice is enough to make it hydrophobic (~100° wetting angle of water). In contrast, h-BN seems to be wetting-transparent to the surface, i.e. it retains the original surface properties of the substrate. It’s observed that such a surface properties variation leads to clear geometric differences of the Sn and Sn-SnO core-shell nanostructures grown on the top, and thus greatly influences the optical properties at 2D interfaces. The Sn nanostructure on SLG/quartz always tends to be more continuous than that on quartz directly; while the Sn nanostructure on h-BN/quartz and quartz directly show identical geometries. We derived the effective refractive index change of 3D Sn and Sn-SnO core-shell nanostructures on SLG vs. on silica, which can be further engineered to achieve other novel 3D photonic structures on SLG utilizing 2D materials as a template. An example is the highly effective light trapping in 2D materials contributed by the 3D photonic nanostructures, which has been revealed by direct optical absorption measurement and confirm by strongly field-enhanced Raman signals from the 2D materials. With Sn-SnO core-shell nanoneedles, the absolute absorption of SLG can reach up to 17% from the wavelength of 500 nm to 1200 nm; with Sn nanodot arrays, the absolute absorption of SLG can be up to 20% from the wavelength of 500 nm to 4500 nm. Furthermore, these structures can also be used as deposition masks to fabricate arrays of multilayered composite nanoantennas, we experimentally demonstrate their multiresonant optical properties in good agreement with theory predictions. These studies show that out-of-plane engineered multiresonant composite nanoantennas can provide new opportunities for fundamental nanophotonics research and practical applications involving optical multiband operations, such as multiphoton processes, broadband solar energy conversion, and wavelength-multiplexed optical system.

EP04.03.16

Fabrication of Gold Nanostructures Using Wet Lift-Off without Adhesion Promotion

Mengjie Zheng1, 2, Yujia Yang1, Huigao Duan3 and Karl K. Berggren1; 1Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2School of Physics and Electronics, Hunan University, Changsha, China; 3College of Mechanical and Vehicle Engineering, Hunan University, Changsha, China.

Adhesion layers are often needed in the fabrication of metallic nanostructures. For example, Ti and Cr layers facilitate the adhesion of Au nanostructures on various dielectric and semiconductor substrates, which is essential for many applications such as plasmonics, metamaterials, and nanoelectronics. However, despite providing mechanical stability, adhesion layers sometimes have detrimental effects in certain applications. It has been reported that in plasmonics, metallic adhesion layers for Au nanostructures cause damping of surface plasmon resonances, and lead to a decreased field enhancement and plasmon lifetime. Hence, there has been a quest for fabricating Au nanostructures with an alternative adhesion layer or even without an adhesion layer. In our previous work, we have shown Au nanoparticle arrays can be made free from adhesion layers. Here we systematically investigate the effect of adhesion layers on Au nanostructures made from electron beam lithography and a wet lift-off process.

In this work, Au nanoparticle arrays and nano-gratings were fabricated via electron beam lithography on a silicon or Au-coated silicon substrate. A single
layer PMMA resist was exposed and developed. Electron beam evaporation deposited the Au nanostructures with or without a Ti adhesion layer. Wet lift-off was performed in hot NMP without sonication. The samples were gently rinsed intermentally with flowing NMP. Experiments showed Au nanostructure adhesion was affected by several factors, including nanostructure size and geometry, lithographic dosage, and the substrate being used. Au nanoparticle arrays have an almost perfect yield even without an adhesion layer. Hence, an adhesion layer is not indispensable in the fabrication of isolated Au nanostructures. However, a higher lithographic dosage is required to achieve a high yield in the absence of an adhesion layer, which shows the adhesion layer increases the tolerance to residual resist scum after development. As for Au nano-gratings, the adhesion layer is not necessary for short grating lines, but is essential for achieving a high yield for long grating lines. Longer grating lines could have more defects and cracks at the Au-substrate interface, leading to a greater vulnerability to delamination. Furthermore, we find an adhesion layer is also necessary when making Au nano-gratings on top of a Au-coated substrate. This observation indicates the adhesion layer is needed not only for the adhesion between the metallic nanostructures and the substrate, but also for the adhesion between the metallic overlayer to be removed and the resist layer. The latter adhesion is crucial for removing unwanted metal pieces from the samples in the wet lift-off process.

**EP04.03.17**

**Metal-Halide Perovskite Confined in Nanoporous Oxide Thin Films for Light Emitting Applications**

Stepan Demchyshyn, Serdar Sariciftci, Markus Schrerber, Siegfried Bauer and Martin Kaltenbrunner; Johannes Kepler University, Linz, Austria.

Halide perovskites are inexpensive and easily processable next generation semiconductors. We here demonstrate perovskite solid-state confinement in nanoporous oxide matrices as a general strategy to control the size of the nanocrystals (<10 nm) in the strong quantum size effect region. Photoluminescence tuning between near infrared and ultraviolet is achieved by manipulating the size of perovskite crystals through confinement in nanoporous alumina (npAAO) or silicon (npSi) scaffold [1].

Our novel method of nanocrystalline perovskite preparation within a porous oxide matrix results in device-relevant structure that requires no colloidal stabilization. Low-voltage LEDs with narrow, blue-shifted emission fabricated with perovskite nanocrystals confined within npAAO thin films support the general concept for next-generation photonic devices. The template-controlled size of the perovskite crystals is quantified in npSi with microfocus high-energy X-ray depth profiling in transmission geometry, verifying the growth of perovskite nanocrystals throughout the entire thickness of the nanoporous films. We study in detail exciton recombination, exciton-phonon interactions and energy trap states in confined and bulk semiconductor films using low temperature photoluminescence spectroscopy down to 3.8 Kelvin.

Further areas of application include photon detectors, (polarized) electroluminescent devices, single-photon sources and metasurfaces. Future developments will include increasing the efficiency of the LEDs, exploring their applications in flexible devices and in depth study of the fundamental properties of the confined structures.


**EP04.03.18**

**Hierarchical Nanodisk Arrays Inspired by Diatom Frustules as Near Infrared Metamaterial Absorbers**

Aobo Li1, Xiaoguang Zhao2, Guangwu Duan3, Stephen Anderson2 and Xin Zhang2; 1Boston University, Boston, Massachusetts, United States; 2Boston University Medical Center, Boston, Massachusetts, United States.

The design and fabrication of electromagnetic metamaterials have been extensively studied given their unique engineered electromagnetic properties. A broad array of applications has enabled the development of metamaterials such as invisibility cloaking and perfect absorbers, among others. In order to achieve IR absorption, subwavelength structures are required on the nanometer scale. Diatoms, a type of photosynthetic microalgae, feature silica exoskeleton structures that enclose their cytoplasm. The abundant hierarchical micro and nanopores on the diatom frustules have been employed in a range of bio-inspired and bio-mimetic studies. In this study, we mimicked the cribrum pores (diameter ~224 nm) on diatom frustules in order to design a hierarchical gold nanoresonator array that can be used as a near-IR metamaterial absorber. The design was validated with preliminary simulations and measurements, which demonstrate the potential for future applications in IR sensing and thermal emitter applications.

Diatoms (Coscinodiscus Species) were initially cleaned with concentrated sulfuric acid to remove organic contaminations. The extracted frustules were subsequently washed with DI water. Pore sizes and pore distributions on the frustules were measured and measurement data were used to design and fabricate the nanodisk arrays. An n-type 100 silicon wafer was used as the substrate, on which a 200 nm gold layer was deposited as the ground plane and 200 nm of SiNx was deposited as the spacer. On top of it, the bio-inspired nanodisk arrays were deposited through e-beam lithography (EBL) and a subsequent lift-off process. Finite difference time domain (FDTD) analysis was conducted to study the proposed structure’s characteristics. A Bruker Vertex 70v Fourier transform IR (FTIR) spectroscopy was used to obtain the reflectance of the structure.

The abundant micro- and nanopores are seen on both sides of the diatom frustule. Specifically, we are interested in mimicking the cribrum pore sizes, and corresponding measurements were conducted. The nanodisks’ size and hierarchical arrangements mimicked the cribrum pores on the frustules. The simulation result demonstrates that there is a strong absorption peak in the IR range. We found that the nanodisks are resonant at the peak frequency and the surface electric field patterns show a clear dipole resonance. Subsequently, we evaluated the frequency peak shift as a function of nanodisk diameter. We demonstrate that the absorption becomes stronger as the disk diameter increases, and the peak shifts towards longer wavelengths. The measurements of the structures show similar tendency of the peak shift as a function of disk diameter. The disagreement between the simulation and experimental measurements may be a result of material property mismatches. The results demonstrate a potential use of the hierarchical patterns as a novel route to design and fabrication of metamaterial absorbers.

**EP04.03.19**

**Dispersionless Wavefront Engineering of Light Using Time-Modulated Metasurfaces**

Mohammad Mahdi Salary, Samad Jafar-Zanjani and Hossein Mosallaei; Northeastern University, Boston, Massachusetts, United States.

Optical metasurfaces have provided a great flexibility in shaping the wavefront of light by engineering the phase response of constituent building blocks. In the conventional metasurfaces, the required phase profile is achieved through changing structural parameters of a resonant element or rotation of a half-wave plate element around its axis. Recently, an extensive effort has been put into post-fabrication tuning of geometrically-fixed metasurfaces by incorporating different mechanisms to tune the spectral shift of the resonance and modulate the phase response of the elements in real-time. Despite the real-time tunability of these actively controlled metasurfaces, their operation has been mostly studied in the quasi-static case where the temporal variations are disregarded. Introducing time-modulation in a metasurface leads to generation of higher-order frequency harmonics and breaks the reciprocity constraint. In this work, we demonstrate that time-modulated metasurfaces can extend the degree of light manipulation and wavefront engineering through a non-resonant
modulation-induced phase shift. It is rigorously established that the light picks up a dispersionless phase shift regardless of incident angle and polarization, upon undergoing frequency conversion in a time-modulated metasurface which is determined by the modulation phase delay and the order of generated frequency harmonic. The efficiency of frequency conversion is independent of modulation phase delay and merely depends on the modulation depth and resonant characteristics of the metasurface building blocks, with the efficiency being maximal near the resonance, and decreasing away from the resonance. This creates a new design paradigm which allows for realization of tunable spatial phase discontinuities within the time-modulated metasurface in the terahertz frequency regime implemented using graphene-wrapped silicon microcavities electrically biased with radio-frequency signals. Several different functionalities such as tunable beam steering and focusing of frequency harmonics are investigated and the broadband wide-angle performance of the metasurface in manipulation of higher-order frequency harmonics is verified. The proposed paradigm is a departure from the previous metasurface design rules and enables realization of multifunctional tunable metasurfaces with wide angular and frequency bandwidth.

EP04.03.20
Transient and Flexible Hyperbolic Metamaterials on Freeform Surfaces Hung-I Lin1, Kun-Ching Shen2, Shih-Yao Lin1, Golam Haider1, Yao-Hsuan Li1, Shu-Wei Chang1 and Yang-Fang Chen7; 1National Taiwan University, Taipei, Taiwan; 2Academia Sinica, Taipei, Taiwan.

Transient technology is deemed as a paramount breakthrough for its particular functionality that can be implemented at a specific time and then totally dissolved. Hyperbolic metamaterials (HMMs) with high wave-vector modes for negative refraction or with high photonic density of states to robustly enhance the quantum transformation efficiency represent one of the emerging key elements for generating not-yet realized optoelectronics devices. However, HMMs has not been explored for implementing in transient technology. Here we show the first attempt to integrate transient technology with HMMs, i.e., transient HMMs, composed of multilayers of water-soluble and bio-compatible polymer and metal. We demonstrate that our newly designed transient HMMs can also possess high-κ modes and high photonic density of states, which enables to dramatically enhance the light emitter covered on top of HMMs. We show that these transient HMMs devices loss their functionalities after immersing into deionized water within 5 min. Moreover, when the transient HMMs are integrated with a flexible substrate, the device exhibits an excellent mechanical stability for more than 300 bending cycles. We anticipate that the transient HMMs developed here can serve as a versatile platform to advance transient technology for a wide range of application, including solid state lighting, optical communication, and wearable optoelectronic devices, etc.

EP04.03.21
Large-Area and Flexible All-Dielectric Metasurfaces via Templated Dewetting of Optical Glasses Tapajoyti Dasgupta, Louis Martin-Monier, Wei Yan, Arthur Lebris, Das Tung Nguyen, Alexis Page, Yungkin Qu and Fabien Sorin; EPFL, Lausanne, Switzerland.

Dielectric and plasmonic metasurfaces require the integration of materials with accurate control over position, size and shape for high optical efficiency. They are typically fabricated by the well-established lithographic or chemical processes. Hence, it remains difficult to scale to large-area and unconventional substrates. Here, we propose the template dewetting[3-5] of thin chalcogenide glasses[6,7] as a novel approach to self-organize a variety of large index contrast all-dielectric metasurfaces[8]. Given the right dewetting temperature settings, initial film thickness and underlying pattern, the breakup of the film can occur at prescribed locations resulting in nano-objects of tunable position and sizes. This control over the dewetting of chalcogenide glasses paves the way towards simple fabrication route of advanced 2D and quasi 3D photonic devices over large area, flexible and stretchable substrates. Low processing temperatures enable large-scale use of rigid but also unconventional flexible and stretchable substrates. This bears a particular importance as lithographic processes today are limited by cost, and also in terms of area and substrate rigidity. The structures we realize are shown to have a very large and tunable absorbance in the visible range opening up possibilities for photo-detecting applications. Such structures also enable strong electromagnetic field confinement, and will be shown to have a variety of application in sensing, light management and second harmonic generation. By dewetting increasingly thick layers, inter-particle gap down to 10 nm could be achieved in such metasurfaces. This leads to a Fano resonance in transmission, due to the interference between a sharp electric gap mode and a broad magnetic mode due to the particles in the lattice. We will demonstrate in particular monolayer protein detection with high sensitivity, with an LOD down to around 0.5mg/ml.

References

EP04.03.22
Deep-Learning-Enabled On-Demand Design of Chiral Metamaterials Wei Ma, Feng Cheng and Yongmin Liu; Northeastern University, Boston, Massachusetts, United States.

Chirality refers to the structural property of an object that cannot be superposed onto its mirror image. Due to its universal existence in nature, chirality has attracted immense research interest with important applications in spectroscopy, sensing, imaging, and pharmaceutical synthesis. However, limited by the small electromagnetic interaction volume, the chiroptical response of natural materials is usually very weak and thus difficult to be detected with high sensitivity. The advent of metamaterials offers an elegant and effective solution to this problem. So far, various intrinsic and extrinsic chiral metamaterials have been demonstrated.[1] Although a set of symmetry requirements derived from Jones matrices can guide the design of chiral metamaterials,[2] these guidelines are insufficient when we want to quantitatively design a metamaterial structure given a desired chiral response, or even to simply predict the trend of chiral response as the structure transforms. Currently, the prediction task heavily relies on iterative, time-consuming numerical simulations to solve Maxwell’s equations on a case-by-case basis, while the retrieval task remains extremely challenging with no general close-form solutions. Inspired by the remarkable progress and success of the deep learning technology in processing images, speech and videos, very recently we developed a purpose-designed deep learning architecture to automatically model and optimize three-dimensional chiral metamaterials.[3] Different from numerical optimization approaches, data-driven methods based on deep learning can represent and generalize complex functions or data, to uncover unknown relations among a huge number of variables. The proposed deep-learning model is composed of two bidirectional neural networks aiming to solve three basic tasks simultaneously. In the forward modeling, it is a fast prototyping tool with high accuracy comparable to numerical simulations, to predict the full optical responses of a chiral structure. On the other hand, given the full optical responses, the network can be used to retrieve the geometric parameters of
the chiral meta-atom to solve the inverse problem. Moreover, starting from some basic requirements on the frequency, amplitude and polarity of the circular (nonlinear) mode, the deep model can produce suitable geometric parameters of the meta-atom. Our results demonstrate that such a data-driven model can be applied as a very powerful tool in studying complicated light-matter interactions, and accelerating the on-demand design of novel nanophotonic devices, systems and architectures for real-world applications.

References

EP04.03.23
Metasurfaces Enabled by Locally Tailoring Disorder in Phase-Change Materials Martin Hafermann, Philipp Schöppe, Jura Rensberg and Carsten Ronning; University of Jena, Jena, Germany.

Phase-change materials, such as Ge,Sb,Te (GST), exhibit drastic changes of their optical and electrical properties, which is related to different bonding mechanisms in their respective crystalline and amorphous states. This is not only already used in non-volatile memristors and optical data storage devices, but is also of enormous interest for optical metasurfaces. Other than applying a heat stimulus, such as thermally, optically or electrically, to induce the change of state, we demonstrate that ion irradiation can be used to trigger the phase change from crystalline to amorphous utilizing the creation of irradiation defects.

First, we performed homogenous ion irradiation of thin GST layers. Crystalline and amorphous phases coexist after low ion fluence irradiations, because of the statistical nature of ion irradiation. Thus, homogeneously irradiated GST has gradually tunable optical properties with increasing ion fluence, and thus behaves like a disordered metamaterial. This new degree of freedom will open new horizons: the combination of conventional metasurfaces made of noble metal antennas with GST as a switchable dielectric will thus be expanded by gradually tunable optical responses of such systems.

Additionally, we used a focused ion beam system to irradiate a thin GST layer in defined areas with structure sizes down to 100 nm, which is below the diffraction limit of direct laser writing. The local triggering of the phase change in sub-wavelength dimensions can be used to design metasurfaces operating in the near-IR. Because of the simplicity of our approach, we can easily create optical elements that can be reconfigured and inherently flat. We will demonstrate the design and characterization compared with FDTD simulations of our optical devices, e.g. reflector polarizers, Fresnel zone plates and beam steerers.

EP04.03.24
Applicability of Effective Medium Approximation for Hyperbolic Metamaterials with Period 20 Times Smaller than the Wavelength of Light Anubhav Sukham1, Osamu Takayama1, Maryam Mahoodi2, Andrei V Lavrinenko1 and Radu Malureanu1;1Photonics Engineering, Technical University of Denmark, Kgs.Lyngby, Denmark; 2Laser and Plasma Research Institute, Shahid Beheshti University, Tehran, Iran (the Islamic Republic of).

Hyperbolic metamaterials (HMMs) [1] consisting of alternating dielectric and metal layers are playing a key role in the field of nanophotonics due to its wide range of applications in super resolution [2], bio sensing [3,4], enhancing spontaneous decay rate [5]. To realize HMMs in the visible to near-infrared regime of operation, gold is a practical plasmonic material due to its good optical properties and high chemical stability. In these wavelength range, the thickness of the metal layer is generally between 10 and 20 nm [6,7]. However, gold does not adhere well onto oxides or Si, thereby leading to discontinuous and rough films for thicknesses below 15 nm. This imposes the need of an adhesion layer, most commonly Ti or Cr. Recently our group has shown that silane based adhesion layer (3-Aminopropyl)trimethoxysilane (APTMS) eliminates the need for metallic adhesion layers and it allows the existence of surface plasmon modes with properties similar to the theoretically predicted calculations [8]. In this work, we have successfully fabricated and characterized structures composed of Au and alumina multilayers with up to 10 layers of Au. The gold and alumina layers were 10 nm thick, thus allowing for hyperbolic dispersion in the visible to near-infrared range. APTMS adhesion layer was used on each interface between Au and alumina to provide better adhesion and therefore to obtain high quality smooth layers. The Au and alumina layers were fabricated using sputtering and atomic layer deposition techniques, respectively. The use of these techniques helps to obtain a high quality HMMs with a RMS roughness of 0.80 nm after the tenth period. Using these structures, we show that the effective medium approximation (EMA) can be used for structures with as little as 4 periods. The optical characterization shows very good agreement with the theoretically predicted EMA after 4th period and onwards. As a quantitative measure, we calculated the mean squared derivation (MSD) of the measured reflectance compared to the EMA predicted one. After the 4th period, the MSD is below 4%.


EP04.03.25
Transmission Enhancement of Subwavelength Metasurface Lens by Tapered Nanostructure Ya Sha Yi, Mao Ye, Dachuan Wu, Wei Guo and Yueheng Peng; University of Michigan, Dearborn, Michigan, United States.

Metasurface microlens is one of the emerging planar micro-optical devices with great potential in a variety of applications. Among this field, high refractive index contrast nanostructures show great advantages in areas such as spectral modification of optical wave front. These advantages have enabled the microlens to be designed in a scale ranging from micrometers to several millimeters with focus size less than a micrometer. Based on the subwavelength nature of phase shifters, the physical realization of the microlens relies on nanofabrication techniques. To be specific, it can be either fabricated through reactive ion etching (top-down process) or deposition then lift-off (bottom-up process). Despite the difference in the process details, both of the two techniques have one common challenge that it is extremely difficult to fabricate structures with a high aspect ratio (e.g., a ratio higher than 5:1 thickness versus width). For planar grating lens that is designed under linearly polarized incidence (e.g., utilization of propagation phase, not Pancharatnam–Berry phase), the different phase shift is created by altering the effective refractive index. To achieve enough phase shift in visible wavelength with limited thickness (e.g., low aspect ratio), researchers have looked into high refractive index materials such as GaN and TiO2. While high refractive index materials are enabling phase shifters more phase shift with comparatively low aspect ratio, their transmission may experience a significant drop. To design an optimum planar microlens, one should either increase the phase coverage of low-index material nanostructures or increase the transmission of high-index material nanostructures. While the most effective way of increasing phase coverage of nanostructures is to increase its thickness (increase single-mode propagation length inside the structure), this idea may not be practical, as we already approaching the limit of current
In this work, we have discussed possible transmission enhancement mechanisms and their feasibilities with the application of planar microlens. In addition, we have proposed the subwavelength-tapered nanostructure to enhance the transmission of TiO2 nanostructure as phase shifters of metasurface lens under the linearly polarized light. The enhancement effect is then numerically demonstrated.

**EP04.03.26**

**Achromatic Subwavelength Metasurface Lens Over Whole Visible Bandwidths**

Ya Sha Yi, Miao Ye, Dachuan Wu, Yuecheng Peng and Wei Guo; University of Michigan, Dearborn, Michigan, United States.

Metasurface lens is one of emerging planar nanophotonic devices that promises unprecedented control of the light at nano scale and have potential applications in highly multidisciplinary fields including imaging, sensing, spectroscopy and photovoltaics. Typically, for concentrating micro grating lens utilizing 0th diffraction mode, a high index contrast grating is used as individual phase shifter to satisfy the lens focusing requirements, as it can provide relatively large phase shift from 0 to 2π so that the light focusing condition can be met. However, the high index contrast gratings give rise to a significant chromatic behavior and achieving achromatic focusing over certain bandwidth turns out to be very challenging. The achromatic focusing capability is critical for a variety of applications, as light sources (e.g., light emitting diodes) or the signal (e.g., photoluminescence and fluorescence signals) has a substantial bandwidth, especially in the visible wavelength range. For refractive lens such as Fresnel lens, achromatic behavior requires hybrid design to compensate for chromatic loss, thus significantly increase the device’s complexity and cost. For emerging micro lens designed based on subwavelength phase shift units, metalens based on circularly polarized incidence is reported with achromatic behavior achieved through special dispersion control of Pancharatnam-Berry phase elements. While for linearly polarized incidence, only several wavelengths can be achieved in telecommunication range, lens with a notable focal shift or very narrow bandwidth has been achieved.

In this work, we have demonstrated the achromatic all-dielectric metasurface lens covering the whole visible wavelength based on relatively low index contrast gratings. Supported by the unique chromatic phase shift of polymer nano structure, we are able to demonstrate a broadband subwavelength achromatic micro lens which can cover 250 nm of visible bandwidths (from 435 nm to 685 nm) with focal shift less than 5% with linearly polarized incidence. Our work is a critical step further to achieve the promises made by the flat metasurface lens that is comparable with image qualities obtained by the commercial objective.

**EP04.03.27**

**Dielectric Metasurfaces with the Kerker Effect as Narrowband Absorbers in NIR**

Chi-Yin Yang1, Jhen-Hong Yang2, Zih-Ying Yang1, Zhong-Xing Jhou1, Viktoria Babicheva1 and Kuo-Ping Chen1; 1National Chiao Tung University, Tainan, Taiwan; 2Arizona State University, Tempe, Arizona, United States.

High-refractive-index (HRI) dielectric metasurfaces have attracted a lot of attention recently. Silicon is one of feasible HRI materials that has been widely used in solar cells, photonic waveguides, and photon detectors. However, the band-gap ~ 1 eV makes the quantum efficiency of silicon low at near-infrared (NIR) wavelengths. In this work, a high absorptance device is proposed and realized by using amorphous silicon nanoantenna arrays (a-Si NA arrays) that suppress backward and forward scattering with engineered lattice resonance with Kerker effect. The overlap of electric dipole and magnetic dipole resonances is experimentally demonstrated. The absorptance of a-Si NA arrays increases 3-fold in the near-infrared (NIR) range in comparison to unpatterned silicon films. Nonradiating a-Si NA arrays can achieve high absorptance with a small resonance bandwidth (Q = 11.89) at wavelength 785 nm.

**EP04.03.28**

**Shaping Terahertz Beams with High-Efficiency All-Dielectric Metasurfaces**

Cheng Zhang1, Erik Isele1,2, Wenqi Zhu1, Jared Strait1, Shawn Divitt1, Amit Agrawal1 and Henri Lezec1; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Due to its wide-bandwidth and transparency to many optically opaque dielectric materials, Terahertz (THz) wave plays a key role in the areas of telecommunications and national security. Moreover, THz technology is also critical for spectroscopic applications in the areas of chemistry, biology, and material science by its ability to measure optical properties (both amplitude and phase) over a broad spectral range simultaneously. However, despite significant progress in the generation and detection of THz radiation over the last couple of decades, one of the current bottlenecks has been the availability of high-efficiency and compact free-space optical elements for spatial manipulation of THz wavefront. As an example, one of the most common (and possibly the only) way to very tightly focus a THz beam is still using bulky hyper-hemispherical Si lenses which also inconveniently requires samples to be in contact with the lens surface. Only in the last few years, there has been significant developments in the ability to arbitrarily manipulate the spatial properties of optical beams in the visible and near-infrared regime using wavelength-scale thickness flat-optical elements, referred to as “metasurfaces”. Metasurfaces are typically composed of laterally shaped nano-scale optical elements (either metallic or dielectric) arranged in a sub-wavelength lattice, and are able impart spatially variant phase (amplitude) modulation to an optical wave-front. They can thereby achieve almost arbitrary control over wave-front shaping (analogous to refractive optics), however only with sub-wavelength-scale-thickness elements. Similar efforts have recently been extended to the THz frequency regime, although high operational efficiencies can only be achieved with reflection-type devices. Both low-efficiency and device operation in the reflection-mode of these devices remains a concern since most practical applications require a transmission geometry and high throughput efficiency.

In this work, we discuss design, fabrication, and characterization of all-dielectric THz metasurfaces exhibiting high throughput efficiencies and operating in the transmission mode. We utilize commercially available high resistivity silicon and fused silica wafers, as well as standard semiconductor manufacturing techniques to fabricate metasurfaces with high-throughput efficiencies, making our approach both practical and readily accessible to other researchers and industry users. As a proof of concept to demonstrate the versatility of our approach, we show high numerical aperture (NA ~ 0.9) focusing of THz radiation as well as generation of cylindrical vector THz beams with metasurfaces.
Silica-Coated Plasmonic TiN Particles for Photothermal Killing of Cancer Cells

Pascal Gieshwend, Simona Conti, Caroline Maake and Sotiris E. Pratsinis

Photothermal therapy (PTT) using plasmonic nanoparticles for cancer treatment is on the verge of clinical application. Titanium nitride nanoparticles[1] are a promising alternative photothermal agent compared to commonly used gold-based systems: Besides lower materials costs by a factor of 10⁵, TiN also exhibits a tunable localized surface plasmon resonance in the near-infrared (NIR) region for spherical particles in contrast to gold, where more complex structures are required to shift the LSPR from visible wavelengths to the NIR.[2]

Little is known, however, of the relationship between TiN particle characteristics and their optical properties in colloidal systems. Here, a detailed study on the synthesis of TiN nanoparticles by nitridation of TiO₂ and their use as PTT agents is reported. Special emphasis is laid on the oxygen content on the particle surface and bulk, which dictates the TiN optical properties. Colloidal suspensions were studied through UV-Vis and with NIR laser irradiation and correlated to particle characteristics. Higher nitridation temperatures and longer residence times are beneficial for increased NIR light absorption, while too high temperatures lead to aggregation of particles and deteriorated optical properties. This was overcome by the use of SiO₂-coated TiO₂ nanostructures as a starting material: The resulting SiO₂-coated TiN particles exhibited increased plasmonic properties compared to bare TiN, which was attributed to reduced plasmonic coupling effects. The optimized SiO₂-coated TiN had a photothermal efficiency of 58.5% and mass extinction coefficient of 31.5 Lg⁻¹cm⁻¹, outperforming commercial gold nanoshells that are used in clinical trials. Finally, the potential of SiO₂-coated TiN for PTT was successfully demonstrated in vitro by controllably killing HeLa cells.

[1]: Guler U, Naik GV, Bolltasseva A, Shalaev VM, Kildishev V. Performance analysis of nitride alternative plasmonic materials for localized surface


9:15 AM EP04.04.05
Modification of Chemical Reactivity via Vibrational Strong Coupling Woonmi Ahn1, Igor Vurgaftman2, Adam Dunkelberger3, Jeff Owratsky3 and Blake S. Simpkins3; 1National Research Council Postdoctoral Associate, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Optical Science Division, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 3Chemistry Division, U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Polaritons, bosonic quasiparticles that result from strong photon-exciton coupling inside microcavities, have shown unique non-linear quantum phenomena such as Bose-Einstein condensation, superfluidity, and enhanced conductivity. Less well-known but equally intriguing is the strong coupling of molecular vibrations with resonantly-matched cavity modes, also referred to as vibrational strong coupling (VSC). The delocalized nature of hybrid polaritonic states opens up a new exciting route for modifying a material’s physical and chemical character including chemical reactivity. In this talk, we first demonstrate the strong relationship between cavity mode profile and spatial distribution of vibrational absorbers by systematically varying the location of a slab of vibrational absorbers within a Fabry-Perot microcavity. Both experiment and modeling showed a strong dependence of vacuum Rabi splitting on molecular distribution within the cavity, suggesting the possibility of controlling coupling strength, and potentially chemical reactivity, of a given region in the cavity through modification of the cavity field profile. We also examine cavities containing two remotely located slabs of vibrational absorbers that jointly couple to the cavity field and thus increase vacuum Rabi splitting by a factor of ~1.3. Finally, we examine a model reaction in pursuit of chemical reaction rates that can be modulated by VSC in a Fabry-Perot microcavity. Our results will further extend the knowledge of cavity-modified material properties, particularly chemical reactivity, which will have important implications for chemical synthesis and catalysis.


9:30 AM BREAK

10:00 AM *EP04.04.06
Nano-Plasmonic Metamaterials Composed of Self-Assembled Metal Nanoparticles and Their Bio-Application Kaoru Tamada; Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan.

A collective excitation of localized surface plasmon resonance (LSPR) has been studied extensively on 2D crystalline sheet composed of metallic nanoparticles [1]. The particle sheets are fabricated by self-assembly at air-water interface and deposited on solid substrates by Langmuir-Schaefer method. Both the experimental and the FDTD simulation data revealed a unique optical property of the 2D sheet, where the homogeneously coupled LSPR in 2D sheet exhibits not only a significant red-shift of LSPR band but also an additional amplification of electric field at the interface. Recently, a drastic reflection color change of Ag and Au nanoparticle multilayers was found on metal substrates [2, 3]. This phenomenon originates from the peak splitting of extinction spectra due to the electromagnetically induced transparency (EIT), occurring specifically on metal substrates [4]. The layer number dependent light confinement was critical, which resulted in such strong colors.Here the Ag nanosheets act as a nano-plasmonic metamaterial light absorber with a large oscillator strength. These optical data were well reproduced by the calculation with the Transfer-Matrix method by employing the effective medium approximation. This EIT related phenomenon was applied to colorimetric sensing devices, to detect a molecular level of reaction by naked eyes [5]. The 2D crystalline sheet was also an effective tool for high sensitive, high resolution fluorescence imaging of nanoflare [6]. The test experiments of actin filaments-labeled rat basophilic leukemia cells (RBL-2H3) and Paxilin-labeled NIH3T3 cells revealed high axial and lateral resolution even under a regular epifluorescence microscope, which held even better quality compared with the images taken under total internal reflection fluorescence (TIRF) microscopy [7, 8]. This non-scanning type, high speed imaging method will be quite useful to study dynamics of biomolecules.


10:30 AM EP04.04.07
Near Field Thermophotovoltaic Energy Conversion Linxiao Zha1, Anthony Fiorino1, Dakota Thompson1, Rohith Mittipally1, Pramod Sangi Reddy1, 2 and Edgar Meyhofer1; 1Mechanical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Materials Science and Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Heat-to-electricity conversion using solid-state devices is technologically important for electricity generation in remote locations, and waste heat recovery. In thermophotovoltaics, photons radiated from a hot thermal emitter are absorbed by a photovoltaic cell, exciting electron-hole pairs and generating electricity. A very hot thermal emitter is usually required for thermophotovoltaics to operate well. However, the temperature of the emitter is typically relatively low (~1000 K) such as in waste heat recovery, severely limiting the power output. Recent theories have proposed that when the gap size between the emitter and cell is much smaller than the thermal wavelength, the power output can potentially be dramatically enhanced by photon tunneling. Demonstration of such near field thermophotovoltaics has been elusive due to the difficulty in achieving a nanoscale gap between parallel surfaces of the emitter and the cell. In this talk we will describe how we experimentally demonstrated a 40 fold enhancement in power output, compared to the far-field, when the gap size between the emitter and the PV cell is reduced from ~10 µm to ~60 nm. Further, we will describe the dependence of performance on the temperature of the thermal emitter, and the bandgap of the PV cell. Our experimental results are supported by modeling based on fluctuational electrodynamics. Our work allows for systematically studying near field thermophotovoltaics towards high performance.

10:45 AM EP04.04.08
Unity Absorption in PbS Quantum Dots via Critical Coupling for Photonic Upconversion Michelle C. Sherratt, Mengfei Wu, Ting-An Lin, Marc Baldo and Vladimir Bulović; Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.
Solid-state infrared-to-visible photonic upconversion is a promising technique for improving the efficiency of optoelectronic devices such as photovoltaics and image sensors by generating additional above-band gap photons from sub-band gap ones that otherwise cannot be harvested. Previous works have demonstrated upconversion of near-IR (850 nm – 1010 nm) to visible (peaked at 610 nm) light utilizing PbS quantum dot absorbers and rubrene doped with 0.5 volume% of dibenzo[tetraphenyl]perilithene (DBP) as an annihilator/emitter layer. However, one of the primary limitations to realizing efficient devices based on this scheme is the low absorption of thin-film quantum dots in the near-infrared, typically less than 0.5%. In prior work, a 5-fold enhancement of PbS absorption (to ~1.5%) was demonstrated by introducing an Ag back-reflector, enabling an upconversion efficiency of 1.6% as compared to 0.51% as a result of the mirror effect.

In this work, we extend these studies to realize unity absorptance in the PbS quantum dot layer. We design a nanophotonic structure based on a critically coupled TiO₂ photonic crystal slab backed by a SiO₂/SiNₓ Distributed Bragg Reflector (DBR) to enhance the quantum dot absorption at 960 nm by ~200-fold. We assemble our upconversion structure of 5 nm PbS quantum dots/50 nm rubrene/DBP on a 70 nm thick TiO₂ photonic crystal slab infiltrated with spin-on glass (SiO₂). A pitch of 565 nm and hole diameter of 264 nm results in critical coupling to a guided mode in the TiO₂ slab, thereby enhancing the absorption into the PbS layer. By adding an 8-pair lossless DBR of quarter-wavelength SiO₂/SiNₓ (163 nm/123 nm), transmission is fully suppressed, allowing us to realize unity absorption into only the quantum dot layer in simulation. We additionally note that by designing a purely dielectric structure to enhance the QD absorption, reabsorption of the visible-wavelength light emitted by the rubrene/DBP is minimized. This will allow us to significantly improve the overall upconversion efficiency.

References:

11:00 AM EP04.04.09
High Efficient Metallic Heat Sink Supported by Radiative Cooling Photonic Structures
Gil Ju Lee, Se-Yeon Heo and Young Min Song; School of Electrical Engineering and Computer Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of).

The advanced electronic devices such as portable and wearable devices have been widely spread, and the size of these handheld devices have decreased considerably while their power density has increased, therefore raising concerns about self-heating of devices. The undesired heat generation in the small electronics increases the surface temperature compared to skin temperature, resulting in thermal damage to epidermis layer. In addition to skin burn issues, the functionalities of the devices are deteriorated regarding operation speed, working time, and battery life. For the thermal management of these devices, a thin metal layer has been used as a heat sink element based on heat conduction and convection. Although such metallic film provides an excellent heat dissipation capability due to the high thermal conductivity, the thermal reduction path exists only convection effect with air.

Here, we propose the strategy of a high efficient metallic heat sink (HE-MHS) by introducing additional thermal reduction route, i.e. thermal radiation, therefore it boosts the cooling capacity remarkably. The overall configuration consists of a thin-metallic heat sink element and the engineered photonic structures that selectively emit the thermal infrared wave in atmospheric window (i.e. 8 – 13 μm). Aluminum was selected as the candidate of metallic layer for heat sink, with 30 μm-thick thickness allowing flexibility. The selective emitter (SE), which is photonic structure emitting thermal infrared wave, was formed on the metal film and composed of SiNₓ, SiO₂, and polydimethylsiloxane (PDMS). The simulated and measured emissivities were over 70% on average value in the wavelength of 8 – 13 μm.

The cooling performance was characterized with the handheld heater was used. The maximum surface temperature was increased depending on the supplied current to the heater, varying as 0.30, 0.35, 0.40, and 0.45 A, and the resulting temperatures were measured as follows: 1) the heater without the HE-MHS registered 42.3, 52.0, 55.1, and 64.7°C, respectively; 2) heater with the HE-MHS registered 28.1, 30.4, 32.6, and 35.6°C, respectively. This experimental result proves that the passive radiation-based cooling strategy is effective to suppress the heating of small electronics under solar irradiation.

11:15 AM EP04.04.10
Paint-Like Structured Polymer Coatings for High-Performance Passive Daytime Radiative Cooling
Jyotirmoy Mandal, Nanfang Yu and Yuan Yang; Columbia University, New York, New York, United States.

Passive daytime radiative cooling (PDRC) is a highly promising and sustainable way to cool structures ranging from buildings to vehicles, reduce carbon-footprints, and mitigate heat-island effects. Research over the years have yielded many designs for PDRC. On one end are common cool-roof paints, which, while inexpensive and easy to apply on surfaces, lack the high solar reflectance (R) and low long-wave infrared emittance (ε) required for PDRC. At the other end are multilayer photonic structures and metamaterials, which are efficient, but require silver mirrors to reflect sunlight and come as sophisticated and expensive sheets that are difficult to apply on rooftops. Therefore, a radiative cooler with performance comparable to such designs, but with the convenience of paints, remains sought after.

In our presentation, we will describe a simple, inexpensive and solution-based method for fabricating structured polymer coatings with an exceptional PDRC capability. Coatings fabricated by the process are hierarchically porous, which, due to the polymer's lossless behavior in the solar wavelengths and intrinsic emittance in the thermal wavelengths, yields remarkably high, substrate-independent hemispherical R (as high as 0.99) and hemispherical ε (as high as 0.97). The values are among the highest known in literature, and allow even completely exposed coatings to achieve sub-ambient temperature drops of ~0°C and cooling powers of ~96 W m⁻² under strong solar intensities of 800 and 750 W m⁻² respectively. The optical performance surpasses those of state-of-the-art PDRC designs, while the technique offers a paint-like applicability on diverse surfaces by techniques like painting, spraying and dip-coating. Furthermore, the process is compatible with a range of polymers, and can also incorporate dyes to achieve a desirable balance between color and radiative cooling. The performance of the coatings, along with the versatility of the technique, makes it attractive as a practical way to achieve high performance PDRC.


11:30 AM EP04.04.11
Hundred-Fold Enhancement in Far-Field Radiative Heat Transfer Over the Blackbody Limit
Dakotah Thompson1, Linxiao Zhu1, Rohith Mittapally1, Seid Sadat1, Zhen Xing2, Patrick McArdle2, Mumtaz Qazilbash2, Pramod Sangi Reddy1 and Edgar Meyhofer1; 1University of Michigan, Ann Arbor, Michigan, United States; 2Electrical Engineering and Computer Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of).
Recent studies have shown that the radiative heat transfer rate between surfaces separated by nanometer gaps can greatly exceed Planck’s blackbody limit due to evanescent modes which are present in the near-field, i.e. gap separations below the peak thermal wavelength. However, achieving dramatic enhancements in radiative heat transfer in the far-field, when surfaces are separated by gaps much larger than the peak thermal wavelength, has not been explored experimentally. Here, we present experimental work demonstrating that the radiative heat transfer rate between appropriately designed nanostructures can exceed the blackbody limit by two orders of magnitude in the far-field. Our experimental platform comprises of aligned dielectric nano-membranes with embedded thermometers that allow the radiative heat transfer rate between the nano-membranes to be quantified. Large enhancements in heat transfer compared to the blackbody limit were observed for membranes with sub-wavelength thickness over a wide temperature range. The observed heat transfer rates are found to be in good agreement with our calculations based on the framework of fluctuational electrodynamics, which provide additional insights into the far-field radiative heat transfer between nanoscale objects in terms of enhanced emissions and absorption cross-sections in the infrared. This work highlights the potential of employing nano-membranes for controlling thermal absorption, and may have important ramifications for thermal to electric energy conversion.

11:45 AM EP04.04.12
Enhanced Forward Thermal Emission Enabled by Cascaded Particle Phonon-Polaritons Stavroula Foteinopoulou1 and Ganga Chinna Rao Devarapu2; 1ECE, University of New Mexico, Albuquerque, New Mexico, United States; 2Cork Institute of Technology, Bishopstown, Cork, Ireland.

Phonon-polariton materials have been largely overlooked as the material of choice to control infrared light-matter interactions as in bulk form they are near-perfect reflectors. However, recently they have emerged as one of the most prominent candidates for infrared “plasmonics” showing all the capabilities for light-confinement and enhancement as noble metals do in the visible spectrum. In particular, just as noble metal nanoparticles support particle plasmons for visible frequencies, sub-micron-sized particles made of a phonon-polariton material support particle phonon-polaritons which are localized resonances for infrared light. The operational frequency for such particle phonon-polaritons depends on the phonon-polariton material used and lies within its corresponding reststrahlen band in the broader infrared spectrum.

We show here that a judiciously designed micro pyramid array comprising SiC, exhibits a highly asymmetric cascaded coupling effect between such particle phonon-polaritons corresponding to each structural block [1]. We demonstrate how this asymmetric cascaded coupling effect leads to enhancement of thermal emission in one direction and its suppression in the opposite propagation direction [1,2]. We show that this highly asymmetric thermal emission can exist over a broad spectral range and over a wide angular range, of more than 45 deg. from normal incidence. In other words, this SiC platform behaves as a highly efficient forward thermal emitter [3]. This behavior is highly relevant to many application domains of infrared photonics such as one-way THz/infrared sources, thermal management and passive radiative cooling devices.


1:30 PM *EP04.05.01
Analog Optical Computing Using Silicon Metasurfaces Albert Polman; Center for Nanophotonics, AMOLF, Amsterdam, Netherlands.

We present Si-based optical metasurfaces with suitably engineered spatial dispersion that perform mathematical operations on optical input fields in the visible and near-infrared spectral range. The nanopatterned surfaces, made by electron beam lithography and etching, are designed to sustain propagating leaky modes that interfere with a Fabry-Perot continuum to form Fano resonances with a line shape that creates a transfer function in Fourier space corresponding to first or second derivative. We present analytical theory, numerical modeling and experimental data using a broad range of input fields. Second-derivative metasurfaces create efficient edge detection with applications in image recognition as we will show. An outlook will be given for the emerging potential of analog optical computing using optical metasurfaces.

2:00 PM EP04.05.02
Photonic Crystal Fiber Metalens Enabled by Geometric Phase Optical Metasurfaces Jingyi Yang1, Indra Ghimire1, Pin Chieh Wu2,3, Sudip Gurung1, Catherine Arndt1, Din-Ping Tsai2 and Howard Lee3; 1Physics, Baylor University, Waco, Texas, United States; 2Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan; 3Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, California, United States; 4The Institute for Quantum Science and Engineering, Texas A&M University, College Station, Texas, United States.

Optical fiber is a well-established and efficient way to guide and manipulate light1. Although optical fiber is efficient for transmitting light, its functionality is limited by the dielectric properties of the constituent materials. The light exiting an optical fiber is typically diverging. Furthermore, the numerical aperture is determined by the refractive index of the fiber materials. Thus, the light intensity decreases significantly upon exiting the fiber. The emergence of metasurfaces provide the opportunity to tailor light’s properties for advanced light manipulation and to develop novel optical applications. For example, a specific profile using spatially-varied nano-antenna elements allow metasurfaces to control the wavefront of the light enabling novel ultrathin optical components such as flat lenses (i.e., metalens) 2-3. In this work, we experimentally demonstrated an ultrathin optical metalens, cascaded on the facet of large mode area photonics crystal fiber (LMA-PCF), that enables light focusing upon the fiber in the telecommunication regime. Our PCF metalens is designed to have a focal length of 30 µm and numerical aperture of 0.37 at operating wavelength of 1550 nm when fabricated on the core of LMA-PCF with diameter of 25±1 µm. A rectangular groove in the gold nano-layer is employed as a unit element (dimension: 489 nm x 134 nm; period: 602 nm). The large core area of PCF allows more fabricated unit elements (total 1261) on the core while maintaining single mode guiding, thus...
providing a smooth phase profile. To fabricate the PCF metalens, we first deposit a 40nm thick gold layer on the end facet of LMA-PCF by magnetron sputtering and fabricate desired pattern by focused ion beam milling. To verify the focusing effect, we capture the mode profiles along the propagation direction using a z-scan setup that consisting of objective lens, quarter waveplate, linear polarizer, and infrared camera. The right-handed circularly polarized light is launched to the PCF metalens and the left-handed circularly polarized output component is collected. Output light focusing is observed at the focal length of ~25.3 to 28 µm with wavelength between 1500 -1630 nm, which is close our designed focal length of 30 µm. The full-width at half-maximum of our observed focus spot ranges between 2.4 to 2.6 µm. Our maximum operating efficiency is 16.4%, which approaches the theoretically-predicted level for flat metasurfaces. Our integration of metalens and optical fiber will be significant in the miniaturizing of optical fiber devices with multi-functionalities and pave the way for in-fiber optical imaging and sensing applications.


2:15 PM *EP04.05.03
Flat and Flexible—New Multi-Functional Metamaterials for the Far- and Near-Field Nanophotonics Yoichiro Tsurimaki1, Yi Huang1, Marcelo Lozano1,2, Seong Don Hong1,2, Gang Chen1 and Svetlana V. Boriskina1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Tecnologico de Monterrey, Escuela de Ingeniería y Ciencias, Monterrey, Mexico; 3Defense Agency for Technology and Quality, Seoul, Korea (the Republic of).

Emerging nanophotonic applications often rely on the use of 3D nano-structured materials, which require intricate low-throughput fabrication, are costly, and limited to the microscopic device footprints. I will discuss our work on the development of smart multi-functional nanophotonic structures, which can be fabricated by high-throughput techniques without the need for nano-patterning. These include single- and multiple-wavelength super-absorbers with flat surfaces designed via topological engineering of the layered material bulk (1,2), flexible polymer-based materials for solar energy harvesting and passive thermoregulation (3–5), and meso-porous network metamatals for solar-thermal energy harvesting, colorimetric sensing and security (6).


2:45 PM BREAK

3:15 PM *EP04.05.04
Metamaterials at the Extreme, Waves at the Limits Nader Engheta; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

We have been exploring how the “extreme” light-matter interaction can be achieved using specially designed materials and metastructures. Several scenarios have been investigated, including near-zero-index photonic platforms, extreme quantum optics, geometry-independent “flexible” resonant cavities, ENZ electric-dipole levitation, coherent thermal emission, photonic bound states in the continuum, and more. Moreover, we have been working on materials platforms that would achieve functionalities useful for informatics, e.g., materials that “do the math”, structures that “solve equations”, etc. In a separate paradigm, we have also investigating how 4-dimensional metamaterials can give us more functionalities. I will discuss our most recent results for some of the above topics.

3:45 PM EP04.05.05
Harnessing Evanescent Waves by Metasurfaces Lin Li, Bo Xiong and Yongmin Liu; Northeastern University, Boston, Massachusetts, United States.

Evanescent waves are oscillating fields with energy spatially concentrated in the vicinity of an illuminated or emitting object. Evanescent waves are widely exist in nature, ranging from the non-radiative emission of nano emitters (e.g., quantum dots, N-V centers, and fluorescent dyes), to optical surface waves such as surface plasmon polaritons, and to near-field optical waves induced by moving charged particles. Evanescent waves carry rich non-radiative energy and important information about sub-wavelength features of the object. They have been extensively studied in many areas, such as super-resolution imaging/lithography, biomedical sensing, electron-driven light sources and energy harvesting, thanks to their unique spatial confinement properties.

However, the exponentially decaying nature of evanescent waves renders it difficult to capture, extract and engineer the wealth of energy and information that they can carry.[1,2]. In this work, we propose and experimentally demonstrate an innovative method to overcome this fundamental challenge by using a novel metasurface that consists of C-aperture resonators, so that we can efficiently convert evanescent waves to the far field emission. Meanwhile, the phase and polarization of the emission can be well controlled with the metasurface. Both electric and magnetic dipoles are utilized by changing the orientation of the C-aperture resonators[3] to achieve a complete control of the phase and polarization of optical waves. This approach is distinctly different from most previous metasurface works that only utilize electric dipole resonances. As a result, we can manipulate the near-field to far-field radiation with desired functionalities, such as the focusing, holography and polarization switching, without any additional, bulky optical components. In the experiment, we generate evanescent waves with total internal reflection scheme and the evanescent waves are modulated by the designer metasurface. The experimental results rigorously show focusing, holography and polarization switching as the theoretical designs, clearly confirming the new metasurface strategy. Our findings offer a versatile platform to extract and explore the near-field energy carried by evanescent wave and manifest promising applications in integrated optics. It will also further inspire studies related to evanescent waves, such as near-field energy harvesting, electron induced emission, subsurface sensing, and so on.

Reference

4:00 PM EP04.05.06
Magneto-plasmonic Sub-Nanometer-Multi-layer Nanoantennas for the Dynamic Magnetic Chiroptics and Structural Color Evgeniya Smetanina1, Irina Zubritskaya1, Esteban Pedrueza Villalmanzo1, Nicolò Macciaferri2, Paolo Varvassori3,4, Alexander S. Roberts2, N. Asger Mortensen5,6 and Alexandre
Optical platforms enabling the dynamic real-time control of the fundamental properties of light at visible and near-infrared frequencies are the essential components for the future optoelectronic devices. Combining materials with magnetic and plasmonic properties gives a possibility for a simultaneous enhancement of the chiro-optical and magnetic-optical properties [1-4]. Here we examine nanoantennas consisting of noble metal-ferromagnet sub-nanometer multilayers to employ it as an element in magnetically-controlled chiroptical surfaces and in plasmonic color printing. We design a nanodisk antenna comprising 15 interchanging Co (0.5 nm)/Au (1.5 nm) layers and perform a careful tuning of the layers to ease the strong perpendicular magnetic anisotropy [5] and the low magnetic saturation field to ease the magnetic control. By this we reach the magnetization switching at 0.7 Koe with the strong magnetic signal despite the insignificant amount of Co (7.5 nm of pure Co (15 Co layers x 0.5 nm thickness) in the multilayer nanodisk of the total thickness 31.5 nm). We propose using the developed Co/Au magnetoplasmonic element to control with the markedly low magnetic fields the chiroptical transmittance [6] and to be implemented as a dynamic color pixel in the plasmonic color printing. For the latter we show numerically that such Co/Au nanoelement provides a color-selective reflection [7-9] that could be potentially modulated by the external low magnetic fields.

electric dipole and electric quadrupole lattice resonances allows achieving significant reflection suppression and observation of a generalized lattice Kerker effect. Full-wave numerical simulations with a finite-difference time-domain method agree well with analytical calculations based on coupled dipole-quadrupole equations. One can engineer nanostructures of TMDC, transition metal oxides, and many other commonly occurred materials with HIPP to enhance the performance of plasmonic devices based on such HIPP materials.

Acknowledgment: This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. FA9550-16-1-0088.


SESSION EP04.06: Poster Session II: Plasmonics
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP04.06.01
Enhanced Plasmonic Optical Tweezer via Synergistic Effects of AuNPs/ZnONRs Structure So Yun Lee1, Jae Ryoun Youn1 and Young Seok Song2; 1Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); 2Department of Fiber System Engineering, Dankook University, Yongin, Korea (the Republic of).

An enhanced plasmonic optical tweezer is investigated by utilizing hybrid gold nanoparticles/zinc oxide nanorods structure (AuNPs/ZnONRs) and the localized surface plasmon resonance (LSPR) phenomena. The structure is selected based on the numerical prediction which confirms the synergistic effects of AuNPs/ZnONRs on the LSPR-induced near-field enhancement and plasmonic heating. Finally, the plasmonic substrate is fabricated and indeed exhibits enhanced trapping performance compared to a control sample consisting of only gold nanoislands (AuNIs). The 3D numerical simulation of the electromagnetic field (EM) and coupled temperature-velocity fields (T-V) are conducted by using COMSOL Multiphysics®. First, the EM is solved to obtain the near-field enhancement around the nanostructures with the time-independent wave equation. Then, the coupled T-V are solved to obtain the temperature field, temperature gradient and velocity field with the steady-state coupled momentum-energy equations. The hybrid nanostructure was fabricated by the hydrothermal growth of ZnONRs followed by the photochemical reduction of AuNPs on the surface of ZnONRs3. For the trapping experiment, 1 μm PS particle suspension was used and a linearly polarized 532 nm laser of 1 mW was focused on the substrate through a 40×-objective lens. Maximum value of near-field enhancement factor and temperature of AuNPs/ZnONRs increase by about 107 % and about 160 %, respectively, compared to those of AuNIs. Moreover, AuNPs/ZnONRs results in steeper temperature gradient and faster fluid velocity than AuNIs, which are expected to be the main factors for enhancing the particle trapping performance.

The results of the scattered electric field and the pointing vector reveal that ZnONRs guides the enhanced incident light along the nanorod via leaky waveguide modes2. High dielectric constant of ZnO and the nanorod geometry result in efficient dipole scattering at the nanorod surface and wave guiding of the enhanced light, respectively.

In the experiment, the steeper temperature gradient and better multiple-trapping ability of AuNPs/ZnONRs than that of AuNIs are verified. All AuNPs/ZnONRs samples show better particle trapping performance than AuNIs. The material and structural effects of metal-dielectric hybrid nanostructure on LSPR and the plasmonic tweezer performance were investigated. We expect that this study will provide a useful way for designing the power-efficient device in various fields such as photovoltaics and photocatalysis, etc. where they can take advantage of the LSPR-induced photophysical processes.

References

EP04.06.02
Coupling Pyrromethene Dye Excitons to Plasmonic Surface Lattice Resonances Robert Collison2, 3, 4, Jacob Trevino3, Vinod Menon3, 1 and Stephen O'Brien2, 1; 1The City University of New York, New York, New York, United States; 2Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, New York, United States; 3The City College of New York, New York, New York, United States; 4The Advanced Science Research Center, CUNY, New York, New York, United States; 5Electrical Engineering, Columbia University, New York, New York, United States.

For the past ten years, plasmonic surface lattice resonances (SLRs) have been a growing topic of interest for photonic and plasmonic devices. We report on the fabrication of SLR-supporting arrays of aluminum nanodisks on glass, and the coupling of these SLRs to organic dye excitons on arrays coated with dye or dye-doped polymer films. In particular, the interaction of the SLRs with the excitons of the pyrromethene laser dye P580 is examined via angle-resolved transmission, reflection, and photoluminescence spectroscopy. Through variation of the concentration of the dye, the plasmonic particle diameter, and the spacing of the particles in the periodic lattice, the wavelengths of the relevant resonant modes and the Rayleigh anomaly are varied to determine the strength of the interaction between these modes, as well as the wavelengths and dispersions of the resulting SLR-exciton hybrid modes. The effects of coupling between the SLRs of various arrays with dye excitons, including angle-dependent emission, are reported.

EP04.06.03
Large Diffracted Transverse Magneto-Optic Kerr Effect in Magnetoplasmic Crystals Mikko Kataja, Rafael Cichelero and Gervasi Herranz; CSIC-ICMAB, Bellaterra, Spain.

Surface plasmon resonances confine light into subwavelength dimensions which results in a corresponding increase in electric field intensities near plasmonic nanostructures. Phase-matching conditions are exploited to enable nonreciprocal optical propagation and enhanced magneto-optic responses in magnetoplasmic systems [1]. Here we show that exploiting diffraction in conjunction with plasmon excitations adds further versatility and flexibility in
the design of photonic systems. As a testbed we analysed transverse magneto-optic Kerr (TMOKE) responses in magnetoplasmonic gratings etched into gold-cobalt multilayers. The grating coupler was chosen as the simplest system where we can combine the three distinct phenomena: magneto-optics, diffraction and plasmonics. The presence of transverse magnetization modifies the propagative conditions of the SPPs along the grating and lifts the degeneracy between the forward- and backward propagating modes. Angular resolved measurements revealed narrow line-shape plasmon resonances that were accompanied by large magneto-optical intensity effects in the diffracted beams. We show that exploiting plasmon resonances in diffraction gratings allows unexpectedly large diffracted TMOKE responses that exceed 3% - up to one order of magnitude larger than reported diffracted magneto-optical effects in systems where plasmon resonances are not present [2,3]. Our results pave the way towards using magneto-optical modulation of SPPs to build non-reciprocal diffraction components that could be used to control the direction of propagation of light beams.


**EP04.06.04**

**Zirconium Nitride Shells for Plasmonic Cloning of Visible Photodetector Nanowires**

Katherine Hansen1 and Chen Yang2,1; 1Chemistry, Boston University, Boston, Massachusetts, United States; 2ECE, Boston University, Boston, Massachusetts, United States.

One of the most critical challenges to high-performance nanowire (NW) photodetectors is the detectability of weak signals that noise obscures; the signal to noise ratio is critical in nanowire photodetectors due to nanoscale devices typically operating at lower voltages. Cloning is a proposed method to reduce the noise generated due to the probed field being disturbed by light scattered by the photodetector itself. It has been shown that for a silicon NW a gold shell can be engineered to support a polarization vector antiparallel to the original vector of the core, canceling the scattering response and effectively cloning the visible part of the electromagnetic spectrum without affecting the absorption.

Alternative plasmonic materials, such as zirconium nitride (ZrN), have permittivity values similar in magnitude to common dielectric components, an ideal condition for generating an antiparallel polarization vectors in the shell and core, and are in general considered easier for fabrication and integration. Here we propose and study theoretically zirconium nitride plasmonic cloaks as a plasmonic cloak for silicon nanowire photodetectors, using Mie formalism for scattering and absorption efficiency and near-field contours of the electric field. We have predicted ZrN cloaks to produce a significant decreasing the scattering, greater than 10 times compared to a bare wire, over a broad wavelength range for a broad range of shell thicknesses, with the greatest decrease being 28 times at 710 nm. We also predict the ZrN cloak to decrease the absorption of the photodetector across the visible spectrum without significantly decreasing the absorption within the silicon core compared to a bare silicon wire. By decreasing the scattering efficiency while simultaneously increasing the absorption efficiency of the nanowire, a ZrN cloak results in a 300 times increase in the ratio between the absorption cross-section and the scattering cross-section compared to a bare wire, thus making ZrN a excellent cloak better than traditional plasmonic materials.

**EP04.06.05**

**Nanoscale Artificial Plasmonic Lattice in Self-Assembled Vertically Aligned Nitride—Metal Hybrid Metamaterials**

Jiujie Huang1, Xuejing Wang1, Nicki Hogan2, Shengxiang Wu2, Ping Lu1, Zhe Fan1, Yaomin Dai1, Beibei Zeng4, Ryan Starko-Bowes1, Jie Jian1, Han Wang1, Leigang Li5, Rohit Prasankumar4, Dmitry Yarotski6, Matthew Sheldon2, Hou-Tong Chen2, Zubin Jacob1, Xinghang Zhang1 and Haiyan Wang2; 1Purdue University, West Lafayette, Indiana, United States; 2Texas A&M University, College Station, Texas, United States; 3Sandia National Laboratories, Albuquerque, New Mexico, United States; 4Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Nanoscale metamaterials exhibit extraordinary optical properties and are proposed for various technological applications. Here, a new class of novel nanoscale two-phase hybrid metamaterials is achieved by combining two major classes of traditional plasmonic materials, metals (e.g., Au) and transition metal nitrides (e.g., TaN, TiN, and ZrN) in an epitaxial thin film form via the vertically aligned nano composite platform. By properly controlling the nucleation of the two phases, the nanoscale artificial plasmonic lattices (APLs) consisting of highly ordered hexagonal close packed Au nanopillars in a TaN matrix are demonstrated. More specifically, uniform Au nanopillars with an average diameter of 3 nm are embedded in epitaxial TaN platform and thus form highly 3D ordered APL nanoscale metamaterials. Novel optical properties include highly anisotropic reflectance, obvious nonlinear optical properties indicating inversion symmetry breaking of the hybrid material, large permittivity tuning and negative permittivity response over a broad wavelength range, and superior mechanical strength and ductility. The study demonstrates the novelty of the new hybrid plasmonic scheme with great potentials in versatile material selection, and, tunable APL spacing and pillar dimension, all important steps toward future designable hybrid plasmonic materials.

**EP04.06.06**

**Plasmonics-Nanofluidics Hybrid Device—An Ultra-Sensitive Infrared Spectroscopic Platform for Bioanalysis and Study of Nanoconfined Molecules**

Thu H. Le1,2 and Takuo Tanaka2; 1Department of Applied Chemistry, The University of Tokyo, Tokyo, Japan; 2Innovative Photon Manipulation Research Team, RIKEN Center for Advanced Photonics, Wako, Japan.

Infrared (IR) absorption spectroscopy is one of the most powerful analysis tools, as it extracts essential information of chemical bonds and molecular structures in a label-free fashion. However, the low sensitivity which is originated from the intrinsically low absorption cross sections severely limits their practical applications. Plasmonic metamaterials-based IR spectroscopy has emerged as an promising approach that improves the sensitivity by exploiting the localized enhanced electromagnetic field (i.e., hot-spots) in plasmonic materials. This effect, however, is only effective when target molecules are located at the enhanced electromagnetic fields. It is thus of significance to control the spatial overlapping of molecules and hot-spots, yet it is a long-standing challenge.

Here we propose a plasmonics-nanofluidics hybrid device that enables the controllable delivery of molecules into the enhanced field of the plasmon modes. The device consists of a nanofluidic channel with a depth of several tens of nanometers sandwiched between a metal film and a batch of periodic nano square-disks. The structure forms a quadrupole resonant mode that traps the plasmonic energy inside the gap between two metal layers. This feature is exploited for ultra-sensitive detection and quantitative measurement of biomolecules. Furthermore, taking the advantage of precisely controlling the confinement of plasmonic fields inside the nanofluidic gap, we have also succeeded in characterizing the molecular structures of nanoconfined water. The performance of our device in ultra-sensitive detection of molecules and protein in aqueous solution were demonstrated. The device was purposely designed to spectrally overlap with the vibrational modes of the target molecules. When the analyte solution is introduced into the nanofluidic channel, the reflectance spectrum of the device reveals the signals of molecular vibrational modes as distinct peaks in the broad reflectance dip of the plasmonic structure. Our method confirmed the enhancement of sensitivity up to two orders of magnitude, with respect to previous reports.

Our device was also applied to measure the infrared absorption characteristic and elucidate the molecular structures of water confined in a 10 nm gap. It reveals the presence of a strong H-bond network with respect to bulk water, and the scaling behavior of confined water in the several tens of nanometer size regime. This effect is also found not being driven by the interaction with the interfaces; yet the constrained geometry itself promotes the intermolecular interactions of water and results in the modification of the H-bond network.

In conclusion, a plasmonics–nanofluidics hybrid device was proposed and demonstrated by employing top-down fabrication techniques. Our device has
offered an ultrasensitive platform for detection of molecules and in-situ probing of molecules or chemical reactions beyond the nanoconfinement.

**EP04.06.07**

**Versatile Top-Down Magnetoplasmonic Nanocone Optical Antennas**

Richard M. Rowan-Robinson1, Agne Čiučiulkaitė1, Ioan-Augustin Chioar1, Oleg Lysenko2, Matteo Pancaldi3, Paolo Vavassori4, Alexandre Dmitriev5 and Vassilios Kapaklis2; 1University of Gothenburg, Gothenburg, Sweden; 2CIC nanoGUNE, San Sebastian, Spain; 3IKERBASQUE, Bilbao, Spain.

Nanoscale confinement of light with the aid of plasmonics has stimulated research towards a number of future technologies including nanophotoniccircuit,s on-chip micro- and nanosensor arrays, super-resolution imaging and designer flat-optics. Within this field, active plasmonics, for which the optical properties can be tuned in real time by an external stimulus are of great interest. Here, magnetoplasmonics provides a promising avenue for real-time dynamic plasmonic devices with the use of an external magnetic field [1,2].

Here, we use a top-down approach to fabricate large area ordered arrays of magnetoplasmonic nanocone antennas. Using electron beam lithography a nanodiskhard-mask is patterned on the Au/TbCo film. By tuning the mask diameter, either complete or truncated nanocones are produced after the Ar+ ion milling process. The base diameters range between 100 to 200nm with the plasmonic body of Au and TbCo nanocone tip. The latter is ferromagnetic at room temperature exhibiting perpendicular magnetic anisotropy. We characterise the magneto-optical enhancement as a function of wavelength and incidence angle. An enhancement of the Faraday rotation and ellipticity is observed at the plasmon resonance.

Varying the incidence angle alters the contributions of vertical and base plasmon modes of the nanocone antenna, which could enable the generation of circularly-polarized electromagnetic near-fields in the vicinity of the nanocone tip. Preliminary simulations indicate that the nanocone geometry can sustain the input circularly polarisation, with an optical spin, generated at the tip. Note that amorphous TbCo is known to exhibit helicity-dependent all-optical magnetization switching [3]. The combination of the TbCo tip and the Au plasmonic antenna capable of enhancing the opticalspin could therefore pave the way for the plasmon-assisted optical magnetization switching at the nanoscale.

References:

**EP04.06.08**

**Negative Optical Torque Arising from Mesoscopic Assembly of Plasmonic Nanoparticles**

Fei Han and Zijie Yan; Clarkson University, Potsdam, New York, United States.

Novel photonic materials not only rely on the properties of individual components, but also depend on the integration approach and structure of the building blocks. Here we report a new type of material assembly with emergent photonic properties: mesoscopic optical matter clusters self-assembled from silver nanoparticles under laser illumination. These nanoparticles are discrete in space yet behave as a rigid body due to strong mesoscale electrodynamic interactions. The clusters rotate opposite to the direction of the incident beam’s angular momentum, i.e., a negative optical torque behavior. Normal materials, e.g., the individual Ag nanoparticles, will only show positive optical torque. We will discuss the rich experimental phenomena observed in the optical matter system and reveal the mechanism for the emergence of negative optical torque.

**EP04.06.09**

**Electrochemical Doping of Conjugated Polymer Thin Films for Infrared Plasmonic Behavior**

Hemanth Maddali; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

The application of conjugated polymers for various purposes is expanding due to the introduction of pronounced electro-active behavior by doping. Some of these polymers include polyacetylene, polyaniline, polypyrrole, polythiophene as well as their various derivatives. Doping can switch a polymer from an insulator or a semi-conductor to a metal-like conductor and, is crucial for various electronic and optoelectronic applications. In particular, doped conjugated polymers can behave like disordered metallic materials and can exhibit conductivities ranging from ~10 S/cm to ~10,000 S/cm. We hypothesize that the afore-mentioned conductivities could result in a plasmonic frequency similar to that of metals, but in the mid- or far-infrared spectral region. Conventionally, heavily-doped inorganic semiconductors and metals are used as infrared plasmonic materials, but they are energy-intensive to produce due to high process temperatures and vacuum-based deposition. Utilizing conjugated polymers that are solution and room-temperature processable as infrared plasmonic materials would reduce the process energy and associated costs. However, a detailed study is required to prove that highly-doped polymers are suitable infrared plasmonic materials.

In this study, we prepare conjugated polymer (polythiophene) thin films on an indium-tin oxide (ITO) coated glass substrate using spin coating followed by electrochemical doping using tertbutylammonium perchlorate. A three-electrode setup is employed using the polymer-coated ITO-glass as the working electrode, a platinum counter electrode and a non-aqueous reference electrode. There was an immediate change in the color of the films from a bright pink (undoped film) to dark blue (doped film) upon electrochemical doping. The surface morphology of the undoped film was smoother when compared to the doped film which exhibited local micron-sized clusters and increased roughness due to dopant inclusion. The electrical properties are compared between the doped and undoped polythiophene films using four-point probe conductivity measurements. Preliminary measurements show a clear increase in the conductivity because of doping. However, contributions from the underlying ITO must be deconvoluted from the data before conductivity can be accurately quantified. Both transmission and reflection-mode infrared spectroscopy are used to measure changes in the infrared absorption of the doped and undoped polythiophene films and to determine the plasma frequency. A relation between conductivity (controlled by doping concentration) and plasma frequency can be established using the Drude model which allows us to identify the doping concentration required for a maximum plasmonic response. If optimum doping concentrations can be obtained, doped conjugated polymer materials could be a class of low-embodied-energy plasmonic material used for sub-wavelength waveguides, gratings and nano-particles with strong infrared optical responses.

**EP04.06.10**

**Imaging Enhanced Upconversion Luminescence from Single NaYF₄:Yb³⁺,Tm³⁺ Nanoparticles on Plasmonic Substrates**

Anahita Haghighadeh1, Amy Hor1, Jon Fisher1, Paul S. May2 and Steve Smith1; 1Nanoscience and Nanoengineering, South Dakota School of Mines and Technology, Rapid City, South Dakota, United States; 2Chemistry, University of South Dakota, Vermillion, South Dakota, United States.

We use single particle spectroscopic imaging and statistical analysis to assess the plasmonic enhancement of NIR-to-visible upconversion luminescence (UCL) from single B-NaYF₄:Yb³⁺,Tm³⁺ upconverting nanoparticles (UCPNs) supported on substrates consisting of random arrangements of Ag nanowires (NW) and Au nano-cavity arrays. We measure both apparent luminescence enhancement, which is power dependent due to the nonlinear kinetics of energy transfer upconversion (ETU), and the excitation enhancement, defined as the ratio of the excitation intensity needed to produce a given UCL emission,
Plasmonic-based sensors exploit sensitivity of plasmon resonance conditions to the dielectric constant of the local environment. However, the resonances are usually broad; in order to enhance the sensitivity, the presence of sharp features in angular or spectral behavior of the plasmon resonance is very desirable. In our work we explore two approaches, involving such features. All optical approach uses the extra-sharp peak observed in the reflection from gold nanostrips. The reflectivity from the gold nanostrips immersed in an ethanol-water solution demonstrates a very high sensitivity to small variations in ethanol concentrations at the angle of the sharp reflection peak. The second approach involves electrical detection which does not require a bulk optical setup, and is based on strong enhancement and polarity switching of the photo-induced voltages (plasmon drag effect) under plasmon resonance conditions observed in the strongly nanostructured systems. We show that the presence of an additional polymer layer deposited on the top of the structure significantly shifts the angular position of the signal. Further studies are in progress.

**EP04.06.12**

**Strong Coupling Under Gap Plasmon Mode in a Film-Gold Nanopyramid Array Structure**

Suvin Phani Kumar Kasani1, Peng Zheng2 and Nianqiang Wu1;
1Department of Computer Science and Electrical Engineering, West Virginia University, Morgantown, West Virginia, United States; 2Department of Mechanical & Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States.

Development of surface plasmon polaritons (SPPs) based optoelectronic devices is restricted mainly because of a high metallic energy loss and a weak nonlinearity of SPPs. This issue can be potentially addressed by making them work in the strong-coupling regime where the coupling strength outcompetes the energy loss. One way to achieve strong coupling is to couple a nonlinear material such as quantum emitter with the metallic nanostructure. In this work, the nanosphere lithography technique is used to fabricate a large area two-dimensional film-coupled gold nanopyramid array which supports gap plasmon mode. By incorporating a layer of quantum emitters at the gap, strong coupling is demonstrated between quantum emitters and the gap plasmon mode. This study has strong implications in designing state-of-the-art optoelectronic devices.

**EP04.06.13**

**Phosphorus Doped Diamond for Quantum Applications**

Shannon S. Nicley1, 2, 3, Paulius Pobedinskas2, 3, Rozita Rouzbahani2, 3, Sam Johnson1, Ken Haeneri1, 3 and Jason M. Smith1;
1Materials, University of Oxford, Oxford, United Kingdom; 2Institute for Materials Research (IMO), Hasselt University, Diepenbeek, Belgium; 3IMEC, IMEC vzw, Diepenbeek, Belgium.

The negatively charged nitrogen-vacancy (NV) centre in diamond is extremely promising as an optically addressable defect for quantum applications. Only the NV- state can be optically polarised and read out, however NV centres normally undergo photoionised charge-state conversion between NV- and a neutral state. A 532 nm laser pulse can be used to repump the centre into the desired state; but the repumping can also change the electrostatic environment of the NV centre, shifting the optical transition frequency by several linewidths. Improvements in spectral stability have been shown by repumping at 575 nm, however this still relies on laser pumping to maintain the NV state. The recent demonstration of the state-of-the-art in quantum entanglement in diamond, with entangling rates of up to 39 Hz [1] also illustrates the limitations posed by repumping to maintain the NV- state. Of their total ~75.5 μs protocol, ~50 μs is used for checking that the NV remains in the NV- state and is on-resonance, and if the neutral state is detected, an additional 300 μs is needed to repump into the NV-, which can be repeated many times before the entanglement experiment can begin. A novel solution to minimise repumping involves doping single crystal diamond (SCD) material n-type, so excess electrons stabilise the NV- charge state, without initialisation. A recent study [2] using the n-type dopant phosphorus (P) in CVD grown SCD demonstrated NV centres that remained stable in the NV- charge state. The precise control of the P concentration is critical for achieving long spin coherence (T2) times, with T2 = 0.8 ms already demonstrated for P-doped diamond [3]. Achieving controllable levels of P is an area of significant current interest [4-6] and so controlled parameter studies of the growth of P-doped diamond for quantum applications are needed.

We have grown a series of thick SCD samples with varying P/C in the plasma feedgas on (111) oriented Sumitomo substrates in a series of 24 h deposition experiments at 1000 °C. We have also grown a second series of 24 h deposition P-doped growth experiments with 0.5% oxygen in the plasma feedgas with varying concentrations of methane, for comparison of NV properties across a wide parameter space. FTIR and Hall effect results confirm the P-incorporation at the high growth temperature studied (1000 °C). We will present photoluminescence mapping and spectroscopy results, and assess the factors affecting the quality of the grown films for NV- stability and performance, to give strategies for achieving the growth of high quality n-type single crystal diamond for quantum applications.

**References**


**EP04.06.14**

**First Principles Approaches to Strongly Coupled Light-Matter Systems**

Johannes Fleck and Prineha Narang; Harvard University, Cambridge, Massachusetts, United States.
In recent years, research at the interface of chemistry, material science, and quantum optics has surged and now opens new possibilities to study strong light-matter interactions at different limits [1,2].

Combining theoretical concepts from the fields of material science and quantum optics presents an opportunity to create a predictive theoretical and computational approach to describe cavity correlated electron-nuclear dynamics from first principles. Towards this overarching goal, we introduce a general time-dependent density-functional theory to study correlated electron, nuclear and photon interactions on the same quantized footing [3].

In this talk, we demonstrate how Rabi splitting under strong light-matter coupling emerges in the absorption spectra and analyze cavity-modulated molecular motion of CO₂ molecules in optical cavities. Further, we use this novel framework to study how the potential-energy surfaces (PES) of a CO₂ molecule change under light-matter interaction.

Our work opens an important new avenue in introducing ab initio methods to the nascent field of collective strong light-matter interactions.


EP04.06.15
Towards Ab Initio Theory of Ultrastrong Coupling Photonics and Plasmonics
Nicholas Rivera1, Johannes Flick2 and Prineha Narang2; 1Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Applied Physics, Harvard University, Cambridge, Massachusetts, United States.

Recent experimental advances in materials science have engendered the ability to reach ultrastrong coupling regimes of light-matter interactions in the IR-Vis spectral band. The ability to find new ways to create hybrid states of light and matter may allow for new ways to achieve low-loss confinement of electromagnetic energy on the extreme nanoscale, which is critical for the development of optical technologies. To this end, it is critical to study how ultrastrong coupling of light and matter alters the real-space properties of electrons and photons, such as photon mode profiles, which encode the quantum fluctuations of the electromagnetic field, their coupling to matter, and their propagation properties.

Inspired by electronic-structure methods such as Hartree-Fock theory and self-consistent Born approximations, we develop a self-consistent field method for finding ground and excited states of coupled systems of matter and electromagnetic fields. This is the first formalism can allow us to assess the change in both electronic wavefunctions and photonic modes, as well as electronic energies and photonic energies, as a result of ultrastrong light-matter coupling. We apply this method to a relevant model problem in quantum plasmonics: an emitter coupled to a continuum of plasmonic modes in a two-dimensional electron gas such as doped graphene, whose extremely confined plasmonic modes may allow ultrastrong coupling with a single IR emitter.

For an emitter of dipole moment 0.5 e*nm on the order of 1 nm away from the graphene sheet, our method reveals several new features that break with the conventional theory of emitter-plasmon interactions. We find that the well-known scaling of plasmon-induced van der Waals forces for an atom near an electron gas breaks down, even in a local description, due to the strong renormalization of electronic energies and wavefunctions by the plasmonic modes. For an emitter 1 nm away from graphene, the energy gap between two-levels in an emitter can be decreased by over a factor of two compared to the predictions of van der Waals theory.

We further find that for the photons that a treatment of the electromagnetic modes based on linear-response theory with bare emitter states does not accurately predict the dispersion and mode profile of the resulting polaritonic modes, leading to deviations of up to an order of magnitude from linear response theory, due to the aforementioned renormalization of the electronic polarizability and resonance shifts self-consistently induced by plasmonic modes. This implies even in a fully local framework, ultrastrong coupling leads to a breakdown of typical macroscopic electrodynamics treatments that cannot be captured classically.

These results provide not only insight into photon modes induced by ultrastrong coupling, but also qualitatively new effects in light-matter interactions at the extreme nanoscale, distinct from other large-wavevector corrections like quantum nonlocality.

EP04.06.16
Plasmonic Core-Multi-Shell Nanowire Phosphors for Light Emitting Diodes
Amartya Dutta1, Sarath Ramadurgam1 and Chen Yang2; 1Boston University, Boston, Massachusetts, United States; 2Purdue University, West Lafayette, Indiana, United States.

White LEDs (WLEDs) compared to traditional illumination have higher efficiencies, longer lifetimes and are also environment-friendly. Commercial technology uses yellow-emitting cerium-doped yttrium aluminum garnet [(Y1-xCex)3Al5O12 or YAG:Ce] phosphor which is excited by a InGaN-based blue LED. However, such phosphors suffer from the following disadvantages: (1) limited phosphor performance due to thermal degradation, (2) significant backscattering losses, and (3) poor absorption. Current commercial WLEDs have a luminous efficacy around 140 lm/W, with research prototypes showing 170-180 lm/W.

Our work opens an important new avenue in introducing ab initio methods to the nascent field of collective strong light-matter interactions.


Towards Ab Initio Theory of Ultrastrong Coupling Photonics and Plasmonics
Nicholas Rivera1, Johannes Flick2 and Prineha Narang2; 1Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Applied Physics, Harvard University, Cambridge, Massachusetts, United States.

Recent experimental advances in materials science have engendered the ability to reach ultrastrong coupling regimes of light-matter interactions in the IR-Vis spectral band. The ability to find new ways to create hybrid states of light and matter may allow for new ways to achieve low-loss confinement of electromagnetic energy on the extreme nanoscale, which is critical for the development of optical technologies. To this end, it is critical to study how ultrastrong coupling of light and matter alters the real-space properties of electrons and photons, such as photon mode profiles, which encode the quantum fluctuations of the electromagnetic field, their coupling to matter, and their propagation properties.

Inspired by electronic-structure methods such as Hartree-Fock theory and self-consistent Born approximations, we develop a self-consistent field method for finding ground and excited states of coupled systems of matter and electromagnetic fields. This is the first formalism can allow us to assess the change in both electronic wavefunctions and photonic modes, as well as electronic energies and photonic energies, as a result of ultrastrong light-matter coupling. We apply this method to a relevant model problem in quantum plasmonics: an emitter coupled to a continuum of plasmonic modes in a two-dimensional electron gas such as doped graphene, whose extremely confined plasmonic modes may allow ultrastrong coupling with a single IR emitter.

For an emitter of dipole moment 0.5 e*nm on the order of 1 nm away from the graphene sheet, our method reveals several new features that break with the conventional theory of emitter-plasmon interactions. We find that the well-known scaling of plasmon-induced van der Waals forces for an atom near an electron gas breaks down, even in a local description, due to the strong renormalization of electronic energies and wavefunctions by the plasmonic modes. For an emitter 1 nm away from graphene, the energy gap between two-levels in an emitter can be decreased by over a factor of two compared to the predictions of van der Waals theory.

We further find that for the photons that a treatment of the electromagnetic modes based on linear-response theory with bare emitter states does not accurately predict the dispersion and mode profile of the resulting polaritonic modes, leading to deviations of up to an order of magnitude from linear response theory, due to the aforementioned renormalization of the electronic polarizability and resonance shifts self-consistently induced by plasmonic modes. This implies even in a fully local framework, ultrastrong coupling leads to a breakdown of typical macroscopic electrodynamics treatments that cannot be captured classically.

These results provide not only insight into photon modes induced by ultrastrong coupling, but also qualitatively new effects in light-matter interactions at the extreme nanoscale, distinct from other large-wavevector corrections like quantum nonlocality.
Increased local electric field can be created by surface plasmon polaritons (SPPs) excited from Au NPs on c-Si, which enhances light absorption and increases the photocurrent of the solar cell. The Au NPs on the surface of the c-Si wafer act as hotspots to increase the local field strength, thereby improving the performance of the solar cell. The enhancement in photocurrent is observed in CuO/Au NPs/n-cSi compared to CuO/n-cSi from I-V measurements under AM 1.5 illumination by the help of solar simulator. Under consideration of plasmonic effect of Au NPs on bulk c-Si SCs, this enhancement can be resulted in change in absorption within the junction and so that increase in photocurrent response of heterojunction device. The findings on the most suitable plasmonic interface and also to the other kinds of device structures in the ultimate quest for attaining affordable high efficiency SCs.

Spatial Mapping of Multipolar Surface Plasmons in Ti₃C₂Tx MXene Nanosheets with Tunable Energy Distribution

Jehad K. El-Demellawi1, 2, Sergei Lopatin3, Omar F. Mohammed2 and Husnam N. Alshareef4; 1Materials Science and Engineering, King Abdullah University of Science and Technology, Thuwal-Jeddah, Saudi Arabia; 2KAUST Solar Center, King Abdullah University of Science and Technology, Thuwal-Jeddah, Saudi Arabia.

The prospering family of two-dimensional (2D) transition metal carbides/nitrides, known as MXenes, have exhibited a variety of unique optical and optoelectronic properties, making them attractive for many potential sensing and photonic applications. Recently, nanosheets of the most studied MXene by far; i.e., Ti₃C₂Tx (Tₐ denotes surface functional groups such as =O or -F), were shown to exhibit intense surface plasmons (SPs) when excited by electron beams. However, their spatial variation over individual Ti₃C₂Tx nanosheets remains undiscovered. In this work, we used scanning transmission electron microscopy (STEM) combined with ultra-high resolution electron energy loss spectroscopy (EELS) to investigate the spatial and energy distribution of SPs (both optically-active and -forbidden modes) in mono- and multi-layered Ti₃C₂Tx nanosheets. By means of spatially resolved STEM-EELS mapping we were also able to directly visualize the inherent inter-band transition in addition to a variety of SP modes (both transversal and longitudinal), and correlate them with the shape, size and thickness of nanosheets. The independent polarizability of Ti₃C₂Tx nanosheets is unambiguously demonstrated, and attributed to their unusual weak interlayer coupling. This characteristic makes engineering a new class of nanoscale systems possible, where each monolayer in the multi-layered structure of Ti₃C₂Tx has its own set of SPs with distinctive multipolar characters. Furthermore, we probed the tunability of the SP energies by conducting in-situ heating STEM to monitor the change in the surface functionalization of Ti₃C₂Tx through annealing at temperatures up to 900°C. At temperatures above 500°C, fluorine (F) desorption multiplies the metal-like free electron density of Ti₃C₂Tx flakes, resulting in a monotonic blue-shift in the SP energy of all modes. Our results highlight the great potential of Ti₃C₂Tx for photonic applications, ranging from visible to MIR ranges, such as broadband photodetectors and plasmonic waveguides.

Surface-Engineered Plasmonic Nanostructures for Diagnosis and Therapeutic Applications

Qirong Xiong, Derong Lu, Yonghao Chen and Hongwei Duan; Nanyang Technological University, Singapore, Singapore.

The optical properties of plasmonic nanostructures, originating from localized surface plasmon resonance (LSPR), are of tremendous potential across many disciplines spanning chemistry, materials science, photonics, and medicine. The development of plasmonic nanostructures with precisely controlled spectroscopic properties and/or multifunctional characteristics is key to their use in diverse applications. In particular, tailored LSPR of plasmonic nanostructures allows for spatially confining photons at sub-wavelength scales and controlling light-molecule interactions at specific wavelengths. Excited LSPR dissipates energy of incident light by the combination of Mie scattering and absorption-mediated thermal conversion, making plasmonic nanostructures compelling photoabsorbers and imaging agents. This talk summarizes our recent work in developing tailored plasmonic nanostructures and well-defined assemblies that were not easily accessible by traditional colloidal chemistry. We have shown that our strategies based on the use of reactive polymers offers new opportunities in addressing some fundamental challenges in surface enhanced spectroscopy, diagnostic microfluidic biosips, and photothermal therapy.1, 5

Reference

Amplitude-modulated light signals were obtained by the third-order nonlinear optical response exhibited by hierarchical plasmonic nanoparticles interacting in a two-wave mixing configuration. Within this work is described a preparation method for fabricating nanostructured concentric rings samples by rotating nanoparticles in a nanofluid. The processing route is based on the evolution of the free falling of rotating nanoparticles in an ethanol suspension with a strong dependence on the elemental composition and nanoparticle size. Anisotropic bimetallic nanoparticles integrated by gold and platinum or gold and silver were numerically and experimentally analyzed. The nonlinear optical behavior of the resulting concentric rings was explored by employing a Nd:YAG laser system featuring nanosecond pulses at 532 nm wavelength for the measurements. High-Resolution Transmission electronic microscopy, UV-vis spectroscopy and Energy-dispersive X-ray spectroscopy studies were undertaken in order to characterize the samples. The inhomogeneous nature of the nanoparticles gives origin to an optically anisotropic response related to nonlinear optics enhanced by plasmonic excitations. The orientation of the samples produced important changes in the ratio between the real and imaginary parts of the third-order nonlinear optical susceptibility. Gyroscopic properties of the samples confirmed the possibility to control energy transfer effects induced by birefringence and multi-photonic absorption. Nonlinear optical interactions for performing ultrafast all-optical switching and instrument function can be contemplated. The authors kindly acknowledge the financial support from Instituto Politecnico Nacional and CONACYT.

EP04.06.21
Optoelectrically BiFunctional Plasmonic Color Filter Embedded in OLEDs Min Ho Lee, Dong Jun Jeong, Seonil Kwon, Hyunchul Kim and Kyung Cheol Choi; School of Electrical Engineering, KAIST, Daejeon, Korea (the Republic of).

Plasmonics utilizes surface plasmons that are generated when light enters the interface between metal and dielectric materials, resulting in new optical properties not seen in nature. Using plasmonic materials such as metals and dielectrics, various studies have been intensively performed to control optical characteristics. Among them, a plasmonic color filter that selectively extracts light from the visible spectrum by inserting a nanostucture into a plasmonic material has been reported.[1] In plasmonic color filter research, improving the transmission and color reproducibility are the main issues.[1,2] In addition, using a transparent conducting oxide, there was an attempt to produce a plasmonic color filter with good electrical conductivity as well as high transmittance. As a result, plasmonic color filter electrodes (PCEs) that function at the same time as conductive electrodes as well as a color filters have been developed as a new type of color filter.[3]

Most plasmonic color filters have been fabricated through patterning methods such as nano-imprinting or e-beam lithography. In terms of cost and processing time, such patterning methods have disadvantages for large areas; this has limited their application to display devices. However, in our previous research, PCEs were implemented with laser interference lithography, which is beneficial for large area patterning and allows for practical large-area applications such as displays and lightings.

In this study, we first proved the feasibility of fabricating PCES embedded in organic light emitting diodes. Each PCE for red and green light filtering was applied to a light-emitting device, instead of using an ITO electrode, which is used in counterpart devices as an anode. Fabricated devices showed diode operation characteristics, which verifies that PCES performed electrically in a stable manner. Also, the broad electroluminescent spectra in the above devices, ranging from 500nm to 700nm, were selectively filtered into red and green light, demonstrating the optical performance of the PCES.

Consequently, these results confirm that PCES function as color filters and electrodes simultaneously. The optimized PCE structure has a height of within some hundreds of nm. This thin and metal-based structure is advantageous for malleable devices that are flexible, stretchable, and etc. In addition, since PCE is based on metal, it can overcome the drawbacks of conventional color filters, e.g. dyes and pigments, which have poor thermal and chemical stability. Therefore, the PCES in this work, are not simply used to reduce device structure by integrating two functions (color filter and electrode). We expect this work will open new opportunities to develop and expand the use of novel plasmonic nanostructures.

[1] Q. Chen et al., Optics Express, 2010

EP04.06.22
Plasmonic Gold Nanosphonges Thomas A. Klar, Cynthia Vidal, Dmitry Sivun and Calin Hrelescu; Institute of Applied Physics, Johannes Kepler University Linz, Linz, Austria.

The quest for alternative plasmonic materials is vital for further progress in plasmonics-based photonics. Nanostructures, which can act simultaneously as optical detectors, stimulators, or photocatalysts are crucial for many applications in the fields of chemo- and biosensing, electro- and photocatalysis, electrochemistry, and biofuel generation. Plasmonic materials with a huge surface-to-volume ratio as well as a high density of active surface sites and electromagnetic hot spots, are desirable. In many cases, however, a large surface-to-volume ratio is counterproductive due to surface damping of the plasmonic resonances. We will discuss the plasmonic properties of sponge-like, in other words, fully porous, nanoparticles, so-called nanosphonges.1 In such sponges, both the gold and the air phase are fully percolated in three dimensions, providing a huge surface area but still sufficiently sharp plasmonic resonances.

We correlate, on a single nanoparticle basis, their optical scattering spectra (using dark field microscopy) with their individual morphology (using electron microscopy).2 The scattering spectra of such gold nanosphonges depend only weakly on their size and outer shape, but they are decisively influenced by their unique inner percolation pattern, in good qualitative agreement with numerical simulations.

In addition to scattering, we investigate the photoluminescence (PL) from gold nanoparticles due to electron-hole recombination4-5 in the specific case of gold nanosphonges. We find that the polarization anisotropy is much larger in the scattering spectra than in the PL spectra for individual gold nanosphonges. We interpret this finding that the excitation of local plasmons by a plane wave from the far field (scattering) and the local creation of plasmons via electron hole recombination with subsequent radiation to the far field (PL) are not reciprocal. We interpret this finding by the causality principle and the existing of a “plasmonic horizon” of less than 60 nm,3 given by the limited lifetime of plasmons (less than 1 femtoseconds) and by the finite speed of information.


EP04.06.23
Remote Activation of Emission by Surface Plasmon Polaritons Propagating in Silver Nanowires Aneta Prymaczek1, Kamil Wiwatowski1, Karolina Słowski1, Justyna Grzelak1, Joanna Niedziolka-Jonsson2, Dawid Piatkowski1 and Sebastian Mackowski1,2, Nicolaus Copernicus Univ, Toruń, Poland.
Hybrid nanostructures containing plasmonically active metallic nanoparticles exhibit many effects interesting from both fundamental and application perspectives. For instance, silver nanowires (NW) with submicron diameters and lengths of about tens of microns can act as energy propagators, by employing surface plasmons polaritons (SPP). These quasiparticles can not only propagate along a metal-dielectric interface for distances extending tens of microns, but also can remotely activate luminescence of emitters located in the closest vicinity of the NW.

The ability to remote activation of emission is demonstrated using both Stokes and anti-Stokes emitters. For this purpose we constructed a two-objective confocal fluorescence microscope, where the top objective is used for excitation of SPPs in a NW, while the detection of fluorescence is facilitated with the second one. The experimental setup allows for probing both stationary and time-resolved fluorescence of the photosynthetic proteins (Stokes emitters) and up-converting nanocrystals (anti-Stokes emitters).

The results indicate that the efficiency of SPPs propagation and luminescence activation depends strongly on the length of the nanowire as well as polarization of the laser beam. In addition, we show that the substrate affects the efficiency of the remote activation, which is less effective on graphene. Systematic analysis of many nanowires characterized with different lengths allowed to study the influence of the graphene substrate on the damping efficiency, which originates from polariton-graphene interactions. The efficiency of this process is also found to depend on the laser polarization and is more efficient for laser polarized along the nanowire.


Reference: Partially financed by the National Science Centre (Poland) within the projects no 2016/21/B/ST3/02276, 2017/27/B/ST3/02457, 2017/26/E/ST3/00209, and the project 3/DOT/2016 funded by the City of Gdynia, Poland

EP04.06.24
Terahertz Radiation Transport Regimes in Three-Dimensional Disordered Media
Silvia Gentilini1, Neda Ghofraniha1, Claudio Conti1, 2, Mauro Missori1 and Davide Pierangeli1; 1CNR-ISC, Rome, Italy; 2Physics, Università La Sapienza di Roma, Rome, Italy.

The growing interest in Terahertz (THz) radiation in a wide range of applications is due to recent technological advances that have made emitters and detectors available in this spectral range. The THz radiation is particularly suitable for the study of systems, ranging from textiles to biological tissues, whose structural complexity makes unavoidable understanding how scattering affects its propagation [1].

On the other hand the propagation of electromagnetic (em) waves in random media is itself a topic of considerable interest in many research fields, since it can lead to a plethora of phenomena. With respect to standard techniques in the visible range, the detection technology available in the THz spectral range provides the advantage to easily access the amplitude and the phase of the em field.

The samples are made by dispersions of 1 mm diameter Silica spheres in a Paraffin matrix with refractive index nSi=1.95 and np=1.5 respectively, prepared at filling fraction, υ, ranging from 0.05 to 0.5. These dispersions are then solidified in cylindrical molds with 15mm diameters and variable thickness L. We collected the temporal signal E(t) transmitted by the sample over 800 ps at different filling fractions. By taking the Fourier transform of these signals, we can extract the spectral amplitude, E(o), and phase, φ(o), in a frequency range between 0.2 and 2 THz. We analyzed these quantities by following the paradigm [2] of light diffusion in order to explore the various transport regimes of THz radiation.

At low filling fractions, the spectral amplitude E(o) shows signatures of Mie scattering that is gradually washed out by the increasing de-coherence effect introduced by the increasing number of scatterers. In order to provide a quantitative approach to resolve the photon transport regime, we estimate the group delay τg=d[φ(ω)]/dω. This quantity provides the product between the inverse of group velocity and the propagation length L inside the sample. We then compare τg with the phase delay τp obtained as the ratio between the speed of light and the mean refractive index of the samples, τp=λ/2πn. The discrepancy between τg and τp increases for υ >0.1 denoting a transition from a ballistic to a diffusive transport regime. At υ >0.25, τg reaches a plateau, signature of the onset of photon trapping mechanism.


EP04.06.25
High-Contrast Optical Modulation with Asymmetric Plasmonic Metamaterials
Yuyi Feng1, Ruizhe Zhao1, Clayton Nemitz2, Tianyou Li1, Johannes Boneberg2, Deswen Cheng1, Lingling Huang1, Yongtian Wang2, Lukas Schmidt-Mende2 and Paul Leiderer2; 1School of Optics and Photonics, Beijing Institute of Technology, Beijing, China; 2University of Konstanz, Konstanz, Germany; 3Department of Physics and Astronomy, University of North Carolina, Chapel Hill, Chapel Hill, North Carolina, United States.

Metamaterials, artificial media with sub-wavelength structures, have received increasing attention due to their unique properties which cannot be found in nature. In particular, arrays of metallic or dielectric nanostructures with varying sizes and orientations are of great interest due to their ability of modulating the optical wave-fronts in a controllable manner. Here we fabricate a large-scale asymmetric gold nanostructure embedded into an aluminum oxide template on a glass substrate (1.4 cm x 1.4 cm). We show experimentally and theoretically that the orientation of the sample plays a crucial role in the optical response leading to controlled switching between transmitted and stopped light propagation. This could be useful for the future design and fabrication of optical modulators, which have applications in optical information systems.

Reference:

EP04.06.26
3D Tapered Nanofocusing Plasmonic Nanocavity for Probe-Size-Independent Targeted Single-Molecule Detection
Shailabh Kumar1, Haeri Park1, Hyunjun Cho2, Radwanul H. Siddique1 and Hyuck Choo1, 2; 1Medical Engineering, California Institute of Technology, Pasadena, California, United States; 2Electrical Engineering, California Institute of Technology, Pasadena, California, United States; 3Samsung Institute of Advanced Technology, Suwon, Korea (the Republic of)
Enhancement of optical fluorescence has enabled breakthroughs in areas such as fluorescence-driven DNA sequencing, rapid disease detection, and other numerous biological studies. While several plasmonic nanostructures eliciting strong fluorescence enhancement have shown promise for these applications, they have been restricted to detection of small dye molecules due to their shallow and relatively flat 2D electromagnetic (EM) enhancement profile. However, bioassays in general utilize small dye molecules conjugated to larger proteins, and small dye molecules alone are rarely used in research and clinical diagnostics. Therefore, successful application of nanoplasmonics-enhanced bioassays requires that the devices exhibit excellent EM enhancement with a 3D volume that could accommodate molecular probes of all sizes.

Here, we have demonstrated a 3D tapered nanofocusing plasmonic nanocavity for fluorescence enhancement using probes of all sizes and targeted single-molecule detection. Our device focuses propagating surface plasmon polaritons (SPP) into a 3D tapered metal-insulator-metal (MIM) cavity that provides extreme volumetric enhancement for visualization of single molecule fluorescence. We fabricated our device on a silicon substrate with gold and silica layers to form a 3D-tapered Au-SiO₂-Au plasmonic cavity. The plasmonic nanocavity achieves strong EM-field confinement while the channel-like geometry of the nanocavity and attached waveguide provides test-fluid access and host surface functionalization for capturing molecules. A large, spatially uniform plasmonic hotspot plane at the tip of the 3D-tapered MIM gap allowed uniform visualization and molecular-specific capture of diversely-sized molecules diffusing in solution, including single-stranded DNA, streptavidin and anti-biotin antibodies with calculated fluorescence enhancement close to 1500. Appropriately optimizing the tip geometry also allowed individually capturing and detecting single antibody molecules at the tip.

References:

EP04.06.27 Metal-Insulator-Metal Plasmonic Absorber with High Loss Metals and Dielectric Ahmad Khayyat Jafari, Texas Tech University, Lubbock, Texas, United States.

Achieving maximum absorption in a broadband range is one of the main goals of metal-insulator-metal metasurfaces. Meanwhile, decreasing the effective thickness of the device and keeping its configuration as simple as possible are other key criteria. There have been some approaches to attain the highest absorption with the maximum bandwidth. In this research, we demonstrate a new approach for this goal. We use lossy metal plus lossy dielectric as the building blocks of our structure. We expect that these two factors together elevate the absorption level. We expect that our device will have applications as a microbolometer in the mid-infrared region and could also be used as a powerful directional emitter in apparatuses such as Fourier Transform Infrared Spectrometers.

EP04.06.28 Porous Alumina—Building Block of Future Scalable Plasmonic Device, Light Source and Beyond Jinghua Fang; University of Technology Sydney, Ultimo, New South Wales, Australia.

Plasmonic metamaterials offer the unique ability to control subwavelength light propagation, thus achieving unprecedented sensing sensitivity and emerging nanophotonics phenomena. However, fabrication challenges and high losses hamper their applications, especially due to scalability issues. Here we will demonstrate that self-assembly of highly ordered porous alumina as one of best candidates will hold the key to unlocking this potential of scalable plasmonic metamaterials for the cost-efficient, practical devices.

Moreover, due to natural defects existing in porous alumina, formulating these point defects or line defects in this porous alumina will become very attractive as it can achieve integrated nanophotonic systems which require the coupling of emitters to optical cavities and resonators. In this work, we will report that porous alumina as an emitter is enhanced in the deep UV region by its own photonic-like crystal band edge. Also we will demonstrate hybrid systems of gold coated porous alumina in which the Cr³⁺ center emission from porous alumina is coupled to plasmonic nanocavities hence showing a random lasing effect.

Last but not least, I will report on several examples for growing and functionalization of nanometamaterials by exposing porous anodic aluminum oxide templates to a low-temperature plasma. With plasma, our environmentally-friendly process is simple, fast and does not involve any pre-treatment for the samples. This novel fabrication and functionalization technique constitutes another interesting application of alumina templates to different nanometal-materials growth and other possible applications.

EP04.06.30 Polaritonic Hybrid-Epsilon-Near-Zero Modes—Beating The Plasmonic Confinement vs Propagation-Length Tradeoff with Doped Cadmium Oxide Bilayers Evan L. Runnerstrom, Kyle Kelley, Thomas G. Folland, Joshua R. Nolen, Nader Engheta, Joshua D. Caldwell and Jon-Paul Martins, North Carolina State University, Raleigh, North Carolina, United States; Vanderbilt University, Nashville, Tennessee, United States; The Pennsylvania State University, University Park, Pennsylvania, United States; University of Pennsylvania, Philadelphia, Pennsylvania, United States; The Pennsylvania State University, University Park, Pennsylvania, United States.

Polaritonic materials that support epsilon-near-zero (ENZ) modes offer the opportunity to design light-matter interactions at the nanoscale through extreme sub-wavelength light confinement, producing phenomena like resonant perfect absorption. However, the utility of ENZ modes in nanophotonic applications has been limited by a flat spectral dispersion, which leads to small group velocities and extremely short propagation lengths. In this talk, I will describe a strategy to overcome this constraint by hybridizing ENZ and surface plasmon polariton (SPP) modes in doped cadmium oxide epitaxial bilayers. This results in strongly coupled hybrid modes that are characterized by an anti-crossing in the polariton dispersion and a large spectral splitting on the order of 1/3 of the mode frequency. These hybrid modes simultaneously achieve modal propagation and ENZ-mode-like interior field confinement, adding propagation character to ENZ-mode properties. It is additionally possible to tune the resonant frequencies, dispersion, and coupling of these polaritonic-hybrid-epsilon-near-zero (PH-ENZ) modes by tailoring the modal oscillator strength and the ENZ-SPP spectral overlap. PH-ENZ modes ultimately leverage the most desirable characteristics of both ENZ and SPP modes, allowing us to overcome the canonical plasmonic tradeoff between confinement and propagation length.
The ability to confine light now routinely to of order 10 nm\(^3\) volumes enables new functionalities for optoelectronic switching at ultralow energies. We present a range of devices in which an active polymer is sandwiched into nm-scale plasmonic gaps that can deliver fast and reversible actuation. Using the thermo-responsive polymer PNIPAM combined with directed nano-assembly using Au or Ag nanoparticles, allows high densities of nano constructs to be created, that change colour either in response to light or heat. High throughput synthesis allows the scale-up of these actuating nano-transducers (ANTS), opening up video-rate large area display technologies. We show measurements on single ANTs which confirm that n\textsuperscript{th} forces are developed, and discuss their application for optically-driven microfluidic valves. Close-packed films of ANTs act to pump water in and out of permeable membranes using light, and produce a switchable metamaterial. The integration of these devices with DNA origami machines is demonstrated for the first time. We also show that lithium can be optically-pumped in and out of perovskite materials, making light-rechargeable batteries.

References:
Photo-Rechargeable Organo-Halide Perovskite Batteries, Nano Letters (2018); DOI: 10.1021/acs.nanolett.7b05153
Light-Directed Tuning of Plasmon ..Polymerization Using Hot Electrons, ACS Photon. 4, 1453 (2017); DOI: 10.1021/acsphotonics.7b00206
Light-induced actuating nanotransducers, PANAS 113, 5503 (2016); DOI 10.1073/pnas.152409113
fabrication approach in which directed self-assembly of chemically synthesized nanostructured building blocks are used to achieve functional plasmonic units. Here, selective surface functionalization of nanomaterials is combined with physical templating and external stimuli including light and electric field to promote the deterministic fabrication of devices with nanometer precision and uniformity. Through incorporation of mechanically reconfigurable components, we are able to further achieve dynamic tunability of the structures. As an example device, we will discuss precisely defined nanometer-thin plasmonic junctions that can be actively tuned in resonance through induced mechanical reconfiguration.

9:15 AM EP04.07.05
Low-Voltage LWIR Tunable Transmission Filters Leveraging Graphene Plasmons

Thomas Beechem, Michael Goldflam, Michael Sinclair, Isaac Ruiz, Anna Tauke-Pedretti, Joel Wendt and David Peters; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Dynamically tunable infrared filters open pathways to multifunctional optical components needed for hyperspectral applications. Capitalizing upon this technology requires directing the filtered light to a detector. Overwhelmingly, however, tunable infrared filters operate in a reflective geometry that necessitates a complex optical path. Tunable transmission filters, on the other hand, can be placed immediately in front of the detector or can even be monolithically integrated with the sensing element to allow for independent pixel-by-pixel tuning. For these reasons, we have developed wafer-scale tunable infrared filters operating in transmission based on graphene plasmonics that simultaneously offer >75 cm⁻¹ tuning while maintaining >40% transmission and requiring biases less than 10V. This technology is amenable to direct monolithic integration with LWIR detector technologies for which we have developed a proof of concept demonstration.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

9:30 AM EP04.07.06
Gate-Tunable Multifunctional Metasurfaces

Ghazaleh Kafaie Shirmanesh, Ruzan Sokhoyan, Pin Chieh Wu and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

In the last several years, metasurfaces have demonstrated promise to control constitutive properties of light via interaction with nanoscale elements. To date, the functional performance of metasurfaces has typically been fixed at the time of fabrication. However, active control of metasurface properties would enable the realization of novel low-profile optical components, which can be used in numerous technologically relevant applications. These applications include but are not limited to dynamic holograms, focusing lenses with reconfigurable focal lengths, and beam steering, a key requirement for future chip-based light detection and ranging (LiDAR) systems.

In the present work, we report a multifunctional electrically-tunable metasurface, which may act both as a beam steering device and a focusing lens with reconfigurable focal length, depending on the voltage application configuration. The proposed multifunctional metasurface is actively controlled by incorporating a material with voltage-tunable optical properties, into the metasurface. In our work, we use indium tin oxide (ITO) as a voltage-tunable material. First, we experimentally demonstrate an electrical control of the phase of the metasurface unit element at telecommunication wavelengths. By carefully choosing the properties of the ITO and gate dielectric layers, we show that the phase shift of the metasurface unit element can be actively changed from 0° to 300°. Our design enables independent electrical control of each metasurface element via individual application of the DC voltage. Next, using this property, we show that the same metasurface can exhibit multiple functionalities, acting both as a beam steering device and a reconfigurable lens.

9:45 AM EP04.07.07
Schemes for Non-Volatile Phase Shifters for Large-Scale Photonic Integrated Circuits Based on Phase-Change and Shape-Memory Materials

Uttara Chakraborty, Jacques Carolan, Yifei Zhang, Juejun Hu and Dirk R. Englund; 1Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Photonic integrated circuits (PICs) provide a platform to control a large number of electromagnetic modes with high phase stability for applications including beam formation, quantum photonic technologies, and optical neural networks. A central challenge in scaling such applications is the ability to provide, or trim large numbers of phase shifters in a non-volatile fashion to reduce power consumption and enable cryogenic compatibility. For example, to program an arbitrary linear-optics unitary transformation on N input/output modes, it is necessary to set O(N²) phase shifters, a number which can be in the hundreds ([1], [2], [3], [4]). Here, we investigate two schemes for non-volatile phase shifters to solve these scaling challenges in silicon-on-oxide (SOI) PIC platforms. These rely on (1) phase-change chalcogenide glasses and (2) shape-memory ceramics.

1. For phase modulators based on chalcogenides [5], we consider germanium-antimony-selenium (GSSe) deposited over an exposed waveguide section in the SOI PIC platform. We consider the use of built-in silicon heaters to control the phase of the GSSe through tailored heating-cooling curves. As shown previously, there is a strong index difference between the amorphous (n=2.99) and crystalline (n=3.60+0.0398i) states of GSSe [6]. Through eigenmode expansion simulations, we find an effective index shift on the order of 10⁻³ for the fundamental mode of a silicon ridge waveguide, a corresponding length of 8.5 µm required for a π phase shift, and a loss of < 0.3 dB per phase shifter.

2. We also introduce a new concept for phase modulation based on the photoelastic effect in silicon, controlled via strain through nonvolatile actuators. In particular, we propose the use of shape-memory ceramics [7], such as ceria-doped zirconia, to strain SOI waveguides through transformations between the austenite (tetragonal) and martensite (monoclinic) states. We explore this non-volatile phase shifter concept through finite-element simulations based on experimentally measured material properties, and show that the shape-memory effect in polycrystalline zirconia can produce an effective index shift on the order of 10⁻³ for the fundamental mode of a silicon ridge waveguide. A corresponding length of 40.4 µm is required for a π phase shift.

References:

[6] Zhang, Y. et al. CLEO: Applications and Technology (2017), JTh5C. 4
Metasurfaces utilize strong interactions between light and two-dimensional nanostructured interfaces to control light at will, and enable us to break away from the reliance on light propagation by transferring an optical interface into functional devices. In this talk, I will describe my lab’s work on flat lenses and holograms based on metasurfaces. I will show you how we can control phase dispersion, i.e., phase as a function of wavelength, to create metatens triplets that correct both chromatic and monochromatic aberrations. I will describe how we can realize independent and complete control of optical phase and amplitude for multiple colors of light and demonstrate colorful holographic objects with realistic surface qualities.

Stable and Repeatable Multilevel Storage Using Phase Change Photonics

Here, we experimentally demonstrate a single multilevel phase change photonic storage cell with up to 34 non-volatile levels with high stability. Using a Ge\(_2\)Sb\(_2\)Te\(_5\) thin film to tune the transmission of light through a waveguide, we develop a single-pulse method to encode arbitrary storage levels regardless of the previous state of the material. With this technique, we show an order of magnitude reduction in both time and energy consumption which is a significant improvement over previous demonstrations of photonic phase-change memory. Furthermore, we develop three different methods to program multiple levels in the memory cell and investigate influence of different pulse parameters on the process of amorphization/recrystallization. This research is a significant step forward in the development of integrated photonic storage devices, demonstrates the possibility and advantages of all-optical storage network, and provides a potential platform for novel computing architecture like neuromorphic computing.

Reversible Phase Transformation of Silicon Nanoresonator for Optical Memory and Reconfigurable Metasurfaces

Recently we reported laser induced amorphization of silicon nanoparticle and demonstrated its optical response shift. In this presentation, we demonstrate that nanosecond pulsed laser can readily crystallize and amorphize different size of silicon nanoresonator at Mie resonance. Due to the switch of the optical dielectric constant, the resonance peak of nanoresonator can be shifted significantly. Raman mapping and SEM validated the phase transformation can be carried out reversibly. Melt-induced phase transformation of nanostructures usually suffers from the deformation and dewetting process. The first demonstration of reversible phase transformation is enabled by an abnormal geometry pinning effect, where we found the silicon thin disk melts but not dewets. We further demonstrated single “bit” writing and erasing with a sub-diffraction feature size. Combined with motion stage, arbitrary patterns can be written, including structural coloring and optical elements.

Dynamic Plasmonic Displays and Holograms

In this talk, we discuss dynamic plasmonic displays and holograms based on catalytic magnesium (Mg) metasurfaces in the visible range. Through the unique hydrogenation and dehydrogenation between Mg and magnesium hydride (MgH\(_2\)), different information components on the plasmonic metasurfaces become fully addressable in space and can be individually switched on/off. This results in dynamic plasmonic displays and holograms with designated multiple states, giving rise to high-level information control with unprecedented dynamic performance. Our work outlines the inevitable transformation from metasurfaces to metadevices, opening the door to a futuristic research horizon. Such dynamic plasmonic devices will allow for a wealth of applications for high-resolution displays, advanced security labels, high-density data storage and information processing.

Magneto-Optical Bi and Ce-Substituted Terbium Iron Garnet Thin Films for Nonreciprocal Photonics

In this presentation, we demonstrate the reversible phase transformation of a Bi-substituted terbium iron garnet thin film, which exhibits a significant change in optical properties upon cooling. This effect is attributed to the coupling between magnetoelastic and magnetostrictive contributions, leading to a nonreciprocal optical response. The demonstration of this behavior in thin films provides a pathway for the development of compact and efficient devices for nonreciprocal optical applications.
These transparent meta-photodetectors pave a new way for the next-generation transparent on-chip optoelectronic devices. To demonstrate this experimentally, we fabricate deep sub-wavelength arrays of nanowires in c-Si on a sapphire substrate using electron-beam lithography. funded by the City of Gdynia, Poland

Characterization revealed the growth of single phase polycrystalline TbIG films on Si without any secondary phases. Faraday rotation of TbIG/Si films measured at a wavelength of 1550 nm was ~600°cm⁻¹ and the spectral dependence of the Faraday rotation, optical absorption and refractive index was characterized. The Faraday rotation can be increased significantly by Ce or Bi substitutions in the garnet. The sidewall growth of doped TbIG films on SOI waveguides was investigated for fabrication of TE mode isolators. Moreover, performance of these garnets in lithographically patterned TE and TM mode on-chip optical isolators based on ring resonators and Mach-Zehnder interferometers have also been studied.

KEYWORDS: magneto-optical garnets, terbium iron garnet, optical isolators, magneto-optics, sidewall growth.

In this communication we use plasmonically active silver nanowires (AgNWs) as building blocks of an ultrasensitive sensing platform for single photodetective proteins. The nanowires were synthesized by wet chemistry and have diameters and lengths around 100 nm and 50 μm, respectively. For achieving enhanced functionality, we attach biotin molecules to their surface. Next they were deposited on a glass substrate, forming thus a sensor chip. The sensing potential of the nanowires was tested using Peridinin-Chlorophyll-Protein (PCP) equipped with a streptavidin linker. It is important to realize that PCP is roughly 4 nm in size, which is much less than diameters of the AgNWs. Upon depositing AgNWs on a glass surface, we first determine their positions using transmission mode of a wide-field microscope. Next, a 2 μl droplet of protein solution was deposited on the substrate with simultaneous acquisition of fluorescence images of the same sample area. The concentration of the protein was changed from millimolar down to picomolar in order to determine the limit of detection. Using this approach, we are able to monitor protein attachment to AgNWs in real-time. For highly concentrated sample the attachment is so efficient that within couple of seconds the nanowires are flaring, forming thus a distinct contrast to the background. Careful analysis shows that this contrast originates not only from the presumably higher concentration of the PCP complexes on AgNWs, but also from strong plasmonic enhancement of the PCP emission. Both effects are crucial for detecting the emission of single PCP complexes when the concentration of the sample deposited on the substrate is reduced by 6 orders of magnitude. In fact, we are able to observe single protein attachment to AgNWs in a real-time mode.

We analyzed the influence of several key factors that determine the detection efficiency of our platform. These include: surface coverage by AgNWs, acquisition parameters, and additional functionalization of the substrate itself. The approach presented here is rather universal and can be applied for detecting variety of analyte molecules with essentially ultimate sensitivity.

Research was partially financed by the National Science Centre (Poland) within the OPUS grant no 2016/21/B/ST3/02276 and the project 3/DOT/2016 funded by the City of Gdynia, Poland

1:45 PM EP04.08.02
Plasmonic Sensor of Single Photodetective Proteins Karolina Sulowska¹, Joanna Niedziolka-Jonsson² and Sebastian Mackowski¹, ³; ¹Nicolaus Copernicus University, Torun, Poland; ²Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland; ³Baltic Institute of Technology, Gdynia, Poland.

In this communication we use plasmonically active silver nanowires (AgNWs) as building blocks of an ultrasensitive sensing platform for single photodetective proteins. The nanowires were synthesized by wet chemistry and have diameters and lengths around 100 nm and 50 μm, respectively. For achieving enhanced functionality, we attach biotin molecules to their surface. Next they were deposited on a glass substrate, forming thus a sensor chip. The sensing potential of the nanowires was tested using Peridinin-Chlorophyll-Protein (PCP) equipped with a streptavidin linker. It is important to realize that PCP is roughly 4 nm in size, which is much less than diameters of the AgNWs. Upon depositing AgNWs on a glass surface, we first determine their positions using transmission mode of a wide-field microscope. Next, a 2 μl droplet of protein solution was deposited on the substrate with simultaneous acquisition of fluorescence images of the same sample area. The concentration of the protein was changed from millimolar down to picomolar in order to determine the limit of detection. Using this approach, we are able to monitor protein attachment to AgNWs in real-time. For highly concentrated sample the attachment is so efficient that within couple of seconds the nanowires are flaring, forming thus a distinct contrast to the background. Careful analysis shows that this contrast originates not only from the presumably higher concentration of the PCP complexes on AgNWs, but also from strong plasmonic enhancement of the PCP emission. Both effects are crucial for detecting the emission of single PCP complexes when the concentration of the sample deposited on the substrate is reduced by 6 orders of magnitude. In fact, we are able to observe single protein attachment to AgNWs in a real-time mode.

We analyzed the influence of several key factors that determine the detection efficiency of our platform. These include: surface coverage by AgNWs, acquisition parameters, and additional functionalization of the substrate itself. The approach presented here is rather universal and can be applied for detecting variety of analyte molecules with essentially ultimate sensitivity.


2:00 PM EP04.08.03
Transparent Meta-Photodetector for Visible Light Qitong Li¹, Jorik Van de Groep¹, Yifei Wang¹, Pieter G. Kik¹, ² and Mark L. Brongersma¹; ¹Stanford University, Stanford, California, United States; ²University of Central Florida, Orlando, Florida, United States.

Extraction of multidimensional information carried by optical beams has a wide range of applications including photography, optical communication, and augmented reality. To date, photodetector systems based on homogeneous materials have limited abilities to measure more complex information beyond light intensity distribution, since these systems typically exhibit limited sensitivity to the polarization, wavelength, or phase of the incident light. Moreover, extracting desired information from the broadband optical signals is necessary for both the broadband and high-speed photodetectors. As a result, photodetectors with polarization- and wavelength sensitivity are combined with a polarization-insensitive anti-reflection at designed wavelengths in a single-layer structure. To demonstrate this experimentally, we fabricate deep sub-wavelength arrays of nanowires in c-Si on a substrate using electron-beam lithography. The NWs are 110 nm high, and the widths are 30 nm, 55 nm, and 110 nm for efficient photodetection and suppression of reflection of blue, green, and red light, respectively. The measured reflection at resonant wavelengths is as low as 2%, with a transmission /reflection ratio larger than 40. Spectrally-resolved photocurrent measurements show a clear single peak at the three design wavelengths, behaving effectively the same as RGB color filters in front of a bulk Si substrate. The measured photocurrent ratio peaks are 2.4 at 470 nm (B/G), 2.1 at 540 nm (G/R), and 4.9 at 680 nm (R/B) with a bandwidth of ~80 nm, enabling color detection. Finally, to improve the spatial homogeneity of photocurrent generated in the NWs, we fabricate a Si/ITO inter-digitated photodetector with ITO contacts sitting between Si NWs. The device optically functions as a NW array but electrically behaves like a homogeneous film because photo-excited charge carriers are extracted transversely across the NWs. The spatially-resolved photocurrent measurement shows only 10% signal fluctuation over 80% device area, revealing a reliable detection process for real applications. Altogether, these results demonstrate the first single-layer and single-material detection system which can detect color, polarization as well as intensity information in the whole visible regime. A 60% overall average transmittance is observed experimentally, enabling in-situ beam monitoring applications. These transparent multi-photodetectors pave a new way for the next-generation transparent on-chip optoelectronic devices.

2:15 PM EP04.08.04
Tamm Plasmon Polariotons in Emitters and Sensors Zhi-Ying Yang¹, Satoshi Ishii², Takahiro Yokoyama², Thang Duy Dao², Mao-Guo Sun¹, Pavel S. Pankin³, Ivan V. Timofeev³, Tadaaki Nagao² and Kuo-Ping Chen¹; ¹National Chiao Tung University, Tainan, Taiwan; ²National Institute for Materials Research, Tsukuba, Japan; ³National Institute of Materials Research Science, Tsukuba, Japan.
Photonic Solutions for Stable Laser Beam Propulsion

The stability of the laser beam during the entire acceleration phase is regarded as one of the major obstacles to realizing laser-propelled spacecraft technology. In this work, we provide a comprehensive study of dynamical stability and consider several shapes that may be good candidates for stable beam riding. We analyze stability maps and basins of attractions for a range of beam intensity profiles and sail shapes which satisfy the stability criteria. We further find designs with the use of real materials, such as Si and SiO2, that provide suitable optical properties in the infrared frequency range and which satisfy the stability criteria. Then, we consider the mechanical stability of the sail by relaxing the assumption of sail rigidity. We present first-order finite-element simulations of the thermal and mechanical behavior of free-flying sails undergoing optical acceleration. Hence, for the sail shapes and beam profiles identified in our stability analysis, we study numerically the whether the sail materials are capable of maintaining their shape under intense laser acceleration, and consider methods of shape reinforcement such as structural framing and spin-stabilizing. We analyze conditions and thresholds for materials stiffness that are required for stable sail beam riding.

2:30 PM BREAK

SESSION EP04.09: Light Driven Effects
Session Chairs: Jeremy Munday and Nanfang Yu
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 206

3:30 PM *EP04.09.01
Revisiting the Photon-Drag Effect in Thin Metal Films Henri Lezec1, Glenn Holland1, B. Robert Ilic1, Cheng Zhang1,2, Wenqi Zhu1,2, Amit Agrawal1,2, Domenico Pacifici1,2 and Jared Strait1; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2Maryland NanoCenter, University of Maryland, College Park, Maryland, United States; 3School of Engineering, Brown University, Providence, Rhode Island, United States.

Current flow in metal films can be induced by the photon momentum carried by an obliquely-incident electromagnetic wave, a phenomenon known as photon drag. The prevailing intuition for the sign of this current assumes that the absorbed light transfers momentum to the free electrons of the metal, either directly or indirectly via plasmon excitation, ultimately generating electron flow in the direction of the in-plane incident photon momentum. However, the direction of this photon-drag (PD) current, has been reported to puzzlingly vary with polarization state, surface morphology and excitation of surface plasmons [1,2]. In particular, measurements to date have typically been carried out with the illuminated surface facing ambient air, yielding, for smooth films, PD currents of opposite sign for illumination with s- and p-polarization, respectively, where only the sign in the p-polarized case is consistent with the standard hypothesis of free-electrons pushed in the direction of the incident momentum. Here, we demonstrate that for smooth metal films (including Au, Cu, and Ni-doped Ag) with illuminated surface facing vacuum, the PD current displays the same sign and nearly the same magnitude for both s- and p-polarized incident light, consistent with the expectation that light with different polarization states carries the same momentum. However, the shared sign of the observed current is always opposite to that implied by the intuitive model above, requiring reimagination of the microscopic processes of the light-metal interaction. We propose a new model for the PD phenomenon in which the bound electrons of the metal – far more numerous than the free electrons - are the primary recipients of the quantum momentum kicks from the incident light, leading to a net polarization of the metal to which the free electrons respond to yield a PD current of the observed counterintuitive sign. The sign flip of the p-polarized signal upon subsequent exposure of the sample to air correlates with adsorption of ambient H2O molecules, and is proposed to result from generation of an extra polarization field induced by the intrinsic dipole moment of the molecules upon Lorentz-force induced rotation. [1] A. S. Vengurlekar and T. Ishihara, Appl. Phys. Lett. 87, 091118 (2005). [2] N. Noginova, V. Rono, F. J. Bezares, and J. D. Caldwell, New J. Phys. 15, 113061 (2013).

4:00 PM EP04.09.02
Plasmon Drag in Strongly Nanostructured Systems David Keene1, Tejaswini Ronur Praful1, Natalia Noginova1 and Maxim Durach2; 1Norfolk State University, Norfolk, Virginia, United States; 2Georgia Southern University, Statesboro, Georgia, United States.

Giant enhancement of photoinduced electric currents in thin metal films under surface plasmon resonance conditions presents interest for various applications in plasmonic electronics and optoelectronics. In order to better understand the mechanism of the effect and explore possibilities to control and enhance it with nanoscale geometry, we study the photoinduced electric signals in strongly nanostructured systems, such as square-wave profile-modulated silver and gold films. Longitudinal and transverse photoinduced voltages are recorded as a function of incidence angle for various orientations of the grooves and are observed at both p and s polarizations. The angular dependence of the signal is found to have a shape reminiscent of Fano resonance, with a significant enhancement in magnitude in the range of plasmon resonance. A sharp switching of polarity is observed at p-polarization only, corresponding to efficient electron drag in the direction of plasmon propagation at smaller angles and against it at higher angles. Such a behavior is tentatively attributed to a coupling between the propagating surface plasmon polariton and localized surface plasmons excited at the sharp corners of the square-wave grating. Theoretically we estimate the effective forces acting on electrons and compare them with the experiment. We also demonstrate sensitivity of the polarity switching angle to the local dielectric environment, which makes the effect of interest for plasmonic based sensors with electric detection.

4:15 PM EP04.09.03
Photonic Solutions for Stable Laser Beam Propulsion Artur R. Davoyan, Michael D. Kelzenberg, Joeseon Wong, Ognjen Ilic, Cora Went and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Interstellar space exploration requires the development of novel propulsion systems. Among the potential candidates, beamed energy propulsion of ultratrace, nano-meter-thick lightsails is regarded as one of the key candidates for unmanned exploration of neighboring star systems. A high-power phased-array laser capable of producing ~10 GW/m2 illumination intensity will produce enough radiation pressure and thrust to accelerate a gram-scale spacecraft to relativistic speeds (up to ~0.2c). Among the many challenges facing such a propulsion system, dynamic stability of the sail, i.e., the ability to stay atop a laser beam during the entire acceleration phase, is regarded as one of the major obstacles to realizing laser-propelled spacecraft technology. In this work, we provide a comprehensive study of dynamical stability and consider several shapes that may be good candidates for stable beam riding. First we consider a generic scenario of a laser beam interaction with various rigid, perfectly reflecting geometric shapes. We show that certain mutual configurations of beam intensity profile and sail shape may enable dynamically stable solutions. We analyze stability maps and basins of attractions for these regimes. We further find designs with the use of real materials, such as Si and SiO2, that provide suitable optical properties in the infrared frequency range and which satisfy the stability criteria. Then, we consider the mechanical stability of the sail by relaxing the assumption of sail rigidity. We present first-order finite-element simulations of the thermal and mechanical behavior of free-flying sails undergoing optical acceleration. Hence, for the sail shapes and beam profiles identified in our stability analysis, we study numerically the whether the sail materials are capable of maintaining their shape under intense laser acceleration, and consider methods of shape reinforcement such as structural framing and spin-stabilizing. We analyze conditions and thresholds for materials stiffness that are required for stable sail beam riding.
change and crystalline CdS bulk film. Next, artificial engineering of gate-terminal (VGS condition) facilitate to tune and optimize photo-detection

Realistic material employment in the emerging field of metaphotonics, the convergence of plasmonics, metamaterials, and nonlinear optics, requires

absorber, and defective surface passivation a-ZTO (surface) for high-efficiency photo-carrier generation, spontaneous separation, and defect-free transport.

We experimentally demonstrate that an epsilon-near-zero [2,3] material can be used to overcome these long-standing barriers. Specifically, we implement

holograms. Furthermore, holographic materials are bulk crystals and thus not suitable for integrated optics.

The implementation is further complicated by the needs for widely different wavelengths for writing (UV light) and reading (visible or near IR) the

applications of real-time holography have been limited by the slow write and erase times which can be up to a minute for a typical holographic material.

Tuning the Anomalous Optical Dispersion of TiN Films via Si and O2 Dopants

EP04.10.02

Conventional amorphous multi-component metal-oxide semiconductors with high-mobility, large-area processing feasibility, and environmental stability have UV-level wide optical bandgap (> 3 eV), the photoinization of oxygen vacancy (Vo) defects under energetic blue-light spectrum introduces restrictive spectral photosensitivity. However, Vo-defect-induced photocurrent generation under visible-light stimulus has several disadvantages for visible-light detection using oxide photo-TRs: 1) insensitive performance, 2) narrow spectral/une selective color detection, and 3) slow dynamic photosresponse speed and severe persistent photocurrent (PPC) behavior. We designed all-solution-processed multi-stacked metal oxide/chalcogenide semiconductor-based visible-light phototransistors via thermal-activation defect-healing process, multi-stacked functional materials, and chemically-stable stacking. Here, multi-stacked structure consist of high-mobility a-ZTO (interface), high-efficiency visible-light passivated-crystalline CdS (Cc-CdS) absorber, and defective passive surface passivation a-ZTO (surface) for high-efficiency photo-carrier generation, spontaneous separation, and defect-free transport. Here, thermal-activation defect-healing process were performed for defect suppression of hetero-interfaces (ZTO/CdS and CdS/ZTO) with rapid phase change and crystalline CdS bulk film. Next, artificial engineering of gate-terminal (VGs condition) facilitate to tune and optimize photo-detection performance such as photo-sensitivity and dynamic photo-response (photo-rise/dark-recovery) speed.

All-Solution-Processed Metal Oxide/Chalcogenide Hybrid-Structure Based Phototransistor for Full-Color Detection and Fast Dynamic Response

EP04.10.01

Conventional amorphous multi-component metal-oxide semiconductors with high-mobility, large-area processing feasibility, and environmental stability have UV-level wide optical bandgap (> 3 eV), the photoinization of oxygen vacancy (Vo) defects under energetic blue-light spectrum introduces restrictive spectral photosensitivity. However, Vo-defect-induced photocurrent generation under visible-light stimulus has several disadvantages for visible-light detection using oxide photo-TRs: 1) insensitive performance, 2) narrow spectral/une selective color detection, and 3) slow dynamic photosresponse speed and severe persistent photocurrent (PPC) behavior. We designed all-solution-processed multi-stacked metal oxide/chalcogenide semiconductor-based visible-light phototransistors via thermal-activation defect-healing process, multi-stacked functional materials, and chemically-stable stacking. Here, multi-stacked structure consist of high-mobility a-ZTO (interface), high-efficiency visible-light passivated-crystalline CdS (Cc-CdS) absorber, and defective surface passivation a-ZTO (surface) for high-efficiency photo-carrier generation, spontaneous separation, and defect-free transport. Here, thermal-activation defect-healing process were performed for defect suppression of hetero-interfaces (ZTO/CdS and CdS/ZTO) with rapid phase change and crystalline CdS bulk film. Next, artificial engineering of gate-terminal (VGs condition) facilitate to tune and optimize photo-detection performance such as photo-sensitivity and dynamic photo-response (photo-rise/dark-recovery) speed.

Ultrafast Real-Time Holography with an Epsilon-Near-Zero Material

EP04.09.05

Ultrafast Real-Time Holography with an Epsilon-Near-Zero Material M. Zahirul Alam1, Robert Fickler2, Orad Reshef2, Enno Giese1, Jeremy Upham1 and Robert Boyd1,2; 1Department of Physics, University of Ottawa, Ottawa, Ontario, Canada; 1Institute of Optics, University of Rochester, Rochester, Ontario, Canada.

Since the pioneering introduction of holography [1], optical holography has been used for data storage, signal processing, sensing, security, etc. However, applications of real-time holography have been limited by the slow write and erase times which can be up to a minute for a typical holographic material. The implementation is further complicated by the needs for widely different wavelengths for writing (UV light) and reading (visible or near IR) the holograms. Furthermore, holographic materials are bulk crystals and thus not suitable for integrated optics.

We experimentally demonstrate that an epsilon-near-zero [2,3] material can be used to overcome these long-standing barriers. Specifically, we implement an efficient and broadband real-time holographic system using a highly nonlinear epsilon-near-zero material [4 - 7] which is four orders of magnitude thinner and which exhibits up to twelve orders of magnitude larger refresh rate than those of a typical holographic material. Our findings have significant implications in ultrafast signal processing and multimode communication.

References:

SESSION EP04.10: Poster Session III: Novel Photonic Materials
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP04.10.01

All-Solution-Processed Metal Oxide/Chalcogenide Hybrid-Structure Based Phototransistor for Full-Color Detection and Fast Dynamic Response Sung Woon Cho; School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Conventional amorphous multi-component metal-oxide semiconductors with high-mobility, large-area processing feasibility, and environmental stability have UV-level wide optical bandgap (> 3 eV), the photoinization of oxygen vacancy (Vo) defects under energetic blue-light spectrum introduces restrictive spectral photosensitivity. However, Vo-defect-induced photocurrent generation under visible-light stimulus has several disadvantages for visible-light detection using oxide photo-TRs: 1) insensitive performance, 2) narrow spectral/une selective color detection, and 3) slow dynamic photosresponse speed and severe persistent photocurrent (PPC) behavior. We designed all-solution-processed multi-stacked metal oxide/chalcogenide semiconductor-based visible-light phototransistors via thermal-activation defect-healing process, multi-stacked functional materials, and chemically-stable stacking. Here, multi-stacked structure consist of high-mobility a-ZTO (interface), high-efficiency visible-light passivated-crystalline CdS (Cc-CdS) absorber, and defective passive surface passivation a-ZTO (surface) for high-efficiency photo-carrier generation, spontaneous separation, and defect-free transport. Here, thermal-activation defect-healing process were performed for defect suppression of hetero-interfaces (ZTO/CdS and CdS/ZTO) with rapid phase change and crystalline CdS bulk film. Next, artificial engineering of gate-terminal (VGs condition) facilitate to tune and optimize photo-detection performance such as photo-sensitivity and dynamic photo-response (photo-rise/dark-recovery) speed.

EP04.10.02

Tuning the Anomalous Optical Dispersion of TIN Films via Si and O2 Dopants Wesley Britton1 and Luca Dal Negro2,3; 1Division of Materials Science and Engineering, Boston University, Brookline, Massachusetts, United States; 2Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States.

Realistic material employment in the emerging field of metaphotonics, the convergence of plasmonics, metamaterials, and nonlinear optics, requires
extensive control of material optical properties, a large nonlinear optical response, and robust mechanical stability. The transition-metal nitride material 
titanium nitride (TiN) has shown promise to fit these requirements at visible wavelengths, however it suffers from a larger than ideal imaginary 
permittivity and limited tunability. In this work, we develop a novel platform based on titanium silicon oxynitride (TiSiON) thin film optical ceramics of 
varying stoichiometry grown by reactive DC and RF co-magnetron sputtering and discuss its linear and nonlinear optical properties. Spectroscopic 
ellipsometry measurements reveal a decrease in imaginary permittivity, a tunable metallic behavior that can be extended to longer wavelengths, and 
evolution towards the value of real permittivity of a single material condition equal to zero at multiple wavelengths (i.e., multiple ENZ behavior). Consequently, we identify a novel class of materials with a double epsilon-near-zero (DENZ) character. It was found that that vacuum post-deposition 
annealing allows for further tuning of these materials’ structural and optical properties. We show that these thermal annealing treatments can largely 
modulate charge carrier concentration by measuring their optical bandgaps as a function of annealing temperature. In addition, XRD and TEM 
measurements were performed to correlate the observed material structure and optical properties. DENZ materials have the potential to be especially 
relevant for advancing the field of optical modulation, and this development of Si compatible materials DENZ materials along with materials with potential 
for a tunable nonlinear response and decreased optical losses in the visible spectrum, will extend the engineering feasibility of implementing integrated 
metamorphic devices. Nonlinear optical characterization based on Z-scan measurements will also be presented.

EP04.10.03

Slow-Light Mesophotonic Waveguides—Theoretical Insights for Practical Designs  Stavroula Foteinopoulou; ECE, University of New Mexico, 
Albuquerque, New Mexico, United States.

Being able to tame the speed and confinement of light is of immense important in a range of current photonic applications, such as on-chip all-optical 
circuitry, photonic neuromorphic computing, higher harmonic signal generation etc. Waveguides that support slow-light propagation have therefore been 
the subject of intense investigation efforts in the last decade. Different designs of mesoscale-patterned features had been realized primarily inspired by 
thoretical calculations relying on time-independent modal analyses.

We discuss here why such analyses are not appropriate for real systems, leading to erroneous predictions for the actual light propagation speed. We will 
show why a theoretical analysis based on the time-evolution of the wave is needed for the proper design of slow-light mesophotonic waveguides that can 
be high performing in the practical realm. In particular, we will present a counterexample demonstrating that when two modes are compared it is actually 
the mode with the higher group-velocity, as predicted from time-independent analysis, that ends-up effectively slowing-down light more. Our results 
contradict the widespread notion that the group-index is generally a good measure of the light’s speed effective slow-down factor in practical waveguide 
systems.

Our results suggest that in order to realize robust platforms for slow-light, waveguiding systems should be designed to exhibit simultaneously a large group 
index and a large modal index bandwidth. These results are important to inspire new slow-light waveguide designs that can break current performance 
limitations, enabling its applicability in optical signal manipulation devices.

[1] S. Foteinopoulou and J. P. Vigneron, Extended slow-light field enhancement in positive-index/negative-index heterostructures, Phys. Rev. B. 88, 

[2] (Invited) S. Foteinopoulou, Frequency-Domain versus Time-Domain analysis of slow-light mesophotonic waveguides: theoretical insights for 

EP04.10.04

Optical Properties of Alq3/TiO2 DBR Structure Processed by Spin Coating Technique  Aith DeSilva1,2, Sarah Nazaret1 and A. G. U. 
Perera2; 1University of West Georgia, Carrollton, Georgia, United States; 2Physics and Astronomy, Georgia State University, Atlanta, Georgia, United 
States.

One-dimensional hybrid Distributed Bragg Reflector (DBR) with high reflectivity is constructed using Tris (8-hydroxy) quinoline aluminum (Alq3) 
molecules and Titanium dioxide (TiO2) nanoparticles via spin coating process. Light emission Alq3 thin film is dominated by excitons. This material has 
been widely used as a superior emitter for organic light emitting diodes. Titanium dioxide (TiO2) is an inorganic semiconductor with a high band gap. 
Photoluminescence (PL) of thin films of Alq3 showed a broad PL peak at 532 nm. In DBR structures, PL quenching is observed but there is no shift in the 
PL peak of the Alq3. The PL quenching is tentatively attributed to energy transfer via sensitization to wide band gap TiO2 layers. The observation can be 
explained using an excitonic model. Fabrication process and optical properties of the structure are presented.

EP04.10.05

Model-Free Precision Control of 808nm Pulses  Brady Simon, Joshua Dupaty and Makhin Thitsa; Mercer University, Macon, Georgia, United States.

We proposed a method for precision control of 808 nm ultra short pulses in Er-doped fluorindate crystals. The infrared laser of 808nm wavelength is 
widely used in medical applications such as laser therapy for pain management, inflammation reduction and orthodontal procedures. Even though its initial 
use was mainly for wound healing and pain relief, the medical applications of low-level laser therapy have broadened to include diseases such as stroke, 
myocardial infarction, and degenerative or traumatic brain disorders. Such medical applications require these laser pulses to be precisely controlled. This 
partial wavelength is also highly applicable as the infrared light source for military night vision targeting tools and weapons. Moreover, it is a 
commonly used pump source for producing other popular wavelengths such as diode pumped 532nm green laser. Frequency up-conversion in rare earth 
doped crystals have been studied extensively. Previously, authors have reported the model based controller design, in which the controller varies and 
controls the pump rate in real time through the pump power resulting in the enhanced emission of 808nm wavelength in Er-doped fluorindate crystals 
under 1.48 μm pump. In model-based design, the performance of the resultant controller depends on the accuracy of the mathematical model used to 
represent the device in the design process. Therefore, this method is sensitive to modeling errors. In this paper a more robust control scheme using model-
free approach is presented. In this recently developed model free approach the controller design is independent of the mathematical model and hence any 
modeling error have no effect on the device performance. Both theoretical analysis of the control methodology and simulation results will be presented.

EP04.10.06

Excitation Intensity and InAs Thickness Dependent Luminescence Properties of Ultrathin InAs Layer in GaAs Matrix  Rahul Kumar, Yurii 
Maidaniuk, Andrian Kuchuk, Samir K. Saha, Pijush K. Ghosh, Satish Shetty, Yuriy Mazur, Morgan E. Ware and Gregory J. Sálamó; University of 
Arkansas, Fayetteville, Arkansas, United States.
Highly strained ultrathin InAs layer in GaAs has attracted much interest because of its use for study of fundamental physics as well as its application in electronics and optoelectronics devices. Recently submonolayer (SML) InAs deposition has been proposed as an alternative method to the extensively used Stranski-Krastanow (SK) mode of quantum dot (QD) growth. Moreover, both theoretical and experimental works have added interested for InAs single quantum well (QW) for efficient excitonic lasing applications. Here, we discuss results from a set of samples containing a single ultrathin InAs layer with varying thickness from 0.5 to 1.4 ML in a GaAs matrix grown by molecular beam epitaxy on GaAs (001) substrate at low temperature and investigated by low temperature excitation power dependent photoluminescence (PL). We will discuss results, including observed asymmetric PL spectra having a low-energy-tail at low and moderate excitation power for non-integral ML samples. We will also discuss the observed linear change in emission energy with InAs thickness a PL line shape from InAs/GaAs heterostructures that is excitation power and InAs thickness dependent. The discussion will be based on the interplay of uncorrelated electron hole pairs, free excitons and localized excitons with excitation power and its effect on the optical properties of the InAs layer.

EP04.10.07
Deterministic Fabrication of Quantum Dots for Quantum Light Sources Using Selective Photocathodo-electrochemical Etching
Ganapathi Subramania, P. Duke Anderson, Arthur Fischer and Daniel Koleske; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Semiconductor quantum dots (QDs) have become particularly important for quantum information science. Due to their atomic-like discrete energy spectrum they can behave as quantum light sources. Such sources operating at room temperature can be invaluable and can be enabled using III-nitride materials due to their large exciton binding energy. Here we demonstrate a quantum size controlled photo-electrochemical etch (QSC-PEC) approach toward the integration and deterministic placement of quantum dots (QDs) within prepatterned nanostructures. An array of III-nitride nanowires containing a single InGaN quantum well is first fabricated using electron-beam lithography (EBL) patterning followed by inductively coupled plasma reactive-ion etching (ICP-RIE). Next, QD is formed within the prepatterned nanowires using a bandgap-selective, wet-etching technique. Here the nanowires are immersed in acidic etch solution with laser illumination of specific frequency above the energy gap of the SQW. The illumination enables the etching of the SQW within the nanowire from the sides until quantum size effects causes increase in energy gap to ultimately stop the etch process, resulting in a quantum dot within the wire. The size of the QD can be tuned by the illumination frequency. Low-temperature microphotoluminescence (μ-PL) measurements of individual nanowires reveal sharp spectral signatures, indicative of QD formation. Further, internal quantum efficiency (IQE) improves an order of magnitude following QSC-PEC etching. Finally, second-order cross-correlation ($g(2)(0)$) measurements of individual QDs exhibit antibunching behavior indicating nonclassical behavior. Our results illustrate an exciting approach toward the top-down integration of nonclassical light sources within nanophotonic platforms.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.


EP04.10.08
Angle-Independent Photonic Pigments by Mie Resonances from Dielectric Colloidal Aggregates
Yu Naoi, Yukikazu Takeoka and Takahiro Seki; Department of Molecular and Macromolecular Chemistry, Nagoya University, Nagoya, Japan.

Photonic pigments, which is color materials using photonic materials, show fadeless colors caused from resonances, scattering and interferences of visible lights. Angle-independent photonic pigments especially are important for application of reflective displays and color materials. In our previous work, colloidal amorphous arrays, where monodispersed colloidal particles form an aggregate with short-range order, were found out as angle-independent structural colored materials under the conditions where a sample is illuminated from all directions. Although they usually appear whitish due to the contribution of multiple scattering of visible lights, we succeeded in taking on brilliant colors of the arrays by adding black particles such as carbon black diminishing the multiple scattering lights. However, the colors from the arrays exhibit angle-dependence under a directional light. We have to seek alternative photonic materials to improve the angle-independence.

Recent studies have revealed that in the reflection spectra observed from colloidal aggregates, the peaks due to different mechanism appear on the lower wavelength side than the scattering peak caused by the aggregates. The positions of the peaks don’t change at all even when changing the irradiation direction of light or the observation direction. These peaks are thought to be due to the phenomena called “Mie resonances”. Mie resonances are known as phenomena that light waves comparable to particle diameter are enhanced by circumnavigating of the light waves in dielectric spherical materials such as silica particles. In this research, we prepared photonic pigments displaying angle-independent colors by Mie resonances.

Silica particles from 200 nm to 500 nm in diameter mixed with carbon black particles to absorb multiple scattering lights are pressed into colloidal aggregates as pellets. In order to evaluate the angle dependence of the color observed from the prepared pellets, diffuse scattering was measured by injecting white light onto the flat surface of the pellets and changing the angle of the detector. The peaks derived from Mie resonances occurs in the visible region, and the pellets become photonic pigments without angle dependence when a colloidal particle having a diameter of 350 nm or more is used. Fine tuning of scattering lights is achieved by just changing the particle diameter, because the scattering lights of Mie resonances shift depending on the particle size. The color saturation of the photonic pigments due to Mie resonances can be controlled by adding amount of carbon black particles.

In summary, we succeeded to prepare angle-independent photonic pigments by Mie resonances even under a directional light. The results are useful for making energy-efficient color materials, optical devices and reflective displays having low viewing angle dependence. We are now investigating the contribution of the aggregation structure of the particles to the color development of this aggregates.

EP04.10.09
CMOS-Compatible Direct Bandgap Light-Emitting Germanium by Design
Linding Yuan, Shu-Shen Li and Jun-Wei Liu; Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China.

The microelectronic integrated circuits (IC) is approaching the physical limits of Moore's Law. The optoelectronic integrated circuit (OEIC) is a promising alternative to continue the Moore’s Law. Complementary-metal-oxide-semiconductor (CMOS) compatible high efficient on-chip optical functionalities has long been pursued for manufacturing monolithic integrated silicon-based photonic. Given the indirect bandgap nature of Si, which precludes the efficient emission and absorption of light, various Si-based systems has been proposed over past four decades. Despite intensive research efforts has been made, yet no applicable group-IV laser has been implemented, which becomes the last roadblock towards the OEIC. Because the direct bandgap is only 140 meV above the indirect bandgap in Germanium (Ge), it is well established that a tiny (~2%) extensile strain could render an indirect-to-direct bandgap transition
and makes it direct bandgap. However, there is no feasible way to create such extensive strain on Ge since the lattice parameter of Ge is even 4.3% larger than Si. Here, we propose inserting external atoms into interstitial sites of Ge, which grows on Si substrate through SiGe buffer layer, to induce an effective tensile uniaxial strain on Ge, a new pathway toward direct band gap Ge. By performing the first-principles calculations, we find that atom implantation in Ge are metastable and are effective ways to engineer the indirect band gap to direct band gap. We predict that the optical dipole transition of atom (Li, He, Ne, or Ar) implanted Ge ($E_g$ ~ 20 eV) is comparable to GaAs ($E_g$ ~ 28.8 eV), indicating an excellent optical property of our designed system. Significantly, we find with a low concentration (0.78%) of Ar atom implanted in Ge, direct band gap of 0.73 eV (~ 1700 nm) can be achieved. Because our proposed scheme is fully compatible with CMOS technology, our new concept would be a solution for on-chip lasers and paves the way towards Si-based OEIC.

EP04.10.10 Application of Large-Scale Flexible Selective Emitter for Deception of IR Detector
Namkyu Lee, Joon-Soo Lim, Injoong Chang and Hyung Hee Cho; Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of).

Research highlights
- Application of large-scale flexible infrared emitter for IR camouflage
- Suggestion of flexible infrared emitter without flexible dielectric materials considering mechanical stress
- Verification of flexible infrared emitter in the various conditions to apply for IR camouflage

Abstract
During several decades, the enhancement of survivability of ally has been one of issues on the modern battlefield. In particular, the infrared regime is important for the increase of survivability because the infrared emission from target occurs continuously from target, which makes the late recognition of target compared to the microwave based on radar using reflection signal. To control the infrared signal, we can control the temperature and emissivity on the surface based on the radiative heat transfer equation. In terms of manipulating emissivity, metamaterials have also superior potentials to apply for the military applications because it can realize the exotic properties contrary to natural resources. Especially, the selective emitter, which is one of metamaterials, has ability to manipulate the emissivity for modifying the emissive power from target. In addition, the IR detector has the limited range of detection wavelength because the atmospheric transparency window exists the range of 3–5 and 8–14 μm due to the existence of molecules to cause high infrared absorption. For this reason, via infrared selective emitter, we can match the infrared emission from target with the consideration of atmospheric transparency window. Furthermore, to apply the arbitrary surface on aircraft, military clothes and others, the selective emitter should have the material flexibility.

Here, we present the large-scale flexible infrared selective emitter for IR camouflage for ally’s survivability. To achieve the material flexibility of selective emitter, we use metal-dielectric-metal (MDM) structures. We adjust the flexible substrate of polyimide. And, contrary to the past research, the discrete dielectric material considering mechanical stress is applied for the selective emitter. In addition, we change the dielectric material to silicone dioxide and nitrile which are common materials to use MEMS fabrication process. The emissivity is measured by FT-IR (Bruker) using Kirchhoff’s law. The results showed that we can achieve the selective emitter with single peak to deceive the emissive power from target. In addition, the presented emitter is high reliability against temperature and peel&stick test. The maximum curvature of presented emitter is down to 250 μm, and the high machinability applies for the various surfaces and sizes. Furthermore, we attach the replicated aircrafts and confirm the performance of IR camouflage in the supersonic flowfields (Ma = 3) with the most severe condition of the aircrafts. This study will be helpful for the enlargement of applications using metamaterials.

EP04.10.11 Laser Micropainting in Visible Regime—Thin Film Interference of Iron (III) Oxide on Platinum Substrate
Younggeum Lee1, Wooseop Shin1, Saewoong Park1, Seongje Park1, Jaemook Lim1, Junyeob Yeo2 and Sukjoon Hong1; 1Optical Nanoprocessing Lab, Department of Mechanical Engineering, Hanyang University, Ansan, Korea (the Republic of); 2Novel Applied Nano Optics Lab, Department of Physics, Kyungpook National University, Daegu, Korea (the Republic of).

Thin film interference is one of the well-known optical phenomena that can be found in many places around us, and numerous optical coatings that utilizes thin film interference are already available in the market at the moment. In general, these optical coatings largely rely on Fabry-Perot interference that occurs between one or more films of dielectric or metallic materials. On the contrary, optical coating that consists of highly absorbing film on a substrate with finite optical conductivity has been investigated recently as a new type of optical coating. In the previous related studies, reflective optical coating at visible frequencies have been successfully achieved by coating Germanium (Ge) film at subwavelength thicknesses on gold (Au) substrate using conventional lithographic techniques. We found that iron oxide film (Fe2O3) on platinum (Pt) substrate, having similar refractive indices trends as Ge and Au, exhibit similar interference effect as the Ge film on Au substrate. In this study, Fe2O3 thin film is grown directly on Pt substrate by laser-induced photothermal reaction and applied as an absorbing dielectric for the optical coating. In brief, Pt substrate is immersed in aqueous Fe2O3 precursor solution and 532 nm continuous wave (CW) laser beam is focused on the substrate at 5 to 10 mW power. It is observed that the reflected spectrum from the substrate varies in full visible regime according to the resultant thickness of Fe2O3 film, which is easily controlled by changing the irradiation time. While on the other hand, the film thickness, and hence the reflected color, can be also altered by the scanning instead of changing the irradiation time. By choosing the proper scanning speed in the range of 10 μm/s to 30 μm/s, continuous line of Fe2O3, which exhibits the designated color in the visible frequencies, is created along the scanning path at microscale width. By utilizing the proposed laser process, thin Fe2O3 absorbing media is easily and selectively created on Pt substrate without any photolithographic techniques. It is also worth mentioning that Fe2O3 films at numerous thicknesses can be created on the same substrate with a single step, while it requires multi-step complex photolithography process with careful alignments to achieve the identical result with the conventional techniques.

Another virtue of the proposed laser process comes from the in-situ measurement of the thin film thickness in real time. The incident laser is absorbed by the substrate at 5 to 10 mW power. It is observed that the reflected color from the substrate varies in full visible regime according to the reflected spectrum from the substrate varies in full visible regime according to the reflected spectrum from the substrate. The laser beam is focused on the substrate at 5 to 10 mW power. It is observed that the reflected spectrum from the substrate varies in full visible regime. The laser beam is focused on the substrate at 5 to 10 mW power. It is observed that the reflected spectrum from the substrate varies in full visible regime. The laser beam is focused on the substrate at 5 to 10 mW power. It is observed that the reflected spectrum from the substrate varies in full visible regime.
The development of devices that can modulate and guide light using electrical stimuli has advanced phase change materials quite recently for beyond data-storage technologies, ranging from high resolution displays to smart windows. Despite the interest, the fundamental understanding of light-material interaction in these materials remains limited to photo-thermal induced crystallization. In this paper we report our observation of strong photovoltaic effect in phase change materials, both their amorphous and crystalline states using opto-electronic measurements on nano-scale crossbar devices; which we attribute to the interplay of photo-crystallization, photo-conductive and thermoelectric effects. We show that through device engineering the contribution of these individual effects to the photo-response can be tuned. We also show that the photo-voltaic effect plays a strong role in the photoreponse of the device, which can potentially make the phase change materials based photonic technologies self-powered, and even enable newer platform such as tunable photodetectors. We find phase change materials are stable under strong irradiance and show strong dependence on irradiance, independent of their states, each providing significant advance to understanding the materials science and photo-physics of these materials. As a demonstrator application we also illustrate the working of phase change materials based artificial retinas.

**EP04.10.13**

**Phase Dependent Photoconductivity in Chalcogenide Phase Change Materials**

Ghazii Sarwat Syed, Jan Mol and Harish Bhaskaran; University of Oxford, Oxfordshire, United Kingdom.

Solid-state microchip lasers attract attention because of their compact size (~cm), high stability, and high efficiency. Giant pulse power and high repetition rate can be realized with active modules and used in proliferation applications. However, these modules are large in size although Q-switches should be small to obtain shorter and higher output pulse. To overcome these issues, we have suggested the use of magnetooptical (MO) materials as Q-switches. Since the rare-earth iron garnet (RIG) film has the similar crystal structure and thermal expansion coefficient as the ones of Nd:YAG, we expected that the combination of RIG and Nd:YAG is suitable for realizing MO microchip lasers, and reported a MO Q-switch laser using Nd:YAG with the output peak power of 1.1 kW[1]. However, the cavity length was 10 mm at the previous report although the physical length limit is 5 mm. Because of the large size of the component holders of the laser optics, there were air gaps between the components and they limited the cavity length. In order to achieve a microchip MO Q-switch laser, the air gaps must be eliminated. In this report, the design and implementation of MO on the RIG film to remove the air gap between the RIG film and output coupler are discussed, and the Q-switching is demonstrated.

We used a matrix approach method to design the BM onto a single crystalline RIG [(Tb, Bi3(Gd, Fe)2O12] film, and SiO2 and Ta2O5 were used as a low and high reflectivity mirror, respectively. The optical constants of the materials were numerically estimated from their transmittance spectra using a simulation software (SCOUT) based on Fresnel interference. Reflective indexes of the RIG, SiO2, and Ta2O5 were 1.70, 1.43, and 2.02, and extinction coefficients of the RIG, SiO2, and Ta2O5 were 1.57×10-4, 2.79×10-3, and 1.48×10-3, respectively. The BM was designed to have a partial reflection of 50%. The BM was coated onto the RIG film via radio frequency ion beam sputtering. The atmosphere was filled with O2, and the ion beam power and voltage were 114 W and 1200 V, respectively. The fabricated structure of the BM was RIG/SiO2/Ta2O5/SiO2/Ta2O5, and the thicknesses of the films were 190 μm, 102 mm, 141 mm, 167 mm, and 129 mm, respectively. Two three-turn coils with diameters of 5.3 mm sandwiched the RIG film. A single crystalline 1 at.% Nd-doped YAG has which has a high reflection BM at the wavelength of 1064 nm on its input surface was used as a lasing material. The cavity length was 7 mm, which is 3-mm smaller than the one of our previous report[1]. The pumping power was 27.4 W and the repetition rate was 1 kHz at the wavelength of 808 nm, and the pulsed current with 2.3 μs width was applied to the coil for Q-switching. The output pulse had the pulse width of 25 ns, and the obtained pulse energy was 40 mJ corresponding to the peak power of 1.6 kW, which is 1.4 times larger than the previous report[1].


**EP04.10.15**

**Enhanced Photoluminescence from Multilayered Quantum Dots 2D Sheet**

Haruka Takekuma1, Junfu Leng1, Kazutaka Tateishi1, Yang Xu1,2,3, Y. Yin T. Chuang1,2,3, Soh Ruyazi1, Pangpung Wang1, Koichi Okamoto1 and Kaoru Tamada1; Chemistry, Kyushu University, Fukuoka, Japan; 1Institute of Materials Research and Engineering (IMRE), Singapore, Singapore; 2Agency for Science, Technology and Research (A*Star), Singapore, Singapore; 3Chemistry, National University of Singapore, Singapore, Singapore; 4Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, Fukuoka, Japan; 5Institute of Systems, Information Technologies and Nanotechnologies (ISIT), Fukuoka, Japan; 6Osaka Prefecture University, Osaka, Japan.

Colloidal quantum dots (QDs) are one of the favorable nanomaterials having outstanding optical properties such as narrow emission bandwidth with high quantum yield. These properties can be useful for optical or optoelectronic device applications like solar cells or flat panel displays. Recently, there are several reports for QDs combining with metal structures, expecting enhance photo-luminescence (PL) by surface plasmon resonance (SPR) [1, 2]. There is another report mentioning that the thickness is an important factor for the PL from QDs spin-coated films [3]. In this study, we controlled the QDs layer thickness precisely by use of layer-by-layer deposition on glass and gold substrates, and compared their emission properties. A self-assembled monolayer composed of colloidal CdSe/ZnS QDs was fabricated by Langmuir-Schaefer (LS) method. The CdSe/ZnS crystal size is 5 nm in diameter and the thickness of organic ligand layer is 1 nm. The sheet was transferred to hydrophobized glass and gold substrates. To avoid a quenching by a Förster Resonance Energy Transfer (FRET), a 10 nm of SiO2 layer was deposited on gold substrate prior to the fabrication of multilayered QDs. The PL images and spectra of the multilayered QDs were taken under an epifluorescence microscope. The PL intensity of the multilayered QDs sheet on glass substrate increased monotonically against the number of QDs layer. However, it showed a different feature on gold substrate. Neither the mirror effect nor SPR effect can explain this layer-number-dependent PL intensity on gold substrate. If SPR is the main reason of PL enhancement, the maximum should appear at 10 to 20 nm layer thickness on gold in consideration of SPR and FRET [2]. Hence, the light confinement effect in the “optical resonator” composed of multilayered QDs sheet needs to be considered. We assume that a similar phenomenon to our previous study with multilayered silver nanoparticle sheets [4] was induced in the multilayered QDs sheet as well (although electromagnetically induced transparency (EIT) was not found in this case). The detailed data analysis with Finite-Difference Time-Domain (FDTD) simulation provides an overall picture of the layer-number-dependent PL profile, which includes three independent contributions of mirror effect, SPR enhancement, and light confinement.

Amorphous Si (a-Si) is used for fabrication of commercial low-cost flat panel image detectors for radiographic applications such as computed tomography (CT) imaging. a-Si photodiodes are known to exhibit a rapid decrease in quantum efficiency near 750nm. While crystalline Si does not suffer from such an early decline, the large-area and low-cost constraints of medical imagers make it challenging and costly to use crystalline Si for such devices. In this work, we report on the development of a sensitive layer for upconversion from 785 nm to green region of the spectrum, which nearly matches the peak quantum efficiency of a-Si detectors. Various host materials have been extensively studied in literature with rare earth ions such as Er³⁺ (emission: green+red), Tb³⁺ (emission: blue), Ho³⁺ (emission: red+green) along with Yb³⁺ as a sensitizer for upconversion to the visible regime at high incident optical power (~100 mW) for colloidal solutions. We carried out a thermal decomposition synthesis of NaYF₄:Yb/Er(18%)/Er(2%)/Gd(15%) at moderate temperature (~320°C), resulting in a nearly pure hexagonal phase material. This is confirmed by powder X-ray diffraction (PXRD) of the unannealed sample with a lattice constant (~5.17 Å). High-resolution transmission electron microscopy (HRTEM) measurements reveal the formation of nearly spherical nanoparticles. The observed plane ([100]) inferred from lattice fringes in TEM data with a visibly estimated interplanar distance (4.4±1.6 Å) is in reasonable agreement with standard data (~5.17 Å) for comparable NaYF₄-based materials. Excitation (785 nm) of the deposited thin films of Gd-doped unannealed material at relatively low incident power (~0.4 mW) exhibits a PL response in green (539 nm) and red (665 nm) region of the spectrum. Gd-based upconversion material based thin films are thus a feasible photonic material for potential effective extension of high quantum efficiency range in a-Si for flat panel image detectors.

Quantum dot light-emitting diodes(QD-LEDs) that allow emission from porous host materials with high color purity can be driven by low power. We can control their wavelength and the full width at half maximum (FWHM) of the emission spectrum by using abilities of size control, therefore, QD-LEDs are expected to be applied for displays with a wide color gamut. Recently, Cd-based QD-LEDs have been reported to show high color purity and external quantum efficiency (EQE). However, because of the toxicity and restrictions on the use of these Cd-based materials, their substitution with Cd-based materials such as InP is highly desired. In this study, we developed QD-LEDs using high-performance Cd-free QDs composed of core/shell spheres of ZnInGaP/ZnS. The Zn added to the InP core improved the crystal growth and the Ga helped control the lattice matching between the core and shell, increasing the stability in air. This is because the interfacial state of the core/shell has a huge impact on the deterioration mechanism. The photoluminescence (PL) emission peak, FWHM and quantum yield (QY) of this material are 521nm, 60.9nm and 73.8%, respectively. We fabricated a QD-LED with an inverted structure using these Cd-free ZnInGaP/ZnS QDs then the relationship between the hole transport materials and EQE. Some of these materials exhibited low EQEs, partially because electrons and holes were not efficiently able to recombine in the light-emitting layer. In other words, electrons were not fully blocked by the hole transport layer and penetrated through it. Therefore, a material with a high Lowest Unoccupied Molecular Orbital (LUMO) level to block and confine more electrons in the light-emitting layer was desired. We found that TCTA (4,4',4"-Tri(9-carbazoyl)triphenylamine) was effective for blocking electrons. The device fabricated with TCTA for the hole transport layer showed an EQE of about 3.4%. This value is comparatively high for common Cd-free QD-LEDs, and a better charge balance was achieved and the recombination probability between electrons and holes was increased compared with those of previously reported Cd-free QD-LEDs. We found that the combination of ZnInGaP/ZnS and TCTA was effective for realizing high-efficiency QD-LEDs.

There is an ever growing interest in organic electro-optic (EO) polymers as the active material in a range of applications from broadband terahertz emitters and detectors [1] to ultrafast electro-optic modulators [2]. Large electro-optic response [3] and ease of tethering on varying device platforms make EO polymers desired over conventional EO crystals (e.g. LiNbO₃) [4]. Push-pull chromophores with large first hyperpolarizability (β) are the key constituent of EO polymeric materials. The translation of their second order molecular nonlinearity into a macroscopic nonlinear optic effect (Pockels effect) depends on their alignment in an acentric orientation. This is achieved by a so called poling process, in which the chromophores dipoles are oriented with a strong external electrical field at elevated temperature [2-5]. One of the challenges of this technology is the long-term stability of the poled arrangement associated with a high EO response [4,5]. Poling efficiency and stability relies crucially on the host polymer and the degree of chromophore mobility after poling. Strategies widely being employed to stabilize the poling induced acentric order include, use of high glass transition temperature host polymers, cross-linking the chromophores with the host after poling, covalently bonding chromophores to the polymeric chain, adding site-isolation groups to the chromophores [4-6]. Presently, there is an intense research interest to achieve a high EO activity together with long-term thermal and photochemical stability.

In this work we focus on the study of host-guest polymeric materials and their EO performance with the purpose of understanding the mechanisms leading to a stable EO activity. We used known polyene-type push-pull chromophores with adequate molecular nonlinearity [4,5]. Miscible amorphous polymeric host materials with different glass transition temperatures were selected. Thin films of host-guest EO materials were poled using contact electric field poling and their EO coefficients were measured using Teng-Man modulation ellipsometry[7]. To understand the mechanism behind change in persistence of poling state with different host, thermally stimulated discharge studies were conducted and parameters governing the relaxation of the chromophores were obtained. The role of the host polymer on the poling efficiency and stability will be discussed. In-device figure of merit of selected materials will be presented for silicon-organic-hybrid (SOH) EO modulators [2,3].
The planar waveguide modes \( T_E \) or \( T_M \) show \( n \) nodes, i.e. positions where the mode intensity equals zero. Within symmetric waveguides one node of all odd modes (odd \( n \)) is situated in the center plane of the waveguide. Remarkably, this accounts for the entire spectral range where the modes exist, which paves the way for tailoring large bandwidth light matter interactions. For instance, light scattering inside a waveguide strongly depends on the filling factor of the scattering film. Placed in the node plane the scattering is strongly suppressed. On the contrary, only slight detuning of the waveguide could efficiently switch that scattering, which paves the way for new display concepts. In planar solar concentrators a diffracting layer placed in the node plane will hardly interact with the excited waves. As a consequence, by exploiting the node plane the same concentration factor and acceptance angle are reached at a much lower thickness of the concentrator.

**EP04.10.20**

**Studies of Morphological Changes Under Electron Beam Irradiation in Cesium Iodide Film**

Puspita Ray1, Radhakrishna V.2, Basishali Garai2 and Rajanna K.2

1Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore, India; 2Space Astronomy Group, U R Rao Satellite Centre, Bangalore, India; 3Department of Physics, Dayananda Sagar University, Bangalore, India.

Remarkable properties of gaseous UV photon detectors make them attractive for relativistic particle identification in high energy physics, sky observation in position and admission emission topography in medical physics. Photocathode used to convert UV photons into electrons play a key role in deciding detection efficiency of these photon detectors. Cesium Iodide (CsI) is one of the most efficient UV photon converter among other alkali halides because CsI has the highest quantum efficiency in the UV wavelength range and is relatively stable in air. However, a major drawback of the photocathode material is ageing process which limits their life time and hence performance of these photon detectors. UV photon detectors used in high energy physics, suffer from a high radiation background. High radiation fluences of electrons or protons are continuously hitting on the detector photocathode surface. Such high flux would significantly affect the morphological, structural and photo-emission properties of the photocathode film.

In this work, we demonstrate the impact of electron bombardment on 50 nm thermally evaporated CsI film. It has been studied by SEM, XRD and HRTEM. A severe modification in surface morphology is observed under high energy electron beam exposure. This surface modification involves the creation of void areas which coalesce upon further exposure. Effect of exposure time and energy of incident electron beam on film continuity will be presented here.

**EP04.10.21**

**Enhanced Room-Temperature Photoluminescence of n+ Ge-on-Si Grown by Metal-Organic Chemical Vapor Deposition (MOCVD) Compared to Delta Doping Approach**

Alessandra V. Quevedo Covian1, Guangnan Zhou2, Ijang Hong Lee1, Xiaoxin Wang1, Chuang Seng Tan2, Guangru (Maggu) Xia3 and Jifeng Liu1

1Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, United States; 2Materials Engineering, University of British Columbia, Vancouver, British Columbia, Canada; 3Low Energy Electronic Systems (LEES), Singapore-MIT Alliance for Research and Technology (SMART), Singapore, Singapore.

Band-engineered Ge has become a promising candidate for monolithically integrated light sources on Si. The direct bandgap of Ge at 0.8 eV corresponds to the most technically important wavelength for telecommunications (1550nm), making Ge an ideal candidate for large scale photonic integration on Si chips for photodetection/optical sensing [1], modulation, and lasing [2]. Even though Ge is an indirect bandgap semiconductor, the energy difference between its direct and indirect bandgaps is only 136 meV [1], which can be compensated by tensile strain and n-type doping. However, growing high quality n+ Ge for efficient light emitters remain a significant challenge. Existing delta-doping approach in chemical vapor deposition (CVD) tends to adversely affect the direct and indirect bandgaps [3,4]. Delta-doping approach results in a low threading dislocation densities of ~10^6 cm^-2 [3], two orders lower compared to 10^8 cm^-2 from as-grown MOCVD samples with n=1x10^19 cm^-3 show a low threading dislocation densities of ~10^8 cm^-2 [3], two orders lower compared to 10^8 cm^-2 from as-grown MOCVD samples with n=1x10^19 cm^-3. Correspondingly, compared to delta-doped samples with a similar doping level, the MOCVD n+ Ge PL intensity is 5-10x higher at room temperature. In fact, their PL intensity is similar to delta-doped samples with 4x higher n-type doping level. Furthermore, the MOCVD samples also show no out diffusion of phosphorus or arsenic dopants upon annealing, in contrast to the delta doping approach. Finally, after annealing the PL intensity of devices decreases by a factor of 2-3 for the MOCVD samples, compared to ~100x for delta-doped samples. However, the PL intensity of the high-temperature annealed MOCVD samples decreases at the PL peak blueshifts mainly due to Ge-Si interdiffusion. These results indicate that it is promising to significantly improve the material quality and light emitting properties of n+ Ge-on-Si via MOCVD growth without high-temperature defect-reduction annealing for better monolithic light emitters on Si.


**EP04.10.22**

**Band Gap Tuning Across the Visible Spectrum Through Cation Sublattice Ordering**

Robert Makin1, Krystal Yock1, Steven M. Durbin1, Nancy Senabulya1, James Mathis1, Roy Clarke2, Nathaniel Feldberg3, Patrick Miska1, Christina Jones1, Logan Williams4, Zihao Dong1 and Emmanouil Kioupakis4

1CE Department W/MU, Kalamazoo, Michigan, United States; 2Applied Physics, University of Michigan, Ann Arbor, Michigan, United States; 3Institut Jean Lamour, Universite de Lorraine, Nancy, France; 4Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

When compared with their binary analogs, heterovalent ternary materials have a degree of freedom not present in the binary materials – specifically the arrangement of atoms on the cation sublattice. An ordered cation sublattice has column-II and column-IV atoms at their specified equilibrium sites. For ZnSnN2 and MgSnN2, this ordered-equilibrium structure is the orthorhombic γ-NaFeO2 lattice. At the opposite extreme of cation sublattice ordering, column-IV and column-II atoms are equally likely to occupy any cation sublattice site. This disorder increases the symmetry of the lattice; for ZnSnN2 and MgSnN2, it shifts the lattice from an orthorhombic structure towards a wurtzite structure. As we show here, it also has a profound affect on the band gap, allowing it to continuously vary over almost 1 eV.

A common method for quantifying the random distribution of atoms on lattice sites is through the long-range order parameter, \( S \). The order parameter of a
material is often determined by calculating the ratio of the integrated area of a superlattice peak, which is a reflection whose structure factor is dependent upon S, to the integrated area of a fundamental peak, which is a reflection whose structure factor is independent of S. There are additional methods as well, such as Raman spectroscopy and reflection high energy electron diffraction (RHEED). We have used all three of these methods to extract the order parameter from both ZnSnN$_2$ and MgSnN$_2$ thin films, and the results agreed to within two decimal places among all three techniques. For ZnSnN$_2$, the S values, averaged using the results from the three different techniques, range from 0.26 to 0.97. For preliminary MgSnN$_2$ films, the S values, averaged using the results from the three different techniques, range from 0.67 to 0.96.

Following the method of Wei and Zunger, who employed an Ising model approach to derive a quadratic relationship between the band gap and ordering in alloy, we find that for ZnSnN$_2$ and MgSnN$_2$, $E_{gS} = E_{gS=0} + S^2[E_{gS=1} - E_{gS=0}]$ where $E_{gS=0}$ is the band gap of the wurtzite structure, $E_{gS=1}$ is the band gap of the orthorhombic structure, and $E_{gS}$ is the band gap of a partially ordered lattice. Consequently, a plot of the band gap as a function of S should yield a linear relationship, with a slope equal to $E_{gS}(a)$ the difference in the band gap of each of the two phases). From a linear fit to the data, we find the band gap ranges between 1.12 eV to 1.98 eV for ZnSnN$_2$, and between 1.87 eV and 3.43 eV for MgSnN$_2$. Thus, the range spanned by the cation sublattice ordering tunable optical band gaps of ZnSnN$_2$ and MgSnN$_2$, approximately 1.12 eV to 3.43 eV, positions these materials as earth-abundant eco-friendly alternatives to GaN alloys capable of spanning the spectrum from the near IR to the UV, without the need for alloying.

EP04.10.23
Polarization Control of Strain-Induced Single-Photon Emitters in Atomically Thin Semiconductor Kwang-yong Jeon$^1$, Jae-Pil So$^2$, Soon-Jae Lee$^2$, Jung Min Lee$^3$ and Hong-Gyu Park$^2$; $^1$Department of Nano Science and Technology, Gachon University, Gyeonggi-do, Korea (the Republic of), $^2$Department of Physics, Korea University, Seoul, Korea (the Republic of).

Quantum emitters in two-dimensional materials have attracted much interest in quantum technologies such as quantum cryptography, computation and metrology. Recently, deterministic creations of the quantum emitter array in two-dimensional transition metal dichalcogenides (TMDCs) by strain engineering has been reported. However, in order to realize the scalable quantum photonic devices, it is necessary to control not only its position but also its polarization. Here, we control the polarization and position of the strain-induced quantum emitters using nanogap arrays fabricated by E-beam lithography and dry etching process on the SiN/SiO$_2$ wafer. Tungsten diselenide (WSe$_2$) monolayer is transferred on the fabricate nanogap arrays. Strain perturbations in WSe$_2$ monolayer can create localized excitons induced by artificial potential energy which can be tuned by nanostructures. Confocal PL mapping shows that the localized emitters are distinct from the neutral exciton which is present uniformly across the WSe$_2$ monolayer with ~10 times higher photon counts. The single-photon nature of emitter is confirmed by Hanbury-Brown and Twiss (HBT) setup. Polarization-resolved photoluminescence (PL) microscopy shows the strain-induced emitter emits the linearly polarized light. The polarization of the emitter is perpendicular or parallel to the nanowires depending on the width of nanogap. We also demonstrate the waveguide coupled on-chip single photon emitter in WSe$_2$. Our results will pave the way for the hybrid integration of passive photonic circuit with single-photon emitters in two-dimensional semiconductors for next generation quantum technology applications.

EP04.10.24
Optoelectronic Design of Thin-Film Infrared Sensitive Photodiodes Based on Lead-Sulfide Quantum Dots Epinitheas Georgitzikis$^{1,2}$, Pawel E. Malinowski$^3$, Vladimir Pejovic$^1$, Jorick Maes$^4$, Zeger Hens$^4$, Paul Heremans$^1$, 2 and David Cheyns$^1$; $^1$imec, Leuven, Belgium; $^2$Department of Electrical Engineering (ESAT), Catholic University of Leuven, Leuven, Belgium; $^3$Budapest University of Technology and Economics, Budapest, Hungary; $^4$Department of Physics, Korea University, Seoul, Korea (the Republic of).

Lead sulfide (PbS) based colloidal quantum dots (QDs) are very attractive materials for the realization of novel optoelectronic devices, combining low cost synthesis and processing, deposition over large area and on any substrate with a tunable band gap that enables selective detection in wavelengths ranging from the visible light to the short-wave-infrared (SWIR). Great effort has been made in the last years to incorporate PbS QDs in thin-film photovoltaic devices (TFPV), leading to improved efficiencies through better ligand passivation schemes of the QD surface. Even though these devices report high external quantum efficiencies (EQE) they lack the required characteristics that would make them suitable for imaging applications, namely a low dark current and high speed. In this work we demonstrate how a combined electronic and optical design PbS QDs can enable high performance infrared sensitive photodiodes.

In the electronic domain, we study devices of QD layers sandwiched between two transparent, thickness tunable transport layers as an n-p junction photodiode. We demonstrate how the proper selection of hole (HTL) and electron (ETL) transport layers through band alignment engineering can decrease the dark current of the device substantially. We argue that a major contribution to dark current in these devices derives from dangling bonds at the surface of the QDs. Time-resolved photoluminescence (TRPL) is used to characterize the recombination processes in the QD films under different ligand termination and to study the relation between the trap states and the dark current of the devices. Taking these data as a feedback we fabricated optimized devices with dark currents below 1 uA/cm$^2$ at 1450 nm and below 10 nA/cm$^2$ at 950 nm.

In the optical domain, we optimize our devices to achieve high EQE at the wavelength of our choice by properly manipulating the optical cavity inside the layers. Using variable angle ellipsometry and reflection/transmission measurements we build an optical model for PbS QD based thin-films. We show that different ligands result in different packing of the QDs, having a crucial effect on the IR light absorption coefficient. Furthermore, we tune the transport layer thickness to optimize the intrinsic cavity effect of the device structure, boosting the absorption of our stack from 40% to above 80% at the wavelength of interest even with very thin QD layers between 100 – 200 nm. Through this path we demonstrate photodiodes with low dark current and high EQE of 30% and 50% at the wavelengths of 1450 nm and 950 nm, achieving specific detectivity of 10$^{12}$ Jones.

EP04.10.25
Crafting Core/Graded Shell-Shell Quantum Dots in the Mid-IR Young Jun Yoon$^1$, Jaehun Jung$^{2,3}$, Yajing Chang$^1$, Chun Hao Lin$^1$, Yeu Wei Harn$^1$, Gill Biesold-Mcgee$^1$, Shengtao Yu$^1$, Zewei Wang$^1$, Cheng-Hsin Lu$^1$, Yihuang Chen$^1$, Zhixiu Kang$^1$, 2, Naresh Thadhani$^1$, Vladimir Tsukruk$^1$ and Zhiqun Lin$^1$; $^1$Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; $^2$Electronic Systems Laboratory, Georgia Tech Research Institute, Atlanta, Georgia, United States; $^3$Materials Science and Engineering, Hongik University, Sejong, Korea (the Republic of).

Quantum Dots (QD) for optoelectronic devices have received much attention over the past decade due to their large-area solution processability as well as
Resonant Optical Studies of GaAs/AlGaAs Multiple Quantum Well Based Bragg Structures at Excited States

Nikesh Maharjan1, Vladimir Chaldyshev2 and Mim Nakarmi1; 1Physics, Brooklyn College and The Graduate Center of the City University of New York, Brooklyn, New York, United States; 2Ioffe Institute, St Petersburg, Russian Federation.

Resonant Bragg Structure (RBS) based on GaAs/AlGaAs multiple quantum wells (MQWs) was designed aiming to coincide the Bragg resonance with the exciton energy of the second quantum state in the GaAs quantum well to achieve double-resonance condition. The RBS samples with 60 periods of GaAs/AlGaAs quantum wells/barriers were grown on semi-insulating GaAs substrates by molecular beam epitaxy. We employed optical reflectance (OR) and electro-reflectance (ER) spectroscopies to study resonant optical properties of the RBS samples. At low temperature optical reflectance measurements, we observed enhanced Bragg reflection intensity when exciton energy coincides with the Bragg energy peak. In the electro-reflectance spectra, we also observed an enhanced and broad ER features related to excitons at the excited states under the double-resonance conditions manifesting a strong light-matter interaction. Bragg peak can significantly be tuned by changing the angle of incidence of the light. Exciton energies can be tuned by changing the temperature and external electric field. The exciton energies are very sensitive to the thickness of the quantum wells. There was noticeable change in exciton energy in the samples in the different regions from the same wafer. We performed the numerical calculations to estimate the possible exciton states. By tuning these variables, we performed OR and ER measurements to study the resonant optical behaviors at the excited energy states. By tuning the Bragg peak for double resonance in the RBS samples of different thicknesses, we observed the electro-reflectance features related to the transitions of \((x(2\text{-}hh}_2), x(2\text{-}hh}_1), x(2\text{-}hh}_3)\) and \((x(1\text{-}hh}_1), x(2\text{-}hh}_3)\) and \((x(1\text{-}hh}_3)\) which are prohibited at zero electric field, were allowed due to the increased overlap of the electron and hole wave functions caused by the electric field, built-in electric field or a DC bias applied. Details about our findings on the resonant optical properties of GaAs/AlGaAs MQW based RBS along with its implications will be presented.

光线性価格を制御するための光学的特性の開発

Dongling Geng, Elena Cabello-Olmo, Gabriel Lozano and Hernán Míguez; Spanish Research Council, Seville, Spain.

Herein we show that nanoporphosphor integration in an optical cavity allows unprecedented control over both the chromaticity and the directionality of the emitted light, without modifying the chemical composition of the emitters or compromising their efficiency. GdVO4:Dy3+/Eu3+ nanoparticles of controlled size and shape are synthesized using a solvothermal method with which highly transparent nanoporphosphor thin films are prepared. Key to the achievement herein reported is the careful analysis of the structural and optical properties of thin nanoporphoshor layers with the processing temperature in order to achieve efficient photoluminescence while preserving the transparency of the films. An optical cavity was photoluminescence produced by embedding one layer of the nanoporphosphors in the middle of a one-dimensional photonic crystal (1DPC) made by ultraviolet (UV) transparent ZrO2 and SiO2 layers. Strict control over the structural parameters yielded a photonic cavity mode that couples to the target emission peak of the nanoporphosphors, which results in an enhancement or suppression of the spontaneous emission of Dy3+ or Eu3+ ions compared with their corresponding reference. As a result the chromaticity and the directionality of nanoporphosphors can be tuned with high precision due to the interplay between photonic resonances and the natural emission of the rare-earth cations. Our approach opens a route towards the development of nanoscale photonics based solid-state lighting and displays.

References


III-As Growth on C-Plane Sapphire by MBE

Samir K. Saha, Rahul Kumar, Andrian Kuchuk, Timothy Morgan, Pijush K. Ghosh, M-Zamani Alavijeh, Shui-Qing Yu and Gregory J. Salamo; University of Arkansas, Fayetteville, Arkansas, United States.

The III-V growth on Al2O3(0001) can create the opportunity to realize monolithic integrated combining high-performance III-V semiconductor light sources, modulators and detectors, low waveguide and passive devices, and CMOS and RF silicon circuits on a sapphire platform. The potential integration of microwave photonics (MWP) functionality on a photonic chip can dramatically increase speed, bandwidth, processing capability and dynamic range. Here we study the initial nucleation mechanism and interface between III-As grown on an Al2O3 (0001) substrate, very dissimilar materials (lattice parameters, crystal structure, thermal expansion). Previous studies for arsenides on sapphire have focused on thick layered growth as opposed to investigating the initial nucleation. In our research, molecular beam epitaxy (MBE) is used to grow ternary (InGaAs) and binary (GaAs, AlAs, and InAs) arsenide materials on well define step and terrace surface of the substrate. At the initial stage of the growth, we observed the 3D growth mode for the InGaAs, GaAs, and InAs from 1ML to 50 nm. For the 50 nm GaAs the faceted crystal structure is observed and from rocking curve measurements of X-ray diffraction (XRD) only one out-of-plane orientation [111] has been detected. Rocking curve of 50 nm GaAs shows small linewidth (242 arcsec) indicating the high quality of the grown crystals. Asymmetric (113) phi-scan shows a weak correlation with the sapphire substrate. The In incorporation is very low for the very small amount of InGaAs deposition on the sapphire substrate and the amount of In incorporation increased with increasing the thickness of
InGaAs. Twin formation is a major challenge for obtaining a single crystalline material and these twin crystals are rotated by 60° to the original phase. We have suppressed the twin formation and improved the GaAs crystal quality by introducing a thin layer of AlAs between GaAs and sapphire as well as the in-plane orientation relationship between GaAs and sapphire has improved. Further in-situ annealing has been found to decrease the twin volume and reduced to less than 2% of the total grown material.

**EP04.10.29**

Investigation of Strain and Stoichiometry of Epitaxial Titanium Nitride on Sapphire

Hadley A. Smith1, 2, Said Elhamri2, Kurt Eyink1, Zachary J. Biegler1, 3, Rachel L. Adams1, 4, Tyson C. Back1, Augustine Urbas1, Brandon M. Howe1 and Amber N. Reed1; 1Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, United States; 2Department of Physics, University of Dayton, Dayton, Ohio, United States; 3Department of Electro-optics and Photonics, University of Dayton, Dayton, Ohio, United States; 4Department of Mechanical Engineering, University of Dayton, Dayton, Ohio, United States.

The metallic, robust and high-melting point qualities of titanium nitride (TiN) make it an interesting and viable material for plasmonics and electrodics. Previously, we analyzed how substrate temperature affects the microstructure and optical properties of TiN films grown with controllably unbalanced reactive magnetron sputtering, with substrate temperatures varying from 280°C to 760°C. The TiN films were analyzed with X-ray photoelectron spectroscopy, which revealed no compositional difference between samples. Additionally, Rutherford backscattering spectrometry on the 550°C film showed that it was stoichiometric. These results indicate that strain is the most prominent component contributing to changes in TiN microstructure, as oppose to stoichiometry changes. To further investigate any present strain, the films were analyzed with high resolution X-ray diffraction (XRD) by completing 2theta-omega scans around the (111) TiN orientation (symmetric) as well as the (113) orientation (asymmetric). Rocking curve scans were also completed around the (111) TiN peak. With the assumption that any strain in the sample would be rhombohedral, the 2theta values from each orientation were compared, and the best estimate for the strained lattice constant and bond angles were extracted. Lattice constants increased with increasing substrate temperature until 490°C. At this substrate temperature, the lattice constants plateaued around 4.245Å, and the deviation from a 90° bond angle remained at a minimum. This trend correlated with plasmonic qualities of the films, with the more relaxed films grown above 490°C yielding greater plasmonic quality. Additionally, two smaller peaks were found symmetrically placed around the film peak in the XRD rocking curve scans for the TiN grown with 550°C, suggesting some planes in the film are unfavourably tilted. The film grown with 550°C had the least amount of background counts, indicating the least amount of point defects in this film. We previously found that TiN grown with 550°C resulted in optimized optical properties for plasmonic materials; this contributes to the previous conclusion that microstructure correlates with optical properties in TiN. The results of this work emphasize the importance of specific deposition conditions—in this case, substrate temperature—to minimize strain and defects for achieving optimal plasmonic properties for TiN thin films.

**EP04.10.30**

Modeling of Type-II InAs/InSb Superlattice Bandstructure and Absorption Spectra Using Time Dependent Density Functional Theory

David G. Gonzalez Alcantara, J Velez and R Palai; Department of Physics, University of Puerto Rico, San Juan, Puerto Rico, United States.

Focal plane arrays (PFAs) based on type II superlattice (T2SL) operating in mid-wave infrared (MWIR- 3-5 mm) and long-wave infrared (LWIR 8-12 mm) are of great importance for many advanced surveillance and imaging systems for a variety of civil and military applications. These detectors have better accuracy and sensitivity with low false alarms even in complicated backgrounds and are promising alternatives to the technologically developed HgCdTe in MWIR and LWIR detection. When the focal plane contains hundreds or thousands of semiconductor elements a single spot of incident energy can stimulate more than one element. The unwanted electrical and optical crosstalk is the most important factor that hinder the performance. It has been found that III-V semiconductor (InAs, InSb, and InSb) strained layer superlattice (SLS) are very promising in terms of reducing the crosstalk, because of the intriguing broken gap alignment and interesting fundamental physics (Bose-Einstein condensation of excitons and the quantum spin Hall effect).

In the present work, the band structure of (InAs)\textsubscript{n}/(InSb)\textsubscript{m}, type-II superlattices is calculated within the density functional theory (DFT) framework using Perdew-Burke-Ernzerhof (PBE) approximation for the exchange-correlation functional using the Quantum Espresso (QE) package. For the calculation of spectroscopic properties of the material (absorption spectra), time dependent density functional theory (TDDFT) package in the QE distribution is used. We investigate the bandstructure of (InAs)\textsubscript{n}/(InSb)\textsubscript{m}, T2SLs with different layer thickness. Understanding and controlling the bandstructure of InAs/InSb T2SL will facilitate to achieve any desired bandgap for infrared detection and the negative bandgap will open a new avenue for the new physics phenomena.

**EP04.10.31**

Charge and Thermal Modeling of a Semiconductor-Based Optical Refrigerator

Shubin Zhang1, Yurii V. Morozov2, Boldizsár Janko1 and Masaru Kunito1; 1Physics, University of Notre Dame, Notre Dame, Indiana, United States; 2Chemistry, University of Notre Dame, Notre Dame, Indiana, United States.

Despite multiple attempts to achieve optical refrigeration in very high (99.5%) external quantum efficiency (EQE) GaAs, no cooling has been observed to date. In this study, we investigate optical refrigeration in GaAs by numerically solving the transient drift-diffusion equation coupled to Poisson’s equation. Obtained charge carrier distributions, together with the heat diffusion equation, allow us to observe the spatial and temporal evolution of cooling/heating within GaAs. Our results indicate that maximum cooling occurs at a laser intensity different from that which maximizes its EQE. A 6-fold difference in cooling power exists. We ultimately find that samples suspended in vacuum using a 100 µm SiO\textsubscript{2} fiber cool to 83 K. These results emphasize the critical importance of choosing an appropriate laser excitation intensity to achieve optical refrigeration along with minimizing the conductive heat load on the refrigerator. Beyond this, results of the study are applicable towards analyzing the optical response of other optoelectronic systems where accurate charge and/or heat diffusion modeling is critical.

**EP04.10.32**

SiO\textsubscript{2} and TiO\textsubscript{2} Sol-Gel Blends with Tunable Optical and Electronic Properties

Stephanie Arouh, Roland Himmelhuber and Robert A. Norwood; University of Arizona, Tucson, Arizona, United States.

Metallic oxide thin films are used for applications ranging from anti-reflective coatings to microelectronics. Sol-gels are useful for creating these films due to the ability to create high quality films without expensive and complex deposition equipment.

In this work, sol-gel blends are created using a combination of previously developed high index (n~2.4) TiO\textsubscript{2}-based sol-gel made directly from the metal chloride and a low index (n~1.5) SiO\textsubscript{2} based sol-gel synthesized by the standard alkoxide route. Blends are prepared with different ratios of these sol-gels and spun onto glass or ITO-on-glass substrates. The thicknesses, refractive indices, and dielectric constants of the resulting films are measured using...
Results show that including more SiO₂ based sol-gel in the initial mixture enables thicker films ranging from 1-10 μm, while resulting in lower refractive indices and lower dielectric constants. Refractive indices measured were 1.5 and 1.75, and dielectric constants up to 8 were observed at 100 kHz. This is consistent with the expected results due to SiO₂ having a lower refractive index and dielectric constant over the range of wavelengths and frequencies explored. The ability to fine tune the properties is explored, with the trade-off between processability and dielectric properties being the primary focus.

In the future, these sol-gel blends can be used within photonic circuitry, or within either stand-alone or integrated capacitors devices.

**EP04.10.33**

**Linear and Non-Linear Optical Properties of a Single Dopant in a Strained Holey SiO₂/Si Nanotube**

Mohamed El-Yadri⁴, Noreddine Aghoutane¹, El Aouami², Elmustapha Feddi², Mostafa Sadoqi¹, F. Dujardin¹, C. A. Duque⁴ and Gen Long¹; Saint John’s University, Jamaica, New York, United States; ²Group of Optoelectronic of Semiconductors and Nanomaterials, ENSET-Mohammed V University, Rabat, Morocco; ³LCP-A2MC, Institut de Chimie, Physique et Matériaux, Université de Lorraine, Metz, France; ⁴Grupo de Materia Condensada-UdeA, Instituto de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, Medellin, Colombia.

In this study, we have investigated the influence of the geometrical confinement and impurity position on the optical properties (linear and third order nonlinear) associated with the 1s-1p intersubband transition of a single dopant in a SiO₂/Si cylindrical core/shell nanotube. Our calculations are performed in the framework of the effective mass and parabolic band approximations and the energies are obtained by using a variational method. Our results show that linear and nonlinear parts of the absorption coefficient and the refractive index associated to the intersubband 1s-1p transition undergoes important changes. There are different interesting results to point out such as the shift of the absorption coefficients and refractive index to high values of photon energy. Another significant result is that the donor position considerably affects theoretical properties and their corresponding magnitudes.

**EP04.10.34**

**Design of Broadband Infrared Selective Emitter for IR Camouflage Through Multiple-Size Structure**

Junesoo Lim, Namkyu Lee, Injoong Chang and Hyung Hee Cho; School of Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of).

Detection techniques using waves are used in many areas such as ultrasound wave, radar, and infrared wave detection. However, these detection technologies also have a side effect that the ally’s operational activities that emit radiation by body temperature are exposed to the enemy. Therefore, it is required to develop anti-detection techniques for protecting our assets. To diminish the detection possibility, many researches about anti-detection for radar and ultrasound wave have been progressed. In case of the Infrared wave, there is difficulty to realize camouflage, because Infrared emission passively depends on the surface temperature of the body. For Infrared detection, Infrared detectors mostly detect wavelengths outside the band of 5 ~ 8 microns, because the absorption by atmospheric air are the largest in the 5 ~ 8 microns band. Therefore, if the emission characteristics can be manipulated that energy is emitted through in 5 ~ 8 micron band to a maximum and out a range of 5 ~ 8 micron to a minimum, the infrared camouflage can be realized. Recently, metamaterials have been cultivated as means to control emission characteristics. By modifying the structure’s size of selective emitters, we can control specific wavelengths to emit. In this study, we design the broadband infrared emitter which emits in 5 ~ 8 microns band through the multiple-size structure for reducing the thermal instability caused by the narrow bandwidth which can cause the out of control emission.

Firstly, to determine the diameter of cylinders, a numerical method was used by using Finite element method. Commercial code (COMSOL 5.2a) was used to simulate the physical phenomenon of MDM structure. For the validation, a single-diameter structure was fabricated by micro-nano fabrication process and compared with numerical results. After the emission characteristics of single-diameter structure are analyzed, we could derive two diameters of the cylinder for having the MDM structure emit in the band of 5 ~ 8 microns. In addition, we simulated the derived structure. As a result, the multiple-diameter structure shows the dual peaks within the in the band of 5 ~ 8 microns. Additionally, we compared the total radiated energy between the selective emitter and broadband emitters for evaluating the radiation performance. Total radiated energy is increased by 33% for comparing the single-diameter structure and multiple-diameter structure and is 120% and 130% more for two layers of MDM and three layers of MDM. In conclusion, through on this study, we derived a structure that emits broadband in 5 to 8 bands to camouflage from infrared detectors. In order to realize the broadband, the absorption peaks could be widened to the left and right through the multi-diameter structure and stacked method and this study will help to understand the effect of the metamaterial structural characteristics on the radiation performance and to understand the application of metamaterials to real life.

**EP04.10.35**

**Corrugated Metal-Electrode Fabry-Perot Cavity for Organic Solar Cells—Near-Perfect Optical Absorption by the Coupling of FP and Propagation Modes**

Sungjun In and Namkyoo Park; Photonic Systems Laboratory, Department of Electrical and Computer Engineering, Seoul National University, Seoul, Korea (the Republic of).

The application of nano-photonic structures for organic solar cells (OSCs) has been quite popular and successful, leading to increased optical absorption and better spectral overlap to solar irradiances. With the introduction of plasmonic cavity structures [1-3], textured light trapping structures [4-5], or multi-plasmonic effects [6-8], signiﬁcant improvements in the power conversion efﬁciency (PCE) have also been reported, now exceeding 11%. Nonetheless, with the limitations of given material properties of OSCs such as low optical absorption and narrow absorption band, together with the high-Q narrow band plasmonic effects, the PCE of single-junction OSCs has been stagnant over the past few years, at the barrier of 12% [9-10].

In this work, we demonstrate an ultra-thin inverted OSC structure which provides near-perfect optical absorption over the entire absorption band of commonly used organic active material. By introducing a smooth spatial corrugation to the vertical plasmonic cavity which encloses the active layer, we successfully derive a strong multi-peak in-plane plasmonic propagation modes, in addition to the signiﬁcant broadening of the Fabry-Perot cavity modes in the UTMF-electrode OSC. As a result, we achieve highly uniform (> 85%) and ultra-low Q (330~775 nm) broadband absorption in the ultra-thin active layer, which directly translates to the record-high PCE approaching ~13%. With the newly introduced concept of long-period spatial corrugation for the UTMF based OSC, we expect further applications of the same concept for solar cells of different materials and structures, targeting for even broader responses and higher PCE. The signiﬁcance of spectral engineering in the PCE of ultrathin OSC will be discussed, together with the detailed study on electrical carrier transport dynamics in the device.

Surface-enhanced Raman scattering (SERS) is a convenient and highly sensitive method for even single molecular level detection. SERS has been extensive use in the field of chemical, material, environmental, and medical sciences. SERS sensitivity is an important role in sensor field because high sensitivity means recognizing target molecule as early as possible. In order to improving SERS sensitivity, advanced and complex metal nano structures have been used to produce a huge electric field in hot spot. Although the metal nano structures have shown high performance, the high cost and poor spatial uniformity are critical drawbacks. In this work, we propose an inexpensive, reliable, and ultrasensitive SERS platform based on M13 bacteriophages (M13 phase) and a simple metal nano structure. The employed simple metal nano structure is a sandwich structure between single silver nanowire and gold film. When the nanowire is well dispersed on the film, the individual hot-spot can be well specified through optical microscope. Therefore, we can believe that each different position of SERS hot-spot shows same properties. Diameter of the silver nanowire is around 300 nm and length is around 30 um. Absorption and localized surface plasmon resonance spectra were measured to understand basic plasmonic properties of the structure. Three-dimensional finite difference time domain simulations (3D FDTD) was also calculated. The most important reason for using the structure is that the shape of its hot-spot is long as like M13 bacteriophage. Because the structure and M13 phase are similar in shape, they can be aligned well. M13 bacteriophage is a promising functional material due to its interchangeability and functionalized peptides on its surface. Genetic manipulated M13 phase can have selective adhesive strength with a target material. When the M13 phase placed in the hot-spot of the structure, the SERS platform can have selectivity for the target material. To verify this, SERS measurement were performed using the structure with and without the M13 phase. Target molecular, 20 microliters of paraquat (PQ), was dropped on the structure and dried. the droplet size is around 0.5 cm x 0.5 cm. Without the M13 phase, the structure shows the limit of detection over picomole range for PQ. When we introduced the M13 phase that was genetically engineered for selective binding of PQ, the structure shows the limit of detection around femt mole range for PQ. M13 phase-based SERS platform exhibited a dramatic improvement of sensitivity compare to the structure without the M13 phase.

Engineering Erbium-Doped Oxide Thin Layers for Integrated Optics

Yttria-Stabilized Zirconia (YSZ) is known to be a thermal and chemical stable functional oxide with a refractive index of about 2.12, which allows good light confinement of the optical mode. Moreover, it has a large energy bandgap avoiding two photon absorption (TPA) in near and mid-IR and its transparency covers the wavelength range from visible to mid-IR. Additionally, Kerr effect has been recently demonstrated. While these optical properties are very appealing for various applications including on-chip optical communications and sensing, YSZ has remained almost unexplored in photonics [1,2]. In this regard, we recently demonstrated YSZ waveguides with propagation losses as low as 2 dB/cm at a wavelength of 1380 nm [3]. Based on the promising results obtained in such passive photonic structures, we have recently looked into the development of active systems based on YSZ thin films. For that, we have introduced optically active rare-earth (RE) dopants into the matrix to investigate the correlation between the luminescence properties and the microstructure of thin films grown under different conditions.

In this work, we report on the optical and structural properties of Er-doped YSZ thin films showing strong emission at 1.53 and 1.536 μm under a continuous-wave pump laser excitation at about 980 nm. Yttrium-to-erbium substitution is performed in the Yttria-Stabilized Zirconia (YSZ) crystal. The observed outstanding luminescence will be analyzed and discussed. Remarkably, the Er-doped YSZ system provides a nearly perfect allocation of Er ions in the host matrix caused by a similar atomic radius between Y and Er, enabling an efficient optical activation of such dopants. These results pave the way towards the implementation of new rare-earth-doped functional oxides into hybrid photonic platforms in a customized and versatile manner, adding new functionalities including light amplifiers that may be instrumental for nanophotonic applications.


Resonant Cavity Enhanced Quantum Well Solar Cells

Resonant cavity enhanced quantum well solar cells (QWSCs) provide significant energy conversion efficiency improvement over standard QWSCs. Recent research in this area has focused on improving the performance of QWSCs through the use of resonant cavity structures. These structures can enhance the light harvesting efficiency of QWSCs by confining the light within the active region of the cell. The use of resonant cavity structures in QWSCs is particularly effective for short-wavelength light, where the bandgap energy of the QWSCs is typically lower than the energy of short-wavelength light. This allows for efficient absorption of the light within the active region of the cell, leading to improved energy conversion efficiency. The use of resonant cavity structures in QWSCs has been shown to improve the energy conversion efficiency of QWSCs by up to 40%. This improvement is achieved through the use of high-Q resonant cavity structures that confine the light within the active region of the cell, leading to increased light absorption and improved energy conversion efficiency. The use of resonant cavity structures in QWSCs is a promising technology for improving the performance of QWSCs and provides a potential solution for the energy conversion efficiency limitation of QWSCs.
Photovoltaic devices can provide a mobile source of electrical power for a variety of applications in both space and terrestrial environments. Many of these mobile power applications can directly benefit from enhancements in the efficiency of the photovoltaic devices. Space-based PV systems can also utilize thin-film technologies that improve radiation hardness, operating temperature range, efficiency, and specific power. To improve the radiation tolerance of multijunction III-V solar cells, we describe a device design which integrates reflector structures and quantum well absorbers into existing space power cell technology.

Prior work has demonstrated that InGaAs wells can be added to a GaAs cell while still maintaining a high open circuit voltage ($V_{oc} \sim 1.05 \text{V}$). Carrier collection efficiency in the wells can then be significantly increased with integrated photon management techniques. In particular, simulations indicate that adding a bottom reflector and a partial top reflector to generate resonant cavity effects can enable thin InGaAs quantum wells to extend infrared absorption and leverage optical cavity effects to increase the path length of near band edge photons. Device structures incorporating these elements we call a resonant cavity enhanced quantum well multijunction solar cell (RCE-QW MJSC). Simulations suggest enhanced absorption via resonant optical cavity effects can enable the GaAs middle subcell to be thinned to less than 1 μm without sacrificing short circuit current density.

We present photonic structures having different heights and color intensities through a flow coating method on a single substrate. Flow coating is one of the solution coatings that use coffee-ring effect. Coffee-ring effect is a non-volatile solute remaining on the surface after evaporation. This pattern originates from the capillary flow that is induced by the different evaporate rate between the edge and center of the droplet. Flow-coater confines the position of droplet with blade on specific position and deposits the solute along the shore. There are various methods of depositing thin films on solid substrates and are of substantial importance in numerous field such as microelectronics, optics and sensors. Flow coating has several important features that are different from other similar methods to fabricate photonic structures. First, lithography or nanocasting need complex steps to achieve photonic structure but flow coating do not need a develop process. Second, deep coating need a long time until liquid evaporate and form a thick film. However flow coating overcome such problems and has more advantages. Especially, flow coating can control the overall thickness easily, it changes spontaneously along the speed of blade. Particles deposit on the substrate forming close packed and well-ordered structure. Photonic structure can be made in that way. And photonic structure is three dimensional periodic structures that influence on incident light lay. When the periodicity of the photonic crystal is about half the light wave, photonic surface diffracts certain range of wave length. It has been found in nature, like avian feathers and wings of butterfly. They exhibit vivid color that reflect depends on their one structure. Two different nano size (195±5 nm and 300±5 nm) of silica Particles are prepared through the stober method. And different particles reflect different wave length showing blue or red colors when is being film structure. Ethanol is good medium to disperse silica and for flow coating. Solution evaporate fast inducing strong capillary follow, it make film quickly. The speed of deposition determines the thickness of film form 0.37±0.1 μm to 2.93±0.3 μm and shows different height of reflection peaks. Therefore, two different colored with different intensity can be made in a one substrate with one step of patterning process.

Exploring Circular Dichroism at Nanoscale by Atomic Force Microscopy Negar Otrooshi, Abraham Vazquez-Guardado, Debashis Chanda and Laurene Tetard; Department of Physics, University of Central Florida, Orlando, Florida, United States.

Studying light-matter interactions at the molecular level is critical to accelerate our understanding of life sciences. Nanoscale infrared spectroscopy, combining Atomic Force Microscopy (AFM) with IR spectroscopy, has made it possible to explore the vibrational modes excited in the sample. Using AFM subwavelength spatial resolution in IR spectroscopy can now be reached. Previous work shows that it is possible to design plasmonic substrate to locally enhance the electromagnetic field used to excite the molecules for higher sensitivity.

Here we use a cavity coupled plasmonic substrate to polarize and enhance the field used to excite the molecular vibration, detected by AFM. Our study focusses in studying the effect of chirality of biomolecules on the nanoscale resolved measurements captured with the AFM. We show that it is possible to generate a stronger confined electromagnetic field in the range of 1500-1800 cm$^{-1}$ by exploiting the cavity-coupled achiral plasmonic structure. We compare the response of the sample to both linearly and circular polarized incoming IR pulsed laser. For circular polarization, we acquire signals resulting from left handed and right - handed circular polarizations before subtracting them to reach information on the chirality. Molecules laying in the confined field at the plasmonic structures show stronger circular dichroism signal. The results suggest that using the “hot spots” of the cavity coupled plasmonic structures are significant and offer great potential for characterizing the chirality of single molecule. By using this approach, we expect to help distinguish chirality of biomolecules at nanoscale.

From Order and Disorder in 1D Photonic Crystals Towards Micro-Glitter Distributed Bragg Reflectors Mirela Malekovic, Esteban Bermúdez-Ureña, Bodo Wilts and Ulrich Steiner; Adolphe Merkle Institute, Fribourg, Switzerland.

Most vivid colours in nature originate from the interference of light with nanostructured materials. In many cases, the nanostructure is not perfect and introducing disorder results in additional optical effects that might change the reflection properties. Our current research is broadly focused on two questions: (i) how are optical properties influenced by disorder? and (ii) can we replicate natural photonic structures with a controlled degree of disorder? For this, we systematically investigate the colour change of distributed Bragg reflectors in relation to its key parameters, i.e. the total numbers of layers, the refractive index contrast and their thickness. Here, we have manufactured distributed Bragg reflectors (DBRs) using different techniques. Using spin coating, we deposit several layers of alternating porous materials where each layer has a controlled thickness and refractive index. We show that a reflector constructed of three repeating series of six layers gives optical properties that are a result of the disorder. In this case, the disorder is not fully random, but small deviations in the structure have a large influence on the colour and still produce a narrowband response. Alternatively, we show a different proof-of-concept solution using lithographically produced multi-layered patterns that readily assemble into a variety of Bragg reflectors with a different number of layers. We discuss the influence of...
disorder and the use of these materials in novel optical applications.

EP04.10.44
Symmetry Induced Transmission in Hybrid Waveguides Mark Meuld, Ivan Shuto Sko and Patrick Görn; Chair of Large Area Optoelectronics, Bergische Universität Wuppertal, Wuppertal, Germany.

Nanostuctured plasmonic systems support strong resonances and have led to new photonic applications. Nowadays, researchers compose metals and dielectrics to build even more sophisticated hybrid devices possessing optical properties exceeding the limits of purely dielectric or plasmonic systems. Here, we focus on a novel symmetric hybrid waveguide system. According to a semi-analytic Fourier Modal Expansion simulation, outstanding optical properties originate from hybridization between plasmonic and dielectric waveguide modes. Due to the symmetry, transmission resonances with remarkably high Q-factors as well as electromagnetically induced transmission (EIT) like phenomena with high refractive index sensitivity are predicted. These predictions were verified experimentally. The hybrid waveguides are fabricated by spin coating, UV-nanoimprint lithography, physical vapor deposition and symmetry-enabling lamination. In comparison to a non-symmetric device, the transmission at resonance is enhanced by a factor of 80 with a Q-factor of 400 through a 100 nm thick silver layer. These results show that both the advantages of plasmon modes and dielectric modes can be combined with our approach, and promise to improve upcoming generations of sensor and filter applications.

EP04.10.45
Low-Threshold, Room-Temperature Visible Lasing From Monolithically Nanostructured Porous Silicon Hybrid Microcavities Valentina Robbiano, Giuseppe M. Paternó, Antonino La Mattina, Silvia G. Motti, Guglielmo Lanzani, Francesco Scotognella and Giuseppe Barillaro; University of Pisa, Pisa, Italy; 2Italian Institute of Technology, Milano, Italy; 3Politecnico di Milano, Milano, Italy.

Since the first report of room-temperature photoluminescence from nanostructured porous silicon (PSi), scientists have fantasized about PSi-based lasers enabling the realization of integrated silicon photonic circuits. Although some trials on the fabrication of Si nanocrystal-based lasers have been attempted after the discovery of Si nanocrystal optical gain, a PSi-based laser has not been reported yet. In the past few years, leveraging a cheap and robust material preparation technique coupled with a high flexibility and high quality in optical structure fabrication, PSi has gained renewed interest in integrated optics and photonics, spanning from gradient refractive index (GRIN) optical elements, capable to finely control light propagation, and resonant microcavities.

Here we report, for the first time, on low-threshold lasing from fully-transparent nanostructured porous silicon (PSi) monolithic microcavities (MCs) infiltrated with a polyfluorene derivative, namely poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO). The hybrid PSi/organic laser is fabricated by electrochemical etching of crystalline silicon, with a square-wave current density profile that produces alternating nanostructured porous silicon (PSi) layers with different porosity and thickness values tuned to achieve a resonant microcavity (MC) operating in the visible region. The as-fabricated PSiMC was oxidized to avoid absorption of silicon, and then peeled off the silicon substrate using a PDMS slab to enable transmittance operation. Eventually, infiltration of PSiMC with PFO was carried out via drop-casting. The hybrid laser supports single-mode blue lasing at the resonance wavelength of 466 nm, with line width of ~1.3 nm and lasing threshold as low as 5 nJ (i.e. fluence of 15 μJ/cm²), which is among the lowest values of state-of-the-art PFO-based lasers.


EP04.10.46
Silk Protein-Based Multi-Responsive and Multifunctional Dynamic Micropatterns Yu Wang, Beom Joon Kim, Berney Peng, Wenyi Li, Yuqi Wang, Meng Li and Fiorenzo G. Omenetto; Tufts University, Medford, Massachusetts, United States.

Smart surfaces with dynamically tunable micro/nanoscale patterns have drawn a great deal of attention because their unique optical, electronic, biological, wetting, and adhesive properties are promising for a wide range of applications. Wrinkle structures, as one kind of mechanical instabilities, have been widely exploited recently to create hierarchical patterned surfaces because of their fast and simple fabrication process, feasibility to generate large-scale patterns, tunability and even complete reversibility in response to various external stimuli. To realize reversibly responsive surface patterns, various smart materials have been applied to wrinkling systems to realize dynamical and on-demand tuning of surface morphology and properties. However, these existing systems have at least one of several challenges such as high sensitivity to external stimuli, multiple and tunable responsiveness, mild and environmentally friendly stimuli condition, or "functional" dynamic patterns.

Reconstituted silk fibrin, derived from the native Bombyx mori silkworm fibers, has been intensively investigated because of its outstanding combination of biocompatibility, biodegradability, all aqueous processing, optical and electronic properties, mechanical flexibility, and the resulting multiple applications in biomedical applications, bio-optics/photonics, electronics, and optoelectronics. Most importantly, silk fibrin undergoes conformational transition when triggered by external stimuli, such as water vapor, methanol or deep UV light. This polymorphic transition of silk fibrin enables the control of the molecular chain movement on the nanoscale, offering the possibility to controllably tune the pattern morphology formed due to mechanical instability.

We report the facile fabrication of reversible, multi-responsive wrinkle patterns using silk protein as the responsive component. We show that the wrinkle structures can be dynamically tuned and/or erased easily by water vapor, methanol vapor or UV irradiation. We demonstrate that the wrinkle evolution rate is dominated by the starting conformation of silk protein, and that the occurrence of conformational transitions accelerated the reversibility of wrinkle patterns. The wrinkle evolution behavior is confirmed by investigating the molecular mechanism governing the conformational transition of silk fibrin. Finally, we demonstrate that the tunable wrinkling systems can be used for information storage, encryption, collection and extraction, as well as light diffusing related smart window with switchable transparency and thermal regulation.

EP04.10.47
Germanium Sulfide Nano-Optics Probed by High-Resolution STEM-Cathodoluminescence Spectroscopy Peter Sutter and Eli Sutter; University of
Nanophotonic studies of confined modes in planar waveguides have attracted significant interest as a means to probe exciton-polaritons and other hybrid light-matter quasiparticles in layered semiconductors, such as transition metal dichalcogenides or boron nitride. There is a need to broaden such studies to other materials and to identify alternatives to scanning near-field optical microscopy for exciting and measuring confined waveguide modes below the diffraction limit. Here, we discuss a novel approach for probing the dispersion of traveling waveguide modes by cathodoluminescence spectroscopy excited by the focused electron beam in scanning transmission electron microscopy (STEM-CL), and apply it to solid-state resonators consisting of mesoscale monocrystalline prisms, plates, and nanowires composed of GeS, an anisotropic layered semiconductor with direct bandgap in the near-infrared spectral range [1, 2]. Structure, crystallography and chemical composition of the GeS mesostructures are analyzed by analytical electron microscopy, STEM-CL maps and spectra. We find pronounced interference effects and sharp emission peaks at photon energies below the fundamental bandgap of GeS. Our analysis shows that locally excited light emission in STEM-CL launches in-plane waveguide modes in the mesoscale GeS structures, which are internally reflected by highly specular GeS edges to cause interference of the confined modes. Reabsorption and secondary luminescence give rise to the intensity modulations detected in the far field. Our results highlight avenues for probing light-matter interactions far below the diffraction limit, correlated with atomic-scale structure and chemical composition determined by (S)TEM, for a wide range of quantum materials. In a broader context, our findings open up the exciting possibility of tuning light emission from semiconductors geometrically using waveguide mode interference rather than by the conventional bandgap engineering.


EP04.10.48

Self-Cleaning, High Transmission, Near Unity Haze OTS/Silica Nanostructured Glass

Youngseok Kim; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

Youngseok Kim; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

High haze, high transparency substrates can increase the power conversion and extraction efficiency of solar cells and light emitting diodes (LEDs), respectively. In this paper, we present a new octadecyl trichlorosilane (OTS)/silica nanostructured substrate that displays high transmission (91.5 ± 0.8%) at 532 nm wavelength) and near unity haze (98.1 ± 0.5% at the same wavelength) with 143° scattering angle. The OTS/silica nanostructures are fabricated through a scalable and facile maskless reactive ion etching (MRIE) process followed by OTS coating. The OTS coating enhances the transmission of the structures by merging silica nanostructures together by capillary forces and effectively grading the index of refraction. The OTS/silica nanostructures display the highest combination of both transmission and haze in the literature as defined by Pareto optimality. The OTS/silica nanostructured glass exhibits lotus leaf-like wetting with a 159.7 ± 0.6° water contact angle (WCA) and 4.9 ± 0.6° contact angle hysteresis. We demonstrate the structures have self-cleaning functionality where about 100% of transparency can be easily recovered after graphite soiled substrates are rinsed with water. This self-cleaning functionality is maintained after 200 cycles of soiling and cleaning. The OTS/silica nanostructured glass may be an important substrate in optoelectronic applications where a combination of high transmission, high haze, and self-cleaning function are important.

EP04.10.49

Dual Layers of Periodic Nanoscale Metal Dot Array Fabricated by Nanoimprint and Dewetting Techniques

Jin Hwan Kim, KeunHwan Park and Youngseok Kim; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

Jin Hwan Kim, KeunHwan Park and Youngseok Kim; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

The nanoscale metal dot array has been used in many plasmonic devices and metamaterials. There are numerous methods to fabricate the nanoscale metal dot array including complex lithography and etching, random dispersion or coating of chemically-engineered metal particles. Here, we use the dewetting of gold (or platinum) thin film on a nano-patterned surface to create a periodically arranged metal dot array. By using nanoimprint techniques, nanohole array patterns are transferred to an alumina thin film and dewetting of gold (or platinum) thin film is followed. The dewetted metal pucks are periodically arranged on the top of the surface and inside the nanohole at the same time. These dual layers of periodic metal dot array can exhibit useful optical properties such as a broadband high absorption. Furthermore, by using FDTD simulation, we calculate the optical properties of the periodic metal dot arrays with different-sized metal dots and show the possible applications with this structure. Experimentally, the dewetting behaviors are presented with different conditions and surface patterns on which the dewetting occurs. The whole process here we use (nanoimprint and dewetting) can create dual layers of periodic metal dot array without complex lithography on various-shaped substrates with great scalability.

EP04.10.50

MAPbI3 and MAPbBr3 Halide Perovskite Super-Lattices for Infrared Emission Applications

Laxman Gouda1; Orin Kigern1; Omree Kapon1 and Yaakov Tischler2; 1Bar Ilan University, Ramat Gan, Israel; 2Chemistry department, Bar Ilan University, Ramat Gan, Israel; 3Cornell University, New York, New York, United States.

Laxman Gouda1; Orin Kigern1; Omree Kapon1 and Yaakov Tischler2; 1Bar Ilan University, Ramat Gan, Israel; 2Chemistry department, Bar Ilan University, Ramat Gan, Israel; 3Cornell University, New York, New York, United States.

Infrared emitting materials are of great importance for LED, Laser, night-vision, and chemical sensor technologies. Superlattice (SL) structures of compound semiconductors such as from A1As and GaAs semiconductors have been studied and used extensively for IR emitting Quantum Cascade Lasers. Until now MBE and MOCVD are the primary fabrication methods for SL fabrication but they are expensive and limited in their scale up. The hybrid organometal halide perovskite (HaP) materials, such as MAPbI3 and MAPbBr3, are a new class of semiconductors which are efficient, cheaper to fabricate, and potential candidates to replace expensive semiconductors which are currently used in solar and LED applications. Here we show a novel and efficient way to fabricate HaP SL's that emit in the Near-IR (NIR) region. We demonstrate that a cascade of layers of MAPbI3 and MAPbBr3 can shift an intense emission peak at 770 nm for 1 pair of layers to 900 nm for 3 pairs. The new technique and resultant SL's of MAPbI3 and MAPbBr3 are a promising candidate for extending the spectral range of HaP emission from NIR to the Mid-IR, with potential to deliver low-cost, efficient, tunable IR emitting LEDs and lasers, and new classes of spectroscopic chemical detectors.

EP04.11.01

Low-Dimensional Photonics

Prineha Narang and Xiaobo Yin; Thursday Morning, November 29, 2018

Hynes, Level 2, Room 206
The isolation of stable atomically thin two-dimensional (2D) materials on arbitrary substrates has led to a revolution in solid state physics and semiconductor device research over the past decade. A variety of other 2D materials (including semiconductors) with varying properties have been isolated raising the prospects for devices assembled by van der Waals forces. A fundamental challenge in using 2D materials for opto-electronic devices is enhancing their interaction with light, ultimately responsible for higher performance and efficiency in the devices. In particular, for photovoltaics, inorganic materials (e.g., Si, GaAs and GaInP) can concurrently maximize absorption and carrier collection. But thin film absorbers have lacked the above ability often due to due to surface and interface recombination effects. In contrast, Van der Waals semiconductors have naturally passivated surfaces with electronically active edges that allows retention of high electronic quality down-to the atomically thin limit.

In this work, we show how the near-field radiative heat transfer (NFHT) can be tuned using Al plasmonics, which spans to broader frequency range, as compared to noble metals, and it oxidizes. The oxide layer (Al2O3) changes the plasmonic response and even inhibits it. The formation of the oxide layer is the basis for our work in the control of NFHT. The NFHT is mediated by the interaction of surface plasmons, in the case of metals and surface-phonons polaritons in polaritonic materials. The hybridization of these two modes changes the heat flux between surfaces [2,3]. Using Rytov theory of fluctuating electrodynamics, we calculate the heat transfer between two Al surfaces at a different temperature, separated by a gap. As the surface oxidizes as a function of time, the surface-plasmon response is inhibited, and the polaritonic modes of the Al2O3 layer begin to play an essential role in the heat transfer, increasing both the spectral heat transfer and the total heat transfer significantly. As the oxidation increases, plasmon modes of the Al and phonon modes of the oxide hybridize favoring the radiative heat transfer.


In this work, we show how the near-field radiative heat transfer (NFHT) can be tuned using Al plasmonics, which spans to broader frequency range, as compared to noble metals, and it oxidizes. The oxide layer (Al2O3) changes the plasmonic response and even inhibits it. The formation of the oxide layer is the basis for our work in the control of NFHT. The NFHT is mediated by the interaction of surface plasmons, in the case of metals and surface-phonons polaritons in polaritonic materials. The hybridization of these two modes changes the heat flux between surfaces [2,3]. Using Rytov theory of fluctuating electrodynamics, we calculate the heat transfer between two Al surfaces at a different temperature, separated by a gap. As the surface oxidizes as a function of time, the surface-plasmon response is inhibited, and the polaritonic modes of the Al2O3 layer begin to play an essential role in the heat transfer, increasing both the spectral heat transfer and the total heat transfer significantly. As the oxidation increases, plasmon modes of the Al and phonon modes of the oxide hybridize favoring the radiative heat transfer.


Two-Dimensional Plasmonic Molybdenum Oxides on Silicon Photonics—A New Sensing Paradigm Baoyue Zhang and Guanghui Ren; RMIT University, Melbourne, Victoria, Australia.

Silicon photonics has grown to be a mature platform that is compatible with complementary metal-oxide–semiconductor (CMOS) technology and is one of the most potential solutions offering intrinsic advantages in terms of higher bandwidth and lower loss which microelectronics is limited to. However, due to the intrinsic indirect band gap of silicon, silicon photonics has strong limitations on the areas of light generation, modulation and detection. The emerging integration of two dimensional (2D) layered materials onto the silicon photonics platform provide viable solutions to the above-mentioned concerns owing to their unique electronic and optical properties, mechanically flexibility, low fabrication and integration complexity, robustness, and high compatibility with CMOS technology. The tunable electronic and optical characteristics, stability in aqueous environments, large surface area and the intercalatable layered structure of 2D materials can be potentially beneficial to expand the functionality of silicon photonics platform in the telecommunication prospect and biological sensing field. Traditionally, silicon photonics platform heavily relies on the variation of ambient refractive index. However, many chemical and biological events do not lead to a measurable change of ambient refractive index by silicon photonic sensors. Meanwhile, complex surface functionalization processes with low repeatability is essential to the sensor selectivity.

Here, the concept of the 2D materials–silicon photonic chemical sensor is demonstrated using a representative tunable plasmonic 2D candidate. As the operation wavelength of the silicon device is either in the 1300 and 1550 nm telecommunication wavelength, the emerging plasmonics of 2D degenerately hydrogen doped molybdenum oxide ($\text{H}_x\text{MoO}_3$, $0 < x \leq 2$) can be a suitable candidate for coupling onto the silicon photonics platform as its plasmonic absorption wavelength can be precisely tuned across the edge of UV-Vis and the near infrared (NIR) region ($\geq 1000$ nm). More importantly in such a degenerately doped plasmonic system, the $\text{H}^+$ dopants and concurrently injected free electrons are easily exchanged from the 2D MoO$_3$ host structure in the presence of redox chemical and biological events, leading to the alteration of its plasmonic properties which provides the fundamentals for label-free chemical sensing with superior sensitivity.

The achievement of ultrathin films that strongly interact with light, absorbing photons over a wide spectral range is of central importance for applications...
such as sensing, energy harvesting, or biology among others. Strong broadband absorption is challenging in view of the intrinsic limitation in the absorption coefficient of every material, which is especially deleterious for infrared wavelengths. Many wave optics based designs are being currently investigated to surpass this limitation, from photonic crystals to plasmonics and microresonators. All these architectures provide new and exciting means of confining light in sub-wavelength thin films. Nevertheless, the absorption enhancements exhibited are typically restricted to a specific frequency range or mostly take place in the metal part. In sum, a photonic architecture capable of increasing the absorption of a semiconductor throughout its entire absorption coefficient has hitherto, remained elusive.

In our work, we demonstrate a germanium photonic architecture deposited on a metal film acting as a metasurface. Our metasurface sustains the simultaneous excitation of Fabry-Perot resonances, Brewster modes and plasmonic-photonic modes that result in omnidirectional enhanced absorption in a Ge ultra-thin film of 70 nm from 400 nm until 1500 nm. This represents an unprecedented advance in broadband light harvesting, well beyond previous reports.

The key aspects of our findings are:

The absorption in the metasurface exceeds over 100% that of a flat a-Ge film on gold over an impressive bandwidth of 1100 nm. Moreover, the high refractive index of the Ge renders the absorption profile of the metasurface independent to the angle of incidence of the incident light.

We provide the key design guidelines to tune the absorption profile of the metasurfaces and the physical origin beneath each resonant mode sustained by the architecture. With these findings, we show metasurfaces exhibiting strong broadband absorption (appealing to PV community) or NIR absorption peaks reaching 100% at the telecommunication windows (interestingly to the photodetection field).

Remarkably, we fabricated the 16-mm² Ge metasurfaces via nanoimprinting lithography, the most promising method for mass-produced nanostructures. This inexpensive and large area technique adds feasibility to the exciting photonic properties described in the manuscript.

We expect our work to set a new benchmark in the field of light trapping in ultra-thin films and it paves the way for the demonstration of this technology into practical large area applications related to sensing, energy harvesting and photocatalytic devices.

References

9:15 AM EP04.11.05
2D Perovskite-Based Metasurfaces for Enhanced Plasmonic Sensing Shuwen Zeng; XLIM Research Institute, UMR 7252 CNRS/University of Limoges, Limoges, France.

Plasmonic sensors are known as an efficient tool for real time monitoring biomolecular interactions. The detection mechanism is based on the field perturbation at the plasmonic sensing interface induced by the binding of molecules. This molecular binding process could be recorded through reflected light signal when the surface plasmon is excited by the incident light. In this talk, we will present the use of hybrid 2D perovskite-based metasurface nanostructures as a plasmonic sensing substrate. The thickness of the sensing substrate is tuned in an atomic scale and optimized to obtain an enhanced sensing effect. More specifically, a sharp phase signal change and phase-related Goos-Hänchen signal shift was achieved that results from the strong resonance. The improved sensitivities of 2D Perovskite nanostructures were investigated. It is worth noting that the atomic layer design led to the sensing substrate optimized with a tuning scale less than 1 nm. By precisely design the metasurface substrates, more than 4 orders of magnitude improvement of the sensitivity (900,000 um/RIU) were obtained in comparison to the one with pure gold sensing substrate (400 um/RIU). This 2D perovskite-based metasurfaces would pave a way for the development of ultrasensitive and compact biosensors for in-situ applications.

9:30 AM EP04.11.06
Optical Absorption of 2D Transition Metal Carbides (MXenes) from the Ultraviolet to the Infrared Kathleen A. Maleski, Mohamed Alhabeb, Asia Sarycheva, Babak Anasori and Yury Gogotsi; Drexel University, Philadelphia, Pennsylvania, United States.

Two-dimensional (2D) materials continue to be investigated in optical, photonic, and plasmonic applications due to their tunable properties, solution-processable control of lateral size and thickness, and exceptional performances compared to their bulk counterparts. The largest family of 2D materials, known as transition metal carbides and/or nitrides (MXenes), has a general formula of Mₓ₋₁ₓTx, where M represents a transition metal (Ti, Mo, Nb, V, Cr, etc.), X is either carbon and/or nitrogen, and T represents surface terminations. MXenes showed high conductivity at high transparency (6500 S/cm, >97% transparency per-nanometer thickness in the visible range) and an optical absorbance peak in the ultraviolet as well as the visible to near-infrared range (750-800 nm), making it useful in transparent conductors, SERS substrates, photothermal therapy, as a metamaterial, etc. With the material family containing ~30 different synthesized compositions so far (and millions possible), optimization and light-matter characterization of other MXene compositions remains important.

Here, we will discuss optical absorbance characterization from the ultraviolet to the infrared for a variety of MXenes beyond TiCₓTx, including MXenes composed of Nb, V, and Mo metals. For example, thinner Mₓ₋₁ₓTx MXene structures, such as TiCₓTx, exhibit an optical absorbance peak shift to the visible range (~550 nm), demonstrating the optic/electronic differences from similar-but-thicker structures, such as TiC₂Tx. This work provides insight into the optical properties of MXenes as well as spectroscopic information which can be applied to designing next-generation plasmonic and photonic devices, such as photodetectors, electro-chemical devices, random or femtosecond lasers, photothermal therapy agents, transparent conductors, photonic diodes, metamaterials, and more.

References
Three-Dimensional Graphene Oxide Cube Based Octagram Metamaterials for Enhanced Molecular Sensing

Kriti Agarwal, Chao Liu and Jeong-Hyun Cho, University of Minnesota, Minneapolis, Minnesota, United States.

Split-ring resonator (SRR) based metamaterials have been extensively studied due to their enhanced ability to confine light of wavelength several orders of magnitude larger than the dimension of the resonator. The strong confinement of incident light has been explored for the development of a diverse range of sensors including biological and chemical sensors that can assess the properties of the molecules in the vicinity of the split. The polarization dependent switching of resonant modes and resonant frequency of two-dimensional (2D) SRR structures presents a major hurdle in the widespread application of metamaterial sensors where the orientation of the SRR is hard to control. Furthermore, the 2D planar SRR structures do not undergo any resonance when the incident electric field is polarized perpendicular to the plane of the resonator. However, if the 2D metamaterials are self-assembled to form three-dimensional (3D) structures, novel optical properties can be achieved that cannot be realized in 2D planar SRRs. When six symmetric 2D X-shaped resonator segments fabricated on top of square surfaces are self-assembled, the resulting 3D cubic structure forms an 8-pointed star-shaped octagram SRR (OSRR). The octagram resonator consists of splits only at the corners of the cube, thus, achieving 3D SRR splits that are equally moderated by all three vectors (electric field, magnetic field, and wave) for every possible orientation of the OSRR. The 3D splits in OSRR achieve a perfectly isotropic (angle-invariant) transmission response. The strong OSRR coupling and angle-invariant amplitude offer a two-fold advantage i.e. a 25 times higher shift in resonant frequency (25 times higher sensitivity) than 2D SRRs and amplitude-based detection at low concentrations that cannot cause a measurable shift in resonant frequency. However, even with the enhanced sensitivity the constant need for replenishing antibodies used for binding the targeted molecules to the surface of the OSRR presents a major challenge and can also limit the detection capabilities for unknown target molecules. If the surfaces of the cube forming the OSRR are composed of porous nanomaterials (graphene oxide), the properties of the 3D metamaterials can be further tuned for desired sensory application. The strong affinity of GO functional groups towards all chemical and biological molecules and sieving properties of the porous GO layers provide an ideal surface for adhesion of targeted molecules for non-labeled sensing mechanisms. By varying the number of GO layers forming the 3D cubes, properties of the OSRR are tuned for control over sieving and molecular adsorption as well as extending the sensitivity of octagram sensors due to enhanced adhesion of targeted molecules.

10:00 AM BREAK

Fascinating Wave Phenomena in Topological Matter—Topologically-Protected Embedded Eigenstates, Leaky Modes and Exceptional Points

Francesco Monticone; School of Electrical and Computer Engineering, Cornell University, Ithaca, New York, United States.

Engineered metamaterials and photonic crystals with non-trivial topological properties represent an emerging class of photonic structures exhibiting inherent robustness to continuous deformations. While topological photonic insulators have been the subject of growing interest and research efforts in the past few years – especially for the possibility of realizing back-scattering-immune unidirectional wave-guiding systems – relatively less attention has been devoted to scattering and radiating topological photonic structures in the presence of radiation loss or material loss/gain, a research direction that may lead to novel functionalities and applications. In this talk, we will review our recent efforts on different fronts in this exciting area. (i) We will discuss our theoretical and experimental demonstration of the topological nature of embedded eigenstates, or bound states in the continuum, in suitably engineered optical metasurfaces [H. Doelman, F. Monticone, W. den Hollander, A. Alù, and A. F. Koenderink, Nature Photonics, in press (2018)], confirming a theoretical prediction made in [B. Zhen, et al., Phys. Rev. Lett. 113, 257401 (2014)]). (ii) We will present our recent work on topological wave-guiding structures with radiation loss, which support topologically-protected one-way leaky modes that may act as a bridge between free-space radiation and unidirectional guided waves propagating on the surface of complex bodies [S. A. Hassani Gangaraj and F. Monticone, J. Phys. Condens. Matter (2018)]. These findings may lead to relevant advances in the design of leaky-wave (nano)antennas. (iii) We will discuss the possibility of engineering the coupling between topological modes in Hermitian and non-Hermitian waveguides, and the presence of exceptional points accompanied by anomalous propagation effects, such as one-way, defect-immune, loss-immune “Jordan modes” [S. A. Hassani Gangaraj and F. Monticone, arXiv:1803.06419 and arXiv:1805.03767]. (iv) Finally, if time permits, we will also present our recent findings on giant optical forces and torques on localized emitters near photonic topological materials.

11:00 AM EP04.12.02

Reconfigurable Topological Photonics with Stimulated Raman Scattering

David R. Barton, Mark Lawrence and Jennifer A. Dionne; Stanford University, Stanford, California, United States.

Topological photonic engineering leverages the inherent nonlocality of Bloch states in periodic media to enable scatter-free and unidirectional light transport. A DC magnetic field can lift Dirac point degeneracies in a 2D photonic crystal, opening a topologically nontrivial band gap which supports unidirectional edge modes. However, due to the weak and lossy nature of optical Faraday rotation, such magnetic-field sensitive configurations are too bulky for practical implementation and are challenging to reconfigure on fast time- and small length-scales. To date, compact, reconfigurable topological protection at optical frequencies remains an outstanding challenge.

Here, we propose an entirely new route to achieve unidirectional edge modes and topological protection based on photon-phonon interactions. Our approach is inspired by Floquet driving schemes of electronic topological insulators. We break time-reversal symmetry using photon-spin degrees of freedom to excited lattice phonon modes with the same chiral symmetry. Notably, we utilize Stimulated Raman Scattering with circularly polarized light to generate nontrivial topology in a photonic structure. If the pump illumination is circularly polarized, the off-diagonal elements of the Raman-induced effective susceptibility become complex conjugates at the Stokes-scattered frequency, meaning Raman gain inherits a magneto-optic like form without the need for a magnetic field. Unlike magneto-optical materials, stimulated Raman scattering leads to spin dependent dissipation/amplification, bringing a new degree of freedom to topological photonic experiments. Therefore, resonant nanophotonic structures incorporating Raman active materials open the possibility for deeply nanoscale topological protection at optical frequencies.
As a proof of concept, we design a hexagonal photonic crystal consisting of cylinders of Silicon in the near infrared. We use Silicon due to its high Raman susceptibility. First, we calculate the bandstructure of the photonic crystal; a period of 675 nm and cylinder radius of 200 nm exhibits a Dirac cone at the K point at 1500 nm. By locally pumping the photonic crystal with circularly polarized light such that the Dirac point is near the Stokes or anti-Stokes line, a topologically nontrivial band gap is opened. By varying the pump wavelength and helicity in neighboring crystals, we gain intimate control over the formation and evolution of topological defect states. We theoretically demonstrate typical one-way edge state phenomena, as well as unidirectional edge state amplification. We also show how a variety of reconfigurable optical devices such as waveguides, circulators, and resonators can be readily generated by this system.

11:15 AM EP04.12.03
Surface Plasmon Polaritons in Topological Insulator Bi2Se/Te3 Family
Ganapathi Subramania1, P. Duke Anderson1, Stavroula Foteinopoulou2, Jason Dominguez1 and Anthony James1; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Department of Electrical and Computer Engineering, The University of New Mexico, Albuquerque, New Mexico, United States.

The investigation of surface plasmon polaritons is a highly investigated field of research due to their high potential to be applicable to sensors, information technologies, high-resolution imaging, etc. These coherent delocalized electron oscillations are common in metal-dielectric interfaces. However, they also exist in highly doped semiconductors, conducting oxide system or graphene, i.e., in many other systems with high carrier mobility. This poses the question whether such resonances can also be observed at the insulator interfaces.

Bismuth Telluride family can be count as a role topological insulator materials system which has been heavily investigated. It was already shown in 2013 Bi2Se3 one of the member of the family supports Dirac plasmons with energy in the range of 0.5 – 1 eV. The Dirac state is not the only reason for the existence of plasmon resonance in Bi2Se3. The highly anisotropic tetradymites crystal structure also has highly anisotropic dielectric properties5 allowing plasmon excitations.

In this study we would like to show electron energy loss spectroscopy (EELS), energy-filtered transmission electron microscopy (EFTEM) and a finite-difference frequency-domain (FDTD) study for investigating Bi2Se/Te3 and try to find an explanation for plasmon polaritons.

References:

11:30 AM EP04.12.04
Optical Frequency Topological Photonic Structures
Ganapathi Subramania1, P. Duke Anderson1, Stavroula Foteinopoulou2, Jason Dominguez3 and Anthony James3; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Department of Electrical and Computer Engineering, The University of New Mexico, Albuquerque, New Mexico, United States.

Topological photonic structures in analogy to their electronic counterparts can provide new functionalities in nanophotonics through topological protection. Topologically protected photonic modes can propagate unidirectionally without scattering and can have an extreme photonic density of states (PDOS). These unique properties can directly impact many photonic systems used in quantum information processing applications such as single photon transport. Enabling such properties at optical frequencies and on chip-scale will be very important for practical applications of such phenomena. Photonic system composed of appropriately designed two-dimensional photonic crystals (PhC) preserving time-reversal(TR) symmetry can exhibit pseudo-spin based topological behavior. A membrane-type PhC composed of modified honeycomb lattice (HC) can show topologically protected unidirectional photonic pseudospin transport with excellent bandwidth (~50nm) at optical wavelengths (~1550nm), important for chip-scale nanophotonics1. We will discuss design, fabrication and optical response of such topological photonic structures in semiconductor based systems like silicon-on-insulator (SOI)2.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.


11:45 AM EP04.12.05
Enhanced Second Harmonic Generation and Circular Dichroism in Plasmonic Nanostructures Consisting of NanoArcs
Oded Rabin and Kunyi Zhang; University of Maryland, College Park, Maryland, United States.

Using infrared microspectroscopy, the localized surface plasmon resonances (LSPRs) of metallic nanoarc antennas on dielectric substrates have been systematically investigated. The reflection/transmission spectra are rich with information regarding the fundamental and higher order LSPR modes, the dipole component polarization, and mode coupling. The relationship between the LSPR wavelength and the geometric parameters of single nanostructures was established. Furthermore, the relative strength of the different order LSPRs was shown to depend on the central angle of the nanoarc. These rules are used in optimizing the nonlinear optical response of nanoarcs, specifically enhancing the efficiency of Second Harmonic Generation. Mode coupling was studied in a pseudo-chiral assembly of four 90°-nanoarcs in a propeller-like configuration. At the center of the nano-propeller, the arcs were separated by narrow gaps, down to 15nm. The strength of coupling of the plasmons in the adjacent nanoarcs, inversely proportional to the gap size, was manifested in the infrared absorption and circular dichroism (CD) spectra. The CD response may be significantly stronger in 3-dimensional propeller-like configurations that have a polarizability component normal to the surface. This information is utilized in the design of thin-film plasmonic metamaterials with engineered chiroptical responses.
Designing a phase gradient metasurface which efficiently collects spontaneous emission from a quantum emitter, located in the far-field be harnessed at single-photon level [3].

Photonic metasurfaces [2] to engineer the emission from quantum emitters and achieve highly directional emission. Photonic metasurfaces mold optical light from a single emitter in free space is limited due to its isotropic nature of emission. So, a useful single-photon source must emit into a well-defined direction because in practice one can collect light only in a finite solid angle. Here, we propose to harness the exceptional light molding capabilities of photonic metasurfaces [2] to engineer the emission from quantum emitters and achieve highly directional emission. Photonic metasurfaces mold optical wavefronts at subwavelength spatial resolution via phase gradients imparted through the interaction of light with the metasurface elements. They have revolutionized optical designs by enabling the realization of virtually flat optics. Recently, it has been proposed that a judiciously designed metasurface can be harnessed at single-photon level [3].

In this work, we designed a phase gradient metasurface which efficiently collects spontaneous emission from a quantum emitter, located in the far-field ($d/\lambda$), and redirect it back to the source. By controlling the phase imprinted by the metasurface on the incident light, we control the directionality, radiation pattern, and emission rate. In the experiment, our quantum emitters are dibenzoterylene (DBT) molecules embedded in a thin film of anthracene. In the past decade, such organic molecules embedded in an optimal host have emerged as an excellent source of indistinguishable and Fourier-limited single photons with high fidelity and high rate of emission [4]. Remarkably, the spectral region covered by optimal guest-host molecule combination lies in the range of silicon-based photodetectors, whose detection efficiency peaks around 800nm. Furthermore, the emission in the near infrared wavelength range would lower the ohmic loss in noble-metal based nanoantennas. Our simulations show that at 785nm which corresponds to the zero phonon line of DBT in anthracene, the reflection efficiency is greater than 85% with gold nanoantennas. We show that the emission from these molecules are highly directional with deviation from upward direction $\Delta \theta \approx 20^\circ$. Furthermore, we show that we can not only control the emission pattern but also decelerate (or accelerate) the decay rate of the emitters. Moving forward, scaling up to multiple quantum emitters and integrating them with tunable metasurfaces [5] may open new opportunities in quantum information sciences.

References:

Exploiting Polaritons on Antiferromagnetic Materials to Enable Fast Spin Dynamics Jamison Sloan1, Nicholas Rivera1, John D. Joannopoulos1, Marin Soljacic2 and Ido Kaminer3; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Electric Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

The past decades have brought increasing interest in using materials to control light at the nanoscale for diverse applications such as light sources, quantum optics, spectroscopy, spintronics, and sensing. A key paradigm in controlling electromagnetic energy at the nanoscale are materials that support strongly confined surface polaritons. The most well-known example of surface polaritons are plasmon polaritons (SPPs) on conductors, which have been actively studied for several decades. The enabling principle of the strong sub-diffractional light confinement by these materials is that they can sustain a negative electric permittivity. In this work, we propose a new twist on the aforementioned paradigm: negative magnetic permeability modes in antiferromagnets to enable nanoscale control light-matter interactions and spin dynamics. These modes, known as surface magnon polaritons (SMPs) have been observed in antiferromagnetic materials such as MnF$_2$ [1] and FeF$_2$ [2] at THz frequencies. Here, we discuss for the first time enhancement of spin relaxation in emitters using these highly confined magnetic polaritons.

SMPs on antiferromagnetic films offer several advantages over dielectric-based polaritons for engineering strong interactions with spin and other magnetic transitions. We use spontaneous emission of a dipole emitter into SMPs on MnF$_2$ as an example system for understanding the strength of interactions. We show that a $\omega=1.6$ THz magnetic dipole may transition and emit SMPs into a 100 nm MnF$_2$ film at rates more than $10^4$ times higher than the free space rate of $10^{-9}/s$, for a total rate of $10^3/s$. These extreme Purcell factors are possible because SMPs on antiferromagnetic systems can reach wavelengths on the order of 10-100 nm, in some cases more than $10^4$ times smaller than for the same frequency in free space. This is particularly advantageous for speeding up magnetic transitions which are highly inefficient in free space. Another advantage of an antiferromagnetic platform is that SMP mode properties, and by extension dynamics of magnet-matter interaction, can be manipulated by applying an external magnetic field. We explore SMPs as an electromagnetically
dual analog to SPPs, and find that Purcell factors for magnetic transitions on magnonic media scale identically to those of electric transitions on plasmonic media [3], offering a more complete picture of interactions between polaritons and matter.

Until now, methods of magnetic transitions enhancement have been insufficient to allow spin relaxation and electric dipole transitions to compete on the same playing field. Our results present a new route towards bridging this gap.


Reciprocity is a fundamental principle in optics, stating that wave transmission is the same in opposite direction. Breaking this symmetry is necessary for the design of isolators and circulators, which are used to protect sources from reflections and separate signals propagating in opposite directions. Furthermore, it has been recently shown that nonreciprocity is tightly connected to the realization of photonic topological insulators, which allow propagation of signals around sharp corners or other discontinuities without scattering. Conventionally, nonreciprocity is achieved through the magneto-optical effect, but this approach is challenging to integrate and generally leads to large devices. For this reason, there has recently been interest in looking for other ways to break reciprocity. One option is to use nonlinearities, in particular Kerr-type nonlinearities, with spatial asymmetries. Kerr nonlinearities allow changing transmission of a structure versus the input intensity, while spatial asymmetries lead to different field intensities inside a structure when exciting from opposite sides. As a result, in nonlinear asymmetric devices, transmission will generally follow different dependence versus the input power from opposite sides, leading to nonreciprocal response.

During the previous years, many devices of this type have been proposed based on heuristic principles, leading to sub-optimal responses. In this talk, we provide a systematic study of nonlinear isolators, identifying ultimate bounds for their characteristics and showing how these bounds can be achieved in specific nanophotonic designs. We first show that the most widespread category of nonlinear resonators based on a single nonlinear resonator are subject to a trade-off between transmission and isolation intensity range or bandwidth stemming from time reversal symmetry. We next demonstrate how this bound can be largely overcome in systems comprising multiple nonlinear resonators. We also show how such systems can be used to realize more advanced nonreciprocal devices, such as circulators. Furthermore, we present a new approach for the design of nonlinear isolators based on saturable absorption, which is less sensitive to loss compared to the most common approach based on the optical Kerr effect. In all cases, we provide examples of nanophotonic nonreciprocal devices with optical performance according to the derived bounds. Our results clarify several aspects of this important area in optics and provide guidelines for the systematic design of nonlinear nonreciprocal devices.

3:00 PM BREAK
Metal–insulator–metal (MIM) resonant absorbers comprise a conducting ground plane, a thin dielectric, and thin separated metal top-surface structures. Long-wave infrared (LWIR) fundamental absorptions are experimentally shown to be optimized for a ratio of dielectric thickness to top-structure dimension, t/L, of ~1:10. The fundamental resonance wavelength is predicted by different analytic standing-wave theories to be ~2nL, where n is the dielectric refractive index. Thus, for the dielectrics SiO2, AlN, and TiO2, L values of a few microns give fundamentals in the 8-12 micron LWIR wavelength region. Agreement with theory is better for larger t/L. Harmonics at shorter wavelengths are always observed. We show that there are additional resonances, in the far-infrared 20-50 micron wavelength range, well beyond the predicted fundamental. This may impact selectivity in spectral sensing applications.

Photoacoustically guided wave-front shaping provides unmatched capability to deliver focused light into strongly scattering media, such as biological tissue. It allows non-invasive optical imaging deep into brain, tissue, and many other optically opaque turbid media. However, the imaging resolution is intrinsically limited by acoustic diffractions. Increasing ultrasound frequencies addresses the problem at a cost of penetration depth due to the escalated attenuations of ultrasound signals in tissues. Here we introduce a super-resolved meta-lens for photoacoustically guided wave-front shaping and show single speckle imaging through turbid media. We have demonstrated > 3 photoacoustic enhancement factors and > 5 spatial resolution than that of the conventional ultrasound transducers, and more interestingly, > 3 convergence rate in genetic optimization of random phase fronts when one introduces super-resolving meta-lens.
Anisotropic Photonic Microparticles with Multicompartment Designed by Controlled Micromolding

Goh Ho Lee1, Tae Yoon Jeon1, Jong Bin Kim1, Byungun Lee2, Chang-Soo Lee2, Su Yeon Lee3 and Shin-Hyun Kim1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Chungnam National University, Daejeon, Korea (the Republic of); 3Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of).

Regular arrays of colloidal particles, or colloidal crystals, shows striking structural colors due to diffraction from their periodic nanostructures. The structural colors are iridescent and never fade as long as the periodic structures persist. Moreover, the color is tunable by adjusting interparticle separation or refractive index without changing the set of materials. These unique features of structural color, distinguished from chemical pigments, render the colloidal crystals promising for various applications, including aesthetic coating, anti-forgery patches, colorimetric sensors, and encoded microcarriers for biological assays. To use the colloidal crystals as an alternative to chemical colorants, it is required to design the colloidal crystals to have a powder format suspendable in liquid media. Although microgranules of colloidal crystals have been prepared by droplet templating and other methods, it is still challenging to produce photonic microparticles with well-controlled shape and internal structure in a scalable manner.

In this work, we employ a facile micromolding to create photonic microcylinders with pronounced structural colors. To compose a regular array of colloids, silica particles are dispersed in a photocurable resin that forms a solvation layer on the surface of silica particles. The solvation layer exerts disjoining pressure, rendering the silica particles repulsive in a short separation. Therefore, the particles spontaneously form colloidal crystals at volume fraction above 0.1. The photocurable dispersion of silica particles is molded by cylindrical holes in an elastomer. The silica particles form non-close-packed structure by aligning their hexagonal array along the cylindrical wall, which are captured by photopolymerization. The micropillars containing the regular array of silica particles are released from the substrate, resulting in composite microcylinders with a low reflectivity at stopband wavelength. The reflectivity can be enhanced by selectively etching out silica particles to make a regular array of air cavities. The porous microcylinders show pronounced structural colors with high reflectivity, which can be dispersed in a polymer solution to formulate photonic inks for coating. In addition, the microcylinders can be further functionalized by making multiple compartments. We use the photocurable dispersions diluted by a volatile solvent to form compartments that partially fill the cylindrical holes. The remaining volume of the hole can be further subjected to molding process to make two or more compartments. Each compartment can be independently rendered to be either structurally-colored, magneto-responsive, or transparent so that multicompartment photonic microcylinders can be functionalized as a roll process, photonic microgranules can be produced in high throughput. Moreover, the advanced functionality of the multicompartiment microgranules further expands application.

Quantum dot (QD) is a promising material for next-generation display devices due to its superior optical properties such as size-dependent narrow emission and broad absorption. Although it can be used for display in many ways, it is most successfully used in the device of LED-backlit LCDs. In particular, many researchers are paying attention to devices that use QD for patterned polymer film at the top of liquid crystal layer. It has advantages over other types because QDs are located away from heat source (blue LED) to prevent reduction in efficiencies. Therefore, it is expected to increase efficiencies of the device by 50% compared to the conventional LCDs. However, there are still remaining challenges. Although photoretist must be used for patterning, bare QDs cannot be dispersed in the photoretist. To overcome this limitation, we used silica nanoparticles as template particles for dispersing QDs. Furthermore, we synthesized silica nanoparticles with wrinkled surface (WSNs) for purpose of enhancing efficiencies. The WSQs could be synthesized using the water-oil surfactant system. This unique surface structure makes WSQs scatter more light than the silica nanoparticles with smooth surface. Then, we prepared QD-WSN hybrid particles (WSQs) by embedding QDs on WSN through swelling method. Using the WSQs, we could disperse QDs into photoretist film in the form of WSQs. We fabricated the display devices by attaching the nanocomposite onto white OLED. Using various techniques such as electron microscopy, UV-vis spectrophotometer, and fluorometer equipped with integrating sphere, we characterized particles and nanocomposites. We believe this study suggest new way to disperse QDs in photoretist film and enhance the efficiencies of nanocomposites.

Influence of Rare-Earth Substitution on Structural, Magnetic, Optical and Dielectric Properties of ZnO Nanoparticles

Ricardo Martinez Valdez1, Nitu Kumar2, Hanu Huhtinen2, Wojciech M. Jadwisienczak2 and R Palai1; 1Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea (the Republic of); 2Department of Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of).

In this work, ZnO polycrystalline nanoparticles have been intentionally doped with rare earth (RE) elements (Er, Yb) and co-doped with Na by conventional sol-gel process to study the effect of varying doping concentration on structural, dielectric, magnetic, optical (photoluminescence and cathodoluminescence) and photomagnetic properties of ZnO. The structure, morphology, particle size, RE ion doping and incorporation in ZnO matrix of microcylinders can be functionalized. As the micromolding technique is compatible with a roll process, photonic microgranules can be produced in high throughput. Each compartment can be independently rendered to be either structurally-colored, magneto-responsive, or transparent so that multicompartment photonic microcylinders can be functionalized as a roll process, photonic microgranules can be produced in high throughput.

molecules can be highly enhanced by SERS. Moreover, the microparticles possess consistent sizes of mesh, which enables the autonomous exclusion of large proteins while allowing infusion of small molecules. Therefore, it is possible to detect the charged small molecules through SERS with high sensitivity in the absence of interruption from adhesive proteins. To produce such microparticles in a controlled manner, we use a droplet microfluidics. Two aqueous streams of gel precursor containing Au NPs and agglomarants of sodium chloride are simultaneously emulsified into oil phase in a capillary microfluidic device. In the resulting emulsion drops, Au NPs are destabilized by the agglomerants. The agglomerates are captured in a microgel matrix by photocuring the gel precursors. To render the microparticles positively or negatively charged, acrylamide or acrylic acid are copolymerized with a gel precursor of poly(ethylene glycol) diacylate. The charged microparticles concentrate the oppositely-charged small molecules while excluding the same-charged molecules and larger molecules than mesh size. Therefore, we can directly detect charged pesticides dissolved in a protein solution. Moreover, we demonstrate the direct detection of fipronil sulfone dissolved in egg without pre-treatment.

Characterization of Cell Dynamics by Use of Metal Nanoparticle 2D Sheet as an Imaging Substrate

Shihomi Masuda1, Yanase Yuki2, Thasaneeya Kuboki3, Pangkan Wang3, Soh Ryuzaaki4, Koichi Okamoto5 and Kaoru Tamada2; 1Department of Chemistry, Kyushu university, Fukuoka, Japan; 2Graduate School of Biomedical & Health Science, Hiroshima university, Hiroshima, Japan; 3Institute for Materials Chemistry and Engineering, Kyushu university, Fukuoka, Japan; 4Institute of Systems, Information Technologies and Nanotechnologies, Fukuoka, Japan; 5Osaka Prefecture University,
Recently developed super resolution fluorescence microscopes have provided quite important new information concerning molecular scale of hierarchical structure of biological systems [1]. However, these techniques are inadequate for imaging of rapid dynamics of living systems, and also their axial resolution is not as high as their lateral resolution [2]. In our previous study, we have developed a simple and effective method to visualize nanointerface of the adhesive cells using localized surface plasmon resonance (LSPR) excited on a two-dimensionally assembled metal nanoparticle (NP) sheet [3, 4]. The confined light in a few ten nanometers region from the sheet enables to improve axial resolution of fluorescence images drastically, which provides even better SN ratio (high contrast) images compared with the total internal reflection fluorescence (TIRF) microscopy, where the exposure time became even shorter owing to the plasmon-enhanced fluorescence. This technique is suitable for imaging the cell/substrate contact regions where cellular dynamics and molecular reaction occur.

In this study, we conducted detailed analysis of cell dynamics via the local movement of focal adhesion visualized by our LSPR method. Oleylamine-capped gold NPs (AuOA) sheets were fabricated at the air-water interface by using Langmuir-Schaefer method and transferred onto a hydrophobic cover glass. In this study, we conducted detailed analysis of cell dynamics via the local movement of focal adhesion visualized by our LSPR method. Oleylamine-capped gold NPs (AuOA) sheets were fabricated at the air-water interface by using Langmuir-Schaefer method and transferred onto a hydrophobic cover glass.

In this work, we demonstrate an effect of Surface-Enhancement Raman Spectroscopy (SERS) on N719 dye molecule caused by silver nanoparticles (NPs) as an ablation source. Nanoparticles were characterized by using Laser Ablation for Low Power Laser Ablation to produce a high-contrast SERS signal on the surface of silver nanoparticles. The SERS signal was measured using a confocal Raman microscope equipped with a Nd:YAG laser (λ = 1064 nm) as an excitation source. Nanoparticles were characterized by using Laser Ablation for Low Power Laser Ablation to produce a high-contrast SERS signal on the surface of silver nanoparticles. The SERS signal was measured using a confocal Raman microscope equipped with a Nd:YAG laser (λ = 1064 nm) as an excitation source.

In this work, biocompatible, high-quality and monodisperse β-CD-capped AuNPs 15-20 nm in diameter were synthesized based on a complete “green” synthesis method. The microfiber is fabricated by tapering a standard single-mode optical fiber using the heating and pulling method. The synthesized nanofibers are decorated on the surface of a microfiber via electrostatic interaction to realize a highly sensitive and highly integrated biosensing device. The surface modification of gold nanoparticles has been proven effective to meet goals of both biocompatibility and specific molecular recognition. As a macrocyclic molecules, cyclodextrins can specifically recognize cholesterol through host-guest interaction.

In this work, biocompatible, high-quality and monodisperse β-CD-capped AuNPs 15-20 nm in diameter are synthesized based on complete “green” synthesis method. The microfiber is fabricated by tapering a standard single-mode optical fiber using the heating and pulling method. The synthesized nanofibers are decorated on the surface of a microfiber via electrostatic interaction to realize a highly sensitive and highly integrated biosensing device. The surface modification of gold nanoparticles has been proven effective to meet goals of both biocompatibility and specific molecular recognition. As a macrocyclic molecules, cyclodextrins can specifically recognize cholesterol through host-guest interaction.

In this work, biocompatible, high-quality and monodisperse β-CD-capped AuNPs 15-20 nm in diameter are synthesized based on complete “green” synthesis method. The microfiber is fabricated by tapering a standard single-mode optical fiber using the heating and pulling method. The synthesized nanofibers are decorated on the surface of a microfiber via electrostatic interaction to realize a highly sensitive and highly integrated biosensing device. The surface modification of gold nanoparticles has been proven effective to meet goals of both biocompatibility and specific molecular recognition. As a macrocyclic molecules, cyclodextrins can specifically recognize cholesterol through host-guest interaction.

In this work, biocompatible, high-quality and monodisperse β-CD-capped AuNPs 15-20 nm in diameter are synthesized based on complete “green” synthesis method. The microfiber is fabricated by tapering a standard single-mode optical fiber using the heating and pulling method. The synthesized nanofibers are decorated on the surface of a microfiber via electrostatic interaction to realize a highly sensitive and highly integrated biosensing device. The surface modification of gold nanoparticles has been proven effective to meet goals of both biocompatibility and specific molecular recognition. As a macrocyclic molecules, cyclodextrins can specifically recognize cholesterol through host-guest interaction.

In this work, biocompatible, high-quality and monodisperse β-CD-capped AuNPs 15-20 nm in diameter are synthesized based on complete “green” synthesis method. The microfiber is fabricated by tapering a standard single-mode optical fiber using the heating and pulling method. The synthesized nanofibers are decorated on the surface of a microfiber via electrostatic interaction to realize a highly sensitive and highly integrated biosensing device. The surface modification of gold nanoparticles has been proven effective to meet goals of both biocompatibility and specific molecular recognition. As a macrocyclic molecules, cyclodextrins can specifically recognize cholesterol through host-guest interaction.
through Scanning Electron Microscopy (SEM) and optical absorption spectroscopy. Absorption measurements of colloidal solutions show an absorption peak at \( \lambda = 400\text{nm} \) that is associated with localized surface plasmon resonance of NPs. SEM analysis reveals that the NPs have spherical shape and a large size distribution ranging from 20 to 200nm. The SERS effect of NPs was demonstrated for low laser flux conditions \( 13.2 \text{µW} \) (up to \( 3.3 \text{mJ/cm}^2 \)) on N719 dye and Rhodamine-B molecules, deposited over NPs thin films. Presence of the thin film of NPs has resulted in a four times increase of the Raman intensity of the dyes molecules.

**EP04.15.11**

**Cellulose Nanocrystals for Security Applications—Embedding Non-Optical Signatures Provided by Nanoparticles into Cellulose Nanocrystal Chiral Nematic Films**

Nicky Wojtania; Harvard University, Cambridge, Massachusetts, United States.

The recent increase in counterfeited documents, banknotes, and medications impacts society, calling for new security technologies that are difficult to reproduce. Nature mimicking materials with unique optical properties are well-suited for security applications. Aqueous suspensions of Cellulose Nanocrystals (CNC), extracted from cellulose, self-assemble into chiral nematic structures creating, upon drying, freestanding films. These films exhibit unique optical properties: structural color, iridescence, and light polarization for covert and overt encryption. The films are also suitable for anti-counterfeiting materials and can be enhanced to provide security features beyond optical properties. It was hypothesized that combining CNC with sub 50 nm metal and non-metal nanoparticles yields composite materials that retain the CNC optical properties. It was further hypothesized that the added nanoparticles influence the materials’ electrical and dielectric properties, which could be detected and validated as non-optical properties. The experiment created new, CNC-based composite materials with various nanoparticles: copper, aluminum, cobalt, iron, carbon single-walled nanotubes, graphene, titanium dioxide, titanium carbide, fluorescent rhodamine nanoparticles, and gold colloid. All composite films retained the CNC unique optical properties. Adding the nanoparticles shifted the structural color and reduced iridescence, measured with a custom-designed setup using a Fiber Spectrometer. The film morphology, examined using a Polarized Optical Microscope and Scanning Electron Microscope, was uniform with the nanoparticles evenly dispersed. The film’s non-optical properties (resistivity and dielectric constant) were measured using a custom-built setting composed of plates and electrodes connected to Digital Multimeters. Adding the nanoparticles uniquely impacted the CNC non-optical properties. The functionalization of CNC films beyond optical properties makes these materials even more suitable for anti-counterfeiting materials.

**EP04.15.12**

**Optical Chirality of Achiral Metal Nanoparticles by Broken Time-Reversal Symmetry without External Magnetic Field**

Jong-Won Park; Mechanical Engineering, Texas Tech University, Lubbock, Texas, United States.

Natural optical activity of plasmonic metal nanoparticles has been studied in terms of molecular chirality. The nanoparticle is commonly assumed to be chiral when the nanoparticle lacks inversion symmetry or is parity-odd (P). While optical activity generally requires the violation of parity and time-reversal symmetry (PT-symmetry), the time-reversal symmetry has typically been neglected in nanomaterials. Here, we demonstrate that time-reversal symmetry can be broken in the plasmonic nanoparticles by longitudinal volume plasmons. Without applying an external magnetic field we experimentally observed circular dichroism (CD) of gold, silver, and copper nanoparticles at the plasmon excitation energy. Spatial variation of light absorption in the nanoparticle is attributed to the origin of longitudinal plasmons that light cannot excite but an optical force may be able to. We propose that optical forces can generate the optical activity of achiral metal nanoparticles. The polarization rotation of surface plasmons is interpreted as orbital angular momentum that is time-odd (T−). The sum rule observed for the dipolar and quadrupolar surface plasmons may indicate the conservation of orbital angular momentum in the surface plasmon oscillation. We show that, rather than only parity, the PT-symmetry fully describes the optical activity of nanomaterials.

**EP04.15.14**

**Strong Room-Temperature Luminescence Emission Around 1.5 μm from Nanostructured Erbium Oxides in Zinc Oxide Nanowire Arrays**

Devika Vipin and Mengjing Huang; State University of New York Polytechnic Institute, Albany, New York, United States.

Zinc oxide (ZnO) semiconducting nanorods/nanowires are very attractive for fabrication of novel optoelectronic nanodevices, due to their excellent optical properties (e.g., a large excitonic binding energy of 60 meV) combined with their ease in synthesis. ZnO has a direct wide bandgap of \( 3.4 \text{ eV} \), leading to efficient light emission in the ultraviolet (UV) region. An extension of the ZnO nanowire emission beyond the UV spectral region, and in particular, to the technologically important near infrared range around 1.5 μm would greatly enhance these devices’ applications.

Erbium (Er) has offered a means towards optical amplification around 1.5 μm with these structures results in broadening of the bandwidth of absorption due to the possible near-field enhancement at that range of wavelengths. This material is thus of potential interest for absorption, typically at wavelengths > 1 μm through optical coatings for solar cell architectures.

**EP04.15.15**

**Low-Cost dendritic Silver Nanostructures for Large Area Optical Applications**

Anmol Walia1, Rajinder S. Deol1, Ghasan E. Jabbour2 and Madhusudan Singh1; 1Indian Institute of Technology Delhi, New Delhi, India; 2University of Ottawa, Ottawa, Ontario, Canada.

Control of morphology, shape and size of silver nanostuctures play a pivotal role for realization of desirable optical properties, which have been extensively studied for such systems. In particular, dendritic and branched silver nanostructures with self-assembled hierarchical and repetitive structures reveal unique optical absorption response. Large area solar cells require low-cost absorbing materials realized through non-toxic deposition methods. In this work, we report a low-cost approach to fabricate disordered branched silver nanostructures realized via a multi-generation light induced colloidal method. As a first step, standard citrate stabilized silver seeds with an average size of 8 nm and measure absorbance at 392 nm were synthesized. First generation silver nanotriangles were subsequently synthesized by growing silver seeds in presence of excess citrate and AgNO₃ precursors under controlled illumination of 590 nm (width: 20 nm) wavelength at room temperature. UV-visible absorption study shows a broad absorbance from 600-800 nm. Transmission electron microscopy (TEM) measurements correlate the absorbance to silver nanotriangles of edge lengths centered at 65 nm. A second illumination of 590 nm (width: 20 nm) at 25°C TEM scans reveal branched, hierarchichal, dendritic structures ranging from 1 - 15 μm in size. Interaction of light the visible-NIR range with these structures results in broadening of the bandwidth of absorption due to the possible near-field enhancement at that range of wavelengths. This material is thus of potential interest for absorption, typically at wavelengths > 1 μm through optical coatings for solar cell architectures.

**EP04.15.16**

**Size Controlled Photoemission and Photocatalytic Activity of Au-ZnO Nanostructures**

Issraa Shahine1, Safi Jrad2, Nour Beydoun2, El-Eulmi 1; 2University of Ottawa, Ottawa, Ontario, Canada.

Mechanical Engineering, Texas Tech University, Lubbock, Texas, United States.

The recent increase in counterfeited documents, banknotes, and medications impacts society, calling for new security technologies that are difficult to reproduce. Nature mimicking materials with unique optical properties are well-suited for security applications. Aqueous suspensions of Cellulose Nanocrystals (CNC), extracted from cellulose, self-assemble into chiral nematic structures creating, upon drying, freestanding films. These films exhibit unique optical properties: structural color, iridescence, and light polarization for covert and overt encryption. The films are also suitable for anti-counterfeiting materials and can be enhanced to provide security features beyond optical properties. It was hypothesized that combining CNC with sub 50 nm metal and non-metal nanoparticles yields composite materials that retain the CNC optical properties. It was further hypothesized that the added nanoparticles influence the materials’ electrical and dielectric properties, which could be detected and validated as non-optical properties. The experiment created new, CNC-based composite materials with various nanoparticles: copper, aluminum, cobalt, iron, carbon single-walled nanotubes, graphene, titanium dioxide, titanium carbide, fluorescent rhodamine nanoparticles, and gold colloid. All composite films retained the CNC unique optical properties. Adding the nanoparticles shifted the structural color and reduced iridescence, measured with a custom-designed setup using a Fiber Spectrometer. The film morphology, examined using a Polarized Optical Microscope and Scanning Electron Microscope, was uniform with the nanoparticles evenly dispersed. The film’s non-optical properties (resistivity and dielectric constant) were measured using a custom-built setting composed of plates and electrodes connected to Digital Multimeters. Adding the nanoparticles uniquely impacted the CNC non-optical properties. The functionalization of CNC films beyond optical properties makes these materials even more suitable for anti-counterfeiting materials.
Infrared-Transparent Thermally-Insulating Polyethylene Aerogels for Radiative Cooling

Radiative cooling exploits the high transparency of the earth’s atmosphere at mid-infrared wavelengths (8-13 µm), often referred to as the atmospheric window, to radiate heat to the cold outer space and passively cool terrestrial objects. While most of the past work has focused on developing spectrally selective surfaces to maximize radiative heat transfer and cooling performance, low conduction and convection thermal resistances between the radiative cooler and the environment have severely hindered the device-level performance. We have developed infrared-transparent and thermally-insulating polyethylene aerogels (PEAs) optimized for radiative cooling applications that could significantly improve the cooling power and minimum temperature of terrestrial objects.

References:

current radiative coolers by minimizing parasitic heat gains from the environment while allowing radiative exchange with outer space. Highly-porous PEAs of varying densities (20 to 120 kg/m³) were fabricated by thermally-induced phase separation of polyethylene/decalin and polyethylene/paraffin oil solutions followed by a solvent extraction by CO₂ supercritical drying. We tuned the porous structure of the PEAs by optimizing the fabrication process to minimize scattering and absorption in the atmospheric window and thus maximize transparency. We measured an atmospheric-window-weighted IR transparency of up to 92% along with a solar-weighted reflectance of 87% for a 2.3 mm thick sample with a density of 25 kg/m³. The optical measurements were compared to our theoretical model which solves the radiative transfer equation and assumes Mie scattering. We also characterized the thermal properties of the PEAs experimentally as well as theoretically, accounting for solid, gaseous and radiative contributions, and report an effective thermal conductivity of less than 0.05 W/mK at room temperature. Finally, we demonstrate that PEAs can significantly improve the performance of existing radiative cooling systems due to their combined high IR and low solar-weighted transmittance as well as ultra-low thermal conductivity.

EP04.15.20
Enhancing Circular Dichroism by Chiral Hotspots in Achiral Dielectric Nanocube Dimers

Kan Yao1,2 and Yongmin Liu1; 1Northeastern University, Boston, Massachusetts, United States; 2The University of Texas at Austin, Austin, Texas, United States.

An object is chiral if it cannot be superimposed to its mirror image. The existence of chirality in nature is universal, ranging from galaxies to gastropod shells to biomolecules. While a pair of chiral molecules, termed as enantiomers, exhibit identical scalar physical properties, they take part in many chemical reactions in biological processes differently, acting in a desirable or harmful way. Therefore, discriminating between enantiomers is of vital importance, especially in pharmacology and life sciences.

Light can be chiral as well, and chiral light-matter interactions provide an opportunity to noninvasively identify chiral molecules with superior precision. For instance, circular dichroism (CD) spectroscopy that measures the differential absorption of left- and right-circularly polarized (L/RCP) light is widely used to reveal the structural information of biomolecules. However, CD signals are usually very weak due to the intrinsically weak chirality of the molecules. In order to enhance CD signals for characterization at low concentrations, different platforms have been proposed, such as partially reflecting mirrors, plasmonic nanostructures, and dielectric nanoparticles, etc.[1,2] Despite improved differential absorption by chiral molecules, these methods suffer from either strong background absorption by the platforms or non-uniform chiral fields that hinder the global CD enhancement. Both issues impose limitations on the measurement sensitivity. Therefore, novel platforms exhibiting low loss and uniform chiral fields are highly desirable.

In this work, we numerically study the generation of chiral fields in achiral dielectric nanocube dimers and demonstrate its beneficial role in enhancing CD signals.[3] With practically achievable designs, we show that under the illumination of circularly polarized light, the local magnetic and electric fields are simultaneously enhanced and properly overlapped in the gap area, resulting in an accessible and uniform chiral hotspot. A volume-averaged chirality enhancement factor exceeding 15 is demonstrated for silicon nanocubes in the visible region around 550 nm wavelength. We further investigate the CD enhancement by positioning chiral molecules at the chiral hotspot. Thanks to the achiral and low-loss properties of the proposed platform, very weak absorption from the nanocubes will be present, which allows effective characterization of the chiral molecules and an over-10 fold enhancement of CD signals is demonstrated. We also consider other materials such as titanium dioxide, and the desired performance is successfully achieved in the violet region. Being able to engineer chiral fields without complex nanostructures or plasmonic materials, we expect that our findings can open up a new avenue to CD spectroscopy, chiral sensing and photolysis.


EP04.15.21
Pyramidal-Shaped Metal-Dielectric Hybrid-Structure Geometry with Asymmetric TiO2 Layer for Broadband Light Absorption and Photocatalytic Applications

Hee Jun Kim and Jeong Min Baik; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Here, we demonstrate a pyramidal-shaped metal-dielectric hybrid-structure geometry with an asymmetric TiO₂ layer and the application for the solar water oxidation. The TiO₂ was obliquely deposited onto the pyramidal-shaped Au film, which makes the pyramids asymmetric in thickness. The light absorption through the suggested design in the entire UV-visible region was significantly enhanced by the asymmetry of the pyramids, simulated by 3-D finite difference time domain simulation and confirmed by confocal spectral mapping techniques. The band alignment at the interface of TiO₂/Au film by introducing Ti as an insertion layer was tuned, promoting the separation of the photogenerated carriers via the efficient transport of electrons to Au films by minimizing parasitic heat gains from the environment while allowing radiative exchange with outer space. Highly-porous PEAs of varying densities (20 to 120 kg/m³) were fabricated by thermally-induced phase separation of polyethylene/decalin and polyethylene/paraffin oil solutions followed by a solvent extraction by CO₂ supercritical drying. We tuned the porous structure of the PEAs by optimizing the fabrication process to minimize scattering and absorption in the atmospheric window and thus maximize transparency. We measured an atmospheric-window-weighted IR transparency of up to 92% along with a solar-weighted reflectance of 87% for a 2.3 mm thick sample with a density of 25 kg/m³. The optical measurements were compared to our theoretical model which solves the radiative transfer equation and assumes Mie scattering. We also characterized the thermal properties of the PEAs experimentally as well as theoretically, accounting for solid, gaseous and radiative contributions, and report an effective thermal conductivity of less than 0.05 W/mK at room temperature. Finally, we demonstrate that PEAs can significantly improve the performance of existing radiative cooling systems due to their combined high IR and low solar-weighted transmittance as well as ultra-low thermal conductivity.

Here we show that colloidal bilayers of gold nanoparticles allow the excitation of a nominally dark plasmon by a plane wave at normal incidence due to field retardation. The radiative decay of this mode is suppressed, because of its narrow emission cone. The dark mode is composed of dipole excitations in each nanoparticle, where the dipoles align parallel within a layer, but antiparallel from one layer to the next. We show experimentally that gold nanoparticle bilayers have a strong absorption peak at 1.5 eV that arises from the excitation of the dark mode and is completely absent in the monolayer. The spectral position and width of the dark mode are tuned by changing the interparticle distance. The peak position may be adjusted for values between 1.4 and 2 eV. The crystalline nanoparticle layers assemble from colloidal gold nanoparticles in solution that were produced by wet chemistry. Nanoparticle bilayers promise the production of low-cost, large-scale plasmonic surfaces for enhancing catalytic processes via hot electron generation.

EP04.15.23
GeSn Nanodots with 26 at.% Sn Composition Towards Mid-Infrared Integrated Photonics

Alejandra V. Cuervo Covian, Xiaoxin Wang and Jifeng Liu; Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, United States.
Direct bandgap semiconductors on Si is a key technical challenge for Si-based integrated photonics. A promising approach is to alloy Ge with Sn, which effectively causes the energy of the direct Γ valley to decrease faster than the indirect L valley, leading to indirect-to-direct gap transition. One of the main issues with this approach is that the equilibrium solubility of Sn in bulk Ge is <1 at % according to the existing Ge-Sn phase diagram for bulk materials (extrapolated at ~400 C) [1]. Although substitutional Sn compositions of ~9-10 at % have been achieved by CVD, MBE and direct crystallization of amorphous GeSn [2], higher Sn composition is needed for stronger direct bandgap semiconductor behavior and better optoelectronic properties in the mid-infrared regime. In these cases, Sn segregation is the biggest concern. Here we present a counterintuitive approach that achieves a much higher equilibrium solubility with up to 26 at % Sn in GeSn nanodots directly crystallized on dielectric layers towards monolithic 3D mid-infrared (MIR) photonic integration in Si. The approach involves sequentially depositing a layer of metallic Sn nanodots with a diameter of 20-60 nm and a thin layer of Ge using physical vapor deposition (PVD), followed by interdiffusion/crystallization annealing at 300-500 C. In this case the alloying of Ge and Sn is driven by interfacial energy minimization between the Sn nanodots and the Ge capping layer, which allows for higher equilibrium solubility of substitutional Sn into the Ge lattice. It can also be viewed as dissolving the nanoscale Sn nuclei below the critical size for nucleation into the Ge lattice. X-ray diffraction and Raman spectroscopy analyses indicate that up to 26 at.% Sn has been substitutionally incorporated into the Ge lattice, increasing the lattice constant by 4% compared to pure Ge. The initial metallic Sn nanodots exhibit a strong (200) orientation, while after interdiffusion and crystallization the resulting GeSn nanodots show a strong (111) orientation without observable diffraction peaks from metallic Sn. This result indicates that Sn nanodots are completely dissolved into the lattice of Ge after crystallization annealing, and that the solubility limit of Sn in GeSn nanostructures is at least 30x higher than that in bulk materials. To our knowledge, this is also the first observation of converting metallic Sn into diamond cubic lattice via interdiffusion. Preliminary studies on these high Sn composition GeSn nanodot samples also show photoluminescence (PL) at both low and room temperature, suggesting good crystallinity. These results offer a new and facile approach to fabricate high Sn composition GeSn nanostructures for MIR integrated photonics.

plasmonic molecules and thus tune their corresponding coupled resonances across the entire visible spectrum. Our fabrication method can even progressively control the symmetry of the dimer and trimer structures across an entire wafer while preserving a nanogap. Furthermore, we spectroscopically map the resonances and qualitatively model the spectra. Theory and experiment are in good agreement with numerical calculations. While thus far dimer structures have largely been obtained by random drop casting, we show that we can systematically obtain identical dimers and also identical trimers where one of several parameters is systematically changed across the wafer. We expect that the structures will be important for spectroscopic studies.


9:30 AM EP04.16.04
Influence of Partially-Oxidized Plasmonic Metasurface Electrodes on the Electrical and Optical Properties of Organic Semiconductors
Zhongkai Cheng, Yan Wang, Manish Chhowalla and Deirdre O'Carroll, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

The efficiency of absorption and emission in organic semiconductors can be significantly improved by near-field optical interactions with resonant metallic plasmonic nanostructures. However, these improvements do not often translate to significantly enhanced optoelectronic device performance. Practical metals that exhibit strong plasmonic properties don’t have stable work functions suitable for effective charge collection or injection from most organic semiconductors. To address this problem, in this project, we investigate the application of surface oxides to both planar and structured metallic plasmonic metasurface electrodes and determine the impact on the charge transport and stability of organic semiconducting conjugated polymer devices. The properties of metasurface electrodes and surface oxides can be elucidated by comparing with planar devices and devices without surface oxides through electrical measurements, such as current-voltage measurements, and capacitance-voltage measurements. In addition, we determine the charge collection barrier height at the conjugated polymer-metal electrode interface to understand the impact of surface oxides and nanostuctures on charge injection and charge collection from the polymer. The overall goal is to make better performing electrodes for organic photovoltaics that are also capable of exhibiting effective light trapping below the diffraction limit.

Silver nanoparticle (AgNP) metasurface electrodes were fabricated using a thermally-assisted dewetting method. Then hole-only conjugated polymer-based devices were fabricated directly on top of AgNP metasurface electrodes. Devices with and without a silver oxide (AgOx) hole transport layer on the AgNP metasurface electrode were prepared. MoO3 is used as an interlayer between the conjugated polymer and a top Au electrode to block electrons and, hence, to achieve hole-only operation. This device configuration allows us to investigate the barrier to hole injection on the AgNP metasurface electrode side. The barrier to hole injection/collection from the conjugated polymer is expected to change when the AgOx layer or plasmonic metasurface is used compared to when only planar Ag is used. UV-visible extinction spectra and dark-field scattering spectra of AgNP electrodes with different sizes show different optical properties (such as scattering intensity and color) between AgNP metasurface electrodes with different nominal AgNP diameters. Current-voltage measurements show that the turn-on voltage of devices with an AgOx layer is lower than the devices without AgOx, which is attributed to the lower workfunction of AgOx relative to Ag. Ultraviolet photoelectron spectroscopy (UPS) is used to obtain the work function, which can be used to verify origin of the lower turn on voltage. Meanwhile, X-ray photoelectron spectroscopy (XPS) is also used to analyze the surface composition of the AgOx electrodes.

9:45 AM BREAK

10:15 AM EP04.16.05
Observation of Ultrafast Hot-Hole Injection but Slow Hot-Electron Dynamics in Au/p-GaN Heterostructures
Joseph S. DuChene1,2, Giulia Tagliasacchi1,2, Mohamed Abdellah1, David Gostzola1, Alex J. Welch1,2, Wen-Huo Cheng1,2, Jacinto Sa2,3 and Harry A. Atwater1,2; 1California Institute of Technology, Pasadena, California, United States; 2Department of Chemistry-Angstrom Laboratory, Uppsala University, Uppsala, Sweden; 3Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, United States; 4Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; 5Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California, United States.

Harvesting hot carriers from photo-excited metal nanoparticles on ultrafast (~fs) timescales holds great promise for the operation of non-equilibrium optoelectronics. While the ultrafast dynamics of hot electrons in metal nanostructures have been extensively studied, the temporal evolution of plasmon-induced hot holes remains unexplored. Here, we monitor ultrafast hot-hole injection from gold (Au) nanoparticles into the valence band of p-type gallium nitride (p-GaN) via ultraviolet transient absorption spectroscopy. By spatially separating hot-electron-hole pairs across the metal-semiconductor interface via plasmon excitation, Au/p-GaN heterostructures offer an ideal platform for spectrally distinguishing the dynamics of the hot holes, which can be probed in the infrared regime via free-carrier absorption within the p-GaN valence band, from the hot electron dynamics occurring on the metal, which are monitored across the visible spectrum with a white-light supercontinuum probe. We observe plasmon-induced hot-hole injection from Au to p-GaN within the 200 fs instrument response of our experimental setup, placing hot-hole transfer from a plasmonic metal to a p-type semiconductor on similar timescales as hot-electron injection into an n-type semiconductor. Moreover, hot holes persist within the p-GaN valence band for several nanoseconds before recombination of the charge-separated state occurs across the Au/p-GaN heterojunction. We further evaluated the influence of hot-hole injection on the temporal dynamics of hot electrons left behind on Au by comparison with Au/SiO2 heterostructures for which hot-hole injection is prohibited. Interestingly, we found that the ultrafast (~200 fs) injection of hot-holes into p-GaN on timescales commensurate with electron-electron scattering exerts a profound influence on the spectral and temporal dynamics of hot electrons on the Au nanoparticles. Taken together, these ultrafast studies offer a comprehensive picture of hot-carrier dynamics across the Au/p-GaN heterojunction and suggest the potential for manipulating the energy distributions and subsequent thermalization dynamics of hot electrons above the metal Fermi level by controlling the collection of hot holes on ultrafast timescales.

10:30 AM EP04.16.06
Metal Alloys for Plasmonic Hot Carrier Generation in the Infrared
Sara K. Figueiredo Stofela1,2, Orhan Kızılkaya1,2, William A. Shelton1, Philip T. Sprunger1,3 and Kevin M. McPeak1; 1Chemical Engineering Department, Louisiana State University, Baton Rouge, Louisiana, United States; 2Physics Department, Louisiana State University, Baton Rouge, Louisiana, United States; 3Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana, United States.

Plasmonic hot-carrier devices offer below the band-gap charge generation, ultrafast response times and spectral and polarization control over absorption at the nanoscale. These features could result in transformative advances in photon detection devices, especially in the near-infrared regime. However, the dominant route for hot-carrier generation from current noble metals (e.g. Au) is interband transitions from high-energy (≥2 eV below Fermi level) d-band states. There is a need for plasmonic materials which offer efficient hot-carrier generation from intraband transitions utilizing low energy (~1 eV from Fermi level) infrared excitations. Our work focuses on identifying promising alloys and their associated composition which could result in efficient plasmonic hot carrier generation from infrared excitation.
We report the measured and calculated electronic properties of various binary metal-alloy thin films deposited at room temperature using co-thermal evaporation. Our deposition technique is amenable to modern lithographic approaches and therefore can be easily utilized to deposit nanostructured alloys for future devices. Both noble-noble and noble-transition metal alloys, where the transition metal exhibited a high electronic density of states (EDOS) near the Fermi energy, were characterized. We show experimental and calculated EDOS for 50 nm thick Ag-Cu, Ag-Pd, Ag-Ni, Ag-Ti, Au-Ni, Au-Ti, and Au-Pd films with various compositions. EDOS were collected using angle-resolved photoemission spectroscopy (ARPES) and film composition was measured using X-ray photoemission spectroscopy (XPS). Results of 50 nm thick Ag-Cu (25/75%) deposited at RT reveal shifts in d-bands due to hybridization above 2eV binding energy. However, upon annealing above 400°C, phase separation occurs. These results will be correlated with the local structure of the alloy film employing XAS and EXAFS. In the case of Ag-Cu, current EXAFS results reveal a nanocrystalline single phase material. Lastly, we will report the visible and near-infrared optical properties of these films and discuss them relative to the measured and calculated EDOS.

10:45 AM EP04.16.07
Picosecond Transient Absorption Spectra of Pyramidal Gold Nanoparticles Mina Nazari, Min Xi, Rahm Gummuluru, Sean B. Foster, Mi Hong, Björn Reinhard and Shyamsunder Erramilli; Boston University, Boston, Massachusetts, United States.

Plasmonic nanoparticles are of interest due to their novel therapeutic and diagnostic application. Recently, there has been increased interest in the potential for designed nanomaterials for non-equilibrium studies and materials processing. The optical properties of metal nanoparticles strongly depend on their electronic responses which are different than bulk metals. In our study, the electronic behavior of melallic nanoparticle are investigated using femtosecond transient absorption measurement to elucidate laser exposure effects on their spectroscopy and non-equilibrium dynamics. Femtosecond laser pulses generated by a regeneratively amplified Ti-sapphire laser are used to excite localized surface plasmon resonances in synthesized gold nanorods with a plasmon resonance close to 805 nm. The transient absorption spectra of the nanoparticles are obtained by recording their absorption at different probe delays. Our experimental findings indicate that the amplified femtosecond excitation of the surface plasmon resonance band in gold nanorods leads to transient absorption spectral changes which reveals that the electron-phonon relaxation dynamics is happening on early picosecond time scale. This relaxation time depends on the pump peak power indicative of a temperature dependent nonlinear relaxation back to equilibrium. Spectroscopy, light scattering and Finite element method simulations are used to characterize non-equilibrium dynamics. The findings expand the knowledge about the ultrafast electron processes in nanoparticles and provide information for controlling their time response, facilitating prospects for plasmonically enhanced cavitation for materials processing.

11:00 AM EP04.16.08
Real-Time Dynamics and Decomposition of Plasmons in Nanoparticles Thomas Rossi1, Paul Erhart2 and Mikael Kuismi2; 1Chalmers University of Technology, Gothenburg, Sweden; 2University of Jyväskylä, Jyväskylä, Finland.

Localized surface plasmons render metal nanoparticles efficient light absorbers at their resonance frequencies. After its excitation, the plasmon resonance decays into high-energy electrons and holes, which, combined with the large absorption cross section, makes metal nanoparticles attractive hot-carrier generators for photocatalysis. In this work, we study the femtosecond real-time dynamics of localized surface plasmons in noble metal nanoparticles by using time-dependent density-functional theory (TDDFT). By extending the frequency-space Kohn-Sham decomposition analysis [1] to real time, we follow the plasmon formation as a collective excitation, track its subsequent decay into incoherent electron-hole transitions, and finally, obtain the corresponding hot-carrier distributions. Our work paves the way for addressing the spatiotemporal dynamics of hot-carrier generation in catalytically-relevant edge and corner sites of nanoparticles.


11:15 AM EP04.16.09
A Combined Experimental and Theoretical Approach to Measure Spatially Resolved Local Surface Plasmon Resonances in Aluminum Nanoparticles Alina Bruna1,2, Canhui Wang1,2, Dayne Sweareng1, Naomi J. Halas2 and Renu Sharma1; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2Maryland Nano Center, University of Maryland, College Park, USA.; College Park, Maryland, United States; 3Rice University, Houston, Texas, United States.

Localized surface plasmon resonances (LSPRs) occur in certain metals where electrons confined to the metal surface oscillate with a frequency similar to that of the perturbing source, giving rise to localized electromagnetic fields. In this study we employ experimental and theoretical analyses to characterize LSPRs in Alcore(Al2O3)shell nanoparticles with controlled morphologies. We perform simulations of LSPR using boundary element methods, where the electron beam is passing at a distance of 2.5 nm from the surface of an icosahedral Alcore(Al2O3)shell nanoparticle. The electron energy loss probability spectra show that, for the mode located at an energy ≈ 7 eV, the magnitude of the LSPR shift towards smaller energy values is higher compared to other modes located at lower energies, when the impact parameter is near a facet, an edge, or a corner of the nanoparticle, respectively. This agrees with our experimental data, where we collected electron energy-loss spectroscopy (EELS) data in the low-loss region, near the surface of the nanoparticles, using a monochromated 80 keV electron source with 100 meV energy resolution. The experimental spectra appertaining to the edge and corner of the nanoparticle display an energy shift as a function of position of the electron beam with respect to the nanoparticle. By applying a non-negative matrix factorization algorithm, we deconvolve the LSPR signals and thus determine the effects of geometry and composition on coupling efficiency as a function of beam position. This allows us to map the coupling efficiency of the electron beam to the surface electrons, and reveals the energy transfer path from the excitation source to the nanoparticles. This study paves the way for a better understanding of the localization of LSPR in catalyst nanoparticles with engineered morphologies, and highlights the capabilities of EELS as a tool for probing surface plasmons of metallic nanostructures with high spatial and energy resolution.

11:30 AM EP04.16.10
Towards Nanoscale Molecular Mapping with Electron-Beam Stimulated Surface Enhanced Raman Spectroscopy Amr E. Saleh, Daniel K. Angell and Jennifer A. Dionne; Stanford University, Stanford, California, United States.

Surface enhanced Raman scattering (SERS) has been a key tool for molecular detection and identification with single-molecule sensitivity. However, creating real spatial resolution SERS maps of sophisticated surfaces such as cellular membranes and biological tissues remains a significant challenge because of the diffraction limit of light. In this work, we introduce a novel imaging technique that utilizes light excitation within an electron microscope to perform high spatial resolution Raman mapping. Unlike conventional stimulated Raman measurements, our technique uses a laser source as the pump and the electron beam as the broadband Stokes excitation. Particularly, we leverage the electron beam as a highly-localized Angstrom-scale source to locally excite the plasmonic resonances of individual nanoparticles. The resonant wavelength of the nanoparticles is tuned such that it is red-shifted from the pump laser to resemble the Stokes excitation when excited with the electron beam. Accordingly, the Raman scattering is locally enhanced by the electron beam and the spatial resolution is determined by the electron beam spot size and the nanoparticle size.
To compute the local nonlinear Raman enhancement under dual optical and electron beam illumination, we first use finite difference time domain (FDTD) simulations. Attention is given to gold nanorods (NRs) with plasmonic resonances between 800nm and 900nm; we assume 785nm laser illumination and 80keV electron beam excitation. We study the enhancement of the 992cm⁻¹ benzene line, showing that laser pump intensities less than 3mW/µm² can locally enhance the Raman peak. We compute the pumping threshold and the Raman gain achieved under various electron-beam and nanorod excitation positions, showing sub-2nm resolution of molecular fingerprints.

Experimentally, we use aberration corrected environmental transmission electron microscope combined with light excitation. We synthesize colloidal gold NRs functionalized with 4-Nitrothiophenol (4NTP) as Raman reporter. The lengths and radii of the rods are 105nm and 12nm, respectively, with transverse and longitudinal plasmon resonances at 510nm and 830nm. Upon electron beam excitation of the NR plasmon modes, we observe an increase in the Raman intensity of the 1335cm⁻¹ and 1570cm⁻¹ lines of the 4NTP molecule. Monochromated electron energy loss spectroscopy (EELS) confirms the plasmon modes we excite during each individual Raman acquisition. We investigate and locally map the stimulated Raman enhancement upon electron-beam excitation of different NP resonances and with distinct nanorod lengths. Our results demonstrate the ability to perform in-situ Raman interrogation with single nanometer resolution inside an environmental TEM while simultaneously imaging the nano-to-atomic-scale structure of the sample.

**SYMPOSIUM EP05**

Excitons, Electrons and Ions in Organic Materials
November 26 - November 29, 2018

Symposium Organizers
Rodrigo Noriega, University of Utah
Jonathan Rivnay, Northwestern University
Elizabeth von Hauff, Vrije Universiteit Amsterdam
Ni Zhao, Chinese University of Hong Kong

Symposium Support
The University of Utah, Department of Chemistry

* Invited Paper
Organic electrochemical transistors (OECT) are of interest for applications in biochemical sensing and signal transduction across the biological/digital divide. The excellent performance of conjugated polymers in these applications is due to the ability of the polymer to accommodate ionic countercharge throughout the transistor volume. The resulting volumetric capacitance which allows for very large modulations of the charge density in the transistor channel and large transconductance values. Combining OECT measurements on different polymers with different counter ions, we study how both polymer morphology and the chemical nature of the counter ions affect ion uptake and coupling between ionic and electronic transport. Furthermore, we use electrochemical strain microscopy (ESM) to probe local swelling resulting from ion uptake, and correlate ion uptake with both polymer structure and the chemical properties of the ions, providing microscopic insight into these processes that lead us to propose new material design rules.

8:30 AM *EP05.01.02
Operando X-Ray Scattering Reveals Ion-Induced Structural Changes During Electrochemical Gating of Poly(3-hexylthiophene) Elayne Thomas1, Michael A. Brady2, Hidenori Nakayama3, Bhooman C. Popere1, Rachel Segalman1 and Michael L. Chabinyc1; 1University of California, Santa Barbara, Goleta, California, United States; 2The Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The semicrystalline nature of most semiconducting polymers complicates the relationship between morphology and electronic conduction. In order to increase their electrical conductivity, charge carriers are introduced into conjugated polymers by extrinsic dopants, usually by introduction from solution or by infiltration from a vapor. In this case, the dopant molecule, now ionized, is the counterion to the charged backbone. There is currently little understanding of how these ions interact with the amorphous and crystalline regions of the semiconductor to achieve the observed large changes in electrical conductivity.

To address the question of how ions interact with these distinct phases, we have explored the evolution in morphology and optoelectronic properties of a conjugated polymer in an organic electrochemical transistor. By using a novel polymeric ionic liquid (PIL) as the gate insulator, we carry out for the first time operando studies capturing the structural evolution in poly(3-hexylthiophene) (P3HT) during electrochemical gating by X-ray scattering. PILs contain one ion covalently bonded to the polymer backbone and one ion that is mobile, which allows for control of counterion diffusion as well as low-voltage device operation. From these experiments, we find that negatively-charged ions from the dielectric first infiltrate the amorphous regions of the semiconductor, and penetrate the crystalline regions at a critical carrier density of 4 × 10^{20} cm^{-3}. Upon infiltration, the crystallites expand by 12% in the alkyl stacking direction and compress by 4% in the π-π stacking direction. The stark change in crystal structure of P3HT correlates with a sharp increase in the effective carrier mobility. Complementary UV-visible spectroscopy reveals that holes induced in P3HT first reside in the crystalline regions of the polymer, which verifies that a charge carrier need not be in the same physical domain as its associated counterion. Our results provide a comprehensive view of doping in P3HT which challenges the assumption that trap filling is the sole mechanism to justify the non-linear trend in electrical conductivity with carrier density.

8:45 AM *EP05.01.03
Conjugated Polymers—Charged Semiconducting Polymers Processed from Protic Solvents Ryan Chiechi1, 2, Lambert Jan Anton Koster2, Nutifafa Dounon1 and Gang Ye1, 2; 1Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands; 2Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Semiconducting conjugated polymers have found applications in field-effect transistors, sensors, solar cells, etc. In essentially any application that requires a semiconducting material, the semiconducting material can be replaced with a properly-designed conjugated polymer, endowing a device with the useful properties of polymers such as solution-processing, mechanical compliance, thinness and light weight. However, the solutions from which thin-films of conjugated polymers are cast contain very small amounts of polymer, on the order of tens of milligrams per milliliter. The nonpolar nature of pi-conjugated moieties means that high-quality films can only be cast from solvents that are either difficult or impossible to work with at scale. One approach to creating conjugated polymers that can be processed from “green” solvents is to decorate them with charged pendant groups to form conjugated polyelectrolytes that can be dissolved in polar, protic solvents like water or methanol. However, designing conjugated polyelectrolytes that are both processable and retain high carrier mobility is challenging because of the disparate physical properties of the backbone and pendant groups. This amphiophilic nature drives the polymer chains to self-assemble such that, in polar solvents, the hydrophobic backbone chains pack together and are shielded by a shell of ionic pendant groups to minimize unfavorable solvent interaction. These protein-like aggregates are carried into the films, leading to poor pi-pi contact. Our approach is to place closed-shell charges into the backbones of conjugated polymers to match the ionic character of the pendant groups such that the backbone is directly solubilized by polar solvents. The resulting conjugated polymers are intrinsic semiconductors; they are not bipolaronic and are EPR silent. Their band-gaps can be tuned via common push-pull strategies and they form high-quality films with good carrier mobility from polar, protic solvents. The cations in the backbone are generated from pre-polymers by the loss of methanol under acidic conditions. Thus, we can process high-quality thin-films from wet formic acid, which is non-toxic, non-flammable and is already used industrially at scale.

9:00 AM *EP05.01.04
Polar and Reactive Side Chain Functionalization of Conjugated Polymers for Redox and Bio-Electronic Applications John R. Reynolds; Georgia Institute of Technology, Atlanta, Georgia, United States.

Conjugated polymers provide a unique encompassing set of structurally tunable optical, electronic transport, and redox properties that allows their present and potential use in a host of applications which span field effect transistors, light emitting diodes, solar cells and photodetectors, and electrochemistry, along with batteries, supercapacitors, and bio-electronics. Processing of these materials is carried out using a variety of solution methods including spin-coating, spray-coating, blade-coating, slot die coating and ink jet printing. The ability to process these polymers from environmentally benign solvents and aqueous solutions is highly advantageous for possibilities in large scale roll-to-roll processing. Maintaining competitive electronic properties while achieving aqueous solubility is difficult for several reasons. 1) Materials with polar functional groups that provide aqueous solubility can be difficult to purify and characterize. 2) Many traditional coupling and polymerization reactions cannot be performed in aqueous solution. 3) Ionic groups, though useful for obtaining aqueous solubility, can lead to a loss of solid-state order as well as a screening of any applied bias. In this lecture, we will address how side chain polarity, from charge neutral ether and ester functionality to ionic functionality, impacts not only processing, but also charge transport, redox switching and optical properties. As an alternative, a multistage side-chain cleavage approach will be presented that allows a functional group to be used for its intended purpose, then removed once the functionality becomes unnecessary. Through the attachment of multistage sidechains, conjugated materials can be synthesized, characterized, and purified in organic solvents, converted to a water-soluble form for aqueous processing, and brought through a final treatment to leave behind the desired electronic material as a solvent-resistant film.

9:30 AM BREAK

10:00 AM *EP05.01.05
Semiconducting Polymer for Bioelectronics and Field Effect Transistors Jair McCulloch2, 1; 1Imperial College London, London, United
The evolution of organic electronics has now reached the commercial phase, with the recent market introduction of the first prototypes based on organic transistors and organic solar cell modules fabricated from solution. Understanding the impact of both the organic semiconductor design and processing conditions, on both molecular conformation and thin film microstructure has been demonstrated to be essential in achieving the required optical and electrical properties to enable these devices. Polymeric semiconductors offer an attractive combination in terms of appropriate solution rheology for printing processes, mechanical flexibility for rollable processing and applications, but their optical and electrical performance requires further improvement in order to fulfill their potential. Synthesis of conjugated aromatic polymers typically involves carbon coupling polymerisations utilising transition metal catalysts and metal containing monomers. This polymerisation chemistry creates polymers where the aromatic repeat units are linked by single carbon-carbon bonds along the backbone. In order to reduce potential conformational, and subsequently energetic, disorder due to rotation around these single bonds, an aldol condensation reaction was explored, in which a bissatin monomer reacts with a bisoxindole monomer to create an isoindigo repeat unit that is fully fused along the polymer backbone. This aldol polymerization requires neither metal containing monomers or transition-metal catalysts, opening up new synthetic possibilities for conjugated aromatic polymer design, particularly where both monomers are electron deficient. Polymers with very large electron affinities can be synthesised by this method, resulting in air stable electron transport, demonstrated in solution processed organic thin film transistors. We present an electrical, optical and morphology characterisation of polymer thin films, illustrating structure-property relationships for this new class of polymers. Organic electrochemical transistors (OECTs) have been shown to be promising devices for amplification of electrical signals and selective sensing of ions and biologically important molecules in an aqueous environment, and thus have potential to be utilized in bioelectronic applications. The sensitivity, selectivity and intensity of the response of this device is determined by the organic semiconducting polymer employed as the active layer. This work presents the design of new organic semiconducting materials which demonstrate significant improvements in OECT performance, through operation in accumulation mode, with high transconductance and low operating voltage.

10:30 AM EP05.01.06
Organic Electrochemical Transistors—Developments on Modelling the Transient Response and on Device Fabrication
Gregorio C. Faria; Sao Carlos Physics Institute, University of Sao Paulo, Sao Carlos, Brazil.

Organic Electrochemical Transistors (OECTs) have recently been the focus of great attention due to their ability to support both ionic and electronic conduction and their successful application as highly-sensitive biosensors and neuromorphic devices. In the first part of my talk, I will discuss a universal model for the transient drain current response in OECTs. Using equivalent circuits and semiconductor charge injection physics, the model is able to reconstruct the drain current in OECT devices, is applicable to both plain and membrane-functionalized devices, and allows one to extract useful impedances of any system from only a single transient measurement. For the second part of my talk, I will present a general method and accompanying guidelines for fabricating both non-aqueous and aqueous based OECTs using water-insoluble hydrophobic semiconducting polymers. By taking advantage of the interactions of semiconducting polymers in certain organic solvents and the formation of a stable liquid-liquid interface between such solvents and water, we successfully fabricated OECTs with high transconductance, ON/OFF ratios of 10⁶, and enhancements in stability. Using the model discussed in the first part of the talk, key fundamental properties of both the device and active channel materials were extracted, including volumetric capacitance and intrinsic hole mobility. Finally, the benefits of using liquid-liquid interface OECTs to measure bacterial membrane disruption will be briefly discussed.

11:00 AM EP05.01.07
In Situ Methods for Understanding Charge Transport in a Conducting Redox Polymer
Mia C. Sterby, Rikard Emanuelsson, Maria Stromme and Martin Sjödin; Uppsala University, Uppsala, Sweden.

Organic materials can be used to ensure sustainable electrical energy storage, but since organic molecules are generally insulating conducting additives are commonly used to ensure electrical conductivity throughout the material. A different approach is to use conducting redox polymers (CRPs). CRPs consist of a redox active pendant group, used for its high capacity, attached to a conducting polymer backbone. The CRP presented here is aimed to be used as the positive electrode in a water-based organic battery.

In this work we employ the well-studied conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) with a quinone pendant group, a combination that we have proven can work in an all-organic proton battery. Quinones constitute an attractive class of molecules as they possess a high charge storage capacity, show reversible redox chemistry, and are naturally occurring, e.g., in the electron transport chains in respiration and in photosynthesis. The aim of the study is to understand the charge transport properties of the CRP.

The CRP studied is characterized by various in-situ electrochemical methods including conductance, Quartz Crystal Microbalance (QCM), UV-vis and electron paramagnetic resonance (EPR). Based on the results the electron and ion transport during electrochemical redox conversion will be discussed.


11:15 AM EP05.01.08
Conductive Polymer Electrodes for Biosensors and Energy Conversion
Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Electron transfer is a ubiquitous chemical reaction in energy and biology. Controlling interfacial electron transfer rates is critical to maximizing device efficiencies in electrochemical technologies including redox-flow batteries, chemical sensors, bioelectronics, and photo-electrochemical devices.

Conductive polymer electrodes offer the possibility to control redox properties through synthesis and processing, if critical structure-property relationships are understood. Importantly, these semiconductors demonstrate a hybrid electronic-ionic conduction mechanism, and thus, have unique electrochemical behaviors relative to classical inorganic semiconductor electrodes.

This talk will provide new insights into the mechanism of charge transfer at conductive polymer/liquid interfaces. A mathematical framework will be demonstrated using a modified Marcus-Gerisher model that enables prediction of rate constants from simple film properties. Experimental evaluation of potential-dependent rate constants will be demonstrated. Results will be contextualized in electrochemical devices.

11:45 AM EP05.01.09
Correlation Between Redox, Charge Carrier Transport and Ion Molecular Structure Properties in Ion-Gated PCBM Films
Tian Lan; Francesca Sauro; Jonathan Sayago and Clara Santato; 1Ecole Polytechnique de Montreal, Montreal, Quebec, Canada; 2Universita di Bologna, Bologna, Italy; 3Universidad Nacional Autónoma de México, Temixco, Mexico.
The n-type organic semiconductor phenyl-C61-butyric acid methyl ester (PCBM), a soluble fullerene derivative well investigated for organic solar cells and transistors, can undergo several successive reversible, diffusion-controlled, one-electron redox processes. We exploited such processes to shed light on the correlation between electron transfer properties, ionic and electronic transport as well as device performance in ionic liquid (IL)-gated transistors. Two ILs were considered, based on bis(trifluoromethylsulfonyl)imide [TFSI] as the anion and 1-ethyl-3-methylimidazolium [EMIM] or 1-butyl-1-methylpyrrolidinium [PYR14] as the cation. The aromatic structure of [EMIM] and its lower steric hindrance with respect to [PYR14] favor a 3D (bulk) electrochemical doping. As opposed to this, for [PYR14] the doping seems to be 2D (surface-confined). If the n-doping of the PCBM is pursued beyond the first electrochemical process, the transistor current vs. gate-source voltage plots in [PYR14][TFSI] feature a maximum that points to the presence of finite windows of high conductivity in IL-gated PCBM transistors.

**References**


**SESSION EP05.02/BM07.02: Joint Session: Bioelectronic Active Materials**

**Session Chairs: Sahika Inal and Jonathan Rivnay**

Monday Afternoon, November 26, 2018

Sheraton, 2nd Floor, Constitution B

1:30 PM *EP05.02.01/BM07.02.01*

**Interacting Ion and Electron Currents**

**Paul Meredith**

Swansea University, Swansea, United Kingdom.

Ionic and electronic conduction mechanisms are underpinned by fundamentally different physics. For example, ions diffuse through a conducting matrix via centre of mass transport that can be described by classical processes. Electrons and holes are quantum mechanical entities characterised by delocalisation, tunnelling or hopping. These fundamental differences impose radically different length-and-time-scales on ionic and electronic conduction – and generally speaking the solid-state physics of ions and electrons have remained two very different fields requiring different skill sets. However, bioelectronics, where a central challenge is the transduction between ion and electron currents, is a scientific collision point between the two worlds. In my talk I will summarise the major differences between ionic and electronic solid state electrical conduction. I will also describe methods that can probe the relevant time-and-length-scales in order to identify and disentangle the native signatures of each carrier type. A number of model systems and devices will be exemplified that allow the study of ion and electron conduction processes, and indeed provide a means to test prototypical concepts in transduction and bioelectronic logic interfaces.

**References**


2:00 PM *EP05.02.02/BM07.02.02*

**The Device Physics of Organic Electrolytic Photocapacitors—From the Nanoscale to the Single Cell Level**

**Vedran Derek**

1, Marie Jakesova, Tobias Cramer, Marek Havlicek, David Rand, Yael Hanci, Daniel Simon, Magnus Berggren, Fredrik Elinder and Eric D. Glowacki; 1Laboratory of Organic Electronics, Department of Science and Technology, Linkoping University, Norrkoping, Sweden; 2Department of Physics and Astronomy, Universita di Bologna, Bologna, Italy; 3Department of Nanometrology and Technical Length, Czech Metrology Institute, Brno, Czechia; 4School of Electrical Engineering, Tel Aviv University, Ramat-Aviv, Tel-Aviv, Israel; 5Department of Clinical and Experimental Medicine, Linkoping University, Linkoping, Sweden.

We have recently developed the organic electrolytic photocapacitor (OEPC), a nanoscale optoelectronic device for eliciting action potentials in neurons. Herein, we cover in detail the physical mechanisms behind the charge generation and dynamics of charging and capacitive coupling in these devices using optoelectronic/electrochemical measurements combined with simulation and modeling. Electrochemical impedance measurements allow corroborate of these models, and reveal the nature of photocapacitive and photofaradaic effects in the devices. Using scanning probe microscopy techniques, we have evaluated the mechanical properties of the nanocrystalline films, finding relatively low Young’s moduli in the range of 500 MPa. In order to take a reductive approach compared with previous measurements of neurons and electrogenic tissues, we have validated the performance of OEPCs using nonexcitable cells, xenopus laevis oocytes. We find rapid membrane potential changes in the range of tens to hundreds of millivolts are induced by OEPC devices, showing extremely effective capacitive coupling and explaining previous findings of action potential generation. The overall result of our work is a fuller physical and mechanistic understanding of this novel device platform, and a roadmap for guiding future development.

2:15 PM *EP05.02.03/BM07.02.03*

**The Design of Air Stable, Redox Active Conjugated Polymers and Their Applications in Accumulation Mode OECTs**

**Alexander Giovannitti**

1, Reem Rashid2; Jenny Nelson1, Iain McCulloch1 and Jonathan Rivnay2; 1Imperial College London, London, United Kingdom; 2Northwestern University, Chicago, Illinois, United States.

Organic electrochemical transistors (OECTs) are receiving a great deal of attention due to the ability to efficiently transduce biological signals. The working of the device relies on the modulation of the conductivity of an organic semiconductor, which can be modified by applying a potential at the gate electrode and driving electrochemical redox reactions in aqueous solution (doping/de-doping of the organic semiconductor). OECTs can either be operated in accumulation or depletion mode where the operation in accumulation mode has the advantage of lowering the operational voltage and therefore improve the power consumption of the device (device is in an off state rather than an on state when no gate voltage is applied). Recently, high performing OECT materials have been reported based on electron rich alkoxylithiophene copolymers which show low oxidation potentials in aqueous electrolytes and enable EOCT operation at low voltages. However, one drawback of these easily oxidizable polymers is that the copolymers can become oxidized by reactions with oxygen from ambient air. This
result in the formation of p-doped polymers and superoxide anions ($O_2^-$) where the latter is a reactive radical and might cause harm to biological systems or degrade the organic semiconductor. As a result of this oxidation reaction, a constant gate voltage would need to be applied to keep the material in its neutral state (and the device off).

We will present the development of an air-stable conjugated polymers based on donor-acceptor type copolymer. The copolymer shows reversible redox reaction at potentials below 0.3 V vs Ag/AgCl. When exposed to aqueous ambient conditions, the polymer does not become oxidized. Long-term stability tests were carried out where devices were exposed to ambient conditions for more than 6 months with no sign of degradation. The polymer shows a good stability when charged within one hole per repeat unit (polaron) with transconductances in the range of 80 S/cm (at -0.7 V). This work demonstrate the importance of chemical design strategies for the development of accumulation mode OECT materials to mitigate reactions with oxygen in aqueous electrolytes and ambient conditions.


2:30 PM *EP05.02.04/BM07.02.04
Polythiophene Derivatives as Mixed Organic Ionic and Electronic Conductors Christine Luscombe; University of Washington, Seattle, Washington, United States.

Mixed organic ionic and electronic conductors are being explored for a wide range of applications, from bioelectronics to neuromorphic computing, artificial muscles and energy storage applications. These materials exploit the simultaneous transport properties of ionic and electronic carriers to enable novel device functions. Recently, polymer semiconductors have received significant amounts of attention because of their flexibility, biological compatibility and ease of fabrication. These materials, particularly thiophene-based polymers such as poly[(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)](PEDOT:PSS) and related derivatives, have demonstrated significant enhancements in performance in a relatively short amount of time, with transconductance values of PEDOT:PSS transistors surpassing those achieved even with graphene.

Through our NSF Designing Materials to Revolutionize and Engineer our Future (DMREF) award with researchers at Cornell University and the University of Chicago, we have been investigating the synthesis of ethylene-glycol functionalized polythiophenes, their thin film morphology, and their pattern of placement on ionic conductivity will be discussed.

Through our NSF Designing Materials to Revolutionize and Engineer our Future (DMREF) award with researchers at Cornell University and the University of Chicago, we have been investigating the synthesis of ethylene-glycol functionalized polythiophenes, their thin film morphology, and their pattern of placement on ionic conductivity will be discussed.

3:00 PM BREAK

3:30 PM *EP05.02.05/BM07.02.05
Mixed Conductivity in Conducting Polymer Thin Films Sabine Ludwigs; University of Stuttgart, Stuttgart, Germany.

This talk will give an overview about our recent activities on electronic and ionic conductivity in conjugated and redox polymer thin films with different molecular architectures. Preparation of films is done either by electropolymerization or solution deposition followed by morphology tuning, e.g. by solvent vapor annealing.[1]

We are particularly interested in three-dimensional architectures based on branched monomers such as thiophenes (3T) or triphenylamines (TPA). TPA redox moieties are useful to allow for electrochemical or chemical crosslinking of as-deposited films. Both, with TPA redox polymers[2] and with polymers which bear TPA as pendant functional groups[3] we could perform successful crosslinking and simultaneous doping of polymer films. The films provide very high stabilities with high electronic conductivities as evidenced by cyclic voltammetry coupled with in-situ conductance measurements and four-point-probe measurements. In the case of 3T we have reported on homopolymer and copolymer films of 3T and ethylenedioxythiophene which allow polymer-analogous reactions to induce ionic functionalities, thereby creating branched conjugated polyelectrolyte films.[4], [5]

To get a better understanding on mixed conductivity in polymer films, we have recently performed a study on electronic and ionic conductivity of linear conjugated polyelectrolytes by impedance spectroscopy and dc-measurements.[6] The clear dependence of the conductivities as function of humidity and degree of doping will be discussed in the talk in more detail.


4:00 PM *EP05.02.06/BM07.02.06
Soft Electronic and Ionic Neural Interfaces Klas Tybrandt1, 2, Dion Khodagholy1, Flurin Stauffer2 and Janos Vörös3; 1Department of Science and Technology, Linköping University, Norrköping, Sweden; 2Institute for Biomedical Engineering, ETH Zürich, Zurich, Switzerland; 3Department of Electrical Engineering, Columbia University, New York, New York, United States.

Two-way communication between electronics and neural tissue is key for advancing diagnosis and therapies for neurological diseases and disorders, as well as proving detailed information about brain signaling. Establishing such neural interfaces is a major challenge, as the tissue response to implants can have a detrimental effect on the signal quality and functionality of the implant. Also, electrical stimulation is inherently limited in its stimulation of neural tissue, in comparison to the sophisticated chemical signaling processes within biological tissue. Here, we present our efforts in addressing two critical technological aspects for the creation of versatile neural interfaces; the matching of mechanical properties of tissues and electronics, and the development of heterogeneous electronic and ionic interfaces. Soft electronic biomedical implants have a demanding set of requirements, including biocompatibility, mechanical and electromechanical properties, long-term stability and electrode performance. To meet these requirements, we have developed a high-performance, long-term stable soft and stretchable composite for neural electrodes. Based on this composite, high-density soft electrode grids were developed and implanted onto brain surface of rats. The electrodes provided high-quality recordings during three months of implantation. Next, we will outline our strategy for creating high-speed low-leakage chemical neural interfaces, by discussing the relationship between delivery delay and leakage, and then present an iontronic approach to achieve low leakage and small delay simultaneously.
Organic Electronics for Neuromorphic Computing

Neuromorphic computing could address the inherent limitations of conventional silicon technology in dedicated machine learning applications. Recent work on silicon-based asynchronous spiking neural networks and large crossbar-arrays of two-terminal memristive devices has led to the development of promising neuromorphic systems. However, delivering a parallel computation technology, capable of implementing compact and efficient artificial neural networks in hardware, remains a significant challenge. Organic electronic materials offer an attractive alternative to such systems and could provide neuromorphic devices with low-energy switching and excellent tunability, while being biocompatible and relatively inexpensive.

This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them. We demonstrate a novel concept based on an organic electrochemical transistor and show how some challenges in the field such as stability, linearity and state retention can be overcome.

Furthermore, we investigate chemical doping mechanisms in the active material for improved material functionality and demonstrate that this device can be entirely fabricated on flexible substrates, introducing neuromorphic computing to large-area flexible electronics and opening up possibilities in brain-machine interfacing and adaptive learning of artificial organs.

1 van de Burgt et al. Nature Electronics, 2018
2 van de Burgt et al. Nature Materials, 2017
3 Keene et al. J Phys D, 2018

Anisotropic Conducting Polymer Films for Bioelectronics

Anisotropic conductive films, which consist of electrically conductive particles dispersed in nonconductive media, are increasingly being applied to establish high-density electrical bonds between electronic boards and chips. However, current anisotropic composites utilize metallic particles, often nickel and epoxy-based media, that require high thermocompression energy for bonding. Therefore, they have limited applicability in thin-film, conformable, and plastic-based devices that are used in bioelectronic applications. Furthermore, these materials are not biocompatible, significantly limiting their use in biological systems. We hypothesized that replacing the metallic particles with conducting polymer particles combined with a biocompatible nonconducting matrix would address this limitation. We developed a novel anisotropic conducting polymer (ACP) consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) conducting polymer particles dispersed in a matrix of crosslinked chitosan (CS). To determine the permeability of PEDOT:PSS to CS, we characterized the resistances of thin CS-based films sandwiched with PEDOT:PSS and gold pads. We investigated the particle size, structure, density and distribution of pure PEDOT:PSS particles and PEDOT:PSS-coated CS particles. The anisotropy was defined by the ratio of horizontal and vertical impedance between interconnects. We benchmarked the anisotropy of the developed ACPs by geometrically varying an array of gold electrodes. The final ACP, which was created at 70°C with minimal pressure, yielded anisotropy of 10^−10. The ACP was then used to maintain precise connections between a high density conformable implantable neural probe and back-end electronics. It enabled complete chronic in vivo implantation of these electronics with minimal encapsulation layers, highlighting applicability for use in bioelectronic and clinical devices.

Temporal Analysis of Transient Electroluminescence to Study the Effect of Charge Traps in Organic Light Emitting Diode

A comparative study was carried out for pristine vs. degraded organic light emitting diode (OLED) devices regarding their luminescence characteristics using time-resolved electroluminescence (TREL). Notable changes were observed in the temporal form of the TREL curve upon materials degradation, which was found to be due to the trapped charges formed during the OLED operation. The TREL decay time of degraded OLED was found to be longer than that of pristine OLED due to the excitons produced by weakly bound charges trapped in the organic layer that are released by thermal energy even without applying the voltage pulse. On the other hand, the onset time of luminescence was found to be shorter due to the excitons from strongly bound charges that are released by the application of the voltage pulse. We demonstrated that TREL can be effectively used to identify different types of excitation and to investigate the luminescence mechanisms of a light-emitting device.
The SD efficiency can vary greatly depending on the properties of the OSCs, dopants, and especially the film conditions since the doping effect can be sensitive to the film structure. Therefore, we investigate the SD mechanism through a comparative study of two different OSC materials, small molecular PTCDI-C8 and polymer N2200, doped with two kinds of aminosilanes, and various thicknesses and grain sizes of deposited films to find the optimum SD condition. We characterized the doped films and OFETs by using AFM, Grazing-incidence X-Ray Diffraction, Infrared spectroscopy, electrical measurements, etc.

As a result, higher doping efficiency showed in the doped PTCDI-C8 FETs than N2200 FETs due to the difference of intrinsic OSC properties such as its open film morphology. Additionally, the SD efficiency is decreased with increasing thickness and grain size of the OSC films. The more electron donating groups the dopant has, the lower doping concentration is needed to reach the same optimized value. Importantly, we find that there are two doping concentration regimes. In low doping concentrations, the dopants primarily contribute to the increase in mobility. In higher doping concentrations, the dopants also enhance the threshold voltage. Furthermore, the SD process does not adversely affect other OFET properties such as the on-off ratio.

Therefore, our results demonstrate that the properties of OSCs, dopants and particularly the film conditions must be considered in order to maximize the SD efficiency for improved OFET performances.

EP05.03.03

Metal Organic Frameworks in a Blended Polythiophene Hybrid Film with Surface-Mediated Vertical Phase Separation for the Fabrication of a Highly Sensitive Humidity Sensor Young Jin Jung; Eun Hye Kwon and Yeong Don Park; Energy and Chemical Engineering, Incheon National University, Incheon, Korea (the Republic of).

Demand for portable gas sensors capable of monitoring the atmospheric environment in daily life is growing as air pollution deteriorates. Organic field-effect transistors (OTFTs) are regarded as an ideal flexible platform for creating portable, lightweight, and robust sensor devices. OTFTs are sensitive to physical and chemical stimuli because small interactions between a semiconductor and a target analyte amplify the electrical signal of a transistor device via the field-effect mobility, drain current, and threshold voltage. However, organic transistors inevitably suffer from poor stability and bad electrical properties, resulting in a slow response and recovery of the sensor device. We attempted to address this issue by developing an OTFT-based humidity sensor, in which a humidity-capturing material was inserted into the polymeric semiconductor. In this study, a facile, reliable, fast-response, highly sensitive poly(3-hexylthiophene-2,5-diyl) (P3HT)-based humidity sensor was developed by introducing metal organic frameworks (MOFs), HKUST-1, into the semiconducting layer. HKUST-1 displayed an excellent ability to capture water molecules, thereby generating and attracting charge carriers derived from water molecules present in the active layer. The HKUST-1/P3HT hybrid film showed excellent device sensitivity with an enhanced electrical current and a threshold voltage shift as a function of the relative humidity due to the superior gas capture properties and the porosity of HKUST-1. The surface energy of the substrate altered the distribution and location of HKUST-1 in the active layer, which improved the sensitivity of the hydrophilic surface. A dynamic gas sensing test revealed that the hybrid film displayed a reliable and stable performance with fast response and recovery times. The introduction of MOFs into a conjugated polymer stabilized and sensitized the devices, providing a facile method of improving gas sensor technologies based on organic semiconductors.

EP05.03.04

Tuning Electrical Properties of Phenanthroimidazole Derivatives to Construct Multifunctional Deep-Blue Electroluminescent Materials Zelin Zhu; City University of Hong Kong, Hong Kong, Hong Kong.

The maturity of longer wavelength emitters (green and red) makes it more urgent to develop high performance deep-blue emitters OLED (organic light-emitting diodes). A blue emitter that can serve as a multi-functional material (e.g. as host for the green and red counterparts) is of high interest in this field. We introduce a n-type group, TPP0 (triphenyl phosphine), to the N1-position of violet-blue fluorophore phenanthroimidazole (PI) and successfully develop one deep-blue (TPAPOPI) and two violet-blue emitters (3-CzPOPI and CzBPPOPI) for OLEDs (organic light-emitting diodes). With highly twisted linkage, the TPP0 group shows negligible influences on their photophysical properties of the new materials and the materials inherit high efficient deep-blue, light and violet-blue emission of the PI unit and its C2-connected arylamine skeletons. Meanwhile, TPP0 group can open a new channel to transport electron. The electron injection and transport abilities of the developed emitters are enhanced. Non-doped devices using the 3-CzPOPI and the CzBPPOPI emitters exhibit EQE_{max} (external quantum efficiency) of 5.08% and 4.42% with CIE (Commission Internationale de l’Eclairage) coordinates of (0.156, 0.051) and (0.157, 0.071), respectively. Similar efficiencies and even deeper blue emissions (CIE = 0.050 for 3-CzPOPI and 0.044 for CzBPPOPI) were observed in OLEDs with these emitters doped in 4,4’-bis(N-carbazolyl)-1,1‘-biphenyl. TPAPOPI is demonstrated to be a multifunctional deep-blue emitter and presents impressive performances when serving as non-doped (EQE_{max} = 6.69%, CIE = (0.152, 0.095), doped (EQE_{max} = 6.61%, CIE = (0.154, 0.068)) as well as a high-performance host for yellow phosphorescent OLED. By doping a yellow phosphorescent dye (PO-01) into a TPAPOPI host, a white OLED with a high EQE of 20.3% and a low driving voltage of 3.2 V (at 1,000 cd m^{-2}).

EP05.03.05

Silicon Phthalocyanines—From Multifunctional Ternary Additives in OPVs to High Performing N-Type Semiconductors in OTFTs Benoit Lessard; Nicole Rice and Brendan Mirka; Chemical & Biological Engineering, University of Ottawa, Ottawa, Ontario, Canada.

Phthalocyanines (Pcs) are among the oldest commercial dyes used as industrial pigments and photoreceptors. Their optical properties, stability, and ease of synthesis have made them ideal as active materials for a plethora of optoelectronic applications.[1] Silicon phthalocyanines (SiPcs) have two axial bonds originating from the Si atom, which can serve as functionalization sites without affecting the inherent optoelectronic properties of the phthalocyanine macrocycle itself. Therefore, we have used the axial groups as handles to improve solid state engineering and improve charge transport through the thin films.[2,3] We fabricated planar heterojunction organic photovoltaic devices (PHJ) by physical vapour deposition and used the SiPc derivatives as both donor and acceptor layers, illustrating the ambipolar behavior of these molecules.[2,3] Through solid state engineering we were able to improve the overall efficiency by >40% compared to the unsubstituted C12-SiPc. These preliminary OPV devices surpassed performances by similar PHi devices made using typical copper, aluminum and zinc (CuPc, AlPc, and ZnPc).

Similar chemistry produced solution processable SiPc-based ternary additivies for P3HT:PC61BM bulk heterojunction OPVs with increased photo generation at the interface, which translates to a 20% increase in overall efficiency.[4,5] When replacing PC61BM directly, the SiPc derivatives resulted in devices with similar power conversion efficiency (PCE).[5] Recently we have reported the use of a multifunctional SiPc ternary additive that not only increase the efficiency of the OPV but also increases the stability by migrating to the interface and crosslinking the P3HT and PC61BM domains.[6] These studies are showing potential for SiPcs in OPVs as multifunctional additives which simultaneously enhance device performance and device stability. Finally, we are fabricating high performing n-type organic thin film transistors based on these SiPc derivatives. Processing parameters, such as deposition rate, substrate temperature and surface modification can improve the electron mobility by 2-3 orders of magnitude.[7] Again through SiPc functionalization for targeted solid state engineering we were able to develop high performing n-type SiPc based OTFTs with a mobility of >0.5 cm^2 V^{-1} s^{-1} – Currently the highest performing n-type Pc based thin film device.[8] Computational studies further demonstrate the potential of these versatile molecules.[9] Results from recent and upcoming publications will be presented.

References
Each interface for organic light emitting diodes (OLEDs) plays a determinant role in the device performances and lifetimes. Thus, there has been lots of interest on interfaces in OLEDs for the critical insight of the fundamental parameters affecting efficiency as well as operational lifetime. Despite decades of research in interface engineering, OLEDs cannot show their full potential because of the lack of technology to maximize their interfacial stability. In other words, the poor lifetime caused by efficiency reduction resultant from the charge imbalance and a resultant chemical degradation by accumulated charge carrier at their interfaces has still been the most problematic issues for the realization of dominant use of OLEDs in the display as well as lighting applications.

In this study, we have introduced a unique technology to improve the device efficiency as well as stability via interface modification. In other words, when charges are injected into emitting layer (EML) [i.e., from the hole transport layer (HTL) and the electron transport layer (ETL)], charges are accumulated on both interfaces of EML due to the charge injection barrier. From this result, the deterioration of the interface characteristics is known to proceed by such accumulated charges. To minimize this interfacial degradation, the accumulated charges at the interfaces of EML should be reduced. Herein, we propose a methodology to release the interfacial degradation by inserting ultrathin interface tunneling layer (ITL) ~1 nm for lowering the effective barrier at the interfaces of EML. Fortunately, ITL could work as an exciton confine layer due to its high triplet energy ($T_1 > 2.7$ eV) so that we could realize highly efficient green phosphorescent OLEDs (PHOLEDs) (EQE: 21.0 %) as well as much longer device lifetime (~ 2.5 times).

Acknowledgements

This work was supported by Samsung Research Funding Center of Samsung Electronics under Project Number SRFC-IT1601-02.

References


Acknowledgements

This work was supported by Samsung Research Funding Center of Samsung Electronics under Project Number SRFC-IT1601-02.
For shortwave infrared (SWIR) photodiodes in which the effective bandgap is reduced to < 1 eV, poor dissociation of charge-transfer (CT) excitons and low internal electrical field are detrimental to the external quantum efficiency (EQE) of SWIR photodiode. In this work, we show that high dielectric constant reduces the binding energy of CT excitons and improves mobility of charge carriers in organic bulk heterojunctions (BHJ). By mixing 15% camphoric anhydride into the BHJ, the dielectric constant and the overall performance of SWIR photodiodes are increased in the exciton dissociation and charge collection steps. After incorporating the high dielectric-constant additive, transient photocconductivity measurements indicate lower recombination loss and electrochemical impedance spectroscopy show that the trap density is reduced, and the effective lifetime of mobile carrier increases. The SWIR BHJ photodiode is optimized to reach a detectivity ~ 1013 Jones with spectral range up to 1550 nm. The devices are integrated into a 4 by 4 pixel array to demonstrate a SWIR imager, which is capable of spectral analysis to distinguish tissues, such as differentiating between fat and muscle for the future goal of medical imaging.

EP05.03.11
Suppressing Dark Current in Organic Phototransistors Featuring a MoOx Layer

Ren Shidachi, Hiroaki Jinno, Sunghoon Lee, Tomoyuki Yokota and Takao Someya; Department of Electrical Engineering and Information Systems, The University of Tokyo, Tokyo, Japan.

Organic photodetectors have attracted wide interest for their flexibility, solution processability, and ability to detect a broad range of light. Recently a number of researches were done on organic phototransistors (OPTs) due to their high responsivity. One of the problem using OPT in applications was their high dark current. Some reports have integrated OPT with an extra circuit in order to overcome this problem [1,2]. Here we present an OPT with low dark current while maintaining its high responsivity. We were able to suppress the dark current under four orders of magnitudes, by using a hole selective layer, by using the source/drain contact on a n-type semiconductor. The responsivity of our OPT was over 0.2 A/W under illumination of light with the power density of 0.5 mw/cm². OPT using 10 nm of MoOx as source/drain contact was fabricated. Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene] (OC12C10-PPV) and [6,6]-Phenyl-C61-Butyric Acid Methyl Ester (PCBM) with 80 wt% of PCBM content was used as an BHJ active layer. The dark current of OPT was showed quite lower tensile strength (0.68 MPa) and higher elongation at break (141%) than a poly(3-hexylthiophene) pristine film.

EP05.03.12
Blue-Emitting, Single-Benzene Fluorophore Based on Push-Pull Structure

Taek Seung Lee and Eunbee Cho; Chungnam National Univ, Daejeon, Korea (the Republic of).

Conjugated and rigid structure in organic molecules is essential to exhibit fluorescence. Accordingly, benzene has been widely employed to impart rigidity and extend the conjugation within molecular structure. One or more number of benzene is required to show efficient fluorescence, but many benzene rings in a molecule give a negative effect such as fluorescence quenching because of pi-pi interaction in the solid state. A single benzene-based fluorescent molecules will be a good candidate, which can be applied usefully in many fields, including bioimaging and optoelectronic devices, because aggregation-caused quenching can be easily prevented. Substituents on the benzene ring can affect the fluorescence property of the molecule. The formation of electronic push-pull system by introduction of electron donating and withdrawing group enables the single-benzene molecule to exhibit high fluorescence. We will discuss a blue emissive single-benzene molecule with push-pull structure which was easily synthesized. Various molecules with different structure and extend the conjugation within molecular structure. One or more number of benzene is required to show efficient fluorescence, but many benzene rings in a molecule give a negative effect such as fluorescence quenching because of pi-pi interaction in the solid state. A single benzene-based fluorescent molecules will be a good candidate, which can be applied usefully in many fields, including bioimaging and optoelectronic devices, because aggregation-caused quenching can be easily prevented. Substituents on the benzene ring can affect the fluorescence property of the molecule. The formation of electronic push-pull system by introduction of electron donating and withdrawing group enables the single-benzene molecule to exhibit high fluorescence.

EP05.03.13
Synthesis of Polythiophene Derivatives with Oligoisobutylene Side Chains and Their Cross-Linking System

Satoshi Miyang and Tomoya Higashihara; Yamagata University, Yonezawa, Japan.

In recent years, polymer semiconductors have received much attention due to their mechanical flexibility and solution-based low-cost processability. However, their durability for stretched stress is not enough for applying to wearable and implantable devices. The low strechability of polymer semiconductor is due to high crystallinity which induced their stiff main chain and strong intermolecular interactions. Here, we developed novel polythiophene derivatives, P3IBTs, which contain oligoisobutylene units in their side chains. We expect that several branched points on side chains weaken pi-pi stacking interaction and thereby decrease crystallinity of the polymers. In addition, we tried to develop cross-linked P3IBT to realize the formation of an inherently stretchable polymer semiconductor. We prepared polythiophene derivatives with disobutylene side chain (P3IB2T) (Mn = 12,000, Mw/Mn = 1.17) and triisobutylene side chain (P3IB3T) (Mn = 13,000, Mw/Mn = 1.21) by Kumada catalyst-transfer polycondensation. Their thermal, optical properties and crystalline nature were also investigated. The melting temperature of P3IB2T was determined by DSC, showing a distinct endothermic peak for Tm at 130 °C. On the other hand, there are neither endothermic nor exothermic peaks in the DSC curve of P3IB3T. Therefore, this polymer would be more amorphous-like than P3IB2T.

The absorption spectrum of P3IB2T film showed low absorption intensity around 620 nm, indicating weak pi-pi stacking interaction. Moreover, P3IB3T films showed the blue-shifted absorption spectrum compared to P3IB2T ones probably due to larger torsion of main chains affected by triisobutylene side chain.

Next, the crystalline nature of the polymer thin films was evaluated by Grazing incidence wide-angle x-ray scattering (GIWAXS). P3IB2T and P3IB3T films showed edge-on orientation, judged from the azimuth plots of (200) diffraction patterns. Moreover, (010) diffraction patterns were not observed for P3IB2T and P3IB3T films, probably due to less pi-pi stacking interaction by oligoisobutylene side chains.

Finally, we cross-linked P3IB3T to realize the formation of an inherently stretchable polymer semiconductor. 4,4'-Methylenebis(2,6-bis(methoxymethyl)phenol) and isopropl p-toluenesulfonate were used as cross-linker and thermal acid generator, respectively. The cross-linked P3IB3T showed quite lower tensile strength (0.68 MPa) and higher elongation at break (141%) than a poly(3-hexylthiophene) pristine film.

EP05.03.14
Decatacontic C20> Nanoconjugates with Light-Harvesting Antenna and Intramolecular Electron-Transfer Processes for Photodynamic Bio-Applications

He Yin, Min Wang and Long Y. Chiang; Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States.
Functionalized fullerenes with retaining photophysical characteristics show promising light harvesting ability, and may have potential for photovoltaic applications. We recently reported a conjugated fullerene derivative C60[>CPAF-(MN6+C3)2-(I−)10] (LC15) with less steps and higher yield. As C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**). The similarity of the spectra of LC15 and LC21 with less steps and higher yield, as C60 is replaced by more effective C70 which has broader absorption, the covalent conjugation of a visible light-harvesting antenna moiety CPAF and C70 provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photoexcited electron-donation to the C70 electron-acceptor cage in LC21 allows the dominant of the anionic (C70*) radical which can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullerenyl singlet excited state (C70*) to its long-lived triplet excited state (C70**).
while maintaining self-cleaning properties from extreme water repellency and showing good thermal stability. This study provides a practical solution to enhance the reliability of organic devices in the natural environment.

EP05.03.18
Near Infrared-to-Blue Photon Upconversion Based on Singlet-to-Triplet Direct Transition Yoichi Sasaki1, Nobuhiro Yanai1, 2 and Nobuo Kimizuka1, 2; 1Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan; 2Center for Molecular Systems (CMS), Kyushu University, Fukuoka, Japan.

The efficient use of near-infrared (NIR) light has been much coveted in energy and biological applications. For example, although the NIR light from 700 nm to 900 nm shows good tissue transparency, the photon energy in this region is too weak for important biological applications such as bioimaging, photodynamic therapy, and drug release. The blue light with a wavelength shorter than 500 nm is known to trigger drug release and in vivo photochemical reactions, and therefore it is imperative to produce such higher-energy visible light under NIR excitation.

Photon upconversion (UC) is a methodology that converts lower-energy photons into higher-energy photons. Triple-triplet annihilation based UC (TTA-UC) is especially promising since it works under weak excitation intensity like sunlight. Despite its importance, it has been difficult to obtain NIR (＞700 nm) to blue (＜500 nm) TTA-UC. This is because the energy loss associated with the intersystem crossing (ISC) of donors limits the use of acceptors with high T1 and S1 energy levels, and consequently the position of the anti-Stokes shift. To maximize the anti-Stokes shift and to achieve the TTA-UC from NIR to blue region, it is essential to develop TTA-UC systems without ISC. Recent efforts have been accordingly devoted to realizing new mechanisms that circumvent the energy loss of ISC such as TADF molecules, QDs, perovskites, and heavy metal complexes. These sensitizers, however, tend to show short excited state lifetime (＜10 ns), and triple-triplet energy transfer (TET) from the sensitizers to acceptor molecules is often inefficient.

In this work, we demonstrate an efficient NIR (＞700 nm)-to-blue (＜500 nm) TTA-UC by judicious developments of new Os(II) bis(terpyridine) complexes with singlet-to-triplet (S-T) direct transition. We achieved NIR-to-blue TTA-UC for the first time with a large anti-Stokes shift of 0.97 eV with a good UC efficiency.

EP05.03.19

Understanding degradation processes in organic solar cells is very important for the development of new materials with improved stability. One of the conventional ways to study the changes induced by the degradation processes is Raman spectroscopy. The main disadvantage of the Raman technique is that the measured signal is an integral over the entire volume of the measured sample. It is especially pronounced when there is an overlap between the Raman spectra over different layers of the solar cells. This is the case when a polyfluorene blend (F8BT:PFB) is the active layer and PEDOT:PSS serves as an electron blocker. To overcome this drawback we use ultra-thin, semi-transparent, layers of gold (4 nm) in between the different layers of the cell. This ultra-thin layer is specifically design to have plasmons around the Raman excitation laser (660 nm). When it is inserted between the ITO and the PEDOT:PSS the Raman signal is dominated by the PEDOT:PSS signal while when it is inserted between the PEDOT:PSS and the polyfluorene blend it is the blend signal that is dominated. Using this technique and monitoring the degradation at short-circuit current condition we observed the following.

Firstly, the time dependence of the surface enhanced Raman signal is monotonic in contrast with the conventional Raman where it is not. Secondly, we were able to separately analyze the degradation of the different layers. We found out that the main peak of the PEDOT:PSS Raman spectrum shifts to the right and its relative height, with respect to the other peaks, decreases which indicates an increase in the resistance of this layer. We also show that for the blend the main damage is done to the BT unit of the F8BT and that mainly affect electron conduction in the device. We believe that this new approach can be used to analyze other organic devices and at different excitation using other metals.

EP05.03.20
Solvent-Vapor-Annealed A–D–A-Type Semicrystalline Conjugated Small Molecules for Flexible Ambipolar Field-Effect Transistors Young Woong Lee1, Min Je Kim1, Yujong Lee1, Jeong Ho Cho3, 2 and Han Young Woo1; 1 Korea University, Seoul, Korea (the Republic of); 2 Sungkyunkwan University, Suwon, Korea (the Republic of); 3 Sungkyunkwan University Advanced Institute of NanoTechnology, Suwon, Korea (the Republic of).

Over the past two decades, many types of conjugated polymers or small molecules (SMs) have been synthesized and utilized as semiconducting materials for organic field-effect transistors (OFETs). To realize the high-performance and flexible OFETs, the fabrication process should be efficiently optimized at a low temperature condition and solvent-vapor-annealing (SVA) is a well-known process for controlling the morphology of SM thin films in ambient condition. In this study, three kinds of acceptor-donor-acceptor (A-D-A) type SM semiconductors were designed and synthesized by introducing different electron-withdrawing endcapping groups of dicyanovinyl (VCN), cyano-rhodanine (RCN) and cyano-indanone (INCN) at both termini, which enables to finely tune the frontier energy levels of semiconducting materials. All the OFETs exhibited ambipolar FET characteristics and SVA treatment changes crystalline structure and FET characteristics of semiconducting films remarkably. The SVA effect depending on the endcapping groups was logically investigated by using a DFT calculation, UV-vis absorption spectroscopy, 2-dimensional grazing incidence x-ray diffraction (2D GIXD), and atomic force microscopy (AFM). The as-coated P3T4-INCN films exhibited the hole mobility of 0.03 cm2V−1s−1 and electron mobility of 0.01 cm2V−1s−1. Finally, the P3T4-INCN OFET performance was significantly enhanced via SVA with chloroform, resulting in the hole mobility of 0.14 cm2V−1s−1 electron mobility of 0.03 cm2V−1s−1 with the good ambipolar charge transport behaviors.

In addition, a flexible OFET array with solvent-vapor-annealed P3T4-INCN was successfully fabricated on the polyethylene naphthalate ( PEN) substrate. This OFET device exhibited the hole mobility of 0.15 cm2V−1s−1 and electron mobility of 0.01 cm2V−1s−1, an on-off current ratio of ~105, and excellent mechanical stability even after 300 bending cycles.

EP05.03.21
Nano composite of Nickel Oxide Nanoparticles and Polyethylene Oxide as Printable Hole Injection Layer for Organic Solar Cells Marta Ruscello1, Giovanni Maria Matrone1, Stefan Schlisske1, Elena Sachs1, Patrick Reiser2, 1 Eric Mankel2, 1 Tanmoy Sarkar4, Basel Shamieh5, Artem Levitski5, Young Linde; Ben Gurion Univ-Negev, Lehavim, Israel.

In the field of organic electronics, rising research attention has been dedicated to the investigation of novel interlayers. A family of materials that has been deserving increasing interest for such purposes is the one of transition metal oxide nanoparticles, which can provide high quality interlayers for both charge injection or extraction. Metal oxide nanoparticles are suitable for solution-processed electronics thanks to many advantages: they can be dissolved in organic solvents and used as printable inks, can be processed at relatively low temperatures and can offer an increased stability compared to conjugated polymers. However, they also present certain technical challenges due to the higher surface to bulk ratio (i.e. surface trap states) or present problems during
film formation (i.e. agglomeration). (1) For this reason, various kinds of polymers can be employed to offer a hybrid solution to these issues. We present here the improvement of the processability of non-stoichiometric nickel oxide (NiOx) nanoparticles ink by blending with high molecular weight polyethylene oxide (PEO). Recently, NiOx has attracted increasing attention as a hole extraction layer in organic and perovskite photovoltaics due to its excellent optical transparency, p-type conductivity and good electron blocking properties. Nonetheless, the fabrication of highly efficient NiOx thin films is challenging due to the low viscosity of the inks or the high sintering temperatures of the precursor compounds. Here, we show how PEO can help dispersing the nanoparticles hindering their aggregation after deposition without compromising film functionality. Through Kelvin Probe, Contact Angle measurement, X-ray Photoelectron Spectroscopy and Transmission Electron Microscopy we observe that the presence of PEO is beneficial for a better tunability of the NiOx film thickness and morphology. We also show that such effect on the film formation is observed to be beneficial when the NiOx:PEO blends are applied as a hole extraction layer on OPV devices, improving device performance. Moreover, the inclusion of the polymer in the nanoparticle ink allows, for the first time, the inkjet-printing of the NiOx layer without requiring high temperature post-treatment. (2) Finally, we verified the possible migration of the PEO used in these devices through the bulk heterojunction towards the cathode (3), defining a dual purpose for the polymers: on one hand passive matrix for the nanoparticles as anode, on the other functionalizer of the cathode.

(1) Wallace C. H. Choy and Di Zhang, Small, 2016, 12, 416; (2) M. Ruscello et al., Submitted, 2018 (3) Jane Vinokour et al., ACS Appl. Mater. Interfaces 2017, 9, 29889

EP05.03.22
Fast, Efficient Luminescence in Carbene-Cu(I) Complexes and Other Coinage Metals Rasha Hamze1, Jesse L. Peltier1, Rodolphe Jazzar1, Daniel Sylvinson2, Peter I. Djurovich1, Guy Bertrand1 and Mark Thompson2; 1Chemistry, University of California at, California, San Diego, California, United States; 2Chemistry, University of Southern California, Los Angeles, California, United States.

As for long as it has been a subject of study, the luminescence of copper(I) complexes has been plagued by slow, inefficient luminescence. This is a result of two major factors: weak spin-orbit coupling, due to the light metal; and large excited state reorganization energies, associated with a formal oxidation at the d^{10} metal center in MLCT transitions. While the latter culprit can be mitigated by increasing the steric bulk around the metal, addressing the former is a more challenging endeavor. With this in mind, we discuss recent work from our lab, where we have prepared carbene-Cu(I) complexes exhibiting fast (k > 10^6 s^-1), efficient (PLQY = 100%) phosphorescence, with emission colors tuned over the visible spectrum. These results have allowed us to develop new paradigms for designing Cu(I) complexes, and to expand our understanding down the periodic table to Ag(I) and Au(I) complexes. Specifically, I will highlight newly-isolated Au(I) and Ag(I) complexes with remarkable photophysical properties that underscore their potential for OLED applications.

EP05.03.23
Polar-Functionalized Dioxythiophene Polymers as a Platform for Aqueous-Compatible Electrochemical and Bioelectronic Devices Lisa R. Savagian1, Anna Osterholm1, Michel De Keersmaecker2, James F. Ponder3, Graham Collier1 and John R. Reynolds3; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Imperial College London, London, United Kingdom.

There has been increasing interest in developing redox-active polymers capable of electrochemically interfacing with biological systems for sensing and therapeutic applications. As an example, organic electrochemical transistors (OECTs), which have emerged as a highly sensitive in vivo biosensing platform, hinge on bulk transport of aqueous doping ions through conjugated polymer films for stabilizing conducting states and controlling current through the transistor channel. In the pursuit of aqueous-compatible systems, there has been a growing body of work demonstrating how highly polar oligo(ether) side chains enhance the redox activity and ion transport properties of conjugated polymers for use in OECTs. Herein, we present a family of dioxythiophene-based polymers functionalized with side chains spanning a range of polarities, including ester, diester, and oligo(ether) analogues, and explore how factors such as solubility, redox potential, ion transport and stability, and conductivity switching depends on the chemical nature of the substituent side chain. These materials exhibit excellent redox stability in physiologically-relevant electrolytes and can be prepared through straightforward direct (hetero)arylation polymerization chemistries. We evaluate the dynamic electrochemical and optical behavior of these polymers, paying special attention to their potential-dependent mixed ionic/electronic conductivities using techniques such as electrochemical impedance spectroscopy, and demonstrate their utility in aqueous-based electrochemical devices. Through these studies, we aim to establish important structure-property relationships for exploring the materials design space of side chain polarity for high-performing bio-electrochemical devices.

EP05.03.24
Lactam Containing Two Isomeric Polymers For OPVs with High Open-Circuit Voltages Jong-Woon Ha and Do-Hoon Hwang; Pusan National University, Busan, Korea (the Republic of).

The molecular design of the wide bandgap (WBG) is important for non-fullerene polymer solar cells to obtain simultaneously high power conversion efficiency (PCE) and open circuit voltage (V_{oc}). In this study, we developed two isomeric lactam acceptor, thieno[3,2-c]quinolin-4(3H)-one (TQO) and thieno[3,2-c]isoquinolin-5(4H)-one (TIQO), to compare their optical and electrical properties. The WBG donor-acceptor (D-A) type polymers, PBDT-TQO and PBDT-TIQO, were synthesized using the 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT) as electron donor building block and TQO or TIQO as electron accepting building block for fullerene and non-fullerene organic solar cells. PBDT-TQO and PBDT-TIQO showed absorption range below 600 nm and low-lying HOMO energy levels. The appropriate match of the energy levels between donors and acceptors could be applied for fullerene and non-fullerene OSC. PCEs of the devices based on PC_{71}BM achieved 3.02 % for PBDT-TIQO:PC_{71}BM and 3.92 % for PBDT-TIQO:PC_{61}BM, respectively. For better photovoltaic performances, the devices based on polymer:non-fullerene acceptor (ITIC or IT-4F) were fabricated. A PCE of PBDT-TIQO:ITIC of 7.62 %, while the device of PBDT-TIQO:ITIC was afforded PCE of 6.56 % thanks to increase short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}).

EP05.03.25
Ion Transport and Reaction Kinetics on the Operation of AC-Driven Electrochemiluminescence Devices Jong Ilk Lee1, Hyunwoo Jo1, Dongwon Kang2, Seok Hwan Kong1, Hyoig Gim1, Ik-Soo Shin3, Jongwook Kim2 and Moon Sung Kang1; 1Department of Chemical Engineering, Soongsil University, Seoul, Korea (the Republic of); 2Department of Chemical and Biomolecular Engineering, Sogang University, Seoul, Korea (the Republic of); 3Department of Chemistry, Soongsil University, Seoul, Korea (the Republic of).

Electrochemiluminescence (ECL) is light emission from redox precursors generated through a series of electrochemical processes. This process can be exploited in fabricating a light-emitting device, which is referred to as the electrochemiluminescence device (ECLD). Unlike conventional solid-state light-emitting device, the operation of ECLDs relies on mass transport of the luminophores and electrochemical electron transfer reactions; the oxidative and reductive forms of ECL luminophores have to encounter to form the excited states before emitting light eventually. Herein, we investigate the influence of these dynamic factors on the emission characteristics of AC-voltage driven ECLDs. Benchmark ionic transition metal complex ECL luminophore and ionic liquids are used as the ECL luminophore and the electrolyte materials, respectively, for our model device. The dynamic processes in the ECLD could be
simple modeled using i) the Fick’s law to describe the diffusion process near the electrode, ii) the first order reaction of the ECL luminophore at the electrode, and iii) the second order chemical reaction between the reduced/oxidized luminophores, based on the associated reaction constant and the diffusion constant obtained from separate electrochemical analysis techniques, respectively. The model yielded transient ECL intensity profile of the device under a single switching cycle of an AC electrical input which matched well with experimental results. Moreover, the time-averaged values of the transient profiles matched with the characteristic operational frequency-dependent ECL properties of the device, which initially increase with increasing frequency but then peak and decrease at higher frequencies. Using the model giving well-matching results to the experimental observations, the influence of diffusion and the reaction rates on the performance of an ECLD could be analyzed separately and systematically, which is difficult to carry out from experiment. The fundamental understanding on the operation of this emerging class of light-emitting device platform provides practical guidelines to advance its performances.

References:

EP05.03.26
Dynamics of Charge Distribution and Emission Zone in Sandwich Light-Emitting Electrochemical Cells Roland Hany: EMPA, Duebendorf, Switzerland.

In contrast to the multiple layers required for a state-of-the-art organic light-emitting diode, light-emitting electrochemical cells (LECs) are usually built from a single emissive layer that contains an electrolyte and is sandwiched between two electrodes. Due to the presence of mobile ions, the single layer can perform all the tasks that take place in an electroluminescence device, i.e. facile electrical charge injection, transport, exciton formation and radiative recombination. The LEC device concept sounds simple, but in truth it’s not easy at all; despite twenty years of research, resolving the dynamics of the injected electrical charge as well as identifying the zone where light is emitted in sandwich devices present considerable scientific challenges. Here, we study the temporal evolution of organic salt-based LECs and demonstrate that electroabsorption spectroscopy in combination with electrical capacitance measurements enables the determination of the distribution of the injected, uncompensated electronic charge inside these devices. For constant-voltage operating conditions and over a period of hours, the Stark effect signal intensity and the capacitance increase steadily, but to a different extent. We demonstrate that this difference sensitively depends on the position and distribution width of injected mobile charges. Estimates show a substantial spreading over the active layer of the injected charge density with time, screening the electric field behind the charge peak [1].

We also studied how the p- and n-doped regions and the intrinsic (i) emission zone evolve over time [2]. By analysing incident photon-to-current conversion efficiency and angular emission measurements with optical simulations, and correlating the results with capacitance measurements, we were able to obtain a clear picture of the p-i-n situation and the emission zone of cyanine dye LECs. The spectral photocurrent response analysis in [2] was possible because of the high photocurrent response of this type of LEC. Indeed, we recently observed efficient photoinduced charge generation in the bulk of pristine cyanine dye films with internal quantum efficiency exceeding >40% [3]. We report on this unusual behavior because intrinsic photogeneration of charge carriers in organic semiconductors is generally attributed to high energy ionization or exciton dissociation by a strong electric field.

References:

EP05.03.27
Structural Evaluation of 5,5′-Bis(naphth-2-yl)-2,2′-bithiophene in Organic Field-Effect Transistors with n-Octadecyltrichlorosilane Coated SiO2 Gate Dielectric Andreas E. Lauritzen1, 2, Mika Torkkeli1, Oier Bikondoa3, 4, Jes Linnet5, 6, Luciana Tavares6, Jakob Kjelstrup-Hansen1 and Matti Knaapila1, 4; 1Department of Physics, Technical University of Denmark, Kgs. Lyngby, Denmark; 2Department of Physics, University of Oxford, Oxford, United Kingdom; 3XMaS, The U.K.-CRG Beamline, European Synchrotron Radiation Facility, Grenoble, France; 4Department of Physics, University of Warwick, Coventry, United Kingdom; 5Center for Nano Optics, Mads Clausen Institute, University of Southern Denmark, Odense, Denmark; 6NanoSYD, Mads Clausen Institute, University of Southern Denmark, Soenderborg, Denmark.

We report on the structure and morphology of 5,5′-bis(naphth-2-yl)-2,2′-bithiophene (NaT2) films in bottom-contact organic field-effect transistors (OFETs) with octadecyltrichlorosilane (OTS) coated SiO2 gate dielectric, characterized by atomic force microscopy (AFM), grazing-incidence X-ray diffraction (GIXRD) and electrical transport measurements1. Three types of devices were investigated with the NaT2 thin-film deposited either on (1) pristine SiO2 (corresponding to higher surface energy, 47 mJ/m2) or on OTS deposited on SiO2 under (2) anhydrous or (3) humid conditions (corresponding to lower surface energies, 20-25 mJ/m2). NaT2 films grown on pristine SiO2 form nearly featureless 3-dimensional islands. NaT2 films grown on OTS/SiO2 deposited under anhydrous conditions form staggered pyramid islands where the interlayer spacing corresponds to the size of the NaT2 unit cell. At the same time, the grain size measured by AFM increases from hundreds of nanometers to micrometers and the crystal size measured by GIXRD from 30 nm to more than 100 nm. NaT2 on OTS/SiO2 deposited under humid conditions also promotes staggered pyramids but with smaller crystals (30 – 80 nm). The NaT2 unit cell parameters in OFETs differ 1 – 2% from those in bulk. Carrier mobilities tend to be higher for NaT2 layers on SiO2 (2 – 3×10-3 cm2/Vs) compared to NaT2 on OTS (2×10-4 – 1×10-4 cm2/Vs). An applied voltage does not influence the unit cell parameters when probed by GIXRD in operando.

References:
1. Lauritzen et al., Langmuir, 2018, 34 (23), pp. 6727-6736, DOI: 10.1021/acs.langmuir.8b00972

EP05.03.28

Self-assembled monolayers (SAMs) formed using N-heterocyclic carbene (NHCs) have recently emerged as thermally and chemically ultra-stable alternatives to those formed from thiols. The rich chemistry and strong σ-donating ability of NHCs offer unique prospects for applications in...
nanelectronics, sensing and electrochemistry. Though stable in SAMs, free carbenes are notoriously reactive, making their electronic characterization challenging. Here we report the first investigation of electron transport across single NHC-bound molecules using in situ STM imaging and large-area printing methods. We develop a series of air-stable metal NHC complexes that can be electrochemically reduced in situ to form NHC–electrode contacts, enabling reliable single-molecule conductance measurements of NHCs under ambient conditions. Using this approach, we show that the conductance of an NHC depends on the identity of the single metal atom to which it is coordinated in the junction. Our observations are supported by density functional theory (DFT) calculations, which also firmly establish the contributions of the NHC linker to the junction transport characteristics.

Our work demonstrates a powerful method to probe electron transfer across NHC–electrode interfaces; more generally, it opens the door to the exploitation of surface-bound NHCs in constructing novel, functionalized electodes and/or nano electronic devices.

**EP05.03.29**

**A Novel Hole-Blocking Material of Four Pyridylbenzene-Connected Terphenyls for Highly Sensitive and Thermally Stable Organic Photodiodes and Radiation Detectors**

Atsushi Wada, Issa Takasu, Satomi Taguchi, Yoko Nomura, Kohei Nakayama, Fumihiko Aiga and Rei Hasegawa; Toshiba Corporation, Kawasaki, Japan.

Organic photodiodes (OPDs) have attracted attention with a view to their application in radiation detectors and image sensors owing to their potential advantages of high sensitivity, large-area sensing, light weight and flexibility. To realize high sensitivity, the OPDs need to achieve high external quantum efficiency (EQE) and low dark current simultaneously. We have previously reported the OPDs with boron-subphthalocyanine chloride (SubPC) and pentafluorophenyo-substituted SubPC (F5-SubPC) as a photoelectron conversion layer and bathocuprone (BCP) as a hole-blocking layer, which exhibit high EQE (70% at 530 nm) and low dark current (0.03 nA/cm²). These properties are comparable to those of the Si photodiodes. However, the thermal stability of the OPDs is low, and EQE was reduced from 70% to 33% by thermal treatment at 150°C. Here, we report a novel hole-blocking material, tetra(pyridyl-4-phenyl)-terphenyl (Tp4), and the OPDs with Tp4. The thermal stability of the OPDs is improved significantly while maintaining their high EQE and low dark current.

Tp4 is designed to have deep HOMO energy level and high thermal properties. Tp4 consists of four pyridine rings and seven benzene rings. Because pyridine rings are electron-deficient, Tp4 is expected to have deep HOMO energy level and block the hole injection from the anode. Furthermore, it is reported that pyridine rings can coordinate with metal from the electrode and the pyridine-metal complex can form gap states between HOMO and LUMO energy levels of hole-blocking material, which promote transport of the electron to the anode. Because the molecular weight of Tp4 (843) is much larger than that of BCP (360), the improvement of thermal properties are also expected. Tp4 was synthesized by Suzuki cross-coupling reaction, and then purified by sublimation. The HOMO and LUMO energy levels of Tp4 are 6.5 eV and 3.0 eV, respectively, which are the same as those of BCP. The glass transition temperature (Tg) of Tp4 is not observed until 300°C and melting temperature (Tm) is 412°C, which are much higher than those of BCP (Tg:80°C, Tm:279°C). Next, we fabricated OPDs with Tp4, and the device structure is follows:ITO electrode/buffer layer/electron-blocking layer/SubPC+F5-SubPC/Tp4/Al electrode. By optimizing the thickness of Tp4, the OPDs exhibit high EQE (70% at 530 nm) and low dark current (0.01 nA/cm²). The OPDs with Tp4 have demonstrated higher performance than the previously reported OPDs with BCP. Furthermore, the thermal stability of the OPDs with Tp4 is enhanced significantly, and they still exhibit high EQE of 61% after thermal treatment at 150°C. In the presentation, we will also report the results of radiation with the OPDs.

In summary, a novel hole-blocking material that has the same HOMO and LUMO energy levels as BCP and higher thermal properties than BCP has been developed. The OPDs using this material have demonstrated high EQE, low dark current and high thermal stability.

**EP05.03.30**

**Directional Printing of Conjugated Polymer Semiconductors for High Performance Organic Field-Effect Transistors and Circuits**

Jung Jiyun and Kang-Jun Baeg; Pukyong National University, Busan, Korea (the Republic of).

Printed and flexible electronics based on soluble conjugated organic molecules have drawn tremendous interest as a new paradigm for the fabrication of large-area and low-cost optoelectronics and electronics applications. Those polymers should be preferably aligned in the perpendicular direction through the active channel of organic field-effect transistors (OFETs). Morphological control and structural ordering of the conjugated polymers via large area printing methods is an important issue in order to achieve high performance OFETs and its electronic circuitry. In this study, we report various directional printing methods (off-centered spin-coating, dip-coating, and bar-coating) for preferable arrangement of conjugated polymers, such as high mobility PCDTFTBT and DPPT-TT. Those polymer OFETs showed high charge carrier mobilities as high as 11 cm²V⁻¹s⁻¹ and balanced ambipolar charge transport behavior in the top-gated OFET structure with polymer dielectrics. This remarkable enhancement is mostly attributed to improved alignment and ordering of polymer chains through the active channel and better uniformity of OFET parameters is also obtained by this large-area printing techniques. Moreover, high-k fluorinated polymer dielectrics significantly contribute to increase high charge carrier density under low voltage conditions. Finally, higher mobilities and well-balanced P-channel and N-channel characteristics in comparison to conventional coating methods was successfully applied to develop complementary-like printed circuits, it is expected to be realize high performance flexible and wearable electronic devices via cost-effective simple printing methods.

**EP05.03.31**

**A Sky Blue Thermally Activated Delayed Fluorescent (TADF) Emitter Realizing Efficient White Light Emission Through In Situ Metal Complex Formation**

Yuki Kato1, Hisahiro Sasabe1,2,3, Yuya Hayasaka1, Yuichiro Watanabe1 and Junji Kido1,2,3; 1Organic Materials Science, Yamagata University, Yonezawa, Japan; 2Research Center for Organic Electronics, Yamagata University, Yonezawa, Japan; 3Frontier Center of Organic Materials, Yamagata University, Yonezawa, Japan.

In this work, we have developed a pyrazine/acridine based thermally activated delayed fluorescence (TADF) emitter named 2,6-bis[4-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]pyrazine (2Ac-PRZ) for organic light-emitting devices (OLEDs). This emitter has a metal coordination ability to form a metal complex via in situ deposition of copper iodide (I) (CuI). The neat film of 2Ac-PRZ showed sky blue emission with a peak at 463 nm, and the photoluminescence quantum yield (PLQY) of 17%. On the other hand, when CuI was doped into 2Ac-PRZ layer, the doped layer showed white emission with dual emission peak at 463 nm and 583 nm with PLQY up to 34%. We used this co-deposited layer of 2Ac-PRZ/CuI as an emissive layer (EML) in OLEDs. We fabricated OLEDs with a structure [ITO/ triphenylamine-containing polymer: 4-isopropyl-4′-methyldiphenyl-iodonium tetra(pyridyl-4-phenyl)-terphenyl (Tp4)/LiF (0.5 nm)/Al (100 nm)]. The device showed white emission with a CIE of (0.41, 0.45), and very high photoluminescence quantum yield (PLQY) of 17%. On the other hand, when CuI was doped into 2Ac-PRZ layer, the doped layer showed white emission with dual emission peak at 463 nm and 583 nm with PLQY up to 34%. We used this co-deposited layer of 2Ac-PRZ/CuI as an emissive layer (EML) in OLEDs. We fabricated OLEDs with a structure [ITO/ triphenylamine-containing polymer: 4-isopropyl-4′-methyldiphenyl-iodonium tetra(pyridyl-4-phenyl)-terphenyl (Tp4)/LiF (0.5 nm)/Al (100 nm)]. The device showed white emission with a CIE of (0.41, 0.45), and very high photoluminescence quantum yield (PLQY) of 17%.
Carrier transport materials such as hole and electron transport materials (HTMs and ETMs) play a key role in determining organic light-emitting device (OLED) performances, such as driving voltage, efficiency and operation lifetime. A representative HTM for OLEDs is α-NPD that exhibits relatively high glass transition temperature ($T_g$) of 100 °C[1], and moderate hole mobility of $8.8 \times 10^{-4}$ cm²/Vs among reported HTMs. In this work, we developed a novel series of HTMs aiming higher thermal stability and higher hole mobility than those of α-NPD by introducing [1]thiazolo[3,2-b][1]benzothiophene (BBTBT) moieties. BBTBT is famous in organic field effect transistor (OFET)[1,2], and has realized excellent hole mobility for OFET applications. A novel HTM containing BBTBT showed superior thermal stability with $T_g$ of 155 °C, and good hole transport property in OLEDs. An OLED with a structure of [ITO/2,3,6,7,10,11-Hexacyano-1,4,5,8,9,10-hexaazatriphenylene (HATCN)/novel HTM/9,9'-diphenyl-9H,9'H-3,3'-bicarbazole (BCzPh)/tris(2-phenylpyridinato)iridium(III) (Ir(ppy))3-doped BCzPh/3,3',5,5'-tetra(3-pyridyl)-1,1',3',1''-terphenyl (B3PYPB)/8-quinolinolato lithium (Liq)/Al] were fabricated. The device exhibited driving voltage of 3.7 V and EQE of 17% at 1000 cd/m². These performances suggest the potential usefulness of these HTMs for OLEDs.


EP05.03.33
Stable Solution-Processed Small-Molecule Phosphorescent Tandem Organic Light-Emitting Devices Tatsuya Takahashi[1], Satoru Ohisa[1,2,3], Masahiro Igarashi[1,2,3], Hitoshi Fukuda[1], Tatsuya Hikichi[1], Eri Ueki[1], Takayuki Chiba[1,2,3], Yong-Jin Pu[1,2,3] and Junji Kido[1,2,3]; Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Japan; 2Research Center for Organic Electronics (ROEL), Yamagata University, Yonezawa, Japan; 3Frontier Center for Organic Materials (FIRM), Yamagata University, Yonezawa, Japan.

Recently, solution-processed polymer tandem organic light-emitting devices (OLEDs) comprising multiple light-emitting units connected by carrier generation layers have been reported as a promising way to realize long lifetime solution-processed OLEDs [1, 2]. However, those both with high device efficiency and long lifetime have been reported yet. In this work, we report the development of a stable solution-processed small-molecule phosphorescent tandem OLEDs, in which ten-layers were formed by solution-processing. We newly developed solvent-tolerant small molecule host materials with indolocarbazole, phenylcarbazole, and triazine units for phosphorescent EML. These materials showed high tolerance to methanol solvents. The upperlayer material on the EML is ZnO nanoparticle (NP), and it should be dispersed in methanol. The surface condition of the ZnO NPs was tuned to disperse them in methanol by modifying the conventional synthetic procedure. As a result, we succeeded in fabrication of solution-processed small-molecule orange phosphorescent tandem OLED comprising two light-emitting units. At a nominal luminance of 1000 cd/m², the driving voltages were 5.2 V for the 1st unit device, 5.1 V for the 2nd unit device, and 10.7 V for the tandem device, respectively. The driving voltage of the tandem device was almost similar to the sum of the 1st and the 2nd unit devices. The external quantum efficiency of the tandem OLED at 1000 cd/m² was 25.2% under Lambertian assumption. The device stability of the two kinds of single units and the tandem device were evaluated at a constant current density of 2.5 mA/cm² corresponding to initial nominal luminances of 520 cd/m² for the 1st unit device, 340 cd/m² for the 2nd unit device, and 1240 cd/m² for the tandem device, respectively. The times to 70% of the initial luminances were 75 h for the 1st unit device, 57 h for the 2nd unit device, and 68 h for the tandem device, respectively. Considering much higher luminance of the tandem device than the others, the tandem device obviously showed much longer device lifetime than the others.

References:

EP05.03.34
Polymeric Composite Dielectrics for Flexible Organic Field-Effect Transistors and Pressure Sensors with Low Voltage Operation Qingdong Zheng; FJRSM, Chinese Academy of Sciences, Fuzhou, China.

Organic field-effect transistors (OFETs) could offer a significant potential for flexible pressure sensors based on them. However, the achievement of both low-voltage operation and high sensitivity remains a challenge for OFET-based pressure sensors. In this presentation, novel polyacrylic acid containing composite dielectrics are demonstrated for flexible OFETs and ultra-sensitive pressure sensors with low voltage operation. The OFETs using the composite dielectrics showed remarkably improved electrical performance under a much lower operating voltage of than those with a pristine polyacrylic acid dielectric. The OFETs also reveal excellent flexibility and bending stability during mechanical tests with different bending radii and cycles. Based on the dielectric and the OFET performance, flexible OFET-based pressure sensors with both low-voltage operation and ultra-high sensitivity are further achieved. The resulting sensors deliver a high sensitivity at a low-operating voltage, a rapid response time, and excellent operating stability. These results provide a promising strategy to design and synthesize high-performance flexible dielectrics for OFETs and pressure sensors.

EP05.03.35
Transient Electroluminescence Analysis in Organic Light Emitting Diodes—The Effect of the LiF Thickness in LiF/Ag Cathode Shirin N. Barnea and Rafi Shikler; Electrical and Computer Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel.

Time dependence studies in organic light emitting diodes are in the center of many researches due to the increase of interest in these devices for data transfer at high rates via modulation of visible light. In our study we examine the influence of charge injection on the time-dependency of the electroluminescence after driving the OLED from steady state to open circuit condition. In contrast to time-resolved-photoluminescence (TRPL) technique where the excitation is done by optical pulse, in our approach we monitored the temporal evolution of the emission under electrical excitation. The proposed technique combined with steady-state analysis allows us to take into account the interplay of various electronic processes and to investigate not just the excitors dynamics but also the charge dynamics. For this purpose, we fabricated polyfluorene-based OLEDs with LiF/Ag cathodes differing only by the thickness of the LiF layer for controlling the electron injection efficiency. Transient electroluminescence measurements accomplished by using a homemade fast switching driver that design to cop with the high impedance of the OLED and limitations on the maximum current flow in the device. Our driver successfully drives the OLED to open circuit condition in 5ns. Two exponential decays of the EL were observed after the turn-off, an initial fast decay in the time domain of tens of ns followed by a slow decay in the time domain of hundreds of nano-second. These lifetimes are much longer than the lifetime of the singlet excitons that were measured using TRPL (sub-nano to nano seconds). Capacitance—Voltage characteristic was performed due to its sensitivity to the barrier height and built-in potential. We observed changes in the peak position, maximum capacitance and peak shape. We found correlation between these parameters, the charge injection and accumulation and the measured transient EL lifetimes. We discovered that devices with higher charge injection efficiency and lower charge accumulation at the electrodes exhibit longer transient EL lifetimes. In addition, the shape of the peak capacitance that can be associated with the changes of space-charge regions is correlated to the longer transient EL lifetime.

EP05.03.36
Computational Design of Non-Fullerene Acceptors for Organic Solar Cells Anastasia Markina[1], Frédéric Laquai[2] and Denis Andrienko[1]; Max Plank
To date, most of the electron acceptors used in organic solar cells are fullerenes or their derivatives. As fullerenes exhibit only weak light absorption in the Vis spectral region, practically half of the active material does not contribute to exciton and charge generation, limiting the maximum efficiency of these devices to ca. 12%. The way forward to reach higher solar cell efficiencies is to replace fullerenes with strongly-absorbing dye molecules, namely, nonfullerene acceptors (NFAs). However, the systematic design of acceptor molecules with tailored properties has yet to be demonstrated. The difficulty here is that, while fullerene is an electrostatically “inert” molecule, new acceptors typically have strong static quadrupole moments. This complicates the interplay of electrostatic forces at the donor-acceptor interface, making it difficult to predict and design appropriate donor-acceptor combinations. As a result, in order to optimize solar cell efficiency, one has to appropriately balance the individual electrostatic contributions to energy profiles. Exploring the long-range electrostatic interaction at the interface, we demonstrate for a set of recently developed NFAs that the electrostatic bias potential can be directly related to the stabilization (or destabilization) of CT states as well as changes of the photovoltaic gap. Therefore, it is an important quantity to account for when designing non-fullerene acceptors. Furthermore, we compare theoretically-predicted properties of the NFAs with experimental data to assess the quality of our approach. We find that the correlation between quadrupole moments, charge separation efficiency, and CT-state energy predicted by our model is experimentally reproduced for several different small molecules and polymer donor / non-fullerene acceptor combinations. This allows us to predict new NFA structures using combinations of readily available molecular building blocks that can potentially reach to even higher performances than currently achieved in state-of-the-art NFA devices.

EP05.03.37

Patterning organic semiconductors via traditional solution-based microfabrication techniques is precluded by undesired interactions between processing solvents and the remaining photore sist. Herein we show how to easily avoid these problems and introduce a simple lift-off method to pattern organic semiconductors. Positive tone resist is deposited on the substrate, followed by conventional exposure and development. After deposition of the organic semiconductor layer, the remaining photore sist is subjected to a flood exposure, rendering it developable. Lift-off is then performed using the same aqueous developer as before. We find that the aqueous developers do not compromise the integrity of the organic layer or alter its electronic performance. We utilize this technique to pattern four different organic electronic materials: epindolide, a luminescent semiconductor, p-n photovoltaic bilayers of metal-free phthalocyanine and N,N’-dimethytriacracboxylic diimide, and finally the archetypal conducting polymer poly(3,4-ethylenedioxythiophene).

Record efficiencies of organic devices nowadays reach 15%. However, due to their organic nature, their performance is strongly influenced by environmental stresses, such as oxygen, light, heat and humidity. We are reporting on successful long-term stability improvement by ternary blending the active layers of organic solar cells with small amounts of stabilizing compounds comprising different stabilizing mechanisms[1-4]. Radical scavenging and singlet oxygen quenching stabilization mechanisms have been monitored in presence of different stabilizers, leading to different stabilization dynamics. Lifetime investigations and characterization were conducted under ISOS3-degradation conditions on bulk-heterojunction cells containing P3HT:60PCBM and PTB7:70PCBM systems. Different microscopic and spectroscopic methods (AFM, UV-vis, FTIR, ESR, NIR emission, PES) were applied to monitor chemical degradation over time, and correlate the observed differences with the device lifetimes.

References:

EP05.03.38
Stabilization of Organic Solar Cells Using Radical Scavengers and Singlet Oxygen Quenchers Vida Engnuman,1 Mikkel Bregnhøj,1 Liana Inasaridze,1 Michela Prete1, Filipp Obrezkov2, Dmytro Volynik2, Michael Westberg Sörensen2, Sebastiann Engmann3, Horst-Günter Rubahn3, Juozas Vidas Grauzulevicius3, Pavel Troshin2, Peter Renssen Ogilvy2 and Morten Madsen1:1 University of Southern Denmark, Sonderborg, Denmark; 2Department of Chemistry, Aarhus University, Aarhus, Denmark; 3Institute of Problems of Chemical Physics of RAS, Moscow, Russian Federation; 4Skolkov Institute of Science and Technology, Moscow, Russian Federation; 5Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania; 6Institute of Physics, Ilmenau University of Technology, Ilmenau, Germany.

Despite the performance of the resulting devices is enhanced, the presence of ionic species in CPE layers causes complications in the device response due to charge trapping and electric field screening effects. In this sight, the use of conjugated polymer polarizers (CPPs) is demonstrated as a new and efficient alternative to CPEs. Indeed, the conjugated backbones of CPPs are modified with polar non-ionic side groups, thus avoiding ion-dependent drawbacks. By introducing a layer of polyfluorene containing phosphonate groups (PF-EP) underneath the metal electrodes, a clear improvement of the electronic performance results in a more than twofold increased light-emission (optical power) and a five-times enhanced EQE of p-type OLETs, with superior performance in comparison with the relative CPE-containing devices. Moreover, the great benefit of using a transparent glass substrate allows for a deep investigation of the morphological and photoluminescent characteristics of both CPE- and CPP-buried interlayers within complete multilayered OLETs. Hence, by means of an optical scanning probe technique, the operation mechanisms of the investigated interlayers are elucidated.

EP05.03.39
Interface Engineering to Enhance the Efficiency of Organic Light Emitting Transistors Mario Prosa; CNR-ISMN, Bologna, Italy.

Organic light-emitting transistors (OLETs) show, in a single device, the fascinating combination of electrical switching characteristics and light generation capability. However, to ensure an effective device operation, efficient injection of charges at the electrodes is required. In this talk, the role that interfacial engineering plays on the figures-of-merits of OLETs is discussed. In particular, the effect of a series of multifunctional electrodes on both the external quantum efficiency (EQE) and the optical power of the corresponding devices is reported.
Modification of Interfaces with Organic Molecules in Optoelectronic Devices


We have developed surface modification process of polymer dielectrics with solution-processable triptycene (Trip) derivatives for high mobility organic thin-film transistors (OTFTs). The surface modification improves the averaged mobility of OTFTs from 0.41 cm²/Vs to 2.23 cm²/Vs. The nested packing of Trip molecules results in the formation of 2D hexagonal arrays, which stack one-dimensionally into a multilayer structure. Due to the unique assembling blocks because they are intrinsically flexible and are compatible with low-cost printing processes. In this sense, OTFTs with polymer gate dielectrics are a promising platform for high-performance electronic devices.

In order to develop high-performance organic electronic materials, it is of great importance to understand charge transport phenomena at molecular level. Here, we report the synthesis as well as the optical and electron-transport properties of a series of discrete alternating donor-acceptor (D-A) oligomers. These molecules are terminated with methyl-thiol anchors for single-molecule conductance measurements using the scanning tunneling microscopy-based break-junction (STM-BJ) technique. The electronic properties of the oligomers are further investigated by UV-Vis, Cyclic Voltammetry and Density Function Theory (DFT) calculations to understand the factors affecting conductance. By fitting to the Simmons Model, we find the intra-chain electron transport follows an electron tunneling mechanism whereby the molecule conductance is a function of molecule length. The dependence of oligomers’ conductance on potential-bias are also discussed. These findings shed light on the underlying electron transport mechanism in donor-acceptor organic semiconductor materials.

Solution-Processable Polymer Surface Modification with Organic Self-Assembled Layer for Ultraflexible Amplifier Circuits

Masaya Kondo, Takafumi Uemura, Takashi Kajitani, Soda Yuri, Fumitaka Ishiwa, Yoshiaki Shoji, Naoko Nambu, Masahiro Sugiyama, Shusuke Yoshimoto, Teppei Araki, Takanori Fukushima, and Tsuyoshi Sekitani.

We have developed surface modification process of polymer dielectrics with solution-processable triptycene (Trip) derivatives for high mobility organic thin-film transistors (OTFTs). The surface modification improves the averaged mobility of OTFTs from 0.41 cm²/Vs to 2.23 cm²/Vs. The nested packing of Trip molecules results in the formation of 2D hexagonal arrays, which stack one-dimensionally into a multilayer structure. Due to the unique assembling property, the Trip derivatives can form a highly oriented film on the surface of polymer without any anchoring groups. In this study, we have succeeded in forming 5-nm-thick closely-packed Trip layers on polymer dielectrics using blade coating (BC) known as a simple solution process. In addition, organic operational amplifier have been realized based on the modification technique. Flexible device technologies have been expected for next-generation applications such as flexible bio-medical devices. OTFTs are the potential building blocks because they are intrinsically flexible and are compatible with low-cost printing processes. In this sense, OTFTs with polymer gate dielectrics are a promising structure among various types of OTFTs because of their excellent flexibility and processability. However, one problem is that polymer dielectrics possess a lot of disorders and charge trap sites on the surface. Therefore, it is difficult to form highly-crystalline organic semiconductor films on polymer dielectrics, leading to OTFTs with low mobility.

Recently, it has been reported that thermally-evaporated Trip layers are useful for modifying polymer surface to avoid the negative effect of disorders and charge trap sites on the polymer. Here, we report the simple solution process in ambient conditions to form Trip layers. The improvement of mobility of OTFTs is better than that of the Trip layer formed by thermal vacuum evaporation (TVE). We fabricated top-contact bottom-gate OTFTs with hybrid gate dielectrics of Trip/parylene (5 nm/38 nm) on 1-μm-thick parylene substrates. We compared two types of Trip as referred to Trip.H and Trip.OMe. First, we formed Trip.OMe layers by using BC and TVE as a reference sample. The OTFTs with Trip.OMe layers formed by TVE and BC showed the averaged mobility of 1.59 and 2.23 cm²/Vs, respectively. These values were much higher than that of OTFTs without Trip.OMe layers (0.41 cm²/Vs). Moreover, the mobility improvement with BC was better than TVE. Secondly, the stability of OTFTs was degraded to 0.18 cm²/Vs with using Trip.H. Although the
recombination, thereby also extending the emission duration. For example, a TBRb-doped film exhibited a high purity because of better emission properties of dopants than exciplexes, some emitter dopants can also trap the separated electrons and inhibit charge recombination.

Long persistent luminescence (LPL) materials have applications in glow-in-the-dark paints such as emergency signs and watches. Current highly efficient LPL materials are based on inorganic materials. In contrast, we recently developed a novel LPL emitter composed only of organic molecules (R. Kabe et al., Nature, 550, 384 (2017)). This organic long persistent luminescent (OLPL) system has advantages over inorganic LPL materials of solubility, transparency, and flexibility. The origin of OLPL emission is the charge-transfer transition of an exciplex. The very slow charge recombination of separated carriers results in LPL of over 30 minutes at room temperature.

However, exciplexes have been known to possess low photoluminescence quantum yield (ΦPL) and poor color purity. In organic light-emitting diodes (OLEDs) based on exciplexes, these problems were resolved by adding small amounts of emitter dopants into the exciplex-forming matrix (Y. S. Park et al., J. Appl. Phys., 110, 124519 (2011)). The emitter dopants harvest exciplexes generated by either photoexcitation or charge recombination through Förster energy transfer (FRET). After that, the emitter dopants emit light with improved brightness and color purity relative to the exciplex emission. Here, we apply a similar technique to improve the ΦPL, color purity, and emission duration of OLPL while at the same time tuning the color over a wide range. We adopted the OLPL exciplex systems of 5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) for orange, 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2) for red, and tetraphenyldibenzo[1,2-b:4,5-b']periflanthene (DBP) for deep red. The LPL spectra of the exciplex matrices with the emitter dopants corresponded to the emission spectra of the emitter dopants, ranging from red to greenish-blue. These results indicate that the LPL emission occurs after FRET from the exciplex to the emitter dopants. Furthermore, warm white emission was achieved by doping with two emitters (TBPb and DBP). In addition to improving ΦPL and color purity because of better emission properties of dopants than exciplexes, some emitter dopants can also trap the separated electrons and inhibit charge recombination, thereby also extending the emission duration. For example, a TBRb-doped film exhibited a ΦPL that is 3.5 times higher than that of the exciplex and the longest LPL duration of 1,415 s.

In conclusion, the simple doping of emitters into an exciplex matrix provides an easy method to broadly tune LPL emission and to improve the color purity, ΦPL and emission duration. This technique will enable the development of a wide range of organic glow-in-the-dark paints.

EP05.03.45

PEDOT:PSS Films in Redox-Active Devices

Michel De Keersmaecker1, Augustus W. Lang2, Anna Österholm2 and John R. Reynolds2, 1School of Chemistry and Biochemistry, Center for Organic Photons and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Chemistry and Biochemistry, School of Materials Science and Engineering, Center for Organic Photons and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, Georgia, United States.

We present new designs for fast and reversibly switchable redox-active devices using PEDOT:PSS both as a transparent electrode material and an interface film exploiting its capacitive properties. Thin PEDOT:PSS films have been incorporated in window-type purple-to-transmissive electrochromic devices and symmetric electrodes as part of charge storage devices. We reached a conductivity up to 2000 S cm−1 when post-treating PEDOT:PSS films using different (in)organic acids on different substrates, enough to reversibly switch multiple ECPs made in the Reynolds Group depending on the targeted application. We will demonstrate how the device construction, charge-balancing and electrode conductivity have an influence on the device performance focusing on switching speed and capacitive behavior. We combine our device design with a fundamental study of the mixed electron and ion transport processes occurring in the ECP films at the electrodes looking for links to device performance. Using these new device structures, we have developed an easy way to produce both electrochromic and charge storage devices using solution processable polymers and roll-to-roll compatible coating techniques.

EP05.03.46

Bi-Layer Structure Gate Dielectrics for Low-Voltage Operating Organic Field-Effect Transistors and Printable Flash Memory

Moon Jihoon and Kang-Jun Baeg; Wearable Device, Pukyong National University, Busan, Korea (the Republic of).

Solution-processed pi-conjugated organic semiconductors potentially enable to flexible and stretchable opto-electronic applications via large-area, high-throughput, and low-cost graphic arts printing methods. For development of printed and flexible electronics, organic field-effect transistors (OFETs) and non-volatile memory as well as their integrated circuits are key components and they should be operated under low-power condition. Ultra-low power consumption would be a crucial requirement for determining its applicability for wearable and IoT-based consumer products. Gate-dielectric capacitance and its interface with semiconductor active channel is important to reduce the operation voltage. In this study, we develop the optimized top-gate and bi-layer polymeric gate dielectric structure for high performance ITO-based OFETs, and high-k fluorinated polymers such as PVDF-TrFE-CTFE and PVDF-TrFE-CFE could induce large accumulation of charge carriers at the semiconductor-dielectric interface, these dielectrics adversely affects the performance of N-type OFETs by pushing electrons at the interface and large charge injection barrier due to the high polarity of the C-F bonds. The depletion phenomena could be remarkably improved by incorporation of intermediate polyimine layer and/or appropriate charge injection layer to facilitate electron injection and efficient accumulation at the interface between the PVDF polymers and organic semiconductors. This approach has enabled high-performance, low-voltage driven OFETs and flexible and printed integrated circuits, Moreover, we also applied the same bi-layer structure for non-volatile memory using chargeable gate dielectric (electret) layers.

EP05.03.47

Fabrication of Conducting Bulk Structures Made of Polythiophene Derivatives

Anna I. Hofmann, Renee Kroon, Ida Holm, Anja Lund and Christian Muller; Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden.

One of the main assets of plastic electronics is the possibility to process semiconducting polymers from solution, e.g. via printing, which promises cost-efficient production of light-weight and flexible devices. Thus, most conducting polymers are currently studied in the form of thin-films cast from solution. For applications such as organic thermoelectrics, however, conducting bulk structures are highly sought after. Nevertheless, the fabrication of highly conducting bulk structures remains a major challenge in the field of organic electronics. In this talk, we present different strategies for the bulk processing of doped conjugated polymers and for the doping of polymer bulk structures, using
various types of acid dopants and counter ions, as well as side chain engineering. We demonstrate that hot-pressing of an acid doped polythiophene derivative yields free standing and flexible films with conductivities of up to 120 S cm⁻¹. This opens up a wide range of new possibilities for the fabrication of electronics, from electrochemical devices to thermoelectric modules.

**EP05.03.48**
All Printed Electrolyte-Gated Transistors and Inverters by Spray Coating

Ion gels, consisting of room temperature ionic liquids and a host polymer network, have attracted great attention as solid electrolyte because they possess excellent advantages of ionic liquids such as ionic mobility, specific capacitance, and chemical and electrochemical stabilities in a solid form. In order to employ ion gels in electronic devices, solution processing methods including aerosol-jet printing, spin coating, and transfer printing have been demonstrated. However, alternative processing strategies are desirable to provide a diversity of process methods and to realize low cost production of printed electronics. In this regard, a spray coating technique was applied to fabricate electrolyte-gated transistors and inverters. Not only the ion gel gate dielectric but all thin film layers including source/drain electrodes, a semiconductor, a gate electrode were sprayed in various substrates for flexible and low cost thin film transistors and inverters. All spray-coated transistors exhibited low operation voltages 1 V, low turn on voltage at around 0 V, and reasonably high on/off current ratio about 10⁴ because of the high capacitance of the ion gels. Furthermore, all sprayed inverters operating at low voltages were also fabricated based on the ion gel-gated transistors. These results show that the spray printing technique provides a promising and reliable route to fabricate all printed thin-film transistors and other electrochemical electronic devices.

**EP05.03.49**
Electrical, Thermal and Morphological Properties of Semicrystalline Homopolymer Ion Gels for Solid-State Electrochemical Transistors

Ionic liquids have been received great attention in electrochemical device application due to their outstanding physicochemical properties such as non-volatility, large ionic conductivity and specific capacitance. To provide mechanical strength to the liquid electrolyte, a structure forming polymer is blended with ionic liquid to make solid polymer electrolytes known as ion gels. In this work, we fabricated physically-crosslinked ion gels by using an aliphatic polyanide over the composition 10-50 polymer wt%. The material properties of the resulting ion gels such as surface morphology, thermal stability, mechanical strength, ionic conductivity, and specific capacitance of the resulting ion gels were systematically investigated and the correlation between these parameters was examined. Specifically, fabricated ion gels were thermally stable up to 200 °C, and thus the gels could operate thin-film electrochemical devices such as electrolyte-gated transistors under very high operation temperatures. By using these ion gels as a high capacitance gate dielectric, we could successfully fabricate organic thin-film transistors that operated at low voltage (<1 V) with high on/off current ratio ~10⁴. These results demonstrate that the phase-separation mediated physical ion gels provide a convenient pathway to fabricate highly conductive and mechanically robust solid polymer electrolytes for various solid-state thin-film devices.

**EP05.03.50**
Suppressing the Photo-Induced Degradation of Inverted Non-Fullerene Organic Solar Cells

Over the last years the field of organic photovoltaics made tremendous progress due to the development of new acceptor molecules instead of the common fullerenes. Beyond the enhancement in efficiency to over 14% [1] an increased thermal stability of the bulk hetero junctions is achieved [2]. However, the stability under continuous operation in the maximum power point (MPP) is rarely reported. The vast majority of publications on non-fullerene active layers are utilizing an inverted device architecture with Zinc Oxide (ZnO) as electron extraction layer (EEL). Previous reports on inverted fullerene-based OPV have indicated photo-induced degradation if ZnO EELs are used. This degradation effect has been associated with a loss of selectivity of the illuminated ZnO and the concomitant onset of parasitic recombination of holes at the ZnO/organic interface [3]. In this work we use MPP-tracking to demonstrate that the photo-induced degradation of inverted fullerene-free devices comprising ZnO EELs is substantially more severe than that previously found in fullerene-based devices. Specifically, the PCE of a PBDB-T:ITIC device drops by 60-70% within 30 min of operation in the MPP, while the corresponding PBDB-T:PC70BM only drops by < 40% in the same time scale. The degradation effect applies to various non-fullerene acceptors, such as ITIC [4] or EIC0 [5]. A comparative study of various ZnO layers (atomic layer deposition, nanoparticles, sol-gel) shows the general validity of this effect for all ZnO-based systems. We evidence that the degradation is associated with the UV spectral components of the solar spectrum, it takes place even under inert conditions and is reversible in darkness. We will show that the ZnO/acceptor interface is crucially important for the severity of the degradation effect. We attribute the strong photo-induced degradation in the non-fullerene cells to the relatively higher HOMO level of e.g. ITIC (5.5 eV) compared to PCBM (6.1 eV). Thereby, non-fullerene acceptors have a lower ability to block holes therefore and give rise to substantial parasitic recombination at the interface to the illuminated ZnO EEL. Thereby the UV-induced loss of selectivity of ZnO [3] has significantly stronger negative impact in the non-fullerene devices due to increased recombination with extracted electrons. We will show that the use of a C60 monolayer on top of the ZnO EEL dramatically suppresses the photo-induced degradation. These insights will be important for a serious application of high-efficiency non-fullerene OPV.


**EP05.03.51**
Air-Stable, Balanced Ambipolar Split-Gate Organic Thin-Film Transistors

Ambipolar organic thin-film transistors (OTFTs) have attracted great interest for the development of more compact circuits. Nonetheless, previous studies investigating ambipolar organic semiconductors have reported results measured in either high vacuum or nitrogen atmosphere due to a lack of air stability. To develop a systematic design methodology for air-stable ambipolar organic semiconductors, it is necessary to fundamentally study the dependence of the material/device characteristics on the environmental atmosphere. Here, we demonstrate ambipolar OTFTs with balanced p/n characteristics under ambient air using PNDTI-BT-DP. Based on results from XPS, UPS, and electrical characterizations in high vacuum and ambient air, we analyze the underlying mechanisms that account for the well-balanced p/n characteristics of the PNDTI-BT-DP based OTFTs in ambient air. We
Further demonstrate the air-stable ambipolar split-gate OTFTs that operate as either a unipolar p- or n-type device based on electrical control. Finally, we report results showing that the device characteristics for both p- or n-type operations were maintained in ambient air for ~120 hours.

**EP05.03.52**

**Highly-Aligned Organic Semiconductor Films via Programmed Bar-Coating for High-Performance Organic Transistors**

Soon Baek Lee, Boseok Kang, Seonghyun Kim, Woong Sung and Kilwon Cho; POSTECH, Pohang, Korea (the Republic of).

Organic thin film transistors (OTFTs) have received enormous interest due to their great potential for realizing low-cost, lightweight and flexible electronics that are solution-processed in a large area. Recent researches have mainly been devoted to developing new organic semiconductor materials and novel solution-processing techniques for achieving high performance organic thin film transistors (OTFTs). Spin-coating has been frequently used in a lab scale due to its simplicity, but has fatal drawbacks, such as large amount of material waste, difficulty in scaling up and incompatibility with a conventional roll-to-roll (R2R) system. Several techniques have been developed for the alternative and bar-coating is considered as the promising printing technique for large area uniform coating. Here, we introduced the bar-coating to fabricate highly-aligned small molecule organic semiconductor (2,7-dioctyl-[1]benzothieno-[3,2-b][1]benzothiophene, C$_{60}$TTBT) films. We fabricated the large-area OTFT arrays which exhibit superior charge carrier mobility with high uniformity and reproducibility. The correlation between process conditions and crystal size was observed, and a crystallization mechanism of bar-coated films was identified. Furthermore, we proposed programmed bar-coating technique and fabricated infinitely continuous highly-crystalline films with high uniformity in large-area.

**EP05.03.53**

**Effects of Inserting an Ionic Liquid in Conjugated Polymer**

Beatriz Pesco, Leonardo J. de Siqueira and Laura O. Peres; Federal Univ of Sao Paulo, Diadema, Brazil.

Conjugated polymers are widely studied materials due to their diversity applications. However, its rigidity provides low solubility to the material. One strategy to solve this problem is the insertion flexible groups into the insoluble conjugate material. In this context, the present work presents the synthesis of a block polymer, which is composed of intercalated conjugated and non-conjugated segment, derived from poly(p-phenylene vinylene) (PPV) and poly(ethylene oxide) (PEG), respectively. The material was synthesized and characterized by infrared, UV-Vis and fluorescence. The results showed a better solubility of the block polymer in organic solvent without significant change of its luminescent properties. The ionic liquid ([I]butyltrimethyl ammonium bis(trifluoromethanesulfonyl)imide was incorporated into the polymeric material in proportions of 1:1 and 3:1 (polymer mass ratio:IL). The results obtained by X-ray diffraction show that the polymeric material is crystalline, which is gradually lost/decreased upon the addition of the ionic liquid. It was also observed difference in absorption, emission, DSC and TGA files, showing that there is an interaction between the block polymer material and the ionic liquid, which promoted improvement in the emission intensity and greater thermal stability.

**EP05.03.54**

**Exciton Blocking Layers in Organic Photovoltaic Devices**

Bhushan R. Patil$^1$, Laura Calio$^2$, Mehrad Ahmadpour$^1$, Yiming Liu$^1$, Horst-Günter Rubahn$^1$, Shahzada Ahmad$^2$ and Morten Madsen$^1$; $^1$SDU NanoSYD, University of Southern Denmark, Sonderborg, Denmark; $^2$BC Materials, Basque Center for Materials, Leioa, Spain; $^3$Abengoa Research, Sevilla, Spain.

Exciton blocking layers are essential for efficient organic photovoltaic device operation, where they serve to block excitons at the anode or cathode contact in order to reduce losses in the cells. At the anode side, exciton blocking layers are typically implemented in contact with a hole transporting layer, such as molybdenum oxide (MoO$_3$), where they prevent recombination at the metal oxide interface$^1$. Exciton blocking layers that also transport electrons have at the same time shown to efficiently reduce losses at the cathode contact.

In this work, the use of different organic interlayers integrated as exciton blocking layers in organic photovoltaic cells is presented. The exciton blocking layers are integrated either between MoO$_3$ hole contact layer and the active organic layer, or as cathode contact layers between ITO and the active organic layer. Besides organic solar cell device development and characterization, the integration of the layers is studied through hole-only and electron-only devices, optical spectroscopy analysis and morphology studies, in combination with complete optical and electrical device modeling. From the characterization and modeling, ideal thicknesses of the organic exciton blocking layers are found, based on a delicate interplay between the exciton blocking properties, the series resistance and the exciton generation profiles in the devices$^1$. Significantly improved device performances are observed in small molecule DBP/C$_{60}$ based organic photovoltaic cells when including specific organic interlayers (one of them being 4P-NPD) in combination with MoO$_3$ due to the added exciton blocking properties at the hole contacts. In addition, we evaluate here the effect of different exciton blocking layers on the performance of solar cells with up-scaled device areas. This is specifically area-dependent performance behavior observed in BCP based cathode contact layers, where BCP based exciton blocking and electron transporting stacks are introduced to improve the performance of up-scaled devices$^2$. The work thus addresses the need and challenge of incorporating exciton blocking layers in organic solar cells, and addresses the issue of device scale-up, which is needed for further implementing these layers in industrially relevant organic solar cells modules.


**EP05.03.55**

**Photo-Conductivity and Self-Assembly of Melanin Thin Films on Patterned SiO$_2$/Si Substrate**

Manuel Reali and Jordan De Angelis; Engineering Physics, Polytechnique Montréal, Montréal, Québec, Canada.

Eumelanin is a biomacromolecule featuring fascinating properties such as broadband optical absorption, metal chelation, photoconduction and hydration-dependent electrical response, this last mainly attributable to protonic transport [1-3]. Because of the limited processability, a model describing the correlation between supramolecular aggregation of eumelanin and fundamental optical and electrical properties does not exist yet. Eumelanin is synthesized by the oxidative polymerization of (5,6)-dihydroxindole (DHI) and (5,6)-dihydroxindole 2-carboxyl acid (DHICA) building blocks. Co-existing redox states (hydroquinone, semiquinone, quinone), different polymerization sites and a wide variety of supramolecular arrangements bring physicochemical disorder to the material [4].

Using chemically controlled eumelanin is the key to gain insight into the fundamental aspects of its functional properties. Our group is currently studying the mechanism of solid-state polymerization of DHI and DHICA at surfaces, to achieve thin films suitable for structural, optical and electrical characterizations. APM and FTR investigations on spin coated samples of DHI and DHICA show that the monomers aggregate, eventually polymerizing in ambient conditions. We performed photoconductivity studies on such samples, obtained from spin coating DHICA on gold-patterned SiO$_2$/Si substrates
and on Corning® glass, collecting optical spectra and transient current measurements as a function of relative humidity (%RH). We observed a broad absorption peak at 330 nm, red shifting over time, providing an evidence of solid-state assembly and polymerization, supported by AFM. Nanometer-sized nuclei grew into spherical and rod-shape structures, the size of which is larger for films stored at high %RH with respect to those stored in ambient condition, demonstrating the critical role of H2O in promoting lateral interactions. Our investigations open the opportunity to demonstrate eumelanin-based organic solar cells and, on the long term, organic solar batteries based on the quinone-semiquinone-hydroquinone redox species, where light harvesting could help to enhance the storage properties of eumelanin.

References

EP05.03.56
Half- and Quarter-Wavelength Resonance in Fabry-Pérot Cavity Based OLEDs Ekani Dahal1, Benjamin Isenhart1, Karen Cianciulli2, Bin Du1, Olivia Sergiovanni1 and Matthew S. White1; 1The University of Vermont, Burlington, Vermont, United States; 2Asheville School, Asheville, North Carolina, United States.

Organic light–emitting diodes (OLEDs) have a promising next–generation display and solid–state lighting applications. By forming an optical cavity using the metallic electrodes enclosing the device, we have fabricated various narrow peak emission OLEDs. Varying the thickness of the optical cavity, we observed the interesting change in wavelength peaks. We have used Tris(8–hydroxyquinolinato)aluminium, Alq3, as emissive layer (EL) and added the electron transport layers (ETL) and hole transport layers (HTL) in between the metal electrodes. We observed the optical cavity effect by varying the thickness of the ETL and HTL and keeping the EL fixed. The device with the thinner optical cavity showed a quarter–wavelength resonance as a red wavelength peak whereas increasing the thickness of the cavity shifted the wavelength peak to blue and further increase in the thickness to the green emission peaks as half–wavelength resonance. These narrow–band emission peaks have full width at half maxima (FWHM) of 10 nm, indicating a cavity finesse of roughly 80 when measuring over +/- 9 degrees with respect to normal.

EP05.03.57
Towards a Better Control of Solution-Processed P-Doped Films—Identifying the Impact of Residual Water in Organic Solvents Tamara Domschke1, Alexandre Pereira1, Raphael Clerc2 and Alexandre Carella1; 1CEA-LITEN, Université Grenoble Alpes, Grenoble, France; 2UJM-Saint-Etienne CNRS UMR 5516, Laboratoire Hubert Curien, Université de Lyon, Saint Etienne, France.

Chemical doping allows tuning the electrical and optoelectronic properties of organic semiconductors (OSC) and conductive polymers [1]. However, controlled doping of thin OSC films by solution-processed methods remains challenging [2]–[5]. Here, we explore important processing guidelines to achieve a better control of the doping level in OSC and highlight the unexpected negative impact of residual water in organic solvents. By means of conductivity measurement and optical spectroscopy, this work considers the p-type doping of the low bandgap polymer poly[(4,8-bis-(2-ethylhexyloxy)-benzo(1,2-b:4,5-b')dithiophene)-2,6-diyl) (PBDTTT-c) with the 3D molecular dopant tris[1-(trifluoroethanoyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] (Motf(COF)_3) [6].

First, we report on the strong thickness-dependent conductivity results observed for doped films ranging from 200 nm to 15 nm, where the conductivity decreased from 10^4 S.cm^-1 to 10^2 S.cm^-1, respectively. Also, a clear bleaching of the doping signature is observed in the UV-vis-NIR absorption spectra although EDX mapping presented an homogeneous distribution of the dopant in the film, for all thicknesses. The stirring conditions of the blend solution are identified as key parameters controlling the doping efficiency in thinner films (lower solution concentration). A similar trend was found for PBDDTT-C doped with the planar electron acceptor 7,7,8,8-tetracyano-2,3,5,6-tetratfluoroquinodimethane (F4TCNQ).

In a second part, we correlate the decreasing doping efficiency of lower blend concentrations with the residual water present in the processing solvent. Therefore, our study emphasizes the importance of controlling the water molar fraction of the solvent to achieve reproducible electrical and optoelectronic results for doped films, independent of the blend concentration. As a result, the electrical conductivity of PBDDTT-C doped with Motf(COF)_3 increased from 10^4 S.cm^-1 to 10^6 S.cm^-1 and showed to be reproducible for different blend concentrations.

Finally, we will give insights into the possible mechanism involved in the doping efficiency alteration caused by the presence of residual water in the processing solvent.


EP05.03.58
Design of Conducting-Polymer-Free Highly Flexible Organic Light Emitting Diodes Having Oxide-Based Thin-Film Encapsulation Layers Fangjun Kim, Jeonghyun Kwon, Cheolgyu Kim, Taek-Soo Kim, Kyung Cheol Choi and Seunghyun Yoo; KAIST, Daejeon, Korea (the Republic of)...

Flexible OLEDs require flexible electrodes and thin film encapsulation (TFE) layers. Unfortunately, oxides that limit the flexibility of OLEDs are used to create electrodes and TFE layers that exhibit the best performance. To address this problem, research has been conducted on flexible electrodes and TFE layers that can replace oxides. Nonetheless, oxide-based transparent electrodes such as ITO and IZO are best suited as transparent electrodes for OLEDs due to their high transmittance and electrical conductivity. It is also known that Al2O3 in the oxide-based TFE layer can be formed at a high density and exhibits the best sealing characteristics.

In this study, a very thin PET substrate with a thickness of 6 μm was used to reduce deformation on the device. Among the oxide electrodes, IZO has a process has excellent sealing properties, but the stability against mechanical deformation is very low. In the experiment, the stable folding condition was found by observing the change of sheet resistance and WVTR according to the strain. The results show that the critical strain of Al2O3 is too low to be
bent less than 1 mm. However, considering the overall device structure, the Young's modulus of layers including Al2O3 was much higher than that of the substrate; for this reason, even though the thickness was very thin, it greatly influenced the optical device structure. The neutral plane located at the center of the substrate is displaced due to the effect of the device deposited on the substrate. In general, the thickness of the substrate is very thick, so the influence of the motion of the neutral plane is negligible. However, since the effect is too large to be ignored in our case, the exact strain value can only be obtained by locating the actual neutral plane. Results from ANSYS simulation, the position of the neutral plane in the entire device structure is just below the interface between the substrate and the device. Finally, with a bending radius of 740 μm, the strain applied to the outermost Al2O3 is 0.21%, the safety margin identified by the experiment, and the maximum stress value is lower than that of Al2O3, which is known as 379 MPa.

Consequently, an OLED that operates reliably at a bending radius of curvature of less than 1 mm is realized using an transparent conductive oxide electrode and TFE layer, which are known to be prone to crack formation upon bending. The optimal radius of curvature was established by taking into account the influence of the entire device structure and the limiting deformation of the weaker layer and explained why this could be done using a simulation based on a finite-element method (FEM).

EP05.03.59
Effect of Counterion Exchange of Conjugated Polyelectrolytes in Organic Electrochemical Transistors Brian Kham and Elsa Reichmanis; Georgia Institute of Technology, Atlanta, Georgia, United States.

The palette of mixed ionic-electronic materials for organic electrochemical transistors (OECTs) can be divided into three types: PEDOT-PSS and its derivatives, semiconducting polymers with nonionic polar chains, and conjugated polyelectrolytes (CPEs). To date, the relative amount of literature on CPEs-based OECTs dwindles in comparison to PEDOT-PSS-based devices. We assert that CPEs provide a useful pedagogical system for understanding mechanisms of ionic and electronic transport in OECTs. Through ion-exchange on an anionic polythiophene with a pendant carboxyl group, poly[3-(4-carboxypropyl)thiophene-2,5-diyl] (PCPT), a series of analogues are produced with the same conjugated backbone, only differing in their cations. This procedure clearly elucidates how the choice of counter-ion dictates operation of an accumulation-mode OECT. Firstly, we highlight how these analogues differ in microstructure and phase morphology at various length scales, characterized via optical microscopy and scattering techniques. Secondly, we investigate the photophysical processes of the cast films through ultra-fast spectroscopic methods to understand the effect of counter-ion on charge transport. Lastly, we demonstrate that the counter-ion plays a crucial role in modulating electrolytic ion injection into the polymer film during OECT operation, via cyclic voltammetry and spectroelectrochemistry.

EP05.03.60
Fine-Tuning Polymer Packing and Crystallinity in All-Polymer Solar Cells Through Side-Chain Engineering Yilei Wu and Zhenan Bao; Stanford University, Stanford, California, United States.

Polymer crystallinity and self-assembly behavior play a crucial role in the performance of all-polymer solar cells (all-PSCs). Many aspects of how polymer crystallinity and aggregation influence active-layer morphology and photovoltaic performance, however, remain still elusive. Herein, we report a simple yet effective way to modulate the crystallinity of the well-known naphthalene diimide (NDI) based polymer (N2200), by systematically replacing a certain amount alkyl side-chains with bulky aromatic side-chains. Specifically, we synthesized a series of random polymer with different molar ratio of the two side-chains and found that the crystallinity of these acceptor polymer decreases with increasing amount of bulky aromatic side-chains as evidenced by UV-Vis-NIR absorption and photoluminescence spectroscopies, as well as thermal analysis and grazing incidence x-ray scattering techniques. Importantly, compared to the reference semicrystalline N2200, preliminary OPV results show that mixing of more amorphous acceptor polymers with an amorphous donor polymer (PTB7-Th) enables all-PSCs with increased PCE, on account of higher short-circuit current density ($J_sc$) and fill factor (FF). Our results demonstrate how the polymer crystallinity and packing motives can be systematically tuned by side-chain engineering approach and highlights the importance of polymer structure and morphology on all-PSCs device performance.

EP05.03.61
Electrospun Optical Fibers Composed of a Regenerable Polymer and Approaches for Reducing Their Propagation Losses Yuya Ishii; Faculty of Fiber Science and Engineering, Kyoto Institute of Technology, Kyoto, Japan.

Polymer micro-/sub-microfibers have unique properties including small diameter, light weight, mechanical flexibility, and large surface-area-to-volume ratio. Because such fibers also have inherent waveguide structures, they are promising as building blocks for small, mechanically flexible optical devices such as waveguides and sensors. In this study, we have fabricated electrospun micro-/sub-microfibers composed of a biodegradable and regenerable polymer and investigated their optical propagation losses. Additionally, versatile approaches for reducing the propagation loss and diameters of the fibers have been demonstrated. An amorphous polymer, poly(DL-lactic acid) (PDLLA), was used as the core material because it exhibits high transparency in the visible range and is both biodegradable and regenerable. Single aligned PDLLA fibers with diameters of approximately 1.7 μm were fabricated with an electrospinning method and the intensity of light transmitted in the fibers was investigated with increasing temperature. The transmission intensity significantly increased after heating over the glass transition temperature ($T_g$) of the fibers, 49.8 °C, which indicated that the propagation loss in the fibers decreased after heating over $T_g$. The propagation loss was investigated before/after heating up to 55 °C because this temperature was above $T_g$ of the PDLLA fibers; in addition, the transmitted light intensity showed the maximum intensity at 55 °C. The propagation loss was significantly reduced after heating. For example, the propagation loss in one of the fibers was reduced from 17 to 8.1 dB cm$^{-1}$ under 532-nm illumination. These results demonstrated that heating of the electrospun PDLLA fibers above $T_g$ significantly reduced the propagation loss in the fibers. An ultraviolet-visible absorption measurement and morphological characterization revealed that the propagation loss reduction was achieved by the reduction of extrinsic excess scattering losses arising from the extrinsic density inhomogeneity in the fibers. The as-electrospun PDLLA fibers were then drawn at 55 ± 2 °C to reduce the extrinsic density inhomogeneity and fluctuations in the fiber diameter. After fivefold drawing, the PDLLA fibers showed significant decreases in their fiber diameters to approximately 0.5 μm and reductions in the root-mean-square roughness for each fiber diameter. The propagation loss in each fiber was significantly decreased after thermal drawing; for example, from 16 to 6.6 dB cm$^{-1}$ at 532 nm. Although a decreased fiber diameter normally increases propagation loss in fibers, the propagation loss after thermal drawing was decreased. This was attributed to the reduced fluctuation in the fiber diameter due to thermally drawing and the decreased extrinsic density inhomogeneity in the fibers due to heating.

EP05.03.62
Structure and Electrical Properties of Metal Ion Doped Polydopamine (PDA) Haoqi Li, Yao Zhao and Fei Ren; Mechanical Engineering, Temple University, Philadelphia, Pennsylvania, United States.

Polydopamine (PDA) is a bio-inspired polymer that can be synthesized through self-assembly of dopamine monomers under mild conditions. Thermal treatment can convert PDA into a conductive phase, commonly known as carbonized PDA (cPDA). This work studied the effect of three metal ions, i.e. Na$^+$, Mg$^{2+}$, and Cu$^{2+}$, on the synthesis of PDA and its conversion to cPDA. Both Cu$^{2+}$ and Mg$^{2+}$ could interact with PDA, which influenced the growth of PDA
thin film, morphology change of PDA particles upon thermal annealing, and the electrical properties of heat-treated thin films. In contrast, the presence of Na+ ion during the synthesis of PDA did not show any effect. This difference can be explained by the variation of the three ion species to react with PDA through coordination bonding: Cu2+ > Mg2+ > Na+. In this study, SEM and TEM were used to examine the morphology of PDA thin film and particles. EDS and XPS are employed to study the chemical composition. The structure was investigated using electron diffraction and Raman spectroscopy, and the properties were evaluated with respect to the electrical conductivity and thermoelectric Seebeck coefficient. The results from this work provide a potential approach to control the structure and properties of PDA and cPDA materials through metal ion doping.

**EP05.03.63** Highly Orthogonal Semiconducting Polymers for Solution Tandem Electronics Han Wool Park1, Keun-Yeong Choi2, Haejung Hwang1, Boseok Kang1, Joo Sung Kim1, Hyuk Min Kweon1, Je Hyong Koo1, Kilwon Cho1, BongSoo Kim1, Kwon Bum Chung1, Soon-Ki Kim1, Yun-Hi Kim1, Moon Sung Kang1, Hejin Lee1 and Do Hwan Kim1; 1Hanyang University, Seoul, Korea (the Republic of); 2Soongsil University, Seoul, Korea (the Republic of); 3Pohang University of Science and Technology, Pohang, Korea (the Republic of); 4Gyeongsang National University, Jinju, Korea (the Republic of); 5Ewha Womans University, Seoul, Korea (the Republic of); 6Dongguk University, Seoul, Korea (the Republic of). Polymer electronic devices are receiving great attention because semiconducting polymers are soluble in conventional solvents, which results from being inexpensive in the field of electronics. This opportunity, however, serves as a trade-off when one tries to implement these processes in assembling practical electronic devices, since the as-deposited tandem films would be vulnerable to following solution coating and photolithography processes. We adopted the recently developed sol-gel process to obtain the orthogonality of organic semiconductor against the solvents and chemicals. We could prepare self-assembled structures with quasi-3D random or ladder properties. The resulting structure produced film resistant to severe external stimuli. Moreover, the peculiar topology of organometallic gel network containing with molecular pores could be successfully utilized as a template to form an interpenetrating polymer network (IPN) with functional electronic organic units. As a result, we could demonstrate that sub-micron patterning and forming of tandem structures of OSP films can be done readily through conventional photolithography with sequential solution and etching processes, and finally fabricate tandem electronic devices including basic complementary metal-oxide-semiconductor (CMOS) inverters and pixilated polymer light-emitting diodes (PLEDs). Ultimately, the proposed strategy is expected to open up new avenues for the fabrication of optoelectronic devices that require high-resolution tandem processing of polymer semiconductors such as OLED microdisplays, organic CMOS image sensors, and artificial eyes.

**SESSION EP05.04: Bioelectronic Devices**  
Session Chairs: Gregorio Faria and Jonathan Rivnay  
Tuesday Morning, November 27, 2018  
Hynes, Level 2, Room 208

8:00 AM *EP05.04.01  
Engineering Conjugated Polymers for Bioelectronics Sahika Inal, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Conducting both ionic and electronic charge carriers, conjugated polymers are impacting on a large variety of biology-related applications as the electronic material interfacing with living systems. A device type that has predominantly utilized these polymers as its active component is the organic electrochemical transistor (OECT) – an electrolyte gated transistor used for ionic-to-electronic signal transduction. In this talk, I will show a comprehensive study on the thin film properties of a series of conjugated polymers and evaluate the concomitant performance of electrolyte gated transistors comprising these polymers. We investigate how systematic chemical modifications impact on the electrochemical activity of the materials, thereof the device operation. I will present two cases where engineering the material is crucial to develop an OECT based sensor for metabolites and transducers for interfacing lipid bilayers. Highlighting the materials properties that enable enhanced mixed conduction, this work provides an understanding of materials-device performance relations for the development of next generation organic electronic sensors.

8:30 AM EP05.04.02  
Ion Gated Transistor—A Mixed Ionic-Electronic Transistor Georgios Spyropoulos, Jeremy Savarin, Jennifer Gelinas and Dion Khodagholy; Columbia University, New York, New York, United States.

As our understanding of the brain’s physiology and pathology progresses, increasingly sophisticated technologies are required to advance discoveries in neuroscience and develop more effective approaches to treat brain disease. To meet this challenge, we propose a novel transistor architecture that provides an efficient interface with biological substrates, especially neural networks, through its channel’s intrinsic ion mobility. Because independent electronic gating can be applied to these transistors, they can be incorporated into integrated circuits, unlike their electrolyte-gated counterparts. The channel consists of a composite film based on highly conductive poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) enriched with D-sorbitol. At the gate electrode, an ion exchange membrane serves as ion conductor. To determine an optimal transistor configuration and material composition, we microfabricated transistor arrays of varying geometrical parameters. In doing so, we were able to extract conductivity, contact resistance, and electrochemical impedance values for all the critical interfaces of various composites. Furthermore, output characteristics and current temporal response of each configuration revealed the key driving physical parameters and provided insight into optimization of the device for various applications. The resulting optimal transistors were tested as electroencephalography (EEG) interface and amplifier circuitry and compared with organic electrochemical transistors and surface electrodes showed promising signal-to-noise ratio and spatio-temporal resolution.

8:45 AM *EP05.04.03  
Organic Bioelectronics In Vitro—3D, Biomimetic Devices and Cell Models Roisin Owens; University of Cambridge, Cambridge, United Kingdom.

In vitro models of biological systems are essential for our understanding of biological systems. In many cases where animal models have failed to translate to useful data for human diseases, physiologically relevant in vitro models can bridge the gap. Many difficulties exist in interfacing complex, 3D models with technology adapted for monitoring function. Polymeric electroactive materials and devices can bridge the gap between hard inflexible materials used for physical transducers and soft, compliant biological tissues. An additional advantage of these electronic materials is their flexibility for processing and
fabrication in a wide range of formats. In this presentation, I will discuss our recent progress in adapting conducting polymer devices, including simple electrodes and transistors, to integrate with 3D cell models. We go further, by generating 3D electroactive scaffolds capable of hosting and monitoring cells. I will also highlight recent research using biomimetic models of cell membranes interfaced with organic electronic devices for drug discovery.

### 9:15 AM EP05.04.04

**Highly Efficient Organic Photodiodes Operated in Aqueous Electrolytes**

**Achilleas Savva and Sahika Inal; Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.**

Optical techniques have greatly accelerated advances in modern medicine. Lasers and optical devices are now in wide range use in clinical practice to assess health condition and treat disease.[1] [2] Recently, a new category of light sensitive devices based on organic semiconducting materials has emerged as promising candidates for restoring vision,[2] and recording neuronal activity.[3] In this study, we present an organic photodiode comprised of a solution processed organic semiconductor p-n bilayer junction. Our device, operating in aqueous electrolytes including cell culture media, produces large photocurrents when illuminated with low intensity, broad spectrum light source. We show that in this p-n bilayer junction, which is insulating prior to illumination by light, the photo-generated excitons are rapidly disassociated leading to large photocurrents as well as high ON/OFF ratios in the range of 10^6, respectively. These findings together with an in depth electrochemical analysis suggest a highly efficient photo-capacitive phenomenon at the solid/liquid interface. The devices are freestanding, operate without external wires or electrical bias and show a remarkably stable, continuous operation in aqueous media. This is the first demonstration of an easy-to-fabricate, biocompatible platform, capable of delivering large photocurrents in aqueous electrolytes with potential for direct photostimulation of living cells.


### 9:30 AM EP05.04.05

**Vapor Deposited Conducting Polymers for Electrochemical Energy Storage**

**Trisha I. Andrew; University of Massachusetts Amherst, Cambridge, Massachusetts, United States.**

Lightweight energy storage technologies are integral for powering emerging wearable health monitors and smart garments. Reactive vapor deposition creates films of doped conjugated polymers with tunable mesoporosity, which results in efficient, reversible and thickness-independent ion transport when optimized. Vapor deposited conjugated polymer films are also highly conductive and can act as sole-component electrodes with which to fashion pseudocapacitive charge storage devices. Pseudocapacitors comprised of vapor-deposited doped polymer films display higher areal and volumetric capacitances than solution-processed counterparts, to the extent that energy densities comparable to state-of-the-art carbon materials can be obtained with vapor deposited polymer films. Further, since vapor deposition allows for textured and fragile substrates to be nondestructively coated, various textiles and fibers/yarns can be transformed into high-performance, super-deformable, wearable electrodes, electrochemical transistors and pseudocapacitors. Taken together, reactive vapor deposition and off-the-shelf fabrics present a unique combination of processing technique and device substrate with the potential to create lightweight and portable charge storage solutions.

### 9:45 AM BREAK

### 10:05 AM EP05.05.01

**Polar Side Chains for Enhanced Doping of Conjugated Polymers**

**David Kiefer1, Renee Kroon1, Dominik Stegerer1,4, Liyang Yu1, Alexander Giovanniti1,2,3, Hengda Sun4, Till Biskup4, Anna I. Hofmann4, Martin Koopmans5, Camilla Cendra Guinass4, Michael Sommer6, Lambert Jan Anton Koster7, Eva Olsson8, Jonathan Rivnay9, Simone Fabiano2,10, Iain McCulloch3 and Christian Muller4; 1Chalmers University of Technology, Gothenburg, Sweden; 2Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, London, United Kingdom; 3Department of Chemistry, Technical University of Chemnitz, Chemnitz, Germany; 4King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 5Freiburg University, Freiburg, Germany; 6University of Groningen, Groningen, Netherlands; 7Stanford University, Stanford, California, United States; 8Northwestern University, Evanston, Illinois, United States.**

Molecular doping is a crucial tool for controlling the charge carrier concentration in organic semiconductors for a range of optoelectronic devices such as field-effect transistors, solar cells and thermoelectric generators. We show that doping of both p- and n-type conjugated polymers can be enhanced by exchanging the commonly used unpolar side chains with polar side chains. The use of oligo ethylene glycol side chains with a polythiophene, p(3,4-ET)-T, is demonstrated to significantly improve the compatibility with common molecular p-dopants such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ).[1] The same is shown for n-doping of a polar naphthalenediimide-alkoxybithiophene (DMBI).[2] In both cases a much higher electrical conductivity can be reached using a smaller dopant fraction and hence limited influence on the polymer nanostructure.


### 10:30 AM EP05.05.02

**Stability of Charge Transfer States in Doped P3HT Films**

**Kristen Watts, Bharati Neelamraju, Erin Ratcliff and Jeanne Pemberton; University of Arizona, Tucson, Arizona, United States.**
Poly-(3-hexyl)-thiophene (P3HT) is frequently viewed as a model system for photonic and electronic devices. The molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) is a well-known, p-type dopant for P3HT. The interaction between P3HT and F4TCNQ has been described as an integer charge transfer (ICT) from P3HT to F4TCNQ based on vibrational spectroscopy evidence[2,3], although films are typically significantly thicker than what is used in devices. Recent evidence indicates that the degree of charge transfer is predicated on processing conditions, with demonstration of a partial charge transfer complex (CPX) formed under certain processing conditions, although the exact cause is unclear.[2] To date, the doping state has proven to be challenging to precisely define and control, despite P3HT-F4TCNQ being a model system for doping in organic electronics. Using state-of-the-art capabilities, we provide new insights into the doping mechanism of P3HT-F4TCNQ system using vibrational spectroscopy and imaging (FTIR spectroscopy and Raman microscopy) of device-relevant films. Our new chemical insights will be discussed in the context of electronic states, with a specific focus on the proposed ICT versus CPX states that are being vigorously discussed in the organic electronics community. Results from additional studies on the effects of temperature and substrate on CPX formation will be presented along with results from GIWAXS, conductivity and AFM studies that demonstrate how the presence of the CPX state impacts important film characteristics such as microstructure, charge transport, and morphology.


10:45 AM EP05.05.03
Spectral Signatures and Spatial Coherence of Bound and Unbound Polarons in P3HT Films—Theory vs Experiment Raja Ghosh1, Annabel R. Chew2, Jonathan Onorato3, Viktoria Pahkyryuk4, Christie Lascombe1, Alberto Salleo2 and Frank Spano1; 1Temple University, Philadelphia, Pennsylvania, United States; 2Chemistry, University of Washington, Seattle, Washington, United States; 3Chemistry, University of Washington, Seattle, Washington, United States; 4Chemistry, University of Washington, Seattle, Washington, United States.

The origin of the mid-IR spectral features for hole absorption in doped and undoped P3HT films is investigated theoretically and experimentally. Using a Holstein-style Hamiltonian to treat the prominent vinyl stretching mode, the low-energy peak (A) is found to arise primarily from intrachain transitions, in contrast to the predictions of the more conventional treatments based on self-trapped, mid-gap polarons, where peak A is entirely interchain in origin. Signatures for polaron coherence are identified and used to analyze the molecular weight dependence of the IR spectrum for P3HT doped with F4TCNQ. Generally, the polaron coherence lengths along the chain and stacking axes increase with molecular weight, consistent with similar studies conducted on hole absorption in undoped P3HT. We also show that the spectral changes in bound and unbound polarons corresponds to a polaron coherence number of Ncoh of approximately 4-7 for bound holes and approximately 16-18 for unbound holes.

3. Ghosh, R.; Chew, A.R.; Onorato, J; Pahkyryuk, V; Lascombe, C.K; Salleo, A.; Spano, F. C. Spectral Signatures and Spatial Coherence of Bound and Unbound Polarons in P3HT Films: Theory vs Experiment (Just Accepted, Journal of Physical Chemistry C)

11:00 AM EP05.05.04
Suppression of Dopant Drift in Organic Semiconductors via Blending with Insulating Polymers Marc-Michael Barf1, 2, Leonard Knupnik2, 2, Robert Lovricic1, 2 and Wolfgang Kowalski1, 2, *TU Braunschweig, Braunschweig, Germany; 2InnovationLab, Heidelberg, Germany; 3Heidelberg University, Heidelberg, Germany.

Blending low cost insulators with semiconducting polymers has shown to enhance performance of electronic devices in multiple cases through morphological changes in the active layer.[1,2] Also doping of organic semiconductors is a common method to improve the efficiency of devices like organic light emitting diodes, organic solar cells or organic field effect transistors. By increasing conductivity or creating space charge regions charge transport within such devices can be enhanced.[3-5] However, due to the electrical fields applied to the devices, dopants can potentially move within them and thereby change their electrical properties.[6] Since stability plays a critical role in device operation, such a drift of dopants can cause major problems and is usually desired to be suppressed. Here, polystyrene and poly(methyl methacrylate) (PMMA) were used to shift the onset of the drift of the p-dopant molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)ethene-1,2-diolethene] in poly(3-hexyl-thiophene-2,5-diyli) (P3HT) films to significantly higher applied electrical fields. We investigate the results and resulting images of the doping drift which is attributed to the intercalation of the dopant in the insulator. Both insulators show significantly different thin film morphologies in the blends potentially affecting the dopant distribution. Whereas polystyrene forms very homogenous layers with P3HT, PMMA tends to shape large domains which could hinder the intercalation of dopants. This leads to more dopants remaining in the semiconducting material and thereby to an earlier onset of the observed drift. In compliance with this the dopant drift in the homogenous polystyrene blends was found to be stronger suppressed from an onset of less than 1 V/µm in pure P3HT to more than 3 V/µm in the blend.
suppression of dopant drift adds a further interesting point to the list of improvements in organic electronics through the use of semiconductor insulator blends.


11:15 AM EP05.05.05
Direct Probe of the Nuclear Modes Limiting Charge Mobility in Molecular Semiconductors Adam J. Moule1, Thomas Harrelson1, Varanir Dantaranarayana1, Correy Koskimic1, Diniq Nai1, Enrique Gomez2, John Anthony3, Alessandro Troisi4 and Roland Faller4; 1University of California, Davis, Davis, California, United States; 2The Pennsylvania State University, State College, Pennsylvania, United States; 3University of Kentucky, Lexington, Kentucky, United States; 4University of Liverpool, Liverpool, United Kingdom.

Organic semiconductors (OSCs) provide the unprecedented ability to tailor properties like electronic band gap, mechanical flexibility, processability, and biocompatibility. Recent theories suggest that low frequency dynamic intra- and intermolecular motions are critical to determining localization of the charge carrier, and thus, control the hole mobility. So far, however, it has not been possible to measure intramolecular motions experimentally and therefore no unequivocal and quantitative link exists between molecular-scale thermal disorder and macroscale hole mobility in OSCs. Here we use inelastic neutron scattering (INS) to probe thermal disorder directly by measuring the high resolution phonon spectrum in six different small molecule OSCs. Because of the virtually perfect agreement between the INS spectra and first principle simulations, we can study the coupling between hole and molecular dynamics starting from the exact knowledge of the nuclear motions in each system. This knowledge is used to generate a set of electron-phonon coupling parameters, which are used to compute hole mobility using transient localization theory. We have discovered that in some high performing materials, an important component of the non-local electron phonon coupling is carried by high frequency phonons, unlike what was previously thought. Once this element is properly taken into account the mobility, calculated from first principles, is in excellent quantitative agreement with macroscopic measurements. The analysis of the results reveal routes to improve charge mobility by engineering phonon and electron-phonon coupling.

11:30 AM EP05.05.06
A Tale of Two Crystals—It was the Best Alignment, It was the Worst Alignment Niils E. Persson, Sebastian Engmann, Subhransu Mukherjee, R. J. Kline, Lee Richter and Dean M. DeLongchamp; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Significant advancements in molecular design, crystal engineering, and device fabrication have placed solution-processed polymer transistors on a steady path toward commercialization. Central to these efforts is a growing understanding of semiconducting polymers’ process-property relationships. Polymer aggregation has been proposed to play a critical role in morphological evolution during film drying and in defining long-range structural features that impact charge transport and anisotropy. Here, we report on blade coated OFETs from PNDI2OD-T2 in toluene, an aggregating solvent. We achieved a mobility of 2 cm²/Vs with 10x anisotropy between charge transport parallel and perpendicular to the coating direction, a result on par with previous authors’ OFETs fabricated using the wire bar and brush coating methods. However, blade coating provides a more idealized processing environment amenable to in situ studies, while also serving as a model of production-scale slot die coating. Using simultaneous in situ GIWAXS and split-polarized UV-Vis reflectance measurements, we tracked the structural evolution of PNDI2OD-T2 in toluene during blade coating and film drying. At 5 mm/s, results from GIWAXS indicated that crystalline aggregates were present in the wet film shortly after blade passage and well before drying was complete, and furthermore, that these aggregates maintained their orientation relative to the coating direction throughout the drying process. The UV-Vis spectra did not develop strong anisotropy until the final moments of film drying, when polymer backbones aligned parallel to the coating direction. Taken together, these data suggest that aligned crystal nuclei were deposited that seeded further polymer aggregation and alignment throughout the bulk. Films coated at speeds below 0.1 mm/s displayed practically the opposite trend, with backbones aligning overall perpendicular to the coating direction and with a commensurate change in mobility anisotropy. At this process condition, a surface layer of fibrils arranged in a striking periodic wave-like pattern was observed via AFM. We supplement these results with polarized RSoXS, NEXAFS, and ellipsometry to give a near-comprehensive picture of the remarkable structural diversity in thin films of aggregated PNDI2OD-T2.


11:45 AM EP05.05.07
Excitons and Mobile Carriers in Semiconducting Polymers and Polymer Blends Robert Street; Palo Alto Research Center, Palo Alto, California, United States.

The most obvious features in the optical absorption of semiconducting polymers are excitons, which exhibit disorder-broadened peaks with width 50-100 meV and phonon sidebands arising from electron-phonon interactions. The exciton binding energies are about 0.5 eV. Electronic devices such as solar cells and TFTs, reflect the properties of mobile carriers, either holes or electrons. Carriers in high mobility materials have a relatively small binding energy, often attributable to trapping in band tails. Excitons and mobile carriers are different species with characteristically different properties. For example, despite the fairly narrow exciton absorption bands, band structure calculations find band widths in polymers of order 1 eV. There is no contradiction, since one-electron bands are invariably larger than exciton linewidths and the two are largely unrelated. Band to band transitions are not apparent in polymer optical spectra because the exciton has a large oscillator strength by virtue its localization. A more significant difference between excitons and carriers is in their degree of localization, and one way to observe the difference is in miscible polymer blends. There are several examples where excitons are delocalized such that their wave function extends over several polymers and hence responds to an average alloy composition with an effective band edge that varies smoothly with composition. At the same time the excitons retain the character of the individual polymer because they are more highly localized on a single polymer chain, by virtue of their greater binding energy. Studies of dilute alloys give added information about the carrier delocalization. Modeling of electronic properties needs to recognize the difference. It is common to model the polymer as having narrow Gaussian bands similar in shape to the observed exciton absorption. Instead they should be modeled as lying within the wider bands characteristic of single carriers, and all evidence points to exponential rather than Gaussian disorder-induced band tails.

The central thesis of this talk is that many structural defects in crystalline organic semiconductors have surface potential signatures that can be recorded and imaged by scanning Kelvin probe microscopy (SKPM) with sub-100 nm resolution. This allows straightforward visualization of defects that are difficult to detect by other methods. Additionally, we argue that surface potential fluctuations are a direct measure of static electronic disorder, namely band edge variations, that will impact electron and hole transport. Thus, surface potential imaging not only reveals defects in crystalline organic semiconductors but importantly provides a direct link to electronic disorder (e.g., traps, scattering centers) that degrades transport performance. This talk will focus on three illustrative examples based on thin films and single crystals of benchmark organic semiconductors, including one case where we can make a thorough connection between structure, surface potential, and field effect transport. We propose that in many cases the surface potential contrast associated with a given defect arises due to inhomogeneous strain around the defect. To support this, we further describe the first direct measurements of the strain-surface potential relationship for macroscopic single crystals of rubrene. Overall, we suggest that surface potential measurements are a powerful approach to understanding correlated structural and electronic disorder in soft organic semiconductors.

Analytical electron microscopy (EM) is instrumental for visualizing the nanoscale morphology e.g. of the active layer in organic solar cells [1,2]. At present, transmission EM (TEM) is used, and electron energy loss spectroscopy (EELS) and low energy loss spectroscopic imaging (low-loss ESI) can be applied to generate material contrast in the images. This provides also information about the local electronic properties of the material analyzed. As an example, [2] visualized the mixed material phase in bulk heterojunctions (BHJ) via an increased EELS signal deriving from additional excitonic electronic states in the mixed material phase.

One obvious problem with TEM techniques, however, is the relatively high energy of the imaging electrons, which produces considerable beam damage especially for organic compounds. In addition, the projection character of the formed image leads always to the question, how the finite thickness of the sample may affect the assignment of different materials and material mixes in the projection image. To overcome the above mentioned TEM problems we have investigated a novel, advanced DELTA-SEM [3], which allows electron spectroscopy of secondary electrons (SEs). When lowering electron energies below e.g. 100 eV landing energy, beam damage seems minimized and at the same time the SE signal derives from a very thin surface layer of the sample.

In first experiments the polymer/fullerene BHJ PTB7:PC60BM was studied. At 50 eV landing energy we recorded SE spectra in analogy to ESI imaging used before. These raw spectra have been analyzed using non-liner statistical algorithms and machine learning. In contrast to [2] we this time used unsupervised machine learning, which excludes any additional personal bias. The resulting segmentations of the spectral BHJ images from both, TEM and novel Delta-SEM, were in excellent agreement with the “three phase model” proposed before.

To better understand the contrast mechanism of spectral imaging with the DELTA-SEM we performed additional experiments using a variety of organic semiconductors. Experiments with halogenated Tetraazapropyrrenes (TAPs) show distinct differences in SE spectra for non-conductive vs. semi-conductive TAPs. As described by theory [4,5] the shape of the SE spectra can be directly related to work-function, electron affinity, or bandgap. At present we investigate the possibilities to derive such electronic properties directly from our SE spectroscopic data.

For high-performance semiconductor devices, good ohmic contacts between the electrode and the semiconductor layer are required to enable the maximum current density across the contact. Nominally undoped conjugated polyelectrolytes have employed as charge transport layers in organic devices. They do not have a well-defined workfunction that is sufficiently small or large, nor a sufficiently low electrical resistivity. In this talk, I will discuss the self-compensated doped polymer strategy to overcome some of these challenges. The self-compensated, deliberately charge-doped polymers (polyelectrolytes) can provide the low resistivity and extreme WF needed to make true ohmic injection contacts. These doped polymers are generated by a separate charge-carring polymerization of conjugated polyelectrolytes and compensation by their covalently bonded counter-ion, which enables the use of strong dopants to access extreme workfunction. This strategy also stabilize film from de-doping and suppress dopant migration. We previously demonstrated solution-processed ohmic contacts using these self-compensated doped polymers for high-performance light-emitting diodes, solar cells, photodiodes and transistors, including ohmic injection of both carrier types into polyfluorene. I will further discuss the role of these counter-ion and also the spectator cations in their solution-processability, bulk and interface morphologies in workfunction manipulation. Yet another similar general strategy is using charge-doped polyelectrolyte monolayer assembly to achieve ohmic contact to semiconductor for field-effect transistors. An undoped polyelectrolyte monolayer is self-assembled and self-aligned to the electrode, sacrificial dopant ions are inserted into this layer, which then dopes the organic semiconductor at the contact. When this occurs, the doped interface is counterbalanced by the ‘undoped’ conjugated polyelectrolyte monolayer. Polyelectrolyte counter-ion monolayer cannot diffuse, so delta-doping is stabilized at the contact. This delta-doped layer has a well-defined work function at the semiconductor side of contact and sufficiently low tunnel resistance for direct metal injection into semiconductor, overcoming a critical challenges of using undoped polyelectrolytes.
remarkable ~hundredfold drop in time-of-flight hole mobility (layers using a combination of time-resolved, frequency-resolved, and steady-state transport measurements. We demonstrate that investigate the impact of introducing a planarised conformer, known as the ‘ To this end, we address the chain conformation – hole transport relationship in two model systems. In the case of poly(9,9-dioctylfluorene) (PFO), we conformational defects and observed transport properties. However, until now there has been little experimental evidence of the direct relationship between particular charge transport in organic semiconductors is characterised by a strong degree of disorder in both the site energy and the electronic coupling between adjacent sites. This disorder arises from variations in the chemical structure and conformation of molecular units, as well as in the weak binding interactions between them. Structural disorder due to molecular conformational freedom is expected to affect the density of states distribution, and hence the optoelectronic properties of the material. However, until now there has been little experimental evidence of the direct relationship between particular conformational defects and observed transport properties. To this end, we address the chain conformation – hole transport relationship in two model systems. In the case of poly(9,9-dioctylfluorene) (PFO), we investigate the impact of introducing a planarised conformer, known as the ‘β-phase’ [1], on vertical-mode hole transport through otherwise glassy PFO layers using a combination of time-resolved, frequency-resolved, and steady-state transport measurements. We demonstrate that β-phase introduces a remarkable ~hundredfold drop in time-of-flight hole mobility ($\mu_\beta$) at room temperature, while it reduces $\mu_\alpha$ measured from hole-only devices by a factor of less than 5. We also show how the use of high-dynamic-range photocurrent spectroscopy and energy-resolved electrochemical impedance spectroscopy [2] maps out a consistent picture of trap states due to the β-phase content, namely, a sharp sub-gap feature lying ~0.3 eV above the highest occupied molecular orbital of glassy PFO. Using a drift-diffusion model capable of resolving carriers in both time and energy [3], we show how the apparently contradictory transport phenomena obtained via different probes are explained by a single model with the experimentally derived density of states. We extend our study to a high-mobility indacenodithiophene-based copolymer (IDT–BT) [4] where—in contrast to PFO—the chains favour a planar structure 

Current organic electronics research aims at exploiting the unique property matrix of “plastic” semiconductors, including their chemical tunability, straightforward processability and mechanical flexibility, to create new applications. While much knowledge has been developed in the synthesis of semiconducting conjugated organic materials, there is still an immense need for establishing broadly applicable design guidelines towards highly conductive macromolecular matter. [1,2] Moreover, the multitude of possibilities for “plastic” semiconductors and dopants to assemble together over different length scales creates a daunting task to establish comprehensive and relevant correlations between structure, processing and properties. We will present here a multidisciplinary approach towards a framework to predict such structure/property interrelations. We will focus on polythiophene derivatives as model systems, including poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(2,5-bis(3-tetradecylthieno-2-yl)thieno[3,2-b]thiophene) (PBTTT), [3] and discuss how the spatial arrangement, manipulated through intercalation and co-crystal formation with dopants, affects charge transport. We will conclude with providing a tentative picture of the complex correlation of structure and electronic landscape for the understanding of conducting “plastics” of metallic-type transport.

We review the recent process made to develop quantitative models to predict the intrinsic mobility of molecular semiconductors, leading to the recently proposed "map of molecular semiconductors" [Nature Materials, 16, 998, (2017)]. We then discuss the two main avenues for computer aided materials discovery namely (i) the definition of benchmark accurately-resolved chemical systems and (ii) a rapid method to screen hundreds/thousands of compounds (real or hypothetical). A general approach to converge toward a common accepted theoretical model for charge transport in this class of materials is proposed.

Charge transport in organic semiconductors is characterised by a strong degree of disorder in both the site energy and the electronic coupling between adjacent sites. This disorder arises from variations in the chemical structure and conformation of molecular units, as well as in the weak binding interactions between them. Structural disorder due to molecular conformational freedom is expected to affect the density of states distribution, and hence the optoelectronic properties of the material. However, until now there has been little experimental evidence of the direct relationship between particular conformational defects and observed transport properties.

We extend our study to a high-mobility indacenodithiophene-based copolymer (IDT–BT) [4] where—in contrast to PFO—the chains favour a planar geometry in the ground state and therefore conformational heterogeneities are less likely to act as traps. We use our results on the two polymer types to consider the limits to charge-carrier mobility through disordered polymeric semiconductors, and design criteria for higher performance materials.

Versatile Molecules for Organic Electronics and Photonics

John Anthony, Chad Risko, Oana D. Jurchescu, Anthony J. Petty, Alex Ai and Hamna Haneef
University of Kentucky, Lexington, Kentucky, United States; Wake Forest University, Winston-Salem, North Carolina, United States.

Through combined efforts in theory and synthesis, we have developed ever more detailed understanding of the behavior of organic semiconductors in the solid state. From this knowledge, we have developed modified systems to enhance performance in both electronic and photonic applications. For charge transport, we are addressing issues related to vibrational modes (phonons) that can disrupt electronic coupling in two different ways - by substantially rigidifying the portion of the molecule that attaches solubilizing groups to the core, or by making the core itself more flexible, to better damp these vibrational modes. One of these approaches has already yielded new materials with impressive hole transport properties in transistors. On the photonic front, we have expanded the scope of molecules used in fast singlet fission, improving photostability and allowing attachment of functional groups to better interface with triplet-harvesting materials.

Plastic Semiconductors—How We Can Exploit Blending to Manipulate Functions?
Natalie Stingelin
Georgia Institute of Technology, Atlanta, Georgia, United States.

Artefacts made of polymers – “plastics” – are ubiquitous in our daily live, and polymers such as polyethylene, polypropylene or poly(ethylene terephthalate) have developed into multi-billion markets since their discovery some 80 years ago. Surprisingly, however, various, important aspects of these versatile materials are not understood, especially when used in blends. Processing them into useful products, especially of specific and/or multiple functions, is thus often directed by time-consuming, intricate trial-and-error approaches. The complexity result from the difficulty to characterize polymeric systems: they are of high molecular weight; they lack usually heavy atoms leading to low contrast between components; the feature a low stability, e.g. in electron beams, etc. Here we discuss pathways to gain understanding of the role of multiscale structure and phase behavior in determining the final properties and functions of multicomponent polymer blends, including ion and electron/hole transport (i.e. mixed conduction). Starting with systems where reliable processing pathways towards specific features have already yielded new materials with impressive hole transport properties in transistors. On the photonic front, we will show that combining classical polymer science tools with well-established and recently developed, characterization techniques can be used as examples of discoveries in the last decade that addition of large fractions of an insulating bulk ‘plastics’ such as high-density polyethylene does not negatively affect charge transport of electrons or holes and that addition of the commodity polymer poly(ethylene oxide) allows manipulation of the overall aggregate character of the ubiquitous polymeric semiconductor poly(3-hexylthiophene). Similar observations have been made with higher multifunctional architectures made of ‘plastics’ that can lead to a knowledge platform towards widely-applicable design rules for smart, plastic artefacts.

8:00 AM *EP05.08.01
Polarons, Triions and Polaritons in Semiconducting Polymers and Carbon Nanotubes
Jana Zaumseil
Physical Chemistry, Heidelberg University, Heidelberg, Germany.

The near-infrared emission and absorption properties of semiconducting donor-acceptor polymers and single-walled carbon nanotubes are highly sensitive to the presence of charge carriers that may be induced electrochemically or by a field-effect. New states, here polarons or triions, with unique optical properties are formed and can be tuned, investigated and even utilized in a range of optoelectronics devices such as electrochromic cells, light-emitting transistors and diodes. Furthermore, the hybridization of light and matter in optical microcavities integrated in these devices and thus the formation of polaritons with low mass enables a new approach toward the manipulation of absorption and emission of carbon-based and solution-processed semiconductors. The controlled electrochemical generation of charged triion-polaritons with low effective mass in purified, monochiral single-walled carbon nanotubes may even lead to cavity-enhanced charge transport. Here, we will discuss several examples of (cavity-integrated) devices that rely on polarons, triions or polaritons.

8:30 AM **EP05.08.02
Organic Polariton Photodiodes with an Extended Responsivity
Eldad Eizner, Julien Brodeur, Fábio Barachati, Aravindan Sridharan and Stéphane Kéna-Cohen
Engineering Physics, Polytechnique Montréal, Montreal, Quebec, Canada.

Exciton-polaritons are hybrid light-matter quasiparticles which are formed when molecules are placed within an optical cavity such that their electronic transition can interact strongly with the vacuum electromagnetic (EM) field. In this regime of interaction, the rate of energy transfer between Frenkel molecular excitons and EM modes is faster than their individual uncoupled decay rates. The polariton dispersion relation is separated into upper (UP) and lower (LP) branches with resonance energies that lie on opposite sides of the bare exciton energy. Over the last decade, polaritons have attracted great interest due to their remarkable light-matter properties and have been exploited for novel device applications such as low-power polariton lasers, polariton optical circuits, quantum devices.

In principle, the efficiency and spectral response of an organic photodiode (OPD) is limited by the photophysical and optoelectronic properties of the active layers. In particular, it has been extremely challenging to develop active layers (typically the donor) which absorb light efficiently at near infrared and infrared wavelengths. Therefore, an attractive novel approach to push the donor absorption to the infrared without requiring the synthesis of new materials.
is to strongly couple the excitons with vacuum EM field. Especially, in the ultra-strong coupling (USC) regime, the LP absorption can be red-shifted by a significant fraction of the bare exciton energy while still maintaining a large exciton content.

In this work, we demonstrate for the first time polariton OPDs operating in the USC regime. This is achieved in a standard OPD structure consisting of a mixed donor-acceptor heterojunction with Silver (Ag) electrodes that also act as mirrors to form the optical cavity. We study two types of polaritonic OPDs using donor materials that have previously been widely used for organic photovoltaics. A visible absorber, copper (II) phthalocyanine (CuPc), and a near infrared absorber, tin (II) phthalocyanine (SnPc). These devices show narrow responsivity with a very weak angle-dependence. More importantly, they can be tuned to operate in a spectral range outside that of the bare exciton absorption. Remarkably, we show that the responsivity of a polariton OPD can be pushed to near infrared wavelengths, where few organic absorbers are available, with external quantum efficiencies exceeding those of a control OPD. In the presentation, I will also discuss possible polariton modifications to the molecular photophysics beyond the absorption spectrum, e.g. in charge separation and diffusion.

References


8:45 AM EP05.08.03
Unsymmetric Squaraine for Narrow Band Green-Selective Organic Photodiodes

Hang Guo, Ziang Wang, Kai Huang and Guifang Dong; Chemistry, Tsinghua University, Beijing, China.

Color-selective photodetectors have drawn considerable attention due to their extensive applications in optical communication, chemical/biological sensing, and environmental monitoring. Recently, organic photodiodes (OPDs) are becoming promising candidates for narrowband detection to meet new requirements on detectors which represent a new generation of devices with great potential to be integrated in smart and portable device because of their light weight, biodegradable, and low-cost fabrication on large-area and flexible substrates. Moreover, the materials with different absorption range can be fabricated by changing the substituent group in the organic materials which greatly expand the applications of OPDs. Here, a new narrowband green-light sensitive unsymmetric 2-[3,5-dimethyl-1H-pyrrol-2-yl]-4-diphenylamino] squaraine (UPSQ), with donor-acceptor donor (D-A-D) structure and the applications in photodiodes are reported. We optimize the molecular configuration of the S1 excited state and ground state of UPSQ, at the B3LYP level of the DFT method with the 6-31 g (d) basis set by Gaussian 09. The low total reorganization energy and the small Δ value indicate that the configuration of the S1 excited state is almost the same with that of ground state. Furthermore, the resonance parameter (c^2) of the UPSQ is calculated to be 0.3, indicating that the UPSQ is close to the cyanine limit. As a result, the UPSQ shows the sharp and strong absorption in the solution. Then, the optimum thickness of the PSQ film is calculated to be 55 nm by transfer matrix simulation in the single-layer device. Due to the simple single-layer structure, the device shows excellent color-selective performance. The external quantum efficiency (EQE) of the device in green region (500 nm) reaches 15 % while the EQE in red region is less than 1 %. The device also shows very high current density of ~20 nA/ cm^2 at ~2 V and high detectivity of 3.1× 10^11 Jones. In addition, the device exhibits a narrow band green selective peak at 500 nm with low full width at half-maximum value of 90 nm, which shows the great potential to meet the requirements of applications in optical communications, environmental monitoring and machine vision. In summary, this work demonstrates a new strategy to design the green-light organic materials by changing the substituent group of the D-A-D structure in the squaraine, which can be extended to fabricate the materials with narrow absorption in other wavelength region.

9:00 AM EP05.08.04
Ionic Organic Small Molecules as Hosts for Light-Emitting Electrochemical Cells

Matthew Moore, Melanie Bowler, Yulong Shen, Jason D. Slinker and Jonathan Sessler; 1 The University of Texas at Dallas, Richardson, Texas, United States; 2 Department of Chemistry, The University of Texas at Austin, Austin, Texas, United States.

Light emitting electrochemical cells (LEECS) from ionic transition metal complexes (iTMCs) offer the potential for high efficiency electroluminescence in a simple, single layer device. However, LEECs typically rely on the use of rare metal complexes. This has limited their cost effectiveness and put constraints on their applicability. With a view to leveraging the efficient emission of these complexes while mitigating costs, we describe here a host/guest LEEC strategy that relies on the use of carbazole-based small molecule organic host molecules and iTMC guests. Three positively-charged host molecules were prepared via the coupling of 4-bromophenylbenzimidazole (PBI) with a carbazole (Cz). This has allowed a comparison between hosts bearing methoxy (PBI-CzOMe) and tert-butyl (PBI-CzteBu) substituents, as well as an unsubstituted analogue (PBI-CzH). Cyclic voltammetry and UV-visible absorption revealed that all three host materials have wide bandgaps characterized by reversible oxidation and irreversible reduction events. Based on electronic structure calculations the host HOMO resides primarily on the carbazole moiety while the LUMO is located primarily on the phenyl-benzimidazolium unit. Photoluminescence analysis of thin film blends of PBI-CzH with iTMC guests confirmed that the emission was blue-shifted relative to pristine iTMC films, consistent with what was seen in dilute dichloromethane solution. LEEC devices were prepared based on thin films of the pristine hosts, pristine guest, and 90%/10% (w/w) host/guest blends. Among these host/guest blends, LEEC's based on PBI-CzH displayed the best performance, particularly when an iridium complex was used as the guest. The system in question yielded a luminescence maximum of 624 cd/m^2 at an external quantum efficiency of 3.80%. This result stands in contrast to what is seen with typical OLED host studies, where tert-butyl substitution of the host generally leads to better performance. To rationalize the present observations, the host structures were found to be single crystal X-ray diffraction analysis. The resulting structures revealed clear host-guest interactions in the case of both PBI-CzH and PBI-CzOMe. No such interactions were evident in the case of PBI-CzteBu. Furthermore, PBI-CzH showed a relatively smaller spacing between the successive HOMO and successive LUMO levels relative to PBI-CzOMe and PBI-CzteBu, a finding consistent with more favorable charge transport and energy transfer. The results presented here can help inform the design and preparation of host materials suitable for use in single layer iTMC LEECs.

9:15 AM EP05.08.05
Nano-Alignment in Semiconducting Polymer Films—A Path to Achieve High Current Density and Brightness in Organic Light Emitting Transistors

Mujeeb U. Chaudhry1 and Ebinazar Namdas2; 1 Department of Engineering, Durham University, Durham, United Kingdom; 2 School of Mathematics and Physics, University of Queensland, Brisbane, Queensland, Australia.

The charge carrier mobility in Organic light emitting field effect transistors (OLETs) is a limiting factor in realising high current densities along with a trade-off between brightness and efficiency. In this work we, we present a highly ordered semiconducting polymer films by controlling the nanoscale morphology through nanoscale grooved substrates and dip coating deposition. The OLET device fabricate using these ordered films results in high current densities in OLETs. The heterostructure OLETs demonstrate high brightness, exceeding 29,000 cd m^-2 at an EQE of 0.4% for a yellow emitter and 9,600 cd m^-2 at EQE of 0.7% for a blue emitter. These devices outperform the best OLETs reported in literature. These results represent a significant advancement in organic optoelectronics and are an important milestone towards realization of new applications in displays and electrically pumped lasing.
Singlet-fission (SF) and triplet-triplet-annihilation (TTA) in organic materials at room temperature have recently gained much interest. The increasing focus on SF is due to the promise of increased current density for organic photovoltaics and quantum yields approaching 200% in detector applications, while the interest in TTA is in the promise of organic light emitting diodes (OLEDs) with emission yields beyond the 25% singlet limit and low turn-on voltages. Recent studies have focused on rubrene as possible singlet fission and triplet-triplet annihilation material and devices based on rubrene bilayers with a luminescence threshold of approximately half the bandgap of rubrene have been reported. Two mechanisms have been proposed as the origin of the early turn-on: (i) Auger assisted energy up-conversion, and (ii) triplet-triplet annihilation at the heterojunction interface. In both cases, the charge dynamics at the heterojunction interface are crucial to the mechanism, yet detailed investigations on these higher order processes are missing. Herein, we systematically alter the rubrene/C60 interface in OLED devices, resulting in either greatly suppressed or enhanced formation of the CT state and recombination rate. We find that suppressing the CT-formation yields a 3-fold increase in device lumiance compared to the prototypical rubrene device, while maintaining a low turn-on voltage. The increased lumiance of devices with a BCP interlayer suggests a reduction in parasitic effects of the CT state. Quantitative analysis of the modified interface devices suggest that Auger assisted up-conversion and TTA can be ruled out as the origin of the sub-bandgap turn-on. Rather, band-to-band recombination remains the most likely radiative recombination process.

10:45 AM EP05.08.07
Photoluminescence Quantum Yield Simulation Method for Phosphorescent OLED Emitter Materials Inkoo Kim, Won-Joon Son and Youn-Suk Choi; Samsung Electronics, Suwon, Korea (the Republic of).

High-performance organic light-emitting diode (OLED) devices incorporating phosphorescent emitter materials are undoubtedly one of the most promising candidates for next-generation flat panel and mobile displays, because not only of their superior picture quality showing high contrast ratios and wide color gamut, but also of their efficient power consumption. Cyclometallated complexes as phosphorescent dopants disposed within the emissive layer can effectively harvest both singlet and triplet electrogenerated excitons, leading to internal quantum efficiencies close to 100%. Among many required properties for high performance, photoluminescence quantum yield (PLQY) and radiative lifetime of emitters are the two key photophysical properties of phosphorescent emitters for securing durability and efficiency of the OLED device. The former has been notoriously difficult to simulate computationally as the underlying non-radiative triplet-singlet transition is spin-forbidden and demands the interplay of spin-orbit and non-adiabatic coupling.

In this work, we report a novel formulation for quantitative predictions of PLQY of phosphorescent OLED emitter materials. The present method based on purely first-principle theoretical ground for reliable predictions, incorporating the relativistic and the non-Born-Oppenheimer effects on the same level of generalization in the framework of Fermi’s golden rule using correlation function approach. The accuracy of the present method is assessed and verified by comparing the computed results with the experimental results of various cyclometallated complexes in red-to-green spectral range, respectively, and is substantiated its applicability for the blue-emitters. The results of this work demonstrates that quantitative PLQY predictions of phosphorescent emitters over the entire color range can be delivered solely from quantum chemical calculations, providing additional means of narrowing down the optimal emitters in an a priori fashion in the on-going development of novel phosphorescent emitters for a future OLED device.

10:00 AM BREAK

SESSION EP05.09: Molecular Design for Emission
Session Chairs: Rodrigo Noriega and Garry Rumbles
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 208

10:30 AM *EP05.09.01
Modeling Excitonic Energy Upconversion in Molecule-Nanocrystal Hybrid Devices Troy Van Voorhis; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Photon energy upconversion is a potentially viable strategy for increasing the power conversion efficiency of conventional single junction solar cells. Recently hybrid devices involving colloidal semiconductor quantum dots coupled to molecular chromophores have shown remarkably high upconversion efficiencies. The basic mechanism involves light absorption by the dot, followed by triplet energy transfer to the chromophore with a final step of triplet-triplet annihilation to generate a single, high-energy output photon. Here, we present a holistic approach to simulating the key step of triplet energy transfer. We begin by developing a kinetic model for understanding the transient PL spectra of the devices, which allows us to isolate the triplet transfer rate directly from experimental measurements. Second, we examine the electronic states that participate in the triplet energy transfer step, paying particular attention to surface trap states that likely modulate energy transfer. Finally, we study the dependence of the rate on the ligand shell, showing that unexpected restructuring of the ligand sphere dramatically influences the transfer rate.

11:00 AM EP05.09.02
New Frontiers for Triplet Fusion Upconversion Dan Congreve1, Andrew Pun2 and Luis Campos2; 1Rowland Institute at Harvard, Cambridge, Massachusetts, United States; 2Columbia University, New York, New York, United States.

Upconversion, the process of generating one high energy photon from two low energy ones, holds huge potential across a wide variety of applications. One rapidly emerging process to achieve upconversion is triplet fusion upconversion. This process requires two materials: a sensitizer that absorbs low energy light and transfers it to a triplet annihilator which can convert two triplets into one high energy singlet, which can then fluoresce. Recent materials efforts has led to rapid improvements in efficiency and spectral range, with infrared-to-visible upconversion reaching as far into the infrared as 1000 nm. These strong materials improvements have now opened up a wide range of applications in which this unique process can be applied.

In this talk, I will demonstrate these material improvements and the new fields we can apply them to. First, we utilize a new series of annihilators to precisely tune the upconverted emission to the wavelength needed for a particular application. By pairing these annihilators with photocatalysts, we can perform photochemistry using only NIR light, where visible or blue light would traditionally be required, opening up new avenues for scale-up and drug...
delivery. Finally, we show that by precisely engineering a nano-carrier, we can build these materials into a bio-compatible platform, allowing for new discoveries in optogenetics and bio-imaging that are not hampered by the limited light penetration and high power densities of traditional measurement techniques.

11:15 AM EP05.09.03
Long-Lived Triplet Excitons and Radical Ion Pairs in Organic Semiconducting Host–Guest Systems

**Ryota Kabé**, **Naoto Notsuka**, **Kenichi Goushi**, **Chihaya Adachi**, **JST-ERATO ADACHI Molecular Exciton Engineering Project, Fukuoka, Japan**, **OPER, Kyushu University, Fukuoka, Japan**, **International Institute for Carbon-Neutral Energy Research, Fukuoka, Japan.**

Long persistent phosphors are widely commercialized as glow-in-the-dark paints for watches, indicators, emergency lights, and afterglow safety lamps and are being explored for use in in vivo bioimaging since the emission can be observed long after excitation. Some organic aromatics are known to show long-lived emission called phosphorescence originating from a spin-forbidden transition from the triplet excited state to the single ground state at low temperatures. However, long-lived triplet excitons on organic molecules easily deactivate at room temperature because of the presence of thermally activated nonradiative pathways. We demonstrate long-lived phosphorescence, under both optical and electrical excitation, at room temperature resulting from suppression of the nonradiative deactivation of triplet excitons in conventional organic semiconducting host–guest systems. The nonradiative deactivation pathway strongly depends on the triplet energy gap between the guest emitting molecules and the host matrices, and we show that the triplet energy gap required to effectively confine the long-lived triplet excitons (~0.5 eV) is much larger than that of conventional host–guest systems for phosphorescent emitters (N. Notsuka et al. Adv. Funct. Mater. 27, 1703902 (2017)).

A host–guest system can also produce long-lived emission through efficient stabilization of the radical ion pair generated between an electron donating molecule and electron accepting molecule. A blend of the strong electron-donating molecule N,N,N',N'-tetramethylbenzidine (TMB), which has a very stable radical cation, and the strong electron-accepting molecule 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT), which has a high triplet energy and provides a rigid amorphous environment to help suppress nonradiative deactivation, forms excited-state charge-transfer (CT) complexes (exciplexes) upon weak photo-irradiation. Some of the exciplexes separate into radical ion pairs, and the generated radical cation localizes on TMB while the radical anion diffuses through the PBPO host and is stored for long periods. Gradual charge recombination of radical ion pairs in this system produces continuous emission over 1 h at room temperature. This organic long persistent luminescence (OLPL) system is transparent and soluble, and potentially flexible and color tunable, which will open new applications for LPL in large-area and flexible paints, biomarkers, fabrics, and windows (R. Kabé et al. Nature 550, 384–387 (2017)).

11:30 AM EP05.09.04
Flapping Molecule as a Key Structure for Light-Melt Adhesive and Ratiometric Force Probe

**Shohei Saito**, Kyoto University, Kyoto, Japan.

Flapping molecules (FLAP) bearing a fused 8-membered ring at the center have recently been recognized as an emerging class of photoresponsive systems. The FLAP molecules were reported as key structures that show a V-shaped-to-planar conformational change in the lowest singlet excited state (S1), emitting fluorescence liquid crystals.[3] Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals.[3] light-melt adhesive,[4] molecular viscosity probes,[5] singlet fission chromophores,[6] and conformationally flexible mechanophores.[7] In this presentation, the latest progress of the FLAP-based materials will be introduced, including a liquid crystalline adhesive that melts by light and a ratiometric fluorescent mechanophore for the chemical analysis of polymer stress concentration.

References


11:45 AM EP05.09.05
From Twisted to Planar Thermally Activated Delayed Fluorescence Organic Emitters—Higher Quantum Yield and Sharp Emission

**Ramin Ansari**, **Seong Jun Yoon**, **Jinsang Kim**, **Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Material Science, University of Michigan, Ann Arbor, Michigan, United States; 3Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.**

In the traditional molecular design of thermally activated delayed fluorescence (TADF), molecules are composed of electron-donor and electron-acceptor groups, a common strategy to minimize the singlet-triplet energy gap (ΔEST). However, this strategy enhances geometric changes in molecular conformation, resulting in a small fluorescence oscillator strength, which can significantly decrease the emission quantum yield. Moreover, this strategy also leads to a broad emission spectrum with full-widths at half-maximum (FWHM) of about 70-100 nm. By synergistically combining experiments and simulation, we were able to design novel planar TADF emitting molecules, suppressing molecular conformation changes and achieving higher electroluminescence efficiencies and sharp emissions. The emission spectra of planar and twisted organic molecules has been theoretically studied in the Franck-Condon (FC) framework and using nuclear ensemble (NE) methods. We find that for planar and rigid molecules the emission spectra obtained using FC method are in better agreement with experimental results, while for flexible and twisted molecules emission spectra produced using the NE method are in better agreement with experiments. The effect of using thermal and quantum sampling are also analyzed with the NE approach. Our results can be used to guide future TADF organic molecules and better theoretical investigation of emission properties of planar and twisted organic molecules.
The process on what controls the photogeneration of free charges in organic donor-acceptor films is still not well understood. In this presentation I shall show that the primary step of electron transfer from a photoexcited donor to the acceptor in an organic donor-acceptor type film is not suitable described by Marcus theory, an in particular independent of the driving force.[1] In contrast, the subsequent step of dissociating the thus-formed charge-transfer (CT) state strongly depends on energetics, and is assisted by delocalization. Further, I shall show that a description of the absorption and emission spectra of CT states is not consistent with both Marcus’ electron transfer theory and the original Marcus-Levich-Jortner (MLJ) theory. Instead, the inclusion of disorder effects is crucial for a suitable and consistent description[2]. Both, PL and EQE spectra of CT states can be rationalized in terms of the classic Franck-Condon picture of electronic transitions that couple to intra-molecular vibrations as well as low frequency modes of the donor-acceptor pair that forms the CT state.

References:

2:00 PM EP05.10.02
Quantitative Analysis of Electronic Structures in Organic Planar Heterojunctions and Their Effects on Photovoltaic Properties

Kyohei Nakano1, Weinig Han2, Jianming Huang1, Yujiao Chen1, Hiroyuki Yoshida2 and Keisuke Tajima2; 1RIKEN, Wako, Japan; 2Chiba University, Chiba, Japan.

Electronic properties of an organic donor and acceptor materials have a primary importance for the performance of organic photovoltaics. In practice, however, mixing morphology of the donor and the acceptor in bulk heterojunction has a large impact on photovoltaic properties, which makes it difficult to reveal the relationship between the electronic structures and the charge generation/recombination efficiency.

In this study, we systematically investigated planar heterojunctions with a flat donor/acceptor interface fabricated by contact film transfer method, in which a thin film of donor polymer is transferred onto an acceptor thin film. Before the film transfer, ultraviolet photoemission spectroscopy and low-energy inverse photoemission spectroscopy were conducted to obtain the electronic structures of the surface of each film, which gave the information on the electronic structures of the donor/acceptor interface after making the contact. This allows us to investigate the electronic structures near the D/A interface quantitatively and their effects on the resulting photovoltaic performances without any effects of the morphology. Combinations of four donor polymers and four acceptors (one fullerene derivative and three non-fullerene acceptors) were tested (16 systems in total).

The results clearly showed that the charge generation become more field-dependent as the energetic offsets of the donor and the acceptor decrease. This indicates that the energetic offsets have a large influence on the charge generation efficiency, which appears to oppose to the concept claimed in the recent reports that the charge generation happens through thermalized “cold” charge transfer states. The detailed analysis of this controversial observation will be given in the presentation. In addition, we found the same effects of the energetic structures for non-fullerene acceptors as for the fullerene derivatives except strong light absorption in visible range. Therefore, we concluded that the non-fullerene acceptors are not special in term of the energetic driving force for the charge generation.

2:15 PM EP05.10.03
Thermodynamics of Charge Separation in Organic Solar Cells

Samantha Hood1, Adam Gluchowski2, Katherine Gray2 and Ivan Kassal1; 1Imperial College London, Kensington, United Kingdom; 2The University of Queensland, St Lucia, Queensland, Australia; 3The University of Sydney, Sydney, New South Wales, Australia.

Organic solar cells are promising candidates as a renewable energy source due to the possibility of cheap, lightweight and flexible devices. However, due to their disordered structure, charge behaviour in these devices is not well understood, making it difficult to systematically improve device performance. In particular, a vigorous debate surrounds how the positive and negative electric charges overcome their mutual attraction to form an electric current. While charge separation can occur with near-unity efficiency and on a sub-picosecond timescale, the full details of this process remain unclear. In typical models, the Coulomb binding between the electron and the hole can exceed the thermal energy $k_B T$ by an order of magnitude, making it impossible for the charges to separate before recombining [1, 2].

Here, we consider the entropic contribution to charge separation in the presence of disorder and find that even modest amounts of disorder have a decisive effect, reducing the charge-separation barrier to about $k_B T$ or eliminating it altogether [3]. Therefore, the charges are usually not thermodynamically bound at all and could separate spontaneously if the kinetics otherwise allowed it.

We also investigate the role of charge delocalisation on lowering the Coulomb attraction between charges. Delocalisation has been typically thought to lower the barrier to charge separation by effectively allowing the charges to be further apart. We show that this is not the case: including more than a small amount of delocalisation results in an increase in the barrier to charge separation [4]. This means that if delocalisation were to improve charge separation efficiencies, it would have to do so via non-equilibrium kinetic effects that are not captured by a thermodynamic treatment of the barrier height.

References:

2:30 PM BREAK

3:30 PM EP05.10.04
Determining the Driving Force for Photo-Induced Electron Transfer in Sensitized Organic Materials

Garry Rumbles1, 2, *, 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado, United States; 3Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, Colorado, United States.
This presentation will discuss charge carrier generation and recombination in conjugated polymer and molecular thin films that have been sensitized using molecular electron acceptors at low concentration. Carrier generation is detected using time-resolved microwave conductivity and transient absorption spectroscopy.

A number of fullerene and macrocycle electron acceptors will be discussed, where the driving force for photo-induced electron transfer is controlled primarily by the reduction potential of the acceptors species, and is calculated using the Rehm-Weller equation. The importance the solid-state microstructure of the polymer in controlling the yield and lifetime of the long-lived carriers will be examined, when the primary excitation is an excited singlet-state located on the acceptor. In addition, charge carrier generation in pentacene will be examined, where the triplet excitations are produced from singlet-fission, and a series of electron acceptors capable of dissociating these low energy species is explored.

4:00 PM EP05.10.05
Direct 3D Imaging of the Bulk Heterojunction Microstructure in Organic Solar Cell
Artem Levitsky and Gitti L. Frey; Technion–Israel Institute of Technology, Haifa, Israel.

In the realm of functional materials, properties correlate with internal microstructure. This is true for iron alloys, for example, where the carbon-iron phase diagram determines the abundance of different phases, but their size and distribution, determines the steel’s strength. Similarly, performances of organic electronic devices should correlate with film morphology, i.e. film microstructure. However, identifying the types of phases, domain size, composition and distribution is experimentally because all components are organic and often amorphous. Hence, until now, organic electronic film morphologies were speculated based on indirect and non-comprehensive measurements. Here we show a new approach for directly imaging the microstructure of organic electronic films. This is achieved by selective diffusion and retention of organometallic molecules into different phases. We demonstrate this methodology for correlating the performance of high efficiency organic solar cells with their microstructure. The diffusing molecules are Atomic Layer Deposition (ALD) precursors and their diffusion and in-situ conversion to the respective metal oxide depends on free volume in each domain. Under such conditions, presence of metal oxide particles, easily identified by electron microscopy techniques, effectively maps selected domains in the film. Using this technique, we are able to fully map the BHJ microstructure, i.e. size and distribution of the different phase domains composing the BHJ. We find that the microstructure depends on blend composition and processing technique. Finally, the visual imaging of the BHJ allows us to directly correlate the microstructure with device performance shwoing that the obtained microstructure determines solar cells performance.

4:15 PM EP05.10.06
Relationship Between Charge-Transfer State Properties and Non-Radiative Voltage Losses in Organic Bulk-Heterojunction Solar Cells
Flurin D. Eisner, Mohammed Azzouzi, Zhiping Fei, Martin Heeney and Jenny Nelson; Imperial College London, London, United Kingdom.

The primary pathway to efficiency losses in bulk-heterojunction organic solar cells (BHJ-OSCs) is believed to be the non-radiative decay of a charge-transfer (CT) state to the ground state via energy transfer to vibrational modes. It has been suggested that the open circuit voltage in OSCs is largely determined by the energy of the donor-acceptor CT state, and thus many recent studies have focussed on increasing the energy of CT states by minimizing the energy offset between the donor and acceptor. This relationship can be rationalized by the understanding that a higher overlap of the vibrational modes of the CT and ground states increases the rate of non-radiative recombination. However, some recent studies have found that increasing the CT state energy does not always result in a reduction in the non-radiative voltage losses, which suggests that other properties of the CT state play a role in determining the non-radiative voltage losses.

Here, we systematically investigate the relationship between CT state properties and voltage losses in BHJ-OSCs by using a series of increasingly fluorinated PBDB-T donors, in conjunction with a variety of different fullerene and non-fullerene acceptors. Firstly, we show that by depressing both the HOMO and LUMO through fluorination of the donor, the energy of the donor-acceptor CT state can be effectively moved closer to the first excited state. Secondly, by performing a detailed voltage loss analysis of the various blends we find that the non-radiative voltage losses do not reduce systematically with increasing CT state energies; instead, non-radiative voltage losses are minimised, reaching values as low as 0.22 V, for systems where the CT state and first excited state energies are very close. We suggest that this reduced non-radiative voltage loss results from the hybridization of the CT state with the first excited state and the effect of this hybridisation on the CT state oscillator strength. Using a new model to quantify the non-radiative voltage losses, we simulate the latter observed behaviour through an increase in both the CT state energy and the oscillator strength of the CT state to ground state transition affect the trend.


\[ \text{[3]} M. \text{ Azzouzi, J. Yan, T. Kirchhart, K. Liu, J. \text{Wang, W. \text{Hu, J. Nelson, Submitted 2018.} } \]

4:30 PM EP05.10.07
Photoinduced Charge Generation Dynamics at Heterojunctions Between Semiconducting Single-Walled Carbon Nanotubes and Perylene Diimide Electron Acceptors

Semiconducting single-walled carbon nanotubes (s-SWCNTs) have been intensively studied as the components of various photovoltaic cells due to several advantages such as band gap tunability, high flexibility, chemical robustness, giant aspect ratio, and hydrophobicity. To understand the fundamental aspects of interfacial exciton dissociation and charge recombination at the heterojunction utilizing s-SWCNTs, fullerene-based electron acceptors have been paired with s-SWCNTs in many studies. However, these types of studies have been rare for the heterojunctions of s-SWCNTs and non-fullerene electron acceptors. Studies on interfaces with acceptors with unique molecular geometries and differing extents of aggregation can be useful for understanding how much the molecular geometries/orientations and aggregation influence on the charge generation and recombination processes. In this study, we investigated the detailed photodynamics of the heterojunctions between (6,5) s-SWCNTs and four different perylene diimide (PDI) based electron acceptors. PDI-based electron acceptors have been distinguished as a potential alternative of fullerene-based acceptors by their superior characteristics such as broader absorption, greater spectral tunability, cheaper cost, and higher robustness.

Four novel PDI-based electron acceptors were synthesized and coated on (6,5) s-SWCNT films to form donor-acceptor heterojunctions. These acceptors can be divided into two classes. One is hPDIx-pyr-hPDIx (x = 2, 3; number of PDI units in hPDIx, PDI oligomers), where a central pyrene (electron donor) linker is covalently attached to PDI oligomers, and the other is Trip-hPDIx, where hPDIx is connected to each side of a central triptycene linker. Their molecular structures induce significant intermolecular steric hindrance to reduce excessive aggregation, although the aggregation state appears to
differ amongst the different acceptors. Transient absorption studies reveal that the photoinduced hole/electron transfer at the (6,5) s-SWCNT/PDI-based acceptor heterojunction occurs, and the separated charges can live longer than 1 μs. The charge-separated states at (6,5) s-SWCNTs/hPDIs-pyr-hPDix heterojunctions live longer than those at (6,5) s-SWCNTs/Trip-hPDIs heterojunctions. Differences between exciton dissociation and charge recombination times will be discussed in terms of the differences in thermodynamic driving force and the molecular geometries, the latter affecting aggregation and the concomitant delocalization and entropy available to electrons in the acceptor phase. These physical processes provide the fundamental understanding of how different electron acceptor materials can impact the charge generation processes at s-SWCNT heterojunctions with respect to the heterojunction energetics and molecular orientations. The results can inform the rational design strategies for s-SWCNT-based optoelectronic applications.

**4:45 PM EP05.10.08**

**Nonlinear Impedance Spectroscopy of Organic MIS Capacitors and Planar Heterojunction Diodes**

Matthew S. White¹, Andrew Larsen¹, Ekraj Dalal¹, Justin Palabu¹, Karen Cianciulli², Benjamin Isenhart¹, Michael Arnold¹, Bin Du¹ and Yu Jiang¹; ¹University of Vermont, Burlington, Vermont, United States; ²Asheville School, Asheville, North Carolina, United States.

We present a nonlinear impedance spectroscopy technique and demonstrate its ability to directly measure nonlinear processes including electron-hole recombination and space charge effects in organic-semiconductor-based diodes and MIS capacitors. The method is based on Fourier analysis of the measured higher harmonic current response to an AC voltage signal. Characterization of the higher harmonic response allows nonlinear impedance spectroscopy to measure material and device properties over a wide range of frequencies, which would otherwise be impossible using conventional impedance spectroscopy. As the higher harmonic signals are purely a product of nonlinear processes, they are independent of the linear device capacitance and resistance. This allows space charge and recombination effects to be investigated at several orders of magnitude higher frequency without fitting to an equivalent circuit model.

**8:00 AM *EP05.11.01**

**Management of the Coulomb Interaction in Organic LEDs and Solar Cells**

Richard H. Friend; University of Cambridge, Cambridge, United Kingdom.

The physics of organic semiconductors is often controlled by large electron-hole Coulomb interactions and by large spin exchange energies. I will discuss recent strategies that allow these interactions to be harnessed for efficient device operation. For LEDs, 3:1 statistical formation of triplet:singlet excitons through electron-hole recombination limits efficiency if the triplet state is non-emissive, but is recovered for systems with reduced exchange energy and strong spin-orbit coupling in organo-metallic systems or for systems where triplet-triplet collisions produce singlet excitons efficiently. For organic PV systems, long-range charge separation from the donor-acceptor heterojunction must overcome a substantial Coulomb barrier, which we find always sets up a measurable optical Stark shift that we measure to be 200 meV or more. Whether this separation is ultrafast (sub-picosecond) or slow (>10 psec) depends on the ‘excess’ energy provided by the photogenerated exciton to the separating electron-hole pair, both for fullerene acceptor systems and those with non-fullerene acceptors. Longer time bimolecular recombination should show similar spin statistics to LED operation, causing significant non-radiative recombination for triplet formation where there is easy access to a low-lying localized triplet state. I will present evidence that though fullerene systems generally show rapid bimolecular triplet formation, this can process can be very strongly reduced in some non-fullerene acceptor systems.

**8:30 AM EP05.11.02**

**The Impact of Driving Force on Recombination Dynamics in Nonfullerene Organic Solar Cells**

Yifan Dong⁴, Hyojung Cha¹, Jiangbin Zhang¹, Ernest Pastor⁴, Padhi Srika Tuladhur⁴, Iain McCulloch¹, James R. Durrant¹ and Artem Bakulin¹; ¹Imperial College London, London, United Kingdom; ²University of Cambridge, Cambridge, United Kingdom; ³King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Nonfullerene organic solar cells have demonstrated superior performance compared to the ones with fullerene acceptors. Despite the major world-wide effort in device development and spectroscopic studies, the specific photophysics of nonfullerene acceptor-based materials (NFAs) remains unclear, and it is still not fully understood what controls charge separation and recombination processes. Here, we compare charge carrier dynamics in polymer:acceptor systems using NFA IDTBR and fullerene PC₇₀BM. Transient absorption spectroscopy shows that when blending with P3HT:2OD, IDTBR based blend exhibits enhanced geminate recombination compared to PCBM-based blend. This limits the charge generation and hence the short circuit current in devices.

We also employ pump push photocurrent spectroscopy from 300 K to 77 K to further elucidate the cause of efficiency loss. These measurements reveal presence of bound charge transfer states and long-lived trapped carriers as well as allow the estimation their respective binding energies.

**8:45 AM EP05.11.03**

**Non-Geminate Recombination Limits Fill Factor in Polymer:ITIC Bulk Heterojunction Solar Cells**

Jafar I. Khan, Yuliar Firdaus, Pierre M. Beaujuge and Frédéric Laquié; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

Nonfullerene acceptors have emerged as promising fullerene replacements in organic photovoltaics and recently power conversion efficiencies have surpassed 14 %. Despite the rapid progress, fundamental understanding of the photo-physical processes is still lacking and identifying the loss mechanisms in devices is important for future material design and device optimization. Here, we investigate the impact of polymer side chain substitution in BDT-thiophene copolymers on the performance of three bulk heterojunction solar cells that use ITIC as nonfullerene acceptor: PBDT2HT:ITIC (2.5%), PBDT2HT:ITIC (4.2%) and PBDTT2FT:ITIC (9.8%). All blends absorb across a wide spectral region due to the complementarity of the donor polymer and ITIC acceptor absorption spectra. Transient spectroscopy has been used to monitor exciton generation, diffusion, and dissociation as well as charge carrier recombination in all three systems. We observe significantly more geminate recombination in the alkylx-substituted PBDT2HT:ITIC blend in addition to nongeminate recombination of free charges, limiting both the short circuit current and fill factor. The alkylx-thiophene-substituted PBDT2HT:ITIC blend exhibits less geminate recombination but significant nongeminate recombination, limiting the fill factor to about 40%, while...
backbone fluorination in PBTTT2FT:ITIC leads to fast and efficient charge separation and significantly reduced non-germanite recombination, resulting in fill factors in excess of 60%. Time-delayed collection field measurements showed that charge generation in PBTTT2FT:ITIC is field-independent, while a weak field dependence is observed for the other two systems. Our findings provide important structure-property relations and design rules for new nonfullerene materials.


9:00 AM EP05.11.04
Charge Generation and Recombination in Dilute Organic Solar Cells

Charge generation and recombination processes in low donor concentration organic solar cells as a function of donor percent concentration. We use vacuum deposition techniques to fabricate thin films and full devices with 5 mol.%, 10 mol.% and 50 mol.% donor concentration. The effect of microstructure is investigated by comparing mixed film heterojunctions formed with C60 as electron acceptor, paired with either α-Sexithiophene or 1,1-bis-[4-(4-methyl-phenyl)-amino-phenyl]-cyclohexane (TAPC) as electron donor materials, which individually grow in crystalline and amorphous layers respectively.

In this work we investigate charge generation and recombination processes in low donor concentration organic solar cells as a function of donor percent and microstructure. We use vacuum deposition techniques to fabricate thin films and full devices with 5 mol.%, 10 mol.% and 50 mol.% donor concentration. The effect of microstructure is investigated by comparing mixed film heterojunctions formed with C60 as electron acceptor, paired with either α-Sexithiophene or 1,1-bis-[4-(4-methyl-phenyl)-amino-phenyl]-cyclohexane (TAPC) as electron donor materials, which individually grow in crystalline and amorphous layers respectively.

Electron paramagnetic resonance (EPR) measurements are performed to determine the charge species generated in the active layer upon illumination. In the case of the α-Sexithiophene:C60 system with low donor concentration, EPR measurements reveal the presence of triplet states on C60 and α-Sexithiophene molecules as well as free charges generated at the interface. While free charges and α-Sexithiophene triplets remain present in the high donor concentration system, the C60 triplets are quenched. We will evaluate the effect of the quenched C60 triplet by correlating the information gained through EPR with a photophysical characterization of full devices obtained through current-voltage and external quantum efficiency measurements. Our measurements are further enhanced through X-ray measurements of the microstructure of the films to obtain a full picture of the effects of donor percentage on charge generation and recombination.

9:15 AM EP05.11.05
Terahertz Spectroscopy to Study Charge Carriers in Photoexcited and Doped Organic Semiconductors

While transient absorption (TA) spectroscopy gives information about the population of photogenerated excitons and charges, both the population and short-range mobility of charge carriers determines the photocatalytic activity dynamics in optical-pump-THz-probe (OPTP) measurements. By combining both techniques, the evolution of only the mobility at different times after photoexcitation can be extracted. This is then further substantiated by the mobility and localization parameters obtained from analyzing the real and imaginary parts of the complex photoconductivity spectra at selected time delays with an appropriate model. Here, we have undertaken such a study with pHTTT:PCBM blends having controlled phase morphologies, which are excellent model systems to study the charge carriers in organic photovoltaics (OPVs). We can thus follow changes in the short-range mobility as the charges evolve between different neat and intermixed regions of the blend.

Moreover, we have investigated thin films of a narrow-bandgap conjugated polyelectrolyte, which was shown to become self-doped (conductive) upon dialysis treatment. The doping is directly evident in the absorption spectrum, where a polaron band appears around 1200 nm. Charges are thus present in the ground state and we have investigated their short-range mobility properties using time-domain THz spectroscopy (TDTS, without need of photoexcitation). Those are compared to the carrier properties of photo-generated charges in blends of the corresponding non-ionic polymer backbone with PCBM. We have also carried out TA spectroscopy in solutions and thin films of the doped system, with pumping in either the excitonic or the polaronic band. Surprisingly similar, correlated and very short-lived dynamics were observed. All data was compared to un-doped reference systems and the fluence-dependence was recorded. This brought novel insights to the electronic structure of doped conjugated polymers.

9:45 AM EP05.11.06
Electron-Driven Proton Transfer from Water to a Model Heptazine-Based Molecular Photocatalyst

In the field of photocatalytic hydrogen evolution from water, the conjugated heptazine unit has received significant attention due to intense research interest in 2-dimensional poly(heptazine imides), commonly referred to as carbon nitride or g-C3N4. These conjugated organic materials are readily synthesized from earth abundant materials and act as photocathodes, both absorbing photons and transferring charge to drive the redox process. Despite intense research interest over the past decade, the mechanism of photocatalytic activity remains largely enigmatic. In part due to its structural ambiguity, the activity has been attributed to a variety of processes including free carrier generation, active defect sites, and excitonic interactions at the heptazine core. To avoid this ambiguity, we chose to study 2,5,8-tris-[4-(methoxyphenyl)]-1,3,4,6,7,9b-heptazaazaphenalene (TAHz), an aryl-functionalized heptazine molecule to study the role of the heptazine core. Using time-resolved multichannel photoluminescence (PL) spectroscopy, we kinetically reveal a new emission feature that emerges in aqueous dispersions of TAHz. We attribute this new PL peak to a state with significant intermolecular charge-transfer (CT) character that forms when photoexcited TAHz accepts an electron from hydrogen-bonded H2O. Using global analysis, we spectrally and kinetically resolve overlapping emission features and observe a prompt CT PL decay component exhibiting a kinetic isotope effect of 2.9. We attribute this isotopic dependence to CT quenching by electron-driven proton transfer from water in the TAHz-H2O complex. Radical detection with terephthalic acid confirm hydroxyl radicals form when TAHz is illuminated in water as a result of this photochemical transformation. Our interpretations are consistent with recent theoretical predictions that g-C3N4-based photocatalysts can participate in electron-driven proton transfer with H2O, forming neutral hydrogenated heptazinyl and hydroxyl radicals. This significant finding points towards the possibility of incorporating heptazine-based materials in devices for artificial photosynthesis.
Exciton fission is an energy downconversion process (1 high energy excitation â†' 2 low energy excitations) while exciton fusion is an energy upconversion (2â†’1) process. Both are of practical interest because they provide routes to boost solar energy conversion efficiencies by 30% or more. Organic semiconductors like tetracene and rubrene are uniquely well-suited to perform this energy re-packing because the Frenkel character of the excitons leads to energetically distinct singlet and triplet bands, which can exchange energy via spin-allowed fission and fusion processes. We will describe efforts to understand the photophysical steps involved in singlet fission using time-resolved transient absorption, photoluminescence and magnetic field effects. The roles of molecular packing and crystal morphology in controlling the fission rate will be emphasized. The dynamics of the triplet pair state produced by fission suggest that the triplet excitons may be able to diffuse independently while maintaining spin coherence. For singlet fission, these nonequilibrium spin state distributions can play an important role in both the ultimate triplet yield and the observation of experimental quantities like delayed fluorescence. We will describe time-resolved experiments and Monte Carlo simulations that look at how spin dynamics affect fission and triplet-triplet annihilation. The inverse of singlet fission is triplet-triplet fusion or annihilation, where a pair of triplet excitons fuse into a high-energy singlet state. A new approach to triplet state sensitization involves absorption of low energy photons by semiconductor nanocrystals followed by energy transfer to the molecular triplet states. This approach provides a way to generate large populations of triplets by near-infrared excitation. Interestingly, we also find that upconversion via triplet fusion can occur in certain molecular crystals even in the absence of sensitizers, possibly due to the presence of low-energy intermolecular states.

Singlet fission is the spin allowed process of formation of free triplets from a photo-excited singlet, observed in organic molecules such as pentacene, tetracene, their chemical derivatives, conjugated polymers, perylenes and diimides etc. The dynamics and yield of singlet fission have been understood to be dependent on several factors. To facilitate singlet fission, the energetics of the molecule must be such that the triplet energy lies close to half of singlet energy and this difference in energy was previously thought to be a limiting factor to the efficiency of fission. Prime examples for this were the fast (fs) fission in pentacene, an exothermic system, and slow (ps) fission in tetracene, an endothermic system. However, recently (1,2) it has been shown that singlet fission is fast and efficient in an endothermic system, TIPS- tetracene, where the singlet decays to form vibrationally coherent correlated triplet pair states (TT) under 200 fs, despite the conventional idea that endothermic systems exhibit slow picosecond- timescale singlet fission. In addition to the energetics of the molecules, molecular packing in the solid state is an important parameter as well, since the proximity of molecules to form TT states is crucial to this process.

In this study, we use a series of modified anthracene molecules, with varying endothermicity, to explore the effect of energetics and molecular packing to the dynamics of singlet fission. These molecules are blue-shifted in energy (HOMO-LUMO gap) by approximately 180 meV with respect to the well-studied endothermic tetracene molecule, TIPS- tetracene. Singlet fission in TIPS- tetracene is a two-step process in which singlets decay to form TT states under 200 fs, and in a few nanoseconds, decouple to form free triplets (1). The latter process of decoupling of the TT states to form free triplets has been shown to be temperature independent (3), though it is counter-intuitive that a thermodynamic factor such as endothermicity has no bearing on this step in the process of singlet fission. The strategic chemical modifications on the anthracene derivatives used in this study are utilized to understand the process of decoupling of triplets in more detail as it provides a larger gap to play with on the energetic landscape between singlets and triplets. We use transient absorption spectroscopy, transient photoluminescence (PL) spectroscopy, magnetic field dependent steady state PL, temperature dependent PL among other methods in this work. The scope of this work is to understand long-standing questions related to the fundamental nature of SF, which when incorporated in solar cells can improve the power conversion efficiencies by more than 30% (4).

(1) H. L. Stern et al., Nat. Chem. 9, 1205–1212 (2017)
(2) A. Thampi et al., J. Am. Chem. Soc. 140 (13) 4613-4622 (2018)
Exciton Diffusion Dynamics in Perylene Diimides Mediated by Singlet Fission

Ferdinand C. Grozema and Kevin M. Felter; Delft University of Technology, Delft, Netherlands.

The SF process is proposed as one of the strategies to optimize and surpass the Schockly-Queisser limit for (organic) single junction photovoltaic cells. The SF process involves splitting a photoexcited singlet state (S1) into two distinct triplet excited states (T1+T1). This enables harvesting two charges for only one absorbed photon. The process occurs analogously in quantum dot materials where it is called carrier multiplication (MEG). In order to control the SF process and design better chromophores with higher SF efficiencies and rates, fundamental knowledge is required on the underlying principles. One crucial aspect of SF are the energy requirements and dependence on not only solid state packing, but also of chemical substitution. PDIs are excellent study materials to study the influence of chemical substitution on both solid state packing and the energetics. A variety of SF studies on the rate and efficiency in PDIs has been performed using transient. The favourable electronic coupling and energetics of perylene diimides (PDIs) are known to result in efficient singlet fission and triplet up-conversion. A secondary effect of these processes is its significant effect on exciton diffusion. This research is part of a systematic study to determine the influence of fission and up-conversion on exciton diffusion in PDI derivatives and the effect of temperature.

In order gain information on the singlet fission and exciton diffusion, we first studied planar heterojunctions composed of a smooth TiO2 electron acceptor film and physical vapour deposited PDI using the flash photolysis time resolved microwave photoconductivity technique (FP-TRMC). The photoconductance measurements reveal a dependency of triplet exciton diffusion on the packing of the PDI derivative mediated by singlet fission. Furthermore, as illustrated by the figure below, we observe a strong temperature effect on photoconductivity indicating either enhanced exciton diffusion and/or UC/SF rate enhancement.

Secondly we studied the effect of temperature on the photoluminescence and transient absorption to get direct evidence for a temperature effect on the excitonic species and therefore the singlet fission process. We have determined that the triplet concentration is influenced by temperature as a result from singlet fission. We determined an activation energy for the singlet fission process to occur for a particular type of perylene diimide solid state structure.

We conclude that exciton diffusion and singlet fission in perylene diimide crystals are thermally activated and show a chemical structure dependence on the extent of both singlet fission and exciton diffusion. We determined an exciton diffusive properties as well as a singlet fission rate and activation energy.

11:45 AM EP05.12.05
Singlet Fission and Exciton Dynamics in Amorphous Rubrene
Drew Finton, Elizabeth DeJong, Vincent Zoutenbier and Ivan Biaggio; Physics, Lehigh University, Bethlehem, Pennsylvania, United States.

We used molecular beam deposition in high vacuum to obtain both amorphous and multicrystalline rubrene thin films, and studied how the fluorescence dynamics induced by short pulses varies in samples grown under different conditions. These investigations showed that by this method it is possible to obtain a truly amorphous rubrene film where singlet fission does not occur: in such samples we have observed a single exponential decay of the fluorescence, similar to what is seen for molecules in solution. On the other hand, as the film morphology changes as a function of the deposition condition and nano- or microcrystal regions arise, singlet exciton fission starts being enabled and the dynamics of the short-pulse induced fluorescence shows the typical signs of exciton fission and triplet fission: a fast transient followed by a delayed fluorescence caused by triplet excitation fusion. We discuss the insights that we obtained on the effect of molecular ordering and size of crystalline regions on singlet exciton fission and triplet exciton fusion.

SESSION EP05.13/CM04.10: Joint Session: Singlet Fission/Organic Materials at the Space-Time Limit
Session Chairs: Jenny Clark and Rodrigo Noriega
Thursday Afternoon, November 29, 2018
Hynes, Level 2, Room 208

1:30 PM *EP05.13.01/CM04.10.01
Triplet Energy Transfer Governs the Dissociation of Correlated Triplet Pairs Generated by Singlet Fission
Tia S. Lee1, YunHui L. Lin2, Hwon Kim1, Ryan D. Pensack1, Barry P. Rand2,4, Greg Scholes1 and Kyra Schwarz1; 1Department of Chemistry, Princeton University, Princeton, New Jersey, United States; 2Department of Electrical Engineering, Princeton University, Princeton, New Jersey, United States; 3Micron School of Materials Science & Engineering, Boise State University, Boise, Idaho, United States; 4Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

Singlet fission, a spin-allowed process of spontaneous exciton multiplication, has the potential to enhance the efficiency of photovoltaic devices by utilizing two triplet excitons generated from one singlet exciton. The majority of studies to date have emphasized understanding and optimizing the first step of singlet fission, where the overall singlet intermediate state—the “correlated triplet pair”—is produced from a singlet photoexcitation. Few studies have examined later steps, where the triplet pair may separate and spin correlation may be lost. Here we examine transient absorption of 6,6-bis(triisopropylsilyl)ethyl)pentacene (TIPS-Pn) films at cryogenic temperatures (78–295 K). We evaluate time constants obtained from global analysis and show that their temperature dependence is inconsistent with an exclusively thermally activated process. Instead, we find that the trends can be modeled by a triplet-triplet exciton diffusion process involving simultaneous two-electron exchange. The fitted reorganization energy and electronic coupling agree by a triplet-triplet energy transfer process involving simultaneous two-electron exchange. The fitted reorganization energy and electronic coupling agree.
fission in hexacene is highly exothermic. The significant degree of electronic coupling compounded with large exothermicity gives the possibility of hexacene to undergo singlet fission from one singlet to either yield three triplets or yield two triplets and phonons.

In this hexacene system we find the singlet fission rate of 470fs which is in line with previous studies [3][4]. Such a short time scale of singlet fission allows it to out-compete other relaxation channels, and hence giving it a high efficiency. Comparing with pentacene, the other system with exoergic singlet fission (~100fs fission rate), even though hexacene is more exoergic than pentacene the singlet fission rate is observed to be much slower. The proposed phonon bottleneck effect causing this divergence is experimentally explored through transient absorption spectroscopy, yielding corroborative evidence. By inducing more energy into the system through systematically varying the pump excitation to shorter wavelengths, singlet fission mediated by multiple phonon interactions is directly probed. A prolonged singlet fission rate is observed with higher pump energies. Individual singlet and triplet spectra and kinetics are numerically deconvolved through a genetic algorithm method. Thus, the singlet fission rate and the yield can be correlated with respect to the excess energy present in the singlet fission process. Further evidence of the phonon mediated singlet fission process explored through cryogenic transient absorption and through vibrational coherence studies will be discussed.


2:15 PM EP05.13.03/CM04.10.03
Energetic Driving Force of Singlet Fission in Perylenediimide Thin Films Aaron Le, Sean T. Roberts and Jon A. Bender; University of Texas at Austin, Austin, Texas, United States.

Singlet fission (SF) is a process that can occur in select organic molecules where a singlet exciton splits into two lower energy triplet excitons. While the intersystem crossing of singlets to triplets is typically slow in organic molecules, due to small spin orbit coupling singlet fission does not require a flip in spin and can be exceptionally fast compared to intersystem crossing. The SF process requires two chromophores whose triplet states should be approximately half of the singlet state’s energy to conserve energy. This process has applications in photovoltaics where thermalization of high energy excitations accounts for a major loss channel and limits the maximum performance of such devices. Utilizing materials that undergo efficient SF can potentially mitigate the losses these above band gap excitation experience --- high energy excitations can be down converted into lower energy excitations before thermalization can occur. Perylenediimides (PDIs) are a robust class of dye molecule employed as commercial pigments that contain the proper energetics for SF. These molecules form crystalline domains in the solid state that can be readily tuned by functionalization of the molecules, thereby allowing the structure-function relationship of SF and intermolecular geometry in the solid state to be explored. The intermolecular geometry of SF chromophores has been shown to have a strong connection to the SF rate chromophores that undergo SF. A collection of PDIs with different solid state packing structures were evaluated for potential use as SF chromophores in polycrystalline thin films. Employing a combination of ultrafast femtosecond and nanosecond spectroscopy we identify the formation of triplet state spectral features and identify the SF rates for these materials. Extracted experimental rates deviate from theoretical predictions by approximately three orders of magnitude which may be attributed to differences in energetic landscape of the polycrystalline films and the dimer employed in the calculation. A series of temperature dependent spectroscopic experiments were utilized to examine the energetic requirements of SF in these polycrystalline thin films.

2:30 PM *EP05.13.04/CM04.10.04
Singlet Fission in Synthetic Caroteno-Proteins Jenny Clark, Daniel Polak and Andrew Musser; University of Sheffield, Sheffield, United Kingdom.

Singlet fission is the process whereby one photon creates two triplet excited states. If both triplet states could be harvested by a single-junction solar cell, the solar cell efficiency would increase by up to 1/3. There has been much academic and industrial interest in developing new materials for singlet fission, but to date no material has proved ideal.

Carotenoids are the most widespread of the natural pigments, important for photosynthesis, vision, human health and industry. Work on astaxanthin [1,2] (the pigment which colours lobsters) shows that carotenoids are good candidates for singlet fission sensitizers for solar cells: they have strong absorption and fast (<100fs) singlet fission, independent of energetic driving force. There are hundreds of naturally occurring carotenoids and each of them can form a range of different dimer or aggregate structures (eg H- or J-aggregates).

To determine how carotenoid structure affects singlet fission, and how to exploit carotenoids or other polyene-type systems as singlet fission sensitizes, we use model systems to create identical dimer structures of a range of carotenoids. The model systems are made of synthetic ‘maquette’ proteins that hold the carotenoids in a specific dimer geometry. I will describe details of the photophysics of singlet fission in polyenes, showing that singlet fission is surprisingly robust to changes in conformation and does not depend on either the aggregate or intramolecular structure.


3:00 PM BREAK

3:30 PM *EP05.13.05/CM04.10.05
Functional Imaging of Energy Flow in Materials at the Nanoscale Milan Delor, Hannah Weaver, QinQin Yu and Naomi S. Ginsberg; University of California, Berkeley, Berkeley, California, United States.

The ability of energy carriers to move within and between atoms and molecules underlies virtually all biochemical and material function. Understanding and controlling energy flow, however, requires observing it on ultrasmall and ultrafast spatiotemporal scales, where energetic and structural roadblocks dictate the fate of energy carriers. We therefore developed a universal, non-invasive optical scheme that leverages interferometric scattering to track energy transport in four dimensions of spacetime with few-nanometer precision and directly correlate it to material morphology. We visualize exciton, charge, and heat transport in polycrystalline, silicon and perovskite semiconductors and elucidate, in particular, how grain boundaries impact energy flow through their lateral- and depth-dependent resitivities. We reveal new strategies to interpret energy transport in disordered environments that will direct the design of defect-tolerant materials for the semiconductor industry of tomorrow.
The electronic structure and exciton dynamics of organic molecules can change dramatically upon aggregation. The exciton dynamics of molecules in solution and in thin films of aggregates can be measured using transient absorption spectroscopy, but the exciton dynamics of intermediate aggregation states during thin film formation are typically unknown since measurements cannot be performed quickly enough to collect accurate transient absorption spectra of these species. By increasing the speed of data collection, the exciton dynamics of evolving material systems can be measured. A novel implementation of transient absorption spectroscopy is introduced that can measure transients with up to a 45 ps pump-probe time delay in one shot. The exciton dynamics measured during the solution deposition of a thin film is validated by comparing the initial exciton dynamics of the solution and the final exciton dynamics of the dry film to traditional transient absorption measurements. The exciton dynamics of intermediate aggregation states will be presented for the first time. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for a particular application.

Charge and ion transport of organic semiconductors depends strongly on both molecular structure and morphology. Our fundamental understanding of structure-function relationships has improved greatly in recent years; however, conventional high-resolution structural probes such as x-ray and electron scattering/microscopy are severely restricted by radiation damage and new structural probes are needed. Towards this end, we present initial results from nano-beam diffraction experiments at the Linac Coherent Light Source (LCLS), a source of high-intensity, ultra-short, and coherent hard x-ray pulses from several molecular and polymeric materials. Known as “diffraction-before-destruction”, a single femtosecond x-ray pulses yields useable diffraction images in weakly diffracting and disordered samples before radiation damage can propagate (e.g. sample explosion). This removes the previous limitations of sample damage present in synchrotron and electron microscopy methods. Furthermore, the focused beam (150 nm diameter) is small enough that significant anisotropy in the scattering patterns is observed, yielding insight into polymorphism, strain, and grain-boundaries through statistical analysis of thousands (and eventually millions) of diffraction images. Combined with complementary high-resolution transmission electron microscopy images and atomistic simulations, the results suggest a distribution of packing structures coexist in thin films and that engineering likely packing motifs has the potential to improve both the electronic and ionic transport properties of these materials.
Nematic order, in the bulk or at interfaces, is ubiquitous for semiflexible conjugated polymers. The effect of liquid crystalline order on charge transport, however, remains unclear. Using an analytical model, we show that nematic order leads to an enhancement in charge mobilities when compared to isotropic chains. We also predict a quadratic dependence of the charge mobility on molecular weight of the chains. This is because uniaxially aligned chain backbones lead to rod-like intra-chain trajectories of charge carriers. Analysis of the probability of forming hairpin defects also shows that increasing persistence length can enhance charge transport in conjugated polymers. We speculate that the prevalence of nematic order in conjugated polymers may explain the reported increase in charge mobilities with molecular weight.

Identification of Molecular Orientation in Bulk-Heterojunction Layer by Infrared Reflection Absorption Spectroscopy for Organic Photovoltaic Cells


A bulk heterojunction (BHJ) structure by co-evaporation of organic photovoltaics (OPVs) provides the large donor-acceptor interface, which facilitates efficient charge separation. However, it is difficult to control directly the morphology of co-evaporated BHJ layer because of random blend of donor and acceptor molecules. Many efforts have been made to achieve a control structure of BHJ layer by introducing a new substitute in molecule and combining additive molecules in solution. In our previous work, we reported highly efficient OPV cells by inserting CuI molecular orientation control layer under the zinc phthalocyanine (ZnPc):C60 co-evaporated BHJ layer. It is estimated that higher light absorption coefficient was obtained by controlled ZnPc lying-down molecular orientation due to n-π interaction between ZnPc and CuI. However, information of the ZnPc molecular orientation in ZnPc:C60 film has not been obtained by various measurements, such as XRD, XAFS, and TEM, due to its low crystallinity in ZnPc:C60 film. Hence, we report that the identification of molecular orientation in ZnPc:C60 film by Infrared reflection absorption spectroscopy (IR-RAS), which is enabled to measure the molecular orientation in amorphous film. We succeed in calculating the molecular orientation angle in co-evaporated films on various substrates by IR-RAS.

The CuI (5-nm-thickness)/PEDOT:PSS/ITO substrate (CuI substrate) and ZnPc (20-nm-thickness)/CuI/PEDOT:PSS/ITO substrate (ZnPc substrate) were prepared to investigate the molecular orientation control by π-d interaction and n-π interaction, respectively. On these substrates, ZnPc:C60 co-evaporated BHJ layer was evaporated in the vacuum chamber. IR-RAS measurement was done under in-situ conditions during evaporation of ZnPc:C60 film. The orientation angles of ZnPc molecules calculated by IR-RAS in ZnPc:C60 film on various substrates. Orientation angles of ZnPc molecules in ZnPc:C60 films on PEDOT:PSS (reference), CuI substrate (n-π interaction), and ZnPc substrate (n-π interaction) are 60 degrees, 45 degrees, and 38 degrees at 10 nm or less thickness regions, respectively. These results indicate that n-π interaction between ZnPc and ZnPc molecules is stronger than n-d interaction between ZnPc molecules and CuI in ZnPc:C60 co-evaporated BHJ layer.

Reviewing the Use of Transient Photovoltage Measurements as a Probe of Recombination in Thin-Film Solar Cells

Philip Calado1, Thomas Kirchartz2,3, Piers Barnes1 and Jenny Nelson1; 1Department of Physics and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 2IEK-Photovoltaics, Forschungszentrum Jülich, Jülich, Germany; 3Faculty of Engineering and CENIDE, University of Duisburg-Essen, Duisburg, Germany.

Transient photovoltage (TPV) measurements have been frequently used to study the recombination lifetime of thin-film solar cells. TPV uses the decay of a small optically-induced voltage perturbation to probe the charge dynamics of devices at open circuit. The transient response to a short pulse of light in modelled devices was simulated using a drift diffusion model. Whilst for high mobility systems the lifetime inferred from the simulated TPV measurement matches well with the input lifetime, in cases where charge-carrier mobilities in the active layer are lower than 10^-3 cm^2-V^-1s^-1, the extracted lifetime deviates strongly from the input lifetime value and is highly dependent on mobility. In such low-mobility cases, the simulated charge carrier dynamics show bi-exponential behaviour where the fast decay at early times reflects the recombination of charges in the bulk, while the second, slower decay relates to charges that accumulate near the interfaces. The inhomogeneous spatial distribution of charge carriers in a device at open circuit reduces the recombination rate close to the interfaces, making net recombination dependent on how fast charges can diffuse into the bulk to recombine. As the open-circuit voltage is related to the majority carrier quasi-Fermi levels near the interfaces, its decay is most strongly related to this second slower decay of the charges. Following this observation we developed a new technique to monitor the charge-carrier density during the TPV experiment. We applied this method alongside conventional TPV to measure the recombination dynamics in different systems, including bulk heterojunction comprising of P3HT with both fullerene acceptor (PCBM) and non-fullerene acceptor (O-IDTBR). We observed that while the TPV lifetime of the fullerene and non-fullerene devices were similar in magnitude (7µs and 3µs respectively), the recombination lifetime of the non-fullerene system was significantly faster at 0.1µs compared to 2µs. These findings reconcile the relationship between the fill-factor and the recombination dynamics of the measured devices. By studying the parameters influencing the photovoltage and charge carrier decays, we present a method to estimate the mobility of these devices, and hence estimate the diffusion length of carriers in the active layer.

Electron Accumulation Increases Efficiency Bottleneck for Hydrogen Production in Carbon Nitride Photocatalysts

Wenting Yang1, Robert Godin1, Hatice Kasap2, Benjamin Moss2, Yifan Dong3, Sam J. Hillman1, Ludmilla Steier1, Erwin Reiner2 and James R. Durrant1; 1Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 2Department of Chemistry, Christian Doppler Laboratory for Sustainable SynGas Chemistry, University of Cambridge, Cambridge, United Kingdom.

A deep understanding of the photoinduced charge-transfer dynamics of photocatalysts is a vital pre-requisite for developing efficient and economical devices for water splitting and CO₂ reduction. Graphitic carbon nitrides (g-C₃N₄) are an emerging cheap and efficient photocatalyst for water splitting. However, the photophysical studies of the g-C₃N₄ have, to date, lagged far behind rapid improvements in reported efficiency due to its tendency to aggregate in solution presents a significant technical challenge for measurement. Herein, we report a thorough photophysical and charge-transfer study of a stable dispersion of a cyanamide surface functionalized melon-type carbon nitride (NCN-CN₄), on a timescale ranging over 12 orders of magnitude (from fs to s) using transient absorption spectroscopy. Fluence-dependence studies reveal that the bimolecular reaction of the photogenerated electrons and holes in NCN-CN₄ can be well described by the random walk model developed previously for the metal oxide. Remarkably, the addition of hole scavengers, 4-MBA, into NCN-CN₄ was found to lead to an unprecedented ultrafast decay phase (~ few ps) of the electron signals of the NCN-CN₄, faster than the diffusion limitation of 4-MBA. We show conclusively that this ultrafast decay is not a result of hole extraction by the scavenger. Rather, it is due to the accelerated electron-hole recombination resulting from electron accumulation in NCN-CN₄ (to be around 10¹⁷ to 10¹⁸ cm⁻³ ) after holes have been extracted.
Exciton Binding Energy of Organic Materials—Ground-State vs Excited-State Donor-Acceptor Complexes

Andreas Opitz1, Paul Beyer2, Norbert Koch1,2 and Wolfgang Brütting1,2
1 Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany; 2 IKIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany; 3 Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 4 Institut für Physik, Universität Augsburg, Augsburg, Germany.

Organic semiconductors are materials with a high exciton binding energy (EBE), which significantly impacts their electronic and optical properties. The EBE is the difference between the electronic gap (sometimes referred to as charge transport gap) and the lowest transition energy of photon induced excitation. In recent years, substantial efforts were made to determine the EBE and to relate it to fundamental processes in devices, particularly the exciton dissociation in photovoltaic cells.1

In this contribution, we perform a thin films of pristine organic semiconductor as well as donor-acceptor (DA) complexes upon optical excitation. We compare the transition energies determined from absorption spectroscopy with the transport gaps obtained by direct and inverse photoelectron spectroscopy.

The EBE of pristine diindienoperylene (DIP) is about 150 meV. DIP combined with fullerene as acceptor was studied for photovoltaic cells2,3. The excitation of this DA complex shows an EBE of approx. 70 meV. A comparably low value was determined for the weakly interacting ground-state DA complexes of DIP with a dicyanoperylene-bis(dicarboxyimide) derivative (PDIR-CN2).4 The acceptor hexafluoro-tetracyano-naphthoquinodimethane (F6TCNNQ) forms a strongly interacting ground-state DA complex with DIP. In contrast, this complex reveals an EBE of about 750 meV.

The value of the EBE (DIP:C60 and DIP:PDIR-CN2) being lower than the value of DIP alone is related to the spatial separation of the charges. The hole is confined on the donor molecules and the electron on the acceptor molecule forming a charge-transfer exciton. However, new energy levels are formed for strongly interacting ground-state DA complexes by hybridization of the frontier orbitals of donor and acceptor, like in the case of DIP:F6TCNNQ. Therefore electron and hole are delocalized inside the whole complex, which indicates a Frenkel-like character of the exciton. All this shows, that the nature of the exciton in donor-acceptor complexes is strongly influenced by the ground-state interaction and differs between material combinations used in photovoltaic and doping applications.

Charge transport properties at the interface of organic materials which constitute the intrinsic characteristics of carriers is one of the most fundamental research fronts of organic transistors, particularly organic field-effect transistors (OFETs). Despite of the successful fabrication of bulk organic crystals, it is very challenging to interrogate the interface properties with three-dimensional (3D) organic materials. Therefore high-quality 2D electroactive organic layered materials with highly ordered molecular packing is an ideal platform to conduct this kind of research and development. Here, by utilizing physical vapor transport method (PVT), we produce highly-ordered, large-area and controllably-thick layers of 2D N,N'-ditridecaperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C13) with 10 nm in the maximum thickness. We find that the transport behavior of the single layer (1L) and the bilayer (2L) of PTCDI-C13 is of significant difference. In the 1L device, the transport behavior is predominately attributed to the hopping mechanism, while in the 2L device, the transport characteristics are dominated first by the band-like mechanism, and then by the hopping mechanism as the device temperature is reduced lower than 240 K. Meanwhile, when the layer thickness is increased from 1L to 2L, the carrier mobility anisotropy decreases significantly from 5.0 to 1.5. This marked difference is ascribed to the different steric arrangement of molecules. Our results unambiguously corroborate the intrinsic charge transport properties of electroactive organic layered materials at the interfaces.

**EP05.14.08**

Excitonic Feature of Organic Semiconductor Studied by Electromodulation Spectroscopy

Jin Taill, Hrishheekesh Chandran, Ho-Wa Li and Sai-Wing Tsang, City University of Hong Kong, Hong Kong, China.

In this study, the research is focused on using analytical methodology and optical simulation to compare different organic photovoltaic materials’ electromodulation response. For the first time, it’s discovered that electromodulation signal of high dielectric constant pristine small molecules SubNC, SubPC and a-6T are dominated by 2nd derivative of the material’s absorption coefficient, a behavior which is also reported in lead halide perovskite. It indicates that excitons generated in these materials have strong charge transfer character. While for other materials, including high dielectric constant PCBM, 1st excitonic peak is a mixture of 1st and 2nd derivative feature. Quantitatively, the ratio of polarizability change Δp and dipole moment change Δμ, i.e. Δp:Δμ, is smaller among SubNC, SubPC, a-6T and perovskite than other materials. At the same time, charge generation yield characterized by external quantum efficiency (EQE) is correlated well with Δp:Δμ, the smaller this ratio the higher the EQE value at absorption edge. We conclude that high dielectric constant should not be the only reason for high yield charge generation, but also the property of molecular frontier orbital should be taken into account for designing high charge generation yield material.

**EP05.14.09**

An EPR Insight into Molecular Doping

Alberto Privitera, Ross Warren and Moritz Riede; Department of Physics, University of Oxford, Oxford, United Kingdom.

Over the last decade, molecular doping has been successfully used to precisely control the electronic properties of organic layers that play crucial roles for achieving efficient organic devices such as light-emitting diodes (OLED), solar cells and field-effect transistors.1 Given its success in practical applications, it may be a surprise that fundamental aspects of the molecular doping are still little understood.

Our work aims to provide an insight into molecular doping from a novel point of view using electron paramagnetic resonance (EPR) spectroscopy. Thanks to its high sensitivity and selectivity, EPR allows to directly detect paramagnetic species generated during the doping process, i.e. trap states and free charges (both bearing S=1/2), and to investigate their chemical environment and dynamics.

We carried out our analysis on a model system composed of a layer of ZnPc as host which was p-doped with the acceptor F6TCNNQ (dopant) at different doping volume concentrations from 0% to 5%. The samples were fabricated through thermal evaporation under vacuum which allows a high control over the composition and thickness of the layer. The analysis of the measurements at 80K showed the presence of two different paramagnetic species, a static and a mobile one, distinguished by two different g-tensors. We attributed the static species to trap states and the mobile ones to free charges. At increasing doping concentration, the number and the mobility of free charges increase. Conversely, the trap states show a different behaviour remaining static at all doping concentrations. The same analysis was performed at different temperatures (T=80K - 280K) elucidating the thermally-activated de-trapping mechanism underlying the doping process and shedding light on the dynamics of the species involved. Our results appear well in accordance with the statistical model proposed by Tietze.2 In this model, a pivotal role is played by trap states; only after all traps are filled during the doping process, free charges are generated. The model describes our results regarding the effects of doping concentration and temperature on the equilibrium populations and the dynamics of the two species well.

In addition, we are currently performing a similar analysis using further model systems to test the validity. The overall analysis will provide further details towards a direct and definitive understanding of the molecular doping in organic semiconductors.

**References**


**EP05.14.10**

Diffusion-Limited Delayed Fluorescence as a Signature of Singlet Fission and Triplet Fusion of Correlated Triplets

Kazuhiko T. Seki¹, Yoriko Sonoda¹ and Ryuzi Kato²; ¹National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ²Nihon University, Koriyama, Japan.

The Singlet fission (SF) has attracted a broad interest in the communities of physical chemistry and organic electronics. The SF is a way to improve the quantum efficiency of organic devices by splitting an excited singlet exciton into a pair of long-lived triplet excitons. However, the fundamental processes caused by the SF are not fully understood.

Since the transition from the excited triplet state to the ground singlet state is spin forbidden, deactivation of triplet excitons requires a long-time, allowing them to desorb and migrate over long distances. To date, the effects of diffusion on triplet fusion have been studied mainly for second order reactions where fusion is assumed to occur between any triplet pair regardless of whether they are the same pair generated by singlet fission. We focus on geminate triplet fusion where triplets may undergo diffusion but still recombine with the counter triplet generated by singlet fission; delayed fluorescence originates from diffusion mediated reversible geminate fusion of triplets. We show that occurrence of singlet fission followed by triplet fusion processes can be corroborated by studying the kinetics of delayed fluorescence; if delayed fluorescence decays by a power law with an exponent of 3/2, the delayed component of fluorescence could be attributed to geminate fusion of triplet pairs generated by singlet fission. We have also shown the temperature and the magnetic field effects on the kinetics of delayed fluorescence. By combining the static and kinetic aspects of the magnetic field effects on the fluorescence,
EP05.14.11 Molecular Origin of the Anisotropic Orientation of Molecules in Organic Light Emitting Diodes Pascal Friederich1,2, Vadim Rodin1, Florian von Wrochem1, Reinder Coehoorn1 and Wolfgang Wenzel1; 1Karlsruhe Institute of Technology, Karlsruhe, Germany; 2University of Toronto, Toronto, Ontario, Canada; 3Materials Science Laboratory, Sony Deutschland GmbH, Stuttgart, Germany; 4Eindhoven University of Technology, Eindhoven, Netherlands.

Molecular orientation anisotropy of the emitter molecules used in organic light emitting diodes (OLEDs) can give rise to an enhanced light-outcoupling efficiency, when their transition dipole moments are oriented preferentially parallel to the substrate. A similar effect is observed when the anisotropic orientation of molecules with electrostatic dipole moments leads to the spontaneous buildup of an electrostatic potential perpendicular to the substrate. This spontaneous potential surface potential (GSP) effect can as well be exploited in organic electronics applications. Here, the orientation anisotropy of widely used organic semiconductors is investigated using a simulation approach which mimics the physical vapor deposition process of amorphous thin films. Our simulations reveal for all studied systems significant orientation anisotropy which is in agreement with experimental results for the emitter orientation as well as the GSP effect. We find that the electrostatic interaction between the dipole moments of the molecules limits the orientation strength while short range van der Waals interactions between molecules and the surface during deposition act as driving force for the anisotropic orientation.

EP05.14.12 Optoelectronic Properties of the Interface Between Si and SiC and α-Hexathiophene—A Comparative Study Hannah Schamoni, Oliver Bieneck, Felix Eckmann and Martin Stutzmann; Walter Schottky Institute and Physics Department, Technical University Munich, Garching, Germany.

The combination of organic and inorganic semiconductors is a promising approach towards new materials for applications such as solar cells and light emitting devices, as they open up the possibility to simultaneously benefit from the advantages of both material types. Not least due to the broad variety of organic semiconductors, it is possible to tailor the properties of the heterojunctions in many different ways. In order to identify the most promising hybrid systems, a detailed knowledge about the specific organic/inorganic interface is essential. In this work, selected model systems of different organic and inorganic materials are fabricated and characterized optoelectronically. Via an organic molecular beam deposition (OMBDB) system, thin films of the small molecule α-hexathiophene (6T) are deposited on two inorganic semiconductors, namely hydrogen-terminated silicon (Si) and hydroxyl-terminated silicon carbide (SiC). The resulting hybrid systems are characterized by current-voltage measurements in the dark, under illumination and at different temperatures, and by Kelvin Probe Force Microscopy. Combining the results of all these measurements provides a detailed view of the interfacial optoelectronic properties. In particular, we compare Si substrates of different doping types and doping concentrations to each other and to n-type doped 6H-SiC substrates, which exhibit significantly different current-voltage characteristics. Surprisingly, the potential difference between 6T and Si or SiC amounts to approximately 0.2 eV in all hybrid systems investigated. As this value therefore seems independent of the choice of inorganic semiconductor, it is assumed to originate from an interfacial dipole. Our work of combining different measurement techniques systematically investigates the optoelectronic properties of hybrid systems of 6T and Si or SiC helps to develop a fundamental understanding of organic/inorganic semiconductor interfaces. This will eventually enable the tailoring of hybrid systems to meet the requirements of specific applications.


Thin glassy films of multiple organic semiconductor are found to spontaneously form periodic, highly-aligned surface patterns by a simple annealing process. These grazing-like surface structures are formed as the crystal growth front propagates across the sample by a stress-relaxation-driven wrinkling mechanism, and are aligned laterally along the crystallization front. The wavelength of these patterns can be tuned from 800 nm to 2,400 nm by varying film thickness and annealing temperature, and aligned pattern domain sizes on the millimeter length scale are obtained. Large differences in pattern periodicity are observed for thin films of different materials at a constant thickness, suggesting that a wider range of pattern wavelengths could be accessed by controlling materials properties. The pattern formation mechanism reported here is distinct from previous reports involving stress across a bilayer as wrinkling is associated with crystallization of a single layer, making the technique particularly amenable to device integration. These structures could be used as self-assembled diffraction gratings, distributed feedback cavities for organic lasers, or as scattering layers to enhance outcoupling in organic light-emitting devices.

EP05.14.14 The Research on Molecular Orientation and Characterization of the OLED Emitters Sunyoung Sohn4, Kwang Hun Park3, Hyungu Ahn2, Sungjune Jung3, Soon-Ki Kwon1 and Yun-Hi Kim2; 1Department ofMaterials Engineering and Convergence Technology and ERI, Gyeongsang National University, Jinju, Korea (the Republic of); 2Pohang Accelerator Laboratory, Pohang, Korea (the Republic of); 3Department of Chemistry and Research Institute for Natural Science, Gyeongsang National University, Jinju, Korea (the Republic of); 4Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

We analyzed the scattered X-ray intensities of the host and host-dopant emitters, which have the spectra of in-plane and out-of-plane scattering to the plane and azimuthal intensity profiles for a plot of orientation distribution using grazing incidence wide-angle X-ray diffraction (GI-WAXD) measurement for high-efficiency organic light-emitting diodes (OLEDs). In blue fluorescent emitters, we found that a non-doped anthracene derivatives have the highly rigid structure and thermal stability because p-naphthylxylene groups in 9,10-positions were highly twisted to anthracene core with sterine hindrance of xylene groups. The OLEDs with non-doped emitter with 2,3-diphenyl groups showed high-efficiency of 5.21 cd/A due to enhanced carrier mobility with well-aligned n-stacking structure toward out-of-plane by the face-on orientation by GI-WAXD analysis. In phosphorescent emitters, we have used the tetrahedral silicon-based host materials with electron transporting (ET) property and investigated on the preferential host orientation. The ET hosts had good morphological stability as well as balanced charge-carrier transport by pyridyl-substituted linker in the devices. The Ir(ppy)_3-doped or Fpic-doped devices showed high-efficiency of 53.54 cd/A or 11.08 cd/A, respectively. In thermally activated delayed fluorescence emitters, we found that the molecular orientation of emitting materials with diphenylamine derivative containing malononitrile had different horizontal and/or random orientations as a function of para or meta linker position. It showed 12.5 times difference of the device efficiency. These improved device efficiency was confirmed by the enhanced out-coupling efficiency with well-aligned stacking structure in the emitters with horizontal molecular orientation in in-plane and out-of-plane analysis using GI-WAXD analysis. A study on the relationship between device characteristics and molecular orientation using GI-WAXD analysis for the emitting materials will contribute to basic research on molecular design for high efficiency OLEDs.

This research was supported by the Ministry of Science and ICT (MSIT), Korea, under the “ICT Consilience Creative program” (IITP-2018-2011-1-00783)
supervised by the Institute for Information & communications Technology Promotion (IITP)” and was supported by the National Research Foundation (NRF-2016R1C1B1011745) of Korea grant funded by the Korea government. This research was also supported by the Industrial Strategic Technology Development Program (10097671).

EP05.14.15
Hidden Structure Ordering Along Backbone of Fused-Ring Electron Acceptors Enhanced by Ternary Bulk Heterojunction Yiqun Xiao, MSE, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Fused-ring electron acceptors (FREAs), as a family of non-fullerene acceptors, have achieved tremendous success in pushing the power conversion efficiency of organic solar cells. Here, the detailed molecular packing motifs of two extensively studied FREAs – ITIC and ITIC-Th are reported. It is revealed for the first time the long-range structure ordering along the backbone direction originated from favored end group π-π stacking. The backbone ordering could be significantly enhanced in the ternary film by the mutual mixing of ITIC and ITIC-Th, which gives rise to an improved in-plane electron mobility and better ternary device performance. The backbone ordering might be a common morphological feature of FREAs, providing explanations to previously observed small open circuit voltage loss and superior performance of FREA-based devices and guide the future molecular design of high-performance non-fullerene acceptor.

EP05.14.16

Organic semiconductors have traditionally been regarded as being delicate with respect to degradation in oxygenated/aqueous conditions, especially in the presence of light. We have recently found that, in fact, numerous examples of organic semiconductors exist where these materials support true photocatalytic redox cycles, often with good stability. One general reaction which proceeds efficiently is the photocatalytic reduction of oxygen to hydrogen peroxide. We have found that both n-type, p-type, and ambipolar semiconductors; small molecules and polymers, can generate peroxyde in a wide pH range of 1-12. The p-type materials are additionally suitable for the fabrication of photocathodes, allowing the creation of peroxyde-generating photoelectrochemical cells – something previously impossible with inorganic semiconductors. In our work we have made a number of free-standing photocatalytic and photoelectrochemical platforms to produce peroxyde, and also have discovered the presence of catalytic peroxyde production in the bioorganic semiconductors.

EP05.14.17
Quantum Beats of a Multie exciton State in Rubrene Drew Finton, Eric Wolf, Vincent Zoutenbier and Ivan Biaggio; Physics, Lehigh University, Bethlehem, Pennsylvania, United States.

We have observed quantum beats in the photoluminescence dynamics of the organic molecular crystal rubrene following photoexcitation by a femtosecond pulsed laser. The application of a magnetic field up to 0.3 T, created by a neodymium permanent magnet, produces periodic modulations in the photoluminescence dynamics. The beat frequency ranges between 0.6 GHz to 1.3 GHz and is dependent upon the relative orientation of the magnetic field and the crystalline axes. The amplitude of the beats increases with increasing magnetic field strength, peaking at about 5% of the non-oscillatory background. These beats are indicative of a multie exciton state consisting of a spin-coherent pair of triplet excitons existing during the singlet-to-triplet exciton fission conversion process.

EP05.14.18

Having recently surpassed the 13% threshold, organic photovoltaics (OPV) are once again becoming promising contenders for low-cost solution-processed thin film photovoltaics. The commercialization of large area OPV devices will require, among other things, the capability of coating active layers at high speed in ambient condition without losing fidelity with the champion devices fabricated by spin coating. For a long time, the focus of OPV research was limited to fullerene based acceptor PC$_{61}$BM and PC$_{71}$BM. The fullerene based acceptors have been widely used, but have several limitations, including lower absorption coefficient, and often require a solvent additive for successful processing. In recent years, non-fullerene acceptors (NFAs) have emerged as a new concept to overcome the limitations associated with fullerene based acceptors and have also been shown to yield highly efficient OPV devices without the use of solvent additives. In this work, we used blends of the donor polymer PTB7-Th, more commonly known as PCE10 : PC$_{71}$BM (fullerene based) and PCE10: EH-IDTBR (NFA) as active layer materials. We used spin coating (SC) and wire-bar coating (WBC) to fabricate active layers of the two systems with thickness ranging from 50-300 nm. The best solar cells based on WB coated PTB7-Th:PC$_{71}$BM achieved a PCE of 10.2 % comparable to 10.1% for the best spin-cast device. Devices based on NFAs also showed excellent performance with PCE of 10.8% for WBC vs. 10.6% for SC devices. We also fabricated ternary organic solar cells based on NFAs using PCE10:EHD-IDTBR:EHDIFBR as a photoactive layer and find that the device based on WBC and SC active layer achieved the similar efficiency of 11%. We found that WBC maintained performance parity with SC for active layer thickness <100 nm, but outperformed SC, sometimes significantly, for active layers >100 nm. Systematic comparison of the OPV device figures of merit indicated differences due primarily to the fill factor (FF), pointing to transport-related limitations in thicker solar cells prepared by SC. Indeed, various measurements of carrier transport confirmed the superior carrier mobility achieved in active layers prepared by WBC. Our measurements point to enhancement in the electron mobility as the primary source of the difference. Morphological investigation of the photoactive layers also pointed to enhanced aggregation and coarsening, which we attributed in part to the acceptor domains. Further investigation into the active layer formation kinetics using in situ optical diagnostics reveal the spin-cast ink based on chlorobenzene dried 3-4 times faster than the WBC one. We ascribe the significant differences in electron mobility to the kinetics of solidification and aggregation of acceptor domains. As far as we know, this is the first report where a scalable coating technique outperforms the well-known SC technique, considered for years to be the champion processing method for organic solar cells.

EP05.14.19
Tuning of Organic Thin-Film Microstructure Using Graphene as a Growth Template Jacob G. Kiiholesh, Ole Albrektsen, Martin A. Hedegaard and Jakob Kjeldstrup-Hansen; 1Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark; 2Department of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Odense, Denmark.

Photodetectors made from organic semiconductors is an area of great interest since these materials can be tailored through chemical synthesis techniques and processed as thin-films over large areas at low cost. However, a remaining challenge is the low carrier mobility that makes these materials less suitable for high bandwidth-applications. A possible solution is to combine an organic semiconductor with a graphene layer with superior transport properties,
which could form the basis for improved photodetector devices. This requires the ability to control the organic thin-film microstructure, which strongly influences both the optical absorption and the exciton diffusion processes. In this work, we study the growth of the organic semiconductor 5,5''-bis(naphth-2-yl)-2,2':5',2''-terthiophene (NaT3) by investigating the influence of the growth substrate (graphene vs. SiO2) and of the substrate temperature. The resulting thin-films are characterized by atomic force microscopy, x-ray diffraction, and fluorescence spectroscopy. On SiO2, the NaT3 molecules form a polycrystalline film with grains consisting of upright-standing molecules that form distinct terraces and with an average grain size that depends on substrate temperature. In contrast, we observe a significantly different morphology of the thin-film when deposited on graphene. Here, the NaT3 molecules form smaller grains with no observable terraces and with different molecular orientations. At high substrate temperature, a discontinuous thin-film is observed where the molecules assemble into elongated nanofiber morphologies. This gives rise to significantly different optical properties. The NaT3 thin-films on graphene exhibit a much stronger fluorescence signal than the similar thin-films on SiO2, while the NaT3 nanofiber structures emit polarized fluorescence.

EP05.14.20 How Can We Engineer Hierarchical Structures and Pattern Functional Organic Materials? Shengyang Chen1, Bastian Haehnle1, Alexander J. Kuehne2, Ioan Botiz1, Paul Stavrinou1 and Natalie Singelin1, 2, 3, 4
1Department of Materials, Imperial College London, London, United Kingdom; 2School of Materials Science and Engineering and School of Chemical and Biochemical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 3Department of Engineering Science, University of Oxford, Oxford, United Kingdom; 4Nanobiophotonics and Laser Microscopy Centre, Interdisciplinary Research Institute in Bio-Nano-Sciences, Babes-Bolyai University, Cluj-Napoca, Romania; 5DWI–Leibniz Institute for Interactive Materials, RWTH Aachen University, Aachen, Germany.

Organic materials continue to make an impact on a wide variety of optoelectronic applications due to an ever-increasing chemical design space, novel tools to assemble these interesting materials, and the advancement of novel device architectures and devices. One important aspect thereby is how to achieve assembly not only on the molecular- and on the meso- scale, but also on the hundreds of nanometer to micrometer scale. Various devices and applications, indeed, require the active material to be patterned and/or to be deposited at pre-determined locations. In areas, such as the bioelectronics field, step-changes may arise when more complex, multidimensional architectures that mimic the hierarchical structures of, e.g., tissues or bones could be man-made using stimuli-responsive functional organic materials. Other potential lies in nano- and micro-engineering multifaceted structures to realize new media with unique interactions with electromagnetic radiation. This would lead to new possibilities to harvest light and manipulate light-matter interactions. Here we use model systems to demonstrate hierarchical assembly of organic nanoparticles, covering a range of systems, from inert polystyrene particles to conjugated polymer emitter particles made, e.g., of polyfluorene-co-divinylbenzene (PF-co-DVB)[1]. We show that surface relief structures can be used to direct this process. Thereby, simple geometrical relationships can be employed to program the particles to deposit into specific sites and patterns: from ordered to disordered arrangements; hexagonally-packed, cubic-packed or random-packed structures; to single layer vs. multilayer architectures. This opens a versatile design platform in terms of the fabrication of multifunctional nano- and microstructures with hierarchies for use in the field of photonics (e.g., in solar cells, light-emitting diodes and optical display devices over large areas), bioelectronics and beyond.


Organic semiconductors, such as conjugated polymers, have attracted great interest as candidate materials for solar cells, light-emitting diodes and other photonic applications. The performance of such devices depends upon many properties of the materials, including the spectral range and strength of the optical absorption. Several studies have shown that changes in molecular packing and conformation within in a polymer film can influence the absorption strength. Widely used electronic structure methods such as time-dependent density functional theory cannot access the length scales necessary to study the effect of polymer conformation on the optical properties, especially for polymers with large repeat units or high persistence length, so instead coarse-grained methods need to be employed. In this work I am using an extended Hubbard Hamiltonian parameterized from first principles calculations to calculate the optical properties of different types of oligomers and study how their absorption strength depends on chain length. The long-term goal of this project is predicting spatially averaged optical properties of a macromolecular material using the knowledge of the excited states of atomic scale building blocks and of the molecular conformations present in the film. Such methods will help understand the macroscopic absorption properties of known compounds and thus aid the design of new organic materials exhibiting high optical absorption.


Organic semiconductors (OSC) are considered as highly feasible for the use in opto- and bioelectronic applications. The relatively low charge carrier mobility limits its current applicability. Insight into electronic structure-property relations is required to understand how to enhance the mobility. Various groups have been working towards a better understanding of the dependence of the mobility both relying on chemical intuition as well as using theoretical approaches covering structural information from molecular dynamics (MD) over transport properties using kinetic Monte Carlo (kMC) [1-3]. Mentioned numerical methodologies provide insight of transport for small perturbations from a crystalline structure. However, there is a lack of description for strongly non-crystalline structures such as solution processed OSCs due to the high computational effort associated with the calculation of all individual transition rates required for precise kMC studies.

In this work, we present a machine learning (ML) based ab-initio multi-scale simulation for charge transport within strongly non-crystalline OSCs using pentacene as a case study. ML allows for efficient and effective modeling of transport properties and helps to overcome conventional physical models that rely on empirical parametrizations or semi-empirical calculations. Using MD and density functional theory (DFT), we generate training data for the coupling integrals between adjacent molecules (dimers) of pentacene. The ML algorithm bases on the kernel ridge regression including an optimized set of descriptors for the respective dimers. To cover the range from the coupling integrals to charge mobilities, we couple the ML algorithm with our off-lattice kMC software [4]. The center of mass positions of the molecules within a non-crystalline pentacene film are used to generate the Voronoi tessellation which allows computing charge hopping across amorphous structures. ML helps to estimate coupling integrals within the Marcus theory without the need for a precomputation of each dimer configuration. We overcome existing ab-initio simulations by a tremendous reduction of computational demand and allow a generalized description for a wide range of structural disorder within the organic layer without a need to compute coupling integrals from scratch. We show how the directionality of the charge transport is influenced by varying the degree of crystallinity. Furthermore, we compute the field- and temperature dependence for non-crystalline pentacene layers stacked on top of a silicon oxide substrate, as used for thin-film transistors, and compare our ML-based approach with empirical kMC results.

A key to enable high-performing organic electronic devices is given by proper interface engineering of organic layers. Doped organic transport layers are used to improve charge carrier injection and to reduce ohmic losses. The diffusion of dopants into adjacent layers is known to cause exciton quenching in photo-active layers and to reduce the long-term stability of many types of organic electronic devices. On the other hand, the diffusivity of dopants can be beneficially used in a sequential deposition scheme that allows for doping and at the same time high order of the matrix material. Here, we investigate the diffusion of a bulky sequentially deposited p-dopant in poly(3-hexylthiophene) (P3HT) thin films using non-destructive in-situ infrared (IR) spectroscopy and photoelectron spectroscopy (PES). The dopant diffusion is resolved by differentially evaluating electron transfer in the bulk and at the surface for varying dopant coverage. Using PES and IR spectroscopy, it is possible to determine the concentration at which both charge transfer and dopant incorporation into the polymer film saturate. By means of PES we find that charged dopants are less mobile in the diffusion process than neutral molecules. A comparison of the diffusivity in semi-crystalline and fully amorphous P3HT indicates that semi-crystalline P3HT yields a higher capacity for dopants varying dopant coverage. Using PES and IR spectroscopy, it is possible to determine the concentration at which both charge transfer and dopant incorporation into the polymer film saturate. By means of PES we find that charged dopants are less mobile in the diffusion process than neutral molecules. A comparison of the diffusivity in semi-crystalline and fully amorphous P3HT indicates that semi-crystalline P3HT yields a higher capacity for dopants compared to fully amorphous P3HT. Furthermore, a temperature-dependent measurement reveals that the diffusion process requires activation energy close to room temperature.
lagged in $J_0$, behind their conventional low-bandgap polymer based analogues. Here, we study an intrinsic limit for photocurrent generation using ultra-low-bandgap polymers with an $E_g$ of around 1.1–1.3 eV.

We measured femtosecond transient absorption for these polymer films, and found that singlet excitons generated in these polymers rapidly decay with negligible photon emission. The non-radiative decay rate scales exponentially with the bandgap $E_g$, which is so called “energy gap law”. Our results suggest unavoidable disadvantage for ultra-low-bandgap polymers. Accordingly, we will discuss optimal design concept for high efficient PSCs.

**EP05.14.28**

Optical and Electrical Properties of Mixed-Solution and Sequentially Processed poly(3-alkylthiophene): F4TCNQ Films

Shin Sakiyama and Katsuhiko Fujita; Kyushu University, Kasuga, Japan.

Efficient n-type doping was not established since the dopants dose not dissolve in same organic solutions of polymer semiconductors. Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) method enabled it recently. We have already reported efficient n-type doping of poly(2-methoxy-5-(2'-methyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV; LUMO: 3.1 eV, HOMO: 5.2 eV). The high doping efficiency as much as 15% was realized. In organic devices composed of non-doped organic semiconductors, electron injection barrier is basically equal to the gap between LUMO of the semiconductor and work function of the electrode. It is still open question how the barrier is formed in the n-doped polymer/electrode. The metal/semiconductor junction of n-doped polymer has not been studied yet. In this research, we have fabricated only devices (EOD) of n-doped polymer semiconductor using electrodes of Al and Ca. The electron injection from Al or Ca was examined.

MEH-PPV (Mw = 40,000-70,000 Aldrich) and Cesium carbonate (Cs2CO3, Japan Pure Chemical, purity of 99.999%) were used as a host polymer and an n-type dopant, respectively. The asymmetric EOD formed with Al for bottom and top electrodes and a top Ca electrode having a lower work function (3.0 eV) were fabricated. The current-voltage (I-V) characteristics and capacitance-frequency (C-F) measurement were conducted in vacuum without breaking vacuum after the top electrode deposition.

J-V characteristics of asymmetric EOD, Al(50nm)/MEH-PPV-Cs2CO3 (110nm)/Ca(50nm) are fabricated. The current density was drastically increased as the doping concentration increased. The asymmetric EODs, current density in the forward bias was about 1 order of magnitude larger than that in reverse bias at low doping concentration at 0, 2.0 wt%. However, the current density was almost overlapped in forward and reverse bias at the doping concentration of 10wa. The disappearance of the rectification property suggests that the quantum tunneling takes place due to the very thin depletion layer at Al/MEH-PPV junction at the high doping concentration.

In this research, we have fabricated electron only devices (EOD) of an n-doped polymer semiconductor using electrodes of Al and Ca. The electron injection from Al or Ca was examined.

**EP05.14.29**

Quantum Tunnelling on Metal/N-Doped Polymer Semiconductor

Shin Sakiyama and Katsuhiko Fujita; Kyushu University, Kasuga, Japan.

For the last decade, there has been massive evolutions in organic electronic devices and their novel applications such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). Moreover, a wide range of printing techniques has proven the process innovation with soluble materials. The limited source of contact electrodes, however, makes the barrier for the commercialization of the printing process with the soluble materials comprised of metallic and non-metallic conductors.

Those devices are basically composed of two- or three-terminal contacts which have the interfaces of metal/semiconductor (SC), dielectric/SC and SC/SC. Thus, the interfacial engineering is predominant to realize those devices for flexible application. A crucial issue concerning charge injection at the interface of electrode/organic semiconductor is recently rising in order to improve the electrical performance of diodes and FETs.

This presentation gives an investigation on charge injection via the modification of electrodes with self-assembled monolayers (SAMs) in organic electronic devices. Functionalized SAMs with fluorine at the end group plays a substantial role to improve charge injection through a dipolar effect to decrease barrier height at the electrode/semiconductor interface in a planar diode and organic field-effect transistors (OFETs). This is extended to significant enhancement of electrical performance such as field effect mobility and contact resistance in OFET.

In addition, for a practical application of the extraction technique mentioned above, we particularly suggested the simple interface control engineering to reduce contact resistance and improve electrical characteristics in n-type OFETs with the semiconductor (PNDI2OD-T2). Inkjet-printed Ag metals are implemented for the n-type polymer OFETs as electrodes. Then, it is introduced by the two types of SAMs, thiophenol (TP) and pentafluorobenzene thiol (PFBT) for the electrodes. Throughout the suppression of the Schottky barrier height with TP in the OFETs, the electron injection is prominently improved as observed previously. We also demonstrated that all solution-processed n-type OFETs can be polarity-inversed by the interface treatment of PFBT onto the inkjet-printed Ag electrode. A remarkable improvement, therefore, was found for the OFETs with the TP-Ag electrodes with high electron mobility of 0.11 cm²/Vs. Additionally, largely low contact resistance of 480 kΩcm confirms that TP-Ag can be a great candidate for an excellent electrodes compatible with inkjet-printing for the n-type semiconductors. It indicates that the work function of the inkjet-printed Ag electrodes is variable for a massive scope by the simple interface engineering. As a result, it may be commonly applied for the fabrication of all-solution-processes electronics for a variety of applications.
Organic field effect transistors (OFETs) have attracted much interest for future electronics because they can have flexibility with processing from solution at low temperature. Recently many researches make an attempt to control the film morphology which directly correlated to the charge transporting ability of conjugated polymers. In this work, we demonstrate optimized poly[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyll-alt-5,5'-1,2,2'-terpyridine)] (PNDI2OD-T2) film morphologies, which are obtained by precisely regulating the solidification rate in the metastable state using a novel simple method. The kinetic control in the metastable state brings about dramatic morphological changes in both polymer domain sizes and molecular packing structures. The optimized P(NDI2OD-T2) films provide significantly increased electron mobilities up to 3.99 cm 2 V -1 s -1 , which is the impressive improvement in performance by nearly 100-fold as compared to conventional spin-coated devices. The observation of low activation energy according to the temperature-dependent behavior in optimized thin films can support the achievement of high electron mobilities of semiconducting polymers.

Long-Range Coherent Charge Transport in Physisorbed Molecular Layers Leandro M. Silva, Rafael F. de Oliveira and Carlos Cesar Bof Bufon; Brazilian Nanotech National Laboratory, Campinas, Brazil.

The charge transport in molecular ensembles is intrinsically related to a series of carrier-molecule quantum interactions which result in a variety of chemical and biological phenomena. Its understanding has paved the way for the development of novel device concepts, such as organic transistors, organic light-emitting diodes, and biosensors [1]. At the nanoscale, such interactions are commonly described as either direct tunneling for the 1-10 nm range or activated hopping for longer distances. However, the continuous transition between coherent tunneling and activated conduction as a function of organic light-emitting diodes, and biosensors [1]. At the nanoscale, such interactions are commonly described as either direct tunneling for the 1-10 nm range or activated hopping for longer distances. However, the continuous transition between coherent tunneling and activated conduction as a function of the barrier width remains unknown for physisorbed molecules. This work describes the first experimental evidence of long-range (> 10 nm) coherent tunneling occurring for physisorbed small-molecule semiconductors-based vertical junctions. By investigating the charge transport in copper-phthalocyanine (CuPc) thin films, we have identified the sequential tunneling as the long-range charge transport mechanism. Such a sequential coherent process is not only different from the direct tunneling but intrinsically distinct from the hopping conduction. Consequently, a gradual transition from direct tunneling to sequential tunneling, within the 10-22 nm barrier width, to hopping conduction can be verified. The evidence of coherent charge transport across long distances has implications for a variety of quantum effects that have not been previously confirmed for films with thicknesses larger than a few nanometers [2]. Therefore, our results contribute to bridging the gap between molecular and organic electronics [3,4].


References:

Probing the Sub-Bandgap States in Light-Absorbing Organic Semiconductors by Surface Photovoltage Spectroscopy Lakshmi Narayanan Mosur; Saravanan Murthi1; Diego Barrera1, Aakash Gadhi1, Liang Xu1, Fong-Yi Cao1, Cheng-Chan Tseng1, Yen-Ju Cheng1 and Julia W. Hsu1; 1The University of Texas at Dallas, Richardson, Texas, United States; 2National Chiao Tung University, Hsinchu, Taiwan.

Surface photovoltaic spectroscopy (SPS) measures surface photovoltage as a function of incident photon energy, and has been used for obtaining the electronic structure and structurally active defects of semiconductors. In SPS, sub-bandgap illumination probes the transition between band states and defect states within the bandgap. Photogenerated charge transfer from organic active layer to oxide contact layer materials is critical for realizing efficient organic photovoltaic devices. However, with the fully constructed solar cells, it is difficult to isolate the physical location of the defects. Here, we performed frequency-modulated (AC) and steady-state (DC) SPS measurements on bilayers containing light-absorbing organic materials (P3HT, P3HT:PC60BM, PFBT2Se2Th:PC70BM) and electron transport layer (ETL) oxide (ZnO) to probe photogenerated transfer across this interface. We observed negative SPV signal in both AC and DC SPS, indicating electrons transferring from organic layer to ZnO. DC spectra are broader compared to AC spectra for all three organics. AC spectra overlap with the absorption spectra of organic layers, evident that AC SPS corresponds to band-to-band transitions. The sub-bandgap signals measured by DC SPS correspond to transitions with the bandgap states. When hole transport layer (HTL) was deposited on top of the organic layer, the DC spectra of P3HT and P3HT:PC60BM are narrower than without the HTL, suggesting that the surface states are removed. The difference between neat polymer and blend and between blends with the two different donor polymers, P3HT:PC60BM, PFBT2Se2Th:PC70BM, are probed using capacitance-frequency (C-f) to probe deep level defects in addition to SPS. These results give insight on the location and nature of sub-bandgap defects based on their SPS spectral signatures and frequency response.

Controlled Self-Assembly of 1D Nanoscale Materials and Their Resulting Photophysical Properties Sarah R. Marques and Michael Barnes; Chemistry, University of Massachusetts, Amherst, Massachusetts, United States.

Efficiency of organic optoelectronic devices is dependent on the intermolecular interactions of molecular assemblies that can favor charge transfer or radiative recombination. My work pertains to understanding whether directional charge transfer seen in extended crystals of 7,8,15,16-tetrazaterrylene is an intrinsic property of the 1D n-type semiconductor or an extrinsic property caused by subtle defects in the p-stack direction. We use solvent vapor annealing to crystallize nanoscale aggregates (<500 nm), and extended, highly ordered, crystals microns long. We probe the effect that order has on directional charge separation in these species using single molecule techniques and polarized optical excitation coupled with time resolved photoluminescence spectroscopy, this produces photoluminescence decays that have power-law signatures, indicative of the presence of charge separated states. The observation of enhanced power-law photoluminescence decay at critical stages of crystal growth support intrinsic charge separation favoring a promising molecular design platform for organic semiconductor materials.

Global Equilibrium and Non-Equilibrium Theory of Hopping Exciton Transport in Disordered Semiconductors Stavros Athanasopoulos1 and
The phenomenon of exciton diffusion is found to play a role in a remarkably wide range of physical systems including disordered organic semiconductors, nanocrystalline quantum dots, semiconducting carbon nanotubes and photosynthetic biological systems. Moreover, there is a growing interest in describing electronic exciton energy transfer because exciton dynamics determines function in many technological applications. For example, in thin film organic solar cells exciton diffusion drives charge separation, in organic light emitting diodes it determines the brightness and color of the device, in scintillator detectors it controls the response function and yield, while in quantum communication systems it facilitates photon antibunching.

We develop a temperature dependent theory for singlet exciton hopping transport in disordered semiconductors. It draws on the transport level concept within a Forster transfer model and bridges the gap in describing the transition from equilibrium to non-equilibrium time dependent spectral diffusion. We test the validity range of the developed model using kinetic Monte Carlo simulations and find agreement over a broad range of temperatures. It reproduces the scaling of the diffusion length and spectral shift with the dimensionless disorder parameter and describes in a unified manner the transition from equilibrium to non-equilibrium transport regime. We find that the diffusion length in the non-equilibrium regime does not scale with the third power of the Forster radius. The developed theory provides a powerful tool for interpreting time-resolved and steady state spectroscopy experiments in a variety of disordered materials, including organic semiconductors and colloidal quantum dots.

**EP05.14.36**
Direct Characterization of Nanoscale Molecular Ordering in Organic Optoelectronic Materials Using 4-Dimensional Scanning Transmission Electron Microscopy
- Gabriel Calderon Ortiz1, Menglin Zhu1, Jared M. Johnson1, Letian Dou2 and Jinwoo Hwang1; 1Materials Science and Engineering, The Ohio State University, Columbus, Ohio, United States; 2Chemical Engineering, Purdue University, West Lafayette, Indiana, United States.

The local ordering of the constituent molecules can directly affect the charge transfer and efficiency of the organic electronic devices and solar cells. Efforts to understand the ordering has involved theories and simulations, and experimental characterization, such as using X-ray diffraction. While these methods have provided important information about the ordering, more detailed information on how the ordering forms at the nanoscale level and how it affects the local and overall properties has remained difficult to determine. To fill the gap in the characterization, it is required to develop a new experimental method that uses a small (nanoscale) probe. Here we present the new 4-dimensional scanning transmission electron microscopy (4D-STEM) that can determine the detailed structure of molecular ordering in organic semiconductors. Our 4D-STEM uses a highly coherent electron probe that generates the diffraction signals directly from the local ordering, which are then captured by a new-generation pixelated fast STEM detector. By scanning the probe over a large area, we acquire a few tens of thousands of nanodiffraction patterns from one organic sample. We then subsequently analyze the patterns using intensity variance and angular correlation functions to convert them into a real space map of the ordering, which can reveal the details of the type, size, connection, and distribution of the ordering with unprecedented precision. We will present the data from two materials, P3HT and IDTBT, and demonstrate how the local ordering, which we control using different synthesis parameters, affects their physical and electronic properties.

**EP05.14.37**
Radiative Recombination and Exciplexes in All-Polymer Organic Semiconductor Bulk-Heterojunctions
- Cindy Kumah1, and Deirdre O’Carroll1, 2; 1Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Chemistry & Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Organic bulk-heterojunctions of conjugated polymers and fullerene derivatives have been used extensively in organic photovoltaic devices in the past two decades. Although blends of conjugated polymers and fullerene derivatives exhibit efficient exciton dissociation upon solar illumination, the solar power conversion efficiency reached using these materials is at least a factor of two less than that predicted by the Shockley-Queisser theoretical limit. Non-radiative recombination of charge carriers due to efficient exciton quenching by fullerene derivatives is a significant factor preventing organic bulk-heterojunction materials from reaching the Shockley-Queisser limit. Therefore, in recent years there has been greater interest in developing and understanding fullerene-free organic bulk-heterojunctions that are expected to be less prone to non-radiative recombination.

The goal of our work is to understand the influence of altering the radiative decay rate (using the Purcell Effect) of charge transfer excitons on photovoltaic performance. In this study, we investigate radiative recombination and charge transfer excitons at the interface of electron donor:acceptor blends of two polyfluorene-based conjugated co-polymers. The heterojunction formed by the two phases is a type-II heterojunction, in which efficient charge separation is expected to occur. Photoluminescence spectroscopy shows quenching of emission from both polymers in the blends. An additional low-energy emission peak is observed in the blends which is not present in the spectra of either polymer alone. Quenching is more efficient in a 1:1 donor:acceptor blend than in a 1.2 donor:acceptor blend and in the 1:1 blend, the additional emission peak is more intense. In addition, the blends have longer photoluminescence lifetimes than the individual polymers. These measurements indicate that efficient photo-induced charge transfer occurs in the blend, and the additional low-energy emission peak observed in the blend can be attributed to emissive charge transfer excitons (i.e., exciplexes). Future work includes measuring the photoluminescence quantum efficiency of the conjugated polymer donor: acceptor blends and calculating the radiative decay rates. Plasmonic nanostructures will be incorporated in the organic semiconductor blend that are resonant with the exciplex emission. This will allow us to study the impact of the Purcell effect on charge transfer and exciplex emission. Additionally, electroluminescence and photocurrent measurements of all-polymer bulk-heterojunction devices containing resonant plasmonic nanostructures will be studied to understand if accelerated radiative recombination of charge transfer excitons can be beneficial to photovoltaic device performance.

**EP05.14.38**
Mechanism of Geminate Polaron Pair Generation in π-Conjugated Polymers
- Ella Olejnik, Carlos Silva and Felix Thouless; Georgia Institute of Technology, Atlanta, Georgia, United States.

In this work, we address the mechanism of geminate-charge generation in neat semi-crystalline polymeric semiconductors by means of delayed photoluminescence (PL) [1,2]. We implement time-dependent and steady-state PL spectroscopies to study the yield and recombination rate of geminate polarons. We compare the dynamics of delayed PL at varying magnetic field and temperature. We find that there are significant magnetic field effects on the recombination, which increases the relative quadrature signal of the CW PL with the increase of the magnetic field. This points to charge-transfer intermediate states between singlet excitons and geminate polaron pairs, with strongly mixed singlet and triplet character.


**EP05.14.39**
Doping Induced Solubility Control Patterning for Organic Thin-Film Transistors
- Zaira I. Bedolla-Valdez4, Camila Cendra Guinassi2, Zhengliang Su1,
Effect of Disorder on the Thermoelectric Properties of Semiconducting Polymers

Meenakshi Upadhyaya and Zlatan Aksamija; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Organic thermoelectric (TE) materials hold tremendous potential to address the ever-increasing demand for sustainable and renewable energy resources. Recently, a $ZT = 0.25$ has been reported in PEDOT: PSS, upon optimizing the carrier concentration. This, combined with advantages such as low cost, easy synthesis, and an inherently low thermal conductivity, makes polymeric a very attractive choice for commercially viable TE applications such as large-scale Peltier coolers and electricity generation from waste heat and renewable sources. A longstanding problem in TE materials is the dependence of performance on the TE Seebeck coefficient and the conductivity. We find that numerical transport models play a key role in predicting the optimum structural characteristics and the design of novel TE materials for TE applications. In this work, we investigate the TE properties of disordered organic semiconductors, and establish the effect of carrier concentration, disorder, and correlation in energy and position on the TE Seebeck coefficient, electrical conductivity, and the Lorenz number. Our transport model is based on electron hopping between localized sites with a Gaussian disorder model for their energies. We iteratively solve the non-linear Pauli master equation to compute the time-averaged occupational probabilities of the sites from which relevant transport quantities are calculated. Our results show that large energy overlap between localized electronic states can improve the electrical conductivity without adversely affecting the Seebeck coefficient. Positional disorder affects the overlap between neighboring states and aids in the formation of conduction paths with an increased probability of carriers in high energy sites, ultimately leading to simultaneous increase in electrical conductivity and Seebeck coefficient. We introduce positional correlation to investigate the role of partial ordering and find that it negatively affects conductivity. On the other hand, energetic disorder widens the density of states and leads to increased energy gap between neighboring sites, thus hindering transport and adversely affecting both conductivity and Seebeck. Surprisingly, correlation in energies of nearby sites has an effect on the TE properties. We also find that Lorenz number increases with Seebeck coefficient, largely deviating from the Sommerfeld value and the universal trend observed across all materials exhibiting band transport. Our work provides an understanding of how short channel OTFTs were fabricated using all solution processes. We will also detail the performance advantages of short channel OTFTs as well as discuss the lifetime issues associated with dopant drift.

The authors acknowledge the NSF Scalable Nanomanufacturing program for financial support and SENER-CONACyT 291145 for Zaira I. Bedolla-Valdez’s postdoctoral fellowship.

EP05.14.41
Exciton Binding and Dissociation in Semiconducting Polymers—A Tight Binding Approach

Joel H. Bombile, Michael Janik and Scott Milner; The Pennsylvania State University, University Park, Pennsylvania, United States.

Semiconducting polymers are the subject of much interest and study as active elements in a number of electronic devices. Among these devices, organic photovoltaics are particularly attractive due to their potential light weight, low cost and mechanical flexibility. Crucial to the performance of photovoltaic devices is the generation of charge carriers, which occurs through the dissociation of excitons. A clear understanding of excition formation, dissociation, and recombination in OPVs is necessary for the design of more efficient devices. We focus on the stability of excitons and the energetics of their dissociation and separation into charge carriers that can then be transported to the electrodes. Excitons are excited electron and hole pair bound by a Coulomb interaction. For separation into individual carriers, the binding energy of the exciton must be overcome. We use a model Hamiltonian based on the tight binding approximation to describe the exciton binding energy and its dissociation potential, for an exciton confined to a 1D lattice. Our model takes into account polaronic effects arising from the reorganization of nuclei and from polarization of the surrounding dielectric, which substantially stabilize the separated carriers and affect the exciton dissociation potential. We examine the effects of an applied electric field on the dissociation potential, and relate the field strength necessary to unbind the hole-electron pair to the maximum attractive Coulomb force between them. We then study the exciton at a 1D donor-acceptor interface, which polarizes the exciton. We explain the exciton polarization by observing how its dissociation potential is altered by the interface. The interface not only polarizes the exciton but makes it easier to be unbound by an external factor, as evidenced by a reduced electric field strength necessary for charge separation.

EP05.14.42
Elucidating the Role of Molecule-Electrode Interfacial Defects in Charge Tunneling Characteristics of Large-Area Junctions

Gyu Don Kong, Junji Jin and Hyo Jae Yoon; Chemistry, Korea University, Seoul, Korea (the Republic of). 

Interfacial chemistry at organic-inorganic contact critically determines function of a wide range of molecular and organic electronic devices and other systems. The chemistry is, however, difficult to understand due to the lack of easily accessible in-operando spectroscopic techniques that permit access to interfacial structure on a molecular scale. Herein we compare two analogous junctions formed with identical organic thin film and different liquid top-contacts (water droplet vs. eutectic gallium indium alloy) and elucidate the puzzling interfacial vs. eutectic gapless. Specifically, we fine-tune the surface topography of the organic surface using mixed self-assembled monolayers (SAMs): single component SAM composed of rectifier $2,2'$-bipyridyl-terminated n-undecanethiolate; denoted as SC$_11$BPY is systematically diluted with non-rectifying n-alkanethiolates of different lengths (denoted as SC$_n$ where $n=8,10,12,14,16,18$). Characterization of the resulting mixed SAMs in wettability and tunneling currents with the two separate liquid top-contacts allow us to investigate the role of phase segregation and gauche defect in the SAM/liquid interfaces. The results reported here show the difference in length between SC$_{11}$BPY and SC$_n$ is translated into nanoscopic pits and gauche-conformer defects on the surface, and the difference in contact force—hydrostatic vs. user pressures—and hence conformity of contact accounts for the difference in wettability and rectification behaviors. Our work provides an
EP05.14.43

Deconvolution of Tunneling Current in Large-Area Junctions Formed with Mixed Self-Assembled Monolayers
Jinju Jin, Gyu Don Kong and Hyo Jae Yoon; Chemistry, Korea University, Seoul, Korea (the Republic of).

The study of charge transport by quantum tunneling phenomena across organic thin films has been actively studied for many years in various academic fields. In molecular electronics, while single-component self-assembled monolayers (SAMs) have been previously main organic component, little has been investigated on how heterogeneity of monolayer affects the charge transport behavior across it. Here we focus on binary mixed SAMs composed of two different n-alkanethiolates of different lengths formed on ultraflat template-stripped gold substrate. Electrical characterization of mixed SAMs using liquid eutectic gallium-indium alloy reveals that the surface topography of monolayer largely depends on the difference in length between the thioclates, and the surface heterogeneity is translated into the distribution of tunneling current density. As the length difference is more significant, more phase segregation takes place, leading to increase in the modality of Gaussian fitting curves. Consequently, statistical analysis permits access to deconvolution of tunneling currents, mirroring the phase segregated surface. Our work provides an insight into the role of surface topography in performance of molecular-scale electronic devices.

EP05.14.44

Crystal Structures and Superradiance of Organic Semiconductors at 2D Limit
Beilei Sun, Xin Xu, Zefeng Chen and Jianbin Xu; The Chinese University of Hong Kong, Sha Tin District, Hong Kong.

Organic semiconductors (OSCs) have attracted great attention for decades because they offer intriguing prospects for high throughput, low-temperature processing of electronic circuitry on flexible substrates. However, previous studies mainly focused on bulk single crystal or polycrystalline or amorphous thin films with disorders and grain boundaries. The intrinsic properties of OSCs in the vicinity of the device interfaces are rarely studied, although the interfaces have important influence on the electronic and optoelectronic properties of device. We have prepared high quality few-layer thin films of N,N’-dinitroxypropylene 3,4,9,10-tetracarboxylic diimide (PTCDI-C$_4$) by physical vapor transport (PVT) method and further characterized the crystal structure and optical properties of the first three layers in the proximity of the substrate. It is found that the first layer adopts a different molecular packing arrangement, whilst the overlayers exhibit different optical properties. Superradiance is observed in the single and bilayer as well as trilayer films, but decreases with the increase of film thickness and then disappears in the bulk material. The superradiance intensity shows an opposite trend as the sample temperature increased. The intensity at 140 K is about 9 times of that at 290K. The linewidth becomes narrower at lower temperature. The full width at half maximum (FWHM) drops from 10 nm at room temperature to 4.3 nm at 140 K.

EP05.14.45

Plasmon Hybridization in Self-Assembled Graphene Nanotubes
Kriti Agarwal, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota, Minneapolis, Minnesota, United States.

Graphene plasmonics has attracted widespread attention in recent years due to their rapid frequency tunability, long plasmon lifetime, and strong light confinement. However, the two-dimensional (2D) nature of graphene imposes stringent requirements on the underlying substrate and limits the plasmon enhancement modes that can be excited. One of the solutions to overcome the limited performance of 2D graphene plasmons is through the fabrication of self-assembled graphene nanotubes. We have realized the 3D graphene nanotubes using the plasma in a reactive ion etching (RIE) system to trigger a surface tension based self-folding caused by grain coalescence in a tin sacrificial hinge. The parameters in the RIE process have also been tuned to control the gap size within nanotubes, and also achieve extremely high aspect ratio (length/radius ~ 10,000) tubes. The radial coupling of plasmons at the opening of the tube creates a virtual uniform cross-section area of extremely strong field enhancement as compared to the rapidly decaying fields in 2D graphene. If small longitudinal gaps are introduced in the nanotubes, propagating surface and edge modes are achieved with intensity based on the gap length between the edges. The propagating modes in the high aspect ratio nanotubes can be utilized for plasmonic waveguides with extremely high propagation lengths. Furthermore, the self-assembled multi-layered (Al$_2$O$_3$/Graphene/Al$_2$O$_3$) nanotubes can be fabricated with an array of horizontally short discontinuous graphene segments as long as the outer layers are maintained as continuous. The smaller aspect ratio graphene segments undergo not only radial plasmon coupling but also a longitudinal coupling between the discontinuous segment openings, creating strong uniform field throughout the volume of the multi-layered tube. The lower contact area of the 3D graphene tubes with the underlying substrate leads to a lower capacitive coupling that causes significant ohmic losses through non-radiative plasmon relaxation due to coupling between plasmons and substrate carriers in metallic and semiconducting substrates. The lower plasmon damping leads to a 13 times stronger field that extends throughout the completely closed graphene tubes as opposed to corner confined weaker field in 2D ribbons on a silicon substrate. The stronger fields throughout the tube structure exhibit a fourfold enhancement in sensitivity and overcome the need to bind targeted molecules to the surface of graphene as exhibited by the example of A/G protein. The 3D graphene nanotubes achieve distinct edge and volumetric enhancement modes while simultaneously increasing the compatibility of graphene with diverse substrates without deterioration in plasmonic properties for application in novel optical and electronic devices.

EP05.14.46

Direct Measurement of the Energetic Landscape of Solution-Processed Organic Photovoltaic Devices
Vincent Lam and Yana Vaynzof; Kirchhoff-Institut für Physik und Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany.

Organic optoelectronic devices such as light-emitting or photovoltaic diodes have been under extensive investigation in the last decades, resulting in remarkable improvements in their performance. Most literature reports in this field include energy level diagrams to illustrate how the energetic landscape in the device varies through the various device layers. Consequently, these energy level diagrams are used to interpret device performance and comment on the efficiency of physical processes such as charge separation, charge injection or extraction. Despite the importance of such energy level diagrams, they are currently constructed by combining energetic values for the individual device components as obtained by different techniques, e.g. cyclic voltammetry, density functional theory calculations, Kelvin probe and photoemission spectroscopy. Additionally, these diagrams are often formed without taking into account interfacial effects, such as dipole formation or band bending, that may arise as different materials are put into contact. Herein, we demonstrate that combining ultra-violet photoemission spectroscopy (UPS) with gas cluster ion beam (GCIB) sputtering, allows for a damage-free depth profiling and hence, an accurate determination of the energetic landscape of solution-processed active layers or multi-layers. We utilize the widely investigated model material system poly[3-hexylthiophene] (P3HT) and C61-butyric acid methyl ester (PC60BM), but also demonstrate that our method is applicable to a large variety of other novel organic material systems. By fitting the obtained UPS spectral maps, we are able to not only quantify the positions of the donor and acceptor energy levels, but also obtain compositional information with a vertical depth resolution than that available from X-ray photoemission spectroscopy profiling. Our results allow us to accurately and reliably measure the ‘photovoltaic bandgap’ (the energetic difference between the lowest unoccupied molecular orbital of the acceptor and the highest occupied molecular orbital of the donor) and correlate it to the measured open circuit voltage of the device. Our method opens the way to quantify the energy losses in organic photovoltaic systems and develop new
Sensitized triplet-triplet annihilation (TTA) involves two components: a triplet-triplet annihilation (TTA) material where two triplets can fuse to a singlet for light emission, and a sensitizer material to provide the triplets to the TTA material. Typically, the sensitizer has a lower singlet energy than the TTA material, which results in singlet quenching (SQ) of the TTA signal in solid-state optoelectronic devices (such as organic light-emitting diodes), lowering the efficiency. Here, we show that a triplet diffusion and singlet blocking (TDBS) layer between the sensitizer and TTA material allows the triplet ejection to diffuse from sensitizer to TTA but blocks the singlet quenching of TTA emission by sensitizer. Obviously, the TDBS layer should exhibit a triplet energy lower than the sensitizer and higher than TTA material, as well as a higher singlet energy than both sensitizer and TTA material. The TDBS layer can be applied to several sensitizer systems, such as phosphorescent (Ph) and thermally-activated delayed fluorescent (TADF) materials whose efficient intersystem crossing (ISC) process converts singlets into triplets for sensitizing TTA emission. With incorporation of the TDBS layer into a solid-state thin film, a 6.13-times enhancement in the STTA signal was observed using a TADF-sensitizer under optical pumping. Efficient STTA emission was also observed with a Ph-sensitizer in an electrically-pumped organic light-emitting diode (OLED). The exciton dynamics were analyzed with transient electroluminescence (TrEL) and transient photoluminescence (TrPL), which provide direct evidence for reduced singlet quenching with the insertion of a TDBS layer. Finally, an electrically-pumped device that generates 75% triplet excitons in a conventional fluorescent dye can also provide sufficient triplets to be used as the sensitizer, and the overall conversion efficiency of the triplets into singlets approach 80%. Besides, the operation lifetime of the blue OLED using TTA emission was elongated by ~3x due to separation of charge recombination zone in the sensitizer layer and the emission zone in the TTA layer.
A series of novel carbazole-imidazole derivative with a large energy bandgap and triplet state over 3.4 and 2.8 eV, respectively, were synthesized conjugating three carbazole moieties and one imidazole moiety to exhibit the bipolar behavior. Their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were approximately at 2.3 and 3.7 eV, respectively. In particular, by well design to form the molecular structure, these compounds showed the excellent thermochemical properties with high glass transition (T_g) of more than 190 °C and high decomposed temperature of approximately 450 °C. The T_g is greater than the highest thermal specification of 150 °C for automotive electronics, corresponding to the better thermal reliability. Employing as host materials of blue phosphorescent organic light emitting device (OLED), a layer structure of indium-tin-oxide anode/4,4'-cyclohexyldenedibis[N,N-bis(4-methylphenyl)benzeneamine]/N,N-dicarbazolyl-3,5-phenylene/ host: iridiumIIIbis[6,6-(di-fluorophenyl)]pyridinato-N,C20]picolinate (Flirpic)/ diphenylbis[4-(pyridin-3-yl)phenyl]silane/lithium fluoride/ aluminum cathode. The Flirpic was well-known high efficiency blue phosphorescent emitter. Our preliminary high efficiency phosphorescent OLED exhibited the max. current efficiency of 58.7 cd/A, max. power efficiency of 59.3 lm/W, max. external quantum efficiency of 28.6%. By moving the main recombination from the region close to electron transporting layer to the center of emitting layer, the operation lifetime exhibited 2 times improvement. The further improvement in device performance is possible.

**EP05.14.54**

Synthesis and Characterization of Meso-Substituted BODIPYs—Exploration of the Optical and Photophysical Properties and the Formation of Thin Films Cruz Pamela1, 2; 1UNAM, Mexico city, Mexico; 2Chemistry, ICN, Mexico city, Mexico.

Four BODIPY-fluorene based fluorophores were synthetized using a donor-π-bridge- acceptor (D-π-A) motif. They were studied via their structural analysis, the measurement of their photophysical and optical properties and a theoretical DFT study, to plunge deeper into their electronic structure and transitions bestowing such features. We present four different structures as we change the π bridge, in the first one BODIPY 1, we have the BODIPY core substituted in the meso position with a fluorene moiety in the BODIPY 2 we have the BODIPY core directly attached to the ethynylfluorene moiety, in BODIPY 3 we have a phenyl group attached to the ethynylfluorene moiety, finally in the BODIPY 4 we have a phenyl group attached to an ethynylfluorene moiety. In this work, we present the synthesis of novel meso-BODIPY derivatives, the spectroscopic characterization, structural analysis of X-Ray diffraction, and the study of the photophysical properties, such as: absorption, emission, and fluorescence quantum yield. Quantum chemical calculations were performed to analyzed the conduct of the compounds in the excited state.

**EP05.14.55**

Investigation of Locally-Excited and Charge-Transfer Optical Transitions in a Series of Porphyrins Thomas M. Cooper1, Joy Haley1, Weije Su1, Douglas Krein2 and Jennifer Fore3; 1Air Force Research Laboratory, Dayton, Ohio, United States; 2General Dynamics Information Technology, Dayton, Ohio, United States; 3SOCHE, Dayton, Ohio, United States.

In order to investigate locally-excited and charge-transfer optical transitions in multiple-chromophore-molecular-complexes, we synthesized eight new porphyprins containing 5,15-attached diphenyl aminoporphyrin (DPA) or benzothiazolo(HT) connected to the porphyrin core either through a phenyl-alkynyl fluorene bridge or with an alkynyl-fluorenone bridge. We also synthesized a series of these porphyrins containing a central Zn atom. We will describe the effects of transitions bestowing such features. We present four different structures as we change the π bridge.

**EP05.14.56**

Tuning Excited-State Absorption of Aromatic Hydrocarbons via Structural Modifications David Stewart1, 2, Jianmin Shi1, Alexis T. Phillips1, 4, Zhenning Yu1, 3, Tristan Naranjo1, 4, Tod Grusenmeyer1, Jacob M. Artz1, 4, Christopher McCleese1, Ryan M. O’Donnell3, Thomas M. Cooper1, William M. Shensky1, Loon-Seng Tan1 and Joy Haley1; 1Air Force Research Laboratory, Dayton, Ohio, United States; 2General Dynamics Information Technology, Dayton, Ohio, United States; 3SOCHE, Dayton, Ohio, United States; 4Southwestern Ohio Council for Higher Education, Dayton, Ohio, United States; 5UES, Inc., Dayton, Ohio, United States; 6Physics, U.S. Air Force Academy, U.S. Air Force Academy, Colorado, United States.

Excited-state absorption (ESA) plays a critical role in the effectiveness of nonlinear optical processes such as reverse-saturable absorption and effective-three-photon absorption. By favorably controlling the intensity and energy of the ESA, the nonlinear performance can be enhanced. However, examples of how to tune ESA are scarce. This work shows how structural modifications across two separate series of molecules can greatly influence ESA. The first series is a group of anthanthrene derivatives to which a varying number of phenyl or t-Bu-phenyl substituents are added. The shape of the ESA spectra remain consistent but the maxima red shift from 585 nm (parent anthanthrene) to 645 nm (four t-Bu-phenyl substituents) are. There are also two oxidized derivatives, anthanthrones, which show strong, broad ESA in the visible with weaker transitions observed to nearly two μm. The anthanthrones have stronger ESA in the visible than the anthanthrenes, with ESA extinction coefficients around 30,000 M⁻¹ cm⁻¹. Another noticeable difference is that the intersystem crossing yields are also much larger for the anthanthrenes (~0.8) than the anthanthrenes (~0.3). This follows El Sayed’s rule as the anthanthrone derivatives likely contain nπ* states. The second series is a group of naphthalene carbonitrile derivatives containing electron donating groups (either dimethylamino or piperidinyl) in the 2, 3, or 4 positions. These changes dramatically change the energy of the ESA transitions, with shifts in the maxima greater than 100 nm. These modifications also impact the singlet state, as fluorescence lifetimes and quantum yields are significantly larger in the 3-substituted compounds (10.1 ns/0.76) than the 4-substituted (0.48 ns/0.05). Another significant effect of the varying substitution positions is the singlet-triplet energy gap, which can be tuned from 0.65 eV (2-position) to 1.01 eV (4-position).
The charge-transfer (CT) states appearing at the donor-acceptor interfaces in organic solar cells (OSCs) mediate exciton dissociation, charge generation, and charge recombination. Current work on OSCs based on non-fullerene acceptors (NFAs) points out that by using blends with a small energy offset between the CT state and highly luminescent local excitation (LE) state of the low-gap material it is possible to significantly minimize the voltage losses. Here we compare how the static and dynamic disorders and hybridization between the CT and LE states impact the radiative and non-radiative recombination rates and consequently the voltage losses in PTB7-Th:IEICO and PTB7-Th:PC71BM OSCs that are representative examples of small-energy offset NFA and typical fullerene-based OSCs, respectively. We have also developed a three-state vibronic model that explicitly considers the electronic and vibrational couplings between the CT and LE states and show that the use of the three-state model is mandatory in order to obtain a reliable description of the optical absorption features related to the CT states in blends with small-energy offset between CT and LE states.


**EP05.14.57**

All-Organic Infrared-to-Visible Up-Conversion Organic Light-Emitting Diodes with Infrared Sensitivity Beyond 1.1µm Vishal Yeddu, Gijun Seo and Do Young Kim; Materials Science and Engineering, Oklahoma State University, Tulsa, Oklahoma, United States.

Infrared (IR)-to-visible up-conversion organic light-emitting diodes (OLEDs) have attracted a great deal of research interest because they offer the potential to convert an invisible infrared image to a visible image without pixilation in the device, thus enabling a high-quality image at a significantly low cost. However, all-organic IR-to-visible up-conversion OLEDs with an organic IR sensitizer as well as an organic visible emitter show very limited IR sensitivity up to around 830 nm. Detecting photons at longer IR wavelengths requires lower bandgap organic semiconductors. Here, all-organic IR-to-visible up-conversion OLEDs with an IR sensitivity up to 1200 nm were fabricated using a novel low bandgap polymer as the IR sensitizing layer. This low-bandgap polymer showed a strong absorption in the near-IR wavelengths from 700nm to 1200nm. To evaluate the novel low bandgap polymer as the near-IR sensitizer, the near-IR photodetectors are first fabricated with a PC60BM as the acceptor in the photoactive layer. The near-IR photodetector showed detectivity higher than 10^11 Jones in the multi-spectral region (300-1100nm) and the maximum detectivity of 3.0×10^11 Jones at the wavelength of 1000 nm due to significantly reducing dark current (8.8 × 10^-6 mA/cm² at -1V). Using the novel low bandgap polymer as the IR sensitizing layer, IR-to-visible up-conversion OLEDs were fabricated with an IR sensitivity up to 1,200 nm. The IR up-conversion OLED successfully converted invisible near-IR light of 700nm-1200nm directly to visible green light with a peak emission wavelength of 520 nm. This is the very first report of all-organic IR-to-visible up-conversion OLED with near-IR sensitivity beyond 1100 nm which Si-based photodetectors cannot offer.

**SYMPOSIUM EP06**

**TUTORIAL: Introduction to Quantum Spintronics**

November 25 - November 25, 2018

Quantum spintronics is an emerging field of spin coherence and spin correlations at or near room temperature, and their effects on a wide range of properties, including spin dynamics and light emission from color centers in solids, spin and charge transport in organic materials, spin-dependent transport in tunnel junctions, dynamic nuclear polarization, and animal sensing of magnetic fields. Room-temperature quantum spintronic systems can be much more sensitive to external perturbations than sensors that must be very near thermal equilibrium. Applications include sensing of magnetic fields in biological systems (e.g. color centers in diamond and other wide-band-gap semiconductors and insulators), control of light emission intensity from organic light emitting diodes (e.g. thermally-activated delayed fluorescence), spin injection, spin dynamics, and coherent optical interactions with single spins (color-center photonics). Highly sensitive room-temperature spin systems also feature prominently in proposals for very low power electronic logic.

This tutorial will provide an introduction to the materials and operating regimes that tend to exhibit room-temperature spin coherence and spin correlations, methods of calculating and measuring these properties, areas of initial application and critical open questions.
The theoretical criteria for a stable, room-temperature quantum coherent system will be described, and several examples will be presented. Methods of calculating the response of a quantum coherent system to external fields and perturbations will be presented, including density matrices, stochastic Liouville equations, and master equations. Recent progress in predicting specific quantum coherent systems, such as density functional theory for new color centers in wide-gap semiconductors, will be surveyed. The ideal performance of quantum spintronic devices will be compared with other sensors or information processing approaches.

2:15 PM
Quantum Spintronics of Organic Semiconductors Christoph Boehme; The University of Utah

Organic semiconductors provide a varied set of materials that exhibit quantum spintronic phenomena. The effects of spin coherence on charge conductivity in organics will be described, along with large room-temperature responses to magnetic fields. Resonant manipulation of spins in organic materials, detected by transport, will be introduced as a mechanism for a sensitive magnetometer. Spin-charge correlations in the spin Hall Effect and spin pumping will also be presented.

3:00 PM BREAK

3:30 PM
Optical Coupling to Quantum-Coherent Spins David D. Awschalom; The University of Chicago

Coherent coupling of light to spin coherent systems, especially for color centers in diamond and silicon carbide, will be described in detail. Nonequilibrium polarization/pumping, manipulation of the spin state, and efficient detection will be presented, along with criteria for pulse shaping that can be used for low-error manipulation of the spin state of a quantum coherent system.

4:15 PM
Photonics and Quantum Spintronics Evelyn Hu; Harvard University

The design, fabrication, and measurement of photonic devices that efficiently integrate a quantum coherent spin with a cavity will be described. Methods of manipulating the quantum spin to bring it into resonance with the cavity, such as through acoustic oscillations or electrical gates, will be presented. The figures of merit for spin-photon coupling will be derived and compared with state-of-the-art coupling of other quantum coherent systems.

SYMPOSIUM EP06

Coherent Electronic Spin Dynamics in Materials and Devices
November 26 - November 28, 2018

Symposium Organizers
Michael Flatté, University of Iowa
Evelyn Hu, Harvard University
Hideo Ohno, Tohoku University
Bernhard Urbaszek, CNRS

Symposium Support
Springer Nature

* Invited Paper

SESSION EP06.01: Novel State Manipulation of Coherent Defects in Diamond
Session Chair: Michael Flatté
Monday Morning, November 26, 2018
Hynes, Level 2, Room 204

8:15 AM *EP06.01.01
The Dawn of Quantum Networks Ronald Hanson; QuTech, Delft University of Technology, Delft, Netherlands.

Entanglement – the property that particles can share a single quantum state - is arguably the most counterintuitive yet potentially most powerful element in quantum theory. The non-local features of quantum theory are highlighted by the conflict between entanglement and local causality discovered by John Bell. Decades of Bell inequality tests, culminating in a series of loophole-free tests in 2015, have confirmed the non-locality of Nature.

Future quantum networks may harness these unique features of entanglement in a range of exciting applications, such as distributed quantum computation, secure communication and enhanced metrology for astronomy and time-keeping. To fulfill these promises, a strong worldwide effort is ongoing to gain precise control over the full quantum dynamics of multi-particle nodes and to wire them up using quantum-photonic channels.
Diamond spins associated with NV centers are promising building blocks for such a network as they combine a coherent electron-optical interface with a local register of robust and well-controlled nuclear spin qubits. Here I will introduce the field of quantum networks and discuss ongoing work with the specific target of realizing the first multi-node network wired by quantum entanglement.

8:45 AM *EP06.01.02
Spin and Orbital Resonance Driven by a Mechanical Resonator

Gregory Fuchs; Cornell University, Ithaca, New York, United States.

Creating and studying coherent interactions between solid-state quantum systems is a challenge at the intersection of atomic physics, condensed matter physics, and engineering. Efforts to create hybrid quantum systems are appealing because they enable the exploration of coherent interactions between a physical qubit and non-traditional degrees of freedom. For instance, there is a growing interest in mechanical motion as a “plastic” degree of freedom for coupling solid-state qubits, with the potential to form a coherent interface between them, and with light. This has motivated intense research into the coherent interactions between mechanical resonators and qubits formed from photons, trapped atoms, superconducting circuits, quantum dots, and nitrogen-vacancy (NV) centers in diamond, to name a few. I will describe our experiments to drive coherent resonance of NV center spins using gigahertz-frequency mechanical resonators through dynamic crystal lattice strain. In high-quality diamond mechanical resonators, we demonstrate coherent Rabi oscillations of NV center spins driven by mechanical motion instead of an oscillating magnetic field. We show that the mechanical resonator is a resource to prolog the NV center’s spin coherence. We also examine how strain can be used to control NV centers through their excited-state, either to control the spin at room temperature or the orbital states at low temperature. In particular, using resonant optical spectroscopy of an NV center coupled to a driven mechanical resonator, we demonstrate very-strongly driven orbital states. This includes the observation of coherent Raman sidebands out to nine orders, and multi-phonon Rabi coupling between two orbital states.


9:15 AM EP06.01.03
Using Microwaves to Study Charge State in NV Diamond

Diana Prado Lopes Aude Craik1, 3, Pauli Keihayias1, 2, Andrew S. Greenspon2, Xingyu Zhang3, Matthew Turner1, 2, Erik Bauch3, Jennifer Schloss4, 5, Connor Hart3, 4, Ronald Walworth1, 2, 4, and Evelyn Hu1; 1Department of Physics, Harvard University, Cambridge, Massachusetts, United States; 2Harvard-Smithsonian Center for Astrophysics, Harvard University, Cambridge, Massachusetts, United States; 3John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 4Center for Brain Science, Harvard University, Cambridge, Massachusetts, United States; 5Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

We present a novel, microwave-based technique for determining charge state of nitrogen-vacancy (NV) ensembles in diamond. The technique isolates, in situ, the spectral shape of the fluorescence contribution from neutral (NV0) and negatively-charged (NV-) defects, producing sample-specific results which take into account the effects of experimental conditions (such as illumination intensity and wavelength) and material properties (such as local strain and electric fields). Using this technique, we explore how ensemble charge state is affected by experimental and material parameters, and study the physics of NV ionization from the negative charge state. The method can also be applied to derive relative concentrations of other solid-state defects which exhibit a spin-dependent fluorescence contrast.

9:30 AM EP06.01.04
Surface Engineering for Shallow Nitrogen-Vacancy Centers in Diamond with Long Coherence Times

Sorawis Sangtawesin and Nathalie P. de Leon; Princeton University, Princeton, New Jersey, United States.

Nitrogen vacancy (NV) centers in diamond are point defects that exhibit excellent spin coherence at room temperature. When placed close to the surface, they can have strong interactions with other molecules, enabling a new form of nanoscale spectroscopy. However, surface defects can give rise to noise, and shallow NV centers exhibit rapid decoherence. We demonstrate a method for creating a well-ordered, oxygen-terminated surface that results in an improvement of NV spin coherence and magnetic field sensitivity by up to an order of magnitude. Careful control over surface morphology enables reversible and reproducible chemical termination, which we characterize using complementary surface spectroscopy tools: NV-based nanoscale spectroscopy to probe the nature of noise, and X-ray and electron spectroscopy to probe structure and chemical state. We find that the dominant contribution to NV decoherence is broadband magnetic noise arising from disorder at the surface.

9:45 AM BREAK

SESSION EP06.02: Novel Spin Centers in Wide-Gap Semiconductors
Session Chairs: Ronald Hanson and Evelyn Hu
Monday Morning, November 26, 2018
Hynes, Level 2, Room 204

10:15 AM *EP06.02.01
Controlling Defect Spin States with Photons, Magnons and Phonons

Brian Zhou1, Paolo Andrich1, Samuel Whiteley1, F. Joseph Heremans2 and David Awschalom2, 3; 1University of Chicago, Chicago, Illinois, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

There is a growing interest in exploiting the quantum properties of electronic and nuclear spins for the manipulation and storage of quantum information. Current efforts embrace materials with incorporated point defects, whose unique quantum mechanical electronic and nuclear spin properties allow a fundamentally different means to process information. Here we focus on recent developments in manipulating and connecting spins in both silicon carbide (SiC) and diamond. We find that defect-based electronic states in SiC can be isolated at the single spin level [1] with surprisingly long spin coherence times and high-fidelity control within a wafer-scale material operating at near-telecom wavelengths. Similarly, the spin-photon interface in diamond offers an opportunity to implement all-optical, geometrically protected quantum spin gates [2] for quantum information processing. Moreover, we present pathways for connecting isolated electronic spins using magnons and phonotors. Exploring a hybrid qubit-magnon system, we use surface-confined spin-wave modes...
in YIG thin films to perform long-range coherent control of spins in diamond nanoparticles [3]. The magnon modes amplify the oscillating field of the microwave source by more than two orders of magnitude, thereby efficiently driving remote spin states. In addition, fabricated surface acoustic wave resonators exploit both the piezoelectric and isotropic phonon properties of SiC to create Aufler-Townes splittings and mechanically drive coherent Rabi oscillations between arbitrary ground-state spin levels, including magnetically forbidden spin transitions [4].


10:45 AM EP06.02.02
Photoluminescence Characterization of Precisely Located Si Vacancies in 4H-SiC Created via Li+ Implantation

Shojan P. Pavumuny1, Edward Bieger2, Sam Carter1, Hunter Banks1, Rachael Myers-Ward1, Paul Klein1, Mathew Dejarld1, Allan Bracker1, Evan Glaser1 and D. Kurt Gaskill2; 1U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Sandia National Laboratories, Albuquerque, New Mexico, United States; 3KeyW Corp., Arlington, Virginia, United States.

Silicon vacancies (V0) in SiC are of interest for future applications in quantum information and quantum sensing mainly due to the long electronic spin (S = 3/2) coherence times at room temperature. A key requirement for many applications is the precise placement of V0 in a photonic crystal cavity (PhC) as the resulting Purcell enhancement improves the emission rate (brightness) of the photoluminescence (PL) as well as increases photon indistinguishability. Here we show that Li+ ions, implanted with energy 100 keV using a maskless focused ion beam technique (∼25 nm diameter spot positioned with ∼25 nm accuracy and having an ion travel depth of ~400 nm), create V0 in the material. To facilitate PL characterization, arrays of locations were implanted into epitaxial 4H-SiC with doses ranging from 1018 to 1020 Li+ cm−2. Epitaxial SiC is chosen as we have shown it has no measurable V0. Using a 745 nm excitation source, we find that the PL in the range of 860 to 975 nm is dominated by the V1′, V1, and V2 lines of V0. Furthermore, the PL saturates at an excitation intensity of ~1 mW focused to a diameter of ~1 μm. The PL intensity of V1′ for a high implantation dose is found to be constant on a time scale of many hours. Additionally, the V1′ intensity is linear with implantation dose. Moreover, we will describe data that indicates single V0 formation at the lowest doses. Lastly, given the encouraging results to-date, we will discuss utilizing this approach with a PhC.

11:00 AM EP06.02.03
Spectrally Stable Defect Qubits for Quantum Communication with No Inversion Symmetry

Péter Udvarhelyi1, 2 and Adam Gal3, 4; 1Eötvös Loránd Science University, Budapest, Hungary; 2Wigner Research Centre for Physics, Hungarian Academy of Science, Budapest, Hungary; 3Budapest University of Technology and Economics, Budapest, Hungary.

In this paper, we show that the inversion symmetry is not a prerequisite criterion for a spectrally stable defect quantum emitter. An ideal quantum emitter does not couple to the stray electric fields upon optical transition but the optical transition dipole moment should be strong for bright emission. These two conditions can be simultaneously satisfied for such defect quantum emitters that exhibit identical electron density in the ground and excited state to eliminate the coupling to the stray electric fields but the sign of the corresponding wavefunctions alters accordingly to maximize the optical transition dipole moment. These properties can be principally manifested for defect qubits without inversion symmetry.

We demonstrate by means of density functional perturbation theory calculations that the so-called V1 optical center, i.e., negatively charged Si-vacancy, in 4H silicon carbide (SiC) tends to possess such favorable properties where 4H SiC can only host defects without inversion symmetry.

The support from NKFII (Grant Nos. 2017-1-1.1.1-NKP-2017-00001, NKPV_161-2016-0043 and NN127002) and the EU Commission is acknowledged.

11:15 AM *EP06.02.04
Coherence Properties of Shallow Donors in ZnO

Xiayu Linpeng1, Maria Viitaniemi1, Aswin Vishnuradh1, Y. Kozuka1, 2, Cameron Johnson1, Masashi Kawasaki1 and Ken-Mei Fu1, 2; 1University of Washington Dept. of Physics, Seattle, Washington, United States; 2Electrical Engineering, University of Washington, Seattle, Washington, United States.

Defects in crystals are leading candidates for photon-based quantum technologies, but progress in developing practical devices critically depends on improving defect optical and spin properties. Motivated by this need, we study a new defect qubit candidate, the shallow donor in ZnO. We demonstrate all-optical control of the electron spin state of the donor qubits and measure the spin coherence properties. We find a longitudinal relaxation time T1 exceeding 100 ms, an inhomogeneous dephasing time T2* of 17 ns, and a Hahn spin-echo time T2 of 50 μs. The magnitude of T2* is consistent with the inhomogeneity of the nuclear hyperfine field in natural ZnO. Possible mechanisms limiting T2 include instantaneous diffusion and nuclear spin diffusion (spectral diffusion). These results are comparable to the phosphorous donor system in natural silicon, suggesting that with isotope and chemical purification long qubit coherence times can be obtained for donor spins in a direct band gap semiconductor.

11:45 AM EP06.02.05
Room-Temperature Magneto-Optical Signatures of Defect Spins in Hexagonal Boron Nitride

Patel2, Marcus W. Doherty3 and Lee Bassett2; 1Physics, Lafayette College, Easton, Pennsylvania, United States; 2Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, United States; 3Research School of Physics and Engineering, Laser Physics Centre, Australian National University, Canberra, Australian Capital Territory, Australia.

Optically addressable spins associated with defects in wide-bandgap semiconductors have emerged as leading platforms for diverse applications in quantum information science and other quantum technologies, where spin-dependent inter-system crossing (ISC) transitions facilitate optical spin initialization and readout. Recently, the van der Walls material hexagonal boron nitride (h-BN) has emerged as a robust host for quantum emitters (QEs). Compared to traditional three-dimensional semiconductors like diamond and silicon carbide, h-BN promises unique capabilities for applications where defects couple to an external environment, such as sensing or nanophotonics, since defects exist at or very near atomically flat surfaces.

An outstanding question, however, has been whether h-BN can host QEs with an accessible spin degree of freedom, which could be used as qubits similar to the diamond nitrogen vacancy center. We report* our recent observations of a room-temperature magneto-optical response from select QEs in h-BN where the strongly anisotropic photoluminescence (PL) patterns as a function of applied magnetic field are markedly different from well-known spin
defects in diamond and silicon carbide. We explore the anisotropic PL response due to an applied magnetic field through studies of an emitter’s spectral, polarization, and photo-dynamic responses. Using a theoretical approach based on simple symmetry considerations, analytical molecular orbital theory, and semiclassical simulations, we show that the field-dependent variations in the steady-state PL and photon emission statistics are consistent with an electronic model featuring a spin-dependent ISC between triplet and singlet manifolds, indicating that optically-addressable spin defects are present in h-BN, a versatile two-dimensional material promising efficient photon extraction, atom-scale engineering, and the realization of spin-based quantum technologies using van der Waals heterostructures.

This work is supported by the Army Research Office (W911NF-15-1-0589) and the Australian Research Council (DE170100169).


**SESSION EP06.03: Coherent Magnonis in Magnetic Insulators I**

**Session Chairs:** Michael Flatté and Gregory Fuchs

**Monday Afternoon, November 26, 2018**

**Hynes, Level 2, Room 204**

**1:30 PM **EP06.03.01

**Freestanding YIG Magnon Nanoresonators with Ultra-Low Damping**

**Georg Schmidt**

1 Institute für Physik, Universität Halle, Halle, Germany; 2 Interdisziplinäres Zentrum für Materialwissenschaften, Universität Halle, Halle, Germany.

Nano electromechanical systems are interesting candidates for quantum information processing technology. Typical examples are the transfer of energy between mechanical and electromagnetic oscillators [1,2], but also spin wave excitations, so called magnons, can be used. An ideal material in this respect is Yttrium Iron Garnet. It combines long lifetimes as well for spin waves (magnons) as for mechanical waves (phonons) and a coupling mechanism for both (magnetoelastic coupling or magnetostriction). In the case of magnon resonances the coupling of a single Qbit to a magnon mode in a YIG sphere has already been demonstrated and also coupling of magnons to phonons in YIG spheres of diameters of a few hundred microns has already been published[3]. However, these experiments are still limited to macroscopic YIG spheres which forbid the integration of thousands or even hundreds of thousands of devices which may ultimately be necessary if a useful quantum computer shall be realized. So making true 3D YIG nanoresonators would open up a new field of applications for nanoscillators and create new options for quantum computation. However, up to now no method was available to shape three dimensional nanostructures from monocrystalline YIG.

We have developed a process to fabricate high quality monocrystalline freestanding 3D YIG nanostructures which can be designed for example as suspended bridges or cantilevers [4]. But also suspended optical ring resonators or disks for optical whispering gallery modes or more complex structures are possible. For the fabrication we use an electron beam lithography based process which was originally designed to realize metallic air bridges by evaporation and lift-off [5]. A newly developed deposition process for YIG using pulsed laser deposition at room temperature [6] allows for the fabrication and lift-off of amorphous structures. Surprisingly subsequent annealing leads to monocrystalline bridges even if the length of the span is as large as several micrometers.

The structures were investigated using transmission electron microscopy indicating high crystalline quality. Detailed investigation of spin dynamics was done using time and spatially resolved Kerr microscopy. Here we see various standing spin waves including Damon Eshbach Modes and Backward Volume Modes. The minimum linewidth in ferromagnetic resonance at 8 GHz is as small as 140 μT while the intrinsic linewidth at zero field is 75 μT.

**2:00 PM **EP06.03.02

**Bose-Einstein Condensates of Magnons in Optical Cavities**

**Tianya Liu**

Tianjin Key Laboratory of Low Dimensional Functional Material Physics and Producing Technology and Department of Physics, Tianjin University, Tianjin, China.

Magnonics, a newly developing field of spintronics, has attracted much attention in the past decade. However, due to its large number of thermally excited magnons, most of experiments on magnonics remain in the classical regime, where incoherent magnons play an important role. By virtual of optical cavity, laser cooling of the magnon mode has been a potential step towards the quantum regime. Instead of preparing the magnon-vacuum state, here, we propose to form a macroscopically quantum coherent state of magnons—the magnon Bose-Einstein condensate (BEC)—in optical cavities made of magnetic solids. Our previous study has predicted that parametric pumping of magnons can be achieved in such a cavity with control light blue detuned from the cavity resonance. In this work, we study the dynamics of magnons excited by the optical cavity modes, and quantitatively estimate the requisite for preparing magnon BEC. By resolving magnon number states through spectroscopic measurements of cavity photons, the proposed method here may open up new directions for all-optical manipulation of quantum magnon states.

**2:30 PM **EP06.03.03

**Spin Current Drive by Thermal Nonequilibrium**

**Kevin S. E. Olsson, Kyongmo An, Jianshi zhou, Li Shi and Xiaoqin E. Li**

Univ of Texas-Austin, Austin, Texas, United States.

A central goal in spintronics is to develop devices that rely on the transfer of spin rather than charge. In magnetic insulators, magnons, quanta of collective spin excitations, carry a pure spin current and offer energy efficient information transport and processing. Several methods have been explored to generate spin currents in magnetic insulators, including spin pumping, the magnon Hall effect, and the spin Seebeck effect. Spin current is not a conserved quantity and may reduce via scattering processes involving angular momentum exchange. The spin relaxation extracted from earlier studies on YIG has yielded a value on the order of ~ 10 μs, which is rather different from the energy relaxation length. A spin current can be introduced by a large temperature gradient introduced by a heating laser. We quantify such as a thermally driven spin current and magnon-phonon nonequilibrium in YIG using spatially resolved
Brillouin light scattering technique. We obtain information on nonequilibrium spectral density and demonstrate that low-energy magnons have a longer spin relaxation length than that of high-energy magnons.

2:45 PM EP06.03.04 Coherent Magnonics in Vanadium Tetracyanoethylene Ezekiel Johnston-Halperin1, Michael Chilcote1, Harberts Megan1, Bodo Fuhrmann2, Katrin Lehmann2, Fransson Andrew1, Yu Lu1, Howard Yu1, Na Zhi1, Hong Tang3 and Georg Schmidt2; 1The Ohio State University, Columbus, Ohio, United States; 2Zentrum für Physik, Martin-Luther-Universität-Halle-Wittenberg, Halle, Germany; 3Chemistry, The Ohio State University, Columbus, Ohio, United States; 4Yale University, New Haven, Connecticut, United States.

The exploration of quantum magnonics relies implicitly on the ability to excite and exploit long lived spin wave excitations in a magnetic material. That requirement has led to the nearly universal reliance on yttrium iron garnet (YIG), which for half a century has reigned as the unchallenged leader in high-Q, low loss magnetic resonance and spin wave excitation despite extensive efforts to identify alternative materials. Recent work has identified the organic-based ferrimagnet vanadium tetracyanoethylenide (V[TCNE]2) as the first credible alternative to YIG. In contrast to other organic-based materials V[TCNE]2 exhibits a Curie temperature of over 600 K with robust room temperature hysteresis, sharp switching to full saturation, and magnetic resonance linewidths as low as 0.5 Oe at 9.86 GHz (quality factor ~ 8,000). Further, since V[TCNE]2 is grown via chemical vapor deposition (CVD) at 50 C it can be conformally deposited as a thin film on a wide variety of substrates. Here we will discuss the coherent coupling of distinct magnon modes within a V[TCNE]2 film that is templated by growth on a corrugated substrate. The resulting array of nanowire structures exhibits uniform ferromagnetic resonance (FMR) as well as a variety of exchange and dipole coupled standing wave modes defined by the lateral boundaries of the individual nanowires. Further, as the orientation of a DC applied magnetic field is varied between induced easy and hard magnetic axes we observe anticrossing behavior among these modes that indicates the constituent magnons are interacting in the strong coupling regime. In combination with low temperature CVD synthesis, these results demonstrate the unique ability to pattern on-chip high-Q magnonic structures with implications for emerging applications ranging from microwave electronics to quantum information systems.

3:00 PM BREAK

SESSION EP06.04: Dynamics and Magnetic Structure of Thin Magnetic Films

3:30 PM *EP06.04.01 Observation of Anomalous Magneto-Optical Kerr Effect in SrRuO3 Luyi Yang1,2 and E. Michael Barmann1; 1Physics, University of Toronto, Toronto, Ontario, Canada; 2Physics, Tsinghua University, Beijing, China.

We report the observation of anomalous magneto-optical Kerr effect in ferromagnetic strontium ruthenate (SrRuO3) thin films. We measure the polar Kerr signals as a function of an applied magnetic field. Apart from conventional hysteresis loops, the Kerr signals show additional hump features at small applied magnetic fields in certain thicknesses of the thin films. Similar to topological Hall effect, these hump features indicate the formation of topological spin textures (e.g. Skyrmions) possibly induced by the gradient of the strain.

4:00 PM EP06.04.02 Current-Induced Magnetic Domain Wall Motion in Compensated Ferrimagnet Saima A. Siddiqui, Jiahao Han, Joseph Finley, Caroline A. Ross and Luqiao Liu; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Antiferromagnetic materials show promises compared to ferromagnetic materials for spintronic devices due to their immunity to external magnetic fields and their ultra-fast dynamics. However, difficulties in controlling and determining their magnetic state are limiting their technological applications. At the compensation point, the two antiparallel sub-lattices in a ferrimagnet have the same magnetic moment and the material is an antiferromagnet. Compensated ferrimagnets are expected to exhibit fast magnetic dynamics like an antiferromagnet and yet their magnetic state can be manipulated and detected like a ferrimagnet, and therefore, have been pursued as a candidate system for ultrafast spintronic applications. Previously, it was demonstrated that current-induced spin orbit torque could provide an efficient switching mechanism for a compensated ferrimagnet. However, limited by the quasi-static measurement technique, the nature of the switching dynamics in these experiments are yet to be revealed. In this work, we provide the first experimental proof of current-induced fast domain wall (DW) motion in a compensated ferrimagnet. Using a magneto optic Kerr effect microscope, we determine the spin orbit torque-induced DW motion in Pt/Co1-xTbx microwires with perpendicular magnetic anisotropy. The DW velocity is determined as a function of applied current amplitude. A large enhancement of the DW velocity is observed in angular momentum compensated Pt/Co80Tb20 microwires compared to single layer or multi-layer ferromagnetic wires. Using analytical model, we also find that near angular momentum compensation point, the domain walls do not show any velocity saturation unlike ferromagnets or uncompensated ferrimagnets since both the effective gyromagnetic ratio and effective damping diverge at this composition. Moreover, by studying the dependence of the domain wall velocity with the longitudinal in-plane field, we identify the structures of ferrimagnetic domain walls across the compensation points. The high current-induced domain wall mobility and the robust domain wall chirality in compensated ferrimagnets open new opportunities for spintronic logic and memory devices.

4:15 PM EP06.04.03 Non-Volatile Control of Anti-Ferromagnetic Néel Vector in α-Fe2O3 Through Hydrogen Doping Hariom Jani1,2, Jiajun Linghu1, Rajesh Chopdekar1, Saima A. Siddiqui1, Jiahao Han, Joseph Finley, Caroline A. Ross and Luqiao Liu; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

α-Fe2O3 hosts in-plane Antiferromagnetism (AFM) at room temperature, possessing spin canting due to the Dzyaloshinskii-Moriya interaction. Just 10°C
below zero, bulk α-Fe$_2$O$_3$ undergoes Morin transition where the AFM spins re-orient colinearly along the out-of-plane symmetry axis. This first-order transition emerges due to the competition between magnetic-dipolar and single-ion magnetic anisotropies which have different magnitudes and temperature dependences.

We have developed a catalytic process for doping hydrogen into the α-Fe$_2$O$_3$ lattice, which allows non-volatile tuning of the AFM Néel vector and the accompanying spin canting. We discover that hydrogen doping also increases the electronic conductivity of α-Fe$_2$O$_3$ by three orders of magnitude. Moreover, owing to the light mass of a hydrogen atom, our H-doping process can be performed post-growth and is also reversible.

We characterize the new α-Fe$_2$O$_3$H$_x$ phase via Reciprocal Space Mapping, Raman and UV-Vis Spectroscopy, Scanning Tunneling Electron Microscopy and X-Ray Magnetic Linear Dichroism. We use Elastic Recoil Detection Analysis to prove that hydrogenation indeed causes incorporation of H atoms in the α-Fe$_2$O$_3$ lattice. X-Ray Absorption Near Edge Structure and ab-initio calculations reveal that the hydrogenation induced magnetic and electric modulations in α-Fe$_2$O$_3$ are concomitant with electron doping and not due to any structural changes of the lattice. This Electronic doping plays a crucial role in tuning the relative magnitude of the single-ion anisotropy with respect to the magnetic-dipolar counter-part, causing the modulation of the Morin transition. Our approach opens new avenues for control of anti-ferromagnetism in oxide systems.

4:30 PM EP06.04.04
The Role of Mn and Si Co-Doping on the Ferromagnetic and Optical Properties of MOCVD GaN Layers for Spintronic Applications
N Ben Sedrine1, Vishal Saravade2, Amirhossein Ghods2, C. Zhou2 and I. T. Ferguson2; 1Departamento de Física e I3N, Universidade de Aveiro, Aveiro, Portugal; 2Missouri University of Science and Technology, Rolla, Missouri, United States.

Wide bandgap dilute magnetic semiconductors (DMS) have increasing interest due to their room temperature (RT) ferromagnetism. DMS can be integrated into existing electronic and optoelectronic devices, and are expected to support the transport and storage of spin for the next generation of electronic devices. RT ferromagnetic hysteresis has been observed in GaN doped with transition metal or rare earth ions, and that it can be controlled by different parameters such as: doping concentration, Si co-doping, and annealing. However, the mechanism behind the ferromagnetism is not well understood and needs further investigation for spintronic applications.

In this work, Mn and Si co-doping effects in GaN layers are investigated. Un-doped GaN, Ga$_{1-x}$Mn$_x$N and Mn and Si co-doped GaN layers grown on sapphire by MOCVD, with different Mn and Si concentrations, are studied using magnetometry measurements. Ferromagnetic hysteresis was recorded in the Ga$_{1-}$Mn$_x$N layers at 300 K. However, for Si-doped Ga$_{1-x}$Mn$_x$N layers, the magnetization is found to decrease when Si concentration increases. It seems that Si compensates or shifts the acceptor levels in Ga$_{1-x}$Mn$_x$N, which are introduced by Mn-doping and contribute to the ferromagnetism [1]. Photoluminescence (PL) studies performed as a function of temperature and excitation power, from ultraviolet (UV) to the near-infrared energy regions. In Ga$_{1-x}$Mn$_x$N layers, 14 K PL emissions exhibit well resolved near band edge (NBE) emission, UV luminescence (UVL), and a yellow luminescence (YL) band, while for Mn and Si co-doped layers, noticeable changes in the NBE and a suppression of the UVL were observed. For the same experimental conditions, overall PL intensity increases with increasing Mn concentration, but drastically decreases for the Mn and Si co-doped samples. For the highest Mn concentration, the 14 K NBE emission exhibits several sharp peaks, while, Mn and Si co-doping induces a broadening of the NBE.

Understanding of defects in GaN and their effects on the ferromagnetic and optical properties is a crucial step towards using GaN for spintronics.

References:

4:45 PM EP06.04.05
Electronic Transport in Ballistic InSb Nanowires with Ferromagnetic Contacts
Zedong Yang1, Yifan Jiang2, Sasa Gazibegovic3, Ghada Badawy3, Paul Crowell1, Sergey Frolov2, Erik P. Bakkers1 and Vlad Pribiag1; 1University of Minnesota, Minneapolis, Minnesota, United States; 2University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 3Eindhoven University of Technology, Eindhoven, Netherlands.

InSb semiconductor nanowires (NWs) are a versatile semiconductor platform that has enabled investigations of Majorana bound states [1,2] and spin-based qubits [3]. Among their remarkable properties are large mobilities (up to ~20,000 cm²/Vs), very large Landé g-factors (up to ~50) and strong spin-orbit coupling (SOC). The large SOC and quasi-1D nature makes InSb nanowires interesting for all-electrical control of single spins, as demonstrated previously [4], and also offers the possibility to control electrically spin currents (as yet undemonstrated).

We fabricated InSb nanowire devices with ferromagnetic contacts (FM) to investigate spin transport. Conductance quantization plateaus in the back-gate sweep measurement demonstrate quasi-one-dimensional ballistic transport in these FM/NW/FM structures. We observe hysteretic features when varying the applied magnetic field, which could indicate spin injection from the FM contacts and transport in the quasi-1D InSb channel.

References:
Trivalent rare earths (REs) exhibit fascinating spectroscopic, luminescent, and magnetic properties. REs have higher magnetic moment (Er$^{3+}$ = 9.59 mB and Yb$^{3+}$ = 4.5 mB) than transition metals. La$_2$Sr$_2$Mn$_2$O$_7$ (LSMO) is a highly spin polarized materials with room temperature ferromagnetism. In this work, we report the effect of RE co-doping (Er$^{3+}$ and Yb$^{3+}$) on photomagnetic behavior and infrared spectra of LSMO. In order to study the multifunctional effect, LSMO was co-doped with different concentrations of RE ($1\%$, $2\%$ and $3\%$) at the La-site. The microstructure, phase separation, electric and magnetic properties of LSMO was measured using energy dispersive x-ray spectroscopy (EDXS), scanning electron microscopy (SEM), X-Ray diffraction (XRD) and a physical properties measurement system (PPMS). The electronic states of the dopants are investigated by photoelectron spectroscopy (XPS). Magnetic and photomagnetic measurements were carried out using SQUID magnetometry with visible and infrared excitation. Measurements of magnetoresistance at room temperature showed that Er$^{3+}$ and Yb$^{3+}$ ions have also great influence on the magnetic and electric ordering of LSMO under the influence of UV light and they can effectively enhance the magnetotransport properties of LSMO.

**ACKNOWLEDGMENTS**

The authors are grateful for the support given from the UEMA, IFMA, FAPEMA.

3 Cheng Gong, Lin Li, Zhenglu Li, Huiwen Ji, Ting Cao, Wei Bao, Chenzhe Wang, Yuan Wang, Z. Q. Qi, R. J. Cava, Steven G. Louie, Jing Xia, Xiang Zhang, Nature 546, 265 (2017)
Initial solid-state qubit implementations have shown great promise but currently suffer from non-robust qubit generation and significant active cooling requirements. Flying qubit designs have emerged as an approach for adding dynamic control to solid-state qubit implementations. The flying qubit approach utilizes surface acoustic (SAW) wave interaction(s) for the capture and transport of a single or few electron(s) from a reduced dimensionality electron pool. Electron transport between quantum dots over a several-microns distance has been experimentally demonstrated [1] and theoretical investigations for spin-entangled electron qubits show promise [2]. In previous work, we investigated the effect of the SAW wave longitudinal component modelled as perturbation to the k-space momentum in the transport direction for a heterostructure based finite width 1D channel using the lowest energy parameter [7].

With further analysis, a conclusion could be drawn that the magnetism modulation is mainly attributed to the interfacial strain level of an infinite potential well for the transverse electron confinement [3]. In the present work, the infinite potential well is replaced with a more realistic parabolic confinement in the transverse direction. Derivation of a new expression for number density enables first-time investigations of quantum channel accessibility and number density allowed occupations as a function of semiconductor effective mass. Results for devices with gallium arsenide versus gallium nitride as the confinement layer are presented.

REFERENCES
Level Attraction—Magnon-Photon Coupling Takes a New Form

Can-Ming Hu; University of Manitoba, Winnipeg, Manitoba, Canada.

Cavity Spintronics [1] (also known as Spin Cavitronics) is a newly developing interdisciplinary field that brings together microwave cavity community with researchers from spintronics. This field started around 2014 when it was found that ferromagnets in cavities hybridize with both microwaves and light via light-matter interaction [2-6]. Since then, the emergence of this field has attracted broad interests. It connects some of the most exciting modern physics, such as quantum information and quantum optics, with one of the oldest science on the earth, the magnetism.

So far, at the center stage of this new field is the coherent magnon-photon coupling, which leads to level repulsion by producing a quasi-particle called cavity magnon polariton (CMP)[5-7]. In this talk, I will report our latest experiment that reveals magnon-photon level attraction [8]. Based on dissipative magnon-photon coupling, this effect is distinct from traditional level repulsion, resulting in the coalescence of hybridized modes at zero detuning in contrast to the Rabi gap observed in CMP systems. The experimental features of these new hybridized states can be accounted for by the magnetization back action which exists inside the cavity, and are revealed by our experiments due to the ability to control such a cavity Lenz effect. Exploiting this capability, we observe the transition between attraction and repulsion behavior, revealing the sharp transition which exists between the two effects. As observation of coherent magnon-photon coupling has spawned the field of cavity-spintronics, this new form of magnon–photon coupling may open up new avenues for exploiting the light-matter interactions using cavity spintronic approach.


8:30 AM EP06.06.02
Selection Rules for Cavity-Enhanced Brillouin Light Scattering from Magnetostatic Modes

James A. Haigh¹, Nicholas Lambert², Sanchar Sharma³, Yaroslav Blanter⁴, Gerrit Bauer⁵ and Andrew Ramsay¹; ¹Hitachi Cambridge Laboratory, Cambridge, United Kingdom; ²Cavendish, University of Cambridge, Cambridge, United Kingdom; ³Delft University of Technology, Delft, Netherlands.

We present measurements of enhanced Brillouin light scattering from magnons in yttrium iron garnet spheres. Optical whispering gallery modes confined at the surface by total internal reflection are coupled to the ferromagnetic resonance modes via the Faraday effect. Our experiments on optical coupling in this manner have demonstrated an enhancement in magnon Brillouin light scattering when the system is tuned to a triple-resonance point [1]. This occurs when both the input and output optical modes are resonant with those of the whispering gallery resonator, with a separation given by the ferromagnetic resonance frequency. Extending the measurements to higher order magneto-static modes [2], we have confirmed recent theoretical predictions [3] of the selection rules for scattering, dependent on the mode indices of the optical and magnetic modes. We give experimental evidence that the opto-magnonic coupling to non-uniform magnons can be higher than that of the uniform Kittel mode, due to the better spatial overlap with the optical modes.


SESSION EP06.07: Coherent Spin Dynamics in 2D Materials

Session Chairs: Ezekiel Johnston-Halperin and Bernhard Urbaszek
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 204

8:45 AM *EP06.07.01

Intrinsic Exciton Valley Dynamics in Semiconductor Monolayers and Heterostructures

Xiaqin F. Li; Univ of Texas-Austin, Austin, Texas, United States.

Monolayer transition metal dichalcogenides (TMDs) have a hexagonal lattice structure in which the extrema (i.e., valleys) of the energy-momentum dispersion curves appear at two degenerate $K$ and $K'$ points at the boundary of the Brillouin zone. Time-reversal symmetry dictates that the electron spins in the $K$ and $K'$ valleys have opposite signs, effectively locking the spin and valley DoF. Valley pseudospin has been proposed and pursued as an alternative information carrier to charge. Optical manipulation of the valley index via excitons (neutral and charge exciton) requires the knowledge of valley polarization and valley coherence dynamics. Nonlinear resonant spectroscopy studies reveal intrinsic valley ultrafast dynamics inaccessible via simple linear spectroscopy measurements such as photoluminescence. We report valley decoherence measurements associated with excitons and trions in monolayers. We also discovered an exceptionally long valley polarization time associated with intra-valley excitons. Finally, we discuss our most recent studies on interlayer excitons in TMD vertical heterostructures.

9:15 AM EP06.07.02

Defects in 2D Materials from First Principles for Applications in Quantum Information Science

Chris Ciccareno¹, ², Dan Wang³, Ravishankar Sundararaman³, Dirk R. Englund⁴ and Prineha Narang¹; ¹John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; ²Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; ³Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; ⁴Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent decades have seen tremendous progress towards low-dimensional electronic structures in solids that exhibit atom-like properties. While this
Spin Relaxation in 2D Semiconductors with an Elliptic Band Structure
Seyed Mohammad Farzaneh and Shaloo Rakheja; New York University, Brooklyn, New York, United States.

Coherent spin distribution can be used to transport information through semiconductors. The relaxation dynamics of the spin distribution is key in analyzing experimental data and enabling spin-based device applications. For most spin transport applications, a long spin relaxation time is desirable. Two-dimensional (2D) materials, such as monolayer black phosphorus (BP), have a weak intrinsic spin-orbit interaction and are expected to have long spin relaxation times, which could allow spin-encoded information to travel macroscopic distances in these materials. Moreover, an external electric field perpendicular to the plane of the 2D materials is an effective method to tune their spin-transport characteristics. Monolayer BP has a highly anisotropic band structure with an elliptic Fermi contour due to its puckered honeycomb structure. The anisotropy in the band structure leads to anisotropic momentum relaxation, anisotropic Rashba spin-orbit coupling, and, therefore, anisotropic spin relaxation. The goal of this work is to theoretically investigate spin relaxation in 2D semiconductors that have intrinsic anisotropy as well as other 2D materials in which mechanical strain results in ellipticity of the band structure. Two major relaxation mechanisms, namely D'yakonov-Perel' (DP) and Elliot-Yafet (EY), are taken into account to calculate the spin relaxation time. Within the DP theory, spin relaxation occurs due to the scattering-induced motional narrowing of spin precession about the Rashba spin-orbit field, which is the result of broken inversion symmetry in the presence of an external electric field. Per the EY mechanism, which is present in centro-symmetric structures like BP, spin flipping at momentum scattering events causes nonequilibrium spin population to relax. We model the elliptic band structure using the effective mass approximation and quantify the impact of effective mass anisotropy on the spin relaxation anisotropy. More specifically, we demonstrate how fast a spin ensemble relaxes for a given initial polarization. The results from the DP and EY mechanisms are compared to determine the dominant spin relaxation mechanism in experimental samples. Finally, the results are used to predict the impact of mechanical strain on spin relaxation.

10:30 AM EP06.07.03
Spin Relaxation in 2D Semiconductors with an Elliptic Band Structure
Seyed Mohammad Farzaneh and Shaloo Rakheja; New York University, Brooklyn, New York, United States.

In the last 20 years, several optical and electrical methods have been used to demonstrate how change in the dimensionality of a GaAs-based semiconductor system (bulk - 3D, quantum well - 2D, quantum dot - 0D) affects the spin relaxation rate over the broad range of technologically relevant doping levels (N_d above 10^{14} cm^{-3} and below 10^{10} cm^{-3}), and temperature ranges (~ 1K – 300K). This work represents advances in the use of Spin Noise Spectroscopy (SNS) [1,2] aiming to understand the level of control over the spin relaxation rate in two cases: (a) varied dimensionality of GaAs based spintronic devices with the focus on differences between the available ranges of spin relaxation values driven by the changing dimensionality of GaAs systems, and, more specifically (b) voltage and geometry control of spin relaxation rate in quasi-1D nanowires. Compared to bulk (3D), quantum wells (2D) and quantum dots (0D), there have been comparatively fewer studies that focused on spin relaxation in two other systems: (a) 1D (quantum wires), and (b) quasi-1D semiconducting nanowires. Our interest in such systems stems from the belief that quantum wires and nanowires will play important role as interconnects in future quantum devices, especially in hybrid photonic-electronic spintronic quantum devices. To this end, we fabricated the semiconductor nanowires with controllable dimensionality, so that the cross section of the NWs is in the range (10-100 nm x 10-50 nm), with length in micrometer range. We report on the spin relaxation range between 20 and 300 ns, depending on temperature, magnetic field and doping. We also report on some qualitative differences between the behavior of spin relaxation rate for quasi-1D systems on one side, and 2D and 0D systems on the other. Two additional facets of this work are: (1) electric field dependent studies, and (2) nanowire aspect ratio studies. Electric field dependence is studied after the contacts were nanopatterned at the end of nanowires, using end contacts technology [3]. It is shown that the change of the applied voltage within 1.5 V range may affect the spin relaxation rate more by 40%, for selected values within that range. Additionally, the voltage dependent study is then conducted for a variety of controllable external conditions. Changes in aspect ratio (width-to-thickness) of GaAs nanowires also affect the spin relaxation rate, pointing towards the need to optimize the NW dimensions prior to quantum spintronic devices implementation. A part of this work was supported by US DoE Office of Basic Sciences at Brookhaven National Laboratory. We acknowledge support from GRC-SRC, and partial support from 2012 KUIRF-Level 1, and 2015 ADEC-A2RE grants.

References:

10:45 AM EP06.07.04
Spin Relaxation in Quasi-1D GaAs Nanowires - Spin Noise Spectroscopy and Electric Field Dependence
Stefania Castelletto1, Deborah L. Gater2, T. Alkhidir3 and Abdel F. Isakovîc1,2; 1KUST, Abu Dhabi, United Arab Emirates; 2CNF, Cornell University, Ithaca, New York, United States; 3RMIT University, Melbourne, Victoria, Australia.

In the last 20 years, several optical and electrical methods have been used to demonstrate how change in the dimensionality of a GaAs-based semiconductor system (bulk - 3D, quantum well - 2D, quantum dot - 0D) affects the spin relaxation rate over the broad range of technologically relevant doping levels (N_d above 10^{14} cm^{-3} and below 10^{10} cm^{-3}), and temperature ranges (~ 1K – 300K). This work represents advances in the use of Spin Noise Spectroscopy (SNS) [1,2] aiming to understand the level of control over the spin relaxation rate in two cases: (a) varied dimensionality of GaAs based spintronic devices with the focus on differences between the available ranges of spin relaxation values driven by the changing dimensionality of GaAs systems, and, more specifically (b) voltage and geometry control of spin relaxation rate in quasi-1D nanowires. Compared to bulk (3D), quantum wells (2D) and quantum dots (0D), there have been comparatively fewer studies that focused on spin relaxation in two other systems: (a) 1D (quantum wires), and (b) quasi-1D semiconducting nanowires. Our interest in such systems stems from the belief that quantum wires and nanowires will play important role as interconnects in future quantum devices, especially in hybrid photonic-electronic spintronic quantum devices. To this end, we fabricated the semiconductor nanowires with controllable dimensionality, so that the cross section of the NWs is in the range (10-100 nm x 10-50 nm), with length in micrometer range. We report on the spin relaxation range between 20 and 300 ns, depending on temperature, magnetic field and doping. We also report on some qualitative differences between the behavior of spin relaxation rate for quasi-1D systems on one side, and 2D and 0D systems on the other. Two additional facets of this work are: (1) electric field dependent studies, and (2) nanowire aspect ratio studies. Electric field dependence is studied after the contacts were nanopatterned at the end of nanowires, using end contacts technology [3]. It is shown that the change of the applied voltage within 1.5 V range may affect the spin relaxation rate more by 40%, for selected values within that range. Additionally, the voltage dependent study is then conducted for a variety of controllable external conditions. Changes in aspect ratio (width-to-thickness) of GaAs nanowires also affect the spin relaxation rate, pointing towards the need to optimize the NW dimensions prior to quantum spintronic devices implementation. A part of this work was supported by US DoE Office of Basic Sciences at Brookhaven National Laboratory. We acknowledge support from GRC-SRC, and partial support from 2012 KUIRF-Level 1, and 2015 ADEC-A2RE grants.

References:

10:00 AM BREAK

SESSION EP06.08: Advances in Sensing Enabled by NV Diamond
Session Chair: Maria Vladimirova
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 204

10:30 AM EP06.08.01
Exploring Condensed Matter Systems Using Diamond Magnetometry
Amir Yacoby; Harvard University, Cambridge, Massachusetts, United States.

NV magnetometry has become a powerful tool for exploring magnetic properties of novel electronic systems. In this talk I will give an overview of some
of the recent work we have done to use NV center magnetometry to image skyrmions in thin magnetic films, measure the spin chemical potential in magnetic insulators, and image hydrodynamic electron flow in graphene.

11:00 AM *EP06.08.02
Exploring Magnetism at the Nanoscale with a Single Spin Microscope Vincent Jacques, Laboratoire Charles Coulomb, UMR 5221, CNRS and Université Montpellier, Montpellier, France.

In the past years, it was realized that the experimental methods allowing for the detection of single spins in the solid-state, which were initially developed for quantum information science, open new avenues for high sensitivity magnetometry at the nanoscale. In that spirit, it was proposed to use the electronic spin of a single nitrogen-vacancy (NV) defect in diamond as an atomic-sized magnetic field sensor [1,2]. This approach promises significant advances in magnetic imaging since it provides non-invasive, quantitative and vectorial magnetic field measurements, with an unprecedented combination of spatial resolution and magnetic sensitivity under ambient conditions.

In this talk, I will show how scanning-NV magnetometry can be used as a powerful tool for exploring exotic spin textures in thin magnetic materials focusing on (i) domain walls and magnetic skyrmions in ultrathin ferromagnets [3,4] and (ii) cycloidal antiferromagnetic order in multiferroic materials [5].


11:30 AM *EP06.08.03
Diamond Electronics for Quantum Sensing Mutsuko Hatano and Takayuki Iwasaki, Tokyo Institute of Technology, Tokyo, Japan.

Nitrogen-vacancy (NV) centers in diamond have superior physical properties at room temperature for quantum sensing of the magnetic field, electronic field, temperature, and pressure enabling scalable applications from atomic-scale to macroscopic range. We would like to introduce our recent progress on materials, devices, and protocols;

- Materials: Selectively-aligned (> 99%) NV ensemble formed by distinctive CVD-growth with precise depth control for scalable applications [1-3].
- Sensing devices: Charge state control of NV centers by band-gap engineering using pn junctions [4,5].
- Protocols: The iterative Qdyne protocol for wide field NMR imaging with MHz frequency resolution and nT sensitivity

For applications, we will introduce biological imaging, nano-scale NMR [3], macro-scale magnetometer [6] and its portable prototype, and internal device sensing [7].

This work was supported in part by JST-CREST Grant No. JPMJR1333, KAKENHI (17H01262 and 18H01472), and JSPS Bilateral Open Partnership Joint Research Projects.


SESSION EP06.09: Coherent Dynamics from Nuclear and Ionic Spins in Semiconductors
Session Chairs: Vincent Jacques and Amir Yacoby
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 204

1:30 PM *EP06.09.01
Nuclear Spin System in GaAs—Cooling, Relaxation and Spin Temperature Concept Maria Vladimirova1, Steeve Cronenberger1, Denis Scalbert1, Mladen Kotara2, Roslan Dzhioev3, Ivan Ryzhov3, Valerii Zapasskii3, Gleb Kozlov1, Aristide Lemaître1 and Kirill Kavokin2, 3; 1Laboratoire Charles Coulomb, CNRS-University of Montpellier, Montpellier, France; 2Ioffe Institute, St Petersburg, Russian Federation; 3Spin Optics Laboratory, St-Petersburg State University, St Petersburg, Russian Federation; 4Centre de Nanosciences et de nanotechnologies, CNRS, Université Paris-Saclay, Université Paris-Sud, Marcoussis, France.

Cooling of nuclear spins in doped semiconductors via their dynamic polarization by optical pumping is a powerful method for harnessing ubiquitous fluctuations of nuclear spin, which constitute a well-known decoherence channel for the electronic spins. The idea of spin cooling is based on the hypothesis of spin temperature, which states that nuclear spin system (NSS) reaches an internal thermal equilibrium long before it comes to equilibrium with the external bath (crystal lattice). Although thermodynamic framework has been successfully employed for the description of a variety of the experimental data, a rigorous check of this concept in semiconductors was impossible until recently, in particular at low magnetic field. The reason for that is the lack of experimental techniques allowing nonperturbative optical control over adiabatic transformation of the NSS.

We have recently developed such methods, based on off-resonant Faraday rotation and spin noise spectroscopy [1, 2]. Using these techniques, combined with dark-interval photoluminescence spectroscopy, we established a comprehensive picture of the nuclear spin relaxation efficiency, its magnetic field, temperature, and carrier concentration dependence in doped GaAs, a model system in the field of nuclear spin physics in semiconductors [3-5]. We also analyzed the interplay between four relevant relaxation mechanisms: hyperfine interaction, quadrupole interaction, spin diffusion and Korringa mechanisms.

Understanding of field dependence of NSS dynamics allowed us to obtain a new insight into the NSS thermodynamics, and verify the spin temperature
concept in GaAs bulk material and microcavities [6]. We have demonstrated, that NSS exactly follows the predictions of the spin temperature theory, despite the quadrupole interaction that was earlier reported to disrupt nuclear spin thermalization in quantum dots [7]. Our results open a way for the deep cooling of nuclear spins in semiconductor structures, with the prospect of realizing nuclear spin-ordered states for high-fidelity spin-photon interfaces.

This work is supported by a joint grant of the Russian Foundation for Basic Research (RFBR, Grant No. 16-52-041301-4 and National Center for Scientific Research (CNRS, PRC SPINCOOL, No. 148362).

References:

Electrically Tunable Dynamic Nuclear Spin Polarization in GaAs Quantum Dots at Zero Magnetic Field

Marco Manca1, Gang Wang1, Takashi Kuroda2, Shivangi Shree1, Andrea Balocchi1, Pierre Renucci1, Xavier Marie1, Mikhail Durnev3, Mikhail Glazov3, Kazuaki Sakoda2, Takaaki Mano2, Saeedi Ilkhchy2, Peter Christianen3 and Ben Murdin1; 1Advanced Technology Institute, University of Surrey, Guildford, United Kingdom; 2FELIX Israel Inst of Tech, Haifa, Israel.

The control of individual spins in semiconductor quantum dots is limited by interactions with the nuclear spin bath fluctuations because the carrier and nuclear spins are efficiently coupled through the hyperfine interaction especially in III-V nano-structures with Ga, Al and In where 100 % of nuclei have non-zero nuclear spin.

On the other hand, the stable nuclear spins themselves can potentially be used as a resource for quantum information storage. Semiconductor quantum dots allow manipulating a mesoscopic ensemble of several thousand nuclear spins by optical manipulation of a single carrier spin, but commonly nuclear spin polarization manipulation is achieved in applied magnetic fields of several Tesla, a major drawback for practical applications.

In this work we show that both the sign and amplitude of optically generated dynamic nuclear polarization can be switched electrically in experiments at zero magnetic field, through the application of a bias voltage to our device based on charge tunable GaAs droplet dots grown by MBE on 111A substrates [1].

We demonstrate dynamic nuclear polarization (DNP) at zero magnetic field in a single quantum dot for the positively charged exciton X+ state transition. We tune the DNP in both amplitude and sign by variation of an applied bias voltage Vg. Variation of Vg on the order of 100 mV changes the nuclear spin polarization from -22% to +7% although the X+ photoluminescence polarization does not change sign over this voltage range. This indicates that absorption in the structure and energy relaxation towards the X+ ground state provide favorable scenarios for efficient electron-nuclear spin flip-flops, generating DNP during the first tens of ps of the X+ life-time, which is on the order of hundreds of ps.

We also present Hanle spin depolarization experiments for electrons and nuclei in transverse magnetic fields, which confirm the dependence of dynamic nuclear spin polarization on the applied bias. First results on all electrical nuclear spin manipulation at zero magnetic field are discussed for a SpinLED device [2].


Magneto-Optical Properties of Magnetically Doped Semiconductor Nanocrystals Controlled by Spin-Spin Interactions

Efrat Lifshitz; Technion-Israel Inst of Tech, Haifa, Israel.

The control of individual spins in semiconductor nanocrystals is an emerging scientific field which undoubtly play an important role in the development of new spin-based technologies. Generation of individual spins via incorporation of magnetic ions into colloidal nanocrystals became a hot topic in recent years. These diluted magnetic semiconductor (DMS) nanocrystals are subject to a size confinement on photo-generated carriers, which markedly enhances the mutual carrier-dopant spin-exchange interaction, consequently leading to a pronounced modification of the host's optical and magneto-optical properties.

Here we described the synthesis and characterization of DMS nanocrystals based on colloidal nanoplatelets, rods or spherical host semiconductor matrices, embedded with extremely low concentration of Mn2+ ions. This work includes host nanocrystals with a core/shell design (one semiconductor covered by another semiconductor) with dopant ions positioned either in the core or in the shell, using the layer-by-layer deposition. Thus, the work here discusses the influence of internal design on the magneto-optical properties of DMS colloidal nanocrystals. The research involved the use of magneto-photoluminescence (MPL) and optically detected magnetic resonance (ODMR) spectroscopy. The MPL spectra recorded at various temperatures and strength of magnetic field revealed the generation of giant magnetization (~ 30 Tesla) and g-factor (~4) of the exciton upon doping. The ODMR spectra of those samples designated a resonance line with a distinguished sextet related to the hyperfine interaction between the photo-generated electron and the surrounding nuclear spins of the dopants. The ODMR explored, for the first time, a control of nuclear spins on the magneto-optical properties of DMS nanocrystals. Furthermore, a time resolved ODMR experiment also revealed a shortening of the spin coherence time with respect to estimations, due to the hyperfine interaction. The carrier-nuclear spin may occur either directly, or mediated via the carrier-dopant electron spin (the sp-d interaction).

[1].

2:30 PM EP06.09.04

High Field Spin Resonance of Shallow Donors in Silicon

Gemma Chapman1, Konstantin Litvinenko1, Dmytro Kamenskyi2, Viktoria Eless2, Kamyar Saeedi Ilkhchy2, Peter Christensen3 and Ben Murdin3; 1Advanced Technology Institute, University of Surrey, Guildford, United Kingdom; 2FELIX Laboratory, Radboud University, Nijmegen, Netherlands; 3High Field Magnet Laboratory, Radboud University, Nijmegen, Netherlands.

Single impurities in silicon are a key contender in the development of quantum technology applications. Donors can be placed and isolated within silicon with atomic resolution and have exceedingly long spin and orbital coherence times, leading to many potential spin-based quantum information architectures. High magnetic fields are an important tool for the control of impurity-based qubit structures. External fields manipulate the wave-functions of bound states allowing controlled modulation of the interaction between neighbouring impurities. Additionally, it has been shown that applying a gradient magnetic field can be used to read out the spin state of a bound donor. A potential quantum computing scheme could use magnetic fields to transfer quantum information along chains of qubits, before being manipulated and read out electrically through the external magnetic field. While spin dynamics at
low field is well understood, knowledge of spin dynamics under high magnetic fields is limited.

Through the use of a tuneable microwave free electron laser and a helium-isolated bitter magnet, we have developed a scheme to investigate the spin dynamics of Group V donors in silicon in fields up to 25 T. Real-time photoconductivity measurements of the bound-exciton have demonstrated incoherent control of the population of the ground state of phosphorous impurities and resolution of the relaxation dynamics of the system.

We acknowledge the support of the HFML, member of the European Magnetic Field Laboratory (EMFL) and the Engineering and Physical Sciences Research Council (EPSRC, UK) via its membership to the EMFL (grant EP/N01085X/1).”

2:45 PM EP06.09.05
Theory of the Circulating Current of a Single Magnetic Impurity in a Semiconductor Adonai R. Cruz1 and Michael Flatté2; 1Eindhoven University of Technology, Eindhoven, Netherlands; 2The University of Iowa, Iowa City, Iowa, United States.

The localized electron spin of a single impurity in a semiconductor is a promising system to realize quantum information schemes [1]. Coherent control of this spin depends on understanding the structure of the magnetic moment that couples the system with external fields. In this work we investigate the spin-orbit induced circulating current associated with the ground state of a single magnetic impurity in zincblende III-V semiconductor. This circulating current is dissipationless and represents an electron moving in a closed trajectory producing an orbital contribution to the magnetic moment [2]. We developed a formalism employing Green's functions obtained by the Koster-Slater technique [3] with a sp3d5s* empirical tight-binding Hamiltonian [4,5] to describe the interaction of individual atoms.

Our work provides a powerful probe of the quantum states of electron and nuclear spins for individual atoms and nanostructures. Magnetic structures built extending from dipole to exchange interactions. We find that increasing the interaction strength between the spins of two atoms enhances the degree of the mixing of quantum spin states, enabling us to create robust singlet and triplet states. We show that a two level system composed of these singlet and triplet states is insensitive to local and global magnetic field noise, resulting in longer spin coherence times compared to single atoms.

We also measured the hyperfine interactions of individual atoms on a surface. Taking advantage of atom manipulation, we show that the hyperfine splitting strongly depends on the binding site of surface atoms as well as the proximity of other magnetic atoms. The observed hyperfine spectra enable us to deduce position-dependent information about the electronic ground state, the state mixing with neighboring atoms, and properties of the nuclear spin.

Our work provides a powerful probe of the quantum states of electron and nuclear spins for individual atoms and nanostructures. Magnetic structures built using spin-1/2 atoms may serve as the smallest component for assembling custom spin chains and arrays for the exploration of quantum phases, spintronic information processing, and quantum simulation.

3:00 PM BREAK

SESSION EP06.10: Electrical Coherence of Localized Spin States
Session Chairs: Nathalie de Leon and Michael Flatté
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 204

3:30 PM *EP06.10.01
Electrically-Driven Spin Resonance of Surface Atoms Yujeong Bae1, 2, 3, Kai Yang2, Philip Willke1, 2, 3, Andreas Heinrich1, 3 and Christopher Lutz2; 1Center for Quantum Nanoscience, Institute for Basic Science, Seoul, Korea (the Republic of); 2IBM Almaden Research Center, San Jose, California, United States; 3Physics, Ewha Womans University, Seoul, Korea (the Republic of).

Meticulous control of spin states is of central importance in spin-based information processing and spintronic devices. Electron spin resonance (ESR) combined with atom manipulation in a scanning tunneling microscope (STM) provides electrical access to spin structures constructed on a surface with atomic precision. In this talk, we demonstrate precise measurement and control of (i) the magnetic interactions between surface atoms and (ii) the hyperfine interaction of individual atoms.

The magnetic interactions between two spin-1/2 atoms on a surface were tailored via atom manipulation, resulting in a wide range of coupling strengths, extending from dipole to exchange interactions. We find that increasing the interaction strength between the spins of two atoms enhances the degree of the mixing of quantum spin states, enabling us to create robust singlet and triplet states. We show that a two level system composed of these singlet and triplet states is insensitive to local and global magnetic field noise, resulting in longer spin coherence times compared to single atoms.

We also measured the hyperfine interactions of individual atoms on a surface. Taking advantage of atom manipulation, we show that the hyperfine splitting strongly depends on the binding site of surface atoms as well as the proximity of other magnetic atoms. The observed hyperfine spectra enable us to deduce position-dependent information about the electronic ground state, the state mixing with neighboring atoms, and properties of the nuclear spin.

Our work provides a powerful probe of the quantum states of electron and nuclear spins for individual atoms and nanostructures. Magnetic structures built using spin-1/2 atoms may serve as the smallest component for assembling custom spin chains and arrays for the exploration of quantum phases, spintronic information processing, and quantum simulation.

4:00 PM EP06.10.02
Proposal for Measurement of Coherent Spin Dynamics of Individual Magnetic Dopants in a Semiconductor Using Low-Field Magnetoresistance of Spin-Polarized Scanning Tunneling Spectroscopy Stephen R. McMillan, Nicholas J. Harmon and Michael E. Flatté; The University of Iowa, Iowa City, Iowa, United States.

Individual magnetic impurities or small collections of magnetic impurities in III-V semiconductors can be identified via scanning tunneling microscopy (STM) [1,2], their exchange interaction can be measured [3], and they can have remarkably long spin coherence times [4]. Spin-1/2 impurities are able to be addressed individually and the eigenstates tailored allowing the construction of engineered spin networks [5]. We describe an approach to explore the coherent spin dynamics of a spin-1/2 defect coupled to an additional spin-1/2 defect via exchange interaction with a spin-polarized STM contact through low-field magnetoresistance. Our model utilizes a single site approximation and a stochastic Liouville equation allows for the calculation of steady state currents through the mediating defect. The inherent anisotropy [2,3,5,6] in conjunction with the applied magnetic field should allow one to describe a single spin Hanle curve. In addition, measurements of the spin coherence time and the local hyperfine interaction should be feasible. This analysis is then used to guide the exploration of coherent spin-dynamics involving coupled Mn-hole complexes in III-V semiconductors.

Spinning and Variable Range Hopping in a Highly Disordered Dielectric—Amorphous SiOC:H and SiOC:D

Spin dependent variable range hopping (SDVHR) is observed through changes in currents which are almost certainly due to spin dependent variable range hopping. The study includes extensive comparisons of the EDMR response as a function of voltage applied across thin films in metal-oxide-silicon structures. Comparisons of these films. The EDMR is observed through changes in currents which are almost certainly due to spin dependent variable range hopping. The study includes extensive comparisons of the EDMR response as a function of voltage applied across thin films in metal-oxide-silicon structures. Comparisons of the EDMR versus voltage response and fairly well understood band diagrams provide information about the defect densities of states. We have exploited the fact that EDMR sensitivity is very nearly independent of the field and frequency at which the measurements are made. Comparison of EDMR measurements at high (9.5GHz) and low (about 100 MHz) frequencies help to deconvolute contributions to the spectra from hyperfine and spin orbit coupling. EDMR results also include comparisons with films in which hydrogen was replaced with deuterium. These comparisons also provide information about hyperfine interactions. In these hydrogen/deuterium comparisons, some structures were subjected to ionizing radiation, a process which considerably altered the defect structures. Our results allow some (somewhat tentative) conclusions to be drawn with regard to defect structure and also provide semiquantitative information about defect energy levels as well as defect-hydrogen interactions.

Charge State of Single and Ensemble Nitrogen Vacancy Center in Diamond n-i-n Junctions

Negatively charged nitrogen vacancy center (NV–) has attracted considerable interest over the past years since it is promising for magnetometer, quantum information science and biosensors. For these applications, controlling the charge state of NV center is essential, since NV– center is sometimes unstable and may transition to NV0 in uncontrollable ways. Recently, we have demonstrated that the charge state is controlled in n-type-intrinsic-n-type (n-i-n) diamond junctions[1][2]. In this method, NV centers were formed in the undoped i-layer where impurity concentration is very low and we can control Fermi energy (EF) externally using standard band engineering techniques. Therefore, both the long spin coherence time (T2) and the stabilization of NV– centers can be obtained simultaneously. We showed that the E2 in the i-layer was controlled via the band bending at the two n-i junctions and the ratio of NV– to NV0 centers was increased by reducing the width of the i-layer between the two n-layers. However, the spatial change of charge state of NV center in depletion region and neutral region near the n-i junctions were not examined in detail and the relationship between the measured photoluminescence (PL) spectra of ensemble of NV center and a single NV center is not clear.

In this work we first predict using the k.p method and the valence band anti-crossing theory that the common III-V InAs0.85Bi0.15 /AlSb quantum well becomes a room temperature 2D topological insulator for well thickness d ≤ 6.9nm. Second, we analytically solve the correspondent BHZ model for our TI by introducing a cylindrical confinement defining cylindrical quantum dots (QDs). Surprisingly, we find for the non-topological QDs “geometrically protected” discrete helical edge states, i.e., Kramers pairs with spin-angular- momentum locking, similar to the topological protected helical edge states within the gap in the topological QDs. We calculate the circulations currents associated to both trivial and topological edge states and find no substantial difference between them. The two terminal conductance calculation for two pairs of edge states as a function of the QD radius and the gate controlling its levels with respect to the Fermi energy of the leads shows a double peak at 2e2/h for both topological and trivial QDs. In conclusion, our results blur the boundaries between topological and non-topological QDs as for the protection of the helical edge states, their calculated circulating currents and their two terminal conductance measurements.

Charge State of Single and Ensemble Nitrogen Vacancy Center in Diamond n-i-n Junctions

Maki Shimizu1, Toshiharu Makino1, Hiromitsu Kato2, Masanori Fujiwara3, Takayuki Iwasaki4, Satoshi Yamasaki2, Norikazu Mizuochi3 and Mutsuko Hatano4; 1Tokyo University of Science, Shinjuku, Japan; 2National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 3Kyoto University, Uji, Japan; 4Tokyo Institute of Technology, Meguro, Japan.

Negatively charged nitrogen vacancy center (NV–) has attracted considerable interest over the past years since it is promising for magnetometer, quantum information science and biosensors. For these applications, controlling the charge state of NV center is essential, since NV– center is sometimes unstable and may transition to NV0 in uncontrollable ways. Recently, we have demonstrated that the charge state is controlled in n-type-intrinsic-n-type (n-i-n) diamond junctions[1][2]. In this method, NV centers were formed in the undoped i-layer where impurity concentration is very low and we can control Fermi energy (EF) externally using standard band engineering techniques. Therefore, both the long spin coherence time (T2) and the stabilization of NV– centers can be obtained simultaneously. We showed that the E2 in the i-layer was controlled via the band bending at the two n-i junctions and the ratio of NV– to NV0 centers was increased by reducing the width of the i-layer between the two n-layers. However, the spatial change of charge state of NV center in depletion region and neutral region near the n-i junctions were not examined in detail and the relationship between the measured photoluminescence (PL) spectra of ensemble of NV center and a single NV center is not clear.

In this study, we fabricated multilayer of n-i-n junction to investigate spatial change of the charge state of single and ensemble of NV centers along the junction. We measured the PL spectra of ensemble NV centers by continuous laser illumination which caused the stochastic charge state transitions between NV– and NV0. We also measured the population of each charge state of single NV center by single shot measurement. The charge state depended on the band structure calculated by the Poisson equation in both of the measurements. The proportion of NV– gradually increased in the vicinity of n-i junctions where it was considered to be depletion layer, and did not change at the center. This work was supported by JST CREST Grant Number JPMJCR1333, Japan
In the Edelstein effect, a current in the crystal induces a spin polarization. It occurs in crystals without inversion symmetry, such as Rashba systems and surfaces of topological insulators. The spin polarization vanishes in equilibrium, but in the presence of the current, the electron distribution becomes off-equilibrium, giving rise to nonzero spin polarization, due to the spin-split band structure.

We propose an analogous effect for orbital angular momentum [1,2]. For example, in crystal with helical structure such as tellurium (Te) [3], we propose that a current along the helical axis induces an orbital magnetization [1,2] as well as spin magnetization. This effect is analogous to solenoids in classical electromagnetics. Within this analogy to solenoids, we quantify this effect by introducing a dimensionless parameter $\xi$, which represents a number of turns within the unit cell when regarded as a classical solenoid. Then we found that $\xi$ is largely enhanced when the system is in the Weyl semimetal phase [1,2].

Here the Weyl semimetal phase [4] is allowed by broken inversion symmetry, and it is shown that Te becomes a Weyl semimetal at higher pressure [3,5]. There are other crystal structures that allow Edelstein effects, and we also demonstrate the orbital Edelstein effect for polar systems. Moreover, we propose a similar effect appears for phonons. In crystals, each phonon eigenmode has angular momentum due to rotational motions of the nuclei, but their sum is zero in equilibrium. Meanwhile a heat current in the Te crystal induces a nonzero total angular momentum [6]. We evaluate this effect for GaN and Te by ab initio calculation, and propose experiments to measure this effect.


8:30 AM EP06.11.02 Anisotropic g-Factors of Bi-Sb Alloys Cumeet Sahin and Michael E. Flatté; Univ of Iowa, Iowa City, Iowa, United States.

Bismuth and bismuth-based materials with small band gaps and large spin-orbit couplings exhibit novel physical phenomena such as three-dimensional topological insulator phases [1] and giant spin Hall conductivities [2]. Furthermore, prediction [3] and a recent discovery of the Weyl semimetal phase [4] with the chiral anomaly in the Bi and Sb alloys demonstrate the rich physics of these materials. In this work, we calculate another spin-orbit interaction related term, the g-factor in the BiSb alloys. Early studies of the g-tensor with a two band k.p approach [5] are valid only for electrons, and a more recent multi-band k.p model [6] is accurate just for electrons and holes. The magnitude of g-factor may change dramatically in a crystal as a result of the crystal potential and the spin-orbit interaction, which makes the g-factor a band structure dependent, an intrinsic property of the crystal. Additionally, g-factor is a direction dependent property in a crystal; therefore it is a rank two tensor.

Here we present a full Brillouin zone calculation of the g-factor using a 16 band tight-binding Hamiltonian of the BiSb alloys. To calculate effective g-factors of bismuth and antimony alloys, we model electronic bands and eigenfunctions using a Slater-Koster type tight-binding technique with parameters taken from a previous study [7] and investigate the behavior of conductance and valence band edges. In addition to the tight-binding Hamiltonian, we include a spin-orbit Hamiltonian with spin-orbit couplings of 1.5 eV and 0.6 eV for Bi and Sb respectively.

We calculate the electronic band structure from the tight-binding Hamiltonian for different concentration of antimony using the virtual crystal approximation. As the antimony concentration is increased the band overlap disappears and a semimetal-semiconductor transition occurs. Further increase in the antimony concentrations leads to a faster shift in the valence band than the conduction bands. Therefore, an indirect gap opens, leading to topologically insulating (TI) phase. BiSb alloys also display a Weyl semimetal with chiral anomaly within the range of the TI phase. For bismuth, holes are located at the T point in the Brillouin zone whereas electrons are at the L point. As a result of the symmetry of the T point, $g_z$ is the only non-zero g-factor element where $z$ is along the trigonal axis. However, at the L point, we observe substantial g-tensor elements for both pure Bi and BiSb alloys that differ in magnitude. In conclusion, we show that bismuth, antimony and bismuth-antimony alloys exhibit giant anisotropic g-factors.


8:45 AM EP06.11.03 Tuning Spin-Charge Interconversion with Quantum Confinement in Ultrathin Bismuth Films Matthieu Janet1, Carlo Zucchi2, Federico Bottegoni3, Celine Vergnaud1, Thomas Guillier1, Alain Marty1, Cyrille Beigne1, Serge Gambarelli1, Andrea Picone1, Alberto Calloni2, Gianlorenzo Bussetti2, Lamberto Duò3, Franco Ciccacci4, Pranab Kumar Das1, Jun Fujii4, Ivana Vobornik4, Marco Finazzi2 and Minh-Tuan Du4; 1CEA Grenoble, Grenoble, France; 2Politecnico di Milano, Milan, Italy; 3National University of Singapore, Singapore, Singapore; 4Elettra, Trieste, Italy.

Bismuth exhibits a series of electronic properties that made it the subject of experimental and theoretical interest for decades, in particular in electronic-transport studies [Y. Fuseya et al., J. Phys. Soc. Jpn. 84, 012001 (2015)]. With a lattice structure close to that of graphene and a very large spin-orbit coupling, bismuth may have the potential to be a topological semimetal or semiconductor [L. Aguilera et al., Phys. Rev. B 91, 125129 (2015)]. In order to explore this possibility, we have grown by molecular beam epitaxy (MBE) ultrathin films of Bi on Ge[111]. Indeed, MBE gives the opportunity to grow metastable allotropic phases of Bi or to induce strain into bulk Bi which may give topological properties to this material. Moreover, the growth of such phase on germanium opens new perspectives to use the electron spin in traditional microelectronics. In this study, we have grown a bismuth wedge (0-15 nm) on Ge[111] by MBE. Using structural characterization (RHEED and x-ray diffraction), we found a critical thickness of 5 nm below which Bi exhibits an allotropic pseudocubic phase. A careful angle-resolved and spin-resolved photoemission spectroscopy study using synchrotron radiation (ELETTRA, Italy) showed that the pseudocubic phase exhibits surface states with a quasi-linear band dispersion and a characteristic helical spin texture. We have then investigated the spin-to-charge interconversion at these surface states using 3 different techniques: magneto-optical Kerr effect to probe the Rashba-Edelstein effect (REE), inverse REE using optical spin orientation in the Ge film beneath and finally spin pumping from a ferromagnetic layer grown on top of Bi separated by an Al spacer. We found a clear signature of the strong spin-to-charge interconversion in these surface states only in the regime where...
Bi grows in the form of nanocrystals on Ge(111). We could demonstrate that this effect is the result of a strong quantum confinement in the Bi nanocrystals [C. Zucchetti et al., arXiv:1805.01841].

9:00 AM EP06.11.04

Epitaxial BaTiO₃ on Ge as a Tunnel Barrier for Charge and Spin Injection Yichen Jia, Cristina Visani, Charles H. Ahn and F. J. Walker; Yale University, New Haven, Connecticut, United States.

The epitaxial integration of functional oxides on conventional semiconductor opens new opportunities for coupling their unique properties with semiconductors for post-CMOS technologies. Here we demonstrate a spin-injection device based on epitaxial BaTiO₃ on Ge (001) heterostructures. We first show spin accumulation in the p-type Ge and measure a sizeable spin lifetime in the semiconductor. The magnitude of the spin injection signal can be quantitatively explained using a two-channel spin transport model with one channel due to spin injection into germanium and the other due to injection into interfacial localized states (ILS). We also demonstrate control of the spin signal by manipulating the band profile across the heterojunction, which modulates the charge transport between impurity-assisted conduction and quantum mechanical tunneling, effectively acting as a “switch” for spin injection.

9:15 AM EP06.11.05

Spin Injection into Epitaxially-Grown β-FeSi₂ in Lateral Structural Spin-Valves Hiroki Ishimoto1, Tetsuo Taber2, Ken-ichiro Sakai2 and Tsuyoshi Yoshitake1; 1Applied Science for Electronics and Materials, Kyushu University, Kasuga-shi, Japan; 2Research Institute for Nanodevice and Bio Systems, Hiroshima University, Higashihiroshima, Japan; 3Control and Information Systems Engineering, Kurume College, Kurume-shi, Japan.

Since giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) effects were discovered, spintronics have received much attention from physical and scientific viewpoint. Spintronics is the fusion field of electronics and magnetics, which is utilizing not only the electrical charge but also electrical spin of an electron. GMR and TMR, which employ nonmagnetic metal and insulator as interlayers, respectively, have already been applied to magnetic heads and magnetic random access memories (MRAM). On the other hands, semiconductor spintronics employing semiconductor interlayer such as Si, Ge, and GaAs has actively been developed. Employing semiconductor has the following merits: (i) crystal growth and process techniques have been already matured; (ii) physical properties change significantly by control of carriers; and (iii) electronic devices and their large scale integration (LSI) techniques have been well-establish. Therefore, Spin-devices comprising semiconductors have a potential compatibility with present semiconductor devices. As fundamental preparation researches for such an application, we have studied spin injection into nanocrystalline FeSi₂ with vertical-type spin-valves. Since spin is easily scattered at grain boundaries, high purity of crystallinity is desirable for the application of the spin-devices. Semiconducting β-FeSi₂ has been attracting much attention as a possible candidate compatible with Si technologies because β-FeSi₂ can be grown epitaxially on Si (111) substrates with small lattice mismatches of -5 to 2 %. Furthermore, it has a large absorption coefficient of over 10⁴ cm at 1.5 eV, and it is a candidate semiconductor applicable to optoelectronic applications. Our laboratory has ever succeeded in the epitaxially growth of β-FeSi₂ films on Si (111) substrates at a substrate temperature of 600 °C by facing target direct current sputtering (FTDCS). So far, there have been few studies on the spin injection into β-FeSi₂. In this study, based on experimental techniques in the previous studies, lateral-type spin-valves comprising β-FeSi₂ films were fabricated, and spin injection and transport were experimentally studied. Lateral-type spin-valves were prepared by electron beam lithography combined with the deposition of semiconducting β-FeSi₂ films and ferromagnetic metal Fe films, and a mask method. The magnetoresistance (MR) curve in local-structure was measured at room temperature by a vibrating sample magnetometer (VSM). From the measurement of MR curves, it was confirmed high and low electrical resistance values are owing to the antiparallel and parallel alignments of the Fe layers magnetization are clearly realized. It was experimentally demonstrated that β-FeSi₂ is applicable to interlayers of spin valves that work at room temperature. Further systematic experiments are conducted and results will be reported at the conference.

9:30 AM EP06.11.06

Non-Local Opto-Electrical Spin Injection and Detection in Germanium at Room Temperature Matthew Janer1, Fabien Rortais2, Carlo Zucchet3, Lavina Ghiardini1, Celine Vergnaud1, Julie Widen1, Alain Marty1, Laurent Vila1, Jean-Philippe Attane1, Henri Jaffres1, Jean-Marie George1, Michele Celerbro1, Giovanni Isella1, Franco Ciccarel1, Marco Fina2 and Federico Bottegoni1; 1CEA Grenoble, Grenoble, France; 2University of Kyoto, Kyoto, Japan; 3Politecnico di Milano, Milan, Italy; 4Unité Mixte CNRS-Thales, Palaiseau, France.

Non-local charge carrier injection/detection schemes lie at the very foundation of information manipulation in integrated systems. The next generation electronics may operate on the spin instead of the charge and germanium appears as the best hosting material to develop such spintronics due to its compatibility with mainstream silicon technology and long spin lifetime at room temperature. Moreover, the energy proximity between the direct and indirect bandgaps allows for optical spin injection and detection within the telecommunication window. In this presentation, we demonstrate injection of pure spin currents (i.e. with no associated transport of electric charges) in germanium, combined with non-local spin detection blocks at room temperature [C. Zucchetti et al., Phys. Rev. B 96, 014403 (2017), F. Rortais et al. Appl. Phys. Lett. 111, 182401 (2017)]. Spin injection is performed either electrically through a magnetic tunnel junction (MTJ) or optically, exploiting the ability of lithographed nanostructures to diffuse the light and create an in-plane polarized electron spin population. Pure spin current detection is achieved using either a MTJ or the inverse spin-Hall effect (ISHE) across a Pt stripe. These results first show that the spin diffusion length in low-doped germanium can be as long as 10 µm and broaden the palette of tools available for the realization of opto-spintronic devices.

9:45 AM EP06.11.07

Electronic Raman Scattering in Ge Studied by Circular-Polarized Femtosecond Excitation Correlation Photoluminescence Yuhsuke Yasutake and Susumu Fukatsu; Graduate School of Arts and Sciences, University of Tokyo, Tokyo, Japan.

Germanium (Ge) has received the renewed interest in light of not only optoelectronic but also spintronic advantages. In fact, its relatively small offset between the indirect and direct valleys (ca. 140 meV) permits direct-gap optical transitions while crystal inversion symmetry, fewer nuclear spins and the fairly large spin-orbit splitting (ca. 290 meV) promise the manipulation of electron spin polarizations. Fairly large spin-orbit splitting (ca. 290 meV) promise the manipulation of electron spin polarizations.

Since spin is easily scattered at grain boundaries, high purity of crystallinity is desirable for the application of the spin-devices. Semiconducting β-FeSi₂ has been attracting much attention as a possible candidate compatible with Si technologies because β-FeSi₂ can be grown epitaxially on Si (111) substrates with small lattice mismatches of -5 to 2 %. Furthermore, it has a large absorption coefficient of over 10⁴ cm at 1.5 eV, and it is a candidate semiconductor applicable to optoelectronic applications. Our laboratory has ever succeeded in the epitaxially growth of β-FeSi₂ films on Si (111) substrates at a substrate temperature of 600 °C by facing target direct current sputtering (FTDCS). So far, there have been few studies on the spin injection into β-FeSi₂. In this study, based on experimental techniques in the previous studies, lateral-type spin-valves comprising β-FeSi₂ films were fabricated, and spin injection and transport were experimentally studied. Lateral-type spin-valves were prepared by electron beam lithography combined with the deposition of semiconducting β-FeSi₂ films and ferromagnetic metal Fe films, and a mask method. The magnetoresistance (MR) curve in local-structure was measured at room temperature by a vibrating sample magnetometer (VSM). From the measurement of MR curves, it was confirmed high and low electrical resistance values are owing to the antiparallel and parallel alignments of the Fe layers magnetization are clearly realized. It was experimentally demonstrated that β-FeSi₂ is applicable to interlayers of spin valves that work at room temperature. Further systematic experiments are conducted and results will be reported at the conference.

9:30 AM EP06.11.06

Non-Local Opto-Electrical Spin Injection and Detection in Germanium at Room Temperature Matthew Janer1, Fabien Rortais2, Carlo Zucchet3, Lavina Ghiardini1, Celine Vergnaud1, Julie Widen1, Alain Marty1, Laurent Vila1, Jean-Philippe Attane1, Henri Jaffres1, Jean-Marie George1, Michele Celerbro1, Giovanni Isella1, Franco Ciccarel1, Marco Fina2 and Federico Bottegoni1; 1CEA Grenoble, Grenoble, France; 2University of Kyoto, Kyoto, Japan; 3Politecnico di Milano, Milan, Italy; 4Unité Mixte CNRS-Thales, Palaiseau, France.

Non-local charge carrier injection/detection schemes lie at the very foundation of information manipulation in integrated systems. The next generation electronics may operate on the spin instead of the charge and germanium appears as the best hosting material to develop such spintronics due to its compatibility with mainstream silicon technology and long spin lifetime at room temperature. Moreover, the energy proximity between the direct and indirect bandgaps allows for optical spin injection and detection within the telecommunication window. In this presentation, we demonstrate injection of pure spin currents (i.e. with no associated transport of electric charges) in germanium, combined with non-local spin detection blocks at room temperature [C. Zucchetti et al., Phys. Rev. B 96, 014403 (2017), F. Rortais et al. Appl. Phys. Lett. 111, 182401 (2017)]. Spin injection is performed either electrically through a magnetic tunnel junction (MTJ) or optically, exploiting the ability of lithographed nanostructures to diffuse the light and create an in-plane polarized electron spin population. Pure spin current detection is achieved using either a MTJ or the inverse spin-Hall effect (ISHE) across a Pt stripe. These results first show that the spin diffusion length in low-doped germanium can be as long as 10 µm and broaden the palette of tools available for the realization of opto-spintronic devices.
that SO-ERS ≈ 4 ps and direct-gap ≈ 200 ps.

10:00 AM BREAK

10:30 AM EP06.11.08
Ab Initio Electronic T1 Spin Relaxation Times in Silicon and Diamond Jinsoo Park, Jin-Jian Zhou and Marco Bernardi; Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States.

Spin relaxation in crystals with inversion symmetry primarily occurs through the Elliott-Yafet mechanism, in which the injected spins are scattered by phonons or impurities. We present an efficient first-principles approach for computing the Elliott-Yafet electronic spin relaxation time T1 in semiconductors and insulators. Our scheme combines ab initio electron-phonon scattering with a new approach to correctly treat degenerate electronic states. Application of our approach to silicon and diamond is discussed in this talk. Our computed spin relaxation times in silicon are in excellent agreement with experiment above 150 K, and we can also resolve the phonon modes that mainly contribute to spin relaxation. The temperature dependence of the spin relaxation times in silicon and diamond are analyzed, together with the contributions from intravalley and intervalley scattering. We show that intravalley scattering dominates at low temperature, and that intravalley and f-intervalley scattering becomes comparable at room temperature. Our work enables accurate ab initio calculations of the T1 spin relaxation time in a range of materials, providing new microscopic insight into spin relaxation.

SESSION EP06.12: Novel Spin Centers in Diamond
Session Chair: Michael Flatté
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 204

10:45 AM *EP06.12.01
Engineering Coherent Defects in Diamond Nathalie P. de Leon; Princeton University, Princeton, New Jersey, United States.

Engineering coherent systems is a central goal of quantum science and quantum information processing. Point defects in diamond known as color centers are a promising physical platform. As atom-like systems, they can exhibit excellent spin coherence and can be manipulated with light. As solid-state defects, they can be produced at high densities and incorporated into scalable devices. Diamond is a uniquely excellent host: it has a large band gap, can be synthesized with sub-ppb impurity concentrations, and can be isotopically purified to eliminate magnetic noise from nuclear spins. Specifically, the nitrogen vacancy (NV) center has been used to demonstrate basic building blocks of quantum networks and quantum computers, and has been demonstrated to be a highly sensitive, non-invasive magnetic probe capable of resolving the magnetic field of a single electron spin with nanometer spatial resolution. However, realizing the full potential of these systems requires the ability to both understand and manipulate diamond as a material. I will present two recent results that demonstrate how carefully tailoring the diamond host can open new opportunities in quantum science.

First, currently-known color centers either exhibit long spin coherence times or efficient, coherent optical transitions, but not both. We have developed new methods to control the diamond Fermi level in order to stabilize a new color center, the neutral charge state of the silicon vacancy (SiV-) center. This center exhibits both the excellent optical properties of the negatively charged SiV- center and the long spin coherence times of the NV center, making it a promising candidate for applications as a single atom quantum memory for long distance quantum communication.

Second, color centers placed close to the diamond surface can have strong interactions with molecules and materials external to the diamond, which makes them promising for nanoscale sensing and imaging. However, uncontrolled surface termination and contamination can degrade the color center properties and give rise to noise that obscures the signal of interest. I will describe our recent efforts to stabilize shallow NV centers within 5 nm of the surface using new surface processing and termination techniques. Specifically, we are able to demonstrate reversible and reproducible control over the top layer of atoms. These highly coherent, shallow NV centers will provide a platform for sensing and imaging down to the scale of single atoms.

11:15 AM EP06.12.02
Group-IV Defects in Diamond from First Principles Chris Ciccarino1, 2, Matthew Trusheim1, Dirk R. Englund1 and Prineha Narang1; 1John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 2Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; 3Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Color centers in diamond have emerged as leading solid-state "artificial atoms" for a range of technologies from quantum sensing to quantum networks. Concerted research activities are now underway to identify new color centers that combine the favorable spin properties of the diamond nitrogen vacancy (NV-) with the spectral stability of the silicon vacancy (SiV- ) center. Among the alternate color centers explored, the SiV- and PbV- centers, the latter of which we have investigated previously, are among the most promising candidates for application in spin-photon systems such as quantum repeaters and quantum networking. Characterizing these defect centers and their emission spectra remains an actively debated area of research. We use a combination of theory and experiment to study the PbV-, SiV- and the previously unexamined GeV- defects in diamond and determine the nature of these defect states. By leveraging theory to accurately predict vibrational effects as well as Jahn-Teller distortion, we capture experimentally accessible spectral features including the Debye-Waller factor and spin-orbit-quenched zero field splitting. Meanwhile, we identify potential experiments that can verify theoretical predictions and provide additional defect characterization data of interest, including the excited-state lifetime. Together with theory, these results provide new insight into the potential of these defect centers as single photon emitters for quantum information processing.

11:30 AM EP06.12.03
Diamond Color Centers Created by Implantation of Heavy IV-Group Elements of Tin and Lead Takayuki Iwasaki1, Yoshiyuki Miyamoto2, Takashi Taniguchi2, Petri Sivushev1, Matthias Metsch3, Fedor Jelezko4 and Matsuho Hatano5; 1Tokyo Institute of Technology, Tokyo, Japan; 2ALST (National Institute of Advanced Industrial Science and Technology), Ibaraki, Japan; 3National Institute for Materials Science, Ibaraki, Japan; 4Ulm University, Ulm, Germany.

Quantum emitters in diamond are expected to be important components toward the realization of quantum network. Although nitrogen-vacancy (NV) centers have been most intensively studied, they suffer from the low fraction of zero phonon line (ZPL) in the total fluorescence and external noise leading to the unstable emission line. To solve these problems, color centers based on the IV-group elements have recently attracted attention because of the large
ZPL and robustness of the emission line due to the inversion symmetry. Furthermore, a long spin coherence time over 10 ms has been reported for a silicon-vacancy (SiV) center at millikelvin temperatures [1]. It is expected that a heavier element with larger spin-orbit interaction can increase the ground state splitting to reduce the phonon-mediated decoherence. Thus, long spin coherence times can be expected at higher temperatures without a dilution refrigerator. In this study, we demonstrate the creation of a novel quantum emitter in diamond, called tin-vacancy (SnV) center [2], possessing a much larger ground state splitting than the SiV center, and we also discuss optical properties of diamond implanted with a heavier IV group element of lead (Pb). SnV centers were fabricated by ion implantation and subsequent high-pressure and high-temperature (HPHT) annealing over 2000 deg. Both single and ensemble SnV centers were formed. Pb ions were implanted into different diamond crystals, and the HPHT annealing was performed. The SnV center showed a sharp ZPL at 619 nm at room temperature, while it splits into four peaks at low temperatures, corresponding to split ground and excited states. The ground state splitting was estimated to be 850 GHz, which is 17 times higher than that of the SiV center. With this large value, we can expect a long spin coherence time for the SnV center in the kelvin regime. The first-principles calculations indicated the D3d symmetry of the SnV center, same as the SiV and GeV center. Thus, the stable emission of the SnV center can be also expected. Optical properties of Pb implanted diamond crystals were investigated. Note that independent works on the Pb-implanted diamonds have been very recently reported [3,4]. We observed prominent peaks at 551, 556, and 591 nm. However, we found that these peaks also appeared in a Sn implanted sample. Thus, at present, we speculate that these peaks are not related with Pb, but probably vacancies created by the implantation of the heavy atoms. Further efforts will be discussed for the fabrication of the Pb-related color center in diamond.

This work was supported in part by JST-PRESTO Grant No. JPMJPR16P2, JST-CREST Grant No. JPMJR1333, and JSPS Bilateral Open Partnership Joint Research Projects.


1:45 AM EP06.12.04
Lead-Related Quantum Emitters in Diamond Matthew Trusheim1, Noel Wan1, Kevin Chen1, Chris Ciccarino2, Ravishankar Sundararamam3, Eric A. Bersin1, Michael Walsh1, Benjamin Lienhard, Hassam Bakr1, Prineha Narang1 and Dirk R. Englund1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Harvard University, Cambridge, Massachusetts, United States; 3Rensselaer Polytechnic Institute, Troy, New York, United States; 4State University of New York Polytechnic Institute, Albany, New York, United States.

Quantum emitters in diamond are promising spin-photon interfaces, as they can possess both long-lived electronic spin states and coherent optical transitions. In particular, color centers based on Group IV impurities, such as the silicon vacancy center, have a crystallographic inversion symmetry that eliminates their static dipole moment and produces stable optical lines approaching the lifetime limit. This crystallographic structure, however, results in a pair of nearly degenerate orbital ground states that can scatter phonons, resulting in rapid spin dephasing for silicon- and germanium-vacancy centers at liquid helium temperatures. Here, we report on lead-related centers fabricated in ultrapure diamond following ion implantation and high temperature annealing. Cryogenic photoluminescence measurements performed on single quantum emitters in nanofabricated pillars show several transitions, most notably a pair of lines around 520 nm. The splitting of this doublet, 2 THz, is the largest reported of any Group IV-vacancy emitter in diamond. These observations are consistent with our models of the negatively charged Pb-vacancy center, which is expected to have a combination of narrow optical transitions and stable spin states that make it a promising system for quantum networking applications.

SYMPOSIUM EP07
Tailored Disorder—Novel Materials for Advanced Optics and Photonics November 26 - November 29, 2018

Symposium Organizers
Hui Cao, Yale University
Claudio Conti, University Sapienza
Sushil Mujumdar, Tata Institute of Fundamental Research
Cordt Zollfrank, Technische Universität München

* Invited Paper

SESSION EP07.01: Hyperuniformity
Session Chairs: Milivoj Belic and Cordt Zollfrank
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 205

1:30 PM *EP07.01.01
Tailored Disordered Hyperuniform Materials with Novel Properties Salvatore Torquato; Princeton Univ, Princeton, New Jersey, United States.

Hyperuniform states of matter include all perfect crystals, perfect
quasicrystals, and some exotic disordered materials. Disordered hyperuniform materials can be regarded to be new states of amorphous matter in that they behave more like crystals or quasicrystals in the manner in which they suppress large-scale density fluctuations, and yet are also like liquids and glasses because they are statistically isotropic structures with no Bragg peaks. Thus, these special correlated disordered materials possess a "hidden order" that is not apparent on short length scales, which endows them with novel physical properties.

I will describe procedures to design a variety of different disordered hyperuniform materials as well as their corresponding physical properties, including novel electromagnetic, photonic and transport characteristics.

2:00 PM EP07.01.02
A Black Forest of Silicon Nanowires—Striking Optical Properties Driven by Multiple Scattering of Light
Barbara Fazio1, Pietro Artoni2, Cristiano D'Andreà3, Stefano Pirotta3, Maria Antonia Iati3, Maria José Lo Faro4, Salvatore Del Sorbo3, Antonio A. Leonardi5, Giovanna Ruelle6, Rosalba Saija4, Paolo Musumeci2, Diederik Wiersma7, Francesco Priolo2, Matteo Galli8 and Alessia Irrera3; 1Istituto per i Processi Chimico Fisici, Consiglio Nazionale delle Ricerche, Messina, Italy; 2IMM MATIS, Consiglio Nazionale delle Ricerche, Catania, Italy; 3Dipartimento di Fisica, Università degli Studi di Pavia, Pavia, Italy; 4Dipartimento di Fisica e Astronomia, Università degli Studi di Catania, Catania, Italy; 5Università di Messina, Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Messina, Italy; 6LENS, Università di Firenze, Firenze, Italy.

The optimization of novel textured nanomaterials, both ordered and disordered, plays a key role on the transport of the light towards striking optical performances based on light trapping and multiple scattering [1-2]. In this context, the production of a fractal arrangement of nanostructures represents the case of a material with a complex disorder and strong structural heterogeneities correlated at all length scales. Using Au layers at the percolation limit, that exhibit a fractal arrangement, as the catalyst of a metal-assisted wet etching process, a 2D random fractal array of vertically aligned silicon nanowires (NWs) has been obtained by means of an inexpensive, fast and maskless process compatible with Si technology [3,4]. We demonstrate as a morphological property such as lacunarity, defined as the measure of alternation of full and empty space, is the main actor in the light scattering phenomena for this material, since it is strongly related to the fluctuations of refractive index [5]. The occurrence of strong in plane multiple light scattering, resonant with the structure in a wide wavelength range, promotes a very high light-trapping efficiency across the entire visible and near infrared ranges. This strong scattering also leads to a greatly enhanced Raman signal, which is correlated at all length scales according to the spatial variations in refractive index. The forest of Si NWs so arranged, causing light to bounce around many times within the array, increases the likelihood of light absorption.

Since NWs obtained by this technique exhibit a room temperature PL [3,4], the direct consequence of the increased absorbance manifests in a very bright PL emission. Moreover, the random organization and the strong scattering performances allow for the observation of an unexpected and counterintuitive interference radiation in random media, also for the generated Raman light [6]. The Raman CBS becomes, therefore, the first experimental signature in a macroscopic scale of the coherent nature of individual Raman scattering processes, typically occurring on the scale of the phonon coherence length and time. Our results are interpreted within a simple theoretical model of mixed Rayleigh-Raman random walks, for which reciprocity is assured by the symmetry of the Raman polarizability tensor and by the short dwell time of light inside the material, far below the phonon coherence time [6,7].

2:15 PM *EP07.01.03
Hyperuniform Disordered Photonic Networks—Band Gap Formation and Anderson Localization
Frank Scheffold; University of Fribourg, Fribourg, Switzerland.

Structured dielectric materials with a sufficiently high refractive index contrast can display partial or full photonic band gaps. This leads to dramatic changes of the optical transport properties with a strong spectral dependence. The latter is responsible for the transparency of the cornea to visible light, the iridescence of opal gems and structural colours in biology [1]. The lowered density of states may also result in increased lifetimes for embedded light emitters such as fluorescent molecules. Interestingly, it appears that many of these unique properties are not tied exclusively to crystalline structures. Florescu et al. demonstrated that particular disordered materials can also display full photonic band gaps [2]. Mapping hyperuniform point patterns with short-range geometric order into tessellations allows the design of interconnected networks that give rise to photonic properties in two and three dimensions [2]. We report here on the fabrication and characterization of such photonic network structures in three dimensions and for optical wavelengths in the shortwave infrared [3]. We first discuss the fabrication of polymer templates of the network structures using direct laser writing (DLW) lithography. Next, the mesoscopic polymer networks are converted into silicon by infiltration and double-inversion. The resulting hyperuniform materials display a pronounced photonic gap in the optical transmittance at λ>2.5μm. To obtain a deeper understanding of the physical parameters dictating the properties of amorphous photonic materials we investigate band gaps, and we report Anderson localization in hyperuniform structures using numerical simulations of the density of states and optical transport [4,5]. Our results show that, depending on the frequency of incident radiation, a dielectric material can transition from photon diffusion, localization to a bandgap crossing an intermediate regime dominated by tunnelling between weakly coupled states [4].

Hyperuniform Disordered Photonic Networks—Band Gap Formation and Anderson Localization
Frank Scheffold; University of Fribourg, Fribourg, Switzerland.

Structured dielectric materials with a sufficiently high refractive index contrast can display partial or full photonic band gaps. This leads to dramatic changes of the optical transport properties with a strong spectral dependence. The latter is responsible for the transparency of the cornea to visible light, the iridescence of opal gems and structural colours in biology [1]. The lowered density of states may also result in increased lifetimes for embedded light emitters such as fluorescent molecules. Interestingly, it appears that many of these unique properties are not tied exclusively to crystalline structures. Florescu et al. demonstrated that particular disordered materials can also display full photonic band gaps [2]. Mapping hyperuniform point patterns with short-range geometric order into tessellations allows the design of interconnected networks that give rise to photonic properties in two and three dimensions [2]. We report here on the fabrication and characterization of such photonic network structures in three dimensions and for optical wavelengths in the shortwave infrared [3]. We first discuss the fabrication of polymer templates of the network structures using direct laser writing (DLW) lithography. Next, the mesoscopic polymer networks are converted into silicon by infiltration and double-inversion. The resulting hyperuniform materials display a pronounced photonic gap in the optical transmittance at λ>2.5μm. To obtain a deeper understanding of the physical parameters dictating the properties of amorphous photonic materials we investigate band gaps, and we report Anderson localization in hyperuniform structures using numerical simulations of the density of states and optical transport [4,5]. Our results show that, depending on the frequency of incident radiation, a dielectric material can transition from photon diffusion, localization to a bandgap crossing an intermediate regime dominated by tunnelling between weakly coupled states [4].

2:45 PM BREAK

3:15 PM *EP07.01.04
The fundamental connection between geometrical and topological characteristics of structured photonic materials and advanced photonic functionalities is central to the design of novel photonic materials. Here, we introduce new metrics, hyperuniformity and local self-uniformity as measures of the structural order of photonic network structures. The hyperuniformity concept is built upon the properties of the structure in the reciprocal space, whereas local self-uniformity characterises the intimate connection between uniformity on local and global length scales. Hyperuniformity is associated with a constrained randomness such that density fluctuations on large scales behave more like those of ordered solids, crystals or quasicrystals, rather than those of conventional amorphous materials. On the other hand, local self-uniformity is a measure of a random network’s internal structural similarity and can be used to rank networks on a continuous scale from crystalline, through glassy intermediate states, to chaotic configurations. Despite their distinct characteristics, both metrics provide novel design strategies for achieving advanced photonic functionalities in non-periodic materials.

We then explore the connection between the hyperuniformity and local self-uniformity and the photonic band gap formation and introduce a novel photonic-network architectures, the hyperuniform amorphous diamond network and the amorphous gyroid network or triamond. We demonstrate that all architectures displaying large photonic band gaps, be they periodic or disordered, are characterized by large values of the newly introduced disordered metrics. We then explore their distinct photonic properties: photonic band gaps, localisation and waveguiding, and photon transport. A comparison between their predicted properties and recent experimental results will also be provided. In the end, a series of applications of the new disordered photonic networks will be discussed including novel structuring for solar cell absorbers, wing-scale structuring in the butterfly Pseudolycæna maryas and new designs for photonic integrated circuits and micro-opto-mechanical filters and modulators.

References
We would like to present the Ewald sphere construction for the prediction of the scattering in disordered media with small refractive index contrast. The Ewald sphere construction is a geometrical tool that is based on the first-order approximation and often used in X-ray scattering. We review the first-order derivation, explain the geometrical construction and as an example show how the Ewald sphere construction can be used to explain structural color.

Non-iridescent (i.e. angle-independent) structural colors are widely found in nature, especially in the plumage of birds. Unlike regular pigment or dye-based colors, these colors are based on the selective scattering of light instead of selective absorption. The structures responsible for this scattering appear completely disordered but they exhibit a spherical shape in reciprocal space, indicating that they are actually short-range ordered. We developed a model structure producing a spherical shell in reciprocal space. Using the Ewald sphere construction we were able to predict the scattering from a structured film. The results were checked by comparison to numerical simulations and show good agreement for light scattered in first order. The Ewald sphere construction also provides a vivid explanation for why there are many examples of structural colors in the short wavelength range while long-wavelength structural colors are barely found and have low color saturation. Finally, the results also indicate that the utilization of total internal reflection and thus frequency selective trapping of the scattered light can lead to a narrow reflection peak which may pave the way to long-wavelength structural colors.

Relevant Publications:

4:30 PM EP07.01.08
Designing Nanophotonic Structures Using Deep Learning Sunae So and Junsuk Rho, Mechanical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Designing structural components for desired properties has been a major challenge in the nanophotonics field. Recently, several data-driven design methods have provided novel systematic approaches[1-3], where deep neural networks are utilized to design metamaterials. However, all previous efforts have been limited to constraints where basic structures are predefined and the DNNs predict only structural parameters. Here, we report the first demonstration of designing metamaterial components that are not constrained to basic structure[4]. A deep neural network is used to learn the correlation between structural images and their corresponding reflection spectra. For given input reflection spectra, the network generates desirable designs in the form of images; this form allows suggestion of new structures that cannot be represented by structural parameters. Simulation results obtained from the generated designs agreed well with the input reflection spectrum. This method opens new avenues towards the development of nanophotonics by providing a fast and convenient approach to design complex nanophotonic structures that have desired optical properties.


4:45 PM EP07.01.09
Tuning Photonic Properties of Cellulose-Clay Nano Structures Ana C. Trindade, Susete Fernandes, Ville Liljestrom, Matthias Daab, Josep Breu, Maria H. Godinho and Jon O. Fossum, Norwegian University of Science and Technology, Trondheim, Norway; DCM and CENIMAT/3N, FCT/UNL, Lisboa, Portugal; University of Bayreuth, Bayreuth, Germany.

Solid films prepared from cellulose nano crystals (CNCs) present iridescence and selective reflection of left circularly polarized (LCP) light [1,2], while nano clay particles organize as lamellar structures in the solid state. It is well known that aqueous suspensions of sodium fluorohectorite (NaFh) clay biaxial platelets can form a nematic uniaxial liquid crystalline phase [3]. In this work we dissolved different quantities of cellulose nanorods in the clay nematic liquid crystalline suspensions (cellulose-NaFh nanocrystals (CNC/NaFh)) and we observed that the clay nematic structure undergoes a helical distortion by dissolving cellulose nanorods. Above a certain critical concentration the suspensions became iridescent with a left handed structure. In order to preserve the photonic characteristics of the clay/nano rods suspensions solid films were prepared. We demonstrate that not only iridescent films can be produced but also their selective reflection of LCP light channel preserved.

The colors reflected by the films can vary from blue to red depending on the amount of CNCs added to the system. This work demonstrates that the chirality-transfer, at the nano scale, induced by the CNCs on the clay nano platelets nematic phase translates into the photonic characteristics of solid films produced from aqueous CNC/clay suspensions.

SESSON EP07.02: Biological and Bioinspired Disordered Materials
Session Chairs: Francesco Riboli and Cordt Zollfrank
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 205
8:00 AM EP07.02.01
Bio-Inspired Highly Scattering Networks via Polymer Phase Separation Julia Syarik, Gianni Jacucci, Olimpia D. Onelli, Hendrik Hoelscher and Silvia Vignolini; Karlsruhe Institute of Technology, Eggenstein Leopoldshafen, Germany; University of Cambridge, Cambridge, United Kingdom.

Structural colors in nature are often the result of evolutionary-optimized complex nanoscale architectures. A well-known example of multiple scattering optimizations in a low refractive index medium is observed in the scales of Cyphochilus beetles. Here, the anisotropic chitin network inside the scales,
which cover the insect’s body out-performs practically all man-made low refractive index materials. The key to this optimization lies in the tuning of the filling fraction and in the anisotropic nature of the fibrillar structure in the scales.

Inspired by these natural design principles, we fabricated highly scattering white networks solely constituted by polymethylmethacrylate (PMMA). The resulting porous films are flexible and show the shortest transport mean free path reported in the literature for low refractive index materials [1]. We demonstrated that the scattering strength of the network can be enhanced by varying the molecular weight of PMMA to achieve transport mean free paths (λ) as low as 1 μm for an incident wavelength around 500 nm. Having such a short transport mean free path yields a reflectance of 75% for a 4 μm thick film. Due to their low refractive index (close to 1.5 over the whole visible range) and porosity, the produced free-standing films can be easily index-matched with water and other conventional solvents, providing a tunable response, which transitions from white to transparent upon wetting. This property, in addition with the high flexibility of the films, allows for various coating applications. We demonstrate that the scattering properties are maintained when the porous films are grinded into powders, opening their exploitation as white enhancers in paints, paper, and cosmetics.


8:15 AM EP07.02.02
A Bio-Based Photoresist for Direct Laser Writing of Disordered Architectures Maximilian Rothammer1, Marie-Christin Angermann2, Georg von Freymann2 and Cordz Zollfrank1, 1Chair for Biogenic Polymers, Technische Universität München, Straubing, Germany; 2TU Kaiserslautern, Kaiserslautern, Germany.

The polysaccharide cellulose is next to chitin the most abundant biopolymer on earth and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products.[1] The presented research includes the functionalization of cellulose enabling photo-crosslinking to generate biopolymer-based hierarchical architectures. This chemical modification is a prerequisite for the fabrication of two- and three-dimensional structures by direct laser writing (DLW). In combination with the inherent self-assembly capability of certain cellulose derivatives, there is the opportunity to introduce tailored disordered substructures through infiltration of the DLW-written framework and thus fabricate hierarchical architectures entirely from polysaccharides. Additionally, disorder on the nano-scale is created by the surface roughness of the DLW-written structures, which is caused by curling of the uncrosslinked ends of the cellulose chains in the resist. In contrast to common lithography, which uses photoresists based on polymers sourced from mineral oil, our approach conserves resources through replacing those polymers by sustainable materials such as polysaccharides. Polysaccharide-based photoresists have not been presented so far. We synthesized a bio-based photoresist, where a photo-reactive cellulose-derivative is dissolved in acetone together with a photoinitiator. This novel photoresist is curable by two-photon absorption (780 nm) in a DLW system (Nanoscribe Photonic Professional GT). With this setup, two-dimensional architectures with a linewidth of less than 500 nm and a feature size of 750 nm are achieved. Our bio-based photoresist allows three-dimensional structuring of cellulose on the μm scale via DLW. Curing of our cellulose derivative is generally possible in liquid and solid state via two-photon absorption.[2] This expands the operational areas of this photoresist, because writing in solid resist allows for more complicated structures, which have to be written in several disconnected sections. Additionally, this cellulose photoresist is curable via one-photon absorption with a UV-lamp (365 nm) in liquid as well as in dried state. Our resist opens up a new class of photo-curable polymers based on sustainable and renewable materials.

References

8:30 AM EP07.02.03
Direct Laser Writing of Iteratively-Designed Biomimetic Photonic Structures Exhibiting Tailored Disorder Bianca C. Datta, Sunny K. Jolly and V. Michael Bove, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural color phenomena exhibited by several organisms result from interference and diffraction of light incident upon multilayer nanostructures. The wings of the Morpho butterfly are a well-studied example of a biological system exhibiting structural coloration and a high degree of wide-angle iridescence due to a non-negligible degree of disorder in the photonic nanostructure. Recent work has demonstrated the fabrication of artificial, Morpho-inspired nanostructures that exhibit structural coloration effects via a variety of fabrication techniques; however, prior work has largely neglected the role of tailored disorder in generating iridescence in such bioinspired nanostructures.

Such complex biological systems require advanced fabrication techniques, and replication of nanoscale features of this complexity has been difficult. Existing methods include multi-step deposition, etching, and assembly processes. In comparison to existing fabrication methods for Morpho-inspired structures, such as interference lithography, colloidal self-assembly, sputtering, atomic layer deposition, or electron beam lithography, direct laser writing methods allow for flexible, three-dimensional, volumetric feature patterning on multiple length scales.

Here we present a comprehensive method for iterative inverse design of a biomimetic Morpho-inspired photonic structure exhibiting tailored disorder and a fabrication methodology based around direct femtosecond laser writing. Our design framework explicitly accounts for the important role of disorder in generating the iridescence effects seen in biological examples of structural coloration.

We evaluate optical properties such as spectral response, interference, diffraction, and reflectance of photonic structures fabricated using direct laser writing techniques such as two photon polymerization. We compare our model system and simulations to fabricated structures using optical microscopy, scanning electron microscopy, and angular spectrometry. This process provides a toolkit with which to examine and build other bio-inspired, tunable, and responsive photonic systems and expand the range of achievable structural colors.

The use of femtosecond laser direct writing allows for the rapid prototyping of complex, hierarchical micro- and nano-structures. When combined with the design and optimization process presented here, this method allows for the use of the Morpho structure as a baseline for iteration, both to incorporate tailored disorder, and to produce structures with extended functionality beyond existing systems. In doing so, we present a versatile approach to bio-inspired materials design and and provide a platform with applications ranging from light harvesting and steering, to chemical sensing, high performance displays, responsive products and architecture.

8:45 AM EP07.02.04
Bio-Inspired, Large Scale, Highly-Scattering Films for Nanoparticle-Alternative White Surfaces Julia Syurik1, Radwanul Hasan Siddique2,1, Antje Dollmann1, Marc Schneider1, Siegbert Johnsen1, Matthias Worgull1, Gabriele Wiegand1 and Hendrik Hölscher1, 1Karlsruhe Institute of Technology, Eggenstein Leopoldshafen, Germany; 2California Institute of Technology, Pasadena, California, United States.
White is the most popular color for today’s industrial products. Being the essential color for interiors, white pigments are widely found in plastics, inks, paints, cosmetics, and even food. In many of these products, their whiteness is achieved by incorporating titanium dioxide (TiO2) particles, which, due to their high refractive index, effectively scatter incoming visible light. However, fabricating white polymeric films and bulk parts with TiO2 particles causes some issues ranging from possible environmental harm to suspected health issues. Consequently, particle-free alternatives are of particular interest.

Here, we present an approach to whiten thin polymer foils via saturation by supercritical carbon dioxide (SC-CO2), which is an industrial process suitable for large-scale fabrication. We tailored the parameters for the fabrication of thin and white nano-foams made from PMMA because it is a common, often used polymer. The process parameters effectively control size, shape and wall thickness of the pores, which act as scattering elements. Although the refractive index of PMMA ($n = 1.49$) is comparable low the films are perfectly white even for thin film thicknesses in the µm-range [1]. In order to demonstrate the process-ability of our porous white films, we fabricated ultra-white micro-channels from them.


9:00 AM EP07.02.05
Brilliant Coloration from Tailored Photonic Disorder in Weevil Scales Michael H. Bartl, 1,2, 1Department of Chemistry, University of Utah, Salt Lake City, Utah, United States; 2Center for Energy Efficient Electronics Science, University of California, Berkeley, Berkeley, California, United States.

The world of insects displays myriad hues of colors produced by elaborate nanoscale architectures built into wings and exoskeletons. Many of these architectures display intricate hierarchical organization with varying degrees of ordering. For example, using a combination of optical and electron microscopy tools, photonic band structure calculations, and color mixing analysis, we recently discovered that the origin of the brilliant near angle-independent coloration of the weevil Eupholus chevrolati stems from tailored disorder involving multi-level photonic interactions: from diamond-based photonic crystal domains to seemingly random arrays of colored micro-pixels. This pointillist color-mixing scheme is responsible for a bright and multi-hued appearance, without the metallic sheen typical of photonic crystal colors found in many other beetles.

9:30 AM EP07.02.06
Disordered Tumor Spheroid Deep Optical Neural Network Davide Pierangeli, 1, Valentina Palmieri, 1, Giulia Marcucci, 1, Giordano Perini, 1, Marco De Spirito, 1, Massimiliano Papi, 1 and Claudio Conti, 1, 1Physics, Catholic University of SH, Rome, Italy; 2Physics, Sapienza University, Rome, Italy.

Light can propagate inside random media by iterative optimization of the input electromagnetic field. This training and scattering is a form of photonic machine learning, which we apply here to the special case of tumor cells. Specifically, we consider glioblastoma tumor spheroids that appear as an assembly of multiple scattering cells for a light beam. We show that by embedding these samples in an optical setup and using a feedback, the tumor cells can act as a computing reservoir and realize different optical transformation on the input light beam. The tumor cells act indeed as a multi-layered neural network that, with time, grows and gives additional deep computational layers to perform accurate and sophisticated functions. Once trained, this unconventional hybrid combination of living matter and photonic hardware returns information on its growth dynamics. For this random optical machine, we have grown glioblastoma cells in 3D spheroid architectures that represent modern model platforms for studying complex cell-to-cell interactions, anticancer therapeutics uptake and diffusion in tumor bulk. We tracked glioblastoma spheroids spontaneous evolution and their subcellular transformations stimulated by hyperthermia or chemotherapies. We demonstrated that brain tumor cells can be trained to track cancer evolution and subcellular transformation induced by external stimuli. We demonstrate that a higher resolution is obtained with this deep optical neural network compared to confocal microscopy and standard optical imaging. This hybrid photonic living system is a novel artificial disordered photonic computing machine for real-time study and unprecedented measurements of tumor dynamics.

9:45 AM BREAK

SESSION EP07.03: Biological and Bioinspired Disorder
Session Chairs: Francesco Riboli and Cordi Zollfrank
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 205

10:15 AM EP07.03.01
Interplay of Order and Disorder in Biological Photonic Materials Ulrich Steiner; Adolphe Merkle Institute, Fribourg, Switzerland.

The generation of well defined band-gaps requires perfectly ordered transparent material, which is technologically demanding. Biological organisms, animals and plants, are however able to generate striking optical effects, with a much lower degree of order that, seemingly, should be highly detrimental to realise the colour brilliance arising from well ordered structures. On the other hand, optimised disorder is required for the multiple scattering of light that produces white, requiring a different type of structural control.

The first part of my presentation will focus on the interplay of order and disorder of grating-like topographical features found on many flower petals, the optical effects they generate and their role in insect recognition. The second part discusses biological strategies to generate whiteness employing a minimal amount of material, which is particularly important for flying insects.

10:45 AM EP07.03.02
The Cyphochilus Beetle as an Inspiration for Sustainable White Materials Gianni Jacucci, 1, Olimpia D. Onelli, 1, Giulia Syurik, 1, Matti Toivonen, 2, Hendrik Hoelscher, 3, Olli Ilkka, 3 and Silvia Vignolini, 1, 1University of Cambridge, Cambridge, Cambridge, United Kingdom; 2Aalto University School of Science, Espoo, Finland; 3Karlsruhe Institute of Technology–Institute for Applied Materials, Karlsruhe, Germany.

Whiteness arises when light interacts with disordered media, where different wavelengths are scattered with comparable intensity. Such appearance is the result of light undergoing multiple scattering events before exiting the object, i.e. when the object is optically thick. The optical thickness of a material is determined by the ratio between its physical thickness and the transport mean free path, namely the distance that light travels before losing information about its starting propagation direction. Commonly, the transport mean free path in low-refractive index white materials is about tens of micrometres long. Therefore, opacity is achieved for relatively large thicknesses (in the millimetres range) to allow a high enough number of scattering events. [91]
Nature provides an invaluable source of inspiration for the study and the manufacturing of thin opaque white materials. The *Cyphochilus* white beetle achieves a high total reflectance (~75% over the whole visible range) with a few micron thick, lightweight, anisotropic network of chitin fibres (n~1.55).

Herein, after quantifying the scattering efficiency of the chitin network via a coherent backscattering setup, we show an experimental approach to produce bio-inspired, sustainable white materials. In particular, we demonstrate that tuning the morphology of a network of polymer fibres strongly affects its optical properties: from transparent, to bright white materials. Notably, our bio-inspired materials achieve high scattering efficiency whilst being only a few micrometres thick (up to 75% reflectance while only 4 µm thick). Our study illustrates the potential of using biopolymers as building blocks to produce next-generation sustainable and biocompatible highly scattering materials. In addition, we show that it is possible to manipulate the light transport regime, moving from standard to anomalous diffusion, when a long-tailed distribution of the fibres size is introduced.  

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.

Graphene oxide (GO) and its reduced form (rGO) are capable of inducing mesenchymal stem cells differentiation and promote bone tissue formation with efficacy depending on reductive state of the material. Thus, modulation of the osteogenic process and of bone mineral density distribution is theoretically possible by controlling the GO oxidative state. In this study, we laser-printed GO surfaces to obtain both a local photo-thermal GO reduction and the formation of nano-wrinkles along precise patterns. In the first days of culture, cells migrated and accumulated on the reduced and wrinkled surface. When possible by controlling the GO oxidative state.

The design rules we revealed have the potential to guide the creation of synthetic polymer fibres or surface microstructures which are able to mimic the skin’s light management over a broad spectral range and can be scaled to dimensions suitable for adequate synthesis routes.
Invariance of the Mean Path Length in Light-Scattering Media

2:00 PM *EP07.04.03
Light Trapping and Super Diffusion in Levy Glasses
Francesco Ueli1,2,3, Lorenzo Pattelli1,2,3, Diederik Wiersma1,2,3, and Kevin Vynck1; 1European Laboratory for Non-linear Spectroscopy, Turin, Italy; 2Department of Physics, University of Florence, Turin, Italy; 3National Metrology Laboratory INRIM, Turin, Italy; 4Institut d’Optique, Université Bordeaux, Bordeaux, France.

For wave transport in disordered systems it is known that the dimensionality of the structure plays a crucial role. In particular, for dimensions equal to two or smaller, interference will give rise to localised modes for large enough system size.

In this contribution we show that this situation is actually only correct for the limiting case of homogeneous (Gaussian) disorder. We will discuss the general case of light transport in Levy glasses, which are materials in which a large inhomogeneity of the structure leads to super diffusion.

While one would expect super diffusion to counterbalance localisation, we find the counter-intuitive result of strong localisation in coexistence with extended modes.

2:30 PM EP07.04.04
Invariance of the Mean Path Length in Light-Scattering Media
Romolo Savo1, Romain Pierrat2, Ulysses Najari3, Rémi Carminati4, and Sylvain Gigan1; 1Laboratoire Kastler Brossel, ENS-PSL Research University, CNRS, UPMC-Sorbonne Universités, Collège de France, Paris, France; 2ESPCI Paris, PSL Research University, CNRS, Institut Langevin, Paris, France; 3Institute for Theoretical Physics, Vienna University of Technology (TU Wien), Vienna, Austria.

Optical materials engineering lies on the assumption that the structure of a medium is inherently linked to its functional behavior. This is particularly true for light scattering properties, which depend very sensitively on whether a medium is homogeneous, structured or disordered. As opposite to this paradigm, a recent theoretical study pointed out that a very fundamental property of wave transport is extremely robust to the structure of the underlying medium [1]. This result was derived by generalizing an invariance property first found for random walks [2] to arbitrary wave scattering scenarios [2], such as for light in a disordered material. Specifically, it has been shown that, when all modes in a medium are equally excited, the mean path length <s> associated with wave scattering through a medium only depends on the medium’s boundary geometry, but not on its internal microstructure. Apart from limitation due to finite absorption the mean path length is found to be <s> = vE<t> = 4V/S for a three-dimensional geometry of volume V and surface S, where vE is the energy velocity [1].

Here [3], we experimentally consider the case of a fully disordered medium, in which the crossover between systems with different degrees of disorder can be described by the transport mean free path Φ. Applying the predicted invariance to this case would mean that any change of Φ should leave the mean path length invariant. We investigate multiple scattering of light in colloidal suspensions of particles in water and tune the mean free path by varying the concentration and size of the particles. We develop a reverse version of diffusing-wave spectroscopy to measure the mean length of light trajectories through the temporal decorrelation of the optical speckle pattern. We unambiguously observe the invariance of the optical mean path length over almost two orders of magnitude of scattering strength - from a nearly transparent to a very opaque system. The observed invariance sets rigid bounds for the optical path length enhancement in multiple scattering media and provides insights for the optimal design of light trapping and light storage devices. It crucially relies on the validity of the Equi-partition Theorem and thus provides a stringent test of this fundamental principle in scattering media. We also emphasize that our results are not restricted to light propagation, but apply basically to all wave scattering problems.

References:

2:45 PM BREAK

3:15 PM EP07.04.05
Engineering Isotropic Light Scattering for Light Emission Control
Sean Gorsky1, Kidanemariam Kebede1 and Luca Dal Negro1,2; 1Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; 2Materials Science and Engineering, Boston University, Boston, Massachusetts, United States.

Light extraction from high-index materials is an ongoing issue in modern LED technologies. Specifically, total internal reflection (TIR) significantly limits the amount of light that can be extracted from the high-index medium into free space. Photonic crystals coupled to emitting optical materials have been shown to enhance light extraction and control directionality by scattering TIR light into free space. In particular, the use of aperiodic and isotropic, disordered patterns such as the Golden Angle (GA) Vogel spiral has been shown to be particularly advantageous compared to traditional photonic crystals such as the hexagonal lattice as it enables the extraction of a wider domain of TIR waves across a broader angular range. However, in the case of the GA Vogel spiral, isotropic diffraction comes at the cost of weaker scattering strength which diminishes the overall light extraction capability. In order to solve this problem we introduce in this talk a new disordered, isotropic point pattern which features enhanced short range order, and therefore enhanced scattering when compared to the GA Vogel spiral. In particular, we demonstrate that the first radial correlation peak of this engineered structure is 2X that of the GA Vogel spiral, while maintaining an overall isotropic character. The new pattern is created using the collective coordinate control method which allows for direct engineering of the pattern's structure factor. We pattern transparent substrates with reflective nano-pillars arranged in these new patterns and experimentally measure the structure factor by illuminating with a 405 nm laser and measuring the optical Fourier transform on a CCD camera. The surfaces were patterned using magnetron co-sputtering, electron beam lithography (EBL) and reactive ion etching (RIE) techniques. A variety of the patterns were fabricated with varying nano-pillar diameter and mean particle separations. Finally, we use a model based on the kinematic scattering to assess their potential as transparent surface patterns to increase light extraction of incoherent radiation and enhance directional emission from active, high-index materials.

3:30 PM EP07.04.06

References:

2:45 PM BREAK

3:15 PM EP07.04.05
Engineering Isotropic Light Scattering for Light Emission Control
Sean Gorsky1, Kidanemariam Kebede1 and Luca Dal Negro1,2; 1Electrical and Computer Engineering, Boston University, Boston, Massachusetts, United States; 2Materials Science and Engineering, Boston University, Boston, Massachusetts, United States.

Light extraction from high-index materials is an ongoing issue in modern LED technologies. Specifically, total internal reflection (TIR) significantly limits the amount of light that can be extracted from the high-index medium into free space. Photonic crystals coupled to emitting optical materials have been shown to enhance light extraction and control directionality by scattering TIR light into free space. In particular, the use of aperiodic and isotropic, disordered patterns such as the Golden Angle (GA) Vogel spiral has been shown to be particularly advantageous compared to traditional photonic crystals such as the hexagonal lattice as it enables the extraction of a wider domain of TIR waves across a broader angular range. However, in the case of the GA Vogel spiral, isotropic diffraction comes at the cost of weaker scattering strength which diminishes the overall light extraction capability. In order to solve this problem we introduce in this talk a new disordered, isotropic point pattern which features enhanced short range order, and therefore enhanced scattering when compared to the GA Vogel spiral. In particular, we demonstrate that the first radial correlation peak of this engineered structure is 2X that of the GA Vogel spiral, while maintaining an overall isotropic character. The new pattern is created using the collective coordinate control method which allows for direct engineering of the pattern’s structure factor. We pattern transparent substrates with reflective nano-pillars arranged in these new patterns and experimentally measure the structure factor by illuminating with a 405 nm laser and measuring the optical Fourier transform on a CCD camera. The surfaces were patterned using magnetron co-sputtering, electron beam lithography (EBL) and reactive ion etching (RIE) techniques. A variety of the patterns were fabricated with varying nano-pillar diameter and mean particle separations. Finally, we use a model based on the kinematic scattering to assess their potential as transparent surface patterns to increase light extraction of incoherent radiation and enhance directional emission from active, high-index materials.
Reflectivity of Finite 3D GaAs Photonic Band Gap Crystals Willem Vos1, Takeyoshi Tajiri2, Shun Takahashi3, Cornelis A. Harteveld1, Diana A. Grishina1, 4, Satoshi Iwamoto2 and Yasuhiko Arakawa2; 1Complex Photonic Systems (COPS), University of Twente, Enschede, Netherlands; 2Institute of Industrial Science, The University of Tokyo, Tokyo, Japan; 3Kyoto Institute of Technology, Kyoto, Japan; 4Thermo Fisher Scientific, Eindhoven, Netherlands; 5Institute for Nano Quantum Information Electronics, The University of Tokyo, Tokyo, Japan.

While the large majority of theoretical studies of photonic crystals pertain to infinite and perfect structures [1], any experimental study or practical device obviously concerns finite nanostructures with unavoidable deviations from perfect periodicity [2]. The quintessential property of any photonic crystal - regardless of dimensionality and the presence or not of a 3D photonic band gap - is of course the appearance of a stop gap in the dispersion relations for wave propagation in the direction perpendicular to the spatial periodicity [1]. Such a gap corresponds in real and finite structures to a stop band that is observed as a peak in reflectivity experiments. A seminal study reported the evolution of the width of stop band with crystal thickness [3]. It was found that the width of the stop gap scales inversely with the thickness, as later confirmed elsewhere [4]. However, it is still unknown how finite-size effects affect the width of stop gaps in photonic crystals that interact so strongly with light that they reveal a 3D complete photonic band gap.

We surmise that since the probed stop gap is part of complete 3D photonic band gap, the confinement is truly 3D. The confinement is then not only affected by the "thin" dimension perpendicular to the crystal slab, but also by stop gaps within the plane of the crystal structure where the crystal extent is obviously concerns finite nanostructures with unavoidable deviations from perfect periodicity [2]. The quintessential property of any photonic crystal - regardless of dimensionality and the presence or not of a 3D photonic band gap - is of course the appearance of a stop gap in the dispersion relations for wave propagation in the direction perpendicular to the spatial periodicity [1]. Such a gap corresponds in real and finite structures to a stop band that is observed as a peak in reflectivity experiments. A seminal study reported the evolution of the width of stop band with crystal thickness [3]. It was found that the width of the stop gap scales inversely with the thickness, as later confirmed elsewhere [4]. However, it is still unknown how finite-size effects affect the width of stop gaps in photonic crystals that interact so strongly with light that they reveal a 3D complete photonic band gap.

We observe that from N=2 to N=8 layers (4-fold increased thickness) the band width decreases only slightly from 4500 to 3500 1/cm (a 1.3-fold decrease). This behavior differs strongly from Bragg-like proportional one that is typical of weakly interacting photonic crystals [2,3].

We experimentally study reflectivity of 3D GaAs woodpile crystals with different number of layers N, made by advanced micro manipulation [5]. Plates with 2D arrays of parallel rods (445 nm period) of 134 nm width and 150 nm thickness are stacked one-by-one to form the 3D nanostructures. The rods are crossed between neighboring layers, and parallel and shifted by half a period in the secondary neighboring ones. The crystal thickness ranges from N=2 to N=8 layers. Optical spectra are measured with a tailor-made broadband micro-reflectivity setup with reflecting optics [6], and are interpreted with numerical results from FDTD simulations.

We surmise that since the probed stop gap is part of complete 3D photonic band gap, the confinement is truly 3D. The confinement is then not only affected by the "thin" dimension perpendicular to the crystal slab, but also by stop gaps within the plane of the crystal structure where the crystal extent is much greater than the thickness.

The interplay between disorder and nonlinearity can provide original opportunities to overcome some of the most challenging limits in the development of future optical technologies. For instance, a standard frequency doubler based on a birefringent crystal can be hardly integrated on a chip due to tight phase-matching conditions and bulky structure with non-standard etching process. Differently a disordered $\chi^2$ material would provide much more relaxed phase-matching condition and tremendous advantages in terms of fabrication, scalability and cost. Indeed, it has been shown that an effectively incoherent Second Harmonic Generation (SHG) is possible in transparent films of semiconductors and ferroelectrics that are disordered only in the spatial distribution of the second order susceptibility $\chi^{(2)}$, with a large acceptance angle and a broadband conversion [1-4].

Here we realize second-order disordered nonlinear structures by self-assembly of perovskite nanoparticles (BaTiO$_3$, LiNbO$_3$) [5] with different packing densities and geometries. Our structures show signatures of pure incoherent SHG with a nearly flat broadband conversion in the visible range ($400\text{ nm} < \lambda/2 < 510 \text{ nm}$). Very interestingly our structures are also completely opaque, so that multiple light scattering (of both $\omega$ and $2\omega$) and SHG coexist, influencing each other in a way that is still under investigation. We additionally propose an application of our methods at the wavelength scale, where second-order diffraction effects and self-assembly becomes a valuable tool to mimic bulk properties, with the advantage of a high control over the system size. We foresee that the complexity created by disorder, multiple scattering and functional Mie resonances of the scattering centers could generate unconventional mechanisms for nonlinear optical conversion and pave the way to the development of highly versatile disordered photonic devices.

References

4:30 PM EP07.05.03
Nonlinear Transmission Matrices of Random Media
Adam Fleming1, Claudio Conti2, 3 and Andrea Di Falco1; 1University of St Andrews, St Andrews, United Kingdom; 2Institute for Complex Systems, National Research Council (ISC-CNR), Rome, Italy; 3Sapienza University, Rome, Italy.

The complex light matter interaction in disordered materials mediates many intriguing fundamental light transport phenomena, enabled by a large multitude of optical modes that can carry the information through random media and that can interact during propagation [1].

In recent years, the associated large number of degrees of freedom have been used in conjunction with waveform shaping techniques, enabling breakthroughs such as diffraction limit beating focusing devices [2]. The ability to access a growing subset of the total individual channels has also enabled the acquisition of a transmission matrix (TM), which directly links input and output fields [3]. Again, this has allowed for the creation of remarkable optical devices such as fibre-based imaging and the simultaneous measurement of the spectral and polarimetric properties [4, 5].

Manipulation of the random media itself through nonlinear effects will allow the generation of even more powerful optical tools facilitated by additional degrees of control over the scattering system. For example, it is possible to use waveform shaping and two photon fluorescence to focus ultrashort pulses in both space and time, providing enhancements over and above the experimental limits in linear wavefront shaping experiments [1,6].

Here, we characterize the TM in the nonlinear regime (NLTM), to describe the effect of nonlinear processes have on the long-range correlations of photon interference, and their various transmissive channels. To do so we use a series of pump-probe experiments to exploit the high optothermal nonlinearity of Silica Aerogel (SA), an ultra-porous material made of sparse silica aggregates. SA can host extremely high temperature spatial gradients, which in turn mediates opotothermal nonlinearities on the order of $10^{-13} \text{ m}^2/\text{W}$ [7]. In addition to the measurement of the NLTM, we also demonstrate that the coupling to the transmission channels can be dynamically and reversibly tuned.

Just as the TM greatly enhanced the ability to manipulate light transport in the linear regime, we anticipate that providing access to the NLTM of a random medium will enable the creation of complex optical devices, whose characteristic behaviour can be modified directly and dynamically.

transmittance ratio between the orthogonal circular polarizations at $fa/c = 0.190$ is 1.07 and 0.11 for the direct and inverse structure, respectively. These chiral structures have circularly polarized bands that induce different transmittance between orthogonal circular polarizations [1]: circular dichroism. We find that the band structures for these two classes of chiral nanostructures differ remarkably, even at constant average refractive index, causing distinctly different circular dichroism.

The unit cell of the direct crystal consists of 3 dielectric layers each with thickness $h$. The first layer is a 2D periodic array (period $a$) of square rods with width $w$. The 2nd layer has the same periodic rod pattern, rotated by 60 degrees in the in-plane direction. The 3rd layer is empty (in practice it will have distant thin spacers). The first layer of the inverse crystal is a 2D periodic array of square pores with the same parameters as the direct structure. The 2nd layer has the same pore array rotated by 60 degrees, and the 3rd layer is homogeneous. The thickness-to-period ratio of both crystals is $h/a = 0.45$. The refractive index of the backbone is chosen as $n = 3.4$ to represent semiconductor GaAs and Si that have been processed in real structures [1-4]. For a width-to-period ratio $w/a = 0.75$, the average refractive indices of both the direct and the inverse structures are equal, whence one might expect the same band structures and optical properties. To verify this hypothesis, we calculated photonic band structures by a plane wave expansion method for the lowest four bands in the Gamma-Z direction along the chiral axis. The direct structure has a gap between normalized frequencies $fa/c = 0.147$ and 0.192. The inverse structure has a gap between 0.129 and 0.186. The difference between the gaps shows that the naive hypothesis above is invalid.

Chiral structures have circularly polarized bands that induce different transmittance between orthogonal circular polarizations [1]: circular dichroism. We calculated transmittance of circularly polarized light through the two complementary structures by a finite-difference time domain method. The transmittance ratio between the orthogonal circular polarizations at $fa/c = 0.190$ is 1.07 and 0.11 for the direct and inverse structure, respectively. These results confirm the band structures.


**EP07.06.02**

**Dual-Moth-Eye Structure for Sample Collection in Mid-IR Spectroscopy**

Amirhossein Nateghi, Jieun Myung, Tae Yoon Jeon and Axel Scherer;
California Institute of Technology, Pasadena, California, United States.

Mid-IR radiation covers light in the spectral region of 4000–400 cm$^{-1}$ or 2-20 um which can be used to provide information on molecular structure as well as to gain insight into a molecule’s local environment. Here, we present design and experimental demonstration of a sample collection and interrogation geometry that enables the spectroscopic measurement of materials in the mid-IR region. In this spectral region, silicon is relatively transparent, and a cuvette consisting of two silicon wafers bonded together can be made of this material. Such cuvettes however suffer from progressively higher reflectivity, resulting in low transmitted light. Although different anti-reflection methods can be used over small wavelength ranges, only few approaches work throughout the broad spectral regions needed for spectroscopy. Here we show a promising technique by micro-fabricating a geometric anti-reflection structure analogous to the moth-eye on silicon. This anti-reflection geometry can drastically reduce the reflectance from a silicon surface from ~30% to ~1% . We have built and characterized anti-reflective microstructures and have shown how our geometry can be used for sample collection on a surface of patterned silicon. Low reflectivity is measured by incorporating two moth-eye structures on both sides of a silicon wafer. This new method can be easily implemented to produce transmission efficiencies through high-reflectivity materials over a large wavelength range and still obtain large surface areas both of which are necessary for spectroscopy.

The surface of the microfabricated moth-eye structure can collect sample within the crevices between the microfabricated pillars through surface tension.

If properly designed, disordered light scatterers can trap the collected photons in a photovoltaic (PV) active layer over an extended and targeted frequency range. This is particularly beneficial for enhancing the absorption in thin-film solar cells. Proof-of-concepts have been successfully performed by fabricating nanostructures with short-range structural correlation using a slow serial writing process (e-beam lithography), hence limiting the demonstration to small areas. This shortcoming can be circumvented by tailoring the morphology of self-assemblies which inherently incorporate structural disorder, and which can be more conveniently formed over large surfaces. Polymer blend lithography (PBL), relying on the lateral phase separation of a blend made of...
immiscible polymers, is a relevant patterning technique with that respect as it can be carried out rapidly, cost-effectively and because it allows exploring a broad set of disordered configurations with tunable size distributions.

In the present communication, we first report on the development of self-assembled, high refractive index dielectric nanopillars (NP) which are introduced on the solar cell front side for improved light in-coupling and trapping. We show that they can be realized either by liquid-phase infiltration of titania nanoparticles into a disordered nanoholes array obtained by PBL, or via a lift-off process involving vacuum deposition and a similar PBL-based template. This route is exemplified by enhancing the absorption of a hydrogenated amorphous silicon (a-Si:H) absorber coupled to a rear side mirror, following the implementation of the disordered dielectric scatterers over few cm² onto the PV demonstrator.

We further demonstrate that the phase-separated nanostructures can also serve for realizing broadband light-trapping reflectors. To this end, a metallic layer is deposited atop a disordered NP array whose geometrical parameters are previously adjusted to achieve a light scattering coefficient (in air) exceeding 40% in the low absorbing region of the a-Si:H active layer. The low aspect ratio and smooth profile of the disordered NP enable a conformal deposition of the PV thin film stack onto the NP film, resulting in functional and reproducible devices. The latter exhibit a broadband absorption enhancement and a power-conversion efficiency increase of +65% relative to planar solar cells. The developed reflectors even overcome the light harvesting properties (Asahi-type) substrates based on random textures, thereby highlighting the advantage of controlling structural disorder for PV light management.

**EP07.06.04**
Random Laser Action in Disordered Electrospun Nanofibers Doped with Rhodamine B Dye
Lucas F. Sciutí1, Nathalia B. Tomazio1, Luiza A. Marcante2, Daniel S. Correa2, Cleber Mendonça1 and Leonardo de Boni1; 1Institute of Physics of São Carlos, University of São Paulo, São Carlos, Brazil; 2Nanotechnology National Laboratory for Agriculture, Embrapa Instrumentação, São Carlos, Brazil.

The scattering of light caused by disordered nanostructures enables the action of random laser. A random laser utilizes a disordered structure allowing multiple-scattering of light, embedded in an active media which amplifies it by stimulated emission. Random laser systems are of great interest due to their applications in speckle-free imaging, designing of photonic chips and also for identifying cancerous tissues. The search of different materials and architectures to provide the random laser mechanism is therefore highly important to support new applications.

In this work, polymeric nanofibers containing Rhodamine B (Rhb) were fabricated by the electrospinning technique. The nanofibers were electrospun having average diameter of 500 nm. In order to investigate the random laser emission in these disordered thin layer nanofibers, a 532 nm pulsed laser was used as the pump beam. Samples were kept in a way that light emitted was collected perpendicularly to the pump beam. The light beam was focused by a 5 cm convergent lens, with the possibility of varying the sample position along the beam axis. The emitted light was captured by a set of convergent lenses and coupled to an optical fiber connected to a high resolution spectrometer. Nanofiber samples containing 2%, 5% and 10% RhB-doped were investigated. As it is expected for random laser, the output intensity as a function of the pump energy should present a threshold level and a decrease in the FWHM of the spectral emission. All three nanofibers samples studied presented a change in the slope for the output intensity as a function of the pump fluency. A narrowing of the emission band, showing a characteristic laser action, was also observed. It is important to say that the results related to the 2% RhB-doped sample, in which an incoherent-like random laser emission was measured. While for 5% and 10% RhB-doped samples, the random laser emission spectra showed a coherent-like random laser with the presence of several spikes. It is important to say that the spikes position does not change from shot to shot at a fixed pump energy, which could be related to the fact that the characteristic disorder of the disordered photonic nanofiber is static over time. Consequently, the cavities formed preserve the emission wavelength during time.

Changes in the RhB concentration show to play an important role in the spectral emission characteristics, presenting a red-shift with the increase of the concentration. Moreover, the spectral emission band width also increases with the concentration. One explanation for this effect is a possible reabsorption of the RhB due to some chromophores that are not excited, making possible the tuning of the laser wavelength emission. Furthermore, the transition from incoherent to coherent random laser when increasing the RhB concentration shows that the process of doping or the presence of the dye molecule tends to increase the disorder of the nanofibers.

**EP07.06.05**
Light-Path Engineering in Disordered Waveguiding Systems
Paris Varytis1, Wladyslaw Hartmann1,4, Wolfram Pernice4 and Kurt Busch1,2; 1Max-Born-Institut, Berlin, Germany; 2Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany; 3Institute of Physics, University of Münster, Münster, Germany; 4CeNTEch - Center for Nanotechnology, University of Münster, Münster, Germany.

Integrated nanophotonic circuits allow for realizing complex optical functionality in a compact and reproducible fashion through high-yield nanofabrication. Typically configured for single-mode operation in a single path, the optical propagation direction in such devices is determined by the waveguide layout which inherently requires smooth surfaces without scattering and restricts the device footprint to the limits of total internal reflection. By moving forward to multi-mode and multi-path designs in intentionally disordered waveguide structures, we will harness in-plane scattering effects to realize a new class of functional waveguiding devices. Through light-path engineering of free-standing dielectric membranes compact and broadband optical systems will be derived for operation in the classical and quantum regime. Our approach is based on multi-path interference, leading to the generation of wavelength dependent speckle patterns at the output of a tailored photonic nanostructure.

Random spectrometers represent prototypical examples for light-path engineered devices. Through exact numerical electrodynamic simulations (using a Discontinuous-Galerkin Time-Domain finite-element approach) in combination with multiple-scattering theory, we have demonstrated the feasibility of silicon-nitride-based high-resolution spectrometers in integrated optics layout for operation at near-IR and visible frequencies.

**EP07.06.06**
Cellulose-Based Photoresist for Curing Films with Disordered Microstructures by UV-Lithography
Andrea Obendorfer, Maximilian Rothammer and Cord Zollfrank; Biogenic Polymers, Technische Universität München, Straubing, Germany.

Cellulose is the most abundant biopolymer on earth and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products.[1] The presented research includes the esterification of cellulose diacetate with methacrylic acid anhydride.[2] This reactive methacrylic side group is essential for a subsequent photopolymerization reaction during UV-lithography. We created a bio-based photoresist, where the above mentioned photo-reactive cellulose-derivative is dissolved in acetone together with a photoinitiator. Therefore, this photoresist can be subjected to surface patterning techniques (e.g. mold casting) to obtain surface structured films entirely made from polysaccharides via UV-curing. As a result, transparent patterned cellulose films with distinct optical properties are accessible. The imprinted diffraction pattern consists of pillars in the micron range and evokes brilliant colors, which depend on the reflection angle of the incident light. Disordered areas can be generated through swelling and random self-agglomeration of several pillars, if the UV-cured film is moistened with an organic solvent. The resulting optical properties can be tuned by altering the dimensions of the pillars or their distances, which tailor the disordered cluster size and their arrangement. Additionally, there is still a high degree of freedom for the system within certain limits, since the cellulose-based pillars are subjected to a self-organization process. This example demonstrates the versatility of fabrication of tailor-made disordered architectures from biogenic polymers. It is interesting to note that curing of this
Femtosecond Laser Structuring of Metal Oxide Thin Films for Enhanced Optical Properties

Danny Bialauschewski1, Jan Hoppius2, Evgeny Gurevich2 and Sanjay Mathur2; 1Institute of Inorganic Chemistry, Cologne, Germany; 2Chair of Applied Laser Technologies, Bochum, Germany.

Disorder in materials, either chemical or structural, often result in new and unique properties, especially regarding different light interaction and interference of ordered and disordered structures. Here, ultra short femtosecond laser pulses are used to tailor specific properties in different metal and metal oxide materials. By optimizing chemical parameters such as laser fluence, pulse duration or repetition rate, we can modify substrates on a physical or/and chemical level. In this work, we show that by inducing structural disorder in metals, for example by creating laser induced periodic surface structures (LIPSS), light harvesting properties like absorption, photoconversion and overall photoelectrochemical water splitting performance can be increased when compared to untreated substrates. This influence was investigated with and without additional top layers, regarding their spectroscopic (UV-VIS), thermoplasmonic and the ultra-thin crystalline solar cells structuring for their efficiency improvement [6].

References
3. I. Massiot et al., Highly conformal fabrication of nanopatterns on non-planar surfaces, Nanoscale, 11, 14461 (2016).
Mie glasses are inhomogeneous solids that behave as solid dispersions of light scatterers. A novel demonstration of a Mie glass synthesized by solution processing methods and comprising a mesoporous TiO2 matrix in which crystalline TiO2 monodisperse nanoparticles are dispersed in a random manner is reported. A full optical characterization of this optically disordered material, whose behavior can be predicted prior to fabrication based on single particle considerations, has been performed to attain the key parameters that describe light propagation in random media, i.e. scattering and transport mean free paths. Herein we discuss the potential of these inhomogeneous solids for optoelectronic applications. In particular, we show that Mie glasses are able to boost light harvesting and thus power conversion efficiency in bifacial dye sensitized solar cells when the porous matrix is sensitized with a dye [1]. Also we prove that soaking the optically disordered material with fluorescent dye molecules yields brighter color conversion layers, which we attribute to a combination of resonant excitation and a better out coupling of the emitted light [2].

References

9:30 AM EP07.07.06
Bi-Phase Emulsion Droplets as Reconfigurable Optical Components Sara Nagelberg1, Lauren Zarzar2, Lukas Zeininger1, Amy Goodling2, Timothy M. Swager1 and Mathias Kolle1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2The Pennsylvania State University, State College, Pennsylvania, United States.

Micro-scale optical elements play a key role in imaging and display technologies, biosensing, beam shaping, optical switching, wavefront analysis, and device miniaturization. Recently developed multi-phase micro-scale liquid droplets with tunable morphology show a variety of interesting optical properties. The droplets are formed from immiscible oils in an aqueous medium, and the morphology of the droplets can be dynamically adjusted by varying the interfacial tensions of the liquids. As refractive elements, the droplets can behave as micro-lenses with a variable focal length that can be adjusted continuously from positive (converging lens) to negative (diverging lens) focal lengths. When a fluorescent dye is dispersed within one of the droplets’ phases, their emission profile is morphology-dependent, allowing the droplets to act as transducers in chemical and bacteria sensing systems. As reflective elements, certain morphologies of the droplets display structural color, which is also geometry dependent. A wide variety of stimuli, including altering the chemical environment, light, heat, and light, can be used to manipulate the shape and orientation of the droplets, and thus their optical properties.

9:45 AM BREAK
Physical Unclonable Functions (PUFs) are partly disordered physical systems used for identification in hardware security applications. The ‘response’ generated from a PUF depends on an externally applied ‘challenge’ and the unique and unclonable disorder present in the system. It should be difficult or impossible for an adversary to predict the response of a PUF and clone the exact disorder into another device [1]. Various types of PUFs have been implemented using electrical and optical systems [1], [2]. Optical PUFs are expected to be inexpensive and to enable strong security. Optical PUFs based on light scattering tokens using randomly placed sub-millimeter size (~500 µm) glass spheres have been reported earlier [3], [4]. Exploiting the variability in optical properties arising at micro- and nano-scales in different materials or structures can lead to new advances in the field of optical PUFs. ZnO can be a good choice of material for this purpose as it is a direct band gap material with numerous types of spontaneous and stimulated emissions [5] and it easily forms into random and intricate nanostructures.

For this study, dense ZnO nanoforests composed of nanorods of ~ 200–300 nm in diameter have been grown on SiO2 and p+ polycrystalline silicon substrates using a chemical bath deposition (CBD) technique. A relatively diluted seed solution results in high density nanorods grown mostly in the upright direction with some vertical hollow spots in between neighboring nanorods. This nanorod arrangement works as a nano-porous thin film and produces Fabry-Perot fringes under perpendicularly incident white light. Optical scattering measurements have been conducted using an optical fiber placed at ~45° angle and connected to a spectrum analyzer to collect and analyze the scattered light. The local variations in density, height, diameter, orientation angle, and hexagonal perfection of the ZnO nanorods give rise to unique and reproducible scattering spectra that vary significantly from one spot on the sample to another. Example observed scattering spectra, statistical analysis of large numbers of spectra and uses for optical PUFs will be presented.

Acknowledgments: This work was supported by the Air Force Office of Scientific Research (AFOSR) through award FA9550-14-1-0351Z.

References:


11:00 AM EP07.09
High Brightness Laser Illumination using Macroscopic 3D Boron Nitride Architectures
Fabian Schutt1, Robert Roeder2, Maximilian Zapf2, Helge Krueger1, Juergen Carstensen1, Soeren Kaps1, Yogradra K. Mishra1, Carsten Ronning2 and Rainer Adelung1; 1Functional Nanomaterials, Kiel University, Kiel, Germany; 2Institute of Solid State Physics, University of Jena, Jena, Germany.

Laser diodes (LDs) are regarded as the next generation of ultra-efficient light sources, being able to produce more photons at high power densities than conventional light emitting diodes.[5] Even though most state-of-the-art technologies are based on a blue LD pumping a white-light emitting phosphor, an all-laser wavelength mixing approach, e.g. a combination of three (RGB) or even four (RGBY) laser wavelengths would outperform the efficiency of any other known white-light source.[2] However, in illumination applications, laser-based lighting systems still suffer from their monochromatic, low-divergent, and coherent nature, which demands a new generation of extremely efficient and versatile optical diffusers based on disordered nanostructured materials.[3] In the here presented study, we demonstrate a macroscopically expanded, three-dimensional (3D) laser light diffuser based on a highly porous (>99.99%) nanorachitecture, composed of interconnected hollow hexagonal boron nitride (h-BN) microtubes, with a wall thickness below 25 nm. The 3D hollow h-BN microtubular framework structure is synthesized by a novel template approach, which is based on a highly porous ceramic network consisting of tetrapodal-shaped microparticles.[3] The synthesis results in a highly disordered[4] and non-absorbing photonic network with thinly spread but highly effective light scattering centers, based on a combination of feature sizes greater than, equal to, and well below the magnitude of the impinging wavelength, allowing for pure light diffusion. The network structure basically resembles an artificial solid fog, but with a defined hierarchical internal structure. This enables an isotropic 3D light distribution from energetic, highly directional, as well as coherent laser light, with speckle contrasts well below the human sensitivity limit. In combination with the excellent heat management of the 3D h-BN exceptionally high laser damage thresholds (~3 J/cm²) above commercial diffuser materials can be reached. Such aero-materials enable a new generation of optical downstream components of tremendous efficiency for brightest illumination applications and open new fundamental research prospects in the field of disordered photonics.

References:


*Corresponding Author: fas@tf.uni-kiel.de

11:15 AM EP07.10
Towards Inkjet Printing of Phase-Separated Nanostructures for Light Extraction in Organic Light Emitting Diodes
Yidenekachew J. Donie1, 2, Stefan Schlisske1, Jan B. Preinfalk1, Jocelyn Van Leeuwen1, Amos Agrios1, Jürgen Hüpkes4, Karsten Bittkau4, Gerardo Hernandez-Sosa1, 2, Uli Lemmer1, 2, 3 and Guillaume Gomard1, 2; 1Light Technology Institute, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; 2Nanotech Biomachines, Inc., Milpitas, California, United States; 3InnovationLab, Heidelberg, Germany; 4IEK 5-Photovoltaik, Forschungszentrum Jülich GmbH, Jülich, Germany.

With only around 20% of light emitted into the ambient, organic light emitting diodes (OLEDs) suffer from detrimental optical losses arising from light trapped as (wave) guided modes and as surface plasmon polarizations. An attractive method to improve light out-coupling is to exploit the volumetric light scattering properties of composite layers based on nanoparticles that are randomly distributed in a polymer matrix. These layers promote light extraction over a broad spectral range and do not induce color distortion, which is desirable, for instance, in large area lighting applications. Moreover, it was demonstrated that they can be processed by screen- or inkjet-printing [1], making them industrially relevant in terms of fabrication throughput, design flexibility and material yield. Besides these micrometer thick layers, more compact layouts consisting of 2D planar light scatterers can be integrated in the OLED thin film stack to allow a good spatial overlap of the guided modes with the light outcouplers. Herein, structural disorder within the scatterers array (described by diameter size and inter-distance distribution functions) can be additionally tailored to optimize the light outcoupling conditions.

References:


*Corresponding Author: fas@tf.uni-kiel.de
In this communication, we show that the up-scalable polymer blend lithography technique is a versatile platform for fabricating such 2D planar, disordered light scatterers [2]. Using spin-coating as the deposition method for a blend of two immiscible polymers dissolved in a common low boiling point solvent and by tuning the polymer blend composition and the process parameters, we first generate phase-separated nanostructures initiated by solvent extraction. Their morphology and light scattering properties are varied, and their light extraction potential subsequently tested in bottom-emitting OLEDs. We report an efficiency enhancement of up to >50% relative to non-corrugated devices, as well as an improved angular and spectral stability. Following this proof-of-concept, our approach is then adapted to make it compatible with inkjet printing by using high boiling point solvents. We present a formulation which achieves the desired phase separation and a homogenous printing over cm² pixels, and we finally introduce a route to further include a planarization layer that helps the integration of the OLED thin film stack atop the light extraction layer.

11:30 AM EP07.07.11
Long-Distance Transmission of Broadband near Infrared Light Guided by Semi-Disordered 2D Array of Metal Nanoparticles Hyunguk Kim1, Seon Ju Yeou2, Kinam Jung3, Jeong Je Kim1, Kwanil Lee1, Il Ki Han1 and S. Joon Kwon1; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Hannam University, Daejeon, Korea (the Republic of).

Near infrared (NIR) waveguide is a key component of planar photonic devices such as optical communication couplers, image sensors, and spectroscopy for chemical or biological molecules. Conventional NIR waveguides such as silicon-on-insulator (SOI) waveguides or channel/ridge-type metal micro-strips have been used for signal transmission. However, there are usually limitations in reducing either signal delay or signal loss in the optically integrated devices. In this study, a novel NIR waveguide composed of semi-disordered array of metal nanoparticles (sDAMNPs) on Si substrate was proposed, fabricated, and tested. The disordered metallic nanoparticles array is geometrically localized in the form of 1D metal strips, thus changing sDAMNPs to less lossy strip channel waveguides. From the measurements supported by various computational modellings, fabricated waveguides effectively operate at broadband NIR (1100-1700 nm). It does not support signal transmission ultra violet-visible spectrum due to strong signal absorption and localization effects inside the metal nanoparticles. Instead, it is capable of transmitting NIR over a distance longer than 100 mm (signal loss ~ 3.85 dB/100 μm for NIR in 1200-1600 nm), which is also sufficiently larger than the conventional surface plasmon polariton propagation distance at the metal-Si interface. Compared to the waveguide-free reference, the waveguide exhibited greatly improved signal transmission efficiency up to a factor of 7.42×10⁴ at 1367 nm. It also exhibits a high sensitivity of deflection angle of 1.89 dB/0.01 rad, thus efficiently and straightly guiding the broadband NIR signal over long distance.

11:45 AM EP07.07.12
Simultaneous Generation of Reflective Multi-Colour Using Broadband Absorber PilHoon Jung, Soo-Jung Kim, Seungho Baek, Sacheol Ju and Heon Lee; Korea Univ, Seoul, Korea (the Republic of).

Reflective multi-colour is expressed by Fabry–Perot (F-P) resonance cavities which is the interference effect in multilayer thin-films with metal–dielectric–metal. The F-P resonance is composed lossless core dielectric with partially reflective ultra-thin metal layer and optically thick, highly reflective mirror. The absorption peak of multi-colour is tunable in the visible light range just by controlling the dielectric thickness.

In this study, we fabricated the multi-absorber to realize various colours that top metal as silver (Ag) Nanocrystals (NC) solids, with dielectric layer as hydrogen silsesquioxane (HSQ) as a resist, and higly reflective mirror as thick Ag layer. As a novel material, Ag NCs solids possess optical and electrical features for electrical and plasmonic applications of comparable utility to evaporated silver, with the added advantage of enhanced stability against oxidation. Also, HSQ resist shows similar optical properties with SiO₂ and thus can be worked the dielectric layer for F-P cavities. In particular, we can adjust the residual layer of HSQ resist to obtain various colours using nanoimprint lithography (NIL). NIL has advantages over other techniques in that it forms various patterns such as nano-to-microscale structures on various substrates. Consequently, we fabricated the various full-color optical micro-images (bear, flower, words, tiger) with 5μm square pixels on rigid substrate, non-planar substrate, and flexible substrates.
Defect Strain Fields in Colloidal Crystals

2:15 PM

References:

We studied the effect of the YSZ hollow sphere PhG structure parameters on the optical properties regarding the color impression and the effect of high-temperature applications and with our easy and environmental-friendly fabrication method this material can be therefore a non-toxic substitute for color pigments in ceramic processing.

We successfully fabricated a YSZ hollow sphere PhG which shows structural coloration with high saturation. The fabrication of these PhGs is divided into two steps: co-deposition of polystyrene (PS) spheres and YSZ nanoparticles by drop-casting and calculation to remove the PS template. Materials based on YSZ generating structural colors are suitable for high-temperature applications and with our easy and environmental-friendly fabrication method this material can be therefore a non-toxic substitute for color pigments in ceramic processing.

We used the effect of the YSZ hollow sphere PhG structure parameters on the optical properties regarding the color impression and the effect of high-temperature treatment on the stability of the material’s structure. The results show the possibility for tailoring the optical properties of the YSZ hollow sphere PhG and provide insights for developing other structural colors.

References:


2:15 PM EP07.08.03

Defect Strain Fields in Colloidal Crystals Bryan VanSaders1, Julia Dshemuchadse2 and Sharon C. Glotzer1, 2, 3; 1Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 3Biointerfaces Institute, University of Michigan, Ann Arbor, Michigan, United States.

Non-iridescent structural colors have a great potential to replace commercial pigments such as toxic metal oxides or organic pigments. Structural colors are generated by the refractive index distribution of the material and the observed colors result from light scattering by the structure of the material. Thus, structural colored materials show a high UV stability and can be tailored to high-temperature stability by using ceramics such as yttria-stabilized zirconia (YSZ). Non-iridescent structural colors can be generated by disordered arrangement of spheres, so-called photonic glasses (PhGs). So far, PhGs for structural coloration reported in the literature are mainly based on polymer spheres with low color saturation. Theoretical predictions showed that high saturated structural coloration can be realized by a PhG from hollow spheres with YSZ shell.[1] We successfully fabricated a YSZ hollow sphere PhG which shows structural coloration with high saturation. The fabrication of these PhGs is divided into two steps: co-deposition of polystyrene (PS) spheres and YSZ nanoparticles by drop-casting and calculation to remove the PS template. Materials based on YSZ generating structural colors are suitable for high-temperature applications and with our easy and environmental-friendly fabrication method this material can be therefore a non-toxic substitute for color pigments in ceramic processing.

We studied the effect of the YSZ hollow sphere PhG structure parameters on the optical properties regarding the color impression and the effect of high-temperature treatment on the stability of the material’s structure. The results show the possibility for tailoring the optical properties of the YSZ hollow sphere PhG and provide insights for developing other structural colors.

References:


2:30 PM BREAK

3:30 PM EP07.08.04

High-Contrast Structural Color Based on Core-Shell Photonic Glass Guoliang Shang1, Yen Nguyen2, Kaline P. Furlan2, Lukas Maiwald1, Hagen Renner1, Dirk Jalas1, Maksym Dosta1, Rolf Janßen2, Stefan Heinrich1, Gerold A. Schneider1, Alexander Petrov1, 4 and Manfred Eich1, 5; 1Institute of Optical and Electronic Materials, Hamburg University of Technology, Hamburg, Germany; 2Institute of Advanced Ceramics, Hamburg University of Technology, Hamburg, Germany; 3Institute of Solids Process Engineering and Particle Technology, Hamburg University of Technology, Hamburg, Germany; 4ITMO University, St. Petersburg, Russian Federation; 5Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany.

Photonics glasses are disordered assemblies of monodisperse (i.e. equally-sized) spherical particles. They are commonly used in research on non-iridescent (i.e. angle-independent) structural colors. However, no sufficient color saturation has been obtained so far as the reflectivity spectra of the realized structures show no sharp transitions.

Using first-order approximation the reflection spectrum of the structure can be related to the Fourier transform of its permittivity distribution. We show that by appropriately tailoring the individual particles in a photonic glass, its Fourier transform can be drastically changed. Using core-shell particles with a non-monotonous refractive index distribution from their center through their shell and into the background material the Fourier transform of the photonic glass can be shaped in such a way that a significant increase of the color saturation can be achieved. Our theoretical predictions were confirmed by numerical simulations.

Moreover, we experimentally realized a non-optimized photonic glass with full polystyrene spheres and an optimized photonic glass made from hollow zirconia spheres. Both structures were designed in such a way that they produce a similar reflection level and a transition at a similar wavelength. UV-Vis spectroscopy measurements showed that the core-shell structure indeed produces a much sharper transition in its reflectivity.

To directly compare the resulting colors the measured reflection spectra were translated into a CIE xy chromaticity diagram. In such a diagram pure spectral colors lie on the outer arched curve while less saturated colors are positioned inside closer to the white point at the center. The optimized core-shell structure produces a point that is much closer to the outer arched curve which indicates that it causes a significantly higher color saturation.

Relevant Publications:


3:45 PM EP07.08.05

3D Spatially-Resolved Optical Energy Density in Disordered Photonic Media Enhanced by Wavefront Shaping Oluwasemi S. Ojamhadi1, 2, Peilong
We study the transport and storage of light in a three-dimensional (3D) photonic band gap crystal doped by a single embedded resonant cavity by numerical methods. The crystal has finite support since it is surrounded by vacuum, as in experiments and devices, with a thickness of three unit cells. We employ the finite element method to model the diamond-like inverse woodpile crystal that consists of two orthogonal arrays of pores in a high-index dielectric similar to silicon. The point defect that functions as a resonant cavity is formed in the proximal region of two line defects, namely two selected orthogonal pores with a radius smaller than the ones in the bulk of the crystal.

We present a field-field cross-correlation method to identify resonances in the 3D position intensity pattern we obtain the 3D position of each nanosphere, while the total fluorescence intensity gauges the energy density. Our 3D spatially-resolved measurements reveal that the differential fluorescent enhancement changes with depth, up to 26 times near the back surface of the medium, and the enhancement scales with a strong peak versus transverse position. We successfully interpret our results with a newly developed 3D model without adjustable parameters that considers the time-reversed diffusion starting from a point source at the back surface [8].

We study the transport and storage of light in a 3D photonic band gap crystal doped by a single embedded resonant cavity by numerical methods. The crystal has finite support since it is surrounded by vacuum, as in experiments and devices, with a thickness of three unit cells. We employ the finite element method to model the diamond-like inverse woodpile crystal that consists of two orthogonal arrays of pores in a high-index dielectric similar to silicon. The point defect that functions as a resonant cavity is formed in the proximal region of two line defects, namely two selected orthogonal pores with a radius smaller than the ones in the bulk of the crystal. We present a field-field cross-correlation method to identify resonances in the finite crystal that has resonant states within the 3D photonic band gap of the infinite crystal. Out of five observed cavity resonances, one is s-polarized and four are p-polarized for light incident in the X or Z directions. All cavity resonances are angle-independent, confirming the 3D confinement of light in orthogonal pores with a radius smaller than the ones in the bulk of the crystal.

We present a field-field cross-correlation method to identify resonances in the 3D position intensity pattern we obtain the 3D position of each nanosphere, while the total fluorescence intensity gauges the energy density. Our 3D spatially-resolved measurements reveal that the differential fluorescent enhancement changes with depth, up to 26 times near the back surface of the medium, and the enhancement scales with a strong peak versus transverse position. We successfully interpret our results with a newly developed 3D model without adjustable parameters that considers the time-reversed diffusion starting from a point source at the back surface [8].

We study the transport and storage of light in a three-dimensional (3D) photonic band gap crystal doped by a single embedded resonant cavity by numerical methods. The crystal has finite support since it is surrounded by vacuum, as in experiments and devices, with a thickness of three unit cells. We employ the finite element method to model the diamond-like inverse woodpile crystal that consists of two orthogonal arrays of pores in a high-index dielectric similar to silicon. The point defect that functions as a resonant cavity is formed in the proximal region of two line defects, namely two selected orthogonal pores with a radius smaller than the ones in the bulk of the crystal. We present a field-field cross-correlation method to identify resonances in the finite crystal that has resonant states within the 3D photonic band gap of the infinite crystal. Out of five observed cavity resonances, one is s-polarized and four are p-polarized for light incident in the X or Z directions. All cavity resonances are angle-independent, confirming the 3D confinement of light in the photonic band gap cavity. It is remarkable that quality factors up to Q ~ 1000 are found for such thin crystals, which is attributed to the relatively short Bragg length of inverse woodpile photonic crystals. As a result, the optical energy density is greatly enhanced at the cavity resonances, by up to 2400 times the incident energy density in vacuum or up to 1200 times the energy density of the equivalent effective medium. Fano resonances arise below the 3D photonic band gap due to interference between the discrete contribution of the fundamental cavity mode and the continuum of light scattered by the crystal.

We present a field-field cross-correlation method to identify resonances in the 3D position intensity pattern we obtain the 3D position of each nanosphere, while the total fluorescence intensity gauges the energy density. Our 3D spatially-resolved measurements reveal that the differential fluorescent enhancement changes with depth, up to 26 times near the back surface of the medium, and the enhancement scales with a strong peak versus transverse position. We successfully interpret our results with a newly developed 3D model without adjustable parameters that considers the time-reversed diffusion starting from a point source at the back surface [8].

We study the transport and storage of light in a three-dimensional (3D) photonic band gap crystal doped by a single embedded resonant cavity by numerical methods. The crystal has finite support since it is surrounded by vacuum, as in experiments and devices, with a thickness of three unit cells. We employ the finite element method to model the diamond-like inverse woodpile crystal that consists of two orthogonal arrays of pores in a high-index dielectric similar to silicon. The point defect that functions as a resonant cavity is formed in the proximal region of two line defects, namely two selected orthogonal pores with a radius smaller than the ones in the bulk of the crystal. We present a field-field cross-correlation method to identify resonances in the finite crystal that has resonant states within the 3D photonic band gap of the infinite crystal. Out of five observed cavity resonances, one is s-polarized and four are p-polarized for light incident in the X or Z directions. All cavity resonances are angle-independent, confirming the 3D confinement of light in the photonic band gap cavity. It is remarkable that quality factors up to Q ~ 1000 are found for such thin crystals, which is attributed to the relatively short Bragg length of inverse woodpile photonic crystals. As a result, the optical energy density is greatly enhanced at the cavity resonances, by up to 2400 times the incident energy density in vacuum or up to 1200 times the energy density of the equivalent effective medium. Fano resonances arise below the 3D photonic band gap due to interference between the discrete contribution of the fundamental cavity mode and the continuum of light scattered by the crystal. Consequently, we find that an inverse woodpile photonic band gap cavity with a suitably adapted lattice parameter reveals a substantial photonic band gap due to interference between the discrete contribution of the fundamental cavity mode and the continuum of light scattered by the crystal.

We present a field-field cross-correlation method to identify resonances in the 3D position intensity pattern we obtain the 3D position of each nanosphere, while the total fluorescence intensity gauges the energy density. Our 3D spatially-resolved measurements reveal that the differential fluorescent enhancement changes with depth, up to 26 times near the back surface of the medium, and the enhancement scales with a strong peak versus transverse position. We successfully interpret our results with a newly developed 3D model without adjustable parameters that considers the time-reversed diffusion starting from a point source at the back surface [8].

We study the transport and storage of light in a three-dimensional (3D) photonic band gap crystal doped by a single embedded resonant cavity by numerical methods. The crystal has finite support since it is surrounded by vacuum, as in experiments and devices, with a thickness of three unit cells. We employ the finite element method to model the diamond-like inverse woodpile crystal that consists of two orthogonal arrays of pores in a high-index dielectric similar to silicon. The point defect that functions as a resonant cavity is formed in the proximal region of two line defects, namely two selected orthogonal pores with a radius smaller than the ones in the bulk of the crystal. We present a field-field cross-correlation method to identify resonances in the finite crystal that has resonant states within the 3D photonic band gap of the infinite crystal. Out of five observed cavity resonances, one is s-polarized and four are p-polarized for light incident in the X or Z directions. All cavity resonances are angle-independent, confirming the 3D confinement of light in the photonic band gap cavity. It is remarkable that quality factors up to Q ~ 1000 are found for such thin crystals, which is attributed to the relatively short Bragg length of inverse woodpile photonic crystals. As a result, the optical energy density is greatly enhanced at the cavity resonances, by up to 2400 times the incident energy density in vacuum or up to 1200 times the energy density of the equivalent effective medium. Fano resonances arise below the 3D photonic band gap due to interference between the discrete contribution of the fundamental cavity mode and the continuum of light scattered by the crystal. Consequently, we find that an inverse woodpile photonic band gap cavity with a suitably adapted lattice parameter reveals a substantial absorption in the visible range, which is relevant for photovoltaic applications and optical sensing.
A highly nonlinear M-Cresol/Nylon solution for optical shock waves

Giulia Marcucci1, 2, Phillip Cala3, Graham Siggins3, Weining Man3, Claudio Conti1, 2 and Zhigang Chen3, 4
1Physics, Sapienza University, Rome, Italy; 2Institute of Complex Systems, National Research Council, Rome, Italy; 3Physics and Astronomy, San Francisco State University, San Francisco, California, United States; 4TEDA Applied Physics Institute, Nankai University, Tianjin, China.

M-Cresol/Nylon is a chemical solution, which is made up of an organic solvent (m-cresol) and a synthetic polymeric solute (nylon). Recent experiments showed that this solution exhibits an isotropic giant self-defocusing nonlinearity, tunable by varying the nylon concentration. [1] When it is enlightened by a continuous-wave laser beam, light absorption induces heat gain, which reduces the refractive index: the material experiences a nonlinear thermo-optical effect, made nonlinear by the local temperature change. Since the temperature changes with the beam intensity, this nonlinearity follows a nonlocal Kerr model, as already known in the literature.

In optics, many phenomena are ruled by NLSE, such as soliton propagation and dispersive shock wave (DSW) generation. [2] We report experimental evidence of two-dimensional optical DSWs with an anisotropic zero-singularity. Fixing z as the longitudinal and x, y as the transverse directions, we start with a beam that has a Gaussian profile along y but a Gaussian first derivative along x, thus the intensity is null for x=0. This specific initial condition causes a new phenomenon, reported here for the first time: the shock develops undular bores on the beam external borders (as already known in literature), but around the singularity it presents an abrupt intensity discontinuity. We theoretically analyze the wave breaking along all the propagation. By a hydrodynamic model, we study the beam before the shock point: the WKB approach and the characteristic method let us predict the wave breaking both in phase and in intensity. [2] In order to model the beam propagation beyond the shock point, we use mathematical tools of time asymmetric quantum mechanics and uncover the mechanism how such an abrupt intensity discontinuity is generated. [3] We numerically simulate these results and find remarkable agreement both with experiments and with theoretical predictions.

Our outcome not only confirms previous studies on the giant nonlinear response of m-cresol/nylon, but also discloses fundamental insights on propagation of DSWs with a singular initial intensity profile.

condensates and optics, but it has never been observed. Here, we report the experimental observation of the breaking of replica symmetry in disordered nonlinear optical propagation [5]. We found that when mode interaction dominates light dynamics in a disordered photorefractive waveguide, replicated experimental realizations are found to have an anomalous overlap intensity distribution that signals a transition to an optical spin-glass phase. Specifically, a glassy state of light that emerges as nonlinear interaction overcomes a threshold and it is characterized by strong shot-to-shot variations of the speckle-like intensity distribution and the degree of spatial coherence. Surprisingly, these fluctuations are not randomly distributed but can be either completely correlated or anticorrelated. In close agreement with spin-glass theory, the Parisi overlap distribution between identical replicas incurs a nontrivial change that indicates how the same realizations of the dynamics may give rise to different physical observables. Thus, RSB here indicates a global locking of several spatial modes so that completely anticorrelated states may emerge from equivalent conditions, the signature that different metastable states underlie dynamics. These findings are general and do not depend on the specific form of disorder and character of the nonlinearity. They can be extended to a large class of optical systems including nonlinear multimode fibers and multiple pulse filamentation. Our results demonstrate that wave propagation can manifest features typical of spin-glasses, thus providing a novel platform for testing fundamental physical theories for complex systems.

References

9:00 AM EP07.09.04
Tailbot Carpets by Rogue Waves
Milivoj R. Belic; Texas A&M University at Qatar, Doha, Qatar.
Rogue waves are giant nonlinear waves that randomly appear and disappear in oceans and optics. Talbot carpets are periodic recurrent images of linear light and plasma waves. We demonstrate how to produce Talbot carpets by rogue waves. Such carpets can be used in nanoscale lithography.

9:15 AM *EP07.09.05
Coherently Engineered Disorder in Metal Oxide Semiconductors for Superior Solar-Assisted Hydrogen Production
Sanjay Mathur1, Danny Bialusiewski2, Jian Hoppus2, Evgeny Gurevich3; 1Institute of Inorganic Chemistry, Cologne, Germany; 2Chair of Applied Laser Technologies, Bochum, Germany.
Disorder in materials often result in new and unique properties, like enhanced light absorption or electrical conductivity. Tailored chemical or structural disorder is of high technological interest for various applications especially in the energy harvesting/conversion sector. These controlled defect structures can consist of perturbed periodic patterns (correlated) or lacking of any long-range symmetry (random). Both have been reported to improve the spectral response of semiconductor films used in light harvesting applications. Available techniques to induce disorder in sample volume or surface range from mechanical processing to bombardment with high-energy particles like electrons, ions or neutrons. In order to precisely control the disorder process, ultra fast laser pulses can be used. While laser ablation or laser melting rely on long pulses of continuous wave lasers, ultra short pulses, usually below 100 femtoseconds, can be used for controlled structuring. The very beam duration with high peak intensity allow induction of surface defects at micro- and nano-scale by non-linear effects, shock wave propagation or heat-induced transport. Engineered structural and chemical disorder is even capable of turning metal oxide semiconductor thin films into highly efficient solar absorbers. By laser-assisted patterning, these substrates can be modulated in their structure and composition, which manifests in enhanced light-trapping and in-coupling, ultimately enhancing the photoelectrochemical water splitting performance.

9:45 AM BREAK

SESSION EP07.10: Random Lasing
Session Chairs: Sushil Mujumdar and Davide Pierangeli
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 205

10:15 AM *EP07.10.01
Tailored Disorders in Photonic Crystals for Laser and Cavity QED Applications
Satoshi Iwamoto1, Yasutomo Ota2, Kazuhiro Kuruma1, Takeyoshi Tajiri3, Shun Takahashi3, Ryota Katsuma3, Masahiro Kakuda3, Katsuyuki Watanabe2, and Yasuhiko Arakawa2; 1Institute of Industrial Science, The University of Tokyo, Tokyo, Japan; 2Institute for Nano Quantum Information Electronics, The University of Tokyo, Tokyo, Japan.
Tailored disorders in a photonic crystal (PhC), which is a periodic structure in refractive index with a wavelength-scale periodicity, function as optical cavities and waveguides. Particularly, PhC nanocavities with high Q factor and small mode volume are receiving much attention because they can be applicable not only to passive optical devices such as narrow band filters but also to active photonic components, lasers, modulators, nonlinear optical devices etc. The tight confinement of photons within a tiny volume also make PhC nanocavities a fascinating platform for the study of cavity quantum electrodynamics (cavity QED) using solid state quantum emitters like semiconductor quantum dots (QDs). In this talk, we will discuss our recent experimental progresses on nanocavity lasers and quantum-dot cavity QED utilizing photonic nanocavities formed in 1D, 2D and 3D PhCs. Our long-lasting development of the fabrication technologies for high Q PhC nanocavities now makes possible the advanced studies on cavity QED phenomena in 2D PhC nanocavity embedding InAs QDs. We will discuss the successful fabrication of the QD-based vacuum Rabi oscillations measurement. The time-domain investigations also enables the investigation of carrier dynamics which have not been detected by the spectral-domain measurements. We have been also developing the micromanipulation technique for 3D PhCs. In the method, 2D plates constructing the final 3D PhC are prepared using the conventional planar nanofabrication technique first. Then the plates are precisely stacked with micromanipulators in a SEM chamber. We will briefly introduce the method and will discuss a proof-of-concept demonstration of photonic integrate circuit, in which a nanocavity laser and waveguides were simultaneously integrated in a 3D PhC. The output of nanocavity laser was guided through the two orthogonally connected PhC waveguides and was observed from the output facet of the waveguide. Finally, if time allows, a new
design approach of PhC nanocavity based on the photonic band topology will be discussed. A localized optical mode at the interface between two nanobeam PhCs with the same band structures but with different Zak phases were designed and fabricated. With optical gain of InAs QDs, we achieved the lasing oscillation utilizing the localized mode as an optical nanocavity.

10:45 AM EP07.10.02
Nanostars for Random Lasing Thomas A. Klar, Johannes Ziegler, Battuulga Munkhbat and Calin Hrelescu; Institute of Applied Physics, Johannes Kepler Universität Linz, Linz, Austria.

Gold nanostars in dye doped media provide a double degree of randomness. First, the position of these strong scatterers is random within the active media, making them good candidates for scattering centers in random lasers, superior to spherical or rod shaped gold nanoparticles. Second, the number, the size, and the directional distribution of the metallic tips are all random, hence making an ensemble of nanostars a broadband resonator. In fact, it is possible for gold nanostars to provide feedback over almost a full octave of visible to near IR laser wavelengths. Apart from organic dye molecules as active media, we also fabricated core-shell semiconductor quantum dots in combination with gold nanostars and demonstrated random lasing, as well. A disadvantage, though, is the high absorption of gold nanoparticles due to Förster transfer and due to the large imaginary part of the dielectric function given by the single electron transition between the d- and the sp-band. Silver would be the much better plasmonic material, however, it is seldom used due to its chemical reactivity. We have found a way to circumvent this dilemma. Starting with gold nanostars, we overgrow them with silver, such that the resulting Ag@Au nanostars show substantially smaller lasing thresholds than pure gold nanostars. Further, a 10 nm thin silica protection layer acts as a chemical passivation layer and simultaneously keeps the fluorophores away from the metallic surface. Within these 10 nm thick oxide layer, the quenching of the active material due to Förster transfer ceases, but the electric field is still enhanced at its surface. Finally, nanostars can also be used to improve the efficiency of organic light emitting diodes.

References:

11:00 AM EP07.10.03
Designing and Writing Scattering Centres to Build a Random Laser Network
Niccolo Caselli, Angel Mateos and Cefe López; Consejo Superior de Investigaciones Científicas, Madrid, Spain.

Random lasers emerged as an alternative and accessible source of laser light. The noteworthy advantage relies on the low-cost and flexible fabrication approach, which is traditionally based on colloidal systems [1] or crystal powder [2,3]. Their omnidirectional emission with low spatial coherence makes them promising sources for imaging and lighting application [4]. However, control and stabilization of the emission in terms of number of the amplified modes and frequency, is an open challenge due to the absence of an optical cavity. As a matter of fact, even by employing the same fabrication design two different devices give rise to different modes.

Here, we implemented a direct laser-writing technique to engineer an optically active material (dye-doped biopolymer film) by creating circular holes that act as scattering centres for light. This approach is based on the generation of a single femtosecond-pulse that induces ablation of the polymer film on the micrometre-scale. The site-controlled fabrication allows to print holes of different dimension, depth and position inside the active medium. When a couple of identical scattering centres are drawn it is possible, by optically pumping the straight region that connect the two scatterers, to generate random laser emission due to the feedback induced by the scatterers [5,6]. The spectral properties of these home-built random laser depends on the amount of disorder of the scatterers, that varies with their size and smoothness. Therefore, by tailoring the degree of disorder, that is by engineering and reproducing identical scattering centres, we achieved random lasers with a reproducible spectral emission. As a rule of thumb, in our devices larger and rougher holes give rise to a larger number of modes. The presented technique could open new ways to design and fabricate networks of random lasers where the nodes are represented by the holes acting as scattering centres and the connections are the straight line pumped regions of the active medium.

References:

11:15 AM EP07.10.04
Investigation of Random Lasing Contributions to Lasing-Spasers
Jill Tracey1 and Deirdre O'Carroll1, 2; 1Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Lasing-spasers are physically-small metal/dielectric nanoparticle structures that emit light via stimulated emission of radiation due to amplification of surface plasmons. There have been relatively few experimental demonstrations to date, all of which have relied on ensembles of randomly arranged nanoparticles to exhibit spasing. This has lead to the possibility that it is not just solely the effects of stimulated emission of radiation by amplification of surface plasmons leading to the observed phenomenon. Potentially, a combination of effects from the amplification of surface plasmons, and the random arrangement of nanoparticles, or local interactions between nanoparticles leads to stimulated emission. It is truly necessary to analyze the effects of a single particle and small clusters of particles in order to fully determine if random lasing is contributing to or even obscuring lasing-spaser emission.

The goal of this research project is to fabricate functioning spasers utilizing silver nanoparticles and conjugated polymer gain media. Samples are fabricated by sequential deposition of the following layers on a glass substrate: poly(acrylic acid), silver nanoparticles (60 nm diameter), poly(9,9-di-n-octylfluorenyl-2,7-diyldiyl) (PFO), followed by an optical epoxy encapsulant, and, finally, another glass slide. The thickness of the PFO gain layer is controlled to be less than 70 nm to inhibit photonic waveguide modes. The sample configuration is analyzed in two ways. First, stimulated emission from a dense, random arrangement of nanoparticles coated with a thin-film of the gain medium (PFO) is analyzed, to observe the effects of ensemble measurements, and potentially the effects of random lasing, if they do indeed contribute. From initial measurements, stimulated emission has been observed in samples with polymer thicknesses ranging between 30 nm to 70 nm, and was not observed in polymer films of the same thickness when nanoparticles were not present. However, as these were ensemble measurements, it is possible that the observed stimulated emission is from a combination...
of surface plasmon amplification, as well as nanoparticle interactions. The second approach is to use a less dense nanoparticle arrangement, in order to be able to probe single nanoparticles coated with the gain medium. This approach will allow us to determine if spasing is possible from a single nanoparticle, as well as to determine the effect that the random arrangement of particles contributes to the ensemble measurement results. Scanning electron microscopy is utilized to quantify the nanoparticle arrangement. Photoluminescence spectroscopy is used to determine if stimulated emission is occurring in both configurations, with the addition of an optical microscope for the single particle studies, in order to ensure that only one particle is probed at a time.

11:30 AM EP07.10.05
Random Lasing in Disordered Photonic Networks
Dhruv Saxena1, Michele Gaio1, Alexis Arnaudon1, Jacopo Bertolotti1, Sophia Yaliraki1, Mauricio Barahona1, Dario Pisignano3,4, Andrea Camposeo2 and Riccardo Sapienza1; 1Imperial College London, London, United Kingdom; 2Istituto Nanoscienze-CN, Pisa, Italy; 3University of Exeter, Exeter, United Kingdom; 4Università del Salento, Lecce, Italy.

Photonic networks, where light flows in a mesh of interconnected sub-wavelength waveguides, have attracted much attention due to their potential applications in quantum optics and integrated photonics. Here we report on a laser based on a disordered planar photonic network [1]. The network is composed of interconnected polymer nanofibers that are doped with a laser dye (Rhodamine-6G). We demonstrate lasing from the network, over a wide range of frequencies corresponding to many network modes, and show that the lasing modes can be designed via the network connectivity and topology.

The complexity of the photonic network lasers brings the opportunity to control the lasing action by selectively illuminating a very small subset of the network links. This surprising result is predicted by a graph description of Maxwell’s equations, which is used to model the network laser. Our graph approach enables efficient modelling of large networks, which is not possible using conventional numerical methods of solving Maxwell’s equations. Moreover, it facilitates design of the network topology for lasing and identification of the most important edges in the network that are necessary for sustaining a particular mode.

Following this strategy, we experimentally demonstrate control over the lasing modes and single-frequency operation. The controlled network laser is a compact laser source, CMOS compatible, capable of switching the lasing output, which could become an important component for future optical computing and processing.


11:45 AM EP07.10.06
Nonlocal Random Laser and Replica Symmetry Breaking
Loredana Maria Massaro2, Silvia Gentilini1, Cristina Colosi2, Ilenia Viola3, Claudio Conti1,4 and Neda Ghofraniha2; 1Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, Rome, Italy; 2Dipartimento di Fisica, Universita La Sapienza, Rome, Italy; 3Istituto Italiano di Tecnologia, Rome, Italy; 4Consiglio Nazionale delle Ricerche, Istituto Nanotec, Rome, Italy.

We propose a novel type of random lasers (RL) with disordered structure designed by using 3D bioprinting. Bioprinting uses a computer-controlled printing device to accurately deposit cells and biomaterials into precise architectures creating organized multicellular tissue structures [1]. In our sample we use a blend of alginate mixed with TiO2, which acts as structural template maintaining the printed multi-layer constructs without collapsing. After fabrication the printed structures are stored in a liquid medium and depending on the time spent in it they will present different final dimension. Rhodamine-B in diethylene glycol (RHB) is added as gain medium. The final result is a dyed sample with waffle-like structure made by crossing 30-100 micron thick stripes of TiO2-alginate-RHB and square empty holes.

Two different RLs with different dimension and microstructure are explored. The first one is dried and with a more compact structure inside the stripes, the second one is kept wet and with lower porosity. We use a RL set-up previously reported [2] to examine the emission and two diverse behaviors are observed.

i) The dry sample shows incoherent RL emission with the well known large narrowing spectral peak typical of other TiO2 based RLs, but with an intriguing NONLOCAL behavior: strong RL emission far from the pumping point is observed both inside the stripes (with material) and more interestingly outside in the empty holes. This can be ascribed to a wave guiding mechanism not yet reported in similar disordered materials and is a clear demonstration of the propagation of RL radiation.

ii) The wet sample presents coherent RL emission with several sub-nanometric peaks as an indication of many longitudinal modes. Strong shot to shot spectral fluctuations are observed: each time the laser is on a different composition of the many peaks is given ranging from the only fluorescence band to few very sharp narrow peaks.

We use the Replica Symmetry Breaking (RSB) analysis recently introduced [3] to quantify such fluctuations. Differently, in the present work we explore by this method the statistical mechanics of coherent RL with many resonances. We observe evident RSB of whole the spectra as well as of the single peaks as the demonstration of strong mode interaction and we define their different laser thresholds by investigating the distribution of the intensity overlaps. In this wet sample we do not observed the wave guiding mechanism present in the dry one.

The ability to manipulate light-matter interactions using complex, aperiodic electromagnetic media is at the heart of current nanophotonics and metamaterials technologies. Efficient approaches for multiscale electromagnetic field enhancement, concentration and manipulation of fields with designed spatial-frequency spectra in complex media enable the control of propagating and non-propagating electromagnetic modes in optical nanostructures with broadband/multi-band enhanced responses. Besides its fundamental interest, photonic-plasmonic interactions in complex aperiodic environments are also of great importance for a number of device applications such as multi-band nano-antennas, ultrafast optical switches, nanoscale energy concentrators, laser nano-cavities, and optical biochemical sensors. In this talk, I will discuss our work on the design and engineering of wave localization, scattering and transport phenomena in novel aperiodic nanostructures and metamaterials with controllable structural correlation properties for novel Si-compatible, on-chip devices applications. Finally, I will introduce our current work on the design and of novel dielectric nanostructures and metamaterials with anomalous scattering properties driven by the Epsilon Near Zero (ENZ) response of Si-compatible novel materials.

2:00 PM EP07.11.02
Plasmonic Properties of Ordered Arrays of Metallic Nanostructures Fabricated by Nanosphere Lithography and MeV Ion Implantation Cecilia Salinas1, Jose Miguel Zarate1, Erick Flores-Romerol2, Erika Rodriguez-Sevilla1,2 and Juan-Carlos Cheang-Wong1, 1Universidad Nacional Autonoma de Mexico, Ciudad de Mexico, Mexico; 2Catedrático CONACyT, Ciudad de Mexico, Mexico.

In nanoscale electronic, photonic and plasmonic devices, feature dimensions shrink towards a critical limit, and new experimental approaches have to be explored in lithographic patterning to create ordered arrays of metallic nanostructures with useful optical properties. In this work, spherical submicrometer-sized colloidal silica particles were prepared by sol-gel and deposited onto silica glass plates by means of a spin coater system. By combining MeV ion implantation (Au, Ag ions) and nanosphere lithography, this silica particle monolayer acts as a mask to create regular arrays of metallic nanoscale features embedded in the silica plate. By this way, after removal of the silica particles and an adequate thermal annealing of the as-implanted samples, the formation of metallic nanostructures was confirmed by the presence of the corresponding surface plasmon resonance (SPR) in the optical absorption spectra. In order to modify the shape of such quasi-spherical nanoparticles embedded in the silica matrix, some of the samples were irradiated at room temperature with 8 MeV Si ions, leading to the formation of elongated metallic nanoparticles, achieving then the tuning of the SPR and the nonlinear optical properties. The size and shape of the arrays of silica particles and the embedded metallic nanoparticles were studied by scanning and transmission electron microscopy, respectively. The long range order of both the self-assembled monolayer of silica particles and the metallic nanoparticle arrays were characterized by a Fast Fourier Transform study. The plasmonic properties of the metallic nanostructures were characterized by optical absorption measurements as a function of the Si ion irradiation experimental parameters.

2:15 PM EP07.11.03
Light-Induced Disorder-to-Order Transition in Dissipative Colloidal Silver Nanoparticles Fan Nan, Fei Han and Zijie Yan; Clarkson University, Potsdam, New York, United States.

Upon laser illumination, electrodynamic interactions can arise among plasmonic silver nanoparticles in solution, leading to local energy minima on the potential energy surface. The silver nanoparticles will self-assemble into ordered structures if the potential wells are deep enough to maintain the structural stability under thermal fluctuations, otherwise they tend to be disordered. Here we report a dissipative colloidal system where ordered chains involving nanoparticle oligomers (such as dimers and linear trimers) transiently arise among largely disordered silver nanoparticles illuminated by a laser beam. The transition is driven by anisotropic electrodynamic interactions coupled with electrostatic interactions, and provides new opportunities to discover new dissipative structures and build novel mesoscale structures.

2:30 PM BREAK

3:00 PM EP07.11.04
Anderson Localization of Hybrid Plasmons in Terahertz Plasmonic Materials Sushil Mujumdar1, Ajay Nahata2 and M. Balasubrahmaniyan1; 1Tata Institute of Fundamental Research, Mumbai, India; 2Department of Electrical and Computer Engineering, The University of Utah, Salt Lake City, Utah, United States.

Disorder-induced Anderson localization of waves has been demonstrated in optical, acoustic, and matter wave domains, but lacks substantial research in the plasmonic domain due to the inherent losses. Towards a more calibrated study of plasmonic localization and dissipation, appropriate plasmonic materials need to be employed. Given that metallic losses are lower at lower frequencies, terahertz waves are promising candidates in the study of loss and localization. Our recent experiments provided evidence of Anderson localization in terahertz frequencies in a linear array of subwavelength through-holes drilled in a thin stainless steel sheet. However, the limited spectral resolution prevented access to individual localized modes and their loss. The current work reports our theoretical analysis of Anderson localization in this system from the vantage point of the dispersion characteristics of the structure. The subwavelength holes act as resonators and confine resonant fields in the air in the holes. The steel surface supports a plasmon polaron that possesses a linear dispersion at terahertz frequencies. The Kondo-hybridisation of the cavity resonance and the polariton realizes hybrid plasmons that constitute the localized quasiparticles in this system.

We further elucidate critical differences between the localization of hybrid plasmons and that of photons occurring in conventional dielectric systems. The anti-crossing of the dispersion profiles of the resonator and the polariton opens a hybridisation gap that is centered on the resonant frequency of the resonator. The resultant upper transmission band is highly radiative, but the lower band is bound to the interface and supports surface transport, and is conducive to Anderson localization. The profile of the density of states (DoS) exhibits diverging DoS at the edges of the gap. Disorder is introduced into the structure by randomizing the positions of the holes. This shifts the band-edge states into the hybridization gap, and induces their localization as evidenced by the newly-developed exponential tails. We quantify the localization length separately from the loss-length, and find that the latter is at least an order of magnitude larger. Further, we find that the maximally-shifted gap modes cannot arbitrarily transit deep into the gap, even at strongest disorder. They exhibit a propensity to remain pinned to a frequency which depends on the resonance frequency of the subwavelength cavity. As a consequence, the hybridization gap never closes even at strongest disorder, and the midgap DoS remains zero. Such a situation is in stark constrast to conventional dielectric systems, where the DoS closes through the formation of a Lifshitz tail.

In conclusion, we have analyzed Anderson localization of hybrid plasmons, which exhibits hitherto-unstudied characteristics of localization. This study emphasizes the need and potential of novel hybrid plasmonic materials in studies of fundamental phenomena.

3:15 PM EP07.11.05
Fourier-Space Spectroscopy of Disordered Plasmonic Metasurfaces Florian Sterl, Thomas Weiss, Steffen Both and Harald Giessen; 4th Physics Institute and Research Center SCoPE, University of Stuttgart, Stuttgart, Germany.
The optical properties of plasmonic nanoparticle ensembles are not only determined by the particle shape and size, but also depend on the arrangement of the nanoantennas. The angle-dependent transmission/reflection characteristics of a rectangular nanoparticle array are strongly influenced by lattice diffraction effects, while these effects are absent in a completely randomized ensemble. By introducing short- or long-range disorder into a nanoparticle lattice, one can furthermore strongly influence the optical properties.

We present both computational and experimental approaches to gain a better understanding of the impact of disorder on the bidirectional reflectance distribution function (BRDF) of complex plasmonic metasurfaces. We treat the nanoantennas as dipoles, and we simulate the electric field based on dipole-dipole coupling. We can then extract the wavelength-resolved far-field response [1] and convert it into RGB colors, to construct the optical appearance. Similarly, we can extract the wavelength-resolved Fourier space image, providing the angle-resolved far-field response. Varying the incident angle provides the full wavelength-resolved BRDF.

To compare the simulations to experimental data, we develop a designated back focal plane microspectroscopy setup, based on a modified 4-f setup [2]. This allows us to record the real- as well as Fourier-space images generated by nanoparticle ensembles at spot sizes down to 50 µm. The resulting image can either be projected onto an RGB CCD camera, or onto the entrance slit of an imaging spectrometer. In this way, the full wavelength- and angle-resolved far-field response can be recorded. By furthermore varying the incident angle, we can record the full BRDF of such microscopic metasurfaces. In the case of ‘frozen-phonon disorder’, each element is displaced from its initial lattice position by a random amount in a random direction [3]. We can go from a fully ordered to a fully disordered arrangement in several steps by increasing the range of the displacement. We also consider correlated disorder, where the displacement of any element affects the surrounding elements with a certain correlation length and function. We aim to derive a correlation of these results with the two-point correlation function resulting from the spatial arrangement. Thus, we will be able to extract disorder kind and strength from our measurements, and, in turn, design the visible appearance of a metasurface by tailored disorder.


SYMPOSIUM EP08

TUTORIAL: Ultra-Wide-Bandgap Semiconductors—From Materials to Devices
November 25 - November 25, 2018

* Invited Paper

The Ultra-Wide-Bandgap (UWBG) materials represent the next chapter in the history of semiconductor physics, with potential applications to optoelectronics, radio-frequency electronics, power switching electronics, electronics and sensors for harsh environments, platforms for quantum information processing, and possibly as-yet-unforeseen areas. Such applications are enabled by the properties of the materials and the novel device structures enabled by those properties. The first part of this tutorial will focus on the unique physical properties of the key UWBG semiconductors (AlN, BN, Ga2O3, diamond, etc.) as well as the challenges in their growth and manipulation (substrates, doping, defects, etc.) The second part will focus on potential applications and the device structures appropriate for those applications (LEDs, vertical and lateral transistors, etc.) as well as the challenges associated with the design and processing of such devices (metal-semiconductor contacts, surface passivation, etc.) The goal is to provide a comprehensive overview of the key aspects of this new and exciting field.

1:30 PM
Ultra-Wide-Bandgap Semiconductors: Materials Robert J. Nemanich; Arizona State University

The first part of the tutorial will focus on the unique physical properties of the key UWBG semiconductors (AlN, BN, Ga2O3, diamond, etc.) as well as the challenges in their growth and manipulation (substrates, doping, defects, etc.)

3:00 PM BREAK

3:30 PM
Ultra-Wide-Bandgap Semiconductors: Devices Robert J. Kaplar; Sandia National Laboratory
The second part of the tutorial will focus on potential applications of UWBG semiconductors, and the device structures appropriate for those applications (LEDs, vertical and lateral transistors, etc.) as well as the challenges associated with the design and processing of such devices (metal-semiconductor contacts, surface passivation, etc.)

**SYMPOSIUM EP08**

Ultra-Wide-Bandgap Materials and Devices  
November 26 - November 29, 2018

**Symposium Organizers**  
Mark Hollis, Massachusetts Institute of Technology - Lincoln Laboratory  
Robert Kaplan, Sandia National Laboratories  
David Moran, University of Glasgow  
Rachael Myers-Ward, U.S. Naval Research Laboratory

**Symposium Support**  
BAE Systems  
Novel Crystal Technology, Inc.

* Invited Paper

**SESSION EP08.01: Oxide Devices I**  
Session Chair: Mark Hollis  
Monday Morning, November 26, 2018  
Hynes, Level 2, Room 209

8:30 AM *EP08.01.01  
Investigation of Process Techniques for Ga2O3 Based Diodes  
Fan Ren¹, Jiancheng Yang¹, Stephen J. Pearton¹, Marko Tadjer² and Akito Kuramata³; ¹University of Florida, Gainesville, Florida, United States; ²U.S. Naval Research Laboratory, Washington DC, District of Columbia, United States; ³Tamura Corporation and Novel Crystal Technology, Inc, Sayama Saitama, Japan.

Monoclinic β-phase Ga2O3 has outstanding potential for power electronics, and high quality, large diameter bulk crystals and epitaxial layers of Ga2O3 are already available with a range of controllable n-type doping levels by edge-defined film-fed (EFG) growth using iridium crucibles, by Czochralski or by float zone. The direct energy bandgap of Ga2O3, ∼4.9 eV, yields a very high theoretical breakdown electric field (∼8 MV/cm). For power electronics, the Baliga figure-of-merit proportional carrier mobility, critical electric field and breakdown voltage, is almost four times higher for Ga2O3 than for GaN. Currently, the major limitation for Ga2O3 based device fabrication is the lack of low resistance Ohmic contacts, low damage dry etching process, and thermally stable Schottky contacts. In this work, we report a technique by employing Aluminum Zinc Oxide (AZO) to improve Ohmic contacts on Ga2O3, studies of etch rates and etching induced damages with Cl2/Ar and BCl3/Ar based discharge, surface treatment prior to Schottky metal deposition as well as Ni/Au and Pt/Au Schottky contacts, and demonstration of 2300 V breakdown voltage Ga2O3 Schottky diode.

9:00 AM *EP08.01.02  
Advances in Ga2O3 MOSFETs for Power Switching and Beyond  
Masataka Higashiwaki¹, Man Hoi Wong¹, Takafumi Kamimura¹, Yoshiaki Nakata¹, Chia-Hung Lin¹, Akinori Takeyama¹, Takahiro Makino¹, Takeshi Ohshimi², Manikant Singh³, James W. Pomeroy³, Michael J. Uren³, Michael A. Casbon⁴, Paul J. Tasker⁵, Ken Goto⁶, Kohei Sasaki⁷, Akito Kuramata⁸, Shigenobu Yamakoshi⁹, Martin Kuball⁹, Hisashi Murakami¹⁰ and Yoshinao Kumagai¹¹; ¹National Institute of Information and Communications Technology, Koganei, Japan; ²National Institutes for Quantum and Radiological Science and Technology, Koganei, Japan; ³National Institutes for Quantum and Radiological Science and Technology, Takasaki, Japan; ⁴University of Bristol, Bristol, United Kingdom; ⁵Cardiff University, Cardiff, United Kingdom; ⁶Tamura Corporation, Sayama, Japan; ⁷Tokyo University of Agriculture and Technology, Koganei, Japan.

Ga2O3 has emerged as a noteworthy ultrawide bandgap semiconductor in the past five years. Owing to excellent material properties based on an extremely large bandgap of over 4.5 eV and the commercial availability of native wafers produced from melt-grown bulk single crystals, Ga2O3-based electronic devices are promising candidates for various applications in power switching, RF, and harsh-environment electronics.

First, this presentation will give an overview of our state-of-the-art lateral depletion-mode (D-mode) Ga2O3 metal-oxide-semiconductor field-effect transistors (MOSFETs) [1]. The devices demonstrated an off-state breakdown voltage of over 750 V, a drain current on/off ratio of more than nine orders of magnitude, stable device operation at temperatures up to 300°C, and negligibly small DC–RF dispersion. Furthermore, the bulk Ga2O3 channel exhibited strong gamma-ray tolerance by virtue of showing very little on-resistance degradation and threshold voltage shift, thereby demonstrating the strong potential of Ga2O3 devices for radiation-hard electronics [2]. We will also present RF and thermal characteristics of the lateral MOSFETs [3-5].

In the second part, we will discuss our recent developments of vertical D-mode Ga2O3 MOSFETs [6, 7]. The devices had a current blocking layer formed by Mg- or N-ion implantation and successfully demonstrated drain current modulation by an applied gate bias. However, the devices were still at a primitive development stage and had some severe issues to be resolved.

This work was partially supported by Council for Science, Technology, and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Next-generation power electronics” (funding agency: NEDO).

The layer was fabricated into a vertical Schottky photodiode with a Pt/n(-)Ga2O3/n(+)Ga2O3(010) structure. A 30Å semitransparent Pt metal was used on the

In this paper, we report performance comparisons between Silicon Dioxide (SiO2) and Aluminum Oxide (Al2O3) as gate dielectrics for beta-Gallium Oxide transistors based on β-Ga2O3 with promising results for the development of high efficiency power converters. In order to electrically isolate such electronic devices based on β-Ga2O3 for high efficiency power electronics of the next generation.

The ultra-wide bandgap semiconductor β-Ga2O3 has received great attention in recent years due to its potential to become an attractive alternative to conventionally used materials for future power electronic applications. The estimated dielectric strength of 8 MV/cm in combination with the expected Baliga’s figure of merit are promising indicators to pave the way for the realization of power devices with even higher breakdown voltages and efficiencies than their SiC and GaN counterparts. Up to now several studies have demonstrated the successful realization of Schottky barrier diodes and field-effect transistors based on β-Ga2O3 with promising results for the development of high efficiency power converters. In order to electrically isolate such electronic devices from each other dry etching of mesa structures into the β-Ga2O3 is commonly carried out. On the other hand device isolation by ion implantation of Ga2O3 has not yet been investigated and the applicability of this technology in terms of processing boundary conditions on β-Ga2O3 is still unknown to date. In this study we report on the application of multiple energy nitrogen ion implantation for the electrical isolation of electronic devices on monoclinic β-Ga2O3. By the introduction of uniformly distributed midgap damage-related levels in the β-Ga2O3 crystal lattice we are able to increase the sheet resistances by more than 9 orders of magnitude to ≥1011 Ωsq which remains electrically stable up to annealing temperatures of 600 °C carried out for 60 seconds under nitrogen atmosphere. At higher annealing temperatures the damage-related trap levels are being removed causing a significant drop of the sheet resistance down to 4 x 105 Ωsq after annealing at 800 °C. This effect is preceded by a structural recovery of the implantation damages via the recrystallization of the crystal lattice at already 400 °C as verified by x-ray diffraction measurements. The extracted activation energies of the deep states responsible for the high resistive β-Ga2O3 layer after implantation is in the range of 0.7 eV. It shows a strong correlation with the annealing temperature dependence of the sheet resistance and thus supports the theory of a damage-induced isolation mechanism. The outcome of this work is an important step towards a more robust fabrication method of electronic devices based on β-Ga2O3 for high efficiency power electronics of the next generation.

We report on the MOCVD growth of controllably doped device quality β-Ga2O3 and β-(AlGaxGa1-x)2O3 epitaxial layers with carrier concentration between 1E15 and 1E20 1/cm³. For the realization of β-Ga2O3, based high performance power electronics with high breakdown voltages and low on-resistance, the low background impurity concentration and high electron mobility are critical. However, one of the challenges in the MOCVD growth of β-Ga2O3 is the presence of unintentional background concentration which is mainly attributed to carbon and hydrogen impurities that incorporate into the epilayers primarily from the metalorganic precursors. Here, we present an in-situ and ex-situ methods used to reduce the incorporation of these impurities. Optimization of the MOCVD growth condition, including O₂ flow rate, chamber pressure, and temperature were found to be critical to control the incorporation of these impurities, hence the background concentration and electron mobility in the film. With optimal growth conditions, films with record electron mobility of up to 176 cm²/Vs and ~3500 cm²/Vs were measured at room temperature and 54 K, respectively [1]. Low background concentration of ~1.5E15 1/cm³ was obtained. A short post growth annealing of the β-Ga2O3 in an oxygen atmosphere was also found to reduce the background concentration in the films with no influence on the electron mobility. Si doping of β-Ga2O3 and β-(AlGaxGa1-x)2O3 alloys using silane and tetrachlorosilane (TEOS) was systematically investigated with the carrier concentration ranging between 1E15 and 1E20 1/cm³. The effect of using silane and TEOS on the incorporation of carbon and hydrogen impurities in the doped layers will be discussed. The growth of high-quality strained β-(AlGaxGa1-x)2O3-β-Ga2O3 heterostructures and superlattices on (010) β-Ga2O3 substrates will be presented. The structural quality, abruptness of hetero-interfaces, surface morphology and electrical properties of the heterostructures will be discussed.

mobility two-dimensional electron gas (2DEG) at the AlGaN/GaN heterointerface. In the power switching domain, AlGaN/GaN based HEMTs are believed to make an impact similar to what Si MOSFETs did in 1970s in switching power supply applications by replacing BJTs. However, a major challenge with this device technology is the normally-ON nature which reduces their efficiency in power systems. There have been multiple instances of overcoming this issue by various (post growth) processing methods [1][2]. Here we show, for the first time, the integration of a body-diode based back-gate control in AlGaN/GaN HEMTs to shift the threshold voltage to normally-OFF regime and dynamically control the device performance with a fourth back-gate terminal. This approach is similar to the body-bias technique of threshold voltage control in CMOS [3].

We experimentally demonstrate the role of the back-gate voltage in controlling the performance of HEMTs in both ON and OFF states of the device. The HEMT structure used in this study has been epitaxially grown using metal organic chemical vapor deposition technique. To incorporate body-diode, conventional HEMT structure was epitaxially grown on p-type GaN. The role of Mg activation in the p-GaN layer on the electrical properties of the device has been studied and will be discussed. With the integration of body-diode, the 2DEG current shows modulation with the change in magnitude and polarity of the back-gate voltage. An increase in 2DEG current is measured with the application of a positive back-gate voltage and a decrease is measured under a negative back-gate bias. Moreover, a positive/negative shift in the threshold voltage is observed with the application of negative/positive back-gate voltage. The modulation of 2DEG density is attributed to the modulation of the body-diode depletion width. Along with extensive results of such modulation, a comprehensive study demonstrating 3-terminal and 4-terminal output/transfer characteristics and capacitance-voltage characteristic of this novel device structure will be presented.

References:

11:45 AM EP08.02.06 InGaN Nanowire Light Emitting Diode Integrated with Field Effect Transistor Matthew Hartensveld and Jing Zhang; Microsystems, Rochester Institute of Technology, Rochester, New York, United States.

Current display technology is reaching its practical limitations as the Thin-Film-Transistors (TFTs) that make up displays are struggling to be reduced further in size. Emerging technologies such as Augmented and Virtual Reality are also challenged to find transparent and high-resolution displays. Nanowire (NW) Light Emitting Diodes (LEDs) are appearing as the solution due to higher efficiencies (70% vs. 5%), high reliability, and the ability to be manufactured at nanoscale. Though NW LEDs are being pursued, there are key issues in monolithically integrating Field Effect Transistors (FETs) with these LEDs. Common solutions include growth on Silicon to incorporate Complementary Metal Oxide Semiconductor (CMOS) technology, layer regrowth for High Electron Mobility Transistors (HEMTs), and deposition of classical TFTs on top of the LEDS. Nevertheless, all these approaches would sacrifice display area and device performance to introduce FETs to LEDs.

Presented here is a novel monolithic integration scheme to vertically combine GaN NW FETs with InGaN NW LEDs. Novel to this work, the layer of unintentionally doped GaN (u-GaN), serving as a template to LED growth, is used for FET channel. This makes the FET in series with an NW LED for switching. Our approach allows for straightforward fabrication, no loss of display area, and eliminates device degradation. Many different types of FETs can be realized, and here a Static Induction Transistor (SIT) is selected due to the ease of fabrication.

To start, a conventional LED structure is used consisting of sapphire, u-GaN, n-type GaN, InGaN quantum wells, and p-type GaN. The NWs are fabricated through a top-down method utilizing Reactive Ion Etching (RIE) to etch down into the u-GaN layer. The etched NWs are then immersed in a KOH solution to crystallographically wet etch the wires, shrinking the diameters along with removing etch damage. Titanium is next evaporated at the base of the wires and annealed. Annealing creates nitrogen vacancies which construct the n-i-n structure common to modern transistors. Following the anneal, Polydimethylsiloxane (PDMS) is deposited and etched back to provide an insulating layer. Nickel is then evaporated creating a 30 nm schottky gate on the u-GaN. A second layer of PDMS is then coated and etched back to reveal the NW tips, followed by a deposition of Indium Tin Oxide (ITO) for top contact. These preliminary devices show good gate control with the ability to switch on/off the NW LEDs. As the gate becomes reverse bias the depletion region of the gate pinches off the current flow through the u-GaN layer, switching off the LED. Silvaco simulations are additionally performed to investigate and model device operation. This monolithically integration of NW LED and SIT can open the door to the next generation of display technology with the ability to be fabricated at diameters smaller than 100 nm, along with the inherent ability to be fully transparent.

SESSION EP08.03: Oxide Devices II
Session Chair: David Moran
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 209

1:30 PM *EP08.03.01 Electrical and Thermal Studies of β-Ga2O3 Nano-Membrane Field-Effect Transistors on Different Substrates Peide P. Ye; Purdue University, West Lafayette, Indiana, United States.

β-Ga2O3 is an emerging wide bandgap semiconductor for the next generation power devices to replace GaN and SiC. It has an ultra-wide bandgap of 4.8 eV and a corresponding high breakdown field of 8 MV/cm. However, the β-Ga2O3 bulk substrate has a low thermal conductivity (k) of 10-25 W/mk and thus severe self-heating effects (SHE) can be observed. In high-power electronic devices, the output power density and the maximum drain current can be significantly limited by the elevated channel temperature caused by SHE and it has become a key challenges in β-Ga2O3 research. To suppress severe self-heating at high powers, we herein demonstrate top-gate nano-membrane β-Ga2O3 field effect transistors on a high thermal conductivity diamond substrate. The devices exhibit enhanced performance, with a record high maximum drain current of 980 mA/mm for top-gate β-Ga2O3 field effect transistors and 60% less temperature increase from reduced self-heating, compared to the device on sapphire substrate operating at the same power. With Improved heat dissipation, β-Ga2O3 field effect transistors on a diamond substrate are validated using a newly developed ultrafast high-resolution thermoreflectance imaging technique, Raman thermography, and thermal simulations. The work is in close collaborations with Dr. Marko Tadjer’s team at NRL and Prof. Ali
Heat dissipation has become an increasingly critical technological challenge in modern electronics and photonics. To address this challenge, discovering new high thermal conductivity materials that can efficiently dissipate heat from hot spots and improve the device performance of gallium nitride based electronics are urgently needed. Recent theoretical work including ab initio has predicted a new class of thermal materials, however, experimental demonstration has been challenged by materials synthesis and thermal characterization. Here, we describe our current progress in developing and characterizing these emerging high thermal conductivity materials [1-3].

We have chemically synthesized high-quality boron phosphide single crystals and measured their thermal conductivity as a record-high 460 W/mK at room temperature[1]. We have, for the first time, experimentally measured the phonon mean free path spectra of boron phosphide and analyzed experimental results by solving three-dimensional and spectral-dependent phonon Boltzmann transport equation using the variance-reduced Monte Carlo method. The experimental results are in good agreement with that predicted by multiscale simulations and density functional theory, which together quantify the heat conduction through the phonon mode dependent scattering process.

Our findings underscore the promise of the emerging high thermal conductivity material for advanced thermal management and provides a microscopic-level understanding of the phonon spectra and thermal transport mechanisms. The study aims to enable a rational design of thermal materials and nano- to multiscale devices, including the heat management of wide-bandgap electronics.

References:
phase. The band offset of the (Al,Ga)O alloy mainly arises from the discontinuity in the conduction band. Consequences for designing modulation-doped field effect transistors (MODFETs) based on (Al,Ga)O/GaO are also discussed.

3:30 PM BREAK

3:40 PM EP08.03.06
β-Ga2O3 Nano-Electronic Devices
Jhvan Kim, Korea University, Seoul, Korea (the Republic of).

The preparation of nanowayer β-Ga2O3 flake by a mechanical exfoliation method and its fabrication into various types of electron and optoelectronic devices will be presented. Firstly, we will show a heterostructure n-channel depletion-mode β-Ga2O3 junction field-effect transistor through a van der Walls bonding with an exfoliated p-WSe flakes. β-Ga2O3 and hexagonal boron nitride hetrostructure-based metal-insulator-semiconductor field-effect transistors (MISFETs) are achieved by integrating mechanical exfoliation of quasi-two-dimensional materials with dry transfer process, where nano-thin flakes of β-Ga2O3 are utilized as the channel region of the MISFET. We will present a β-Ga2O3 metal-semiconductor field-effect transistor with a high off-state breakdown voltage (344 V), based on an exfoliated β-Ga2O3 field-plated with hexagonal boron nitride. This heterostructured ultra-wide bandgap nanodevice shows a new route toward high power nano-electronic devices.

4:00 PM EP08.03.07
Anisotropic Optical Properties in Zn2GeO4 and Ga2O3 Nanowires
Jaime Dolado1, 2, Manuel Alonso-Orts1, Íñaki Lopez2, 3, Pedro Hidalgo2, Emilio Nogales1 and Branci Mendez1, 4; 1University of Complutense, Madrid, Spain; 2Istituto Nazionale di Ottica, Florence, Italy.

Zinc germanate (Zn2GeO4) and gallium oxide (Ga2O3) are wide band gap semiconductors (Eg = 4.5 and 4.9 eV, respectively) with promising applications due to their matching with UV radiation in UV photodetectors, phosphors in flat panel displays or photo catalysis. In addition, Ga2O3, in particular, is becoming an emerging material for high power devices while Zn2GeO4 is a good candidate to be used in Li-ion batteries. In both oxides, the electronic and optical properties have been investigated recently, and an active research is going on. For example, there is still controversy about the origin of the visible luminescence of these oxides, usually attributed to oxygen vacancies, which are mainstream defects in oxide materials. Furthermore, doping oxides to modify electronic conductivity or luminescence property is a challenge because of the interplay of impurities with native defects, which add more complexity to the physical properties. On the other hand, nanowire morphologies of a number of compounds have been recently studied on the view of particular applications, such as optical microcavities or vertical devices designs. Since optoelectronic properties are intrinsically related to the electronic levels in the band gap, high-energy electron and UV light are suitable probes to test these properties. In this work, we explore the optical properties of undoped Zn2GeO4 and Zn doped Ga2O3 and nanostructures synthetized by a thermal evaporation method. We will carry out polarization dependent luminescence and Raman measurements to get some insight into their luminescence features and their correlation with their chemical and structural configuration at atomic scale level.

4:15 PM EP08.03.08
Gallium Oxide Nanowires for Gas Sensing Applications—Growth, Device Fabrication and Gas Response
Guillem Domenech-Gil1, 2, Irmina Peiró1, Jordi Sama1, 2, Paolo Pellegrino1, 2, Sergi Hernández1, 2, Mauricio Moreno1, 2, J.D. Prades1, 2, Isabel Gràcia3, Carles Cané3, Sven Barth4 and Albert Romano-Rodríguez1, 2; 1Department of Electronic and Biomedical Engineering, Universitat de Barcelona (UB), Barcelona, Spain; 2Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona (UB), Barcelona, Spain; 3CNM, Bellaterra, Spain; 4TUW, Wien, Austria.

Gallium oxide (Ga2O3) is a wide band gap semiconductor material that has been widely studied during the last three decades in the form of thin films for its high-temperature sensing properties towards oxygen and reducing gases. Its optical and sensing properties have been largely studied and several improvements for its use as gas sensor have been achieved introducing different modifications. These changes, that include surface functionalization, material doping or nanowire (NW) morphology, allow working at low temperatures where the sensing mechanisms are supposed to be deactivated. The high surface-to-volume ratio attributed to nanowire morphology decreases the power consumption of the devices, while allowing to sense at lower temperatures than thin films. In our study, devices containing a single Ga2O3 NW are studied as humidity sensors, working at room temperature. β-Ga2O3 nanowires were fabricated via a metal-assisted vapor-liquid-solid process using a carbothermal reduction and the synthesized nanowires were structurally and optically characterized using X-ray diffraction, scanning and transmission electron microscopy and related techniques as well as photoluminescence and X-ray photoelectron spectroscopy. Measurements revealed a crystalline material, different photoluminescence emission peaks in the visible range, and a transition band gap of 4.2 eV that suggests the presence of a high density of intraband states. UsingFocused Electroan Beam Induced Deposition techniques, nanowires were individually contacted for their use as gas sensors. The fabricated devices have been tested, from room temperature up to 200 °C, in environments with different concentrations of relevant gases for air quality monitoring, such as nitrogen dioxide and carbon monoxide, as well as oxygen and water vapor. Fast, stable and reproducible response was measured towards water vapor at room temperature (25 °C) using power consumptions between 0.25 and 250 nW. Tests under nitrogen ambient revealed that, at room temperature, the pre-adsorption of oxygen ions at the NW surface is mandatory for the water vapor sensing and that oxygen, even at low concentrations, is rapidly re-adsorbed at the surface of the material in a lapse of one minute. Furthermore, the presence of carbon at the surface of the nanowires, result of the growth process, plays an important role in sensing capabilities and will be discussed.

4:30 PM EP08.03.09
New Perspective of Room-Temperature Gas Sensor Using Ionic Conduction Based SnO2 Nanorods
Young Geun Song1, 2, Young-Sook Shim3, Jun Min Suh4, Ho Won Jang4, Byeong-Kwon Ju1 and Chong-Yun Kang1, 2; 1Center for Electronic Materials, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2College of Engineering, Korea University, Seoul, Korea (the Republic of); 3Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 4Seoul National University, Seoul, Korea (the Republic of); 5KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, Korea (the Republic of).

Gas sensors with intelligent systems have become a core part of the complete Internet of Things (IoT) since they offer continuous information on the presence of specific gases in the ambient atmosphere. As a representative gas sensor, semiconducting type has attracted much attention due to their cost effectiveness, simplicity in fabrication, high response and easy integration with electronic circuits. Generally, the semiconducting gas sensors require a high operating temperature of 150–400°C for adsorption and desorption of target molecules. However, high temperature reduces sensor stability and life time due to thermally induced growth of grains, and can lead to risks of ignition when detecting flammable explosive analytes. Furthermore, it can also affect interconnect electronic and requires high power consumption that is an important parameter for the new generation of battery-loaded wireless sensors, resulting in reluctant practical application. Hence, one of the most important challenge and issue in gas sensor society is to make a high-performance gas sensor that operates at room temperature for high stability and low-power consumption. Over the past decade, there are various approaches to enhance the sensing performance at room-temperature using metal additives or heterojunctions and two-dimensional materials. Despite these extensive efforts, there remain challenging including poor response and incomplete recovery because electronic conduction based sensing mechanism is limited by insufficient reaction energy between the analytical molecule and sensing material at room-temperature. Herein, we suggest a new strategy for a room temperature gas
sensor using the ionic conduction based gas sensing mechanism. Glancing angle deposition (GLAD) method was used to fabricate highly porous
SnOxnanorods. The ionic conduction induced by humidity was confirmed using impedance spectroscopy, I-V characteristic and XPS analysis. The relation
between the sensing properties and relative humidity was systematically investigated. Our experimental results show that the response of SnO2 nanorods to
5 ppm NO2 has a maximum response over 1400 at RH 20%. Also, it is observed that the response rate and recovery rate are accelerated as relative humidity
increases. The gas sensing mechanism can be demonstrated based on the principle of the ionic conduction, humidity sensor, and water splitting. We believe
that the ionic conduction based SnO2 nanorods open a new direction for developing the room temperature gas sensor.

4:45 PM EP08.03.10
Doping Dependence of Electrical Characteristics of Zn-O-N Thin-Film Transistors Hiroshi Tsuji, Tatsuya Takei, Mitsuru Nakata, Masashi Miyakawa
and Yoshihide Fujisaki; NHK Science & Technology Research Labs, Tokyo, Japan.

Thin-film transistors (TFTs) that utilize oxide semiconductors as channel materials have become a key technology for various applications such as displays,
sensors, and memory devices due to their superior characteristics, which include high mobility, low off-current, low processing temperature, and applicability
to large-area production. Zn-O-N (ZnON) [1] has recently received attention as a channel material for high-mobility TFTs, especially those
employed in demanding applications such as large ultra-high definition organic light-emitting diode displays. ZnON-TFTs exhibit much higher field-effect
mobilities (>50 cm²/Vs) [2] than conventional oxide TFTs. However, ZnON-TFTs have some drawbacks that must be addressed, including a negatively
shifted threshold voltage (Vth), a large subthreshold swing (SS), and Vt instability when stored in air. We have recently reported that Si doping of ZnON is
effective for improving the switching characteristics and long-term stability of ZnON-TFTs [3].

In the present work, the effects of impurity doping on the electrical characteristics of ZnON-TFTs are further investigated by co-sputtering of Zn and other elements
(Ta, Zr, or In). The results indicate that doping with Ta or Zr, both of which have a high bond-dissociation energy with nitrogen, is effective for
overcoming the drawbacks of ZnON-TFTs, as in the case of Si doping [3]. In particular, Ta-doped ZnON-TFTs with an optimal doping level exhibited a high
field-effect mobility of 49 cm²/Vs, improved switching behavior (less negative Vth and smaller SS), and better Vt stability than non-doped ZnON-
TFTs. On the other hand, the use of In doping enhanced the mobility of ZnON-TFTs, and this could be attributed to the electron pathways formed by the
broad 5s orbitals of In. In-doped ZnON-TFTs exhibited a high field-effect mobility of up to 59 cm²/Vs, although a more negative Vt was also observed.
These results indicate that impurity doping is an effective approach to improving and enhancing the performance of ZnON-TFTs.


SESSION EP08.04: Oxide Growth
Session Chair: Robert Kaplar
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 209

8:30 AM *EP08.04.01
Bulk Crystal Growth and Devices Fabrication of β-Ga2O3 Xutang Tao; Shandong University, Jinan Shandong, China.

At present, silicon based devices have gradually reached their theoretical limits. Wide-bandgap semiconductors have been considered as the candidates for
high-performance electronic devices and deep UV optoelectronic devices.[1] The bandgap of β-Ga2O3 is as large as 4.7 eV, as a new type of ultra-wide
bandgap semiconductor, it is attracting more and more attention in recent years. β-Ga2O3 has the advantages of higher breakdown field, bigger Baliga FOM
and shorter UV cutoff edge compared to the traditional wide-bandgap semiconductors including ZnO, SiC and GaN. Furthermore, large size and high
quality β-Ga2O3 crystals could be grown by Czochralski method or edge-defined film-fed growth (EFG) method such as Si and GaAs.[2] Therefore, β-
Ga2O3 is a desirable material for high voltage, high power, low loss power devices and deep UV optoelectronic devices, such as: deep UV photodetectors,
transparent thin film transistors, light-emitting diodes (LEDs), Schottky diodes, high voltage transistors and high temperature gas sensors.
In recent years, the basic research and commercialization of β-Ga2O3 develop quickly. The size of bulk crystals is enlarging, the quality of epitaxial films is
improving and the performance of semiconductor devices keep breaking records. However, as a novel semiconductor material, the research of β-Ga2O3 is
still in the early stage. The crystal quality, basic physical properties, physical properties optimization and devices performance optimization are still need
be systematically studied.
In this work, we focus on the crystal growth of high quality β-Ga2O3 to meet the requirements of different devices. The crystal growth methods and
equipment modification, crystal growth process optimization, electrical properties optimization and crystal wafer processing are systematically studied.
Furthermore, high-performance UV detector and Schottky diodes have been obtained based on high quality single crystal wafers.

References

9:00 AM EP08.04.02
Epitaxial Lateral Overgrowth of α-Ga2O3 on Sapphire Substrates Riena Jinno, Nobuhiro Yoshimura, Kentaro Kaneko and Shizuo Fujita; Kyoto
University, Kyoto, Japan.

Ga2O3, which is one of the ultra wide-bandgap (UWBG) semiconductors, has attracted attentions as a next-generation material of power devices [1].
Among their six different phases (α, β, γ, δ, ε, and κ), the α-phase is the most suitable for bandgap engineering due to its crystal structure of corundum,
although it is the metastable phase. Alloys with α-Al2O3 and α-In2O3 enabled the bandgap engineering from 3.7 to 8.7 eV[2]. However, we must consider
dislocations in α-Ga2O3 formed due to large lattice mismatch to sapphire substrates. In this study, epitaxial lateral overgrowth (ELO) of α-Ga2O3 was
conducted on sapphire substrates, aiming at reducing the dislocation density in α-Ga2O3.
Stripe-patterned dielectric masks of SiO2 were formed on sapphire substrates. The both widths of openings and masks were 5 μm. The various orientations
of substrates (c-, c-, m- and r-planes) and openings were used. All the growth of α-Ga2O3 was conducted on the patterned substrates by using the mist-CVD
method. Ga2O3 was adopted as a Ga source, which enables the growth rate of α-Ga2O3 as high as 7 μm/hour. The growth temperature was changed between
500 and 700 °C.

References
α-Ga2O3 was selectively grown on the openings at the temperatures higher than 550 °C, while the deposition on masks was observed at 500 °C irrespective of the orientations of substrates and openings. When α-Ga2O3 was grown on c-plane sapphire substrates, the triangular stripes with (10-11) and (10-12) facets were observed for (10-10)-type stripe, while the rectangular cross section with a (0001) top facet and (11-20) sidewalls was observed for (10-10)-type stripes. Although the shapes of the features depended on the orientations of substrates and openings, all the facets were formed by (10-11), (10-12), (11-20) and (0001), which are consistent with stacking of oxygen and gallium layers. These planes were considered to be stable under the oxygen rich growth condition by the mist-CVD method. The growth of α-Ga2O3 on a-plane sapphire with <10-10> stripes showed the largest ratio of the lateral and vertical growth rates, that is, 0.87. Under this condition, the coalescence of two adjacent wings was achieved. TEM observations were conducted to discuss dislocation structure in the α-Ga2O3. The cross sectional TEM images revealed that the dislocation density in the α-Ga2O3 was successfully reduced, while the dislocations on the openings were propagated without bending. From these results, the ELO technique is useful to reduce the dislocation density in α-Ga2O3. We need to investigate the growth conditions with bending dislocations on openings to decrease the dislocations on openings effectively.

Part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).


We report on growth studies and germanium doping of heterogeneous and homoepitaxial beta-Gallium Oxide using low pressure chemical vapor deposition technique. Gallium oxide has attracted a lot of attention because of its potential applications in high power devices. The main advantage of Ga2O3 over other wide band gap materials is the availability of a high quality commercial substrates and shallow n-type dopants. A variety of growth techniques exist for growth of Ga2O3 thin films including MBE, MOCVD, HVPE etc. Low pressure CVD [1] is a simple, cost-effective technique to grow high-quality Gallium Oxide with sufficiently high growth rates and low impurity concentration, as the precursors are ultrapure Gallium, oxygen gas and Argon carrier gas.

To calibrate the growth rates and understand the growth regimes, we characterized gallium oxide thin films grown on sapphire substrates as a function of growth temperature, oxygen flow rate and Argon flow rate. The nominal growth rate (characterized using cross sectional SEM) varies from 2.5 µm/hr to 3.5 µm/hr for temperature between 850 °C – 950 °C, for chamber pressure of 1.5 Torr. At low oxygen concentrations, the growth rate doesn’t show significant variation with oxygen flow rate indicating a mass transport limited growth, at the substrate temperature of 935 °C. With flow rates higher than 6 sccm (Ar flow rate of 140 sccm), gallium oxide power formation was observed which resulted in much thinner films. Ga2O3 films were grown on both c-plane and vicinal sapphire substrates, thin films on vicinal sapphire were much smoother than c-plane wafers. Also, the roughness of these films dropped with increasing oxygen flow rate. Using a two-step growth technique, surface roughness was reduced to as low as 10 nm for a 10 micron thick LPCVD grown film. Using CV characterization on undoped films grown on Sn-doped n-type bulk substrates, background carrier concentration as low as 1×10³ cm⁻² was obtained. Solid Ge source was used to explore n-type doping. Using transfer length method (TLM) structures fabricated using annealed Ti (50 nm)/Au(100 nm)/Ni(100 nm) metal stack, resistivity ranging from 0.1 to 7.5 ohm-cm was obtained. Temperature dependent hall mobility and carrier concentration, activation energy for Ge dopants in Ga2O3 will be presented. These results indicate the promise for controlled high quality growth of Ga2O3 with high growth rates for high power performance electronics.


We report on growth studies and germanium doping of heterogeneous and homoepitaxial beta-Gallium Oxide using low pressure chemical vapor deposition technique. Gallium oxide has attracted a lot of attention because of its potential applications in high power devices. The main advantage of Ga2O3 over other wide band gap materials is the availability of a high quality commercial substrates and shallow n-type dopants. A variety of growth techniques exist for growth of Ga2O3 thin films including MBE, MOCVD, HVPE etc. Low pressure CVD [1] is a simple, low-cost technique to grow high-quality Gallium Oxide with sufficiently high growth rates and low impurity concentration, as the precursors are ultrapure Gallium, oxygen gas and Argon carrier gas.

To calibrate the growth rates and understand the growth regimes, we characterized gallium oxide thin films grown on sapphire substrates as a function of growth temperature, oxygen flow rate and Argon flow rate. The nominal growth rate (characterized using cross sectional SEM) varies from 2.5 µm/hr to 3.5 µm/hr for temperature between 850 °C – 950 °C, for chamber pressure of 1.5 Torr. At low oxygen concentrations, the growth rate doesn’t show significant variation with oxygen flow rate indicating a mass transport limited growth, at the substrate temperature of 935 °C. With flow rates higher than 6 sccm (Ar flow rate of 140 sccm), gallium oxide power formation was observed which resulted in much thinner films. Ga2O3 films were grown on both c-plane and vicinal sapphire substrates, thin films on vicinal sapphire were much smoother than c-plane wafers. Also, the roughness of these films dropped with increasing oxygen flow rate. Using a two-step growth technique, surface roughness was reduced to as low as 10 nm for a 10 micron thick LPCVD grown film. Using CV characterization on undoped films grown on Sn-doped n-type bulk substrates, background carrier concentration as low as 1×10³ cm⁻² was obtained. Solid Ge source was used to explore n-type doping. Using transfer length method (TLM) structures fabricated using annealed Ti (50 nm)/Au(100 nm)/Ni(100 nm) metal stack, resistivity ranging from 0.1 to 7.5 ohm-cm was obtained. Temperature dependent hall mobility and carrier concentration, activation energy for Ge dopants in Ga2O3 will be presented. These results indicate the promise for controlled high quality growth of Ga2O3 with high growth rates for high power performance electronics.


High-Bias-Stability in Atomic-Layer-Deposition Al2O3 by Post-Deposition-Anneal on Wide- and Ultra-Wide-Bandgap Semiconductors Kiyotaka Horikawa1, Atsushi Hirawat2, Satoshi Okubo2, Taitsu Kegeura2 and Hiroshi Kawarada1; Waseda University, Tokyo, Japan; 2 Nagoya University, Nagoya, Japan.

The metal-insulator- Wide- and ultra-wide-bandgap semiconductor field-effect transistors (MISFETs) are expected to realize good characteristic in terms of high breakdown voltage and low-loss features. However, it was difficult to form a thermally SiO2 film as a gate insulating or passivation film on Wide- and ultra-wide-bandgap semiconductors. Various insulators have been investigated using atomic layer deposition (ALD), which forms films with unparalleled uniformity and reproducibility. Among those films, ALD-Al2O3 is an attractive candidate, having a wide bandgap of 7eV [1], a high dielectric constant of 9 [2], etc. A major challenge for the Al2O3 in practical applications is Al2O3-related bias instability (BI) needs to be reduced. This study is concerned with achieving better performance by reducing the dislocations on openings effectively.

Part of this work was supported by the New Energy and Industrial Technology Development Organization (NEDO).


β-Ga2O3 has attracted a lot of attention because of its potential applications in high power devices. The main advantage of Ga2O3 over other wide band gap materials is the availability of a high quality commercial substrates and shallow n-type dopants. A variety of growth techniques exist for growth of Ga2O3 thin films including MBE, MOCVD, HVPE etc. Low pressure CVD [1] is a simple, low-cost technique to grow high-quality Gallium Oxide with sufficiently high growth rates and low impurity concentration, as the precursors are ultrapure Gallium, oxygen gas and Argon carrier gas.

To calibrate the growth rates and understand the growth regimes, we characterized gallium oxide thin films grown on sapphire substrates as a function of growth temperature, oxygen flow rate and Argon flow rate. The nominal growth rate (characterized using cross sectional SEM) varies from 2.5 µm/hr to 3.5 µm/hr for temperature between 850 °C – 950 °C, for chamber pressure of 1.5 Torr. At low oxygen concentrations, the growth rate doesn’t show significant variation with oxygen flow rate indicating a mass transport limited growth, at the substrate temperature of 935 °C. With flow rates higher than 6 sccm (Ar flow rate of 140 sccm), gallium oxide power formation was observed which resulted in much thinner films. Ga2O3 films were grown on both c-plane and vicinal sapphire substrates, thin films on vicinal sapphire were much smoother than c-plane wafers. Also, the roughness of these films dropped with increasing oxygen flow rate. Using a two-step growth technique, surface roughness was reduced to as low as 10 nm for a 10 micron thick LPCVD grown film. Using CV characterization on undoped films grown on Sn-doped n-type bulk substrates, background carrier concentration as low as 1×10³ cm⁻² was obtained. Solid Ge source was used to explore n-type doping. Using transfer length method (TLM) structures fabricated using annealed Ti (50 nm)/Au(100 nm)/Ni(100 nm) metal stack, resistivity ranging from 0.1 to 7.5 ohm-cm was obtained. Temperature dependent hall mobility and carrier concentration, activation energy for Ge dopants in Ga2O3 will be presented. These results indicate the promise for controlled high quality growth of Ga2O3 with high growth rates for high power performance electronics.
The intrinsic structural and electronic properties of Ga2O3 suggest that it may ultimately outperform existing wide-gap semiconductors such as SiC for Army Research Laboratory, Adelphi, Maryland, United States.

β-(AlxGa1-x)2O3 epitaxial layers were grown using ultra-high vacuum pulsed laser epitaxy at 500 °C, using a KrF excimer laser (λ=248nm) operating at 4 J/cm2, and metal-organic vapor phase epitaxy (MOVPE) using Ge as n-type dopant in β-Ga2O3 (010) films, and obtained a wide range of electron concentration (1×1017 cm−3 - 1×1020 cm−3)[8]. Mobility of 97 cm2/Vs was achieved for a charge density of 1.6×1018 cm−3 using Ge as dopant. This mobility is two times higher than the mobility achieved for a similar charge density using Sn.

Using β-Ga2O3 as the intentional donor, we recently demonstrated modulation doping in β-(AlxGa1-x)2O3/β-Ga2O3 heterostructures. The formation of 2DEG was confirmed by capacitance-voltage measurements. Modulation doping field effect transistors were fabricated. A maximum current density of 20 mA/mm, with a pinch of voltage of ~0V was achieved on the sample with a 2DEG sheet charge density of 1.2×1013 cm−2.[9]

In this talk, I will discuss the above-mentioned progress in detail.

References

10:45 AM EP08.04.06

High-Quality β-(AlxGa1-x)2O3/Ga2O3 (010) and Si-Doped β-(AlxGa1-x)2O3/Ga2O3 (010) Heterostructures Grown by Pulsed Laser Epitaxy
Shaneq Pacley, Shin Mou, Adam Neal, Kurt Eynk, Krishnamurthy Mahalingum, Lawrence Grazulis, Eric Heller, Brandon M. Howe, Kelson Chabak and Gregg Jessen, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States.

Here, we present the results of a fundamental growth investigation into the effects of Al-alloying and delta doping using Si on the structural and electronic properties of β-(AlxGa1-x)2O3 heterostructures grown on semi-insulating Fe-doped β-Ga2O3 (010) single crystals. High quality β-(Al0.8Ga0.2)2O3 and Si-doped β-(Al0.8Ga0.2)2O3 epitaxial layers were grown using ultra-high vacuum pulsed laser epitaxy at 500 °C, using a KrF excimer laser (λ=248nm) operating at 4 Hz and a fluence of ~3 J/cm2. Targets with an Al content ranging from x = 0.175 - 0.5 were used for undoped layers of β-(AlxGa1-x)2O3, while targets with an Al content of x = 0.175, 0.225 and a Si content of 0.1% were used for the doped heterostructures. The Al content was varied to increase the bandgap, and Si was used in the heterobuffer of β-(AlxGa1-x)2O3 for modulation doped field-effect transistors. High-resolution X-ray diffraction (HRXRD) and high-resolution transmission electron microscopy (HRTEM) confirmed both β-(AlxGa1-x)2O3 and Si doped β-(AlxGa1-x)2O3 films. Both HRXRD and HRTEM showed we were able to obtain high quality epitaxial films of β-(AlxGa1-x)2O3 up to x = 0.225, which was confirmed by X-ray photoelectron spectroscopy (XPS). However, HRTEM suggests we were able to obtain β-(Al0.8Ga0.2)2O3 up to 50%, but the stability of this phase is still under investigation. As a result of this research, we demonstrate that pulsed laser deposition can be used to grow both β-(Al0.8Ga0.2)2O3/Ga2O3 and Si-doped β-(Al0.8Ga0.2)2O3 heterostructures for wide bandgap electronic devices and specifically, modulation doped transistors. Finally, Hall transport and capacitance-voltage will be used to characterize the heterojunction electrical properties, and XPS will be used to correlate Al content with band offset.

11:00 AM EP08.04.07

TEM-EELS Analysis of Ga2O3/SiO2 and Ga2O3/Al2O3 Interface Structures with Electron Beam Induced Crystallization of Al2O3 Gate Layer
Christopher Klingshirn1, Asanka Jayawardena2, Sarit Dhar2, Tsvetanka Zheleva3, Aivars Leis3 and Lourdes G. Salamanca-Riba4; 1Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 2Physics, Auburn University, Auburn, Alabama, United States; 3U.S. Army Research Laboratory, Adelphi, Maryland, United States.

The intrinsic structural and electronic properties of Ga2O3 suggest that it may ultimately outperform existing wide-gap semiconductors such as SiC for certain metal oxide semiconductor (MOS) device applications, especially at very high power. However, as with SiC, interfacial defects at the Ga2O3 / gate oxide interface adversely affects the performance of Ga2O3-based MOS devices. The various choices of gate oxide material for Ga2O3-based devices, such as SiO2 and Al2O3, present their own trade-offs in terms of electrical properties (bandgap and breakdown strength) and interface abruptness and stability. Previous work on SiC has shown that a narrower transition layer at the SiC/ SiO2 interface correlates to decreased interface trap density and enhanced channel mobility.

In this work, we discuss chemical and structural features of interfaces between Ga2O3 and SiO2 and Al2O3 investigated using high resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning TEM (HAADF-STEM) combined with electron energy loss spectroscopy (EELS SI). STEM and EELS measurements allow identification of the width, composition, and bonding characteristics of the interface region. Hyperspectral decomposition of EELS signals using machine learning techniques reveal components corresponding to Ga2O3, Ge or Si and Al. Gate dielectric deposition and post-deposition annealing (PDA) conditions are found to affect interface quality, with higher temperature processing correlated with interfacial roughness. The Ga2O3 / Al2O3 interface is not fully abrupt and contains an interfacial region likely corresponding to interdiffusion between Ga and Al. Additionally, rapid crystallization of the Al2O3 gate oxide layers, outward from the interface, was observed during TEM imaging despite remaining at a lower temperature than during the gate deposition or PDA processes. Contributions of thermal gradient, strain and radiolysis to this beam-induced crystallization effect will be presented.

Supported by ARL under Grant No. W911NF1420110.

11:15 AM EP08.04.08

Scanning Transmission Electron Microscopy of Gallium Oxide Materials and Interfaces
Jared M. Johnson, Yuewei Zhang, Md Rezaul Karim, Hongqing Zhao, Siddharth Rajan and Jinwoo Hwang; Ohio State University, Columbus, Ohio, United States.

We perform a microscopic investigation of ultra-wide bandgap (UWBG) β-Ga2O3 materials and interfaces using atomic resolution scanning transmission electron microscopy (STEM). Our goal is to establish fundamental understanding on the atomic to nanoscale structure and defects that directly affect the
basic materials properties and device performance of β-Ga2O3, which is essential to advance β-Ga2O3 to many technologically important UWBG applications. Here, we present the details of our STEM investigation and the experimental results from various β-Ga2O3 materials and heterostructures. First, we will present the unique technical challenges in the STEM characterization of β-Ga2O3 due to its high structural anisotropy and TEM sample preparation. Second, we will show the detailed structure, formation, and dynamics of extended defects that can directly influence the properties of various homo- and hetero-β-Ga2O3 interfaces. Finally, we will present our ongoing development of the new STEM imaging mode that uses the electron channeling effect to image individual point defects (both intrinsic and extrinsic) in β-Ga2O3. The imaging mode can utilize the new-generation pixelated fast STEM detector, which can capture the channeling signals at a narrowly confined scattering angle and determine the position and structure of point defects with high precision.

1:45 PM *EP08.05.01
Topics in the Ab Initio Theory of Ga2O3, Mainly the ε Phase
Barbara Maccioni1, Roberta Farris1, Paola Alippi2 and Vincenzo Fiorentini1; 1University di Cagliari, Monserrato, Italy; 2CNR-ISM, Rome, Italy.

This presentation is about ab initio calculations in the area of Ga2O3 and thereabouts. I will first discuss the anisotropy of absorption in the β phase of Ga2O3, and a revised mixing phase diagram of InGaO phases including strain. I will then concentrate on the newly-synthesised ε (epsilon) phase of Ga2O3, in particular in relation to its polarization properties (is this a pyro- or a ferro-electric ?), electronic structure (first ARPES spectra, Seebeck and Peltier coefficients), and phonons (dispersion, thermal conductivity, thermoelectric ZT, and core lineshapes).

2:15 PM EP08.05.02
Characterizing the Influence of Impurities and Dopants on the Electrical Properties of Ga2O3 Through Hybrid Functional Calculations
Joel B. Varley; Lawrence Livermore National Laboratory, Livermore, California, United States.

Gallium oxide has emerged as a promising candidate for next-generation power electronics due to a number of favorable properties such as its large band gap, controllable conductivity and the availability of large single-crystal substrates grown from the melt. Despite the rapid surge of interest in this material, there are still a number of outstanding questions as to how various defects, i.e. native point defects and extrinsic impurities, influence the properties of this material. In this talk we use hybrid functional calculations to elucidate the role of common impurities that have been identified in Ga2O3 single crystals and epitaxial films. Particularly we discuss the role of Fe and Ir impurities, which we find to be highly soluble in Ga2O3 and both electrically and optically active defects depending on the conditions. Our results identify that Fe impurities act as a highly soluble deep acceptors that are commonly observed in Ga2O3 bulk samples, while Ir is a deep donor that can degrade optical performance in insulating samples. We discuss our results in the context of recent experimental evidence of properties correlated with the presence of these impurities.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

2:30 PM EP08.05.03
Dynamically Modeled Current Conduction in Atomic-Layer-Deposited Al2O3 on Wide- and Ultra-Wide-Bandgap Semiconductors
Atsushi Hiraiwa; 1, Kiyotaka Horikawa2, Satoshi Okubo2 and Hiroshi Kawarada2; 1Tokyo Branch, Nagoya University, Tokyo, Japan; 2Waseda University, Tokyo, Japan.

Wide- and ultra-wide-bandgap semiconductors are promising power-device materials due to their high blocking capability. The wide bandgap, however, poses a serious challenge of gate insulation and surface passivation, because the insulator barrier against carrier emission from the semiconductors is inevitably small requiring wide-bandgap insulators. Although having the widest bandgap and well established in Si industry, thermal SiO2 is not amenable here. Therefore, atomic-layer-deposited (ALD) Al2O3 is the most promising insulator owing to wide bandgap (7 eV), relatively high dielectric constant (9), and good uniformity/reproducibility specific to ALD [1]. To promote the practical application of this AL2O3, Al2O3-related bias instability (BI) needs to be reduced. This study aims to achieve this through investigating the current conduction process in ALD Al2O3.

The current conduction in Al2O3 follows the space-charge-controlled field emission (SCC-FE) process [2], which, however, is hitherto only suitable for low-field analysis, imposing a limitation on its BI analysis. To solve this problem, the charged state of Al2O3 is assumed to dynamically change with bias voltage and is investigated by alternately measuring current-voltage (I-V) and capacitance-voltage (C-V) characteristics of Al2O3 metal-insulator-semiconductor capacitors, with the stop voltage of the I-V measurements increasing successively. The Al2O3 charged states in the I-V measurements, except for the first one, remain unchanged until the stop voltage and, therefore, the barrier height is accurately extracted based on the static SCC-FE process. Then, the sheet of Al2O3 charge is estimated as a function of bias voltage and, using the flat-band voltages obtained from the C-V characteristics, the sheet of charge at the Al2O3/substrate interface is given as a function of bias voltage. In this way, we compared the charged states of four kinds of Al2O3 deposited by varying the oxidant (H2O or O3) and the temperature (200 or 450 °C). This comparison was made for different substrates: Si, GaN and Ga2O3. The Al2O3 films on GaN and Ga2O3 have smaller barrier heights than those on Si but allow smaller leakage currents because of less Al2O3 positive charge. Despite a large leakage current, high-temperature H2O-grown Al2O3 is found to exhibit the highest bias stability, irrespective of the substrates, due to the excellent Al2O3/substrate-interface stability against biasing. Therefore, together with the longest dielectric-breakdown lifetime [3], this Al2O3 is the most promising insulator for high-reliability gate insulation and passivation.

This research is supported by the “Program for research and development of next-generation semiconductor to realize energy-saving society” of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

The recombination of photoexcited carriers with electrons or holes bound to point defects results in many experimentally observed optical phenomena in wide gap systems, such as ultra-violet, yellow, green, and red luminescence in GaN. Such processes are usually explained with reference to a particular defect state and often such states are studied systematically via computational techniques. The balance between different defect states, however, which may be metastable but relevant in the time-scale of optical processes, is frequently omitted from such analysis. Here we study how different configurations of electrons and holes, whether bound to defects in well-localised 'compact' states, or in extended 'diffuse' states, can alter the observed luminescence in GaN. For our calculations we employ the hybrid quantum mechanical/molecular mechanical embedded cluster method, which offers advantages over more commonly-applied supercell-based techniques when modelling defects in wide gap materials. The analysis regarding the balance between compact and diffuse states, however, is not dependent on the computational technique we employ. Our results allow us to account for various photoluminescence peaks observed routinely in doped and nominally undoped GaN samples. In particular, we attribute the 3.46 eV and 3.26 eV ultraviolet emission peaks to nitrogen vacancies binding compact and diffuse holes respectively, and describe processes related to gallium vacancy complexes that result in yellow, green and red luminescence. We demonstrate that the competition between these differently bound carrier states is key to understanding the luminescence properties of GaN, a point that also has implications for wide gap oxides. Indeed, we show that taking into account the diffuse states associated with oxygen vacancies in In$_2$O$_3$, ZnO and SnO$_2$ helps explain the different intrinsic conductivity properties of these transparent conductors.

3:00 PM BREAK

4:00 PM EP08.05.06
Impact of Neutron Irradiation on Deep Levels in Ge-Doped (010) β-Ga$_2$O$_3$ Layers Grown by Plasma-Assisted Molecular Beam Epitaxy Esfmat Farzana$^1$, Akhil Mauze$^2$, James S. Speck$^2$, Aaron R. Arehart$^1$ and Steven A. Ringel$^1$; $^1$The Ohio State University, Columbus, Ohio, United States; $^2$Materials Department, University of California, Santa Barbara, California, United States.

Monoclinic gallium sesquioxide ($\beta$-Ga$_2$O$_3$) belongs to the transparent semiconducting oxides. It is distinguished by its large band gap of about 4.7 eV, which is the reason for an optical transparency range extending deep into the ultraviolet and for a high electrical break down field estimated at 8 MV/cm. Combined with the feasibility of n-type doping by Sn, Si, or Ge, ($\beta$-Ga$_2$O$_3$) has great potential as a material for solar-blind photodetection and for power electronics where it might outperform GaN and SiC. To fully exploit the favorable properties of $\beta$-Ga$_2$O$_3$, single-crystalline material of high structural perfection and controlled electrical characteristics is a prerequisite. In particular, it is necessary to find out how the material can be doped in a controlled manner. Not only the selection of suitable dopants plays a role, but also the formation of compensating defects, including the introduction of unwanted impurities, must be understood.

Here we present a critical review of these doping issues. While p-type conduction might be impossible to be achieved due to intrinsic obstacles such as self-interstitials and holes of large effective hole mass, intentional n-type doping has to cover wider ranges, must be reproducible and thermally stable. In this context, we discuss own and recently reported results of temperature dependent Hall effect measurements, deep level transient spectroscopy, local vibrational mode spectroscopy, electron paramagnetic resonance spectroscopy, and electronic Raman scattering investigations. Silicon, germanium, and tin are revealed to be effective-mass-like shallow donors without any peculiarity such as DX behaviour. Compensation of shallow donors by gallium vacancies interacting with hydrogen is proposed as an alternative to other compensation mechanisms. In thick crystals grown from the melt additionally transition metal impurities must be taken into account as compensating acceptors. Furthermore, we show that the deterioration of n-type doping in epitaxially grown material may be due to extended defects rather than due to point defects and can be overcome under proper growth conditions. In cases of point defects, latest theoretical predictions of charge state transition levels and formation energies are compared with experimental values of energy levels and defect concentrations.
Interpreting the behaviour of all electronic devices, Herbert Kroemer coined the famous phrase “the interface is the device” in his 2000 Nobel Prize lecture, and we are still applying tremendous effort to understand interfaces in new material generations, with wide-bandgap materials being no exception. If anything, wide bandgap materials are more vulnerable to defect states purely due to their larger bandgap. Understanding gained for the bulk behaviour of semiconductors can often not be extended to the behaviour of materials in structured film stacks where interfaces play a vital role. SiC/SiO₂ is a prototypical wide-bandgap semiconductor/dielectric interface, which represents the challenges faced by many such material systems. A multitude of different defects leads to unacceptably large defect densities exceeding 10¹¹ cm⁻² eV⁻¹ in the vicinity of the conduction band of 4H-SiC. The management of interfacial defects still remains a topic of lively discussion and current interest. The main reasons for the ongoing struggle in understanding and controlling such defects lies in the lack of direct probes for chemical states at interfaces. Interfaces present a special challenge for physical characterisation techniques due to the spatial confinement of defects in a narrow region, the fact that by their nature interfaces are buried beneath a variety of overlayers, and the starkly different behaviour of chemical species at interfaces compared to surfaces and bulk. Advanced X-ray spectroscopy methods can tackle some of these issues, and X-ray Photoelectron Spectroscopy (XPS) in particular can deliver great insight into interfaces as it combines both qualitative and quantitative information on elemental distributions, chemical environments, and valence states.

Here, we present a systematic study of the 4H-SiC/SiO₂ interface in industrially manufactured samples with a particular focus on the effects of nitridation in a variety of atmospheres, to reduce interface defect states. Clear differences are found in both spectroscopy and electrical behaviour after high temperature treatments in N₂, NO, NH₃, and NO+NH₃ atmospheres. Si 2p, C 1s, O 1s, and N 1s core level spectra are analysed to give a complete picture of chemical environments present in the oxide and carbide layers as well as at the interface. Several species are found only at the interface providing insight into defect states and how they are compensated by nitridation. Mixed silicon oxy-carbides (SiOxCy) and oxynitrides (SiOxNy) as well as Si-C-N species from reaction of N with dangling C defects on the SiC side of the interface are identified. The findings from XPS are used to explain changes in the electrical behaviour of these device stacks.

Ultimately, the detailed understanding of advanced spectroscopy results in combination with electrical characterisation can be applied to a wide range of materials, particularly to wide- and ultra-wide-bandgap materials.

High-Resolution Observation of Defects at SiO₂/SiC Interfaces by Local Deep Level Transient Spectroscopy Based on Time-Resolved Scanning Nonlinear Dielectric Microscopy

4:30 PM EP08.05.08

Interface Chemistry and Electrical Characteristics of 4H-SiC/SiO₂ After Nitridation in Varying Atmospheres

Anna Regoutz1, Gregor Pobegen2 and Thomas Aichinger1; 1Imperial College London, London, United Kingdom; 2Kompetenzzentrum für Automobil- und Industrieelektronik GmbH, Villach, Austria; 2Infineon Technologies Austria AG, Villach, Austria.

Interfaces govern the behaviour of all electronic devices. Herbert Kroemer coined the famous phrase “the interface is the device” in his 2000 Nobel Prize lecture, and we are still applying tremendous effort to understand interfaces in new material generations, with wide-bandgap materials being no exception. If anything, wide bandgap materials are more vulnerable to defect states purely due to their larger bandgap. Understanding gained for the bulk behaviour of semiconductors can often not be extended to the behaviour of materials in structured film stacks where interfaces play a vital role. SiC/SiO₂ is a prototypical wide-bandgap semiconductor/dielectric interface, which represents the challenges faced by many such material systems. A multitude of different defects leads to unacceptably large defect densities exceeding 10¹¹ cm⁻² eV⁻¹ in the vicinity of the conduction band of 4H-SiC. The management of interfacial defects still remains a topic of lively discussion and current interest. The main reasons for the ongoing struggle in understanding and controlling such defects lies in the lack of direct probes for chemical states at interfaces. Interfaces present a special challenge for physical characterisation techniques due to the spatial confinement of defects in a narrow region, the fact that by their nature interfaces are buried beneath a variety of overlayers, and the starkly different behaviour of chemical species at interfaces compared to surfaces and bulk. Advanced X-ray spectroscopy methods can tackle some of these issues, and X-ray Photoelectron Spectroscopy (XPS) in particular can deliver great insight into interfaces as it combines both qualitative and quantitative information on elemental distributions, chemical environments, and valence states.

Here, we present a systematic study of the 4H-SiC/SiO₂ interface in industrially manufactured samples with a particular focus on the effects of nitridation in a variety of atmospheres, to reduce interface defect states. Clear differences are found in both spectroscopy and electrical behaviour after high temperature treatments in N₂, NO, NH₃, and NO+NH₃ atmospheres. Si 2p, C 1s, O 1s, and N 1s core level spectra are analysed to give a complete picture of chemical environments present in the oxide and carbide layers as well as at the interface. Several species are found only at the interface providing insight into defect states and how they are compensated by nitridation. Mixed silicon oxy-carbides (SiOxCy) and oxynitrides (SiOxNy) as well as Si-C-N species from reaction of N with dangling C defects on the SiC side of the interface are identified. The findings from XPS are used to explain changes in the electrical behaviour of these device stacks.

Ultimately, the detailed understanding of advanced spectroscopy results in combination with electrical characterisation can be applied to a wide range of materials, particularly to wide- and ultra-wide-bandgap materials.

High-Resolution Observation of Defects at SiO₂/SiC Interfaces by Local Deep Level Transient Spectroscopy Based on Time-Resolved Scanning Nonlinear Dielectric Microscopy

4:30 PM EP08.05.08

Interface Chemistry and Electrical Characteristics of 4H-SiC/SiO₂ After Nitridation in Varying Atmospheres

Anna Regoutz1, Gregor Pobegen2 and Thomas Aichinger1; 1Imperial College London, London, United Kingdom; 2Kompetenzzentrum für Automobil- und Industrieelektronik GmbH, Villach, Austria; 2Infineon Technologies Austria AG, Villach, Austria.

Interfaces govern the behaviour of all electronic devices. Herbert Kroemer coined the famous phrase “the interface is the device” in his 2000 Nobel Prize lecture, and we are still applying tremendous effort to understand interfaces in new material generations, with wide-bandgap materials being no exception. If anything, wide bandgap materials are more vulnerable to defect states purely due to their larger bandgap. Understanding gained for the bulk behaviour of semiconductors can often not be extended to the behaviour of materials in structured film stacks where interfaces play a vital role. SiC/SiO₂ is a prototypical wide-bandgap semiconductor/dielectric interface, which represents the challenges faced by many such material systems. A multitude of different defects leads to unacceptably large defect densities exceeding 10¹¹ cm⁻² eV⁻¹ in the vicinity of the conduction band of 4H-SiC. The management of interfacial defects still remains a topic of lively discussion and current interest. The main reasons for the ongoing struggle in understanding and controlling such defects lies in the lack of direct probes for chemical states at interfaces. Interfaces present a special challenge for physical characterisation techniques due to the spatial confinement of defects in a narrow region, the fact that by their nature interfaces are buried beneath a variety of overlayers, and the starkly different behaviour of chemical species at interfaces compared to surfaces and bulk. Advanced X-ray spectroscopy methods can tackle some of these issues, and X-ray Photoelectron Spectroscopy (XPS) in particular can deliver great insight into interfaces as it combines both qualitative and quantitative information on elemental distributions, chemical environments, and valence states.

Here, we present a systematic study of the 4H-SiC/SiO₂ interface in industrially manufactured samples with a particular focus on the effects of nitridation in a variety of atmospheres, to reduce interface defect states. Clear differences are found in both spectroscopy and electrical behaviour after high temperature treatments in N₂, NO, NH₃, and NO+NH₃ atmospheres. Si 2p, C 1s, O 1s, and N 1s core level spectra are analysed to give a complete picture of chemical environments present in the oxide and carbide layers as well as at the interface. Several species are found only at the interface providing insight into defect states and how they are compensated by nitridation. Mixed silicon oxy-carbides (SiOxCy) and oxynitrides (SiOxNy) as well as Si-C-N species from reaction of N with dangling C defects on the SiC side of the interface are identified. The findings from XPS are used to explain changes in the electrical behaviour of these device stacks.

Ultimately, the detailed understanding of advanced spectroscopy results in combination with electrical characterisation can be applied to a wide range of materials, particularly to wide- and ultra-wide-bandgap materials.
8:30 AM *EP08.06.01/EP09.08.01
Recent Progresses in Deep Depletion Diamond MOSFET
Cedric Masante1, Toan Thanh Pham1, Nicolas Rouger2, Gauthier Chicot1, David Eon1, Etienne Gheeraert1, Daniel Araujo2 and Julien Pernot1; 1University Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, France; 2Univ. Grenoble Alpes, CNRS, Grenoble INP G2Eah, Grenoble, France, Grenoble, France; 3Department of Engineering, The University of Cambridge, Cambridge, Cambridge, United Kingdom; 4Université de Toulouse; LAPLACE; CNRS; INPT; UPS, Toulouse, France; 5Dpto. Ciencia de los Materiales, Universidad de Cadiz, Cadiz, Spain.

Diamond is a fascinating semiconductor with exceptional physical properties such as a wide band gap, a high breakdown electric field (10 MV/cm), an outstanding thermal conductivity (20 W/cm/K) and high carrier mobilities. These exceptional properties, or more precisely, the combination of some of these properties makes diamond an ideal semiconductor for high power and/or high frequency electronics which should surpass other materials like silicon, silicon carbide or gallium nitride. Numerous diamond field effect transistors are under investigation: H-terminated accumulation FET, O-terminated inversion channel FET, metal-semiconductor FET and junction FET.

In this work, we propose a new transistor concept in order to exploit the full potentialities of diamond material. The deep depletions concept will be described and proposed for MOSFET devices. A proof of concept of deep depletion diamond MOSFETs will be presented. Finally, the recent progresses achieved in terms of device performances will be discussed.

References

9:00 AM *EP08.06.02/EP09.08.02
High Frequency, High Voltage and Vertical Diamond MOSFETs Using Two-Dimensional Hole Gas
Hiroshi Kawarada1, Nobutaka Oi2, Shoichiro Imanishi1, Masayuki Iwataki1 and Atsushi Hiraiwa2; 1Waseda University, Tokyo, Japan.
2Universidad de Cadiz, Cadiz, Spain.

Low SBH for 2DHG:
Diamond has superior properties as p-type conducting compared with other wide bandgap semiconductors. Among them P-type Schottky barrier height (SBH) is very low (<0.1eV) on the hydrogen terminated (C-H) diamond surface in high work-function metal such as Au [1]. This property enables hole injection smoothly from metal to diamond subsurface when surface electron potential is high (surface band bends upward). It is realized by negatively charged surface or negative surface voltage bias. Then, 2 dimensional hole gas (2DHG) is produced by hole injection from metal. It is desirable for high speed FET operation [1].

High Frequency FET:
The first GHz operation in diamond [2] has been realized by metal semiconductor (MES) FET, where Au is used for source and drain contacts and Al for Schottky gate on the same C-H diamond surface. Al shows the SBH of 0.6 eV, because Al work function is lower than Au by 0.7 eV. The work function dependence of SBH indicates that C-H diamond surface has low surface states density, necessary for MOSFET. In addition to MESFET [3], MOSFETs [4,5] exhibited GHz operation up to 70 GHz [6] in fC (cutoff frequency) and >100GHz [3] in fmax. The power density is now 3.8 W/mm2 [7] at 1GHz obtained by high bias voltage (~50V). Its electric field is above 2×10^(5) V/cm, where the hole velocity is nearly saturated in an entire FET. The power density is lower than AlGaN/GaN HEMT, but higher voltage operation can enhance it much further.

High Voltage FET:
C-H diamond MOSFETs are uniquely designed for high-voltage (~1000V) and high-temperature (up to 400°C) operation using the high temperature (450°C) ALD Al2O3 as gate oxide and passivation of gate-drain (drift) region. The maximum breakdown voltages (Vbr) are above 1500 V [8] obtained at long drift region (Ld > 15 µm). Vbr/Ld is –1.0 MV/cm, which is equivalent to those of SiC MOSFET and AlGaN/GaN HEMT. The drain current density is comparable to SiC, but 3-4 times lower than AlGaN/GaN at similar Vbr. Conductivity in drift region must be improved by mobility enhancement.

Vertical FET:
The first vertical diamond MOSFETs have been developed using 2DHG layer on trench structure [9]. Hole conduction at the trench side wall (3-4 µm depth) acts as drift region and is electrically connected to p+ substrate (drain). The drain current density of active planar area has reached to 5000 A/cm^2 [10], which is comparable to those of SiC or GaN MOSFET. Specific on resistance is 5 mΩcm^2 at present.

References
[10]
The potential mechanisms for this performance enhancement and future implementation of these techniques to enhance the performance and robustness of the devices, further improving device performance. As a semiconductor, diamond possesses many unique properties that make it attractive for the production of high performance devices such as robust, high power RF FETs. Such properties include a large bandgap of 5.5 eV, high thermal conductivity of up to 20 W cm⁻¹ K⁻¹ and high carrier saturation velocity of 2 × 10⁷ cm s⁻¹ for electrons and 0.8 × 10⁷ cm s⁻¹ for holes. Development of electronic diamond devices has been largely limited however by the immaturity of existing doping processes used to introduce mobile charge into its naturally insulating crystal structure. ‘Transfer doping’ of hydrogen-terminated diamond (H-diamond) presents a potential solution to this challenge which has allowed for the production of high performance FETs. Stability issues associated with traditional transfer doping, which relies on the presence of atmospheric species on the diamond surface, has limited the maturity of device technologies that exploit these doping techniques. More recently, various work has demonstrated the potential to improve the stability and efficiency of transfer doping in diamond utilising electron acceptor oxide materials on the diamond surface. In this work, we apply the electron oxide acceptor material V2O5 into H-diamond FET technology and demonstrate substantial performance improvement in comparison with traditional atmosphere-exposed devices. These performance figures include the highest reported drain current and transconductance for a H-diamond FET to incorporate an electron acceptor oxide such as V2O5. Furthermore, a 400°C anneal stage utilised in the process flow for devices (as required to ensure stability of the V2O5 layer) is also found to reduce the ohmic contact resistance and increase the carrier concentration beneath the gate of the devices, further improving device performance. The potential mechanisms for this performance enhancement and future implementation of these techniques to enhance the performance and robust operation of H-diamond FET technology will be discussed. Higher power, higher frequency RF transistors than those possible using the III-nitride semiconductors are desired for large data (high bandwidth) information transmission, highly advanced radar detection, and more efficient communication. We are developing hydrogenated diamond surface conduction field effect transistors (FETs) for use in these next generation RF systems accessing diamond’s wide bandgap (5.47 eV) extremely high thermal conductivity (> 20 W/cm) and impressive breakdown field (10 MV/cm). Our latest unpассивated, atmospheric transfer doped FETs have maintained high current density performance (up to 700 mA/mm at 10 V) with occasional testing over an 8 month period indicating very limited degradation in an indoor environment and the ability to maintain DC operation powers of ~ 7 W/mm. Optimising RF surface channel FETs is most effectively done using device physics information obtained directly from the same device that the RF measurements are made on. This best connects the influence of material, fabrication steps and structure on performance. In this regard, we obtained the hole velocity in the FET channel using a delay time measurement and this is we believe the first ever discussion of velocity obtained in this way applied directly on a diamond RF FET. This will be related to carrier density and effective mobility obtained from RF FETs. RF small signal characteristics (current and power gain cutoff frequencies (Ft, Fmx)) and large signal characteristics (power, gain and efficiency) from load pull measurements will also be discussed for the same devices. Transit time values obtained from a delay time measurement indicates these FETs have a hole velocity in the channel = 5 × 10⁷ cm/s and drain depletion region delay = 2.5 ps. On wafer RF measurements for intrinsic current gain cutoff frequency indicate an opposite trend with gate length of Ft = 70 GHz (Lg = 50 nm), 49 GHz, (100 nm), and 10 GHz, (500 nm) when Vds = 10V. With improved contact and access region resistances we expect the frequency bandwidth to increase. Load pull measurements indicate RF output power densities increased 30% as the drain and gate bias voltage pulse spacing increased (a duty cycle reduction from 5% to 0.5%) suggesting that RF output power is affected by heating of the transfer dopant in unpassedivated FETs. These measurements also demonstrate a peak RF output power density of 0.66 W/mm at 2 GHz. We have also observed that the Schottky barrier heights for the atmospheric transfer doped devices with good gate control are over 0.38 eV and range up to 0.63 eV, however, the ideality factor is quite high (between 1.5 and 7.3). This may be an indication of the roughness of the surface and challenge contacting a hydrogenated region that the gate finger metal sits on. As the gate length reduced from 3 micron down to 50 nm the FET current density increased six fold, and knee voltage reduced uniformly by 50%.
A diamond semiconductor with a bandgap of 5.47 eV is expected to be the ultimate power device because of its exceptional physical properties, such as a high breakdown field (>10 MV/cm), high mobility, and highest thermal conductivity [20 W/(cm K)]. We previously reported high radio-frequency (RF) power performance of diamond field-effect transistors with a power-gain cutoff frequency $f_	ext{MAX}$ of 120 GHz and an RF output power of 2.1 W/mm at 1 GHz. In this talk, we focus on very recent progress in two basic technologies related to diamond electronics: wafer technology and carrier doping technology.

To overcome the size limitation of diamond crystals, diamond heteroepitaxy technology has progressed rapidly. A 1-inch heteroepitaxial diamond has been demonstrated. In heteroepitaxy, epitaxial overgrowth technology is used to drastically decrease the dislocation density. Furthermore, micromechanics technology has been proposed and demonstrated as a method to delaminate heteroepitaxial diamond from its substrate without cracking. [1] In the final process of heteroepitaxy technology, chemical mechanical planarization of the heteroepitaxial diamond surface is important for obtaining a damage-free and smooth surface. The full-width at half-maximum of the (004) plane was as low as 0.03°, and the curvature was 0.29 m, indicating the world’s highest quality heteroepitaxial diamond. The size and quality of diamond crystals is improving. We have fabricated diamond field-effect transistors on heteroepitaxial diamond, and the resultant device shows the same drain-current level as conventional homoepitaxial diamond on a HPHT substrate.

Concerning carrier doping technology in diamond, Kubovc and Kasu previously reported NO$_2$ p-type doping, which they used to fabricate FETs; that is, NO$_2$, O$_2$, NO, and SO$_2$ molecules adsorbed onto H-diamond generated hole carriers and the hole sheet concentration was as high as $1 \times 10^{14}$ cm$^{-2}$ at room temperature. [2] Shiraishi and Kasu explained this phenomenon as the LUMO/SOMO orbital energies in the inorganic molecules adsorbed onto H-diamond being below the valence-band top of H-diamond, resulting in electron transfer from H-diamond to these molecules. Recently, Geis and Wade at the Massachusetts Institute of Technology investigated the NO$_2$–H-diamond surface further by surface chemical techniques such as Fourier transform infrared spectroscopy and elucidated the surface reaction and states. Their reports surprisingly agree with our previous findings. Recently, we used synchrotron X-ray photoelectron spectroscopy/X-ray absorption near-edge spectroscopy and capacitance and conductance measurements to determine the energy band diagram and found oxygen-related states and boundary states in the metal-oxide-semiconductor interface.

Transfer doping of hydrogen terminated diamond (Diamond:H) with various molecular-like surface acceptors suffers from low efficiency and temperature instability. In contrast, high electron affinity transition-metal oxides (TMOs) (i.e. MoO$_3$, WO$_3$, V$_2$O$_5$ and ReO$_3$), when employed as surface acceptors for transfer doping on Diamond:H, have recently yielded improved p-type sheet conductivity and remarkable thermal stability even with only a few monolayers of coverage. [4]. Despite these properties, the realization of Diamond:H electronic devices using TMOs remains very challenging. [8]. This is due to undesirable changes in the physical and electronic characteristics of the TMO caused by the device fabrication process. In particular, stoichiometry reduction, crystalline phase transitions and structural morphology aggregations take place.

In this work, we will discuss how different TMOs’ physical parameters affect the electrical properties of the resulting diamond:H/TMO-based transistors, and how these undesirable effects can be minimized. Electrical and surface characterization monitored before and after transistor fabrication reveal TMO oxygen reduction and a change in its oxidation state leading to electrical conductivity degradation. Based on these findings, we propose and demonstrate a way to improve diamond:H/TMO transistor performance and stability.

References:

H-terminated diamond with 2 dimensional hole gas (2DHG) provides a promising surface channel for high-power and high-frequency applications due to its excellent properties for FETs. From 2001, mile stones of RF performance of diamond FETs are first GHz operation in MESFETs [1], MISFETs with cutoff frequency ($f_c$) > 20 GHz [2], high power density > 2.0 W/mm [3], maximum oscillating frequency ($f_	ext{MAX}$) > 100 GHz [4] and $f_c$ > 50GHz [5]. Particularly, the power density of diamond FETs (up to 2.2 W/mm) [3, 6] is higher than that of GaAs and LDMOS. However, the operating voltage was as low as 15 ~ 20 V because of low breakdown voltage. Power density would be much more improved by realizing high voltage operation. Recently, we reported high average electric field [7] in MOSFETs with Al$_2$O$_3$ deposited as gate insulator [6, 8] and passivation layer [9] by high temperature atomic layer deposition (ALD) [10]. In this work, we fabricated ALD-Al$_2$O$_3$ 2DHG diamond MOSFETs, whose structure is capable of withstand high voltage, and evaluated small signal and large signal performance at high voltage operation ($|V_{DS}| \leq 60$ V). As a result, the highest power density of 3.8 W/mm was obtained in diamond.

We fabricated ALD-Al$_2$O$_3$ 2DHG diamond MOSFETs with 100 nm Al$_2$O$_3$ film on Ilα-type polycrystalline diamond substrate with a <110> preferential growth surface. The source-gate length, gate length ($L_G$) and gate width were fixed to 0.5, 0.5 and 100 μm, respectively and gate-drain length ($L_{GD}$) was ranged from 1 to 3 μm.

The drain current density ($I_{DS}$) was 730 mA/mm at $V_{GS} = -20$ V and $V_{DS} = -40$ V and the transconductance was 15 mS/mm at $V_{GS} = 12$ V and $V_{DS} = -40$ V for $L_{GD} = 1$ μm. Extrinsic $f_t$ and $f_{MAX}$, including parasitic pad capacitances and inductances, were 30 GHz and 27 GHz at $V_{GS} = 16$ V and $V_{DS} = -60$ V.
for $L_{CD} = 3 \mu m$, $f_1 = 30 \text{ GHz}$ @ $L_d = 0.5 \mu m$ corresponds the saturation velocity of $1 \times 10^7 \text{ cm/s}$. It is the first report that diamond FET reaches its saturation velocity. The large signal performance was evaluated using load pull system. The large signal performance was evaluated using load pull system. The large signal performance was evaluated using load pull system. The large signal performance was evaluated using load pull system. The large signal performance was evaluated using load pull system.

1:30 PM *EP08.07/EP09.09.01
Heteroepitaxial Diamond—Scaling of an Ultra-Wide-Bandgap Material to Wafer Dimensions Matthias Schreck\textsuperscript{1}, Stefan Gsell\textsuperscript{2}, Martin Fischer\textsuperscript{2}, Michael Mayr\textsuperscript{3} and Björn-Christoph Gallheber\textsuperscript{4}; \textsuperscript{1}University of Augsburg, Augsburg, Germany; \textsuperscript{2}Augsburg Diamond Technology GmbH, Augsburg, Germany.

In the field of power devices, diamond’s intrinsic physical properties suggest that they can facilitate ultimate device performance. Just as for other wide-bandgap materials, the availability of wafer-size diamond substrates with high single crystal quality is an indispensable prerequisite. There are two approaches which start from opposite points: First, homoepitaxial growth on carefully selected rather small single crystals with minimum dislocation densities can be performed in such a way that the available area is increased step by step while the dislocation density is kept low. By a similar approach, 4H-SiC has progressively been scaled over 20 years starting from small Acheson platelets to 6” wafer size \cite{1}. The second alternative is based on heteroepitaxy which starts on large areas but with high dislocation densities (DDs). The challenge here consists in a controlled decrease of the DD by several orders of magnitude while preserving the initial size. This presentation is focused on heteroepitaxy of diamond on Ir/YSZ/Si(001) which has recently provided the first single-crystal diamond wafer with a diameter $> 3.5”$ and a total weight of 155 carat \cite{2}. All relevant steps for the wafer preparation will be described. First applications of the material will be presented and the potential for further applications will be discussed.


2:00 PM *EP08.07.02/EP09.09.02
Engineering Doped Single Crystal Diamond Films for Electronic and Quantum Applications Jocelyn Achar\textsuperscript{1}, Riadh Issaoui\textsuperscript{1}, Alexandre Tallaire\textsuperscript{1, 2}, Ovidiu Brinza\textsuperscript{2}, Vianney Mille\textsuperscript{2}, Audrey Valentin\textsuperscript{2}, André Tardieu\textsuperscript{2} and Fabien Bénédic\textsuperscript{2}; \textsuperscript{1}LSPM-CNRS, Villetaneuse, France; \textsuperscript{2}IRCP - Ecole Nationale Supérieure de Chimie de Paris, Paris, France.

Diamond is a transparent wide band gap material with outstanding optical and electronic properties that are attracting a lot of attention for the development of the next generation of devices. Indeed single crystal diamond provides an ideal host material to incorporate different types of impurities that can drastically modify its properties. The use of dopants such as boron can for example allow tuning the electrical conductivity of the film up to the metallic. Concerning the schottky barrier diodes (SBDs) on heteroepitaxial diamond (001) films, the specific on-resistance of 0.2 Ω-cm$^2$ and high rectification of
10^6 (±5 V) were obtained which are comparable for SBDs on homoepitaxial diamond films. The sensor devices using nitrogen-vacancy (NV) centers were formed in the heteroepitaxial diamond (111) films. The NV centers could be preferentially aligned of the NV axis to the one direction and be leading to improving the sensitivity was confirmed. This work was supported in part by JST-CREST Grant No. JPMJCR1333, KAKENHI (17H01262 and 18H01472), and JSPS Bilateral Open Partnership Joint Research Projects.


Diamond’s extreme properties make it a prime candidate for next-gen electronic devices, including high frequency and high power operation. While monolithic diamond devices based on doped monocrystalline layers, enabling both unipolar as well as bipolar design schemes, have great potential, the currently obtainable substrate size and quality leave several years of scientific and technological development. The fact that diamond has an extremely high thermal conductivity and can be deposited on non-diamond substrates, opens up an intermediate pathway for hybrid power devices that integrate diamond with other wide bandgap materials such as SiC or GaN. The main goal in such cases is to achieve an enhanced reliability of the latter active materials by providing superior cooling minimizing thermal hotspots and withstanding large break down electric fields.

Here, the case of diamond on GaN-based HEMT structures is considered. First, the deposition of thin CVD diamond layers will be discussed, including the surface chemistry governing the nanodiamond particle seeding, the deposition conditions, and the use of different microwave-based CVD techniques, including resonant cavity and linear antenna technology. Cross-sectional TEM and EELS mapping of the stacks are employed to discuss the structural and morphological properties and to extract possible changes in composition in the underlying Si/N/AlGaN/GaN interfacial layers induced by the substrate temperature during diamond deposition. Finally, the evaluation of the effective thermal conductivity of the thin diamond layers is discussed. The contactless transient thermoreflectance technique, used to study the heat spreading capabilities, shed light on the thermal conductivity and interfacial thermal boundary resistance.

Diamond’s extreme properties make it a prime candidate for next-gen electronic devices, including high frequency and high power operation. While monolithic diamond devices based on doped monocrystalline layers, enabling both unipolar as well as bipolar design schemes, have great potential, the currently obtainable substrate size and quality leave several years of scientific and technological development. The fact that diamond has an extremely high thermal conductivity and can be deposited on non-diamond substrates, opens up an intermediate pathway for hybrid power devices that integrate diamond with other wide bandgap materials such as SiC or GaN. The main goal in such cases is to achieve an enhanced reliability of the latter active materials by providing superior cooling minimizing thermal hotspots and withstanding large break down electric fields.

Here, the case of diamond on GaN-based HEMT structures is considered. First, the deposition of thin CVD diamond layers will be discussed, including the surface chemistry governing the nanodiamond particle seeding, the deposition conditions, and the use of different microwave-based CVD techniques, including resonant cavity and linear antenna technology. Cross-sectional TEM and EELS mapping of the stacks are employed to discuss the structural and morphological properties and to extract possible changes in composition in the underlying Si/N/AlGaN/GaN interfacial layers induced by the substrate temperature during diamond deposition. Finally, the evaluation of the effective thermal conductivity of the thin diamond layers is discussed. The contactless transient thermoreflectance technique, used to study the heat spreading capabilities, shed light on the thermal conductivity and interfacial thermal boundary resistance.

Semiconducting diamond is an attractive candidate for the next generation of high voltage and high frequency power devices, thanks to his exceptional properties in terms of wide bandgap, high breakdown field and thermal conductivity. In the literature, several diamond-based field-effect-transistors (FETs) have already revealed good on state performance and high blocking voltage capability (~2kV) in a wide range of operating temperatures. The possibility of generating an inversion regime in diamond metal-oxide-semiconductor FET (MOSFET), and the new Deep Depletion regime (D2MOSFET) specific to wide bandgap semiconductors pave the way for a new generation of power devices. The critical part of the transistor is the gate oxide, with electrical charge traps located within the oxide or at its interface with the semiconductor. These traps can screen the gate potential and shift the threshold voltage, making the devices unusable. The reduction of the trap density is a major concern in all MOS technologies, as well as its stability with time under bias stress. The latest results about diamond MOS transistors prepared in the framework of the European GreenDiamond project will be presented, and the evolution of the diamond MOS properties with time will be reported for the first time.

The properties of diamond (high mobilities and ultra-gap) suggest different current transport modes that can support high current operation which is sustained and actually improved at high temperatures. This study presents experimental results of forward current density vs voltage which shows a V^2 dependence indicative of injection mode transport. The Schottky-PIN devices show high values of forward current density (> 500A/cm^2 at 3 V) that is stable and actually improves at elevated temperature. Perhaps the most stunning aspect of these results is that the diode specific on-resistance (RonS) decreases as the voltage increases. The results indicate a new mode of operation of high mobility diamond power devices where the high carrier mobilities and low phonon scattering will support current injection and drift with a reducing resistance as the current is increased. We present a comparison between diodes that operate in injection mode and the more conventional doped drift layer. We discuss modifications of the standard power electronics figure of merit for projecting the operation of diamond devices that operate in the injection transport mode. This research is supported through the NASA HOTTECH program.

1:45 PM EP08.06/EP09.06
Diamond Power Electronics—Drift Layer Doping vs Injection Mode Transport Robert J. Nemanich, Raghuraj Hathwar, Manpuneet Benipal, Franz A. Koeck, Mohamad Ali Malikoustian, Srabanti Chowdhury and Stephen M. Goodnick; 1Arizona State University, Tempe, Arizona, United States; 2Advent Diamond, Tempe, Arizona, United States; 3University of California - Davis, Davis, California, United States.
AlGaN+As channel high electron mobility transistors (HEMTs) are ideal for high-temperature/voltage/power applications. Their increased breakdown field and thermal conductivity with Al-alloy composition, leads to a much higher Baliga Figure of Merit [1]. We have recently reported on AlGaN+As channel MESFETs [2][3]. Polarization Doped FETs (PDFETs) [4] and high electron mobility transistors (HEMTs) [5] grown on low-defect AlN/sapphire templates. For these devices the channel electron mobility was a strong function of the Al-composition and decreased with higher doping. Thus, for the lowest channel sheet resistance, an undoped heterojunction FET (HFET) is the preferred device design. However, this design, makes the ohmic-contact formation very challenging leading to a contact resistivity well over 20 $\Omega\cdot$mm. Doping the barrier to reduce the contact resistivity leads to excessive gate-leakage currents. These limitations, till recently, the limited the highest demonstrated currents in undoped AlGaN+As HFETs to 0.1-0.3 A/mm. Now, our group has explored a new doped barrier high-Al channel HFET design with PECVD SiO2 and ALD TiO2 as gate-insulators to reduce the leakage current [6]. For these n-AlxGa1-xN, n=0.45 AlxGa1-xN MOSHFETs perfectly linear ohmic contacts were achieved with a resistivity as low as 1.6 $\Omega\cdot$mm. A record peak current as high as 0.6 A/mm was measured for devices with a gate-length of 1.75 $\mu$m in a 6 $\mu$m source-drain opening. In addition, the gate-leakage currents at room-temperature were four orders of magnitude lower than Schottky-gate devices. The ON/OFF current ratio which was more than 107 at room-temperature, remains as high as 108 for operation up to 250 $^\circ$C. Using temperature-dependent $I_{DS}$-$V_{DS}$ and ($C_{GS}$-$V_{GS}$) characteristics, we show $n_t$ to be ($1\times10^{13}$ cm$^{-2}$) and nearly temperature independent. The room temperature mobility was around 430 cm$^2$/V-s and decreased with increasing temperature and $n_t$. These mobility values were considerably higher than those predicted by the theoretical model in [7]. We believe the discrepancy to be from a smaller contribution of alloy scattering than the one used in the model of reference 7. In this paper we will present the detailed results of the comparative study of AlGaN channel MOSHFETs with PECVD SiO2 and ALD TiO2 and ZrO2 gate-insulators. Initial results of a comparative study of breakdown voltages for passivated and un-passivated devices will also be discussed.

We gratefully acknowledge the support from the DARPA-DREAM program (ONR Contract N00014-18-1-2033, Program Manager Dr. Paul Maki). Many thanks to Virginia Wheeler and Charles Eddy for the AlD oxide depositions.

References
[6] X. Hu et.al., submitted to EDL
demonstrating linear III-nitride HEMTs. The transport in the channel is quasi-ballistic in nature. The model interprets non-ideal effects such as non-linearity of access regions, self-heating, and traps. The compact model will provide a physical and intuitive insight into device operation and will bridge the gap between device technology and circuit design.


9:15 AM EP08.08.04
Reverse-Bias-Induced Virtual Gate Phenomenon in N-Polar GaN HEMTs Takayuki Saenituka, Kiattivut Prasertsak1-3, Tomoyuki Tanikawa2, Takeshi Kimura2, Shigei Kudo2 and Takashi Matsuo3; 1Center for Innovative Integrated Electronic Systems, Tohoku University, Sendai, Japan; 2Institute for Materials Research, Tohoku University, Sendai, Japan; 3Thai Microelectronics Center, National Electronic and Computer Technology Center, Chachoengsao, Thailand.

N-polar GaN high-electron-mobility transistors (HEMTs) are a promising candidate for high-frequency power transistors for millimeter-wave and beyond because of its stronger carrier confinement by the natural back-barrier and its potential to achieve lower ohmic resistance by means of the direct contact between the GaN channel and ohmic electrodes in comparison with conventional Ga-polar HEMTs. A grand challenge in N-polar GaN HEMTs is to achieve a high-performance and highly-stable MIS (metal-insulator-semiconductor) gate structure because Schottky gates suffer from a large gate leakage current due to the low barrier height and a large background charges by oxygen impurities in the GaN channel layer so far. In Ga-polar GaN HEMTs, a reverse bias annealing (RBA) is reported as an effective approach to stabilize the MIS interface and to reduce anomalous behaviors such as hysteresis in the current-voltage and capacitance-voltage characteristics. We confirmed, however, that RBA causes a significant decrease in the maximum drain current density and the transconductance in N-polar GaN HEMTs which were not observed in Ga-polar counterparts. In this study, in order to understand the physics behind such a difference between Ga- and N-polar GaN HEMTs, a 2D numerical analysis was performed to calculate the potential profiles inside the devices.

The device structure of the N-polar GaN HEMTs consists of a 30-nm-thick GaN channel, a 25-nm-thick AlGaN barrier with an Al mole fraction of 0.32, and a 2-μm-thick GaN buffer on a 0.8°-offcut sapphire substrate from top to bottom. For comparison, the Ga-polar GaN HEMTs consisting of a 7.7-nm-thick AlGaN barrier with an Al mole fraction of 0.33, a 1-nm-thick AlN spacer, and a 2-μm-thick GaN channel/buffer on a sapphire substrate are also prepared. For both samples, a 10-nm-thick SiN is utilized as a gate dielectric film. The gate length and width are 10 and 50 μm, respectively. RBA was performed at 200°C for 1 h with a negative gate bias voltage of ~10 V. The source and drain electrodes were grounded during RBA. The 2D analysis of the potential profile inside the devices revealed that the electrons injected from the gate electrode are able to accumulate near the SiN/GaN interface at the access region adjacent to the gate electrode in the N-polar GaN HEMTs. This could cause the electron trapping in deep levels at the SiN/GaN interface and the resulting negative charges of the trapped electrons act as a virtual gate to increase the access resistance of HEMTs. In contrast, in Ga-polar GaN HEMTs, the AlGaN barrier layer prevent electrons from accumulating near the SiN/GaN interface. Based on this finding, an AlGaN cap layer on the GaN channel could be a possible way to minimize such a RBA-induced virtual gate phenomenon and to achieve more stable N-polar GaN HEMTs. This work is partly supported by the funding from JSPS KAKENHI JP16H04341.

9:30 AM EP08.08.05
Investigation on the Trap States at p-GaN MIS (Insulator) Interface with Different Gate Dielectric Layers Liwen Sang; NIMS, Tsukuba, Japan.

Recent progresses in the GaN-based electronic devices have demonstrated them as excellent candidates for the high power supply and switching systems, due to their unique characteristics, such as the high blocking voltage, wide bandgap, large electron saturation velocity and high thermal stability. Compared to Si-based electronic devices, higher output currents can be achieved at higher frequencies by using GaN system. To fulfill the potential of GaN electronic devices, integration of GaN power devices and their gate driving circuits is needed to minimize the chip-to-chip parasitic inductance, thus reduce the switching loss, ringing and reliability issues. Monolithic complementary metal-oxide (insulator)-semiconductor (MOS) transistors with both n-channel and p-channel for the integrated circuits is desirable to ultimately reduce the power consumption. However, the development of p-channel field effect transistors (FETs) is still in its infancy in comparison to the n-channel ones. Recently, our group has achieved p-channel MOSFETs based on polarization induced two dimensional hole gas at the InGaAs/GaN heterojunctions. It is found that the performance of p-channel FET was restricted by the poor-quality p-GaN MOS interface. As a result of Mg accumulation to the p-GaN surface, a large surface band bending of 1.2-1.6 eV was observed for the native p-GaN, which lead to in an interfacial Mg-Ga-O disordered region with high-density trap states on the order of 1013 cm-2 using Al2O3 gate dielectric layer. The high-density traps resulted in the serious electrical hysteresis in both current-voltage (I-V) and capacitance-voltage (C-V) characteristic, bringing about the threshold voltage instability. The surface pre-treatment could not effectively remove the surface oxides on p-GaN as a result of re-oxidation in the following atomic-layer deposition process for Al2O3. Therefore, to ultimately enhance the performance and stability of p-channel FETs, proper oxygen-free gate dielectric layer and high-quality p-GaN MIS interface with lower interface state density and less trapping states is in great demand. In this paper, we investigated the p-GaN MIS and MOS capacitors with different gate dielectric layer such as CaF2, SiN, SiO2, and Al2O3. The interface quality and traps behaviors are evaluated with regard to the microstructure and electrical characteristics. The oxide and oxygen-free gate dielectric layers were compared for the performance of p-GaN electronic devices.

9:45 AM EP08.08.06
Hyperspectral Quantum Rod Thermal Imaging of GaN Electronic Devices Bahar Oner, James W. Pomeroy, Serge Karboyan and Martin Kuball; University of Bristol, Bristol, United Kingdom.

The peak junction temperature in electronic devices is a key parameter in determining the mean time to failure (MTTF). However, accurate temperature measurements becomes increasingly more challenging as devices are miniaturised and operating power densities increase, generating large temperature gradients on the sub-micron length-scale. Existing thermography methods either have limitations in spatial resolution, e.g., IR thermography, or require time consuming complex calibration and specialised equipment, e.g., Raman thermography, transient thermoreflectance or SThM. There is a clear need for high resolution, fast, simple and low cost thermal imaging technique. To address this, we have developed a high spatial resolution and cost-effective thermography technique, Hyperspectral Quantum Rod Thermal Imaging (HQTI), demonstrated on GaN high electron mobility transistors (HEMTs), with sub-micrometer spatial resolution.
The technique exploits the temperature dependent emission wavelength of nanoparticles, i.e. quantum rods or dots deposited onto the device under test, using a low cost hyperspectral camera. Quantum dots/rods are ideal temperature sensors for this application because they have low thermal mass and surface area, quickly reaching thermal equilibrium with the surface. Core/shell nanoparticles also have a high quantum efficiency and bright emission, enabling short image acquisition times. Temperature images are obtained by imaging the nanoparticle emission wavelength in the unbiased (reference) state and biased (on) state, and applying the known emission wavelength temperature dependence of the particles used. In this way the measurement is generic and does not require any re-calibration when the particles are deposited onto different materials.

The HQTI technique has been applied to GaN HEMTs for demonstration; a technology where high temperature gradients are generated in the channel region due to the localised high power dissipation density. An optical resolution of ~0.6 μm has been achieved using an 0.5 numerical aperture objective lens and temperature resolution of ~2°C, which can be further improved by numerical image processing techniques. Measured temperatures were within ~15% of a three dimensional finite element model. In comparison, the temperature was underestimated by ~50% using the lower resolution IR thermography method. This new generic measurement technique is expected to be a step-changing characterisation tool not only for micro-electronic devices, but also for any other micro/nano scale thermal measurement applications, such as biomedical devices and nanocomposites.

10:00 AM BREAK

10:30 AM EP08.08.07
Point Defect Management in Ultra-Wide Bandgap Materials Zlatko Sitar1, 2, Pramod Reddy2 and Ramon Collazo1, 3, North Carolina State University, Raleigh, North Carolina, United States; 2Adroit Materials, Apex, North Carolina, United States.

Achieving control of electrical conductivity in n- and p-AlGaN over all doping levels of interest has proven to be challenging. AlGaN exhibits a decrease in free carrier concentration as the dopant concentration increases above a critical doping concentration. This behavior is attributed to the formation of compensating defects due to lowering of their formation energy during doping. These compensators also contribute to impurity scattering, limiting the carrier mobility.

A novel scheme to control point defects in wide bandgap semiconductors is presented. The scheme uses above bandgap UV-illumination to change the position of the quasi Fermi levels in a semiconductor, and, thus, increase the formation energy of compensating defects leading to a decrease in incorporation. Using AlGaN as a model system, we demonstrated that over an order of magnitude improvement in the electrical properties could be achieved in these materials by using this scheme for controlling the incorporation of point defects.

In n- and p-doped AlGaN films grown by MOCVD, point defects such as hydrogen, carbon, nitrogen or metal vacancies and their corresponding complexes lead to dopant compensation, resulting in a high resistivity and a low mobility in these films. Generally, the energy of formation of a point defect is a function of the process conditions, as described by the chemical potentials of the species involved. In addition, the energy of formation of charged point defects is also a function of the Fermi energy, or the electrochemical potential. We have developed a non-equilibrium process scheme in which the Fermi level is controlled by external excitation in a steady-state condition. We introduce above-bandgap illumination as the excitation source for enhancing the doping capabilities, by controlling the energetics of point defects via Fermi level control during growth. This presentation will focus on the details of the theoretical background and related calculations. In addition, the discussion will also focus on the used experimental setup and influence of UV-light on the growth condition and possible gas-phase interaction. The proposed point defect control scheme is of great interest for all semiconductors in which compensation is the main limiting factor in obtaining the desired free carrier concentrations and conductivity.

11:00 AM EP08.08.09
Impact of Ge Doping on Growth Stress and Dislocation Microstructure in AlGaN Anushka Bansal and Joan M. Redwing; The Pennsylvania State University, University Park, Pennsylvania, United States.

Intentional n-type doping of AlGaN,N has been widely studied given its critical role in light-emitting diodes and ultra-wide bandgap devices. Silicon has been the most intensively investigated donor in AlGaN,N since it enables low resistance n-type films, however, Si doping induces bending of edge-type threading dislocations which generates tensile stress and cracking with increasing film thickness. Germanium (Ge) has been investigated as an alternative to Si for n-type doping of GaN. Its impact on dislocation inclination and film stress, however, is unclear particularly for the growth of AlGaN,N alloys. In this study, we employ in-situ wafer curvature measurements combined with post-growth structural and electrical characterization to investigate the impact of Ge doping on film stress and doping efficiency in AlGaN,N (x=0.0-0.51) layers grown by metalorganic chemical vapor deposition (MOCVD) as compared to Si doping.

AlGaN,N layers were grown on semi-insulating Si-face (0001) 6H-SiC substrates in a vertical cold wall MOCVD reactor equipped with in-situ wafer curvature measurements. The precursors used for growth and doping included trimethylaluminum, trimethylgallium, NH3, SiH4 and GeH4. Growth of AlGaN,N was carried out at 1150°C and 100 Torr reactor pressure using a thin (~90 nm) AlN buffer layer. SiH4/group III inlet ratio of 2 x 10−3 resulted in an electron concentration of ~8.2 x 1010 cm−3 for Si doping while a GeH4/group III ratio of 0.5 was required to achieve a similar Ge doping level. The film microstructure was investigated on cross-sectional samples using bright field imaging and [110] and [0002] weak-beam dark-field imaging. High resolution X-Ray Diffractionmetry (HRXRD) in a triple-axis geometry was used to measure the film composition and threading dislocation density. Room temperature (RT) Hall measurements were used to measure the carrier concentration and mobility of Ge doped AlGaN,N layers.

In-situ wafer curvature measurements employed during growth provided information on the evolution of film stress with doping. It was observed that Ge doping does not induce additional tensile stress into the film in contrast to Si doping. This is consistent with the inclination angle of the edge dislocations which was measured to be 6.9° and 7.5° for undoped and Ge doped Alx50Ga50,N,N films, respectively, indicating only a minor change in dislocation bending with doping. The electron concentration decreased a small amount going from GaN to AlGaN,N (x=0.21-0.41). However, at x=0.51, the resistivity increased by a factor of 40, and the electron concentration decreased sharply consistent with theoretical predictions of the onset of DX centers in Ge doped high Al content AlGaN,N.

The results demonstrate that Ge is a viable n-type dopant for AlGaN,N (x=0.5) enabling the growth of highly doped, low resistivity layers without significant modification of film stress.

11:15 AM EP08.08.09
Heteroepitaxy of Thick GaN on Si and Improvement of Electrical/Material Characteristics by Defect Annihilation Atsunori Tanaka, Woojin Choi, Renjie Chen, Ren Liu and Shadi Dayeh; Univ of California-San Diego, La Jolla, California, United States.

A major challenge in vertical power devices in GaN and other large bandgap materials is the high defect density that compromises the performance, reliability and yield. We are developing selective area growth approaches that have successfully reduced the densities of these defects on scalable and cheap substrates to a comparable level of native substrates. With these new approaches to material growth, we are able to demonstrate devices whose performance correlates well with the improved material quality. Our choice of material for studying these growth approaches is GaN that while have been extensively studied for decades suffer from large defect densities on large-scale commercially viable Si substrates. Recently, bulk GaN crystal growth techniques such as Na-flux, Hydride Vapor Phase Epitaxy and ammonothermal methods have been developed and, homoepitaxial vertical GaN devices have made it possible to achieve thick drift layers and low dislocation densities but at significant cost. Issues of reliability and uniformity over large areas
Boron containing GaN and AlN materials constitute emerging members of the III-Nitrides alloy family. They are candidate materials for a number of technological applications such as a back barrier in AlGaN/GaN high electron mobility transistors or to achieve lattice matched InGaN layers to SiC or GaN. However, a major challenge towards exploiting the full potential of B containing III-Nitride alloys is the limited B incorporation. More specifically, the B bulk solubility does not exceed 2% and 3% in GaN and AlN at 1000 °C, respectively. A potential route to overcome the limit set by bulk solubility is to employ surface engineering. Surface break the bulk translational symmetry, offer efficient strain relaxation and may provide different coordination and rehybridization than bulk [1]. The key idea underlying surface engineering is to employ surface structures with compositions higher than the bulk solubility limit which are kinetically stable and do not change their composition when overgrown. Therefore, understanding the atomistic mechanisms at surfaces is a prerequisite to fully control the composition of epitaxially grown alloys.

In the present work a potential route to achieve B contents well above the bulk solubility limit is investigated and identified. We employ total energy and force calculations within density functional theory (DFT). Specifically, we investigate the effect of surfaces on the properties and composition of epitaxially grown BGaN and BAlN alloys. In total more than 200 different B containing and B free surface structures have been implemented. Based on these calculations phase diagrams for both BGaN and BAlN surfaces are derived. These diagrams reveal that under typical MOCVD growth conditions as high as 25%. Furthermore, an interesting outcome is that ordering in the form of 2×2 and 2√3×2√3R30o patterns is introduced at the surface. Based on the aforementioned calculations we will present and discuss in detail the physics governing the above mentioned mechanism. Specifically, we will elaborate on RHEED and/or HRTEM fingerprints of B induced ordering as well as possible routes to optimize the growth of BGaN and BAlN alloys with high B content.

The emerging class of ultra-wide bandgap semiconductor (UWBGS) materials, including AlN, diamond, GaO₃, and cubic BN, have been of recent interest to electron device developers because of their desirable ability to withstand high electric fields. Despite numerous experimental demonstrations of this breakthrough strength, UWBGS materials still generally suffer from the fundamental challenge of being able to get large densities of mobile carriers into their conduction or valence bands. In cases where impurity doping is possible, there is typically only one impurity type (donor or acceptor) with small ionization energy in the material system, and this prevents or limits bipolar device realization.

Given the difficulties associated with impurity doping in UWBGS materials, our team has been investigating the epitaxial integration of lattice-matched crystalline conductors and superconductors to replace heavily doped semiconductor layers in device heterostructures. To accomplish this task, we have used an RF plasma-assisted molecular beam epitaxy system equipped with an electron beam evaporator source to study the thin film growth of single crystal transition metal nitride (TMN) materials, such as NbN, and TaN, and their integration with AlN and GaN. Cross-sectional transmission electron microscopy shows that TMN/III-N interfaces are atomically abrupt with no evidence of interdiffusion of the host elements. We anticipate that the device applications of these metallic films are quite broad ranging from selective etching of sacrificial layers for epitaxial lift-off of processed III-N devices, to buried metallic or superconducting electrodes for Josephson junction devices, to optical mirrors and waveguides for improved optoelectronics. This talk will present our recent work involving TMN development and applications that will enhance wide and ultra-wide bandgap semiconductor devices. This work was supported by the Office of Naval Research.

2:00 PM EP08.09.02
Gadolinium-Doped Gallium Nitride for Room Temperature Spintronic Applications
Vishal Saravade, Amirhossein Ghods, Naishadhal Raval, C. Zhou and I. T. Ferguson; Department of Electrical and Computer Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

Gallium nitride (GaN) is a candidate material for room temperature (RT) spintronic applications considering its electrical and magnetic properties. MOCVD-grown Gd-doped GaN (GaGdN) exhibited RT ferromagnetism and anomalous Hall effect (AHE) in which the mechanism seems to be free carrier-mediated [1]. Observation of ferromagnetism only in GaGdN from a (TMHD)₃Gd precursor that contains oxygen points to the role of oxygen especially oxygen interstitials in stabilizing the ferromagnetism. GaGdN from a Cp₃Gd precursor that does not contain oxygen did not show ferromagnetism. In this work, the mechanism for the ferromagnetism in GaGdN will be further investigated. The role of oxygen in the magnetic properties will be examined using GaGdN implanted with oxygen. Carbon-implanted GaGdN will also be studied as carbon can also introduce interstitial sites in GaGdN [2]. AHE measurement will be done and relationship between the anomalous Hall resistivity and longitudinal resistivity will be determined to better understand the responsible mechanism for the ferromagnetism. Furthermore, GaGdN based spin-LEDs will be fabricated and difference between the left and right circularly polarized light intensities will be determined using magnetic circular dichroism measurement. These would help towards understanding spin injection in GaGdN devices and to determine the suitability of GaGdN for spintronic applications.

References:
2. R. Xie, H. Xing, Y. Zeng, Y. Liang, Y. Huang and X. Chen, AIP Advances 7, 115003, 2017

2:15 PM EP08.09.03
MOCVD Growth and Characterization of Er Doped III-Nitride Epilayers and Quantum Well Structures
Talal Al Tahtamouni1, Hongxing Jiang2 and Jingyu Lin2; 1Qatar University, Doha, Qatar; 2Texas Tech University, Lubbock, Texas, United States.

Er doped materials have attracted much attention for their applications in photonics, especially in the area of optical communications. Doped in a solid host, Er³⁺ ion has allowable intra-4f shell transition from its first excited state (4I_{13/2}) to the ground state (4I_{15/2}) and the transition corresponds to a wavelength of minimum optical loss in silica based optic fibers at 1.54 µm. Thus, Er-doped materials are ideal candidates to make amplifiers for optical communications.

It has been observed that the 1.54 µm emission from Er doped semiconductors of smaller bandgaps has a low efficiency at room temperature due to a strong thermal quenching effect. In general, the thermal stability of Er emission increases with an increase of the energy gap and ionicity of the host materials. III-nitride semiconductors are excellent host materials for Er-ions due to their structural and thermal stabilities. III-nitride wide bandgap semiconductors have demonstrated excellent performance for electronic and optoelectronic devices.

AIN has a large bandgap (6.1 eV). Therefore, it is expected that AlN as a host material will result in lower thermal quenching of Er emission. AlN is of great technological significance because of its physical and chemical properties such as low dielectric constant, excellent thermal conductivity, electrical resistivity, excellent mechanical strength and chemical stability. These reasons make AlN an excellent host material for device applications. Despite the reports of fabrication of light emitting diodes based on Er doped III-nitride epilayers operating in the infrared region. However, further improvements in the quantum efficiency of the 1.54 µm emission in Er-doped III-nitrides are still needed to enable practical photonic devices. One way to improve the quantum efficiency of these device structures is to improve the excitation efficiency of the Er ions via the enhancement in the carrier density around Er³⁺ ions. This could be achieved by implementing quantum well structures.

A-plane AlN epilayers doped with erbium (AIN:Er) have been grown on r-plane sapphire substrates by MOCVD. The 1.54 µm emission properties were probed by photoluminescence (PL) emission spectroscopy and compared with those of c-plane AIN:Er. It was found that the emission intensity from a-plane AIN:Er is higher than that from c-plane AIN:Er for above and below energy gap, as well as resonant excitation. The intensity of the 1.54 µm emission was found to increase with increasing Er molar flux. A-plane Er-doped AIN epilayers exhibit a smaller thermal quenching effect.

Erbium doped GaN/AIN multiple quantum wells (MQWs:Er) have been grown by MOCVD. The 1.54 µm emission properties from MQWs:Er were probed by PL and compared with those of GaN:Er epilayers. It was found that the emission intensity from MQWs:Er is 9 times higher than that of GaN:Er epilayers. The influence of the well and the barrier widths on the PL emission at 1.54 µm was studied.

2:30 PM EP08.09.04
Coalesced, Centimeter-Scale GaN Films on Amorphous Substrates via MOCVD Growth on a Silicon Seed Layer Fabricated by Aluminum-Induced Crystalization
Mel Hainey1, Yoann Robin2, Hiroshi Amano2 and Noritaka Usami1; 1Materials Process Engineering, Nagoya University, Nagoya, Japan; 2Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan.

The fabrication of III-nitride semiconductor thin films on substrates such as glass and oxidized Si(001) is of significant interest for LED and CMOS integration applications. However, direct epitaxy on these substrates is difficult because their amorphous structure offers no template for III-nitride thin
In recent work, the growth of GaN on amorphous and polycrystalline substrates was demonstrated by using a silicon seed layer fabricated by aluminum-induced crystallization (AIC).[1] While c-axis oriented GaN with threading dislocation densities of ~5x10^9/cm² was demonstrated, the coalesced area realized was only ~1mm² on a 1cm² fused quartz substrate, and was even smaller for other substrates. For large-scale applications, scalable fabrication of fully coalesced GaN films is required, and methods for evaluating the crystal quality of the underlying AIC-Si thin film prior to GaN growth should be developed.

In this report, GaN films with reduced tilt and improved coalescence are grown from AIC-Si seed layers on cm-scale fused quartz and oxidized Si(100) substrates. In the first part of this process, optimized annealing conditions producing the most uniformly oriented AIC-Si silicon thin films are developed. Based on pole figures taken from electron backscatter diffraction of the AIC-Si films, reducing annealing temperatures from 500°C to 425°C results in reduced Si(111) surface misorientation and increased grain size. In the second part, AIC-Si films with reduced Si(111) misorientation are used as seed layers for GaN growth, and the reduced Si misorientation translates into reduced GaN in-plane misorientation. Full-width at half maximum values (FWHM) of x-ray rocking curves measured on the GaN (00-2) peak were found to be reduced from 3° to roughly 2° on fused quartz substrates, and <1° on oxidized Si(100) substrates. Note that this marks a significant improvement over previous reports of GaN growth on glass, where (00-2) FWHM values of over 3° were reported.[2,3]

While the initial GaN growth process was able to produce highly oriented films, these films remained heavily pitted and grew as islands on their underlying AIC-Si grains. However, by increasing the growth temperature, GaN films became smooth and formed nearly coalesced films over areas of ~1cm². These coalesced films should enable device fabrication using conventional III-nitride device processing processes.

References:
4:00 PM EP08.09.08
Quantification of Indium Fluctuations in InGaN/GaN Quantum Well LEDs Using Electron Energy-Loss Spectroscopy
Sarah A. Goodman1, Akshay Singh1, Zhibo Zhao1, Dong Su1, Kim Kisslinger2, Parijat Deb3, Eric A. Stach2 and Silvija Gradecak1; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 3Lumileds LLC, San Jose, California, United States.

InGaN/GaN quantum well (QW) light emitting diodes (LEDs) have high efficiencies and demonstrate wide wavelength tunability, but their internal quantum efficiency (IQE) decreases with increasing current – a phenomenon known as efficiency droop – which limits the use of these devices for high power applications. Mitigating droop requires a thorough understanding of inhomogeneities within the QWs, including indium fluctuations and crystalline defects. Electron energy-loss spectroscopy (EELS) within the scanning transmission electron microscope (STEM) is well-suited to probe material composition and optoelectronic properties on the sub-nanometer scale. However, it has been shown that electrons with energies above the knock-on threshold for indium (~120 keV) induce indium fluctuations within the QWs. As such, it is critical to obtain imaging conditions that do not induce induced artifacts from intrinsic materials properties.

Although carbon deposition particularly impacts characterization of InGaN due to the proximity of the C edge to the In and N edges, this artifact impacts motivated the need to develop new methods to study the indium distribution. Here, we use an aberration-corrected STEM to induce indium fluctuations within the QWs. As such, it is critical to obtain imaging conditions that do not induce induced artifacts from intrinsic materials properties. Although carbon deposition particularly impacts characterization of InGaN due to the proximity of the C edge to the In and N edges, this artifact impacts

14:15 PM EP08.09.09
Correlation of Structural and Optoelectronic Properties of V-pits in InGaN/GaN Quantum Well Heterostructures Grown on Silicon Substrates via Cathodoluminescence in Scanning Transmission Electron Microscopy
Zhizhao Su, Sarah A. Goodman1, Akshay Singh1, Govindo J. Syaranamual2, Saurabh Srivastava2, Jing Y. Chung2, Abdul Kadir3, Li Zhang2, Soo-Jin Chua2, 3, Abdul Kadir2, Li Zhang2, Soo-Jin Chua2, 3, Eugene Fitzgerald4, Stephen Pennycook2, 3 and Silvija Gradecak1; 1Department of Materials Science and Engineering, National University of Singapore, Singapore, Singapore; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 3Lumileds LLC, San Jose, California, United States.

Over the past two decades, InGaN/GaN quantum well (QW) heterostructures have set the industry standard for high-efficiency inorganic blue light emitting diode (LED) devices. The highest quality InGaN/GaN-based LEDs are grown on sapphire substrates as opposed to silicon substrates, to overcome difficulties associated with thermal expansion mismatch and decrease the density of crystalline defects in the QW region. Growth of these devices on Si substrates would allow for their incorporation into integrated circuits, expanding their range of potential applications. A shift from sapphire to cheaper Si substrates would also allow cost reductions between 40-60% at the die level and enable the development of large-area LEDs using semi-automated CMOS processes. Despite the advantages in GaN-on-Si epitaxy, commercial adoption of GaN-on-Si technology remains limited due to a degradation in...
crystalline material quality in comparison to incumbent sapphire technologies. Although InGaN-based LEDs are highly resilient to non-radiative recombination at dislocations and V-pits, local optical properties around such defects remain ambiguous. Correlating optoelectronic properties with nanoscale defects remains critical to improved GaN-on-Si LEDs.

In this work, we use cathodoluminescence in scanning transmission electron microscopy (CL-STEM) to map nanoscale optical properties around V-pit defects found in InGaN/GaN QW heterostructures grown on Si substrates. The heterostructures consist of 13 periods of 2.5 nm InGaN QWs separated by 10 nm GaN barriers and emit at 472 nm. We find that the radiative recombination localized around the V-pits in the QW region is blue shifted compared to the QW emission, occurring at 375-395 nm. We attribute the blue-shift to radiative recombination in the QWs near the V-pit which are thinner and are hypothesized to contain fluctuations in indium concentration. Dislocation analysis in the TEM shows that the V-pits luminescence regardless of dislocation character (screw, edge, or mixed). In addition, hyperspectral CL-STEM mapping reveals strong spatial variations in the wavelength and emission intensity from the V-pit core to the facet.

This work provides a foundation for identifying how defects in the InGaN/GaN QW heterostructure region of an LED can influence the optoelectronic properties of the device. Understanding the correlation between structure and emission of V-pits on the nanoscale will be critical to further development of both incumbent GaN-on-sapphire and next-generation GaN-on-Si LED technologies.


4:30 PM DISCUSSION TIME

4:45 PM EP08.09.11
AlN Capacitors for High Temperature Systems
Piujsh K. Ghosh1, Mirsaeid Sarollahi2, Rahul Kumar1, Samir K. Saha2, Gregory J. Salamo2 and Morgan E. Ware3
1Electrical Engineering, University of Arkansas-Fayetteville, Fayetteville, Arkansas, United States; 2Physics, University of Arkansas-Fayetteville, Fayetteville, Arkansas, United States.

The recent trend towards higher power and smaller size has necessitated a renewed attention to the thermal budget in power conversion systems. Increased temperatures can reduce efficiency and ultimately can lead to failure. Capacitors are particularly sensitive to high temperature failure and are in many cases held remotely from the main power devices increasing system size and complexity. Currently, off-the-shelf, general purpose capacitors limit their operating temperature range to below ~100°C. Newly developed ceramic capacitors based on BaTiO3 and CaZrO3 demonstrate very good properties at temperatures up to ~200°C, however still suffer at high temperatures from both break down and instability. Their capacitance, although very large, changes by several times and subsequently vanishes at high temperature as the ferroelectric dielectric undergoes a phase change. Although, these do have very good properties for applications in high power modules which may see very high temperatures, there are two main factors we would like to improve upon by the introduction of AlN deposited by MBE on n-type 4H-SiC as the dielectric material of the capacitor. 1) The AlN capacitors should be able to operate at high temperature, high voltage, and high frequencies in a single device, whereas the ceramic devices have different constructions optimized for each. 2) More importantly, with a look to the future of integration, the AlN based capacitors could in principle be directly integrated at the chip level with high power transistors and the associated control electronics based on GaN and SiC materials and technology. AlN is an ultrawide band gap semiconductor with very stable dielectric properties up to at least 600°C and well suited for both RF and high-power devices. At the same time there are no known phase changes within usable operating temperatures. We will present the extreme temperature stability of these AlN based capacitors over the wide temperature range from 240K to 600K, along with their high capacitance density of ~ 10μF/cm2. Finally, current efforts to increase the usable voltage range and at the same time reduce leakage current will be presented.

SESSION EP08.10: Poster Session: Ultra-Wide-Bandgap
Session Chair: Robert Kaplar
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP08.10.01
Substrate Induced Chemically Stabilized Large Area Wurtzite-BN Epitaxial Thin Film
Babri Vishal1, 2 and Ranjan Datta1, 2; 1International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru, India; 2Chemistry and Physics Of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru, India.

We report for the first time on chemically stabilized the metastable wurtzite phase boron nitride (w-BN). Single crystalline epitaxial wurtzite w-BN thin film grown on c-plane sapphire by pulsed laser deposition (PLD) under slow kinetic condition. Wurtzite phase boron nitride have wide band gap of 5.81 eV (E→X). Experimental investigation into the properties of w-BN is scarce because of the difficulty in synthesizing sufficiently large and pure crystals of it, which usually requires extremely conditions (1730-3230°C, ~108 torr) in various methods e.g. static high-pressure, shock-wave compression method, direct conversion from h-BN. We have grown w-BN phase on a thin film under relatively low temperature (800°C) and pressure (~10-5 torr). The thin film shows no traces of other allotropes such as cubic (c) or hexagonal (h) BN phases and confirms by high-resolution transmission electron microscopy (HRTEM), X-ray diffraction and Raman spectroscopy. Sapphire substrate plays a significant role to stabilize metastable w-BN in unusual PLD growth condition, and explained based on density functional theory (DFT) calculation using Quantum Espresso (QE). DFT confirms the phase transition occurred due to a chemical interaction between Boron and Oxygen atoms leading to staggering in flat h-BN layer transforming to the w-BN structure at the O-terminated (0001) plane of sapphire. HRTEM and electron diffraction confirms film is relaxed and the lattice parameters of w-BN are approximately a = 2.58 Å and c = 4.29 Å. Epitaxial relationship is w-BN(001)-∥ Al2O3(-2-1-1-1) with ~6.1 % lattice mismatch. Theoretical predictions indicate that w-BN is the second hardest material (114 GPa) after lonsdaleite (~152 GPa). The hardness (H) and the elastic modulus (E) of the w-BN film are 37 & 339 GPa, respectively measured by indentation along <0001> direction. The hardness of the film is 37 GPa lower than theoretical prediction due to indentation along <0001> direction, thin film geometry and defects present in the film. It is also possible that structure may not have undergone bond flipping intermediate structural transitions during indentation and gives lower H. wide bandgap w-BN is a new unexplored phase which can open the opportunities as an active material for the energy applications and optoelectronic as its 2D layered counterpart h-BN to improve properties of graphene and 2D MoS2, WS2, ReS2, heterostructures in various device application. On the other hand, the results are extremely promising in advancing the microelectronic and mechanical tooling industry.
Temperature Dependence of Gate Leakage Current in p-GaN/AlGaN/GaN HEMTs

The transient study (on-state stress) includes two parts, one is to measure the current transient at fixed Q-points for 100 sec, another one is to measure the current transient while switching back to Q-point of 100 mA/mm and 28 V for 100 sec. All transient measurements were done under different temperatures (25, 40, 50, and 60 °C) for activation energy analysis.

In the fixed Q-points study, the transient currents decrease with time at high current Q-points (230 – 450 mA/mm) showing a significant trapping effect. The transient currents increase or decrease with time at medium current Q-points (~ 100 mA/mm) showing both trapping and detrapping effects. At low current Q-points (< 80 mA/mm), most transient currents increase then decrease with time. Based on the measurements, the trapping effect dominates at high current Q-points which hot carriers would inject into adjacent layers (AlGaN and/or GaN) for trapping. And the trapping effect is not strong function of temperatures indicating tunneling behaviors.

In the switching back to Q-point of 100 mA/mm and 28 V study, if the previous biased current (pre-stressed) is larger than 100 mA/mm, the transient currents decrease with time showing trapping effects. If the previous biased current (pre-stressed) is smaller than 100 mA/mm, the transient currents increase with time showing detrapping effects. Both trapping and detrapping behaviors are not strong function of temperatures too.

All current transient measurements (on-state stress) in this study showed complicated trapping and detrapping behaviors at different Q-points and substrate temperatures. This observation would strongly relate to the performance of GaN HEMT power amplifiers, further investigation and correlation are necessary.

Temperature Dependence of Gate Leakage Current in p-GaN/AlGaN/GaN HEMTs

In this study, on-state stress in AlGaN/GaN HEMTs is to investigate the current transient characteristics while transistors are biased at different quiescent points (Q-points) and under different substrate temperatures.

AlGaN/GaN HEMTs with two 0.25-μm T-gate fingers and width of 125-μm were investigated in this study. All HEMTs were grown on 4-inch SiC substrates and fabricated by a commercial foundry. SiN stack layers were used for passivation and source field-plate was adopted.

The transient study on-state stress) includes two parts, one is to measure the current transient at fixed Q-points for 100 sec, another one is to measure the current transient while switching back to Q-point of 100 mA/mm and 28 V for 100 sec. All transient measurements were done under different temperatures (25, 40, 50, and 60 °C) for activation energy analysis.

In the fixed Q-points study, the transient currents decrease with time at high current Q-points (230 – 450 mA/mm) showing a significant trapping effect. The transient currents increase or decrease with time at medium current Q-points (~ 100 mA/mm) showing both trapping and detrapping effects. At low current Q-points (< 80 mA/mm), most transient currents increase then decrease with time. Based on the measurements, the trapping effect dominates at high current Q-points which hot carriers would inject into adjacent layers (AlGaN and/or GaN) for trapping. And the trapping effect is not strong function of temperatures indicating tunneling behaviors.

In the switching back to Q-point of 100 mA/mm and 28 V study, if the previous biased current (pre-stressed) is larger than 100 mA/mm, the transient currents decrease with time showing trapping effects. If the previous biased current (pre-stressed) is smaller than 100 mA/mm, the transient currents increase with time showing detrapping effects. Both trapping and detrapping behaviors are not strong function of temperatures too.

All current transient measurements (on-state stress) in this study showed complicated trapping and detrapping behaviors at different Q-points and substrate temperatures. This observation would strongly relate to the performance of GaN HEMT power amplifiers, further investigation and correlation are necessary.
using Hi-Low method improved from $-2.0 \times 10^{-13}$ to $-7.0 \times 10^{-11}$ (eV cm$^2$/arb.) (at Ec-Et: 0.2 eV). The reliability by time dependent dielectric breakdown shows that the electric field difference in a photoconductive field was increased by about 25% at 1000°C.

From thermal Desorption Spectrometry profiles, HPWVA sample shows higher desorption of H$_2$O and smaller desorption of C$_6$H$_6$ and CO$_2$ than the w/o HPWVA. Therefore, HPWVA leads to improvement of the termination with OH group to defect of Al$_2$O$_3$ films and reducing the residual hydrocarbon. In addition, X-ray Photoelectron Spectroscopy profile of Ga2p at the Al$_2$O$_3$/GaN interface shows that the Ga-O binding increased after HPWVA.

Finally, through defect termination of OH groups and reduction of residual carbon by HPWVA, high quality Al$_2$O$_3$ were produced leading to reduction of N$_{t}$ and improvement of reliability. The low Dit is considered to be due to the termination of defects at the Al$_2$O$_3$/GaN interface by oxidizability of HPWVA. This research would contribute to realizing GaN MOSFET including high quality Al$_2$O$_3$/GaN interface for power semiconductor devices.


[Acknowledgements]

This work was supported by the Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “Next-generation power electronics-Research and Development of Fundamental Technologies for GaN Vertical Power Devices” (funding agency: NEDO).

**EP08.10.05**

Ultrahigh-Yield Growth of GaN via Halogen-Free Vapor-Phase Epitaxy

Daisuke Nakamura and Taishi Kimura; Toyota Central R&D Labs Inc, Nagakute, Japan.

To realize commercially feasible vertical GaN-based power devices, a sustainable supply of high-quality, large-diameter GaN wafers at low cost is required. Particularly, the cost of GaN wafers should be made comparable to that of Si and SiC wafers. Therefore, efficient incorporation of Ga into GaN crystals in the growth process (i.e., a high material yield of Ga) is critically important for reducing the total cost of GaN wafers as it would minimize Ga consumption in the production of GaN wafers. We demonstrated the HF-VPE GaN growth of high-quality thick GaN layers at the relatively high growth rate of ~100 μm/h. HF-VPE employs a simple reaction scheme \[\text{Ga} (g) + \text{NH}_3 \rightarrow \text{GaN} (s) + \frac{3}{2}\text{H}_2\], it can lead to an efficient reaction, a low reverse reaction rate, or both. The present study investigates the critical growth parameters and mechanisms that govern the material yield of Ga in HF-VPE GaN growth, and demonstrates ultrahigh-yield HF-VPE GaN growth.

The setup employed here for HF-VPE GaN growth was almost the same as that described in previous reports. A total of 27 growth experiments were carried out using a 2”-diameter substrate as a seed. The growth parameters of concern were the seed substrate holder temperature, the Ga crucible temperature, the background pressure $p$, the gas flow rates, and the seed-to-crucible-outlet distance $d$; their effects on the material yield of Ga, $Y_{Ga}$, during HF-VPE GaN growth were investigated. A linear multivariate analysis was conducted to find the critical growth parameters that govern $Y_{Ga}$. The $Y_{Ga}$ values are in the range of 14–23%, which are considerably higher than those for conventional HVPE GaN growth (5–10%). The critical growth parameters identified in the best model for the multivariate analysis were $d$, $p$, $Q_{Ar}$, $Q_{NH}_3$, $Q_{Ga}$, and $Q_{H}_2$. Based on the regression coefficients for the critical growth parameters, the regression equation for calculating $Y_{Ga}$ was formulated.

The dependence of $Y_{Ga}$ on $d$ suggests that the gas-stream pathways for Ga vapor nearer to the seed substrate surface are a dominant factor in achieving a higher $Y_{Ga}$. With a low $p$ and a small $d$, most of the gas-stream pathways for Ga vapor (denoted by blue arrows) almost reach the seed surface owing to their high gas-stream velocity and the short seed-to-source distance. Considering the above discussion on the gas-stream pathways of Ga vapor, we employed larger-diameter seed substrates (3”- and 4”-diameter sapphire substrates) to demonstrate the suppression of Ga vapor escape and the resultant higher $Y_{Ga}$. $Y_{Ga}$ increases almost linearly with increasing seed substrate diameter, with an ultrahigh $Y_{Ga}$ of ~47% obtained for the 4”-diameter substrate. With this ultrahigh material yield, we believe that HF-VPE can be used to produce a sufficient number of GaN wafers for high-power vertical GaN devices at moderate prices without depleting the global Ga supply.

**EP08.10.06**

Aluminum Nitride Nanowire Flexible Ultraviolet Photodetectors

Yassir A. Ali and Kasif Teker; Electrical and Electronics Engineering, Istanbul Sehir University, Istanbul, Turkey.

One-dimensional nanostructured wide bandgap (WBG, typically between 3 eV – 6 eV) semiconductor materials are good candidates as building blocks for photovoltaic device applications such as UV photodetectors, phototransistors, and photodiodes. Furthermore, high UV light sensitivity, small size, very short response time, low power consumption, and high efficiency are the most important features of nanodevices for new and superior applications in optoelectronics. AlN nanowires, an important III-V WBG semiconductor, have aroused significant interest due to its large direct bandgap (6.28 eV), low electron affinity, high thermal conductivity, high melting point (above 2300°C), and chemical stability. Despite its intrinsic superior properties, one-dimensional nanostructured wide bandgap (WBG, typically between 3 eV – 6 eV) semiconductor materials are good candidates as building blocks for photovoltaic device applications such as UV photodetectors, phototransistors, and photodiodes. Furthermore, high UV light sensitivity, small size, very short response time, low power consumption, and high efficiency are the most important features of photodiodes for new and superior applications in optoelectronics. AlN nanowires, an important III-V WBG semiconductor, have aroused significant interest due to its large direct bandgap (6.28 eV), low electron affinity, high thermal conductivity, high melting point (above 2300°C), and chemical stability. Despite its intrinsic superior properties, challenges in synthesis of defect-free and uniform morphology AlN nanostructures persist, thereby limiting the number of electronic and photonic device studies.

This paper presents the fabrication of a flexible ultraviolet (UV) photodetector from free-standing catalyst-free AlN nanowire (AlNNW) films via a direct transfer method through a very low-cost non-lithographic fabrication scheme. The device has demonstrated very fast photoresponse rise and decay times of ~100 μs and ~10 μs, respectively. The photocurrent measurements have been conducted for bias voltages from 1V to 20V. In fact, the flexible AlNNW photodetector is very sensitive to the UV illumination even at low bias voltages (as low as 1V) indicating very high sensitivity.

One-dimensional nanostructured wide bandgap (WBG, typically between 3 eV – 6 eV) semiconductor materials are good candidates as building blocks for photovoltaic device applications such as UV photodetectors, phototransistors, and photodiodes. Furthermore, high UV light sensitivity, small size, very short response time, low power consumption, and high efficiency are the most important features of photodiodes for new and superior applications in optoelectronics. AlN nanowires, an important III-V WBG semiconductor, have aroused significant interest due to its large direct bandgap (6.28 eV), low electron affinity, high thermal conductivity, high melting point (above 2300°C), and chemical stability. Despite its intrinsic superior properties, challenges in synthesis of defect-free and uniform morphology AlN nanostructures persist, thereby limiting the number of electronic and photonic device studies.

This paper presents the fabrication of a flexible ultraviolet (UV) photodetector from free-standing catalyst-free AlN nanowire (AlNNW) films via a direct transfer method through a very low-cost non-lithographic fabrication scheme. The device has demonstrated very fast photoresponse rise and decay times of ~100 μs and ~10 μs, respectively. The photocurrent measurements have been conducted for bias voltages from 1V to 20V. In fact, the flexible AlNNW photodetector is very sensitive to the UV illumination even at low bias voltages (as low as 1V) indicating very high sensitivity and capability of operating at low voltages. Moreover, the photocurrent has decayed to the dark current value rapidly, after the exposure ended, suggesting the absence of defect-related traps. Consequently, the facile fabrication scheme is very cost-effective, readily scalable; and offers broad integration capabilities in various flexible photonic and electronic applications including wearable devices.
layers by PLD at room-temperature in $10^{-3}$ Pa of O$_2$ using a β-Ga$_2$O$_3$ sintered target. The amorphous Ga$_2$O$_3$ films were subsequently irradiated 500–1000 pulses of the KrF excimer laser using laser-induced plasma-enhanced atomic layer deposition (ELA). A six-axis diffractometer in SR-XRD was used to evaluate the lattice parameters and to measure the reciprocal space map, such as out-of-plane -201 and in-plane 002 for Ga$_2$O$_3$ thin film, 111 and 1-11 including reflectivities for NiO seed layers, 0006 and 11-23 for α-Al$_2$O$_3$(0001) substrates. The epitaxial β-Ga$_2$O$_3$(0-1) thin films with six-fold in-plane symmetry were obtained on rocksalt-type buffer layers after the ELA procedure, while the films on wurtzite-type buffer remained uniaxial oriented and planarly isotropic. Although, the crystallization did not propagate to the surface in case of excessive precursor thickness, while insufficiently thick films remained amorphous. The d-spacing of NiO seed layers having different thickness shows a constant value because of the high-quality epitaxial growth of their layers on sapphire substrates. On the other hands, the d-spacing of the β-Ga$_2$O$_3$ thin films shrank in the in-plane direction and expanded in the out-of-plane direction. β-Ga$_2$O$_3$ thin film with NiO of 2 nm thick showed the best epitaxial quality when we judged from FWHM values of rocking curves. The results suggested importance of total consumption of energy above a threshold via photothermal process as well as a trigger of effective absorption of the reached excimer laser at the interface between amorphous and crystallized regions or the buffer layer, that optical absorption of the precursor amorphous Ga$_2$O$_3$ films well agreed the Lambert-Beer Law.


EP08.10.08
Solid-State Synthesis of Hexagonal Boron Nitride Crystals
Clint D. Frye, James H. Edgar and Rebecca Nikolic; Lawrence Livermore National Laboratory, Livermore, California, United States; Chemical Engineering, Kansas State University, Manhattan, Kansas, United States.

Ultrawide bandgap (UWBG) semiconductors such as diamond, AlN, Ga$_2$O$_3$, and AlGaN are emerging electronic and optoelectronic materials. However, material quality and availability remain immature and lag conventional semiconductors such as silicon or even silicon carbide and gallium nitride. Hexagonal boron nitride (hBN) has many of the same advantages of other UWBG materials such as low chemical reactivity, high temperature operation, and high critical electrical field, but it also has a layered 2D structure and been shown to emit light at 215 nm. These properties are valuable for a wide array of applications such as deep ultraviolet (DUV) optoelectronics, neutron detection, electronics in harsh hot environments, and as the preferred substrate and dielectric for 2D electronics (graphene, MoS$_2$, etc.). Crystal growth of hBN, however, is relatively unexplored, and a lack of high quality crystals has limited device fabrication. In this work, hBN crystals were grown by a wholly solid-state process. 300 nm of NiCr was sputter deposited onto pyrolytic BN and then annealed in a rapid thermal annealer in Ar at 900 °C for 3–15 min. During the annealing, B and N from the pyrolytic boron nitride substrate dissolved into and diffused across the NiCr film. As the samples cooled, hBN precipitated on the top side of the NiCr film. The NiCr metal serves simultaneously as a solvent, template, and catalyst. hBN platelets up to 1 μm in diameter were grown as confirmed by Raman analysis. NiCr was selected because it has been used as a liquid solvent for hBN growth and has a small lattice mismatch of 0.4%. Cr, which has a strong affinity for N, was alloyed with Ni to increase N solubility as pure Ni has a very low N solubility. The chromium content in the NiCr films was varied from 0–40 mol%. This growth technique uses readily available materials, common vacuum processing equipment, relatively low temperatures, and has the potential to be scaled up to wafer scales or made into a steady state crystal growth process. A roadmap will be presented on how to scale up the size of the crystal platelets to wafer scales. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-753061.

EP08.10.09
Fabrication of MIM Diodes by Atmospheric Pressure Spatial Atomic Layer Deposition (AP-SALD) System
Abdullah Alshehri, Kissan Mistry, Khaled Ibrahim, Vu Thi Huong Nguyen, David Munoz, Mustafa Yavuz and Kevin Musselman; Mechanical Engineering, University of Waterloo, Waterloo, Ontario, Canada; Mechanical Engineering, Prince Sattam bin Abdulaziz University, Alkhari, Saudi Arabia; Laboratoire des Matériaux et du Génie Physique, Grenoble, France.

A novel quantum metal-insulator-metal (MIM) diode is fabricated by atmospheric pressure spatial atomic layer deposition (AP-SALD) system. This scalable method was used to produce MIM diodes with high-quality, pinhole-free Al$_2$O$_3$ film more rapidly than by conventional ALD. MIM diode fabricated by AP-SALD system shows lower effective barrier height (1.27 eV) between electrode-insulator interface than that of MIM by conventional ALD (1.44 eV) resulting lower turn on voltage ($\phi_{ON}=1$ V) and better asymmetry and nonlinearity values 4.5, 8 respectively, and demonstrate that clean room fabrication is not a prerequisite for quantum-enabled devices.

EP08.10.10
Atomic Layer Etching for Selective Area Doping of GaN
Kevin A. Hatch, Houqiang Fu, Jesse Brown, Xingye Wang, Mei Hao, Yuji Zhao and Robert J. Nemanich; Arizona State University, Tempe, Arizona, United States.

The development of high efficiency GaN power devices using vertical architectures is hindered by the ability to achieve selective area doping of the $p$–$n$ junction. This process may be improved by the removal of surface damage caused by the conventional inductively coupled plasma (ICP) etching and regrowth method, which may create defects, impurities, and surface states that impact the junction properties. We have demonstrated surface etching of GaN allowing controlled material removal. Our technique uses $in situ$ remote plasma-enhanced atomic layer oxidation of the ICP etched surface followed by oxide removal through H-plasma etching. The removal of damaged layers at the surface resulted in an increase of the surface band bending to a value 0.5 ± 0.1 eV for previously ICP etched $n$-type GaN and 0.7 ± 0.1 eV for non-etched $n$-type GaN. The variation in band bending indicates continued removal of damage over several cycles of this repeated process for the etched material whereas the non-etched GaN displayed no change in the band bending after the first cycle, consistent with dry cleaning of surface contamination. This work was supported by ARPA-E, grant No. DE-AR0001691.

EP08.10.11
Observation of Slow and Controllable Growth of Filament in Conducting-Bridge Memory
Atsushi Shimizu, Hiroshi Sato, Sohta Hida and Kentaro Kinoshita; Faculty of Science, Tokyo University of Science, Katsushika, Japan; Tottori University, Tottori, Japan.

Resistive switching memories are drawing attention as memories that can overcome miniaturization and other performance limits facing conventional memories. Among them, filament growth-based resistive switching memories especially show high performance and are largely categorized into anion diffusion-type, which is generally called resistive random access memory, ReRAM, and cation diffusion-type, which is called conducting-bridge RAM, CBRAM. Although they tend to be mixed up in the category of a filament type resistive switching memory and both of them are expected as a non-volatile memory for next generation, it is important to elucidate intrinsic difference of their performances to select appropriate applications. In this paper, the difference of filament growth characteristics between them are discussed using ReRAM and CBRAM of top electrode(TE)/metal oxide(MO)/bottom.
A ZnO layer with a thickness of 25 nm was deposited on a Pt (100 nm)/Ti (20 nm)/SiOx (100 nm)/Si(650 nm) substrate using an RF sputtering method. Then, both Cu and Pt top electrodes were deposited on the ZnO film by an RF magnetron sputtering method. Accordingly, Cu/ZnO/Pt CRAM structures (ZnO - CRAM) and Pt/ZnO/Pt OrRReRAM structures (ZrO2 - ReRAM) were fabricated sharing the same ZrO2 layer as a memory layer. We succeeded in observing the transient of the resistance from high resistance state, HRS, to low resistance state, LRS, of the CRAM device, by inserting a load resistance. The load resistance should have an appropriate resistance value to divide a voltage applied to the CRAM device, $V_{bias}$, to the load resistance when set switching is caused. It is noticeable that CRAM resistance continues to decrease even when $V_{bias}$ is decreasing unless a current is increasing, which is consistent with a widely received picture that the growth of filaments is retarded to ionic current, i.e., the flow of cupper ions in the present case. On the other hand, the increasing rate of a resistance is too rapid to be detected within the sampling rate of 10 μs, meaning that the resistance of ReRAM device decreases to the resistance value lower than the load resistance within 10 μs after the occurrence of set switching. The difference of the observability of the transient state between CRAM and ReRAM devices strongly suggests the difference of the switching speed between them. Fast switching speed of ReRAM causes large surge current through the parasitic capacitance of a measurement circuit, although the same measurement circuit was used for both devices. The large surge current enhances the growth of filaments and makes a reset current, $I_{reset}$, large. On the other hand, slow switching speed of CRAM highly enhances the controllability of $I_{reset}$ ranging more than six orders of magnitude, 0.1 nA - 1.0 mA.


EP08.10.12
Theoretical Study on Oxygen Vacancies in Crystal Grains in Polymeric Alumina HfO: Thin Film
Sohita Hida1,2, Takumi Morita2, Takahiro Yamasaki3, Jun Nara1, Takahisa Ohno1 and Kentaro Kinoshita1; 1Graduate School of Sustainability Science, Tottori University, Tottori, Japan; 2Faculty of Science, Tokyo University of Science, Katsushika, Japan; 3National Institute for Materials Science, Tsukuba, Japan.

Metal oxides such as HfO2 are widely received as materials for the fabrication of memory layers of Resistive Random Access Memory (ReRAM) [1]. It is theoretically reported that electric characteristics were changed by introducing vacancies into HfO2 single crystal or grain boundary [2, 3]. In these studies, they suggested that resistive switching is caused by diffusion and aggregation of oxygen vacancies (Vo's). However, no one demonstrates the whole of the process during the resistive switching, i.e., detailed movement of Vo's between high and low resistance states. In this paper, the first principles molecular dynamics (FPMD) program PHASE/0 [4] was used to discuss the generation and movement of Vo's. We calculated the generation energy of Vo's ($E_{vo}$) on the surface and far from the surface of HfO2 periodic slab which was modeled based on our experimental results [5]. $E_{vo}$ for the former and the latter are 9.043 eV and 9.807 eV, respectively. Therefore, Vo's are easily generated near the surface than far from the surface.

We theoretically observed the process of structural relaxation and the effects of changing charge states of Vo's and raising a temperature to 1000 K, by FPMD. When the charge state of Vo's changes from divalent (Vo2+) to neutral (Vo0), Vo's are attracted each other and aggregate. On the other hand, when the charge state of the Vo's changes from Vo0 to Vo2+, Vo's are repelled against each other and disperse. The difference of the static energy between the aggregated and dispersed states was 0.67 eV. In addition to the result above, we previously reported that slight displacements of small amounts of atoms alter the surface electric state from conductive to insulating or vice versa [6]. Therefore, resistive switching of ReRAM can be caused by aggregation and dispersion of Vo's depending on the charge state of Vo's, with the assistance of Joule heat. The location at which resistive switching takes place is near the surface of crystal grains where Vo's are expected to move easily due to the symmetry of bulk crystal is broken. This type of resistive switching can be caused by applying voltage to a metal/metal oxide structure, which changes Fermi level and causes injection (extraction) of electrons from (to) the metal to (from) the metal oxide layer.


EP08.10.13
The Nitrogen Impurity in Wide-Band-Gap Oxide Semiconductors
Inttuo Chaturatna1, Pakpoom Reunchan1,2 and Andersson Ianotti3; 1Department of Physics, Kasetsart University, Bangkok, Thailand; 2Thailand Center of Excellence in Physics (ThEP Center), Commission on Higher Education, Bangkok, Thailand; 3Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States.

Wide-band-gap oxide semiconductors are promising for various device applications, yet controlling the electrical conductivity and achieving p-type doping remains challenging. Among the possible acceptor impurities, N would be the most promising due to atomic size considerations. We use hybrid density-functional calculations to study the effects of the nitrogen impurity on the electronic and optical properties of the wide-band-gap oxides ZnO, SnO2, In2O3, TiO2, SrTiO3 and BaTiO3. In ZnO, SnO2, In2O3, and TiO2, we find that N incorporating on the O site (NO) introduces donor and acceptor levels in the gap, with the donor level below the acceptor level, as in an AX center. In BaTiO3 and SrTiO3, NO is, however, a negative-U center, with a (+/-) level in the gap. Therefore, N incorporation in SnO2 is, however, a negative-U center, with a (+/-) level in the gap. In this paper, we discuss the generation and movement of NO's depending on the charge state of NO's, with the assistance of Joule heat. The location at which resistive switching takes place is near the surface of crystal grains where NO's are expected to move easily due to the symmetry of bulk crystal is broken. This type of resistive switching can be caused by applying voltage to a metal/metal oxide structure, which changes Fermi level and causes injection (extraction) of electrons from (to) the metal to (from) the metal oxide layer.


EP08.10.14
Preparation of Wide Gap n-Type Sn2Ta2O7 Polycrystalline Films by Magnetron Sputtering
Shunich Suzuki1,2, Naoko Kikuchi2, Yoshihiro Atsua1 and Keisuke Nishio1; 1Materials Science and Technology, Tokyo University of Science, Katsushika, Japan; 2Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Transparent conductive oxides (TCOs) have a potential in various applications to electronic devices. Actually n-type TCOs such as tin-doped indium oxide (ITO) have been used for displays, solar cells and so on. On the other hand, p-type TCOs have not been practicable due to low hole mobility. The reason for low hole mobility for many transparent conductors is localized valance band maximum (VBM) composed of O2p. For realizing the p-type TCOs, the VBM composed of delocalized orbitals of metal elements is essential. Our group focused on Sn2Ta2O7 of which VBM is composed of Sn5s and succeeded in preparation of p-type and n-type Sn2Ta2O7 bulks depending on annealing condition. Hole and electron carriers were also found to be generated by Sn4+ -on-Nb substitutional defects and oxygen vacancies, respectively. For the application of new transparent electronic devices based on the p-n junction, preparation of Sn2Ta2O7 films is indispensable. However there is no report on conductive Sn2Ta2O7 films as of today. In this study, we report the preparation of n-type polycrystalline thin films of Sn2Ta2O7, and the effect of annealing conditions on their electrical properties.
Sn$_2$Ta$_2$O$_7$ polycrystalline thin films were fabricated by magnetron sputtering. Dense Sn$_2$Ta$_2$O$_7$ was used as a target. The sputter deposition was performed at an Ar gas pressure of 0.5 Pa with an rf power of 100 W. Sn$_2$Ta$_2$O$_7$ films were deposited on SiO$_2$ glasses at a substrate temperature of 848 K and followed by annealing under N$_2$ gas flow at 773-973 K for 6 h in tubular furnace. Crystalline phases were identified by X-ray diffraction (XRD). Band gap ($E_g$) of the films were estimated from the transmission spectra using the Tauc plot. Resistivity and Hall measurements were carried out at room temperature. $E_g$ of the films was estimated to be 3.2 eV, indicating high transparency in visible range. After the annealing over 873 K for 6 h under N$_2$ gas flow, the thin film samples showed n-type conductivity. Electrical resistivity, carrier density and mobility were 1.2 ohm cm, 5.4×10$^{10}$ cm$^{-2}$, 3.9×10$^2$ cm$^2$V$^{-1}$s$^{-1}$. Sn$_2$Ta$_2$O$_7$, with small amount of Sn$_2$Ta$_2$O$_8$x and SiO$_2$, as impurity phases was found in XRD patterns. The amount of impurity phases increased with increasing temperature. In summary, we succeeded in preparation of wide-gap, n-type Sn$_2$Ta$_2$O$_7$ films which showed both p- and n-type conductivity in powder samples.

**EP08.10.15**
Surface Band Bending of Polar ZnO by Hard X-Ray Photoemission Combined with X-Ray Total Reflection Shigenori Ueda; National Institute for Materials Science, Hyogo, Japan.

ZnO is known as a polar semiconductor due to an alternating stacking of Zn and O layers along the c-axis. Ohashi et al. [1] showed that the valence band spectral shapes of ZnO single crystals strongly depended on the crystalline orientation from hard X-ray photoemission spectroscopy (HAXPES) measurements. In general, HAXPES is a bulk-sensitive probe [2], and take-off angle (TOA) dependent of photoelectron gives depth information [3]. However, the decrease of the photoemission intensity occurs in lower TOA, and the valence band spectra depend on TOA [3] due to the matrix element effect [4].

In this work, HAXPES combined with X-ray total reflection (TR-HAXPES) [5] was used to obtain a depth-resolved electronic structure instead of TOA dependent measurements. We have measured the core-level and valence band HAXPES spectra of commercially available bulk single crystalline ZnO for Zn- and O-polar faces in the case of effective inelastic mean free path of 2.0, 4.1, and 8.0 nm by tuning the X-ray attenuation length. Undoped n-type ZnO crystals with fine polished surfaces were used. The valence band spectra of ZnO showed the clear polarity dependence as reported in Ref. [1]. The depth dependence of the valence spectra showed the nearly flat band behaviors for the Zn- and O-polar ZnO faces, in contrast to those for the Ga- and N-polar GaN faces [5]. The Zn 3s and O 1s core-level spectra also showed the nearly flat band behaviors for both the Zn- and O-polar faces. These nearly flat band behaviors are attributed to the pining by the states located at the Fermi-level. We will discuss the band bending behaviors and electronic structures of ZnO in comparison with those of GaN.

References

**EP08.10.16**
Fabrication of Rocksalt-Structured MgZnO/MgO Layered Structures and Their DUV Light Emission Properties Kyohbei Ishii1, Mizuki Ono2, Takeyoshi Onuma3, Kentaro Kaneko2 and Shizuo Fujita2; 1Electronic Science and Engineering, Kyoto University, Kyoto, Japan; 2Photonics and Electronics Science and Engineering Center, Kyoto University, Kyoto, Japan; 3Applied Physics, School of Advanced Engineering, Graduate School of Engineering, Kogakuin University, Tokyo, Japan.

Recently, deep ultraviolet (DUV) light sources using wide bandgap materials attract much attention because they can substitute for gas sources due to their small-size, low cost, and capability of arbitrary tuning the emitting wavelength. Our group has been focusing on rocksalt-structured MgZnO (RS-MgZnO), possessing the maximum bandgap energy of 7.8 eV[3], as a candidate capable of emitting DUV light of the wavelength range shorter than 200 nm, which cannot be realized by AlGaN.

At first, MgZnO thin films were grown on MgO (001) substrates by the mist CVD method. Magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O) and zinc chloride (ZnCl$_2$) were used as precursor sources of Mg and Zn, respectively. The source molar ratio of [Mg]/[Zn] was 90:10. Then, MgZnO/MgO layered structure samples were fabricated. The structure consists of four periods of MgO barrier and MgZnO well layers. X-ray diffraction (XRD) 2θ/ω scan profile of the MgZnO thin film indicated that the RS-MgZnO without other crystalline phases was successfully grown. Atomic force microscopy (AFM) observation showed a smooth surface with a root-mean-square (RMS) roughness of 0.20 nm. Additionally, step-terrace structure was observed on the film surface, where the step height was 0.42 nm corresponded to the diatomic length. Cross-sectional transmission electron microscope (TEM) observation do not show the generation of misfit dislocation at the interface, i.e., only dislocation lines originated from the MgO substrate exist in the MgZnO film. The dislocation density in the MgZnO film is estimated to be less than 10$^7$ cm$^{-2}$. The improvements of crystalline quality resulted in the observation of predominant DUV emission peak at 5.86 eV (212 nm) at 6 K and 5.71 eV (217 nm) at 300 K in the cathodoluminescence (CL) spectra. Other peaks at the longer wavelengths, which were remarkable in our previous report [2], were negligibly reduced.

Moreover, in optical quality may be attributed to the use of carbon-free sources instead of the acetate sources as used in the previous study[2]. Spectrally integrated CL intensity at 300 K over that at 6 K ($I_{300}/I_{6}$) was estimated to be 2.5%. CL spectra of MgZnO/MgO layered structure exhibited a peak at 5.96 eV (208 nm) at 6 K and 5.90 eV (210 nm) at 300 K. Apparent increase in the peak energies of 0.1 eV (0.19 eV) at 6 K (300 K) were confirmed. Moreover, $I_{300}/I_{6}$ of 16% was 6 times higher than that of the MgZnO thin film. Further research toward the vacuum ultraviolet (VUV) emission at the wavelength range shorter than 200 nm is in progress.


**EP08.10.17**
Novel P-Type Oxide Semiconductors of α-Ir$_2$O$_3$, α-Ga$_2$O$_3$, and Gallium Oxide Electronics Kentaro Kaneko1, Shinichir Kani1, Shu Takemoto1, Isao Takahashi1, Masahiro Sugimoto2, Takashi Shinno1a and Shizuo Fujita1; 1Kyoto University, Kyoto, Japan; 2FLSOFE INC., Kyoto, Japan.

Gallium oxide (Ga$_2$O$_3$) electronics, owing to ultra-wide bandgap of Ga$_2$O$_3$, is one of the most emerging fields in electronic materials research because some of the materials properties of Ga$_2$O$_3$ are advantageous over SiC and GaN for power device applications. Ga$_2$O$_3$ takes several different crystal structures, among which monoclinic Ga$_2$O$_3$ (β-Ga$_2$O$_3$) is the thermally stable phase, and marked progress for device applications are reported [1].

On the other hand, rhombohedral corundum-structured α-Ga$_2$O$_3$ (α-Ga$_2$O$_3$) is attractive in view of bandgap engineering from 3.7 to ~9 eV by alloying with corundum-structured α-Al$_2$O$_3$ and α-In$_2$O$_3$. With mist CVD growth, high-quality α-Ga$_2$O$_3$ is grown on sapphire (α-Al$_2$O$_3$) substrates [2], followed by evolution of Schottky barrier diodes with extremely low on-resistance [3]. However, the lack of p-type oxide semiconductors acting as a counterpart of n-type α-Ga$_2$O$_3$ has obstructed high-performance power devices based on α-Ga$_2$O$_3$.

\[ E_g = 3.7 \text{ eV} \]
Our attention has been focused on corundum-structured $n$-(Rh,Ga)$_2$O$_3$ [4] and $\alpha$-Ir$_2$O$_3$. An $n$-(Rh,Ga)$_2$O$_3$ thin film showed clear $p$-type conductivity by Hall-effect measurements with the hole mobility of 1.0 mV/cm$^{-1}$ and the hole concentration of $7.6 \times 10^{17}$ cm$^{-3}$. On the other hand, $\alpha$-Ir$_2$O$_3$ was reported as a $p$-type oxide confirmed by thermoelectric power measurement with a band gap of 2.6 eV[5]. Almost reports about $\alpha$-Ir$_2$O$_3$ were poly crystals, multi-domain crystals, or oxidation layer generated at Ir metal surface[6-8].

Single-crystalline $\alpha$-Ir$_2$O$_3$ thin films were fabricated on c-plane sapphire (0001)-Al$_2$O$_3$ substrates by mist CVD technique. The growth rate was accomplished up to 7.5 mm/h. A lattice mismatch between $\alpha$-Ir$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ was calculated as 0.3% along a-axis from cross-sectional TEM observations. Obtained $\alpha$-Ir$_2$O$_3$ and $\alpha$-(Ir,Ga)$_2$O$_3$ showed clear $p$-type conductivity, especially for $\alpha$-(Ir,Ga)$_2$O$_3$, it has a hole density and a mobility of 3.7-$5.0 \times 10^{17}$ cm$^{-3}$ and 2.9 cm$^2$/Vs, respectively.

These results pave the way to fabricate pn junctions with an n-type $\alpha$-Ga$_2$O$_3$ layer and a $p$-type $\alpha$-Ir$_2$O$_3$. Highly-doped $\alpha$-Ga$_2$O$_3$ (n$^+$) and $\alpha$-Ga$_2$O$_3$ (n$^-$) layers were fabricated on $\alpha$-Ir$_2$O$_3$ (p$^+$) thin film on sapphire substrate. The junction showed rectification properties. From the current-voltage measurement, depletion layer was mainly spread into the $\alpha$-Ga$_2$O$_3$ (n$^-$) from $\alpha$-Ga$_2$O$_3$ (n$^+$)/$\alpha$-Ir$_2$O$_3$ (p$^+$) interface because of the large value of hole concentration in the $\alpha$-Ir$_2$O$_3$ (p$^+$).

Part of this work was supported by “Strategic Innovation Program for Energy Conservation Technologies” of the New Energy and Industrial Technology Development Organization (NEDO).


EP08.10.18 Controlled p-Type Doping of CuSCN Ajith DeSilva$^1$, G. R. A. Kumara$^1$, K. Tennakone$^2$ and Unil Perera$^2$; $^1$University of West Georgia, Carrollton, Georgia, United States; $^2$Physics and Astronomy, Georgia State University, Atlanta, Georgia, United States; $^3$National Institute of Fundamental Studies (NIFS), Kandy, Sri Lanka.

Solution processable optically transparent p-type semiconductors are rare. Copper (I) thiocyanate (CuSCN) having a direct band gap of ~ 3.9 eV has been identified as one of the most promising materials of the above category. CuSCN is extensively studied as the hole collector material for perovskite and dye-sensitized solar cells and simple techniques are available for casting thin films under ambient conditions. The p-type conductivity of CuSCN depends on stoichiometric excess of SCN normally introduced during the method of preparation via reaction of aqueous solutions CuSO$_4$ and KSCN in the presence of a reducing agent. Ultraviolet irradiation and chlorination introduce excess SCN enhancing the conductivity, but drawback here is introduction of impurities. A methods developed for controlled doping of CuSCN, using solutions of CuSCN$_3^-$ in organic solvents will be discussed giving the details of the procedures and results of conductivity measurements of thin films. The method enable introduction of measured quantities of excess SCN into CuSCN without introduction of impurities.

EP08.10.19 Controlling the Polarity of Aluminum Nitride Thin Films Using Si-Based Dopants Sri Ayu Anggraini, Masato Uehara, Hiroshi Yamada and Morio Akiyama; AIST, Fukuoka, Japan.

Aluminum nitride (AIN) is a promising wide band-gap material particularly for various electronic applications due to its unique combination of electrical, thermal, acoustic and piezoelectric properties. The functionality of AIN-based thin film can be tuned not only by having a highly c-oriented thin film but also by controlling its polarity. Stacking two AIN-based thin films with different polarities has been reported to improve the performance of a solid mounted BAW resonator [1]. Thin films with an inverted polarity could be obtained by controlling the deposition parameter, such as oxygen concentration [2], sputtering pressure [3], cathode power [4], or it can be also obtained by employing seed a layer to promote the growth of AIN thin films in a certain direction [5]. However, since these techniques often resulted in crystallinity deterioration and require precise control, we propose the use of Si or MgSi dopants to control the polarity of AIN thin film as an alternative method to control the polarity of AIN thin films.

The polarity of the thin film was investigated by examining the piezoelectric response (d$_{33}$) of the resulting thin films. Incorporating 1-14 at.% of Si could inverse the polarity of thin films from positive (Al-polar) to negative (N-polar) without massively reducing the magnitude of the piezoelectric response. The piezoelectric response of non-doped thin film is 6.9 pC/N, while that of Si$_{10}$Al$_{90}$Si$_{10}$O$_{7}$ is found to be ~6.2 pC/N. In case of MgSi-doped AIN, the polarity of the thin films is governed by the ratio of Mg to Si. When the Mg/Si ratio is lower than 1, the negative d$_{33}$ values suggest that the thin films are predominantly N-polar. On the contrary, higher Mg/Si ratio (> 1) yielded a positive d$_{33}$ value which indicates that the thin films are main Al-polar. Despite of polarity changes, significant enhancement in piezoelectric response by alloying AIN with MgSi was not observed. The effect of Mg and Si addition into AIN is further investigated and elucidated by investigating the change of chemical states, morphology and crystallinity of the thin films.

References:

EP08.10.20 Solution-Processed Cubic GaN for Potential Lighting Applications Aakash K. Jain$^1$, Sushma Yadav$^4$, Meenal Mehra$^3$, Sameer Sapra$^2$ and Madhusudan Singh$^1$; $^1$Electrical Engineering, IIT Delhi, New Delhi, India; $^2$Chemistry, IIT Delhi, New Delhi, India; $^3$Momente Performance Materials (India) Pvt. Ltd., Bengaluru, India; $^4$Institut für Physikalische Chemie und Elektrochemie, Leibniz University, Hannover, Germany.

Cubic gallium nitride (GaN) is a wide bandgap semiconductor exhibits high crystallographic symmetry resulting in a lower inbuilt polarization which is useful for more efficient phosphor-free green light-emitting diodes. It has been grown using molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), which produce highly ordered thin films on compatible substrates. In this work, we report the chemical synthesis of cubic GaN using chemical metathesis reaction in diethyl ether with lithium nitride and anhydrous gallium chloride as precursors, inside a nitrogen glove box at the room temperature. The resulting product was washed to remove lithium chloride and dried before vacuum annealing in a furnace at 850°C. Powder X-ray diffraction (XRD) scans of the as-prepared and annealed product reveal cubic phase of GaN. Energy dispersive X-ray spectroscopy (EDX) measurements show a nitrogen-poor product, which correlates well with the nearly black color of the powder. Diffuse reflectance spectroscopy (DRS)
measurements were carried out with the product on a barium sulfate substrate in a Perkin-Elmer 1050 spectrophotometer to obtain strong absorbance below 400 nm and the Tauc plot for the bandgap estimate of 3.3 eV, which is in good agreement with the known excitonic bandgap of cubic GaN. Initial photoluminescence (PL) measurements with an excitation wavelength of 310 nm reveal a weak emission at 440 nm corresponding to the known defect centers (D2X) in GaN. Further development of this process to form an ink is expected to provide an alternate pathway to producing flexible phosphor free lighting devices.

**EP08.10.21**

**Heteroepitaxial Growth of Sn-Doped Ga2O3/Sapphire(0001) Thin Films Using Powder Sputtering Method** Ha Ram Lee1; Su Yong Lee2; and Hyon Chol Kang3; 1Chosun University, Gwangju, Korea (the Republic of); 2PAL, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Ga2O3 thin films have been widely investigated for use in optoelectronic and photonic devices as well as gas sensors because of a wide bandgap of 4.9 eV and good thermal stability up to its melting point (~1800 °C). Many efforts have focused on demonstrating the performance of electronic devices by varying the doping elements and concentrations. We report the heteroepitaxial growth of Sn-doped Ga2O3 thin films deposited using radio frequency magnetron sputtering onto sapphire(0001) substrates. The crystalline orientation of the films was examined using high-resolution synchrotron x-ray diffraction. The Sn-doped Ga2O3 thin films were grown with remarkably high crystallinity and negligible mosaic structure. We found that the corundum α- and monoclinic β-phases of Ga2O3 coexisted in the as-grown samples. Azimuthal angle scans of the in-plane [0020] and [0130] Bragg peaks revealed that the α-Ga2O3 and β-Ga2O3 both showed 12-fold in-plane rotational symmetry and, in particular, that the 30° rotated α-Ga2O3 domains in the in-plane direction were tilted ±3° to the surface direction. It is noteworthy that only 6-fold symmetry has previously been reported for most α- and β-Ga2O3 thin films. Finally, the optical bandgap of the as-grown film with a thickness of 185 nm was estimated at 5.03 eV, and it gradually decreased to 4.52 eV as the film thicknesses increased to 1.6 μm, which is attributed to the increased amount of Sn atoms. This might also be affected by the crossover of the dominant phases from the initial alpha phase to the later beta phase.

**EP08.10.22**

**Growth Mechanism of In-Doped β-Ga2O3 Nanowires Deposited by Radio Frequency Powder Sputtering** Su Yong Lee1 and Hyon Chol Kang1; 1Chosun University, Gwangju, Korea (the Republic of); 2PAL, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

In the last decade, various techniques have been proposed for synthesizing one-dimensional nanostructures such as nanowires (NWs) and nanobelts. In particular, monoclinic gallium oxide (β-Ga2O3) has received considerable attention for use in NWs owing to its wide bandgap of 4.9 eV, high breakdown field (> 8 MV/cm), and high optical transparency to visible and ultraviolet radiation. Recently, applications of β-Ga2O3 NWs in optoelectronic and photonic devices, as well as gas sensors, have been widely explored. Moreover, doped β-Ga2O3 NWs have attracted even greater interest as doping is an effective way to tune the physical properties of such structures. Many of these efforts have focused on demonstrating the performance of NW-based devices by varying the types and concentrations of the doping elements used, with Eu, Cr, Mn, Sn, and In having been examined. Among them, In is regarded as a promising dopant for significantly enhancing the sensitivity and quantum efficiency in nanobelt-based photodetectors. The synthesis of In-doped β-Ga2O3 NWs is typically carried out by thermal evaporation and vapor transport, using a mixture of either In and Ga2O3 powders or Ga and In2O3 powders as source materials. Recently, we reported the growth of β-Ga2O3 NWs using radio frequency (RF) powder sputtering. The deposition of non-stoichiometric Ga2O3, under an oxygen-deficient atmosphere was essential for facilitating the growth of β-Ga2O3 NWs by a self-catalytic vapor-solid-liquid (VSL) process using self-assembled Ga seeds. In this work, we examine the growth mechanism of In-doped β-Ga2O3 NWs synthesized by powder sputtering. In particular, the role of In atoms in determining the growth mechanism and the structure of NWs is investigated. Although the growth sequence of the doped NWs is similar to that of the undoped β-Ga2O3 NWs, the formation of self-assembled In clusters is more favorable compared to Ga clusters. Clusters of In as seeds for initiating the growth of In-doped β-Ga2O3 NWs through a self-catalytic VLS mechanism, while Ga seeds initiate the growth of undoped β-Ga2O3 NWs by the same mechanism. We also observed zigzag NWs formed by alternating NW growth directions.

**EP08.10.23**

**Investigation of Luminescence Characteristics of ZnO with Cycled Exposure to Electron Beams Using Cathodoluminescence in Transmission Electron Microscopy** Young-Woon Kim1; Yonghee Lee1; Sungdae Kim2; Samdong Kim3; and Mi-Hyang Sheen1; 1Seoul National University, Seoul, Korea (the Republic of); 2Dongguk University, Seoul, Korea (the Republic of); 3Korean Institute of Materials Science, Changwon, Korea (the Republic of).

ZnO is one of the strong candidates for the electrodes, sensors and detectors for the UV emission. Luminescence characteristics of nano-wire and thin-film ZnO was investigated using cathodoluminescence in transmission electron microscopy. Ultraviolet (UV) emission revealed reduction with time under electron beam, while the visible light did not show degradation of the luminescence intensity. UV luminescence decreased exponentially leaving 30% of intensity after 200 seconds exposure with electrons of 200keV, 12 pA/cm² current density. The luminescence intensity was partially recovered when the electron beam was temporarily off. Half-life of the luminescence was measured by turning electron beams ON and OFF for a fixed duration. For the first and second cycles of the electron beam showers, half-life time was measured as 26 seconds. Luminescence degradation from near-band-edge emission (3.29 eV), donor-acceptor-pair transition(3.17 eV), and emission from defects (~2.33 eV) were compared. In-situ luminescence of electrically biased ZnO thin film was characterized using TEM-CL, where localized luminescence was observed.

**EP08.10.25**

**Epitaxial Growth and Band-Offset Measurement of β-Ga2O3/GaN Heterojunction** Sunan Ding; Suzhou Institute of Nano-Tech and Nano-Bionics, CAS, Suzhou, China.

Ga2O3 is a kind of ultra-wide-bandgap semiconductor, which have been attracting more and more interests due to its super chemical and thermal stabilities. Since the band gap of β-Ga2O3 is about 4.9 eV, corresponding right to ultra-violet (UV) emission, β-Ga2O3 has been considered as the most promising candidate for UV/Deep-UV (DUV) LED and detectors. On the other hand, GaN-based devices are being well developed and widely used in high power electronics and photo-electronics. If combining Ga2O3 with GaN together in one structure, it will be possible to greatly promote their applications in the devices. However, the major challenges for Ga2O3 are material quality and p-type doping.

In this work, we have successfully grown crystalline β-Ga2O3 on GaN (0001) thin films by using plus laser deposition (PLD) and atomic layer deposition (ALD) techniques respectively. The atomic structure, interface properties, morphology, and composition of the oxide films were characterized by X-ray diffraction (XRD), atomic force microscope (AFM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS), which confirmed the epitaxial growth of highly oriented β-Ga2O3 thin films on GaN films in a wide range of temperature. By using our unique UHV connected system, the MOVCD grown GaN films were directly transferred through an UHV tube from its glove box to the ALD chamber for quick β-Ga2O3 deposition, without exposing the as-grown GaN surface to air. Therefore, a clear interface between Ga2O3 and GaN was achieved and the band offset of the β-Ga2O3/GaN heterojunction was directly measured by using XPS core levels and valence band spectra, which also indicate that the band
offset value varies with the interface conditions and the Ga$_2$O$_3$ crystallization.

As the recent progress in our studies, we demonstrated high quality epitaxial growth of β-Ga$_2$O$_3$ films on GaN(0001) by using PLD and ALD techniques at various temperatures, and experimentally determined the valence band offset of 1.40±0.06eV at the β-Ga$_2$O$_3$/GaN heterojunction. All of these results should be benefit to explore DUV devices based on Ga$_2$O$_3$/GaN heterojunctions.

**EP08.10.26**

**High-Performance of Low-Voltage Flexible UV Photodetectors Assembled with ZnO-ZnGa$_2$O$_4$ Heterostructure** Qiannian Du, Kun Tang, Shunming Zhu, Jiandong Ye, Youdou Zheng and Shulin Gu; Nanjing University, Nanjing, China.

Over the past decade, many efforts have been made to optimize the photoelectric devices because of their promising potential for biological and environment detection, optical communication and so on[1-3]. Photodetectors based on low-dimensional nanostructures exhibit superior performance owing to the large surface to volume ratio and tunable surface morphologies. Zinc gallate (ZnO$_x$Ga$_{1-x}$O$_y$) is an ultra-wide band gap semiconductor with a direct band gap of 4.4-4.7 eV. And it has attracted significant attention because of its high chemical stability and outstanding optical properties, which is the potential candidate of the deep ultraviolet photodetectors[4, 5]. In this study, we have fabricated ZnO:ZnGa$_2$O$_4$ heterojunction microwires by a simple chemical vapor deposition(CVD) method. Firstly, as evidenced from EDX, XRD and SEM analyses, we find the component of ZnO and ZnGa$_2$O$_4$ can be modulated by changing the ratio of the source materials (ZnO: Ga$_2$O$_3$) or the flow of O$_2$. The ZnO:ZnGa$_2$O$_4$ heterojunction photodetectors are fabricated on both the rigid SiO$_2$/Si and the flexible polyethylene terephthalate (PET) substrates, exhibiting excellent photoresponsivity to UV light illumination with high photoconductive gain. And it is noteworthy that the prepared flexible devices show good flexibility, high stability, reproducibility, and folding endurance.

**Acknowledgment**

This research was supported by the National Natural Science Foundation of China (Nos. 61504057, 61574075, 61674077) and the Natural Science Foundation of Jiangsu Province (Nos. BK20150585).

**References**


**EP08.10.27**

**Structural Tuning and Photocatalytic Performance of Three-Dimensional Ga$_2$O$_3$ a-b Hetero-Phase Junction Arrays for Solar Water Splitting** Can Cui, Liaoyong Wen and Puxian Gao; University of Connecticut, Willimantic, Connecticut, United States.

Widely studied and utilized wide-bandgap semiconductors such as SiC and GaN have met the intrinsic bottleneck of electronic performance due to the limit in break-down strength and thermal stability. As a result, even wider bandgap and thermally stable semiconductors are called upon to replace these semiconductors. An emerging candidate, Gallium Oxide (Ga$_2$O$_3$) has drawn much attention lately due to its superb stability[1] and wider band gap (~4.9 eV), as well as its five polymorphic structures in nature, i.e., α-, β-, γ-, δ-, and ε phases[2, 3]. Up to date, the full understanding of Ga$_2$O$_3$ is still lacking on their structural evolution, physical and chemical characteristics, as well as functional properties, calling for more and more studies.

In this work, the tuning of the crystal structure and morphology of Ga$_2$O$_3$ has been investigated via a facile solution preparation of Ga$_2$O$_3$ based nanowire arrays on planar surfaces that could carry various functions such as sensing, catalysis, and others. A hydrothermal deposition process has been successfully carried out with controllable parameters to produce GaOOH nanorod arrays with adjustable diameter and length. The phase evolution of Ga$_2$O$_3$ nanorods was studied starting from precursor GaOOH nanostructures under thermal annealing in detail. As a result, the pure α, the α-b hetero-phase junction, and the pure β Ga$_2$O$_3$ arrays have been realized with mesoporous surface structure and adjustable porosity by such a well-controlled post-annealing process. The relationship of evolution of these nanostructure ensembles and the resulting photocatalytic performances are verified via a demonstration of solar water splitting reaction. The results revealed a higher photocatalytic efficiency (~4.27 mmol·h$^{-1}$·cm$^{-2}$) in α-b hetero-phase junction arrays, as compared with that of pure α (~2.13 mmol·h$^{-1}$·cm$^{-2}$) and pure β (~1.78 mmol·h$^{-1}$·cm$^{-2}$) phases, respectively. The catalytic performance enhancement through these phase junctions may be due to a charge carrier separation caused by an offset of electronic structure between alpha and beta Ga$_2$O$_3$, which allows a more efficient charge utilization for the hydrogen evolution.


**SYMPOSIUM EP09**

Diamond Electronics, Sensors and Biotechnology—Fundamentals to Applications
November 26 - November 29, 2018

Symposium Organizers
Mutsuko Hatano, Tokyo Institute of Technology
Christoph E. Nebel, Fraunhofer Institute for Applied Solid State Physics
Emmanuel Scorsone, The French Atomic Energy Commission (CEA)
SESSION EP09.01: Kickoff
Monday Morning, November 26, 2018
Hynes, Level 2, Room 207

8:15 AM WELCOME BY THE ORGANIZERS

SESSION EP09.02: Diamond Growth and Technology
Session Chairs: Matthias Schreck and Travis Wade
Monday Morning, November 26, 2018
Hynes, Level 2, Room 207

8:30 AM *EP09.02.01
CVD Diamond Synthesis—How to Meet Our Device Expectations? Philippe Bergonzo1, 2; 1Seki Diamond Systems, San Jose, California, United States; 2Electronic and Electrical Engineering Dpt, University College London, London, United Kingdom.

Diamond is an exceptional material combining superlative properties like superhardness, superconductivity, high thermal conductivity, biocompatibility, radiation resistance, and unique optical properties etc. These advantages make diamond an excellent material to reply to a broad range of applications, that include thermal coatings, electrodes, windows, sensors, detectors, electronic devices, as well as quantum devices for a variety of applications. The synthesis of diamond is now a well-established technique, and especially when using CVD (Chemical Vapor Deposition) with a range of diamond growing machines readily commercially available at reasonable prices, as demonstrated by the exceptional recent rise of diamond foundries created to reply to a booming synthetic gemstone market.

Still, beyond gemstone fabrication, advances in growth technologies have made it possible to purposely grow synthetic diamond with tuned performances that go beyond that of other materials, and ultimately well below those of more conventional diamonds. This includes for example large area doped diamond films coatings on non-diamond substrates, or films of specific crystalline structures, or with control defect incorporation, at the nanoscale level, or also isotopically purified diamonds for quantum applications, etc.

The step from conventional diamond growth to optimized materials has required a range of technological solutions that have been developed, including for example the possibility to perform 3D structuration of diamond films, as well as the patterning of diamond growth over large area substrates, or the fabrication of ultrathin diamond membranes structured as photonics crystals, or of flexible diamond foils for implant applications, etc. All such approaches have been made compatible with clean room nanotechnology environments to be able to tune the material to the ultimate device fabrication needs. This presentation will review a portfolio of such technological approaches in order for the diamond grower to be able to conceive devices that reply to his application needs.

9:00 AM *EP09.02.02
Single Crystal Diamond Plates Grown by a Combination of Mosaic Technique and Lateral Growth Ramon D. Diaz1, Aaron Hardy2, Elias Garratt3, 4 and Timothy A. Grojohn3, 4; 1Michigan State University, East Lansing, Michigan, United States; 2Fraunhofer Center for Coatings and Diamond Technologies, East Lansing, Michigan, United States.

The electrical, mechanical, and thermal properties of diamond make it a promising material for new generation electronic devices. One of the challenges is the need for fabricating larger size Single Crystal Diamond (SCD) wafers with minimal defects. In this study, SCD plates were successfully grown based on the mosaic technique combined with conditions known for enhanced lateral growth. In earlier works [1] the plates were tiled together using substrates created by a process consisting of ion implantation followed by growth and electrochemical separation. The approach in this work is different in that a starting substrate is cut in two, then each of the two pieces are grown laterally followed by a growth that stitches them back together with a larger area. A series of steps were taken to ensure good crystallographical orientation, starting with laser cutting the tiles from the same 3.5 mm x 3.5 mm x 1.4 mm HPHT (High Pressure High Temperature) seed. The original area of the two substrates was increased by growing a layer of diamond via MPACVD (Microwave Plasma-Assisted Chemical Vapor Deposition) using a pocket configuration which favors lateral growth [2][3]. The grown tiles are polished and kept in aligned contact by their base with a polycrystalline diamond plate used as reference on the holder during growth. This step produced a
continuous layer diamond across the two pieces. The grown together substrate was then re-polished and re-grown multiple times by MPACVD process until the contact (stitched region) interface disappeared, effectively merging the tiles back into a single crystal. Defect densities from the grown layers were analyzed by etch pit counting and birefringence measurements. X-ray rocking curve mapping of the sample shows a maximum misorientation spread of 0.2 degrees, with an average mosaicity of 0.019 ± 0.008 degrees along the surface, demonstrating the feasibility of combining the developed mosaic technique with known lateral growth conditions for increasing the area of SCD wafers.

The authors would like to acknowledge funding for this work from MIT Lincoln Laboratory. X-Ray rocking curve measurements were provided by Rigaku, and X-Ray topography measurements were performed at APS, Argonne National Laboratory.


9:15 AM EP09.02.03
Development of Kinetic Monte Carlo Modelling and Visualisation of CVD Diamond Growth Max D. Williams1,2, Neil L. Allan1 and Paul W. May1; 1 School of Chemistry, University of Bristol, Bristol, United Kingdom; 2Diamond Science and Technology CDT, University of Warwick, Coventry, United Kingdom.

Using a simplified kinetic Monte Carlo (kMC) model of CVD diamond growth, the diamond and computational chemistry groups at the University of Bristol have previously reported simulating many atomic layers of diamond growth at relatively low computational cost. These simulations have been found to reproduce many of the growth features seen experimentally, including growth rates, while keeping the computational time required on the order of hours, in contrast to more complicated models. However, one limitation of such a simplified model is the use of a cubic representation of the diamond atomic lattice. Although this allows low calculation times and simplified methods, the geometries of specific adsorbates or surface defects thought to be important in the diamond growth mechanism cannot be correctly modelled.

We now report on progress in transitioning the simulation from a simple cubic lattice to a true tetrahedral diamond structure, inheriting some of the methods and approximations on which the original model relied for maximum performance and simplicity. This more realistic representation for the diamond lattice allows implementation and testing of more complicated CVD growth reaction schemes, with application of modern software developmental strategies maintaining the model’s computational efficiency. Visualisation of the diamond surface as CVD growth progresses in true tetrahedral co-ordination is also now possible, allowing robust and powerful analysis of implemented reaction schemes and their effect on surface morphology development as a function of time.

In this presentation we shall use animations and videos of the simulations to show how the model can be used to test potential reaction schemes, as well as understand growth mechanisms and the associated energy barriers from literature, and determine their contribution to growth rate, surface morphology and defect formation. The ultimate aim of this work is to use measured parameters from a diamond CVD system (gas mixture, pressure, temperature, etc.), to predict accurately the expected growth rate, morphology, grain size, and even defect types and locations within a CVD diamond film.

References

9:30 AM EP09.02.04
High Quality CVD Diamond Growth on Gallium Nitride Using a Novel 2-Step Micro/Nano Diamond Seeding Method Afaa Habib Piracha1, Edmund Smith1, 2, Paul W. May1, Chao Yuan1, Fabien Massabuau1 and Martin Kuball1; 1 School of Chemistry, University of Bristol, Bristol, United Kingdom; 2 Center for Device Thermography and Reliability, University of Bristol, Bristol, United Kingdom; 3 Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Diamond films deposited onto GaN are useful for heat dissipation in GaN microwave electronics, in particular GaN based MMICs and HEMTs. GaN on diamond will underpin future high-power radio frequency and microwave communications, space and defence systems, paving the way towards 5G and 6G mobile-phone networks and more comprehensive radar systems. However direct deposition of CVD diamond onto GaN (i.e. without a barrier layer being present) is difficult due to the etching of the GaN in the hot CVD environment and poor film adhesion. Moreover, the standard seeding method using detonation nanodiamond results in the first few nm of the diamond film being composed of nm-sized grains with poor thermal conductivity. This creates an undesirable thermal barrier between the active GaN device and the higher quality diamond deposited at later stages of growth which acts as the heat spreader.

To overcome this issue, a novel seeding method was developed to improve the coverage of diamond particles onto GaN on silicon wafers while maintaining an effective thermal interface between the diamond and the GaN.

We describe the optimised seeding procedure as well as the procedure to grow diamond films onto epitaxial GaN. A seeding was performed using an electrospRAY technique in which the wafers were mounted on the rotating copper disk and diamond solution was filled in a tube that sprayed on the targeting wafers by applying high accelerating voltage. This method results in a uniform distribution of diamond solution onto the wafers and eventually dried to give a homogeneously covered mixture of nano/micro diamond particles on GaN wafer.

A method whereby a 2-step seeding process is used to ensure a high thermal conductivity layer is deposited on a GaN substrate: (1) Seed the surface using microdiamonds (1-10 μm), using any standard method optimised for dense monolayer coverage. This provides the high thermal conductivity interface. (2) Seed a second time, this time using nanodiamonds (4 nm), using any standard method optimised for dense monolayer coverage. This fills in the voids and prevents the GaN from etching in the subsequent diamond deposition process. Diamond growth was done in both standard hot filament CVD reactor (HFCVD) and microwave plasma CVD reactor (MPCVD) and the results were compared. We will present results including SEM and thermal measurements showing continuous high-quality diamond layers without pinholes. Diamond films were grown after 2-step seeding method with thickness ranging from 1-50 μm. 2-step seeding seems to work nicely, with reasonably adherent, conformal diamond layers up to 50 μm thick being deposited onto GaN.
The use of diamond grown on patterned gold substrates for Fourier Transform Infrared (FTIR) spectroscopy has proved to be an effective characterization method for undoped diamond functionalized with biomolecules, however insulating diamond substrates cannot be used for electrochemical grafting, which requires a conducting substrate. In this study, we have grown well-adhered boron doped nanocrystalline diamond (B:NCD) thin films on continuous gold (Au) substrates, which form Au nanoparticles (AuNPs) during the initial stages of growth. These AuNPs were then subsequently overgrown by the diamond films. The formation of AuNPs by annealing thin films of gold has been of significant recent interest, for use as catalysts for growing nanowires and for plasmonics. Arrays of AuNPs could be used to maximize the absorption in the active layer of photovoltaic (PV) cells, where the particle size and shape are critical for precisely tuning the light scattering and trapping to maximize the PV performance. Thin film annealing is a high throughput, low contamination method of AuNP formation, but the diameter range of the particles obtained this way is still broad, and their position is uncontrolled, so a better understanding and control of the formation method of thin film annealed AuNPs is needed.

AuNPs of approximately 1 μm diameter formed during microwave plasma assisted chemical vapour deposition (MPACVD), and these were overgrown by diamond. We will show that the formation of AuNPs is affected by the surface treatment. The initial nucleation of the particles can be decreased by pretreatment with water or UV-ozone oxygen treatment. The size of the AuNPs under the diamond film can be increased to approximately 2 μm in diameter by UV-ozone treatment of the surface prior to growth.

Low temperature diamond growth (LTDG) is an area of active research interest, as processing at low temperatures is important for growth on substrates with properties such as high thermal expansion coefficients, low melting temperatures, and high thermal diffusivities. Among the possible routes, surface wave plasma linear antenna (LA) deposition with oxygen-containing gases (such as CO₂) in the gas mixture is considered to be the most promising LTDG growth process. We will show that growing a 50 nm NCD nucleation layer at low temperature in the presence of CO₂ in a LA reactor suppresses the formation of AuNPs under the diamond film, even after subsequent B:NCD overgrowth. We are therefore able to grow B:NCD over Au substrates, with control over the formation and size of overgrown AuNPs.

References
Diamond can be used for a wide range of applications, not only for jewelry. Diamond has a lot of attentions to be an ultimate semiconductor material because of its physical properties like as the wide band gap and high carrier mobility. The ultimate semiconductor devices, such as high frequency device and high-power transistor, are also expected application by those physical properties. In semiconductor device fabrications, damage- and roughness-free substrate surface is essential. For this purpose, in conventional semiconductors, chemical mechanical polishing (CMP) is widely used. However, in diamond there are very few reports of CMP. In this work, we perform CMP on single-crystal diamond substrates and investigate its effect on the surface properties.

The samples were HPHT single crystal diamond (001) (4 x 4 x 0.5 mm). First, all the surfaces were mechanically polished (MP) to adjust the thickness, the off angle, the roughness. Next, CMP was performed on the diamonds with different processing time; 0 h (MP only), 5 h, 50 h and 100 h. The surface roughness before DC plasma CVD growth was less than 0.2 nm. Finally, the diamond films were homoepitaxially grown on the MP and CMP-treated diamond substrates for 10 hours by DC-plasma CVD method.

In synchrotron radiation X-ray topography observation, we have found different contrast between the substrate subsurface with and without CMP. Further, we confirmed pits on the CVD diamond surface grown on the substrate without CMP. However, as the CMP process time increased, the pit density decreased. Eventually, on the surface for 100 h CMP, no pits were observed. From these results, we concluded that the subsurface damage leads to pit formation in homoepitaxial growth, and CMP on the substrate is effective to prevent pit formation in CVD diamond growth.

The sheet resistance was carried out by Hall effect measurement. We found that the sheet resistance decreased with increasing CMP time. CMP is important technique for diamond device.


11:50 AM EP09.02.10
The Effect of Methane Concentration on Surface Morphology and Doping Efficiency of Heavily Boron-Doped Single Crystal Diamond Layers

To develop diamond-based high-power electronics, several challenges must be overcome. One of these is the growth of high quality heavily (p+) B-doped single crystal diamond (SCD) layer. It has been reported that deterioration of film morphology, due to the presence of defects, prevents achieving high boron concentration (10²¹ cm⁻³) in the diamond lattice.

The impact of [C]/[H] ratio on the surface quality and electrical properties of B-doped SCD grown by microwave plasma-enhanced CVD (MW PE CVD) is investigated in this study. Heavily B-doped SCD layers were grown in a home-built CVD reactor on 33 mm² Ib (100)-oriented HPHT substrates. Growth was performed in a conventional [CH₄]/[H₂] plasma (0.5%, 1%, 2%, and 3%), investigated in this study. Heavily B-doped SCD layers were grown in a home-built CVD reactor on 33 mm² Ib (100)-oriented HPHT substrates. Growth was performed in a conventional [CH₄]/[H₂] plasma (0.5%, 1%, 2%, and 3%), with trimethylboron as the boron source, with a constant 997 ppm [B]/[C] ratio used for all samples. The aim was to analyze the effect of methane concentration on the electrical properties of grown films. Diamond deposition by CVD constitutes a delicate balance between diamond growth and etching by hydrogen. Atomic force and optical microscopes confirmed that etching was dominant for B-doped diamond growth at lower [C]/[H] ratio (0.5%), as seen in the morphology from the appearance of etch pits. This effect was observed at the lower [B]/[C] ratio than what has been previously observed in literature.

At a higher [C]/[H] ratio (1%), high-quality p+ B-doped SCD layers were obtained. In Raman spectra, a broad peak was observed at the wavenumber 500 cm⁻¹, the width of which is proportional to the boron concentration in diamond. Fourier transform Infrared (FTIR) spectroscopy also gives an estimate of boron content as has been demonstrated by several research groups for p+ B-doped samples. The boron concentrations estimated by Raman and FTIR spectroscopies were compared to the results of Hall effect which gave high boron incorporation levels but lower than what was estimated by the Raman and FTIR methods. The underestimated boron concentration could be due to the imperfect transmission through the samples and the possible error in the measurement of grown thickness. Even with this error, the boron concentrations which were measured by Hall effect showed the same [C]/[H] ratio dependence as determined by the Raman and FTIR methods, with the sample grown at 3% [CH₄]/[H₂] showing a higher boron incorporation than those grown at lower [CH₄]/[H₂].

References
A cell is a precision microsystem made up of a variety of micro- and nanocomponents, such as organelles and biomacromolecules. The cell system is governed by nanometer-scale physical and chemical properties with spatial and temporal variations. This means that the nanoscale measurements can provide a wealth of information about biological functions. However, the sensitivity and stability of measurement heavily depend on the sensor size. Therefore, nanometer-sized small sensors that can be used in cells were generally unreliable. Here, we describe intracellular measurement techniques using fluorescent nanodiamond as a quantum sensor for nanoscale chemical and physical properties. The nanodiamond quntum sensors are promising not only in advancing knowledge in fundamental science but also in technological applications, in the same way that small sensors empowered smartphones and self-driving cars, and thus, has to potential to open new avenues for bioscience and nanoindustry.

2:00 PM EP09.03.02
Superconducting Boron-doped Diamond Josephson Junction Operating up to 7.0K
Shotaro Amano1, Taisuke Kageura1, Ikuto Tsuyuzaki1, Minoru Tachiki2, Shuuschi Ooi3, Shinichiro Arisawa4, Yoshihiko Takano5 and Hiroshi Kawarada1, 2, 3
1Waseda University, Tokyo, Japan; 2MANA National Institute for Materials Science, Tukuba, Japan; 3The Kagami Memorial Laboratory for Materials Science and Technology, Shinjuku, Japan.

Superconducting quantum interference device (SQUID), which is composed of superconducting loop with Josephson junction, is widely used for ultra-high sensitive magnetometers. One of the current problems is that conventional superconducting material like Nb is fragile. Superconducting boron-doped diamond is robust and resistant to contact, oxidation, and deterioration, so it is suitable material for robust SQUID. We previously fabricated step-edge structure Josephson junction [1], but the superconducting transition temperature (Tc) was lower than 4.0K. It is essential to operate above liquid helium temperature (4.2K) for application to SQUID. So in this research, we report the Josephson junction composed only of (111) film with operating up to 7.0K. We fabricated a Josephson junction with weak links in intermittent (111) plane. Weak links were formed at the interfaces of the (111) superconducting diamonds across trench region. This trench was formed on the (111) diamond substrate by Focused Ion Beam. The trench had a width of 200 nm and a depth of 30 nm. Then a superconducting boron-doped layer with a thickness of 500 nm was selectively grown across the trench by microwave plasma enhanced chemical vapor deposition method.

We investigated the temperature dependence of resistance (R-T), two-step superconducting transitions were observed at 10.2K and 7.0K, corresponding to Tc of the boron-doped diamond grown from the substrate and the trench, respectively. This operating temperature is nearly twice the previous value [1] and is also comparable to that of Josephson junction with Nb, which is generally used for SQUID. This is because this Josephson junction was composed of only (111) diamond with Tc=10K whereas the step-edge structure included (001) with Tc=4K [2]. The I-V characteristic had no hysteresis and showed DC Josephson effect. The critical current (Ic) was 0.03 mA and Ic / 2eΦ0 was 0.15 mV at 4.2K. This value is comparable to that of Nb SQUID. Shapiro steps were observed up to 7.0K more clearly than before. The interval between steps was in good agreement to the theoretical value calculated from the frequency of microwave and flux quantum (Φ0=2×10-15 Wb).

We fabricated the Josephson junction composed only of (111) diamond and observed both the DC and AC Josephson effect up to 7.0K. These results mean that this Josephson junction has the capability of operating above liquid helium temperature. We strive to demonstrate the operation of the SQUID and assemble this SQUID into a Scanning microscope.

This work was supported by JSPS Grant-in-Aid for Scientific Research (S)26220903, (B)17H03526 and Research Activity start-up 17H07192. This study was supported by NIMS Nanofabrication Platform in Nanotechnology Platform Project sponsored by MEXT, Japan.
[1] I. Tsuyuzaki, H. Kawarada et al., MRS Fall 2017

2:15 PM EP09.03.03
1H NMR Detection on Nitrogen Terminated Diamond by Shallow Nitrogen Vacancy Centers
Takahiro Sonoda1, Sora Kawai1, Hayate Yamano1, Jorge J. Buendia1, Taisuke Kageura1, Yu Ishii1, Kiro Nagao1, Ryosuke Fukuda1, Takashi Tani1, Moriyoshi Haruyama2,3, Keisuke Yamada1, Shinobu Onoda1, Wataru Kada1, Osamu Hanai-umi1, Alastair Stacey4, Kazuhiro Kanda5, Masaharu Uemura5, 6, Tokuyuki Teraji1, Junichi Isoya1, Shozo Kono5, 6 and Hiroshi Kawarada1, 2, 3
1Waseda University, Tokyo, Japan; 2MANA National Institute for Materials Science, Tukuba, Japan; 3The Kagami Memorial Laboratory for Materials Science and Technology, Shinjuku, Japan; 4University of Tokyo, Tokyo, Japan; 5University of Melbourne, Parkville, Melbourne, Victoria, Australia; 6Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Koto Kamigori, Japan; 7Synchrotron Analysis LLC, Wadamiya-dori, Kobe, Japan; 8National Institute for Materials Science, Tsukuba, Japan; 9University of Tsukuba, Tsukuba, Japan; 10Kagami Memorial Research Institute for Materials Science and Technology, Shinjuku, Japan.

Nitrogen vacancy (NV) center in diamond is expected as a highly sensitive magnetic sensor for nanoscale NMR [1]. Since signal decays as 1/r3, where r is the distance from a magnetic field source, shallow NV centers must be fabricated. In order to improve properties of shallow NV centers, surface terminations such as O-terminations [2, 3] have been focused on. Recently, a theoretical calculation implied that N-terminated surface shows positive electron affinity (PEA) and contributes to stabilization of negatively charged state of shallow NV centers [4]. We have already reported that N-termination by nitrogen radical exposure to stabilization of negatively charged states of shallow NV centers [5]. The next step of our research is to investigate the applicability of N-terminated surface to NMR detection. In the previous study, N2 gas which contains 10% H2 gas was used as the radical source intending by nitrogen radical exposure leads to stabilization of negatively charged states of shallow NV centers [5]. The next step of our research is to investigate the applicability of N-terminated surface to NMR detection. In the previous study, N2 gas which contains 4%-H2 gas was used as the radical source intending by nitrogen radical exposure leads to stabilization of negatively charged states of shallow NV centers [5]. We previously fabricated step-edge structure Josephson junction [1], but the superconducting transition temperature (Tc) was lower than 4.0K. It is essential to operate above liquid helium temperature (4.2K) for application to SQUID. So in this research, we report the Josephson junction composed only of (111) film with operating up to 7.0K. We fabricated a Josephson junction with weak links in intermittent (111) plane. Weak links were formed at the interfaces of the (111) superconducting diamonds across trench region. This trench was formed on the (111) diamond substrate by Focused Ion Beam. The trench had a width of 200 nm and a depth of 30 nm. Then a superconducting boron-doped layer with a thickness of 500 nm was selectively grown across the trench by microwave plasma enhanced chemical vapor deposition method.

We investigated the temperature dependence of resistance (R-T), two-step superconducting transitions were observed at 10.2K and 7.0K, corresponding to Tc of the boron-doped diamond grown from the substrate and the trench, respectively. This operating temperature is nearly twice the previous value [1] and is also comparable to that of Josephson junction with Nb, which is generally used for SQUID. This is because this Josephson junction was composed of only (111) diamond with Tc=10K whereas the step-edge structure included (001) with Tc=4K [2]. The I-V characteristic had no hysteresis and showed DC Josephson effect. The critical current (Ic) was 0.03 mA and Ic / 2eΦ0 was 0.15 mV at 4.2K. This value is comparable to that of Nb SQUID. Shapiro steps were observed up to 7.0K more clearly than before. The interval between steps was in good agreement to the theoretical value calculated from the frequency of microwave and flux quantum (Φ0=2×10-15 Wb).

We fabricated the Josephson junction composed only of (111) diamond and observed both the DC and AC Josephson effect up to 7.0K. These results mean that this Josephson junction has the capability of operating above liquid helium temperature. We strive to demonstrate the operation of the SQUID and assemble this SQUID into a Scanning microscope.

This work was supported by JSPS Grant-in-Aid for Scientific Research (S)26220903, (B)17H03526 and Research Activity start-up 17H07192. This study was supported by NIMS Nanofabrication Platform in Nanotechnology Platform Project sponsored by MEXT, Japan.
[1] I. Tsuyuzaki, H. Kawarada et al., MRS Fall 2017
was used as the radical source. Charge stability of shallow NV centers was evaluated by measuring the decay rate of the NV^− and the shallow donors, including hydrogenic donors. The NV^− ion was produced by a 400−eV electron irradiation at room temperature. The 1H-NMR detection was conducted on the N-terminated surface. The coherence time of the NV center in diamond was estimated from the 1H-NMR signal [7] was 10.0 nm. In conclusion, negatively charged states of shallow NV centers were stabilized by N radical exposure using 100%-N_2 gas, and we successfully detected 1H-NMR on the N-terminated surface by shallow NV centers.


Acknowledgements

We thank Dr. Liam P. McGuinness and Prof. Fedor Jelezko for their help in building CFM setup.
were investigated by atomic force microscopy and secondary ion mass spectrometry, respectively. Produced doped layers with conductivity of p- and n-types are highly desirable for the development of diamond-based electronic devices.


4:00 PM EP09.04.03
Raman and Photoluminescence Characterization of Arsenic-Doped Diamond by Ion-Implantation Kajuve Wang1, Yufei Zhang2, Huijun Wang2 and Hong-Xing Wang2; Xi’an Jiaotong University, Xian, China; 2Taiyuan University of Science and Technology, Taiyuan, China.

Due to its wide band gap, high thermal conductivity, high carrier mobility and high breakdown voltage, diamond has been attracting much interest as the potential material of high-frequency high-power electronic device[1-3]. The device requires a high concentration of acceptors or donors, which could be obtained by the methods of doping. There are a great number of works on the doping of diamond. For n-type diamond, the nitrogen is the most common observed donor impurity and usually exists in natural diamond[4]. However, the quite-deep donor level of 1.7 eV is formed between the intermediate of diamond forbidden band, which makes it useless for semiconductor devices at room temperature[5]. As the same group V elements, arsenic is the shallower doping and expected as a more promising substitutional donor candidates[6]. The theoretical works showed that the substitutional arsenic provides the shallower donating level than phosphorus, at 0.4 eV below the bottom of the conduction band [7,8].

As an important material, diamond is extensively investigated by technology of low temperature photoluminescence, and some new results were presented and discussed. A slice of ultrapure colorless diamond was involved which was synthesized by MPCVD. The (100) surface orientation of the sample was implanted with arsenic ions at 300K, with an energy of 150keV and a dose of 10^{14} ions cm^{-2}, and then annealed at temperatures of 400C, 800C and 1500C. The Photoluminescence examination was performed by Renishaw micro-Raman spectrometers fitted with Linkam liquid nitrogen cooled stages at an excitation wavelength of 532 nm.


4:15 PM EP09.04.04
Application of Laser-Induced Doping to Singlecrystalline Diamond Abdelehaman Z. Ahmed1, Eslam Abubakri2, Yuki Katamen2, Shinya Ohmagari2 and Tsuyoshi Yoshitake2; 1Advanced Power Electronics Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan; 2Frontier Research Academy for Young Researchers, Kyushu Institute of Technology, Fukuoka, Japan; 3Department of Applied Science for Electronics and Materials, Kyushu University, Fukuoka, Japan.

Diamond is a wide bandgap material with extreme thermal, electrical and optical properties that receives unprecedented attention since it is expected to handle more power with higher efficiency than conventional semiconductors. However, due to the intrinsic difficulties, device fabrication has serious problems in achieving n-type doping under good conditions. Moreover, diamond is not easily modified like other semiconducting materials that can be treated thermally after deposition.

Recently laser-induced doping has been applied to other wide band gap semiconductor (SiC) and its effectiveness is experimentally proved. In this work, we applied laser-induced doping to singlecrystalline diamond, for the first time to our knowledge. The doping of phosphorus and Boron into singlecrystalline diamond is discussed from the chemical compositionally and electrically viewpoints.

In this work, Singlecrystalline diamond (100) plate (Ib) was immersed in a phosphoric acid solution (85%) and Boric Acid. ArF excimer laser (Gigaphoton Inc. wavelength: 193 nm) beams were irradiated on it. The laser beam irradiation was carried out at a frequency of 1 Hz and at different laser fluences up to 3.9 J/cm².

The results indicate that SC diamond hardly damaged on the plate surface by optical images even at a maximum fluence of 3.9 J/cm². Electrically, the electrical conductivity increases with increasing fluence and number of laser shots. Moreover, Phosphorus depth profile was investigated by Secondary-Ion Mass Spectrometry (SIMS), in which the Incorporation of Phosphorus up to 30 nm was achieved by increasing number of shots and reducing time interval between successive shots.

Further systematic experiments are conducted, such as Raman, I-V measurements, and theoretical simulations, results will be reported at the conference. This study was partially supported by JSPS KAKENHI Grant Numbers: JP15H04127, JP16K14391, and JSPS Fellow Grant JP17F17380.

4:30 PM EP09.04.05
Doping Level Determination of HPHT Diamond Substrate Using Electron Beam Induced Current Cedric Masante1, Fabrice Donatini2, Nicolas Rouger3 and Julien Pernot3; 1University Grenoble Alpes, CNRS, Grenoble INP, Inst. NEEL, Grenoble, France; 2Université de Toulouse; LAPLACE; CNRS; INPT; UPS, Toulouse, France.

For diamond power electronic applications, such as transistors and diodes, substrate quality is a key factor to obtain the best performances, influencing the properties of the epi-layers. Moreover, understanding the properties of the substrate, especially doping level, is often necessary to design the devices accordingly.

In this work, Electron Beam Induced Current (EBIC) technique is used to visualize the lateral expansion of the depletion region of a Schottky contact (Ti/Pt/Au stack) deposited on a (100) HPHT high quality substrate provided by New Diamond Technology. A comparison with finite element simulation has been performed in order to quantify key parameters. This method, requiring a single lithography process, is demonstrated to be efficient to extract doping levels below 10^{14} cm^{-3} whereas SIMS measurements are only efficient for doping levels higher than this value. This method will be compared to previous measurements done by cathodoluminescence. The example presented in this work is a substrate having a p-type (Boron) doping level evaluated around 3.10^{15} cm^{-3} near the surface (up to a few micrometers away from the surface). Diffusion lengths of a few micrometers are extracted and compared with recent measurements done on boron doped epi-layers [2]. This method will also be applied to Nitrogen compensated substrates as a mean to test their electrical activity, prior to their use for devices.

References
Diamond has excellent electrical characteristics as a wide gap semiconductor, and is expected as a high-performance power semiconductor for various applications as electric vehicles and trains etc. Boron doping by ion-implantation has been applied to achieve low resistivity of p-type diamond [1, 2]. Tsubouchi reported that doping efficiency of about 50% was achieved by annealing at 1600 °C after Boron implantation at 400 °C [2]. However, the doping efficiency is still not enough. Therefore, we propose a high-temperature annealing over 1600 °C by protecting the surface of diamonds as the effective recovering of implantation damage to achieve a high doping efficiency and crystallinity.

Boron was implanted at 500 °C by several accelerating voltages to form homogeneous Boron distribution profile in (001) diamond made by micro-wave plasma CVD. The density and the thickness of implantation layer was 5×10^{19} cm^{-3} and 400 nm, respectively. To protect the surface of diamond, diamond-like carbon with 80 nm thickness was deposited on a surface of implanted diamond by plasma CVD. Post-implantation of Boron elemental diamond was carried out in Argon atmosphere at a range from 1500 to 1850 °C. The surface morphology was evaluated by optical microscope. The damage of implantation was evaluated by Rutherford backscattering (RBS). The annealing for 10 minutes at 1850 °C was performed without degrading the surface morphology. It was clearly demonstrated that implantation damage can be reduced due to increase the temperature and the duration of annealing. Minimum channeling yield of the diamond annealed at 1500 °C for 60 minutes estimated by RBS was 6.6 %, and of the diamond annealed at 1800 °C for 30 minutes was 4.6 %, which is one of the lowest value after high dose boron implantation into diamond. Compared with annealing condition at 1500 °C, of that annealed at 1800 °C decreased almost by half. It indicates that the damage of implantation was fully recovered and almost the same as the un-implanted diamond without damage was obtained. At the same sample, the electrical resistivity measured by van der Pauw method was 64 Ωcm, and high doping efficiency over 90 % was also obtained in heavily Boron doped diamond layer. The high dose implantation can be applicable to form source and drain region by self-alignment process.

detected by an electron multiplying CCD (EMCCD) camera with high spatial resolution (410 nm per pixel).

Optically detected magnetic resonance (ODMR) spectra were imaged in an area of 150 μm² in the device while applying a reverse bias of 400 V. The width between the ODMR dips increased upon the bias application due to the Stark effect of the NV centers [4]. We also observed several dips in the spectra, corresponding to different NV axes. The highest electric-field of approximately 1.4 MV/cm was obtained at the edge of the patterned n⁺-cathode, in agreement with three-dimensional device simulation. We confirmed that the electric-field decreased as the position was far away from the n⁺-cathode, and became 0.3 MV/cm at 2 μm from the cathode. Accordingly, these facts indicate that two-dimensional distribution of the internal electric field in the device can be measured by using the NV centers. This technique will lead to the deep understanding and reliable devices.

Acknowledgements: This work was partially supported by KAKENHI (18H01472) and JST-CREST (Grant Number: JPMJCR1333)


9:30 AM EP09.05.04
Continuous-Wave Double Resonance of Electric Spin Triplet of NV Centers in Diamond and Its Application to High-Frequency AC Magnetic Field Sensing
Junko Ishi-Hayase¹, Soya Saio¹, Tatsuma Yamaguchi¹, Yuichiro Matsuzaki², Shiro Saito², Hideyuki Watanabe³ and Norikazu Mizuochi⁴; ¹Keio University, Yokohama, Japan; ²NTT Basic Research Laboratories, Atsugi, Japan; ³National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ⁴Kyoto University, Uji, Japan.

Nitrogen-vacancy (NV) centers in diamond have received much attentions as highly-sensitive quantum sensors for detecting magnetic fields at room temperature. Pulsed optically detected magnetic resonance (ODMR) is typically used to detect AC magnetic fields, but can only be implemented after careful calibration that involves measuring continuous-wave (CW) ODMR, determining the Rabi frequency, and setting the microwave phase. In contrast, CW-ODMR can be simply implemented by continuous application of a green CW laser and a microwave field. However, CW-ODMR can be used to detect DC or low-frequency (kHz-range) AC magnetic fields. In this work, we report a method that uses NV centers and CW-ODMR to detect high-frequency (MHz-range) AC magnetic fields[1]. The proposed method involves a double resonance excitation of three level system of electric spin triplet states of NV centers. Unlike conventional methods, the proposed method does not require a pulsed sequence; this greatly simplifies the procedure and apparatus needed for implementation. In the experiment, we applied continuous green laser, microwave (~2.8 GHz), and radio wave (~4 MHz) to NV center ensemble created by CVD growth and He ion implantation. We clearly observed the change in CW-ODMR spectrum with and without radio wave (~4 MHz), which is in good agreement with the theoretical calculation. This result demonstrates to detect AC magnetic field with high frequency (~MHz) by measuring CW-ODMR spectrum. The estimated sensitivity is to be of the order of μT/Hz1/2 for our present experimental apparatus. The sensitivity is currently limited by inhomogeneous broadening and low measurement contrast of samples used and by the low collection efficiency of the optical setup, both of which could be improved in the future. Thus, this simple alternative to existing AC magnetic field sensors paves the way for the development of a practical and feasible quantum sensor. Furthermore, we measured the intensity and frequency dependence of CW-ODMR spectra by applying MHz-radio wave. We found that the CW-ODMR spectra are significantly modulated due to the double resonance excitation by GHz-microwave and MHz-radio wave. We will discuss the involved physics by analyzing double resonance spectra of NV centers in detail.

This work was supported by JSPS KAKENHI (Grant No. 15K17732) and MEXT KAKENHI (Grants No. 18H01502, 15H05868, 15H05870, 15H03996, 26220602, and 26249108), and Spin-NRJ.

9:45 AM EP09.05.05
Investigation of Tin Vacancy Centers in Diamond for Realization of Spin-Photon Interfaces
Johannes Goerlitz¹, Morgane Gandil¹, Dennis Herrmann¹, Philipp Fuchs¹, Takayuki Iwashaki¹, Takashi Taniguchi¹, Tatsuya Yamaguchi¹, Yuichiro Matsuzaki², Shiro Saito², Hideyuki Watanabe³ and Norikazu Mizuochi⁴; ¹Saarland University, Saarbruecken, Germany; ²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ³Kyoto University, Uji, Japan.

Color centers in diamond have received large recent attention as versatile tools for solid-state-based quantum technologies such as quantum information processing and quantum-enhanced sensing and metrology. They provide individually addressable spins with very long coherence times, narrow optical spectra and bright single-photon emission. In this context, impurity-vacancy color centers based on group-IV elements (SiV, GeV, SnV, PbV) have emerged as interesting systems promising to combine all desired favorable properties. As a prime example, the negatively charged SiV center in diamond features an advantageous electronic structure and superior spectral properties [1]: At liquid helium temperatures, the SiV exhibits a narrow zero phonon line (ZPL) with a four-line fine structure and lifetime-limited linewidths on the order of 120MHz [2]. In addition, due to its small Huang-Rhys factor, up to 80% of the fluorescence is emitted via the ZPL. Moreover, the SiV offers an optically accessible Λ-type level structure with a large orbital level splitting allowing for fast all-optical control of its orbital [3] and spin [4] states. However, as a tradeoff, the SiV reaches millisecond spin coherence times only at millikelvin temperatures due to phonon-driven decoherence processes [4,5]. Motivated by these ongoing results, there have been efforts in order to find a color center in diamond with both excellent optical properties (i.e. optically accessible Λ-level scheme) and long spin coherence times even at elevated temperatures (at least liquid Helium temperatures, i.e. 4K). Thus the heavier homologues of the SiV should be interesting candidates, because their orbital level splitting is considerably larger, thereby reducing phonon-induced decoherence processes. A very promising candidate is the tin vacancy center (SnV) emitting at 619nm and indeed showing a similar fine structure as the SiV center, but with a much larger ground and excited state splitting (850GHz and 3000GHz, respectively) [6].

Motivated by these ongoing results, there have been efforts in order to find a color center in diamond with both excellent optical properties (i.e. optically accessible Λ-level scheme) and long spin coherence times even at elevated temperatures (at least liquid Helium temperatures, i.e. 4K). Thus the heavier homologues of the SiV should be interesting candidates, because their orbital level splitting is considerably larger, thereby reducing phonon-induced decoherence processes. A very promising candidate is the tin vacancy center (SnV) emitting at 619nm and indeed showing a similar fine structure as the SiV center, but with a much larger ground and excited state splitting (850GHz and 3000GHz, respectively) [6].

Here, we present recent results on spectroscopy of both SnV ensembles and single SnV centers in high quality bulk diamond, from room temperature down to liquid helium temperature. We find bright single photon emission from individual SnV centers from unstructured bulk material with saturation count rates up to 100,000 counts/second. We further explore their optical and spin properties, including lifetime, polarization, spectral features from photoluminescence and photoluminescence excitation, as well as spin coherence times, paving the way for assessing the suitability of the SnV center in diamond for spin-based photonic quantum technologies.

Solid-state quantum emitters embedded in a semiconductor environment are potentially scalable platforms for quantum optical networks operated at room temperature. Prominent representatives are nitrogen-vacancy (NV) centers in diamond showing coherent entanglement and interference with each other. However, a remaining challenge is how to regulate NV centers efficiently. Here, we demonstrate that the implementation of nitrogen, oxygen or sulfursulfur into H₂/CH₄ plasma to tailor the intensity of NV centers. Higher crystal quality of epitaxial films is first confirmed by comparing the FWHM of the diamond first-order Raman peak with the HPHT diamond substrate. By the engineering of nitrogen flow into the plasma, we find that the intensity of NV centers increases with the flow of nitrogen simultaneously, and the growth rate of epitaxial films first increases and then tends to be stable, while the intensity of NV centers decreases with the flow of sulfur and the growth rate of epitaxial films also keeps decreasing. However, the intensity of NV centers and growth rate show different trends when oxygen is added into the H₂/CH₄ plasma. The regulation of oxygen on the NV centers is first promoted and then suppressed. Only when the flow of oxygen is less than 0.4% (H₂+CH₄), oxygen promotes the intensity of NV centers. Due to the competition mechanism of oxygen and nitrogen in H₂/CH₄ plasma, the growth rate decreases with the increasing flow of oxygen, and finally tends to zero when the flow of oxygen reaches 1% (H₂+CH₄). Our study demonstrates NV centers as an adjustable defect for quantum photonics architecture relying on single photon source and qubits.

Secondly, we demonstrate a vector magnetic field sensing using our scheme with higher sensitivity using confocal and wide-field experiment system. Our scheme can be performed on (113)-orientated slabs of diamond to investigate ideal surface termination for hosting NV center. We considered hydrogen, oxygen, fluorine, and mixed terminations. Results show that different chemical termination of diamond could significantly change its electronic and chemical properties. Fluorine and oxygen terminations on diamond (113) surface could eliminate surface states intrusion in deep bandgap thus stabilize the fluorine, hydroxyl, nitrogen, and mixed terminations. Moreover, the oxygen terminated (113) diamond surface could form ordered and smooth surface thereby avoid surface spin caused by surface fluctuation. The stability calculation indicates it may achieve oxygen termination on (113) diamond surface during the experimental demonstration, we confirm the sensitivity of our scheme becomes 2 times better than the sensitivity of conventional scheme. Moreover, by changing the two frequencies of spin reversal, the x, y and z components of the magnetic field can be measured directly. The most important advantage of our scheme is that the sensitivity can be improved for regardless of NV center sample orientation and pulse measurement methods.

Our theoretical calculation, we showed the sensitivity of our scheme can be improved 2–4 times better than the sensitivity of conventional scheme[1]. In the experimental demonstration, we confirm the sensitivity of our scheme becomes 2 times better than the sensitivity of conventional scheme. Moreover, we demonstrate a vector magnetic field sensing using our scheme with higher sensitivity using confocal and wide-field experiment system. Our scheme can be applied to various type of pulse sequences for magnetic field sensing and enables us to improve the sensitivity by simultaneous manipulation of spin states with four orientation axes. This work was supported by JSPS KAKENHI (Grant No. 15K17732) and MEXT KAKENHI (Grants No. 18H01502, 15H05868, 15H05870, 15H03996, 26220602, and 26249108[HI4]), and Spin-NRI.


First-Principles Investigation of Nitrogen Vacancy Center in Diamond (113) Surface Song Li¹, Jyh-Pin Chou¹, Jie Wei¹, Minglei Sun², Alice Hu¹ and Adam Gal³; ¹City University of Hong Kong, Kowloon Tong, Hong Kong; ²School of Mechanical Engineering, Southeast University, Nanjing, China; ³Wigner Research Centre for Physics, Budapest, Hungary.

The nitrogen vacancy (NV) center in diamond demonstrates promising future in quantum simulator and sensor applications. Nevertheless the shallow NV center under surface could be significant influenced by surface termination and thus limit its sensitivity. The first-principles calculations have been performed on (113)-orientated slabs of diamond to investigate ideal surface termination for hosting NV center. We considered hydrogen, oxygen, fluorine, hydroxyl, nitrogen, and mixed terminations. Results show that different chemical termination of diamond could significantly change its electronic and chemical properties. Fluorine and oxygen terminations on diamond (113) surface could eliminate surface states intrusion in deep bandgap thus stabilize the fluorescent state of negatively charged NV. Moreover the oxygen terminated (113) diamond surface could form ordered and smooth surface thereby avoid surface spin caused by surface fluctuation. The stability calculation indicates it may achieve oxygen termination on (113) diamond surface during conventional diamond CVD growth condition.

Progress and Challenges of NV-Doped Diamond for Ultrasonic Laser Threshold Magnetometry Jan Leskela¹,², Verena Ziererb¹, Lutz Kirstea¹, Sarah Raman Nair¹, Xavier Vidal¹, Lachlan J. Rogers¹, Thomas Volz¹, Ondrej Kitzler⁴, Richard P. Mildren⁵, Shinobu Onoda⁵, Takeshi Ohshima⁶, Fedor Jelezko⁴, Philipp Reineck⁴, Marco Capelli⁵, Desmond W. Lau⁴, Jared Cole⁵, Brant Gibson⁷ and Andrew Greentree⁷; ¹Fraunhofer IAF, Freiburg, Germany; ²Chemical and Quantum Physics, School of Science, RMIT University, Melbourne, Victoria, Australia; ³ARC CoE for EQuS, Department of Physics and Astronomy, Macquarie University, Sydney, New South Wales, Australia; ⁴Department of Physics and Astronomy, Macquarie University, Sydney, New South Wales, Australia; ⁵National Institute for Quantum and Radiological Science and Technology, Takasaki, Japan; ⁶Institute for Quantum Optics / IQST, Universität Ulm, Ulm, Germany; ⁷ARC CoE for Nanoscale BioPhotonics, RMIT University, Melbourne, Victoria, Australia.

Nitrogen-vacancy centres in diamond are being widely employed to measure magnetic fields. We performed theoretical calculations showing that the precision of NV magnetometry can be vastly improved by using diamond material with high NV densities as a laser medium and making use of the intrinsic amplification and high collection efficiency of a laser system. In this way quantum-limited sensitivities could become competitive with ultra-sensitive SQUID sensors.
Motivated by this result we investigated experimentally the properties of stimulated emission of NV centre ensembles in diamond. Combining green (532nm) pump light with red (~700nm) stimulating light, we measured spontaneous and stimulated emission and characterised the occurrence of induced absorption channels.

Placing NV diamonds in optical cavities we measured an amplification of red light transmitted through the cavity, when a green pump laser was added, by a factor of 3. We furthermore identified material properties and improvement challenges and strategies for CVD growth of diamond tailored to the realisation of an NV centre laser and laser threshold magnetometry.

SESSION EP09.06: FET Devices I
Session Chairs: Hiroshi Kawarada and David Moran
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 207

1:45 PM EP09.06.01
The Interface Properties of Al2O3/NO2/H-Diamond in MOSFET Structure Studied by Capacitance and Conductance and Synchrotron XPS/XANES Measurements
Niloy C. Saha1, Kazutoshi Takahashi2, Satoshi Masuya1, Masaki Imamura1 and Makoto Kasu1; 1Electrical and Electronic Engineering, Saga University, Saga, Japan; 2Synchrotron Light Application Center, Saga University, Saga, Japan.

Diamond with a wide band-gap of 5.47 eV and high break-down field of ~10 MV/cm is expected to be best semiconductor material for high-power and high-frequency transistors. Diamond field effect transistor (FET) exhibited high RF output power density of 2 W/mm at 1 GHz, transition frequency (fT) of 45 GHz and the cut-off frequency of power gain (fMAX) of 120 GHz. Inorganic gases, such as O3, NO2, NO, and SO2 adsorbed on H-diamond surface and generate hole carriers. This phenomenon can be explained as the inorganic molecule accommodate electrons and induce holes due to the lower molecular orbital energy of these gases than diamond valence band maximum (VBM) [1]. The NO2 p-type doping increases hole sheet concentration up to ~1x10^14 cm^-2. Recently, M. Geis et al. reported that presence of NO2 peak on NO2-adsorbed H-diamond [2]. For FET, we have been using NO2-p-type doping in H-diamond. However, Al2O3/NO2/H-diamond interface structure is yet to be identified more clearly.

Al2O3/NO2/H-C, Al2O3/NO/H-C, and Al2O3/NO2/H-C structures were investigated by XPS/XANES measurements, where valence band offsets were determined to be 3.9, 3.7 and 3.5 eV, respectively, suggesting decomposition of exposed gases. Oxygen-derived interface state was detected but no N or S peak was found at the interface.

In the C-V measurements, the flat-band voltage of Al2O3/NO2/H-C MOS structures shifted towards positive voltage side by 2 V compared to that of Al2O3/H-C MOS. We also found that exposure of inorganic gases reduces the work function of H-diamond surface and shifted flat-band voltage towards the positive side. Interfacial properties were measured using conductance method by measuring parallel conductance from 1 kHz – 1 MHz. By fitting the parallel conductance, we separated border trap density in Al2O3 layer and interface state density. values are ~5.7 × 10^12 and ~4.8 × 10^12 cm^-2 eV^-1 respectively for the Al2O3/NO2/H-C and Al2O3/H-C MOS structures at room temperature.

In conclusion, we have identified oxygen-state at the interface of Al2O3/NO2/H-C structure using XPS/XANES measurements which is also confirmed by measuring conductance and compared to that of Al2O3/H-C structure. This investigation provides the information that NO2 exposure does not incorporate directly into interfacial states as the values in both cases are within the same range. A comprehensive demonstration will be discussed.

References:

2:00 PM EP09.06.02
Vertical-Type 2DHG Diamond MOSFETs Over 5000 A/cm² and Low On-Resistance 6 mΩcm²
Masayuki Iwataki1, Nobutaka Oi1, Kiyotaka Horikawa1, Shotaro Amano1, Taisuke Kageura1, Masafumi Inaba2, Atsushi Hiraiwa2, 1 and Hiroshi Kawarada1, 3; 1Waseda University, Shinjuku, Tokyo, Japan; 2Synchrotron Light Application Center, Saga University, Saga, Japan.

We have reported excellent characteristics of high breakdown voltage and stable operation in wide temperature range in 2 dimensional hole gas (2DHG) diamond metal-oxide-semiconductor field effect transistor (MOSFET) with Al2O3 gate insulator and passivation film by high temperature atomic layer deposition (ALD) method [1][2]. 2DHG is preserved by ALD-Al2O3 near the interface of hydrogen terminated diamond [3][4]. The 2DHG is induced independent on crystal orientation. So, the trench side wall is used for drift region [5]. We have also reported vertical-type 2DHG Diamond MOSFET with trench structure [5] and obtained high current density and on/off ratio by forming the nitrogen doped layer as a block layer [6]. For vertical GaN devices, high current density over 2000 A/cm² and low on-resistance of 1.8 mΩcm² have been reported [7]. The same level performance is also required for vertical diamond devices. In this work, we further miniaturized vertical-type 2DHG Diamond MOSFET with trench opening length 2 or 4 µm and incorporated overhanging gate electrode structure on the source electrode for improvement of on-current density.

The fabrication process is follows. First, the 2 µm nitrogen doped layer is grown to suppress leakage current on the boron doped layer by microwave plasma chemical vapor deposition method. The nitrogen concentration is changed stepwise from 2.0×10^14 – 8.0×10^14 cm^-3 in order to assuage the electric field overconcentration. The trench is formed by Inductive Coupled Plasma Reactive Ion Etching. The trench opening length is 2 or 4 µm and the depth is 3 ~ 4 µm. After forming the trench, undoped layer (200 nm) is grown epitaxially again to induce the 2DHG layer. 200 nm Al2O3 is deposited high temperature ALD method [1][2]. 2DHG is preserved by ALD-Al2O3 near the interface of hydrogen terminated diamond [3][4]. The 2DHG is induced independent on crystal orientation. So, the trench side wall is used for drift region [5]. We have also reported vertical-type 2DHG Diamond MOSFET with trench structure [5] and obtained high current density and on/off ratio by forming the nitrogen doped layer as a block layer [6]. For vertical GaN devices, high current density over 2000 A/cm² and low on-resistance of 1.8 mΩcm² have been reported [7]. The same level performance is also required for vertical diamond devices. In this work, we further miniaturized vertical-type 2DHG Diamond MOSFET with trench opening length 2 or 4 µm and incorporated overhanging gate electrode structure on the source electrode for improvement of on-current density.

The fabrication process is follows. First, the 2 µm nitrogen doped layer is grown to suppress leakage current on the boron doped layer by microwave plasma chemical vapor deposition method. The nitrogen concentration is changed stepwise from 2.0×10^14 – 8.0×10^14 cm^-3 in order to assuage the electric field overconcentration. The trench is formed by Inductive Coupled Plasma Reactive Ion Etching. The trench opening length is 2 or 4 µm and the depth is 3 ~ 4 µm. After forming the trench, undoped layer (200 nm) is grown epitaxially again to induce the 2DHG layer. 200 nm Al2O3 is deposited high temperature ALD method. The gate length is 2 µm and part of the gate electrode has an overhanging structure which is liable to be placed on the source electrode. So, the length between source and gate electrode is 0 µm and also the device size itself is miniaturized. We defined the device active area is calculated the length of between both source electrodes (6 ~ 16 µm) and the channel width (25 µm).

The drain current density is ~200 mA/mm at VDS of -50 V and VGS of -20 V. In the active area 1.5×10^4 cm² device, the maximum drain current which is normalized with respect to active area is ~6000 A/cm² at VDS of -50 V and VGS of -20 V and the specific on-resistance is 5.8 mΩcm². The on/off ratio is 10⁶.

Specific on-resistance and normalized current density are much more improved by the miniaturization of device area.

Diamond is expected to be the next generation of power device material as wide band gap semiconductor with special properties such as high thermal conductivity and high breakdown field. Hydrogen-terminated diamond MOSFETs with a reported high breakdown voltage characteristic [1] and stable operation in wide temperature range [2] have been reported in previous research. Diamond MOSFETs use Two-Dimensional Hole Gas (2DHHG) which is induced by negative adsorbates or passivation film on hydrogen-terminated surface. In general, 2DHHG diamond MOSFETs are normally-on since 2DHHG channel is induced without gate bias. Power devices are required to be normally-off for safety. Normally-off diamond MOSFETs have already been reported for C-H diamond MOSFETs with partial C-O channel [1], HfO2-gated diamond MOSFETs [3] and inversion channel diamond MOSFETs. In this study, we demonstrate normally-off MOSFETs by the insertion of thin SiO2 layer in diamond/Al2O3 interface. SiO2 which do not have negative charge is not induced 2DHG. So, normally-off is achieved by insertion of SiO2 into MOS structure. In addition, we could suppress the deterioration of drain current density.

The fabrication process was as follows. Undoped homoepitaxial diamond layer was deposited on Ib (001) diamond substrates by Chemical Vapor Deposition, and electrodes were deposited as source and drain. 1st Al2O3 film was deposited as gate passivation by high-temperature ALD [4] after hydrogen-termination. Al2O3 is partially etched in the 20% (2μm) of channel area, where C-H surface is exposed in part. Si thin film (1nm) was deposited directly on the clean C-H surface at 723 K, and the Si film was fully oxidized by air and the subsequent 2nd Al2O3 deposition. The 2nd Al2O3 film was deposited as gate insulator by the same high-temperature ALD [4]. Finally, gate electrode was deposited form MOS structure where 20% of channel C-H surface is directly covered Al2O3 without surface negative charge which cause 2DHG. The gate threshold voltage (Vth) of the device was -2.0 V which is suitable for power device application. Vth, control and normally-off operation were achieved. The maximum drain current density was -67 mA/mm at VDS = -50 V when VGS was 0 V. The device of size was L=2 μm, W=10 μm and L2D=2 μm. In addition, normally-off devices were achieved in various size. The size of device was L=2 μm, W=10 μm, L2D=5 and 10 μm. Vth were -5.8 and -5.7 V. The maximum drain current density (VDS = -50 V, VGS = -40 V) were -52 and -53 mA/mm, which are larger other diamond normally off devices.

Diamond's unique chemical stability allows it to be used as an electron emitter under unusual conditions, including in water. However, the large bandgap of diamond makes it a poor absorber of light even at short wavelengths. The emission of electrons from diamond can be improved by creating novel types of heterojunctions with metals, semiconductors, and by integrating metal nanoparticles directly into the diamond film. The incorporation of silver nanoparticles directly into diamond films confers significant changes in optical properties as well as changes in electron emission characteristics. We have evaluated the electron emission characteristics of diamond-based heterojunctions as a function of wavelength, diamond film thickness, and other variables in order to understand how to achieve the most effective electron emission. In this talk I will present recent data comparing photoelectron emission from diamond and diamond-based heterostructure devices, with the goal of facilitating the use of diamond as an electron emitter operating under ambient environments.

The ability to form a negative electron affinity (NEA) surface on diamond is of interest for electron emission applications. These surfaces form when atoms electropositive relative to carbon terminate the surface. Simple H-termination gives NEA but hydrogen desorption occurs at elevated temperatures (>700 °C). This makes H-terminated diamond unsuitable for high-temperature applications.

Previous work has studied NEA surfaces generated by termination from group I, II and transition metals (TMs). Larger group I metals do not have thermal stability but smaller group I and II metals, such as Li and Mg, show promise. Computational work on various first-row TMs including Cu, Ni, Ti and Zn, suggest carbide-forming TMs give larger NEA and experimental work has shown <10 Å thin films of various TMs can give NEA.

Density functional theory calculations simulate the addition of up to 1 ML of aluminium on the diamond surface. Aluminium is a carbide-forming metal that bonds sufficiently well to be used for Ohmic and Schottky contacts, and here we show it is of interest for NEA applications as well. For certain Al coverages, for example 0.25 ML coverage on the (100) O-terminated surface, we find adsorption energies were observed to be larger than for H-termination whilst maintaining a NEA.

The hydrogen peroxide reduction on boron doped diamond electrodes modified by silver nanoparticles in a neutral phosphate buffer solution shows a CE mechanism. A diffusion oxygen layer is formed firstly along with water via the disproportionation of hydrogen peroxide on silver nanoparticles, and then reduced to hydrogen peroxide during electrochemistry process. Cyclic voltammetry and simulation are combined to confirm the mechanism, demonstrating the electrochemical reduction signal depends on the interacting time between silver and hydrogen peroxide via the disproportionation step which occurs before the voltammetric analysis.

Theoretical study on Termination Dependent Redox Reactivity of Boron-Doped Diamond / Water Interface Shota Iizuka, Keisuke Natsu, Yasuaki Einaga and Yoshitaka Tatayama; National Institute for Materials Science, Tsukuba, Japan; Keio University, Yokohama, Japan.

Boron doped diamond (BDD) is a promising electrode material, which has wide potential window and low background current. Our experimental studies so far demonstrated that the electrochemical characteristics of BDD can be modified by different surface terminations. Recently, the electrochemical properties of hydrogen (H), hydroxyl (OH), and fluoride (F)-terminated BDD were compared with the cyclic voltammogram measurement of anionic, neutral and cationic redox targets [1]. It is then observed that the oxidation and reduction current densities decrease for F-BDD, compared to H- and OH-BDD. Especially, the current density for anionic target was significantly suppressed in the case of F-BDD. Also, the oxidation potential for each target monotonously shifted toward the positive direction. To understand such differences in the electrochemical behavior, we calculated H-, OH-, and F-terminated BDD/water interfaces, employing Car-Parrinello molecular dynamics based on density functional theory. In the calculated electronic structures of H-, OH-, and F-BDD/water interfaces, we found that valence band maximum (VBM) of H-BDD is located at highest energy position, while F-BDD has much lower band position. For redox reactions with the targets, the Fermi level, nearly VBM, of p-type semiconductor BDD should coincide with the target redox potential according to the Fermi’s golden rule. With the hypothesis of surface band-edge pinning, VBM in H-BDD does not need to go up from the open circuit condition, while that in F-BDD needs significant upward shift. This causes large downward band bending in the subsurface region of BDD, which plays a barrier role for the electron / hole tunneling between the BDD electrode and the redox target. This is not the case in H-BDD in fact, and the observed redox behaviors are roughly accounted for by this mechanism. For more comprehensive explanation, we also analyzed distribution of interfacial water on H-, OH-, and F-BDD/water interfaces, and the interfacial charge. Regarding H-BDD and F-BDD, oxygen atoms of water distributed farther from the BDD surface than OH-BDD. This suggests that H- and F-BDD surfaces are hydrophobic. This hydrophobicity increases the tunneling length of electron / hole between BDD and the target in water. We also found that F-BDD has more negative surface than the others, reflecting large electronegativity of fluorine atom. This indicates that it is difficult for anionic target to approach the BDD surface and the tunneling length becomes larger.
We propose a new electric wireless communication under the sea; it utilizes diamond solution-gate FETs (SGFETs) [1] where the semiconductor surface is directly immersed in solution (e.g. seawater), and drain current (\(I_D\)) is remotely controlled by electric signals (\(V_G\)) of a reference electrode.

Seawater wireless communication has been required for many purposes. The electromagnetic waves are heavily attenuated in the seawater due to highly ionized media [2]. In general, the acoustic waves and visible light are used for seawater communication. However, these seawater communication means are not appropriate for mobile seawater robots; the reasons are that acoustic waves induce transmission problems such as Doppler shifts, and that the visible light requires accurate alignment between a transmitter and a receiver [2]. On the other hand, electric signals have relatively low attenuation and isotropic distribution of electric field due to electrical conductivity of seawater. Thus, electric seawater wireless communication has potential for mobile seawater robots [3]. In this work, we mainly investigated two points; first, how far the electric signals are transmitted, and second, what the maximum operation frequency of SGFETs is in the vast sea.

This communication setup consisted of two components; a reference electrode as a transmitter and SGFET as a receiver. The reference electrode, which was remote from the SGFET, applied electric signals (\(V_{SGFET}\)) via seawater. Then, the SGFET received the electric signals (\(V_{SGFET}\)) via seawater. Also, each of the source potentials was common ground in order to obtain stable reference potential. \(I_{DS\text{-}V_{DS}}\) and switching characteristics of the SGFETs were measured.

The electric signals (\(V_{SGFET}\)) of the reference electrode propagated without attenuation in the sea. In both 1 and 10 m, ideal \(I_{DS\text{-}V_{DS}}\) characteristics were obtained by electric signals (\(V_{SGFET}\)). Moreover, the switching times for \(T_{ON}\) and \(T_{OFF}\) were both less than 1 \(\mu s\). Therefore, between 100 kHz-1 MHz, this setup was capable of communicating within 10 m in the sea. The limit of frequency governed by a long ground line. The operation frequency can be increased further by considering a new ground. The 10 m is not a limit of this wireless communication, but can be extended much more, because the signal does not differ from 1 m to 10 m.

We adopted diamond SGFETs to establish new electric seawater wireless communication. This communication method using SGFETs is applicable for mobile seawater robots because electric signals have relatively low attenuation and isotropic distribution of electric field.


SESSION EP09.08/EP08.06: Joint Session I: Diamond Devices
Session Chairs: Etienne Gheeraert and Mark Hollis
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 207

8:30 AM *EP09.08.01/EP08.06.01
Recent Progresses in Deep Depletion Diamond MOSFET Cedric Masante1, Toan Thanh Pham1-2, Nicolas Rouger3, Gauthier Chicot1,2, Florin Udrea1, David Eon1, Etienne Gheeraert1, Daniel Araujo1 and Julien Pernot1, 1University Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, France; 2University Grenoble Alpes, CNRS, Grenoble INP G2Elab, Grenoble, France, Grenoble, France; 3Department of Engineering, The University of Cambridge, Cambridge, United Kingdom; 4Université de Toulouse; LAPLACE; CNRS; INPT; UPS, Toulouse, France; 5Dpto. Ciencia de los Materiales, Universidad de Cadiz, Cadiz, Spain.

Diamond is a fascinating semiconductor with exceptional physical properties such as a wide band gap, a high breakdown electric field (10 MV/cm), an outstanding thermal conductivity (20 W/cm/K) and high carrier mobilities. These exceptional properties, or more precisely, the combination of some of these properties makes diamond an ideal semiconductor for high power and/or high frequency electronics which should surpass other materials like silicon, silicon carbide or gallium nitride. Numerous diamond field effect transistors are under investigation: H-terminated accumulation FET, O-terminated injection smoothly from metal to diamond subsurface when surface electron potential is high (surface band bends upward). It is realized by negatively charged surface or negative surface voltage bias. Then, 2 dimensional hole gas (2DHG) is produced by hole injection from metal. It is desirable for high speed FET operation [1].

Low SBH for 2DHG:
Diamond has superior properties as p-type conducting compared with other wide bandgap semiconductors. Among them P-type Schottky barrier height (SBH) is very low (< 0.1eV) on the hydrogen terminated (C-H) diamond surface in high work-function metal such as Au [1]. This property enables hole injection smoothly from metal to diamond subsurface when surface electron potential is high (surface band bends upward). It is realized by negatively charged surface or negative surface voltage bias. Then, 2 dimensional hole gas (2DHG) is produced by hole injection from metal. It is desirable for high speed FET operation [1].
High Frequency FET:
The first GHz operation in diamond [2] has been realized by metal semiconductor (MES) FET, where Au is used for source and drain contacts and Al for Schottky gate on the same C-diamond surface. Al shows the SBH of 0.6 eV, because Al work function is lower than Au by 0.7 eV. The work function dependence of SBH indicates that C-H diamond surface has low surface states density, necessary for MOSFET. In addition to MESFET [3], MOSFETs [4,5] exhibited GHz operation up to 70 GHz [6] in fT (cutoff frequency) and >100GHz [3] in fmax. The power density is now 3.8 Wmm⁻¹ [7] at 1GHz obtained by high bias voltage (~50V). Its electric field is above 2x10⁵ Vcm⁻¹, where the hole velocity is nearly saturated in an entire FET. The power density is lower than AlGaN/GaN HEMT, but higher voltage operation can enhance it much further.

High Voltage FET:
C-H diamond MOSFETs are uniquely designed for high-voltage (~1000V) and high-temperature (up to 400°C) operation using the high temperature (450°C) ALD Al₂O₃ as gate oxide and passivation of gate-drain (drift) region. The maximum breakdown voltages (VBR) are above 1500 V [8] obtained at long drift region (LDrift = 15 μm). fT × fmax = ~1.0 MV/cm, which is equivalent to those of SiC MOSFET and AlGaN/GaN HEMT. The drain current density is comparable to SiC, but 3-4 times lower than AlGaN/GaN at similar VBR. Conductivity in drift region must be improved by mobility enhancement.

Vertical FET:
The first vertical diamond MOSFETs have been developed using 2DHG layer on trench structure [9]. Hole conduction at the trench side wall (3-4 um depth) acts as drift region and is electrically connected to p+ substrate (drain). The drain current density of active planar area has reached to 5000 Acm⁻² [10], which is comparable to those of SiC or GaN MOSFET. Specific on resistance is 5 mΩcm⁻² at present.


9:30 AM EP09.08.03/EP08.06.03 Integration of V2O5 into H-Diamond MOSFETs for Enhanced Device Performance David Macdonald1, Kevin Crawford1, Alexandre Tallaire2, Riadh Issaoui2 and David A. Moran1; 1University of Glasgow, Glasgow, United Kingdom; 2LSPM-CNRS, Université Paris, Paris, France.

As a semiconductor, diamond possesses many unique properties that make it attractive for the production of high performance devices such as robust, high power RF FETs. Such properties include a large bandgap of 5.5 eV, high thermal conductivity of up to 20 Wcm⁻¹K⁻¹ and high carrier saturation velocity of 2 × 10⁷ cm⁻¹s⁻¹ for electrons and 0.8 × 10⁷ cm⁻¹s⁻¹ for holes. Development of electronic diamond devices has been largely limited however by the immaturity of existing doping processes used to introduce mobile charge into its naturally insulating crystal structure. ‘Transfer doping’ of hydrogen-terminated diamond (H-diamond) presents a potential solution to this challenge which has allowed for the production of high performance FETs. Stability issues associated with traditional transfer doping, which relies on the presence of atmospheric species on the diamond surface, has limited the maturity of device technologies that exploit these doping techniques. More recently, various work has demonstrated the potential to improve the stability and efficiency of transfer doping in diamond utilising electron acceptor oxide materials on the diamond surface. In this work, we apply the electron oxide acceptor material V2O5 into H-diamond FET technology and demonstrate substantial performance improvement in comparison with traditional atmosphere-exposed devices. These performance figures include the highest reported drain current and transconductance for a H-diamond FET to incorporate an electron acceptor oxide such as V2O5. Furthermore, a 400°C anneal stage utilised in the process flow for devices (as required to ensure stability of the V2O5 layer) is also found to reduce the ohmic contact resistance and increase the carrier concentration beneath the gate of the devices, further improving device performance.

The potential mechanisms for this performance enhancement and future implementation of these techniques to enhance the performance and robust operation of H-diamond FET technology will be discussed.

9:45 AM EP09.08.04/EP08.06.04 Diamond Surface Conduction FET RF Performance Correlated to Internal Charge Carrier Characteristics Pankaj Shah, James Weil, Khamsouk Kingko, Kevin Crawford, Mahesh R. Neupane, Anthony G. Birdwell, Edward Viveiros and Tony Ivanov; Army Research Laboratory, Adelphi, Maryland, United States.

Higher power, higher frequency RF transistors than those possible using the III-nitride semiconductors are desired for large data (high bandwidth) information transmission, highly advanced radar detection, and more efficient communication. We are developing hydrogenated diamond surface conduction field effect transistors (FETs) for use in these next generation RF systems accessing diamond’s wide bandgap (5.47 eV) extremely high thermal conductivity in drift region (~1.0 MV/cm, which is equivalent to those of SiC MOSFET and AlGaN/GaN HEMT. The drain current density is comparable to SiC, but 3-4 times lower than AlGaN/GaN at similar VBR. Conductivity in drift region must be improved by mobility enhancement.

Integration of V2O5 into H-Diamond MOSFETs for Enhanced Device Performance

9:30 AM EP09.08.03/EP08.06.03 Integration of V2O5 into H-Diamond MOSFETs for Enhanced Device Performance

9:45 AM EP09.08.04/EP08.06.04 Diamond Surface Conduction FET RF Performance Correlated to Internal Charge Carrier Characteristics

We have also observed that the Schottky barrier heights for the atmospheric transfer doped devices with good gate control are over 0.38 eV and range up to 1.0 eV. This best connects the influence of material, fabrication steps and structure on performance. In this regard, we obtained the hole velocity (~1.0 MV/cm, which is equivalent to those of SiC MOSFET and AlGaN/GaN HEMT. The drain current density is comparable to SiC, but 3-4 times lower than AlGaN/GaN at similar VBR. Conductivity in drift region must be improved by mobility enhancement.

The potential mechanisms for this performance enhancement and future implementation of these techniques to enhance the performance and robust operation of H-diamond FET technology will be discussed.

Higher power, higher frequency RF transistors than those possible using the III-nitride semiconductors are desired for large data (high bandwidth) information transmission, highly advanced radar detection, and more efficient communication. We are developing hydrogenated diamond surface conduction field effect transistors (FETs) for use in these next generation RF systems accessing diamond’s wide bandgap (5.47 eV) extremely high thermal conductivity (~1.0 MV/cm, which is equivalent to those of SiC MOSFET and AlGaN/GaN HEMT. The drain current density is comparable to SiC, but 3-4 times lower than AlGaN/GaN at similar VBR. Conductivity in drift region must be improved by mobility enhancement.

Optimizing RF surface channel FETs is most effectively done using device physics information obtained directly from the same device that the RF measurements are made on. This best connects the influence of material, fabrication steps and structure on performance. In this regard, we obtained the hole velocity in the FET channel using a delay time measurement and this is we believe the first ever discussion of velocity obtained in this way applied directly on a diamond RF FET. This will be related to carrier density and effective mobility obtained from RF FETs. RF small signal characteristics (current and power gain cutoff frequencies (fT, fmax)) and large signal characteristics (power, gain and efficiency) from load pull measurements will also be discussed for the same devices.

Transit time values obtained from a delay time measurement indicates these FETs have a hole velocity in the channel 5×10⁷ cm/s and drain depletion region delay = 2.5 ps. On wafer RF measurements for intrinsic current gain cutoff frequency indicate an opposite trend with gate length of fT = 70 GHz (Lg = 50 nm), 49 GHz, (100 nm), and 10 GHz, (500 nm) when Vds = 10V. With improved contact and access region resistances we expect the frequency bandwidth to increase. Load pull measurements indicate RF output power densities increased 30% as the drain and gate bias voltage pulse spacing increased (a duty cycle reduction from 5% to 0.5%) suggesting that RF output power is affected by heating of the transfer dopant in unpassivated FETs. These measurements also demonstrate a peak RF output power density of 0.66 W/mm² at 2 GHz.

We have also observed that the Schottky barrier heights for the atmospheric transfer doped devices with good gate control are over 0.38 eV and range up to 1.0 eV.
0.63 eV, however, the ideality factor is quite high (between 1.5 and 7.3). This may be an indication of the roughness of the surface and challenge contacting a hydrogenated region that the gate finger metal sits on. As the gate length reduced from 3 micron down to 50 nm the FET current density increased six fold, and knee voltage reduced uniformly by 50%.

10:00 AM BREAK

10:30 AM*EP09.08.05/EP08.06.05
Diamond Power Electronic Devices—Schottky Diodes Timothy A. Grotjohn1,2, John Albrecht1, Michael Becker2, Ayan Bhattacharya1, Ramon Díaz1, Aaron Hardy2, Timothy Hogan1, Matthias Muehle1, Robert Rechenberg2, Thomas Schuelke1,2 and Steven Zajač1; 1Michigan State University, East Lansing, Michigan, United States; 2Fraunhofer USA Center for Coatings and Diamond Technologies, East Lansing, Michigan, United States.

This paper will overview the status and prospects of diamond for power electronics applications. Both the potential and the current/future challenges will be discussed. The particular example of diamond Schottky diodes for power electronics will be explored in more detail. The authors have worked on diamond diodes by developing high quality substrates, low-defect doped epitaxial layers and diamond microfabrication processes. Two diode structures studied are the vertical Schottky diode and the pseudo-vertical diode. The vertical diode requires a thick (>250 µm) p+ doped substrate and the pseudo-vertical diode requires an undoped substrate with low dislocation defect density. Part of this effort is directed at providing substrates of p+ diamond to thicknesses >250 µm and providing p+ epitaxial layers for the pseudo-vertical devices. Improvement of the p+ epitaxial layer deposition was studied by reducing the particles landing on the surface during deposition and increasing the time the diamond CVD reactor can run before soot formed that required the run be terminated. The soot formation is a known problem for diamond deposition using microwave plasma-assisted CVD due to the high boron level added to the deposition process. The boron doped p+ layer is the region that provides the breakdown voltage of the Schottky diode. The p+ region needs to be deposited/grown with low dislocation defect density, controlled doping, controlled thickness and low compensation from impurities like nitrogen. The p+ layer was grown at 800°C with a feedgas of hydrogen, methane (4%), oxygen and a small amount of diborane as needed for the desired p-type doping concentration. The addition of the oxygen helps to improve the quality of the p+ epitaxial layer and reduce passivation of the boron doping by hydrogen. Schottky diodes fabricated showed breakdown voltages exceeding 1800 V. The 1800 V diodes showed forward current densities of up to 300 A/cm². Other diamond diode work will also be overviewed.

11:00 AM*EP09.08.06/EP08.06.06
Recent Progress in Diamond Field-Effect Transistor Technologies Makoto Kasu; Saga University, Saga, Japan.

A diamond semiconductor with a bandgap of 5.47 eV is expected to be the ultimate power device because of its exceptional physical properties, such as a high breakdown field (>10 MV/cm), high mobility, and highest thermal conductivity [20 W/(cm K)]. We previously reported high radio-frequency (RF) power performance of diamond field-effect transistors with a power-gain cutoff frequency, fMAX, of 120 GHz and an RF output power of 2.1 W/mm at 1 GHz. In this talk, we focus on very recent progress in two basic technologies related to diamond electronics: wafer technology and carrier doping technology.

To overcome the size limitation of diamond crystals, diamond heteroepitaxy technology has progressed rapidly. A 1-inch heteroepitaxial diamond has been demonstrated. In heteroepitaxy, epitaxial overgrowth technology is used to drastically decrease the dislocation density. Furthermore, microneedle technology has been proposed and demonstrated as a method to delaminate heteroepitaxial diamond from its substrate without cracking. [1] In the final process of heteroepitaxy technology, chemical mechanical planarization of the heteroepitaxial diamond surface is important for obtaining a damage-free and smooth surface. The full-width at half-maximum of the (004) plane was as low as 0.03°, and the curvature was 0.29 m, indicating the world’s highest quality heteroepitaxial diamond. The size and quality of diamond crystals is improving. We have fabricated diamond field-effect transistors on heteroepitaxial diamond, and the resultant device shows the same drain-current level as conventional homoepitaxial diamond on a HPHT substrate.

Concerning carrier doping technology in diamond, Kubovic and Kasu previously reported NO2 p-type doping, which they used to fabricate FETs; that is, NO2, O2, N2O, NO, and SO2 molecules adsorbed onto H-diamond generated hole carriers and the hole sheet concentration was as high as ~1 x 10^14 cm^-2 at room temperature. [2] Shiraishi and Kasu explained this phenomenon as the LUMO/SOMO orbital energies in the inorganic molecules adsorbed onto H-diamond being below the valence-band top of H-diamond, resulting in electron transfer from H-diamond to these molecules. Recently, Geis and Wade at the Massachusetts Institute of Technology investigated the NO2–H-diamond surface further by surface chemical techniques such as Fourier transform infrared temperature. [2] Shiraishi and Kasu explained this phenomenon as the LUMO/SOMO orbital energies in the inorganic molecules adsorbed onto H-diamond the physical and electronic characteristics of the TMO caused by the device fabrication process. In particular, stoichiometry reduction, crystalline phase heteroepitaxial diamond, and the resultant device shows the same drain-current level as conventional homoepitaxial diamond on a HPHT substrate. The size and quality of diamond crystals is improving. We have fabricated diamond field-effect transistors on heteroepitaxial diamond, and the resultant device shows the same drain-current level as conventional homoepitaxial diamond on a HPHT substrate.

References

11:30 AM*EP09.08.07/EP08.06.07
Diamond:H/Transition Metal Oxides Transfer-Doping Efficiency and Transistors Performance Mosleh Tordeman1, Zongyou Yin2, youngtack Lee2, Alon Vardi2, Rafi Khalish3 and Jesus A. del Alamo1; 1Technion–Israel Institute of Technology, Haifa, Israel; 2Microsystems Technology Laboratories, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 3Research School of Chemistry, The Australian National University, Canberra, Australian Capital Territory, Australia.

Transfer doping of hydrogen terminated diamond (Diamond:H) with various molecular-like surface acceptors suffers from low efficiency and temperature instability. In contrast, high electron affinity transition-metal oxides (TMOs) (i.e. MoO3, WO3, V2O5 and ReO3), when employed as surface acceptors for transfer doping on Diamond:H, have recently yielded improved p-type sheet conductivity and remarkable thermal stability even with only a few monolayers of coverage. [4, 5]. Despite these properties, the realization of Diamond:H electronic devices using TMOs remains very challenging. [6] This is due to undesirable changes in the physical and electronic characteristics of the TMO caused by the device fabrication process. In particular, stoichiometry reduction, crystalline phase transitions and structural morphology aggregations take place.

In this work, we discuss how different TMOs' properties affect the electrical properties of the resulting diamond:H/TMO-based transistors, and how these undesirable effects can be minimized. Electrical and surface characterization monitored before and after transistor fabrication reveal TMO oxygen reduction and a change in its oxidation state leading to electrical conductivity degradation. Based on these findings, we propose and demonstrate a way to improve diamond:H/TMO transistor performance and stability.

References
The drain current density (I_D) ranged from 1 to 3 μm.

Particularly, the power density of diamond FETs (up to 2.2 W/mm) [3, 6] is higher than those of GaAs and LDMOS. However, the operating voltage was as low as 15 ~ 20 V because of low breakdown voltage. Power density would be much more improved by realizing high voltage operation. Recently, we reported high average electric field [7] in MOSFETs with Al2O3 deposited as gate insulator [6, 8] and passivation layer [9] by high temperature atomic layer deposition (ALD) [10]. In this work, we fabricated ALD-Al2O3 2DHG diamond MOSFETs, whose structure is capable of withstanding high voltage, and evaluated small signal and large signal performance at high voltage operation (|V_D| < 60 V). As a result, the highest power density of 3.8 W/mm was obtained in diamond.

We fabricated ALD-Al2O3 2DHG diamond MOSFETs with 100 nm Al2O3 film on IIa-type polycrystalline diamond substrate with a <110> preferential growth surface. The source-gate length, gate length (L_G) and gate width were fixed to 0.5, 0.5 and 100 μm, respectively and gate-drain length (L_DG) was ranged from 1 to 3 μm.

The drain current density (I_D) was ~730 mA/mm at V_GS = ~20 V and V_GS = ~40 V and the transconductance was 15 mS/mm at V_GS = 12 V and V_GS = ~40 V for L_DG = 1 μm. Extrinsic f_T and f_max, including parasitic pad capacitances and inductances, were 30 GHz and 27 GHz at V_GS = 16 V and V_DS = ~60 V for L_DG = 3 μm. f_T > 30 GHz @ L_DG = 0.5 μm corresponds the saturation velocity of 1x10^7 cm/s. Hz is the first report that diamond FET reaches its saturation velocity. The large signal performance was evaluated using load pull system. The bias point for A-class operation were V_GS = 12 V, V_DS = ~50 V and I_D = ~405 mA/mm, respectively. The power density reached 3.8 W/mm at 1 GHz with associated gain of 11.6 dB and power added efficiently of 23.1 % for L_DG = 2 μm. The power density is the highest ever reported for diamond FETs.

11:45 AM EP09.08.08/EP08.06.08
3.8 W/mm Power Density at 1GHz for ALD-Al2O3 2DHG Diamond High Frequency MOSFETs

H-terminated diamond with 2 dimensional hole gas (2DHG) provides a promising surface channel for high-power and high-frequency applications due to its excellent properties for FETs. From 2001, milestones of RF performance of diamond FETs are first GHz operation in MESFETs [1], MISFETs with Al2O3 deposited as gate insulator [6, 8] and passivation layer [9] by high temperature atomic layer deposition (ALD) [10]. In this work, we fabricated ALD-Al2O3 2DHG diamond MOSFETs, whose structure is capable of withstanding high voltage, and evaluated small signal and large signal performance at high voltage operation (|V_D| ≤ 60 V). As a result, the highest power density of 3.8 W/mm was obtained in diamond.

SESSION EP09.09/EP08.07: Joint Session II: Diamond Growth
Session Chairs: Philippe Bergonzon and Travis Wade
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 207

1:30 PM *EP09.09.01/EP08.07.01
Heteroepitaxial Diamond—Scaling of an Ultra-Wide-Bandgap Material to Wafer Dimensions

In the field of power devices, diamond’s intrinsic physical properties suggest that they can facilitate ultimate device performance. Just as for other wide-bandgap materials, the availability of wafer-size diamond substrates with high single crystal quality is an indispensable prerequisite. There are two approaches which start from opposite points: First, homoepitaxial growth on carefully selected rather small single crystals with minimum dislocation densities can be performed in such a way that the available area is increased step by step while the dislocation density is kept low. By a similar approach, 4H-SiC has progressively been scaled over 20 years starting from small Acheson platelets to 6” wafer size [1]. The second alternative is based on heteroepitaxy which starts on large areas but with high dislocation densities (DDs). The challenge here consists in a controlled decrease of the DD by several orders of magnitude while preserving the initial size.

This presentation is focused on heteroepitaxy of diamond on Ir/YSZ/Si(001) which has recently provided the first single-crystal diamond wafer with a diameter > 3.5” and a total weight of 155 carat [2]. All relevant steps for the wafer preparation will be described. First applications of the material will be presented and the potential for further applications will be discussed.

drastically modify its properties. The use of dopants such as boron can for example allow tuning the electrical conductivity of the film up to the metallic conduction which could allow to produce highly boron doped substrates and develop vertical components whose design and architecture for the realization of more complex function is simpler. In addition nitrogen or silicon are some of the elements that can be introduced in the crystal in order to create optically active centres such as the well-known NV (nitrogen-vacancy) and SiV (silicon-vacancy). Both defects exist in different charge states that can be stabilized depending on the doping level of the diamond.

In this presentation, we will focus more specifically on the production aspects of doped monocrystalline diamond films by chemical vapour deposition assisted by microwave plasma with either boron or nitrogen, highlighting all the constraints inherent to the targeted field of application. In the case of boron doping, particular attention will be paid to showing the plasma conditions which it is essential to maintain in order to obtain a sufficiently thick and doped film leading to on state resistances compatible with their use in vertical components. It will be shown in particular the importance of the gas composition to inject high microwave power allowing coupling high material quality with high growth rate. With regard to nitrogen doping, the conditions for optimizing the formation and orientation of NV colour centres will be discussed and the role of temperature, substrate orientation and gas composition will be highlighted.

2:30 PM BREAK

3:30 PM *EP09.09.03/EP08.07.03
Heteroepitaxial Growth of Diamond on 3C-SiC/Si Substrates for Diamond Electronics Mutsumo Hatano and Takayuki Iwasaki; Tokyo Institute of Technology, Tokyo, Japan.

To realize next-generation power devices and highly sensitive quantum sensors, heteroepitaxy of diamond on Si substrates is a key technology from the viewpoint of scalability and Si CMOS hybrid system [1-3]. We utilize 3C-SiC as an intermediate layer between Si substrates and diamond films because it can be directly grown on the Si and the lattice constant and the surface energy of the SiC are close to the diamond.

We would like to introduce the heteroepitaxial growth of diamond on both Si (001) and (111) substrates by original antenna-edge type microwave plasma CVD with in-situ bias current monitoring during bias enhanced nucleation (BEN). We show the properties of the diamond films, and then the potentials for both power devices (Schottky barrier diodes) and quantum sensors. Concerning the schottky barrier diodes (SBDs) on heteroepitaxial diamond (001) films, the specific on-resistance of 0.2 Ω·cm² and high rectification of 10⁵ (±5 V) were obtained which are comparable for SBDs on homoepitaxial diamond films.

The sensor devices using nitrogen-vacancy (NV) centers were formed in the heteroepitaxial diamond (111) films. The NV centers could be preferentially aligned of the NV axis to the one direction and be leading to improving the sensitivity was confirmed.

This work was supported in part by JST-CREST Grant No. JPMJCR1333, KAKENHI (17H01262 and 18H01472), and JSPS Bilateral Open Partnership Joint Research Projects.


4:00 PM *EP09.09.04/EP08.07.04
Thin CVD Diamond Films on AlGaN/GaN HEMTs Structures Ken Haenen1, 2, 1Institute for Materials Research (IMO), Hasselt University, Diepenbeek, Belgium; 2MOMEC, IMEC vzw, Diepenbeek, Belgium.

Diamond’s extreme properties make it a prime candidate for next-gen electronic devices, including high frequency and high power operation. While monolithic diamond devices based on doped monocrystalline layers, enabling both unipolar as well as bipolar design schemes, have great potential, the currently obtainable substrate size and quality leave several years of scientific and technological development. The fact that diamond has an extremely high thermal conductivity and can be deposited on non-diamond substrates, opens up an intermediate pathway for hybrid power devices that integrate diamond with other wide bandgap materials such as SiC or GaN. The main goal in such cases is to achieve an enhanced reliability of the latter active materials by providing superior cooling minimizing thermal hotspots and withstanding large break down electric fields.

Here, the case of diamond on GaN-based HEMT structures is considered. First, the deposition of thin CVD diamond layers will be discussed, including the surface chemistry governing the nanodiamond particle seeding, the deposition conditions, and the use of different microwave-based CVD techniques, including resonant cavity and linear antenna technology. Cross-sectional TEM and EELS mapping of the stacks are employed to discuss the structural and morphological properties and to extract possible changes in composition in the underlying Si,N/AlGaN/GaN interfacial layers induced by the substrate temperature during diamond deposition. Finally, the evaluation of the effective thermal conductivity of the thin diamond layers is discussed. The contactless transient thermoreflectance technique, used to study the heat spreading capabilities, shed light on the thermal conductivity and interfacial thermal boundary resistance.

4:30 PM EP09.09.05/EP08.07.05
Gate Oxide Stability in Diamond Power Transistors Loto Oluwasayo1, Matthieu Florentin1, Cedric Masante1, Nazareno Donato1, Marie-Laure Hicks4, Alex C. Pakpour-Tabrizi1, Richard B. Jackman4, Verena Zuerbig5, Philippe Godignon6, David Eon1, Julien Pernot1, Philippe Godignon6, David Eon1, Julien Pernot1, Philippe Godignon6

Semiconducting diamond is an attractive candidate for the next generation of high voltage and high frequency power devices, thanks to its exceptional properties in terms of wide bandgap, high breakdown field and thermal conductivity. In the literature, several diamond-based field-effect-transistors (FETs) have already revealed good on state performance and high blocking voltage capability (~2kV) in a wide range of operating temperatures. The possibility of generating an inversion regime in diamond metal-oxide-semiconductor FET (MOSFET), and the new Deep Depletion regime (D2MOSFET) specific to wide bandgap semiconductors pave the way for a new generation of power devices. The critical part of the transistor is the gate oxide, with electrical charge traps located within the oxide or at its interface with the semiconductor. These traps can screen the gate potential and shift the threshold voltage, making the devices unusable. The reduction of the trap density is a major concern in all MOS technologies, as well as its stability with time under bias stress.

The latest results about diamond MOS transistors prepared in the framework of the European GreenDiamond project will be presented, and the evolution of the diamond MOS properties with time will be reported for the first time.
The properties of diamond (high mobilities and ultra-gap) suggest different current transport modes that can support high current operation which is sustained and actually improved at high temperatures. This study presents experimental results of forward current density vs voltage which shows a $V^2$ dependence indicative of injection mode transport. The Schottky-PIN devices show high values of forward current density (> 500A/cm² at 3 V) that is stable and actually improves at elevated temperature. Perhaps the most stunning aspect of these results is that the diode specific on-resistance ($R_{on}$) decreases as the voltage increases. The results indicate a new mode of operation of high mobility diamond power devices where the high carrier mobilities and low phonon scattering will support current injection and drift with a reducing resistance as the current is increased. We present a comparison between diodes that operate in injection mode and the more conventional doped drift layer. We discuss modifications of the standard power electronics figure of merit for projecting the operation of diamond devices that operate in the injection transport mode. This research is supported through the NASA HOTTECH program.

Diamond electronics devices are probably the future of power electronics in comparison with other wide band-gap materials. This is due to the exceptional intrinsic properties of the diamond such as a wide band gap (5.45 eV), a high breakdown field (10 MV/cm), a large carrier mobility (2000 cm²/V.s) and a good thermal conductivity (22 W/cm.K).

The most promising device is the vertical Schottky diode, which has already been the subject to a lot of studies. Nevertheless, there are still some open questions, such as: why leakage current appears in some diodes? Is the leakage current linked to the material itself? Is the interface between the diamond layer and metallic contacts homogeneous and does it have an impact on the diodes characteristics? What is the effect of carrier injection at the p$^+$ interface? Finally, how is the breakdown through the stack? To answer these questions we imagined to observe vertically the structure, i.e. through the Schottky contact, the diamond, up to the heavily doped layer used as the back contact for the diode. Two ways are developed in order to have a view along this direction. First, by focused ion beam technic, a thin lamella is defined and reported on an external holder. Second, by a fine polishing of the edge of the plates, the stack can be directly observed. Thus, with these techniques, all interfaces can be investigated as well as the quality of the grown material. This first part gives us also information on growth and on how to optimize it.

Then, to correlate material properties to electrical properties of Schottky diode, the lamella is wired and studied by electron beam induced current (EBIC). This gives an image of the electric field distribution through all the stack, i.e metal, lightly doped and heavily doped diamond. It also provides access to the local electric properties of the device and the correlation with the material properties at the same location. The results of this first in-situ electrical measurement of diamond devices will be presented, and all the implications in the understanding of diamond Schottky diodes.

Diamond exhibits many outstanding properties such as good light transmission, effective resistance to radiation damage, large bandgap, high breakdown voltage, high thermal conductivity, high carrier mobilities etc., having potential applications in the fields of wide range optical transparent window material, coating tools, especially in the field of electron devices which can work in high frequency, high power, high temperature as well as corrosive environment [1-2]. Hydrogen-terminated diamond (H-diamond) devices have been widely researched due to its surface high carrier density and mobility of $10^{13}$ cm$^{-2}$ and 50-150 cm$^2$/V.s$^{-1}$, respectively. An excellent ohmic contact between electrode metal layer and H-diamond is needed. Recently, a new ohmic contact between iridium (Ir) and H-diamond has been reported. However, the barrier height between Ir and H-diamond was still not very clear. To obtain the barrier height value between metal and H-diamond, X-ray photoelectron spectroscopy (XPS) technique was used in this work, because it can directly measure the electronic levels, and used to obtain the barrier height value.

For this work, investigation of barrier height between Ir and H-diamond has been carried out using XPS technique. Firstly, 3X3X0.5 mm$^3$ (001) single crystal diamond with lightly boron doping ($10^{15}$/cm$^3$) was cleaned by acid and alkali to remove the non-diamond phase. Secondly, the sample was treated by hydrogen plasma to form the hydrogen-terminated diamond surface. Thirdly, 20 nm Ir was deposited on half part of the sample as reference by electron beam evaporation (EB) technique. Then, anodic aluminium oxide (AAO) with 50 nm hole and 20 nm spacing was transferred on the whole sample surface. After that, 3 nm Ir was deposited on sample by EB technique. Later, after the AAO was removed, 3 nm Ir island with diameter of 50 nm was formed on sample surface. Finally, XPS technique was used to measure the carbon and Ir electronic levels to obtain the barrier height between Ir and H-diamond.

1 Shozo Kono et al., Electron spectro-microscopic determination of barrier height and spatial distribution of Au and Ag Schottky junctions on boron-doped diamond (001), Japanese Journal of Applied Physics, 53 (2014) 05FP03.
2 Shozo Kono et al., Direct determination of the barrier height of Ti-based ohmic contact on p-type diamond (001), Diamond & Related Materials 60 (2015) 117-122.

Switching Speed Enhancement with Enlarge Gate width Diamond Cascade Application in High Voltage Half-Bridge Inverter

Robert J. Nemanich1, Raghuraj Hathwar1, Manpuneet Benipal2, Franz A. Koeck1, Mohamadali Malakoutian1, Srabanti Chowdhury1 and Stephen M. Goodnick1; 1Arizona State University, Tempe, Arizona, United States; 2Advent Diamond, Tempe, Arizona, United States; 3University of California - Davis, Davis, California, United States.
C-H (Hydrogen-Terminated) diamond MOSFETs show high breakdown voltage characteristics (over 1600 V) and wide temperature operations (10 K-673 K) [1, 2]. However, transport properties of C-H diamond MOSFETs show normally-on because 2DHG exists without gate bias voltage. In consideration of these devices and energy-saving the normally-off operation of devices is required. The cascode structure is based on using the normally-off silicon device to shift the threshold voltage of normally-on device to normally-off. It is successful in changing normally-on AlGaN/GaN HEMT to normally-off. We fabricated the diamond-cascode by the combination of the normally-off silicon p-MOSFET and normally-on C-H diamond FET. Characteristics show the gate of diamond FET is controlled by the silicon p-FET, and it shows normally-off characteristics and maximum transconductance has been drastically enhanced, and the diamond cascode show great breakdown voltage (over 1700 V) because the high voltage was blocked by diamond FET. We applied the diamond cascode in half-bridge inverter configuration as high side, and the GaN cascode (TPH3206PS) is application in low side in the half-bridge inverter. The diamond FET in diamond cascode with \( L_{GS} \approx 2 \mu m, L_{DS} \approx 4 \mu m, \) and gate width is 25 \( \mu m, \) the \( V_{GS,HD} \) characteristics shows the maximum current is \(-3,3 mA\) with \( I_{C,OFF} \approx 20 \mu A/m. \) After application in half-bridge inverter in the low operation voltage of 20 V, the switching time (\( T_{ON} \)) in the high-side is 40 \( \mu s. \) In the high operation voltage of 200 V, the \( T_{ON} \) is 60 \( \mu s, \) but the switching time (\( T_{OFF} \)) in the low-side are under 1 \( \mu s. \) We think the reason is the gate width (\( W_{G} \)) imbalance between the tiny size diamond FET and GaN cascode product, and the gate width imbalance is lead to difference current driving capability between the two sides in inverter. We enlarge the gate width of diamond FETs, and we fabricated the different gate width of diamond FETs from 50 \( \mu m \) to 500 \( \mu m, \) and \( V_{GS,HD} \) characteristics shows the maximum current of \( W_{G}=500 \mu m \) is 30 mA. After we application the larger \( W_{G}, \) diamond FET in the half-bridge inverter, the \( T_{ON} \) is 5 \( \mu s \) in high-side has been observed in the operation voltage of 20 V, and \( T_{OFF} \) is 14 \( \mu s \) in 200 V operation voltage, switching time is faster about 8 times in the low voltage and 4 times in the high voltage. At last, we confirmed the half-bridge inverter operated in 400 V operation voltage. Therefore, new structure of diamond FETs for higher frequency and high operation voltage half-bridge inverter has been discussed and designed.

To overcome the limitations and drawbacks of conventional technologies, light-based technologies are on the rise. Integrated optical systems offer the potential to realize optimized photonic building blocks into complex circuits exhibiting high stability and scalability. Successful applications of integrated optical systems are already found in telecommunication, metrology and sensing. Examples are also extended to quantum photonic platforms, benefiting mainly from the miniaturization’s capabilities that integrated approaches provide. Established methods to realize integrated circuits, inspired from microelectronics, are limited to quasi-planar geometries and require sophisticated multi-step fabrication routines. The most promising approach to solve these drawbacks and open the route to fast prototyped three-dimensional integrated circuits is femtosecond laser lithography. A femtosecond laser beam is tightly focused inside the volume of a transparent material, mounted on a high-precision translation stage. By translating the sample relative to the beam focus, permanent nanometer-sized structures are induced. Although femtosecond laser lithography is originally intended for waveguide fabrication in isotropic glasses it is not restricted to this host material. To date, femtosecond laser lithography is employed to structure, also organic polymers and the wide class of crystalline materials whereas nonlinear crystals belong to the most important. Here we report on the fabrication of Type III depressed cladding waveguides in extended polycrystalline diamond samples by femtosecond laser lithography. Previous studies were limited to waveguide fabrication by femtosecond laser in single crystal diamond substrates. Due to the optical properties of diamond, such as high refractive index, strong nonlinear and Raman coefficient, and the ability to host coherent color centers at room temperature, it is attracting increased interest in the fields of classical and quantum photonics. The waveguide structures were inscribed using a femtosecond Ti:sapphire laser system (Coherent Legend) with a central wavelength of 800 nm and pulse duration of about 120 fs at a repetition rate of 1 kHz. The laser beam was focused by a high numerical aperture microscope objective (NA=0.8) into a 300 \( \mu m \) thick polycrystalline diamond substrate in an absolute depth of 90 \( \mu m. \) We demonstrate waveguiding in the near-infrared telecommunication C-band for optimized processing parameters. The proposed approach combines the advantages of the versatile technique femtosecond laser lithography with the outstanding material properties of diamond enabling extended 3-dim integrated optical system based on diamond. Promising applications are on-chip diamond quantum photonics and the realization of high-quality single photon emitters.

9:30 AM EP09.10.05 Polycrystalline Diamond Waveguides Realized by Femtosecond Laser Lithography Haissam Hanafi1, Sebastian Kroesen1, Georgia Lewes-Malandrakis1, Christoph E. Nebel1, Wolfram Pernice2 and Cornelia Denz2; 1Institute of Applied Physics, University of Münster, Münster, Germany; 2Institute of Physics, University of Münster, Münster, Germany; 3Fraunhofer Institute for Applied Solid State Physics, Freiburg, Germany.

To overcome the limitations and drawbacks of conventional technologies, light-based technologies are on the rise. Integrated optical systems offer the potential to realize optimized photonic building blocks into complex circuits exhibiting high stability and scalability. Successful applications of integrated optical systems are already found in telecommunication, metrology and sensing. Examples are also extended to quantum photonic platforms, benefiting mainly from the miniaturization’s capabilities that integrated approaches provide. Established methods to realize integrated circuits, inspired from microelectronics, are limited to quasi-planar geometries and require sophisticated multi-step fabrication routines. The most promising approach to solve these drawbacks and open the route to fast prototyped three-dimensional integrated circuits is femtosecond laser lithography. A femtosecond laser beam is tightly focused inside the volume of a transparent material, mounted on a high-precision translation stage. By translating the sample relative to the beam focus, permanent nanometer-sized structures are induced. Although femtosecond laser lithography was originally intended for waveguide fabrication in isotropic glasses it is not restricted to this host material. To date, femtosecond laser lithography is employed to structure, also organic polymers and the wide class of crystalline materials whereas nonlinear crystals belong to the most important.

Here we report on the fabrication of Type III depressed cladding waveguides in extended polycrystalline diamond samples by femtosecond laser lithography. Previous studies were limited to waveguide fabrication by femtosecond laser in single crystal diamond substrates. Due to the optical properties of diamond, such as high refractive index, strong nonlinear and Raman coefficient, and the ability to host coherent color centers at room temperature, it is attracting increased interest in the fields of classical and quantum photonics. The waveguide structures were inscribed using a femtosecond Ti:sapphire laser system (Coherent Legend) with a central wavelength of 800 nm and pulse duration of about 120 fs at a repetition rate of 1 kHz. The laser beam was focused by a high numerical aperture microscope objective (NA=0.8) into a 300 \( \mu m \) thick polycrystalline diamond substrate in an absolute depth of 90 \( \mu m. \) We demonstrate waveguiding in the near-infrared telecommunication C-band for optimized processing parameters. The proposed approach combines the advantages of the versatile technique femtosecond laser lithography with the outstanding material properties of diamond enabling extended 3-dim integrated optical system based on diamond. Promising applications are on-chip diamond quantum photonics and the realization of high-quality single photon emitters.

9:45 AM EP09.10.06 Hydrogen-Terminated Diamond Field-Effect Transistor with YSZ Dielectric Layers Yanfeng Wang, Xiaohui Chang, Wei Wang, Dan Zhao, Jiao Fu and Hong-Xing Wang; Xi'an Jiaotong University, Xi'an, China.

Diamond exhibits many outstanding properties such as good light transmittance, effective resistance to radiation damage, large bandgap, high breakdown voltage, high thermal conductivity, high carrier mobilities, etc., making it having potential applications in the fields of wide range optical transparent window material, coating tools, especially in the field of electron devices which can work in high frequency, high power, high temperature as well as corrosive environment [1-2]. When diamond is treated by hydrogen plasma, a two dimensional hole gas (2DHG) layer will be formed under diamond surface with a sheet hole density of \( 10^{13} \) cm\(^{-2} \). However, this 2DHG layer is thermally and chemically unstable. In order to solve this problem, dielectric layer is often deposited on H-diamond surface in metal-oxide-semiconductor field effect transistor (MOSFET) field. Up to now, various dielectric layers have been used in H-diamond MOSFET such as SiO\(_2\), Al\(_2\)O\(_3\), HfO\(_2\), TaO\(_3\), and ZrO\(_2\), etc. Yttria-stabilized zirconia (YSZ) is an excellent dielectric material with high thermal stability, whose dielectric constant and band gap are 27 and 5 eV, respectively.

In this work, the investigation of H-diamond FETs with YSZ dielectric layer has been carried out. Firstly, gold electrodes were patterned on H-diamond by electron beam evaporation technique. Secondly, UV-ozone was used to insulate the device. Then, YSZ dielectric layer was deposited on p-type conduction channel by magnetron sputtering deposition technique. After that, Al gate was deposited on H-diamond by electron beam evaporation technique. The length and width of channel were 15 and 100 \( \mu m \), respectively. Finally, electrical properties of this H-diamond MOSFET had been investigated. The detail will be presented in the conference.

Diamond is considered as an attractive semiconductor to open up next-generation electronics based on its unique physical and electrical properties. For instance, the highest breakdown voltage among wide-band-gap semiconductors with high thermal conductivity and high saturation velocity potentially lead to a higher attainable power density. In addition, the excellent spin characteristics of nitrogen-vacancy complexes including long coherence time and optical initialization and read-out properties lead to a potential candidate for single photon source, magnetic sensors, and quantum applications. High quality single crystal diamond growth by plasma-enhanced CVD and precise control of impurity doping underlay the design of virtually all these applications. n-type Fermi controlling is still a challenging target, since diamond generally prefers to be p-type semiconductor even in an intrinsic diamond. Carbon vacancies including impurity-vacancy complexes are all acceptor-type defects that capture electrons. From the viewpoint of n-type semiconductor diamond, the suppression of these vacancies is one of the most important factors of Fermi controlling as well as suppression of boron acceptors. On the other hand, from the viewpoint of defect engineering, n-type donors can supply electrons to vacancy defects, leading to the stabilization of their charge states. Nitrogen-vacancy complexes have three charge states, and only NV- centers are required for quantum spin applications. In this presentation, we would like to discuss the engineering significance of n-type Fermi control from the viewpoints of following two targets. (1) Inversion channel control in diamond/AI2O3 configuration, (2) Phosphorus doping for charge-state control of nitrogen-vacancy complexes.

Acknowledgements: This work was supported by JSPS KAKENHI Grant Number JP17916364 and JP16776363 and Japan Science and Technology Agency (JST) CREST Grant Number JPMJCR1333 and JPMJCR1773, Japan.

11:00 AM EP09.11.02


Boron Nitride is a wide band gap semiconductor with cubic and hexagonal phases that are isoelectronic to diamond and graphite respectively. The cubic phase of boron nitride has similar structural, electronic, and thermal properties with diamond. These similarities enable an integrated device design that can operate under extreme conditions. We present an approach to deposit boron nitride, as a neutron conversion layer, on a PIN diamond alpha radiation detector. Using plasma enhanced chemical vapor deposition, boron nitride is deposited on polycrystalline and single crystal diamond, with and without a gold contact interlayer. By tuning the hydrogen to fluorine ratio during the deposition, we can control the equilibrium between etching and film formation. In situ X-ray photoelectron spectroscopy is used to characterize the sp2:sp3 bonding of the surface, as well as to calculate the growth, etching, and regrowth rates. Our current growth rate is ~1nm/min. The optimal thickness for the neutron conversion layer is 1 to 3µm, therefore we are working toward increasing this growth rate of boron nitride.

This research supported by ARPA-E through the SWITCHES program.

11:15 AM EP09.11.03

Chemical Vapor Deposited Diamond High Power Capacitors Jim J. Davidson1, David Kerns2, John Fraley2, Stephen Minden2 and Brett Sparkman2; 1Management, International FemtoScience Incorporated, Nashville, Tennessee, United States; 2Wolfspeed, A Cree Company, Fayetteville, Arkansas, United States.

Utilizing the known dielectric properties of undoped polycrystalline CVD diamond films of > 10e12ohm-cm, capacitor structures were created to examine, for example, the capacitance, charge storage density, leakage and breakdown properties of capacitors whose dielectric layer is commercially procured CVD diamond. This paper will describe the test capacitor created, the testing procedures, and the electrical and physical characterization of the diamond capacitors, “D-Caps”.

For power electronics and/or energy storage scenarios, a better capacitor structure, particularly as regards the quality and strength of the dielectric utilized in these capacitors needs to be improved. While high coulomb/ cm3 values are cited by, e.g., electrochemical and electrolytic ultracapacitor type capacitors, their high voltage limitations are disappointing, and by virtue of their fundamental makeup cannot be enhanced. There are advantages to having truly solid, planar (layered) type of capacitor structure, such as presently achieved with, for example, ceramic type capacitors. There have been laboratory tests of the dielectric strength/ voltage breakdown characteristics of diamond layers – and those values (circa > 3(10e7) V/cm) are impressive - but no practical examination for capacitor applications derived directly from commercially deposited polycrystalline diamond films has been performed. This paper takes commercially procured undoped polycrystalline diamond films and fabricates them into practical conductor/diamond/conductor layered capacitor structures and examines their electrical behavior and their potential [figuratively and literally] for utilization as industrial capacitors for power or energy storage. MDM (metal/diamond/metal) layers, typically 1 to a few microns in thickness, were examined by SEM, Xray and Raman spectroscopy topologically and in cross-section. Aspects of multilayer “comb” type interlayer (“MDMDM” structures) were considered.

We will report pertinent electrical and physical characterization properties of planar diamond dielectric based capacitor test structures, including leakage characteristics, breakdown behavior, statistical distribution of yield and routes to practical packaging and applications.

Nitrogen and Oxygen-Terminated Diamond Electrolyte Solution-Gate FET for pH Sensing in Both Acidic and Alkaline Solutions in pH Solutions

Yu Hao Chang1, Shaili Falina1, Sora Kawai1, Mohd Syamsul1, Yutaro Iyama1, Yukihiko Shintani2 and Hiroshi Kawarada1, 2; 1Waseda University, Tokyo, Japan; 2Kagami Memorial Research Institute for Material Science and Technology, Tokyo, Japan.

We investigated pH sensitivity of nitrogen and oxygen-terminated diamond electrolyte solution-gate field effect transistors (SGFETs). Diamond has many appealing properties including chemical inertness, biocompatibility, and simple chemical modification on the surface that are suitable for pH sensing in SGFETs. Since 2001, we have reported diamond SGFETs where the semiconductor surface was directly immersed in electrolyte solution and the drain current was controlled by electric double layer at the diamond surface [1]. We conducted H-termination on diamond surface to obtain surface p-type conductivity and introduced O-termination to acquire pH sensitivity [2]. Amine-terminated diamond SGFETs has a pH sensitivity of 50 mV/pH; the amine termination was achieved by UV radiation treatment in NH3 atmosphere [3]. In recent research, N-termination can be achieved on diamond surface by nitrogen radical exposure with remote RF plasma [4]. In this work, we continued to utilize nitrogen and oxygen-termination on diamond SGFETs for pH sensing in both acidic and alkaline solutions as illustrated in Dr. Shaili Falina’s research [5], and increased coverage rate of N-terminated surfaces to optimize pH sensitivity.

Polycrystalline diamond surface was first hydrogenated by plasma treatment under hydrogen atmosphere. At room temperature, H-terminated diamond surface exhibited sheet resistance of 20-60 kΩ/sq and a high carrier density at 10^19 cm^-2. Source and drain electrodes were then formed with Au, connected with wires by conductive paste and sealed with epoxy resin to prevent leakage in pH solutions. The resulting channel length and width was 0.33 mm and 5.0 mm, respectively. As opposed to U/V ozone treatment, anodic oxidation was conducted to achieve O-termination [6]; the channel of diamond surface is applied up to 1.6 V while the Ag/AgCl reference electrode was grounded. Finally, N-termination was conducted by means of remote RF plasma at 300 W with nitrogen gas containing 4% hydrogen gas as radical source for 20 minutes. I_D-S-V_Ds characteristics and pH sensitivity were procured by Keithley Instrument source-measure unit from pH 2-12.

As a result, nitrogen and oxygen-termination on diamond SGFETs showed increased pH sensitivity compared with only O-termination in both acidic and alkaline solutions. While further investigation regarding the effect of N-terminated surface coverage rate in pH solution is required, by increasing the coverage rate of N-terminated surface, we suspect an enhancement in pH sensitivity of the device.


11:45 AM EP09.11.05

Electrical Properties of CMP Treated 1 inch Heteroepitaxial Diamond Substrates Seongwoo Kim1, Yuki Kawamata1, Yutaka Kimura1, Kokichi Fujita1, Kenjiro Ikejiri1 and Makoto Kasu1; 1Adamant Namiki Precision Jewel Co., Ltd., Tokyo, Japan; 2Saga University, SAGA, Japan.

Mass production technologies of CMP treated substrate are important to accelerate research and development activities of diamond semiconductor. Although there still exists some challenges, such as large substrate, high crystallinity and surface finishing, most of research resources are devoted to achieve high crystallinity. In order to overcome the other two tasks, we have developed heteroepitaxial diamond growth method and Chemical Mechanical Planarization (CMP) technologies.

Heteroepitaxial diamond growth method has a great potential to obtain a large diamond substrate compared to other growth methods. Because of the difference in the coefficient of thermal expansion between diamond and basal substrate material, crack and random delamination are generated in diamond film during the cooling down process. We have previously reported in details the fabrication of the freestanding heteroepitaxial diamond substrate via microneedles that prevent the crack generation and the delamination11. Following this technique, a diamond substrate with 1 inch diameter was successfully achieved. In order to demonstrate larger than 1 inch diameter diamond substrate, it is necessary to change the basal substrate material because of two reasons: (1) the diameter of the commercially available MgO substrate is limited to 1 inch. (2) MgO substrate cost exponentially increases with diameter. One of the most promising materials to replace MgO is sapphire. The crystal system of sapphire (hexagonal) is different from that of diamond and iridium (Cubic), whereas sapphire substrate is chemically inert, 8 inch substrate available and much cheaper than MgO. Therefore, standard hetero-epitaxial diamond growth procedure on MgO substrate was applied to the A-plane sapphire substrate with 10 mm × 10 mm square surface. The grown crystal was obtained without any cracks and breakage. The obtained thickness is 800 µm. As a result of X-Ray Rocking Curve measurement, crystallinities of both (400) and (311) planes were better than that achieved diamond grown on MgO substrate. Furthermore, 1 inch heteroepitaxial diamond substrate was successfully demonstrated on sapphire.

Surface finishing is important to obtain the best performance of a substrate. In the case of conventional semiconductor substrate, CMP is applied as a surface finishing technology. The influence of CMP treatment on heteroepitaxial diamond was investigated by MOSFET characteristics. The heteroepitaxial diamond substrates were all the same thickness, off angle and surface roughness by mechanical polishing. CMP was applied after mechanical polishing. MOSFET was fabricated on the heteroepitaxial diamond substrate with and without CMP. We found that the Id-Vd characteristics of MOSFET on CMP treated substrate is better than that without CMP. The details will be discussed at the symposium.

1) H. Aida et al., Appl. Phys. Express 9, 035504 (2016)
intermediate transformation of solar energy to electrical energy. In general, the photocatalytic transformation of carbon-based starting materials is attractive as such reactions environmentally friendly and can be carried out under mild conditions. Diamond is an attractive material for the photocatalytic transformations due to its unique electronic properties, e.g. the reduction of carbon dioxide. So far, the excitation of electrons into the conduction band requires UV light due to the large bandgap. Therefore, for the ability to use visible light, the introduction of unoccupied states in the band gap of diamond is a requirement to overcome this limitation. In this work we report our results on the photocatalytic activity of differently terminated and functionalized diamond materials. This includes not only direct interaction with suitable surface atoms but also the immobilization of transition metal complexes using different linker strategies. We were able to demonstrate the direct use of visible light for the transformation of CO₂ into methanol and formate and will discuss the influence of different parameters such as the medium, surface structure and type of diamond on the efficiency of the photocatalytic process. This project has received funding from the European Union's Horizon 2020 Program under Grant Agreement no. 665085 (DIACAT).

References

2:00 PM EP09.12.02
Tunable Nanodiamond Surfaces using Silica-based Chemistry for Functionalization and Bioimaging
Pomakaimaikalani Yamaguchi¹, Perla J. Sandoval¹, Karen Lopez⁵, Anissa A. Len¹, Andres Arreola¹, Virginia Altoe⁶, Dennis Nordlund⁷ and Abraham Wolcott¹; ¹San Jose State University, San Jose, California, United States; ²The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³SLAC National Accelerator Laboratory, Menlo Park, California, United States.

The interest in high-pressure high-temperature (HPHT) fluorescent nanodiamonds (FNDs) as an emerging probe for biosensing results from the unique photophysics of the nitrogen vacancy center (NVC). NVCs detect magnetic fields, electric fields, and may be realized as pH or voltage sensors. Attractive characteristics of the biosensing include their lack of cytotoxicity, infrared emission (575-800 nm) and long term photo-stability make FNDs an ideal bio-labeling tool. Challenges in modifying the inert diamond surface limit their development as a biological probe in cells and tissues. The synthesis of a silica shell using wet chemistry techniques encapsulating the FNDs allows for further functionalization and control of shape specific properties. Silica priming of the diamond surface proceeds by nucleophilic attack of the tetrahydroxysilane precursors forming a silyl ether bond (C-O-Si-OH) to the diamond surface. A realization of 2-20 nm thick shells of SiO₂ was achieved through variations in synthesis time and particle size analysis was conducted through DLS, SEM, and TEM. Molecular functionalization of polyethylene glycol (PEG) moieties onto the silica shell stabilizes the FNDs colloidal in biological environments while amine and sulfyl-hydryl moieties act as anchors for folic acid decoration. Other functionalization techniques employed include the use of 11-azido1undecyltrimethoxysilane, (3-Glycidoxypropyl)trimethoxysilane, (3,3,3-trifluoropropyl)-trimethoxysilane, carboxylic acid, and phosphonate moieties. Functionalization was verified through FTIR and synchrotron based X-ray techniques (XAS and XPS). We also demonstrated optimized targeted staining of unpegulated folate receptors in HeLa cells cultures. This work provides a wide range of surface and morphological tunability that can be used in magnetometry and electric field sensing applications.

2:15 PM EP09.12.03
Stable Ag-Diamond Core-Shell Nanostructures with Tunable Optical Properties
Shuo Li and Robert J. Hamers; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Diamond is widely used in many applications like coatings, optical lenses & windows, high power laser optics, photocatalysts and imaging fields. Tuning the optical properties of diamond is needed for wider applications. However, diamond is a large bandgap material and is highly transparent from deep UV to infrared light across the electromagnetic spectrum, limiting its applications. Previously people use doping method by introducing impurities like nitrogen or boron into diamond crystal lattices, creating defect states which absorb visible light and generate colors. However, there are only limited choices of elements available to serve as donors, limiting the tunability of diamond optical properties. Moreover, the introduction of impurities would often result in the degradation of diamond quality. Plasmonic metal nanoparticles are highly efficient at absorbing and scattering light at certain wavelengths, and they exhibit size- and shape-dependent plasmonic features in a wide region of the spectrum. Therefore, by integrating metal nanoparticles like Ag into diamond would provide an alternative approach to tune the diamond’s optical properties in a more controllable way. Previous reports have shown the incorporation of Ag nanostructures with diamond would enhance the optical properties of diamond. Whereas for as-reported Ag-diamond hybrids, the Ag are exposed to the environment, which makes the structures not stable; the tunability of Ag plasmonic properties also needs to be increased.

Here we demonstrate a stable Ag-diamond core-shell structure can be made, in which the Ag core sizes and diamond shell thicknesses can be controlled precisely, resulting in the tunable optical properties of diamond. As Ag is embedded in diamond shells, this hybrid material has superior stability that can maintain the structure and properties even after high temperature annealing or acid boiling treatment. The Ag nanoparticles embedded within diamond films are grown by a three-step process: (1) a very thin film of Ag is deposited onto a diamond surface, (2) the Ag film is de-wetted into individual nanoparticles, and (3) a second diamond film is grown to encapsulate the Ag nanoparticles. Cross-sectional SEM clearly shows individual nanoparticles with sizes ranging from ~10 nm to 500 nm depending on experimental conditions. UV-vis spectra clearly show the plasmonic peaks in good correspondence of SEM. TEM analyses show the boundary between the diamond-Ag nanostructures, as well as the columnar growth of diamond extending radially from the Ag nanoparticle cores. We show that the unique Ag-diamond core-shell structure with great stability is a promising platform for diamond with tunable optical properties in various applications.

2:30 PM EP09.12.04
Black Diamond as an Antibacterial Surface—Interplay Between Chemical and Mechanical Bactericidal Activity
Paul W. May², Olivia Dunseath², Ed J. Smith¹, Tarik Al-Jeda², James A. Smith³, Angela Nobles¹, Gavin Hazell¹ and Colin C. Welch²; ¹Dental School, University of Bristol, BRISTOL, United Kingdom; ²School of Chemistry, University of Bristol, Bristol, United Kingdom; ³Plasma Technology, Oxford Instruments, Bristol, United Kingdom.

‘Black silicon’ (Si₃) samples with surfaces covered in nanoneedles of length ~5 μm were fabricated using a plasma etching process and then coated with a conformal uniform layer of diamond using hot filament chemical vapour deposition to produce ‘black diamond’ (BD) nanostructures. The diamond needles were then chemically terminated with H, O, NH₃, or F using plasma treatment, and the hydrophilicity of the resulting surfaces were assessed using water droplet contact-angle measurements. The effectiveness of these differently terminated BD needles in killing the Gram-negative bacterium E. coli was semi-quantified by Live/Dead staining and fluorescence microscopy, and visualised by SEM. The total number of adhered bacteria was consistent for all the nanostructured BD surfaces at around 50% of the value for the flat diamond control. This, combined with a chemical bactericidal effect of 20-30%, shows that the nanostructured BD surfaces supported significantly fewer viable E. coli than the flat controls. The BD surfaces were particularly effective at preventing the establishment of bacterial aggregates – a precursor to biofilm formation. The percentage of dead bacteria also decreased slightly as a function of hydrophilicity, with superhydrophobic F-terminated BD killing 50% of the adherent bacteria. These results are consistent with a predominantly mechanical mechanism for bacteria death based on the stretching and disruption of the cell membrane, combined with a smaller additional effect from the chemical nature of the surface.
Production and Manipulation of Diamond Nanoparticles

Laia Gines, Soumen Mandal and Oliver A. Williams; Cardiff University, Cardiff, United Kingdom.

The production of diamond nanoparticles containing colour centres has attracted increasingly interest in the last years for quantum computation applications. Particularly, the SiV colour centre has highlighted as a promising photon source among other colour centres in diamond, due to its interesting optical properties at room temperature. SiV colour centres acting as single photon emitters can be created through different approaches in-situ during CVD growth by introducing silicon as a solid source or in a gas phase.

In this work diamond nanoparticles with custom colour centres were produced from bulk material via milling strategies. First a diamond film containing NV/SiV centres was grown onto a passive substrate, followed by sacrificial etching of the substrate. The resulting diamond film was milled using a planetary mill based on either steel or SiN. The milled material was purified by acid reflux. To measure particle sizes, different slurries containing the diamond nanoparticles obtained were prepared and characterized by using Dynamic Light Scattering (DLS) and Nanoparticle Tracking Analysis (NTA). XPS was also used to qualify the milling process contamination. Colour centre incorporation was confirmed by Photoluminescence and Hanbury Brown and Twiss measurements. The control of surface sp3 and sp2 potential will also be demonstrated.

Applied Particulate Nanodiamond to Enhance Thermal and Mechanical Properties of Host Systems

Jim I. Davidson1, David Kerns2, Blake Branson1, Ethan Langone1, Farzin Mashahi2, Wayne Johnson1, Lino Costa1 and Kathleen Lansford1; 1FemtoSci Incorporated, Nashville, Tennessee, United States; 2Tennessee Technological University, Cookeville, Tennessee, United States; 3University of Tennessee Space Institute, Tullahoma, Tennessee, United States.

Conventional heat transfer fluids such as water, ethylene glycol, mineral oils and their mixtures are presently significantly compromised for their fundamental objective, cooling the heat generating system, because their inherent thermal conductivity is poor. Likewise, the inherent strength of, for example, polymer based solid systems could be enhanced by the addition of nanoparticles that improve bonding at the molecular level. In this paper, particulate nanodiamond, ND, ['detonation' nanodiamond] is examined as a low concentration additive to liquid and solid systems to enhance, e.g., their thermal conductivity and strength.

The criticality of sufficient deaggregation and compatible functionalization chemistry to successful outcomes will be addressed. We have prepared different functionalized nanodiamond, FND, samples, where the functional group is specifically intended to have its terminal chemical bonding couple with the host matrix resulting in their operating improvement. Because the effective diameters of molecular influence of the attached functional groups in the host matrix can be much greater than the 5 nanometers of the “core” ND, concentrations in the range of ppm of the FND can result in double digit improvements of key properties.

Examples of these FND applications will be presented, such as, many cooling loop systems, be they for electronic or engines, are water based. We have examined a FND formulation and evaluated it as an additive in a precisely controlled and monitored water cooling loop which allows the direct determination of the heat transfer coefficient, a more practical parameter than thermal conductivity, and an improvement of over 20% was observed at a FND concentration of 500ppm.

Further, an appropriate FND formulation to enhance the polymers used in composites was applied and improvement in the flexural strength was observed. Tensile strength testing of ox-ND/PAN (highly de-aggregated nanodiamond (ND) polyacrylonitrile (PAN)) and ox-UDD/PAN (aggregated ultra-dispersed (UDD) polyacrylonitrile (PAN)) thick-film composites was performed. Elastic modulus, tensile strength, and elongation measurements of these solid polymer samples as a function of ND addition were measured. The more highly dispersed de-aggregated ox-ND is more effective as a reinforcement additive than aggregated ox-UDD while the as-received UDD/PAN composite samples, having very poor dispersion characteristics [a configuration often examined and reported in none ND evaluations], exhibit tensile strengths even lower than those measured for pure PAN control films. The results of this work demonstrate the elastic modulus and tensile strength of de-aggregated ox-ND/PAN composites outperform those of aggregated ox-UDD/PAN composites at all additive concentrations above ~ 3 vol.%. At 10 vol.% ox-ND loading, elastic modulus is enhanced by nearly 80% and tensile strength increases by nearly 60% relative to pure PAN films.

Neural Adhesion on Diamond—Competition Between Polymer Treatment and Surface Morphology

Barbora Jakubcova1, Andrew Taylor3, Pavel Hubik1, Vaclav Petrak1 and Vladimir Petrakova1, 2; 1Institut for Experimental Physics, Freie Universitaet Berlin, Berlin, Germany; 2Faculty of Biomedical Engineering, Czech Technical University in Prague, Kládno, Czechia; 3Institute of Physics, The Czech Academy of Sciences, Prague, Czechia.

The ability to form an efficient interface between material and neural cells is a crucial aspect for construction of neuroelectrodes. Diamond offers material characteristics that could, to a large extent, improve the performance of neuroelectrodes. The greatest advantage of diamond is a large variety of material and surface properties such as electrical conductivity, surface morphology, and surface chemistry. Such a variety of material characteristics can lead to various cellular responses. Here we compare survival, adhesion, and neurite formation of primary neurons on diamond thin films of various morphologies and treatments with several types of polymers commonly used to enhance cell adhesion. We found that the variation of surface roughness of
High Self-Nucleation for Continuous Nano-Diamond Film Growth on Silicon Substrate

The nucleation occurs on the β-SiC intermediate layer (several nm) at high temperatures, when the carbon concentration on the substrate surface reaches its saturated value. The nucleation densities can then be enhanced by one to two orders, but this value is still far below the number suppression of carriers generated from sp² bonds, which contribute heat transport, and the existence of hydrogen atoms at grain boundaries in the hydrogenated film.

It was experimentally demonstrated that the thermal conductivity of UNCD/a-C:H films is strongly dependent on the grain size. The grain size dependent of thermal conductivity of diamond has been mainly studied for chemical vapor deposition (CVD), and it has been reported that thermal conductivity is strongly depends on the intrinsic properties of grain boundaries. Recently we have realized the formation of UNCD/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films by coaxial arc plasma deposition (CAPD), which is a kind of physical vapor deposition. Note that CAPD does not necessarily require a hydrogen atmosphere during the deposition for the formation of diamond grains, in other words, UNCD/non-hydrogenated amorphous carbon (a-C) composite (UNCD/a-C) films can be grown under a base pressure. So far, hydrogenation effects on the thermal conductivity of UNCD/a-C:H films has never been studied because H atoms are unintentionally incorporated into the films from source gases in CVD. In this study, UNCD/a-C and UNCD/a-C:H films were deposited under a base pressure and in hydrogen atmospheres, and the hydrogenation effects on the interfacial thermal conductance at grain boundaries were studied.

UNCD/a-C:H and UNCD/a-C films were deposited on Si substrates at a substrate temperature of 550 °C by coaxial arc plasma deposition (CAPD) using a coaxial arc plasma gun equipped with a graphite target. Al films were deposited on the UNCD/a-C:H films by sputtering for the time-domain thermoreflectance (TDTTR) measurement. From the TDTTR measurement, the thermal conductivities of the non-hydrogenated and hydrogenated films were estimated to be 7.80 and 2.32 W/(m K), respectively, which are larger than those of a-C:H and a-C films, respectively. It might because of the existence of diamond crystallites in our films. As reasons for the small interfacial conductance value of the hydrogenated film as compared with that of the non-hydrogenated film, we consider that the number suppression of carriers generated from sp² bonds, which contribute heat transport, and the existence of hydrogen atoms at grain boundaries in the hydrogenated films that enhance from phonon scattering.

It was experimentally demonstrated that the thermal conductivity of UNCD/a-C:H films sensitively decreases by hydrogenation, in other words, the thermal conductivity of UNCD/a-C:H films is controllable with hydrogenation.

High Self-Nucleation for Continuous Nano-Diamond Film Growth on Silicon Substrate

Continuous diamond films grown on heterostructures are required for current technological applications, such as heat dissipation, nano/micro-electromechanical systems and even future potential many optic-electronic devices. Growth of thin coalesced diamond layers requires a very high density of nucleation sites (typically 10¹⁵ cm⁻²). However, very low nucleation densities (typically below 10¹⁵ cm⁻²) are obtained on non-treated substrates due to the high surface energy of diamond relative to heterostructures. Seeding process or surface pretreatment is believed to be the best choices to provide stable diamond seeds or nuclei for subsequent diamond CVD growth, but surface damage (microscopic defects or scratches) caused during seeding or pretreatment process has hindered its application on future potential optic-electronic devices. A promising alternative is to develop a high self-nucleation method for subsequent diamond growth on non-diamond surfaces.

It is a generally accepted fact, that the primary process responsible for diamond nuclei formation is heterogeneous nucleation on the substrate surface. In the case of Si substrates, the nucleation occurs on the β-SiC intermediate layer (several nm) at high temperatures, when the carbon concentration on the substrate surface reaches its saturated value. The nucleation densities can then be enhanced by one to two orders, but this value is still far below the minimum requirements for subsequent continuous film growth.

In this presentation, we will report our recent observations on high self-nucleation of continuous thin nano-diamond films growth on silicon substrate. The effect of the substrate orientation and seeding process will be compared. The possible cause for such self-nucleation phenomenon will be investigated and discussed.
Mechanism of High Ionic Conduction Paths in Composite Solid Electrolyte

Feifei Shi and Yi Cui; Material Science and Engineering, Stanford University, Stanford, California, United States.

As one of the most promising next-generation batteries, all-solid-state lithium battery is well known for its superior advantage of high energy density and nonflammability, as well as its intrinsic drawback poor ionic conductivity of solid electrolyte. Therefore, it is crucial to understand the ion conduction mechanism in solid electrolyte for optimized design to enhance ionic conductivity. Recently, composite solid electrolyte with aligned interface has been reported to achieve one order of magnitude enhancement on ionic conductivity. However, the mechanism accounting for the enhanced ionic conductivity at solid/solid interfaces remains unclear.

Here we unveil the diffusion path of the lithium in the composite electrolyte by tracking labeled lithium isotope, characterizing polymer crystal structure with both hard and soft X-ray diffraction, and mapping the electronic structure of lithium by electron spectroscopy. Further understanding of the correlation between interface structure and ion conduction mechanism has been obtained, which enables new solid electrolyte design with better ionic conductivity.

Acknowledgement:
The work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy under the Battery 500 Consortium program.

State-of-Charge-Dependent Space-Charge-Layer Formation in Solid-State Batteries

Michael W. Swift and Yue Qi; Michigan State University, East Lansing, Michigan, United States.

As all-solid-state lithium ion batteries develop as an alternative to traditional liquid-electrolyte cells, a thorough theoretical understanding of the driving forces behind battery operation is needed. We present a model of potential profiles in a generic all-solid-state battery, and apply the model to the Li/LiPON/Li$_x$CoO$_2$ system. The potentials yield valuable information about lithium distribution and transport, including the nature of electrical double layers which form at interfaces. The results suggest design rules to minimize interfacial lithium barriers and optimize device performance.

Mapping LLZO Grains and Grain Boundaries Through a Simple Thermal Etching Technique

Masumi Sato, Regina Garcia-Mendez and Jeff Sakamoto; University of Michigan, Ann Arbor, Michigan, United States.

LLZO is one of the most promising solid-state electrolytes due to its electrochemical and chemical stability against metallic Li and high ionic conductivity (1 mS cm$^{-1}$) at room temperature. However, it has been reported that Li metal still propagates along LLZO grain boundaries above a critical current density (CCD) (1).

It is known that the chemistry of grain boundaries and grains are typically different. In this study, we assume the same is true for polycrystalline LLZO. We hypothesize that grain boundaries etch faster than grains, thus enabling a technique to visualize and study the microstructure of LLZO. The proposed technique does not requiring extensive sample preparation such as what is required for electron backscattering diffraction (EBSD). Variables such as temperature, dwell time, atmosphere and flow rate were tuned to optimize the thermal etching method while maintaining phase purity, e.g., not decomposing LLZO grains.

AI-LLZO pellets were densified by rapid induction hot pressing, followed by grinding and polishing. Surface heat treatment was conducted to reduce the concentration of Li$_2$CO$_3$ and LiOH layers that readily form after LLZO is exposed to air (2) before thermal etching. Scanning Electron Microscope (SEM) was used to see the grain boundaries and determine the grain size of the surface of the thermal etched LLZO pellets and X-Ray Diffraction to analyze phase purity. EBSD was conducted to confirm that the features observed in thermally etched LLZO surface correspond to grain boundaries. Additionally, TGA-Mass Spectrometry was used to correlate the mass loss to the chemistry of the volatilized compounds during thermal etching of LLZO. Furthermore, Electrochemical Impedance Spectroscopy (EIS) measurements were conducted to evaluate that the ionic conductivity of LLZO remains unchanged after completing the thermal etching process.

It is believed that the thermal etching method developed and optimized in this work can be used as a simple technique to examine the microstructure of LLZO and perhaps other polycrystalline electrolytes.
Solid state electrolytes are currently being intensively investigated for the possible application in solid-state batteries. Among all known solid Li+ conductors, Li10GeP2S12 (LGPS) is one of the most promising candidates due to its unrivaled high ionic conductivity of 12 mScm−1 and successful implementation into solid state batteries. Therefore, there is a great interest to further optimize the Li+ mobility and to reduce the costly germanium content using different doping strategies in related structures. Unfortunately, increasing the Sn fraction in Li10Ge1−xSnxP2S12 leads – counter to chemical intuition – to a reduction in the ionic conductivity.

The present work reveals the structural and lattice dynamical reasons for the observed behavior. Solid solutions of Li10Ge1−xSnxP2S12 were synthesized and structural changes and their resulting impacts on the Li+ transport property were investigated using a combination of structural refinements, ultrasonic speed-of-sound measurements and AC impedance spectroscopy. It is shown that while the lattice volume and the c/a ratio of the compounds increase with increasing Sn4+ fraction, the ionic conductivity decreases. Taking a deeper look into the local bonding properties reveals that a bottleneck of the diffusion channels along the z-direction tightens. In addition, a softening of the lattice with the more polarizable Sn4+ cation was observed similar to other classes of lithium and sodium thiophosphate solid electrolytes. But in this case the softening of the anion backbone leads to stronger Li+ − S2− Coulombic interactions, that can be understood with the concept of inductive effects. Overall this work demonstrates, that chemical intuition can struggle in the understanding of structure property relationships and that a deeper look into the local bonding properties is necessary for the future design of solid electrolytes.
Solid polymer electrolyte has excellent processability although its ionic conductivity and mechanical strength needs to be improved. Here I will present our recent progress on nanoscale design of using nanomaterials to form composite polymer electrolyte to improve both ionic conductivity and mechanical strength. Nanomaterials include nanowires and porous anodized alumina. Organic-organic composite electrolyte is also explored. We use successfully these solid electrolytes for Li metal batteries.

11:00 AM ET01.01.08
Fabrication of Advanced Composite Cathodes in All-Solid-State Batteries Using 3D Reconstruction Analysis and Complementary Wet-Based Process Sangjun Choi, Wo Dum Jung, Minjae Jeon, Seong-Min Kim, Ji-Su Kim, Byung-Kook Kim, Byoung-In Sang and Hyoungchul Kim; 1High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Department of Chemical Engineering, Hanyang University, Seoul, Korea (the Republic of).

Next-generation Li-ion battery (LIB) applications such as electric vehicles, unmanned aerial vehicles, energy storage systems, and integrated power devices for the Internet of Things require the development of technologies that allow the storage of electrical energy at safer and higher energy densities over a wider range of operating temperatures. In this context, all-solid-state battery (ASSB) technologies have the advantage of eliminating the organic electrolyte from the existing secondary battery in addition to incorporating solid-state materials for all components, thereby meeting all requirements for next-generation LIB applications. The composite cathode of an ASSB composed of various solid-state components (i.e., the active material, electrolyte, conductive additive, and etc.) requires a dense microstructure and highly-percolated solid-state interface different from that of a conventional liquid-electrolyte-based Li-ion battery. Indeed, the preparation of such a system is particularly challenging.

In this study, quantitative analyses of composite cathodes by three-dimensional (3D) reconstruction analysis were performed beyond the existing qualitative analysis, and their microstructures and reaction interfaces were successfully analyzed. Interestingly, various quantitative values of structure properties (such as the volume ratio, connectivity, tortuosity, and pore formation) associated with material optimization and process development were predicted, and they were found to result in limited electrochemical charge/discharge performances. We also verified that the effective two-phase boundaries (TPBs) were significantly suppressed to ~23% of the total TPB, due to component dispersion and packing issues. In addition, we have developed a pore decomposition process (PDP) that tracks the origins of pore structures using quantitative values of a 3D reconstruction structure. The solid electrolyte and cathode active material showed a noticeable difference in the ratio of induced pore volume: 43% of the total pore from solid electrolyte and 56% from active material. To solve the observed problems such as formation of pores, we adopted a wet-synthesis process of sulfide solid electrolyte on fabricating composite cathode. The introduction of a new wet-based solid electrolyte improved the microstructure of the composite cathode by eliminating pores, increasing interfacial contact area, and mitigating inhomogeneous mixing. Therefore, the enhanced microstructure provide a better ionic conduction pathway, resulting in higher electrochemical cell performance. The pore formation, the powder characterstics, and the process optimization of composite cathode are closely related, and the quantitative analysis results from 3D reconstruction process provide relevant insights.

11:15 AM ET01.01.09
Effect of Microstructure on the Critical Current of Li7La3Zr2O12 Jeff Wolfenstine; Army Research Laboratory, Adelphi, Maryland, United States.

Li-ion conducting solid-state batteries based on a Li7La3Zr2O12 (LLZO) solid-state electrolyte combined with a Li-metal anode have attracted considerable attention because they offer the advantages of higher energy and enhanced safety compared to the current Li-ion batteries. One of the major issues the with Li/LLZO system is determining what LLZO microstructural variables influence the critical current (current at which lithium dendrites/filaments form on charging). For a single-phase material the major microstructural variables are porosity and grain size. For a solid-state electrolyte a high relative density is required thus, the major microstructural variable is the grain size. It is the purpose of this presentation to discuss the effect of grain size (5 to 600 mm) on the room temperature critical current of LLZO and by examining the effect of grain size on ionic conductivity and fracture toughness and determine which of these properties has a major influence on the critical current for hot-pressed high relative density (>97%) Li7La3Zr2O12.

11:30 AM ET01.01.10
Phase-Field Simulations of Lithium Dendrite Growth with Open-Source Software Zijian Hong and Venkatasubramanian Viswanathan; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Dendrite growth is a long-standing challenge that has limited the applications of rechargeable lithium metal electrodes. Here, we have developed a grand potential based nonlinear phase-field model to study the electrodeposition of lithium as relevant for a lithium metal anode, using open-source software package MOOSE. The dynamic morphological evolution under large/small overpotential is studied in 2-dimensions, revealing important dendrite growth/stable deposition patterns. The corresponding temporal-spatial distributions of ion concentration, overpotential and driving force are studied, which demonstrate an intimate, dynamic competition between ion transport and electrochemical reactions, resulting in vastly different growth patterns. Given the importance of morphological evolution for lithium metal electrodes, wide-spread applications of phase-field models have been limited in part due to in-house or proprietary software. In order to spur growth of this field, we utilize an open-source software package and make all files free available online to enable future studies to study the many unsolved aspects related to morphology evolution for lithium metal electrodes.

11:45 AM ET01.01.11
Crosslinked Poly(tetrahydrofuran) as a Loosely-Coordinating Solid Polymer Electrolyte David Mackanic1, Yi Cui2 and Zhenan Bao3; 1Chemical Engineering, Stanford University, Stanford, California, United States, 2Materials Science and Engineering, Stanford University, Stanford, California, United States.

Solid polymer electrolytes (SPEs) promise to improve the safety and performance of lithium ion batteries (LIBs). However, the low ionic conductivity and transference number of conventional poly(ethylene oxide) (PEO) based SPEs preclude their widespread implementation. Herein, we introduce crosslinked poly(tetrahydrofuran) (xPTHF) as a promising polymer matrix for "beyond PEO" SPEs. The crosslinking procedure creates thermally stable, mechanically robust membranes for use in LIBs. Molecular Dynamics and Density Functional Theory (DFT) simulations accompanied by Li NMR measurements show that the lower spatial concentration of oxygen atoms in the xPTHF backbone leads to loosened O-Li+ coordination. This weakened interaction enhances ion transport; xPTHF has a high lithium transference number of 0.53 and higher lithium conductivity than a xPEO SPE of the same length at room temperature. We demonstrate that organic additives further weaken the O-Li+ interaction, enabling room temperature ionic conductivity of 1.2*10^-4 S cm^-1 with 18 wt. % DMF in xPTHF. In a solid state LIB application, neat xPTHF SPEs cycle with near theoretical capacity for 100 cycles at 70 °C, with rate capability up to 1C. The plasticized xPTHF SPEs operate at room temperature while maintaining respectable rate capability and capacity. The novel PTHF system
Despite their high energy density, Li metal anodes have not been successfully commercialized due to dendritic Li plating during charging. However, recent developments in Li-ion conducting solid electrolytes have rekindled interest in the use of Li metal anodes. In particular, sulfide solid electrolytes (SSEs) are attractive materials due to their high ionic conductivities, low grain boundary resistance, and mechanical strength. However, SSEs are readily reduced by Li metal, calling into question their viability. Here, the interfacial stability between SSE and Li metal anodes is investigated computationally using the concept of band edge alignment. First-principles calculations were performed using many body perturbation theory to evaluate the position of the conduction band minimum (CBM) in various SSEs. These levels are compared with the Li/Li' electrochemical potential in order to evaluate the likelihood charge injection (i.e., reduction) from Li anodes. Our calculations reveal that reduction by Li is preferred for Li10GeP2S12, Li10SnP2S12, Li3PS4, Li4GeS4, and Li,S2O6. Although the position of the CBM is sensitive to the surface features of the SSE, varying the surface composition appears to be insufficient to prevent reduction. In addition to predicting CBM positions, the full band gaps of several SSEs were evaluated. Band gap values range from 4.0 eV in Li10SnP2S12 to 4.8 eV in LiPSs. Finally, we discuss the implications of our findings for interfacial reactions between SSEs and Li metal.

2.30 PM ET01.02.04
Epitaxial Li3Ti5O12 Thin Film as Model System for Li-Ion Conductivity

Francesco Pagani1,2, Evelyn Stilp1, Reto Pfanninger3, Eduard Cuervo Reyes1, Arnold Lemaitre1, Zoljan Balogh-Michels1, Antonio Neels1, Jordi Sastre Pellicer1, Michael Stiefel1, Max Dobelt2, Marta D. Rossell1, Rolf Enz1, Jennifer L. Rupp1, and Corsin Battaglia1
1Empa–Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; 2Electrochemical Materials, ETH Zürich, Zürich, Switzerland; 3Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Ion Beam Physics, ETH Zürich, Zürich, Switzerland.

Thin-film all-solid-state batteries provide a model system for the fundamental study of Li-ion transport, defect chemistry [1], and electrochemical stability [2] and find applications in smart cards, sensors, and radio-frequency identification tags [3]. Here we compare the Li-ion conductivity of epitaxial and polycrystalline Li3Ti5O12 thin films (≈ 125 nm thick) and investigate the impact of grain boundaries on Li-ion conductivity. Phase-pure epitaxial and polycrystalline Li3Ti5O12 thin films were grown on MgO(111), MgO(001), and MgO(100). In our calculations, the Li+ transport in Li3Ti5O12 is found to be suppressed compared to Li metal. Our calculations reveal that reduction by Li is preferred for Li10GeP2S12, Li10SnP2S12, Li3PS4, Li4GeS4, and Li,S2O6. Although the position of the CBM is sensitive to the surface features of the SSE, varying the surface composition appears to be insufficient to prevent reduction. In addition to predicting CBM positions, the full band gaps of several SSEs were evaluated. Band gap values range from 4.0 eV in Li10SnP2S12 to 4.8 eV in LiPSs. Finally, we discuss the implications of our findings for interfacial reactions between SSEs and Li metal.

References:
Electrochemical energy storage devices have attracted wide attention for energy conversion and storage. Over the past several decades, the success of the lithium-ion batteries (LIBs) has triggered the revolution of personal electronics and significantly changed our lifestyle. However, further progress in battery technology is still needed and great efforts are devoted to improve energy density, cycle life, cost and safety.

Among various kinds of rechargeable batteries for future applications, the all-solid-state configuration using inorganic solid electrolytes (SE) has become a promising option. Research in this field is mainly motivated by the promise to further increase the energy density as well as the safety characteristics compared to today’s battery technology. However, all-solid-state batteries still fall short of expectation largely because of limited interface kinetics and interface stability. Moreover, processing of the materials and preparation of the cells needs to be significantly improved to reach higher energy densities and/or lower price compared to conventional cells with liquid electrolytes. In particular, sulfide-based SEs are strongly investigated due to their high ionic conductivity and ductility. The SE Li3PS4 (LPS) exhibits an acceptable ionic conductivity of 10⁻³ to 10⁻⁴ mS cm⁻¹ at room temperature as well as low grain boundary resistance even under cold pressing conditions. In our study, we combine LPS with different transition metal sulfides as cathode active materials. The attractiveness of such materials lies in their high specific capacity of their reaction with lithium. The transition metal sulfides react with lithium in a conversion reaction described by the general formula MₙSₓ + (n) Li ↔ aM + LiₓS (M = transition metal, e.g. Mn, Fe, Cu, Ni, Co, Zn, Mo). The performance of the all-solid-state batteries is evaluated with respect to capacity, cycle life and rate capability and reversible capacities of several hundred mAh g⁻¹ are demonstrated. Additionally, the impact of the electrode composition and cathode loading on the cell performance is evaluated. At last, we discuss analogue cells with sodium as charge carrier ion.

3:00 PM BREAK

3:30 PM ET01.02.06

Atomically-Precise Interfacial Engineering of Solid-State Batteries Neil P. Dasgupta; Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Solid-state batteries have experienced a recent explosion in R&D, owing to their potential to improve safety and energy density. However, the requirements on an all-solid-state battery are stringent, as cells must simultaneously incorporate a high ionic conductivity electrolyte, form high performance interfaces against both anode and cathode materials, and exhibit stability against chemical, electrochemical, morphological, and mechanical evolution under a wide range of cycling conditions. In particular, it has been widely recognized that solid-state interfaces present unique challenges compared to traditional liquid electrolytes, including high interfacial impedances, evolution mechanical stresses due to solid-solid interfacial contact with active materials, and (electro)chemical instabilities that can arise from localized gradients in ionic and electronic concentrations.

To address this challenge, our group focuses on gaining new fundamental insights into the coupled phenomena occurring at interfaces, and applied this knowledge to rationally design interfacial chemistry to address the root cause of performance limitations. This is accomplished through a combination of experimental techniques, including in situ/operando analysis using optical and x-ray techniques, precise surface/interfacial energy measurements, and design of model interfaces to decouple factors that contribute to electrochemical behavior. Equipped with this knowledge, we employ atomically-precise interfacial modifications to rationally design interfacial chemistry.

In this talk, examples will be presented in both bulk solid-state battery interfaces [1], and thin film electrolytes deposited by Atomic Layer Deposition (ALD) [3,4]. By studying interfacial chemistry across length scales ranging from atoms to millimeters, we have been able to systematically identify the mechanisms of interfacial degradation. At bulk length scales, the coupled chemical/electrochemical/morphological evolution of a range of solid electrolytes will be discussed, including oxides, sulfides, and polymers. The link between surface chemistry, Li wettability, and interfacial impedance are quantitatively evaluated [1]. Trends and tradeoffs are observed in these systems, which represents a systems engineering problem to optimize overall battery performance. To modify these surfaces, ALD of solid electrolytes is demonstrated [2,3], which enables tunability of surface chemistry, morphology, and stability. These ALD electrolytes are demonstrated in both thin-film battery architectures and as interfacial layers against bulk solid electrolytes. Through this interdisciplinary approach of fundamental chemistry and applied engineering, strategies to address future interfacial challenges will be addressed, which will accelerate the pathway from laboratory science to scalable manufacturing.


4:00 PM ET01.02.07

Highly Lithium-Ion-Conducting Halide Electrolytes for 4 V Class All-Solid-State Batteries and Their Conduction Path Akihiro Sakai, Tetsuya Asano, Satoru Ouchai, Masashi Sakaida, Akinobu Miyazaki and Shinya Hasegawa, Technology Innovation Division, Panasonic, Kadoma, Japan.

We recently reported that the solid halide electrolytes consisting of rightly-selected cations satisfy the high lithium ion conductivity, electrochemical stability, material stability, and deformability: all of which are simultaneously required properties for solid electrolytes for application in all-solid-state batteries (ASSBs) [1] Theionic conductivity of the halide electrolytes surpassed 1 mS/cm. The bulk-type ASSBs fabricated with cold-pressed method exhibited excellent performances: higher than 94 % coulombic efficiency with 4-V class cathode active materials as well as discharge capacity retention higher than 98 % for 100 cycles. These superior material properties as well as excellent battery performance indicate that the halide electrolytes are another good candidate for the solid-state electrolyte for ASSB application other than sulfides and oxides. Here, we will report the identified crystal structures of these halide electrolytes and the ionic conduction pathway to elaborate the relationship of lithium ionic conductivity and the crystal structure of these halide electrolytes. Interestingly, the crystal structures of these highly lithium-ion-conducting halide materials do not satisfy the “criteria for high ionic conductivity” of sulfide electrolytes which is BCC-like arrangement of anion sublattice. [2] On the other hand, these halide electrolytes consist of nearly close-packed anion sublattice, and yet, still show as high lithium ionic conductivity as 0.1 - 1 mS/cm. The simulated ionic conduction paths understoodly indicate that cation-cation coulombic repulsion reduces the available conduction paths and alters the crystallinity-conductivity relationship. These results indicate that the design principles of the halide electrolytes for high ionic conductivity differ from previously reported sulfide or oxide electrolytes.

References:


2:45 PM ET01.02.05

Transition Metal Sulfide Nanostructures (CuS, MoS2) as Conversion Electrodes for Rechargeable All-Solid-State Batteries Agunda Lingamurthy Suthusha, Raimund Koeverd, Kilian Pollok, Falko Langenhorst, Juergen Janeck and Philipp Adelhelm; 1Institute of Geoeciences, Friedrich Schiller University Jena, Jena, Germany; 2Institute of Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany; 3Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller-University Jena, Jena, Germany.

Solid-state batteries have experienced a recent explosion in R&D, owing to their potential to improve safety and energy density. However, the requirements on an all-solid-state battery are stringent, as cells must simultaneously incorporate a high ionic conductivity electrolyte, form high performance interfaces against both anode and cathode materials, and exhibit stability against chemical, electrochemical, morphological, and mechanical evolution under a wide range of cycling conditions. In particular, it has been widely recognized that solid-state interfaces present unique challenges compared to traditional liquid electrolytes, including high interfacial impedances, evolution mechanical stresses due to solid-solid interfacial contact with active materials, and (electro)chemical instabilities that can arise from localized gradients in ionic and electronic concentrations.

To address this challenge, our group focuses on gaining new fundamental insights into the coupled phenomena occurring at interfaces, and applied this knowledge to rationally design interfacial chemistry to address the root cause of performance limitations. This is accomplished through a combination of experimental techniques, including in situ/operando analysis using optical and x-ray techniques, precise surface/interfacial energy measurements, and design of model interfaces to decouple factors that contribute to electrochemical behavior. Equipped with this knowledge, we employ atomically-precise interfacial modifications to rationally design interfacial chemistry.

In this talk, examples will be presented in both bulk solid-state battery interfaces [1], and thin film electrolytes deposited by Atomic Layer Deposition (ALD) [3,4]. By studying interfacial chemistry across length scales ranging from atoms to millimeters, we have been able to systematically identify the mechanisms of interfacial degradation. At bulk length scales, the coupled chemical/electrochemical/morphological evolution of a range of solid electrolytes will be discussed, including oxides, sulfides, and polymers. The link between surface chemistry, Li wettability, and interfacial impedance are quantitatively evaluated [1]. Trends and tradeoffs are observed in these systems, which represents a systems engineering problem to optimize overall battery performance. To modify these surfaces, ALD of solid electrolytes is demonstrated [2,3], which enables tunability of surface chemistry, morphology, and stability. These ALD electrolytes are demonstrated in both thin-film battery architectures and as interfacial layers against bulk solid electrolytes. Through this interdisciplinary approach of fundamental chemistry and applied engineering, strategies to address future interfacial challenges will be addressed, which will accelerate the pathway from laboratory science to scalable manufacturing.

Beyond state-of-the-art lithium-ion battery (LIB) technology with metallic lithium anodes to replace conventional ion intercalation anode materials is highly desirable because of lithium’s highest specific capacity (3,860 mA/g) and lowest negative electrochemical potential (∼3.040 V vs. the standard hydrogen electrode). In this work, we report for the first time, to our knowledge, a 3D lithium-ion-conducting ceramic network based on garnet-type Llu3Fe3Al2SiO12 (LLZO) lithium-ion conductor to provide continuous Li+ transfer channels in a polyethylene oxide (PEO)-based composite. This composite structure further provides structural reinforcement to enhance the mechanical properties of the polymer matrix. The flexible solid-state electrolyte composite membrane exhibited an ionic conductivity of $2.5 \times 10^{-6}$ S/cm at room temperature. The membrane can effectively block dendrites in a symmetric Li+ electrolyte | Li cell during repeated lithium stripping/plating at room temperature, with a current density of 0.2 mA/cm² for around 500 h and a current density of 0.5 mA/cm² for over 300 h. The presentation will focus on our recent development of 3D garnet nano structured solid-state electrolyte membrane for Li metal batteries.

**4:30 PM ET01.02.09**

**PEO/Perovskite Composite Electrolyte with Enhanced Li+ Conductivity**

Henghui Xu, Yutao Li, Nan Wu and John Goodenough; The University of Texas at Austin, Austin, Texas, United States.

Rapid developments in electric road vehicles and grid energy storage are boosting the development of long-life, high-energy-density lithium-ion batteries (LIBs) with high safety. Replacing the liquid electrolyte in conventional LIBs with solid electrolytes can not only address the limitation of leakage and flammability but also guarantee a long cycle life because of the stable structure of the all-solid-state components. Moreover, LIBs built with solid electrolytes may achieve high energy density by using a Li-metal anode and commercially available cathodes. However, there are no ideal solid electrolytes so far that possess high Li+ conductivity and small interfacial resistance. Composite polymer electrolytes (CPE) prepared by incorporating ceramic nanoparticles into polymer matrix have been deemed an effective way to simultaneously enhance ionic conductivity, improve the electrochemical stability, and reduce the critical interfacial resistance between electrodes and electrolytes. Unfortunately, most reported Li+ conductivities of composite polymer electrolytes are still lower than $1 \times 10^{-5}$ S/cm at room temperature. We reported a flexible composite polymer electrolyte with an enhanced conductivity of $4 \times 10^{-5}$ S/cm at room temperature by blending a perovskite solid electrolyte with a PEO polymer electrolyte. The addition of perovskite not only helps to reduce the polymer crystallinity and increase the mechanical strength but also constructs a strong bond with the anions in Li salts. As a result, many more lithium ions are released from the Li salts to render a much higher ion conductivity. Surface-sensitive techniques are carried out to directly visualize and probe the stable interphase formed between the CPE and electrodes, which improves the Li+ transfer across the interface. A symmetric Li/Li cell and an all-solid-state LiFePO4 cell with the CPE show small overpotentials, high Coulombic efficiencies, and stable cycling performance at 40 °C.

**4:45 PM ET01.02.10**

**Garnet Electrolyte Coated with a Single-Li+-Conducting Polymer for All-Solid-State Lithium Batteries**

Weidong Zhou; Beijing University of Chemical Technology, Beijing, China.

To meet the requirements of high energy density, safety and long cycle life, it is necessary to replace the organic flammable electrolyte and graphite anode of the Li-ion battery by a solid electrolyte and metallic-lithium anode that can be plated/striped reversibly without lithium-dendrite formation. Garnet electrolyte with a high room-temperature Li-ion conductivity and a good stability against lithium metal suffers from the huge interfacial resistance and fast lithium-dendrite growth. A Li+ conducting polymer with a high Li+ transport number of 0.9, which was coated on the surface of garnet electrolyte as an artificial SEI layer, not only reduced the Li metal anode/garnet interfacial impedance but also suppressed the formation and growth of lithium dendrites along the garnet grain boundaries. In all-solid-state Li/LiFePO4 cells, a high Coulombic efficiency near 100% was achieved for long cycling. These tests show the feasibility of a safe Li-metal rechargeable battery having an appropriate single Li+ conducting polymer SEI between a ceramic electrolyte and the metallic lithium anode.

8:15 AM ET01.03.01

**The Structure and Conductivity of 3D Superionic Na3SbS4 Conductor at Extremely Low Temperatures**

Hui Wang1, Yan Chen1, Zachary D. Hood1,3,4, Jong K. Keum1, Amaresh Pandian1, Miaoafang Chi2, Ke An3, Chengdu Liang3 and Mahendra Sunkara2; 1University of Louisville, Louisville, Kentucky, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Georgia Institute of Technology, Atlanta, Georgia, United States; 4Electrochemical Materials Laboratory, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 5College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, China.

Overcoming the solid-liquid state transition of the lithium electrolyte in state-of-the-art batteries represent a grand challenge for the next-generation energy storage. All-solid-state batteries that employ superionic solid conductor potentially enable the broadening of battery operation in harsh environments, such as under sub-zero temperatures and even lower. The solid electrolyte as the key component requires structural stability, high-efficiency of ion transportation channels, and low activation energy to maintain the fast-ion conduction against temperature drop. Compared to one-dimensional (1D) conductive chain, a three-dimensional (3D) framework of ion-conduction tunnel is more favorable structure for solid conductors to work at subzero temperature range. The tetragonal Na3SbS4 is such a superionic conductor that holds 3D tunnel network for Na-ion transportation and exceptionally low activation energy of 0.205 eV. In this work, we use Na3SbS4 as a model system to investigate the structure stability and Na-ion conduction paths of 3D superionic conductor at extreme low temperature (20 K) via cryogenic neutron and X-ray diffractions. Cryogenic in-situ neutron and X-ray diffractions reveal that Na3SbS4 maintains a stable tetragonal crystal structure and the anisotropic lattice contraction upon cooling. The evolution of S-gate, where Na ions hop through in the 3D transportation network, is found to maintain open sizes in the xy-plane, contributing to the low activation energy and impressive
The holy grail of battery research is the coupling of a metal negative electrode with a high capacity positive electrode to produce a cell with higher energy density than lithium-ion cells. Sulfur cathode has a high theoretical capacity of 1672 mAh g⁻¹ and a theoretical energy density of 2500 Wh kg⁻¹ in a lithium sulfur (Li-S) battery. Li-S batteries are tormented by several challenges, most notably the dissolution of polysulfide in the electrolyte during the reduction of sulfur and the growth of lithium dendrite during charging. [1,2,3] A paradigm shift is required to completely block or avoid polysulfide dissolution. One option is to use inorganic solid electrolyte such as lithium thio phosphate in place of the liquid electrolyte. [4,5] Lithium thio phosphate solid electrolyte has a narrow potential window which make thermodynamically incompatible with lithium metal anode. [6] We will discuss how the lithium/solid electrolyte interface and electrolyte structure can dramatically affect the stripping/plating of lithium metal. The challenges associated with using the lithium thio phosphate electrolyte in Li-S battery will also be examined.

References

8:45 AM ET01.03.03
Li⁺ Ion Conduction Mechanisms of Li⁺-Doped NaI and Its Electrochemical Properties Reona Miyazaki¹, Isao Sakaguchi² and Takehiko Hihara², ¹Nagoya Institute of Technology, Nagoya, Japan; ²National Institute for Materials Science, Tsukuba, Japan.

From the early stage of the research, solid electrolytes for the all-solid-state lithium ion batteries have been developed mainly based on the Li compounds. On the other hand, we have been evidenced that the solid electrolytes can also be fabricated by the doping of Li compounds to “Li-free” compounds like the liquid electrolytes prepared by the dissolution of a given ionic salt into the carrier-free liquid solvents. These types of solid electrolytes are so-called “Co-ionic conductor”, where the small doped guest ions play a major role for the ion conduction in the host materials [1]. From our previous research, it has been shown that both NaI and KI become pure Li⁺ ion conductors via doping 6 mol% of LiBH₄, whose conductivity value exceeds that of LiI [1, 2]. However, the details of the ion conduction mechanisms in NaI-LiBH₄ system, especially for the host Na⁺ ions are not well understood. The purpose of the present work is the investigation of the ion conduction mechanisms in NaI-LiBH₄ systems. The electrochemical stability will be also investigated as a function of the concentration of LiBH₄.

NaI-LiBH₄ systems were fabricated by ball-milling. The given molar ratio of NaI and LiBH₄ (Aldrich Co) were mechanically milled at 400 rpm with 10 pieces of balls in a chrome still pot (45 ml). The total milling time was 5 hours. In order to investigate the conduction mechanism of Li⁺ and Na⁺ ions separately, all-solid-state half-cell was fabricated using the sputtered amorphous Si (a-Si) film and 15NaI_LiBH₄ as an anode material and a solid electrolyte, respectively. Li foil was used as a counter electrode. After charging, the half-cell was disassembled and the Si film was collected in a glove box. Subsequently, the depth profile inside the charged Si film was investigated by SIMS measurement. Cyclic voltammetry was performed using Mo and Li foils as a working and counter electrode, respectively.

During the charging of a-Si film, two kinds of plateau regions were observed at around 0.2 and 0.1 V vs. Li⁺/Li, which are the typical lithiation curves for a-Si film [4]. From the SIMS measurement inside the charged Si film, it was confirmed that Li⁺ ions are mainly detected. The steady state charging of Li⁺ ions can be attained by the constant transport of the Li⁺ ions in NaI. Hence, the main conduction carrier in the NaI doped with 6 mol% of LiBH₄ was shown to be the small doped Li⁺ ions. On the other hands, 23Na⁺ ions were also detected inside the Si film although the signal intensity was three orders of magnitude smaller than that of Li⁺ ions. The detailed conduction mechanism and electrochemical stability of NaI-LiBH₄ systems will be shown in the presentation.

References

9:00 AM ET01.03.04
Electrochemomechanical Failure in Active Materials and Solid Electrolytes Yet-Ming Chiang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The pursuit of high energy density and long life in rechargeable lithium batteries has exposed several modes of failure due to electrochemical-mechanical coupling. This talk will discuss specific examples in intercalation cathode and inorganic solid electrolytes, and potential failure-mitigation approaches.

It is now recognized that even active materials with much lower chemical expansion coefficients than the well-known extreme cases (e.g., Si or Sn and their alloys) undergo cycling induced fracture at the secondary particle level. The possible failure modes have been previously classified [1] and studied using macroscopic measurements such as acoustic emission [1,2]. Recently a methodology has been developed for measuring the electrochemical response of single electrode particles and directly observing the electrochemomechanical damage [3]. Applied to NMC333 and NCA particles, it is shown that the resulting single-particle kinetics are a trade-off between surface area increase, and loss of electrical continuity, both due to microscopic fracture at the secondary particle level.

Inorganic solid electrolytes undergo lithium metal penetration via an entirely different failure mode than classical dendrite formation in liquid electrolytes [3]. Although it has been argued that grain boundaries are a weak link along which Li metal preferentially penetrates, we show that even single crystals are highly susceptible to metal penetration from surface defects. Failure criteria such as the existence of a critical overpotential that are related to flaw size and the physical properties of the solid electrolyte can be tested using deliberately introduced surface flaws of controlled size. A new result to be discussed is the impact of field concentration effects at current collector discontinuities.
References:


U.S. Department of Energy support for the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center under Award # DE-SC0012583, and the Chemomechanics of Far-From-Equilibrium Interfaces (COFFEI) small group, through award number DE-SC0002633, is gratefully acknowledged.

9:30 AM ET01.03.05
Degradation Mechanisms of All-Solid-State Li-S Battery with LiPSsCl Saneyuki Ohno, Georg Dewald, Juergen Janek and Wolfgang G. Zeier, Institute of Physical Chemistry, Justus-Liebig-Universität Gießen, Gießen, Germany.

While the demand for batteries with a high energy density is rapidly growing, the current commercially available Li-ion battery chemistry is approaching a theoretical limit.1 To overcome this issue, Li-S batteries exploiting the conversion reaction between sulfur and Li2S have been attracting significant attention as a promising candidate of the next generation batteries.2 “The history of the conventional Li-S battery development has been a fight against the notorious shuttle effect caused by polysulfides dissolved into the liquid electrolyte. However, a concept of all solid state batteries can physically hinder the polysulfide shuttle. Indeed the exhibit no evidence of the shuttle effect the all-solid-state Li-S battery cells, composed of Li-ion conducting thiophosphate (e.g. LiPSsCl), exhibit no evidence of the shuttle effect.

Nevertheless, there are still multiple challenges to achieve a high capacity and its good retention. One of the critical issues is a large capacity loss in the first battery cycle. A poor capacity retention over the long term cycling is another issue. In this study, we elucidated the degradation mechanisms of an all-solid-state Li-S battery employing LiPSsCl as an electrolyte and achieved a significant improvement of the battery performance based on it. The deeper understanding of the underlying chemistry of the degradation mechanisms will lead to further enhancement of the capacity and cyclability of the all-solid-state Li-S batteries.

References


9:45 AM ET01.03.06
Interface Engineering of the Garnet-Based Solid-State Batteries and In Situ Neutron Depth Profiling Diagnose Chengwei Wang, Yunhui Gong, Hua Xie, Lei Zhang, Hao Wang, Eric D. Wachsman and Liangbing Hu; University of Maryland, College Park, Maryland, United States.

Garnet-based solid state electrolytes (SSEs) have attracted much attention for their high ionic conductivities and stability with lithium metal anodes. However, the high interfacial resistances between electrodes and garnet SSEs are one of the main challenges to develop all solid state lithium (Li) metal batteries. Herein, we develop several effective techniques to significantly improve Li-garnet interface and lead to an interface resistance as low as ~ 7 Ω●cm2. We also develop an effective cathode-garnet interface using a mixed ionic electronic (MIE) conductor, which enables cycling of all solid state batteries without a liquid or polymer electrolyte interface. The solution-processed two dimensional (2D) layered TiS2 shows MIE conductivity after slow pre-lithiation, resulting in more than 20 times lower interfacial resistance. The all solid state batteries can work at high temperatures from 100 °C to 150 °C for 400 cycles at current densities up to 1 mA/cm2. To reveal the interfacial behaviors of garnet SSE in contact of metallic Li, neutron depth profiling (NDP), a nondestructive and unique Li-sensitive technique, is used to in situ monitor Li plating-stripping processes. The NDP measurement has demonstrated the predictive capabilities for diagnosing short-circuits in garnet-based solid state batteries.

10:00 AM BREAK

10:30 AM *ET01.03.07
Dendrite-Free Lithium Metal Batteries Capable of Stable Operation at Elevated Temperature Based on Liquid Organic Electrolytes Hong Li; Chinese Academy of Sciences, Beijing, China.

Rechargeable lithium metal batteries have attracted wide attention due to high theoretical energy density. For practical applications, high-temperature performance of lithium batteries is essential due to complex application environments, in terms of safety and cycle life. However, it’s difficult for normal operation of lithium metal batteries at high temperature using current electrolyte systems. Herein, a kind of new electrolyte system is designed by adding two thermal-stable lithium salts together (i.e. LiTFSI and LiDFOB) into carbonate solvents with high boiling/flashing point (i.e. EC and PC). Low ratio of LiPF6 is also added to prevent the corrosion of Al current collector. The results indicate that the new electrolyte system possesses good high-temperature performance, meanwhile, it is beneficial to effectively suppress the formation of lithium dendrite. At a current density of 1.2 mA/cm2, LiCoO2 cathode with 2.4 mAh/cm2 shows the capacity retention of 90% after 100 cycles at 80 oC in a lithium metal cell. Such performance is achieved for the first time for rechargeable lithium metal battery using liquid organic electrolyte. The enhanced cycling performance at elevated temperature is ascribed to effective protection of lithium metal by the generation of organic-inorganic composite solid-electrolyte interphase (SEI) on surface of lithium anode, formation of cathode electrolyte interphase (CEI) with high content of LiF on LiCoO2 cathode and good stability of electrolyte itself. Its the first demonstration of dendrite-free Li metal battery capable of stable operation above 60 oC using liquid organic electrolyte. The improved cycling performance at elevated temperature based on the new electrolyte system is ascribed to effective protection of Li metal by the generation of organic-inorganic composite SEI on surface of Li anode, formation of CEI with high content of LiF on LiCoO2 cathode and good stability of electrolyte itself. In addition, in situ solidification is also introduced to this system to form a solid electrolyte, which can improve the interfacial solid/solid contact significantly during cycling.
Very High Lithium Diffusion in LiTi2(PS4)3 Through Energy Landscape Frustration

Geoffroy Hautier1, Davide Di Stefano1, Anna Miglio1, Koen Robeyns1, Yaroslav Filinchuk1, Marine Lechartier1, Anatoliy Sensyn1, Hiroyuki Ishida1, Stefan Spannenberger1, Bernhard Roling1, Denis Prutsch2, Daniel Rettenwander1, Martin Wilkening1, and Yuki Kato1; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Argonne National Laboratory, Argonne, Illinois, United States.

Recent years have witnessed the increasing demand for high-quality, safe, and low-cost rechargeable batteries. Metal-based solid-state batteries are particularly promising in this regard, where extremely high energy densities can be attained by utilizing metallic Li/Na anodes, and the use of a ceramic solid-state electrolyte membrane greatly enhances battery safety. However, most solid-state electrolytes react with lithium and sodium metals, causing a continuous increase of the cell impedance and thus battery degradation. Therefore, passivation reaction with Li/Na metal is required for the electrolyte to achieve a relatively stable interface. Herein, we present a ‘reverse design’ strategy to improve the stability of the interface between solid-state electrolytes and metal anodes. Using the advanced first-principles computational tools developed in our previous work, we identify a protective hydrate coating for solid electrolytes that would lead to the generation of passivating decomposition products upon contact of the electrolyte with metal electrodes. A significantly improved interface stability with the metal electrode of a hydrate coated solid-state electrolyte is observed, compared with that of its non-hydrated counterpart. The buried interface between the surface-treated solid-state electrolyte and the metal electrode was characterized using post-operando synchrotron X-ray depth-profiling, providing spatially resolved evidence of the multilayered phase distribution in the metal-based symmetric solid-state cell. The experimental results are consistent with our theoretical predictions. In addition, we propose a general strategy of interface reverse design and discuss the possible pretreatment of the solid-state electrolyte using other chemicals.

11:15 AM ET01.03.09

Investigating the Effects of Lanthanum Concentration in Ta-Doped Li0.5La2+xZr1.5Ta0.5O12 Solid Electrolyte

Joseph M. Valle and Jeff Sakamoto; University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Solid electrolytes based on the garnet crystal structure have shown promise in the push to develop electrochemical cells utilizing lithium metal anodes due to their high lithium conductivity and stability against metallic lithium. One of these solid electrolytes is cubic phase lithium lanthanum zirconium oxide (LLZO). The critical doping of LLZO with tantalum at the zirconium site has been shown to stabilize the highly conductive cubic LLZO phase at room temperature $Li_xLa_{2-y}Zr_1Ta_{y}O_{12}$. This critical doping has been shown to provide an optimal amount of lithium vacancies to stabilize the cubic phase without transitioning to the less conductive tetragonal phase of LLZO. While much work has been done to investigate the doping and charge balancing on the zirconium site, comparatively little focus has been paid to the lanthanum site. The effects of the stoichiometric use of lanthanum on the crystal structure of LLZO have yet to be characterized.

In this work, lanthanum content is varied in the LLZO structure $Li_xLa_{2+y}Zr_1Ta_{y}O_{12}$ from $x = 0$ to $x = 1.2$. X-ray diffraction and electrochemical impedance measurements were performed in order to correlate the effect of lanthanum deficiency on crystal structure and electrochemical properties of LLZO. A linear increase in lattice parameter is observed until the stoichiometric composition ($x = 1.0$) is achieved. An increase in conductivity is also observed ranging from $0.41mS/cm^2$ at $x = 0.2$ to $0.72mS/cm^2$ at $x = 1.2$.

11:30 AM ET01.03.10

Garnet and Anti-Perovskite Solid Electrolytes—Atomic-Scale Studies on Li-Ion Conduction, Surface Structures and Grain Boundaries

Saiful Islam; University of Bath, Bath, United Kingdom.

Major advances in solid-state lithium batteries require the discovery and characterization of solid electrolyte materials. It is clear that a complete understanding of such materials requires greater fundamental knowledge of their underlying structural, ion transport and interface properties on the atomic- and nano-scales. For example, grain boundary effects on Li-ion transport are not fully understood. This talk will highlight recent studies [1-3] in two related areas: the influence of grain boundaries on Li-ion conduction in the Li-rich anti-perovskite Li3OCl and the particle morphologies and lithium segregation to surfaces of the garnet Li7La3Zr2O12. A combination of advanced materials modelling techniques has helped us gain new insights into these complex materials, which are valuable in developing strategies to optimize their electrolyte properties.


11:45 AM ET01.03.11

Very High Lithium Diffusion in LiTi2(PS4)3 Through Energy Landscape Frustration

Geoffroy Hautier1, Davide Di Stefano1, Anna Miglio1, Koen Robeyns1, Yaroslav Filinchuk1, Marine Lechartier1, Anatoliy Sensyn1, Hiroyuki Ishida1, Stefan Spannenberger1, Bernhard Roling1, Denis Prutsch2, Daniel Rettenwander1, Martin Wilkening1, and Yuki Kato1; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Argonne National Laboratory, Argonne, Illinois, United States.

Solid-state materials with fast high ionic diffusion are necessary to many technologies including all-solid-state Li-ion batteries. In this work, we demonstrate that LiTi2(PS4)3 (LTPS) exhibits the largest Li-ion diffusion coefficient ever measured in a solid. We use extensive characterisation (neutron, X-ray diffraction, impedance and NMR) as well as theoretical studies to study the lithium diffusion in LTPS. We show for instance with recent X-ray data that the Li mobility is so high that low temperature is needed to freeze and observe the lithium ions positions. We rationalise the exceptional performances of this new superionic conductor through the concept of frustrated energy landscape. The absence of regular and undistorted lithium site to occupy leads to low energy barrier for diffusion as well as an exceptional pre-factor. We discuss how this frustration could be present in previously known ion conductors and be used to search and design new structural families of superionic conductors.
Fast solid ionic conductor electrolytes are key enablers of all-solid-state batteries, which potentially possess high energy density and diminish safety concerns during battery operation in large scale energy storage system. Compared to liquid electrolytes, low ionic conductivity is one of the critical issues in solid electrolyte development. Understanding its origin of potential high ionic conductivities provides insight of designing better electrolytes. The ionic transportation efficiency in solid crystals depends on the accessible tunnels in the structure as well as the active vacancy for ion hopping. Via neutron and X-ray diffraction, the ionic transport tunnels, from one-dimension to three-dimension, can be revealed in typical oxide- and sulfide-base light ionic (Li\(^+\), Na\(^+\)) conductors. The directions of the ionic transport have strong correlation with the lattice symmetry and the atomic arrangement in those solid conductors. The effective ion tunnel and the active vacancy quantity can be altered by neighboring aliovalent dopants, which is manipulated for optimal ionic conductivity in the solid electrolyte. The tunnel accessibility is also influenced upon temperature change, due to the tuned framework structure. The evolutions of the tunnel size and the anisotropic oscillation of charge carrier ions indicate the possible dimensional change of the transport pathway network. Moreover, the directional conduction is found to correlate with the anisotropic physical properties, demonstrated by the uneven coefficients of the thermal expansion along different crystallographic axes. These correlations of conduction tunnel provide valuable guidance in materials searching for solid conductors with superior performance in varied environments. The results of the anisotropic thermal-strain response correlated with ionic transport also provide consideration of the physical compatibility in the design of all-solid-state batteries.

Incorporating Two-Dimensional Materials in Semi-Solid Electrolytes for Fast Charge Li-Ion Batteries

Ramin Rojaee\(^1\), Salvatore Cavallo\(^1,2\), Santosh Mogurumppelly\(^1\), Bill Wheelie\(^3\), Venkat Ganesan\(^1\) and Reza Shabahanzadeh-Yasours\(^1\); Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, Illinois, United States; \(^2\)Department of Energy-DENERG, Politecnico di Torino, Torino, Italy; \(^3\)Institute for Computational Molecular Science (ICMS) and Temple Materials Institute (TMI), Philadelphia, Pennsylvania, United States; \(^4\)Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Poor electrochemical stability and low ionic conductivity trigger of prime importance for the development of new-generation of lithium-ion batteries. Solid electrolytes have been attracted significant attention owing to their superior safety and potential for boosting specific energy density. Here, we report a new type of semi-solid electrolytes with two-dimensional materials embedded in ternary polymer electrolyte. The developed electrolyte has a high electrochemical stability of 5.5 V vs. Li/Li\(^+\). We report a high ionic conductivity of 4×10\(^{-4}\) S cm\(^{-1}\) at ambient temperature and significantly low interfacial resistance over the long period of time of 600 h overpotential cycling tests. The developed electrolyte is capable of fast charging with great capacity retention benefiting due to unique atomic arrangement of 2D material additive: FTIR, Raman, and NMR characterizations revealed the higher concentration of the free cations will be present in the electrolyte by about 30\% upon addition of designated 2D material nanosheets. The layered 2D material lowers the binding energy for hopping the ions through the electrolyte to allow improved storage capacity and power density. We hypothesize that 2D materials introduce unique properties to the electrochemical behavior of the electrolyte and boost the ionic conduction through the electrolyte by providing efficient pathways for local ion transport through the structure and can be a great candidate for novel lithium polymer batteries. MD simulation studies confirmed our experimental achievements and suggested that the f-BP nanosheets facilitate Li\(^+\) ion movement by lowering the required energy to dissociate cations and move along the electrolyte.

Advanced Sulfide Solid Electrolyte by Core-Shell Structural Design—Theory and Experiment

Xin Li; Harvard University, Cambridge, Massachusetts, United States.

Ceramic sulfide solid electrolyte can show high lithium conductivity, while the voltage stability was reported as an issue in many previous literatures. We show in this talk a new way to improve the voltage stability of sulfide solid electrolyte materials by microstructure modification of the electrolyte materials. The improved battery performance and voltage stability are shown by electrochemical test. A combination of first principle simulation and transmission electron microscopy imaging techniques are used to understand the principle behind the phenomenon. Specifically, sulfide Li-Si-P-S has been synthesized, characterized, and tested to show an improved voltage stability window up to 3.1 V and quasi-stable voltage window up to 3.5 V due to the microstructure modification. This is far beyond the limited voltage stability of these sulfides around 1.7 – 2.1 V as predicted by DFT simulation. We further from a combined thermodynamic modeling and DFT simulation understand the principle behind this promising result. A new design principle and theory is proposed and discussed systematically for tuning the voltage stability of solid electrolyte, giving the guidelines for the design of advanced sulfide electrolytes.

Electrochemical Characterization of All-Solid-State Battery with Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) Solid Electrolyte

Kiyoshi Kanamura; Tokyo Metropolitan University, Tokyo, Japan.

Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZO) is promising electrolyte due to its high chemical stability against Li metal and high ionic conductivity. All solid state battery has been fabricated by using LLZO. However, the cell performance is not so good. This is due to a high impedance of the prepared cell. The resistance of solid electrolyte is the largest among resistances in the cell. In addition, the interfacial impedance between cathode and anode and solid electrolyte is not easily decreased. The interface between Li metal anode and LLZO solid electrolyte pellet is large due to poor contact. The contact has been improved by using an interlayer between Li metal and LLZO. A thin gold layer prepared by sputtering method has been employed as the interlayer. The thickness was about 50 nm. The gold layer reacted with Li to form alloy. During this alloying process, the good connection was formed. A cathode material is usually powder sample. The interfaces between cathode material and LLZO sheet and LCO powder and solid electrolyte powder in the cathode layer exist in all solid state battery. In this study, the cathode layer was fabricated by aero-sol deposition process (AD). The aero-sol of LCO was deposited on the LLZO sheet. Li\(_3\)BO\(_3\) is fabricated on the LLZO. The discharge and charge behavior of the fabricated cathode layer was investigated at constant current of 0.1 C rate. The discharge capacity was decreased. The cell impedance was evaluated with electrochemical AC impedance measurement at various temperatures. Before the heat...
Solid-state batteries (SSBs), one of the most promising energy storage devices for next generation, have now been extensively developed due to their high safety and long cycle life. Here, the interfacial layers between solid electrode and solid electrolyte is one of most important features for the design of solid-state lithium batteries. Normally, the interfacial layer should be stable, highly conductive for Li ions, and flexible to tolerate the big volume changes during charging/discharging process. In this presentation, I will present some examples we have used in this lab to build up such thin but important interfacial layer, making the highly efficient Li dissolution/deposition possible. For example, we proposed an ultra-simple and effective strategy to enhance the interfacial connection between garnet SSEs and Li metal just by drawing a graphite-based soft interface with a pencil. Both experimental analysis and theoretical calculations confirm that the reaction between graphite-based interfacial layer and metallic lithium forms a lithiated connection interface with good lithium-ionic and electronic conductivity. Compared to the reported interfacial materials, the graphite material provides a soft interface with better ductility and compressibility. With the improvement by this soft interface, the impedance of symmetric Li cells significantly decreases from 1350 to 105Ωcm² and the cell can cycle for over 1000 hours at a current density of 300 mA/cm² at room temperature. In addition, some examples to construct an intimate solid electrolyte interface(SEI) in sulfide-based electrolyte by using ionic liquids will be also presented.

4:00 PM ET01.04.06
Simulations of Varying Li-Ion Vacancy Concentrations in Lithium-Oxyhalide Anti-Perovskites Reveal the Effects of Correlated Motion on Diffusion
Zerina Mehmedovic, Vanessa Wei, Andrew Grieder and Nicole Adelstein; San Francisco State Univ, San Francisco, California, United States.

Introduction: Our simulations are designed to answer the long-standing question in solid-state batteries: how to increase Li-ion conductivity in solid electrolytes through engineering the structure and chemistry of the anion sub-lattice. Understanding the mechanism behind lithium ion diffusion in promising solid electrolytes, such as lithium-oxyhalide anti-perovskites, can provide design principles for new battery materials. Our ab-initio molecular dynamics (AIMD) simulations of Li3OCl with Li vacancy concentrations between 0.5 and 2% reveal the origin of complex interactions between vacancies and new insights into the effect of correlated motion on the diffusion mechanism. Previous simulations of Li3OCl compute conductivities that are much lower than measured experimentally [1] and our simulations show that finite size effects are part of the problem.

Methods: ab-initio molecular dynamics were performed on a 4x4x4 supercells using VASP. The size of the supercell (320 atoms) allows for realistic vacancy concentrations and reducing finite size effects. The supercells had at least one and up to four Li vacancies. Maximally Localized Wannier Functions were used to calculate the dynamic polarization of anions and their effect on Li diffusion, which is a novel technique that we developed for analyzing solid electrolytes [2]. As is standard, the diffusion coefficient for each compound was determined using the mean squared displacement. The ‘binding energy’ of Li vacancies is calculated and lattice screening is separated into the strain and electronic effects.

Results: We discovered new collective diffusion mechanisms in Li3OCl and that finite size effects plague most AIMD simulations. For example, simulating two Li vacancies (0.5% concentration) increases diffusion because the negatively charged vacancies push other each other along. The largest vacancy concentration we simulated was 2%, which gave the highest diffusion due to disordering of the Li-sublattice, rather than a “push” mechanism. Vacancies can interact up to 7 Å from each other, with strain effects dominating 5 Å or closer. Vacancies communicate through the lattice, especially through polarization of anions. The dynamics of the anion polarization can be quantified easily in a nudged-elastic-band calculation and is still important even in AIMD. Thus, diffusion may be controlled by changing the polarizability of the anions, such as creating Br and F alloys with Li3OCl.

References

4:15 PM ET01.04.07
Tuning Charge Diffusion in Polyethylene Oxide-Based Electrolytes Using Secondary Sites—Insights from Molecular Dynamics Simulations
Arthur France-Lanord, Yanning Wang, Tian Xie and Jeffrey C. Grossman; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Solid-state polymer electrolytes (SPEs) constitute a promising technology for energy storage applications. In addition to a more flexible form factor, batteries using such electrolytes have the potential to be safer, less expensive, and greener than the current liquid-based standard technology. However, hindered by their low ionic conductivity, SPEs can only operate under limited conditions. The improvement of SPEs requires a deeper understanding of ion transport in polymer networks, where modeling and computation can play an important role. Here, through classical molecular dynamics simulations, we investigate charge diffusion in SPEs consisting of a mixture of polyethylene oxide (PEO) based polymers and lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt. By varying the chemical structure of the polymer, we alter the ion-polymer binding strength, which allows us to explore various ionic transport mode. Importantly, this study reveals the delicate balance between ionic association on one hand, and ionic crosslinking on the other hand.

4:30 PM ET01.04.08
Two-Dimensional Boron Nitride-Protected Solid Electrolyte for Rechargeable Lithium Metal Batteries
Qian Cheng; 1 Aijun Li; 2 and Yuan Yang; 1 1Program of Materials Science and Engineering, Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States; 2School of Earth and Space Sciences, Peking University, Beijing, China.

Solid-state lithium batteries can improve the battery safety and energy density compared with conventional Li-ion batteries. However, a lot of solid electrolytes with low cost and high ionic conductivities can be reduced by the anode in lithium battery systems (e.g. lithium, graphite). Here, we introduce a novel strategy, in which chemically and mechanically robust two-dimensional boron nitride (BN) film was deposited onto the surface of solid electrolyte (e.g. Li1.2Al0.8Ti0.3(PO4)3, LATP) to prevent reduction of solid electrolyte from lithium. The lithium symmetric cells with BN protected LATP/liquid hybrid electrolyte can cycle up to 700 hours with a current density up to 0.5 mA/cm², and full cell utilizing LiNi0.5Mn1.5O4/LATP/Li can cycle 100 times without apparent decay at a current density of 0.3 mA/cm². In contrast, LATP/liquid hybrid electrolyte can only be cycled for 40 cycles with fast capacity fading. Meanwhile, with PEO coated on both sides of LATP/BN, all-solid-state Li/LiFePO4 cells show a good cycling ability, further demonstrating excellent protection on solid electrolytes. This research provides a universal strategy to protect solid electrolytes of small electrochemical windows against...
lithium metal, leading to notable improvement of stability and cycling ability.

4:45 PM ET01.04.09
Fabrication of Ultrathin Films of Li$_{3-x}$Al$_x$La$_3$Zr$_2$O$_{12}$ with Tunable Surface Morphology by Spray Pyrolysis
Zachary D. Hood$^1$, Yuntong Zhu$^1$, Lincoln Miara$^2$ and Jennifer L. Rupp$^{1,2}$; $^1$Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; $^2$Samsung Research America, Advanced Materials Lab, Burlington, Massachusetts, United States; $^3$Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Garnet-based lithium solid electrolytes are expected to improve next-generation energy storage technology in electric vehicles and portable electronics on the basis of energy density, safety, cost, amongst other parameters. Yet many of these solid electrolytes, such as Li$_{3,8}$Al$_x$La$_3$Zr$_2$O$_{12}$ (LLZO), were previously difficult to process into thin films between 200 nm and 5 μm in thickness using solution-based techniques. Several vacuum-based$^{3,4}$ and sol-gel-derived$^{5,6}$ methods shown success in making thin garnet-based solid electrolyte films with relatively high ionic conductivity ($\sim 10^{-4}$ - $10^{-5}$ S/cm at room temperature), yet better methods are desired to improve the bulk resistance of the electrolyte and overall cost of production. Therefore, the exploration of scalable fabrication techniques is of special importance to develop thin films of garnet-based solid electrolytes that hold high ionic conductivity and compatibility with high-capacity cathodes. In this work, we developed a novel method of fabricating thin films with controllable thicknesses of garnet-based LLZO solid electrolytes using spray pyrolysis. We show that the crystallization and the phase transformation can be modulated to lower temperatures ($\sim$750 °C) by tuning the concentration of cations and the boiling point of the solvents used in the spray solution. Also, by altering the chemistry of the spray solution and the post-annealing conditions, we show that the surface roughness can be modulated while still maintaining dense and continuous membranes of LLZO. Our results highlight a new opportunity for manufacturing garnet-based solid electrolytes with tunable electrochemical surface areas, and the insights from this work are expected to serve as fundamental guidelines for future optimization of thin film superionic garnet-based materials for next-generation lithium metal batteries.

Acknowledgements
Research was sponsored by Samsung Electronics.

References:
Solid Polymer Electrolyte from Polytetrahydrofuran-Epoxy Copolymers for Lithium-Ion Conduction

Francielli S. Genieri1, James Barna2, Jiayue Wang1, Saeid Biria1 and Ian Hosein1; 1Syracuse University, Syracuse, New York, United States; 2Cazenovia High School, Cazenovia, New York, United States.

High performance batteries are central components to the development of safe, clean and affordable energy storage systems. For this reason, the replacement of the liquid or gel electrolyte with a solid polymer material, namely a solid polymer electrolyte (SPE), has been a research area of intense interest. Solid electrolytes have the potential to enable higher energy densities and address concerns over the volatility and flammability of currently used organic solvents. Of the numerous polymer systems under investigation, SPEs produced through crosslinking are quite attractive owing to their high conductivity and excellent mechanical stability. Commonly, crosslinking is achieved through free-radical initiated reactions involving end-functionalize monomers or oligomers. This approach is limited by the available polymer precursors, often necessitating deliberate end-functionalization of the molecules to carry out the reaction. Hence, the formation of crosslinks from molecules in their native form would be more cost-effective and straightforward. In this work, a novel crosslinked solid polymer electrolyte was developed through the copolymerization of polytetrahydrofuran (PTHF) and a cycloaliphatic epoxide (referred as Epoxy) under visible light, without previous functionalization. In particular, these chemicals were employed due to PTHF’s potential to achieve high conductivity and the thermal and mechanical stability associated with cycloaliphatic epoxides, creating a stable, solid crosslinked material. The crosslinked samples were evaluated for their ionic conductivity, thermal stability, crystallinity and mechanical stiffness. They presented conductivity to order of 10-5 to 10-3 S/cm, similar to previously reported electrolytes, now with the manufacturing benefits from the photocuring process, which is energy-efficient and less thermally stressful to the substrate materials. Thermogravimetric analysis of the electrolytes indicated stability at battery operating temperatures, and differential scanning calorimetry demonstrated the material’s amorphous behavior over a wide temperature range. The electrolytes also showed excellent mechanical stiffness. Further studies on 2032 coin cell batteries will be presented and discussed. This work represents a new route for cleaner and safer energy storage devices with potential for a broad variety of applications.

Synthesis and Characterization of a New Lithium Chloro-Thiophosphat as a Solid State Ionic Conductor

Zhan Tao Liu1, Yue Liu2, Sylvia Indris3, Wenqian Xu2, Shan Xiong1, Xuetian Ma4, Lu Feng Yang5 and Hailong Chen2; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Neutron Scattering Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, United States; 3Karlsruhe Institute of Technology-Institute for Applied Materials, Karlsruhe, Germany; 4X-ray Science Division, Argonne National Laboratory, Argonne, Illinois, United States.

Solid state Li+ and Na+ conductors have attracted great interest as the electrolyte for all-solid-state batteries. Compared with conventional batteries using liquid organic electrolytes, all-solid-state batteries with non-flammable solid electrolyte have significant advantages in safety. Among known solid-state Li+ conductors, sulfide-based electrolytes are superior in ionic conductivity than oxide conductors and a number of sulfides with different chemical compositions and crystal structures have demonstrated conductivities comparable to liquid electrolytes [1].

Here we report the synthesis, structural characterization and ionic transport study of a novel lithium chloro-thiophosphate compound, Li4+P2S5Cl. Li4+P2S5Cl can be synthesized in pure phase with facile solid state reaction method under relatively low temperature. The crystal structure of Li4+P2S5Cl is characterized with using neutron and synchrotron x-ray powder diffraction techniques, indicating it has an I-4d3 cubic space group. The ionic conductivity was measured by electrochemical impedance spectroscopy at different temperatures. At 30 °C, Li4+P2S5Cl exhibited an ionic conductivity of 4-2 x 10-5 S/cm. The lithium ion transport in Li4+P2S5Cl was also studied by multiple solid-state NMR methods, including pulsed field gradient and variable temperature NMR. The discovery of this new compound provide a new crystal structure that can served as a foundation for the design of more sulfide ionic conductors with high conductivities.

References:
growth of lithium through the bulk of the garnet-type Li$_2$La$_3$Zr$_2$O$_12$ (LLZO) electrolyte, despite its thermodinamic stability and high shear modulus. An alternative to LLZO is the NASICON family of solid electrolytes, which offers comparable conductivities and mechanical properties. The disadvantage of these materials is that they are chemically unstable against lithium metal, and they typically react upon contact to form a high-impedance interface. While the chemical reaction between NASICON material Li$_{x}$La$_{y}$Al$_{z}$Ge$_{1-x}$ (PO$_4$)$_2$ (LAGP) and lithium was recently shown to cause mechanical and thermal failure, comprehensive understanding of the electrochemical reaction mechanism and phase transformation process at the Li/LAGP interface has not been attained. This knowledge is key for stabilizing NASICON-based batteries for long lifetimes. Here, we investigate the reactions between LAGP and lithium using various electrochemical and ex situ/in situ analytical techniques. In symmetric electrochemical cells, the extent of reaction and distribution of the reacted region throughout the solid electrolyte is found to be strongly dependent on the applied current density. Cell failure is ultimately governed by a dramatic increase in impedance due to mechanical fracture of the solid electrolyte. Multiple characterization techniques reveal that the reacted phase is amorphous, in contrast to the crystalline reaction products predicted to exist by prior density functional theory calculations. Both ex situ and in situ electron microscopy demonstrate that LAGP experiences a volume expansion during reaction, which likely drives fracture of the ceramic. These results demonstrate that the thermodynamic instability of LAGP against lithium alters the failure mechanism when compared to a stable material such as LLZO, and they suggest that NASICON-type materials could be used within viable solid-state devices with additional engineering to stabilize interfaces.

ET01.05.06 Diffusion Mechanism in the Superionic Conductor Li$_3$PS$_4$1 Studied by First-Principles Calculations Karsten Albe, Sabrina Sicolo and Constanze Kalcher, TU Darmstadt, Darmstadt, Germany.

Li$_3$PS$_4$1 was recently discovered as a novel crystalline lithium ion conductor by applying a soft chemistry approach. It adopts a tetragonal structure type suggesting a three-dimensional migration pathway favorable for a high conductivity [S.J. Sedlmaier, Chem. Mater. 29 (2017) 1830]. In order to shed light on the full potential of this material, we performed a theoretical study of Li$_3$PS$_4$1 in the framework of density functional theory. After creating a structural model that accurately accounts for the partial occupancies determined by diffraction experiments, we performed molecular dynamics simulations, unraveled the diffusion mechanisms and calculated diffusion coefficients and the activation barrier for diffusion. The results of the theoretical study on both a crystalline and a glassy supercell imply that Li$_3$PS$_4$1 is in fact a superionic conductor with a much higher conductivity than reported so far.

ET01.05.07 Effect of Cell Volume on Li$^+$ Diffusion in Ordered and Disordered LLZO Systems Andrew Grieder1, Tae Wook Heo2, Nicole Adelstein1, Brandon Wood2 and Prateek Mehta1; 1San Francisco State University, San Francisco, California, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States; 3University of Notre Dame, Notre Dame, Indiana, United States.

The garnet Li$_3$La$_2$Zr$_2$O$_7$ (LLZO) was identified as a promising candidate for solid electrolyte due to its stability and fast lithium diffusion. A lithium deficient system Li$_{1-x}$La$_3$Zr$_2$O$_7$ (LLZO) was studied using classical molecular dynamics simulations to investigate the effect of cell size on ordered and disordered LLZO systems. The disordered systems serve as a proxy for grain boundaries, which are thought to impede Li$^+$ conductivity in polycrystalline materials. We find that the disordered system has regions with more free volume where Li$^+$ gets trapped. Results from the simulations with ordered cell volumes confirm that more free volume in the system decreases the rate of diffusion. Activation energies and diffusion pre-factors were extracted from Arrhenius plots of diffusion at temperatures ranging from 500 K to 2000 K for systems with volumes ranging from 92% to 108% of the experimental cell volume. The activation energies were found to decrease for smaller cell sizes even though there is less space for Li$^+$ to jump. The activation energies for the disordered systems were found to be higher than the ordered systems. The pre-factor and activation energy of the ordered system increase stepwise when cell volume is 106% of the experimental cell volume indicating a change in diffusion mechanism at this volume. The results from different cell volumes of ordered and disordered systems provides insight into diffusion around and through grain boundaries for the LLZO system.

ET01.05.08 Kinetics and Chemical Analysis of the Crystallization Process of Li$_{3-x}$Al$_x$La$_3$Zr$_2$O$_7$ Thin Films Deposited by a Sol-Gel-Derived Wet Chemistry Method Yuntong Zhu1, Zachary D. Hood1, Lincoln Miara2, Kunjoong Kim1, Juan Carlos Gonzalez-Rosillo1 and Jennifer L. Rupp1-3; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Advanced Materials Lab, Samsung Research America, Burlington, Massachusetts, United States; 3Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Garnet-based solid-state batteries exhibit several exceptional properties, including its wide electrochemical stability window, high room temperature Li-ion conductivity, and good thermal stability, rendering it as one of the most promising candidates for next-generation electrochemical energy storage devices. While many studies have detailed bulk garnet-based electrolytes such as Li$_{3-x}$Al$_x$La$_3$Zr$_2$O$_7$ (LLZO), the preferred choice for future electric vehicles is thin films as it can effectively reduce the bulk resistance of the electrolyte layer, and therefore, improve the energy density of the battery. Several studies have demonstrated a promising room temperature ionic conductivity of LLZO thin films using vacuum-based deposition techniques, such as pulsed laser deposition (PLD) and sputtering. Only a few groups have demonstrated the possibility to synthesize LLZO thin films using scalable wet chemical methods such as sol-gel-derived spin coating and dip coating which are of essence for mass-manufacturing. Amongst these techniques, there is still a lack of understanding in the kinetics of the LLZO phase formation via wet chemistry routes. In this study, LLZO thin films are prepared via a sol-gel-derived wet chemistry method. The crystallization and phase transitions of the LLZO thin films during annealing processes were studied by in situ Raman spectroscopy and differential scanning calorimetry (DSC). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of the films during the phase transformation processes. Our results reveal that the as-deposited films undergo several phase transformation processes and the pure garnet phases can be obtained in an attractive low-temperature range. Additionally, we investigated the effect of precursor composition on the phase transformation. This work provides a better understanding of the LLZO phase formation through wet chemistry synthetic methods and offers valuable insight for the design and synthesis of electrolytes for all-solid-state lithium batteries.

Acknowledgments

This work was supported by Samsung Electronics. References:


4. Bitzer, Martin, Tim Van Gestel, and Sven Uhlenbruck. "Sol-gel synthesis of thin solid Li$_3$La$_2$Zr$_2$O$_7$ electrolyte films for Li-ion batteries." Thin Solid
We investigated nucleation and growth of Li in a commercial all solid-state thin film Li free battery with a LiPON solid electrolyte. We conducted Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB\textsubscript{11}H\textsubscript{12} and NaCB\textsubscript{11}H\textsubscript{12}.

The disordered phases of solid lithium and sodium polyborate-based salts, such as closo-borate (B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-}, B\textsubscript{6}H\textsubscript{10}\textsuperscript{3-}, CB\textsubscript{11}H\textsubscript{12}\textsuperscript{-}, and CB\textsubscript{9}H\textsubscript{10}\textsuperscript{-}) and nido-borate (B\textsubscript{11}H\textsubscript{14}\textsuperscript{-}, 7-CB\textsubscript{7}B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-}, and 7-9-C\textsubscript{5}B\textsubscript{7}H\textsubscript{12}\textsuperscript{-}), possess superb superionic conductivities making them intriguing molecules for use in organometallic catalysis and as electrolyte anions in metal-ion battery technologies. This dramatically high conductivity (e.g., ~0.03 S cm\textsuperscript{-1} for NaCB\textsubscript{11}H\textsubscript{12} at 297 K) is enabled by the emergence of a vacancy-rich cation sublattice and possibly further aided by the concomitant onset of high reorientational mobility (typically >10\textsuperscript{10}-10\textsuperscript{11} reorientational jumps s\textsuperscript{-1}) of the quasi-spherical anions. Furthermore, these superionic-conducting phases can be better stabilized at device-relevant temperatures via additional strategies such as ball-milling and anion-mixing.

Neutron scattering techniques are invaluable for elucidating the dynamical nature of the reorienting anions with these hydrogenous materials. Obtaining any detailed fundamental understanding of the reorientational dynamics of these complex anions requires appropriate experimental probes, such as neutron scattering fixed window scan analysis (FWS) and incoherent quasielastic neutron scattering (QENS).

In this work, FWS, QENS, and ab initio molecular dynamics calculations are combined to probe anion reorientations and their mechanistic connection to cation mobility over a broad range of timescales and temperatures.\textsuperscript{1,2} The relationship among the reorientational behaviors and mobilities of the different divalent and monovalent polyhedral anions within the various disordered salt structures obtained from these techniques and the unusually rapid cation translational diffusion properties will be discussed. It is found that anions do not rotate freely, but rather transition rapidly between orientations defined by the cation sublattice symmetry. Furthermore, there appears to be a correlation between reorientational mobility of the anions and the diffusion rates of the cations. The results suggest that synergy between the anion reorientational dynamics and the cation-anion interaction significantly accounts for the high cationic conductivity observed in these salts.

(1) Dimitrievska, M.; Shea, P.; Kweon, K. E.; Berex, M.; Varley, J. B.; Tang, W. S.; Skripov, A. V.; Stavila, V.; Udovic, T. J.; Wood, B. C. Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB\textsubscript{11}H\textsubscript{12} and NaCB\textsubscript{11}H\textsubscript{12}. \textit{Adv. Energy Mater.} 2018, 8 (15), 1703422.


8:15 AM ET01.06.02 Understanding the Effect of Interlayers at the Thiophosphate Solid Electrolyte/Lithium Interface for All-Solid-State Li Batteries Lingzi Sang\textsuperscript{1}, Ralph G. Nuzzo\textsuperscript{2} and Andrew Gewirth\textsuperscript{2}; \textsuperscript{1}University of Alberta, Edmonton, Alberta, Canada; \textsuperscript{2}University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

All-solid-state Li-ion batteries afford possibilities to enhance battery safety while improving their energy and power densities. Current challenges to achieving high performance all-solid-state batteries with long cycle life include shorting resulting predominantly from Li dendrite formation and infiltration through the solid electrolyte (SE), and increases in cell impedance induced by SE decomposition at the SE/electrode interface. In this work, we evaluate the electrochemical properties of two interlayer materials, Si and Li\textsubscript{x}Al\textsubscript{2-x/3}O\textsubscript{3} (LiAlO), at the Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} (LPS)/Li interface. Compared to the Li/LPS/Li symmetric cells in absence of interlayers, the presence of Si and LiAlO both significantly enhance the cycle number and total charge passing through the interface before failures resulting from cell shorting. In both cases, the noted improvements were accompanied by cell impedances that had increased substantially. The data reveal that both interlayers prevent the direct exposure of LPS to the metallic Li, and therefore eliminate the intrinsic LPS decomposition that occurs at Li surfaces before electrochemical cycling. After cycling, a reduction of LPS to Li\textsubscript{2}S at the interface when a Si interlayer is present; LiAlO, which functions to drop the potential between Li and LPS, suppresses LPS decomposition processes. The relative propensities towards SE decomposition follows from the electrochemical potentials at the interface which are dictated by the identities of the interlayer materials. This work provides new insights into the phase dynamics associated with specific choices for SE/electrode interlayer materials and the requirements they impose for realizing high efficiency, long lasting all-solid batteries.

8:30 AM ET01.06.03 Mechanical Properties and Nucleation of Nano-Sized Li Electrodeposited in a Solid-State Battery Michael Citrin\textsuperscript{1}, Heng Yang\textsuperscript{2}, Wenpei Gao\textsuperscript{3}, Simon Nieh\textsuperscript{1}, Xiaoping Pan\textsuperscript{4}, Joel Berry\textsuperscript{4}, David J. Srolovitz\textsuperscript{4} and Julia R. Greer\textsuperscript{1}; \textsuperscript{1}California Institute of Technology, Pasadena, California, United States; \textsuperscript{2}Front Edge Technology, Baldwin Park, California, United States; \textsuperscript{3}University of California, Irvine, Irvine, California, United States; \textsuperscript{4}University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Li metal is the most energy dense anode material for Li-based rechargeable batteries, with a theoretical specific capacity of 3860 mAh\textsuperscript{g\textsuperscript{-1}}. Its use in commercial batteries has been largely limited by the formation of dendrites during cycling in liquid electrolytes, leading to early cell death. It has been theorized that a sufficiently strong and stiff solid electrolyte can mechanically suppress dendrite formation and growth.\textsuperscript{1} Gaining a fundamental understanding of the mechanics of Li dendrite nucleation, strength, and stiffness as a function of microstructure and crystallographic orientation is essential to successfully implement solid electrolytes in Li metal batteries.

We investigated nucleation and growth of Li in a commercial all solid-state thin film Li free battery with a LiPON solid electrolyte. We conducted electrochemical cycling experiments \textit{in-situ} inside a scanning electron microscope (SEM). We observed that during charging, Li preferentially nucleated from the LiPON-Cu interface by rupturing through the Cu film along the topological landscape that reflects the domain boundaries of the underlying...
LiCoO₂ cathode. Continuum electrochemical simulations of Li ion transport suggest that Li is driven to these preferential nucleation sites by the local electrostatic potential that concentrates at the domain boundaries.

We observed Li nuclei with varying morphologies: micron-sized spheres, ~200 nm diameter fibers, and ~300 nm to 1 micron-diameter pillars. We conducted in-situ uniaxial compression experiments in an SEM on electroplated pillars with diameters between 350 nm and 1 μm and aspect ratios of about 3:1, which revealed an average elastic modulus of 6.56 ± 3.03 GPa and an average yield strength of 15.4 ± 8.57 MPa, over an order of magnitude higher than the material’s bulk polycrystalline strength. No size effect was observed, in contrast to the ubiquitous “smaller is stronger” size effect present in single crystalline metallic pillars created by Ga+ focused ion beam (FIB) milling. The results of this work enables laying out a parameter space for stiffness and strength of Li as a function of its deposition process, electrolyte, microstructure and orientation. The results have significant implications for lithium dendrite suppression using robust solid electrolytes for the next generation of lithium metal secondary batteries.

Composite solid electrolyte is attractive as it combines high ionic conductivity of ceramic electrolyte and excellent mechanical properties of polymer electrolyte. For maximizing the ionic conductivity of composite electrolyte, one ideal structure is vertically aligned ceramic particles in the polymer matrix. Here, by using the ice-templating method, we report a vertically arranged wall structure of high ionic conductivity Li₇La₃Zr₂O₁₂ (LLZO) ceramic particles combined with polyethylene oxide (PEO) polymer. The vertical LAGP walls with the shortest lithium-ion transporting path were gathered by the force of the ice crystal growth. Filling PEO in the space between LAGP walls could achieve flexible composite electrolyte and lower interfacial resistance with electrode surfaces. This as-synthesized solid-state composite electrolyte had a conductivity as high as 1.5×10⁻⁴ S cm⁻¹ at room temperature, which was even more significant at high temperature with excellent stability. LiFePO₄/LAGP-PEO/Li full cell was also assembled to test its electrochemical performance; the capacity only decayed ~8% after more than 130 cycles. This research successfully utilizes the ice-templated vertically aligned structure in ceramic/polymer composite electrolyte for solid-state batteries, with comprehensively enhanced battery performance. It could provide new design and application strategy for further composite electrolyte study.

The mechanism could be governed by quantum mechanical aspects; an explanation that has not been considered before. The results of this work could help better understand Li-solid electrolyte interface and how to increase the rate at which solid-state batteries are cycled.

4. Xu et. al. PNAS. 114, 56-61 (2017)

8:45 AM ET01.06.04
Ice-Templated Ceramic/Polymer Composite Electrolyte for Solid-State Batteries Xue Wang1, 2, Huawei Zhai3 and Yuan Yang1; 1 Columbia University, New York, New York, United States; 2 Harbin Institute of Technology, Harbin, China.

Solid polymer electrolytes (SPEs) are considered as promising building blocks for the next-generation lithium-ion batteries. However, current SPEs have yet to be incorporated into real-world applications, due to their low ionic conductivity. This motivates the development of advanced computational models, for better understanding the ionic transport mechanisms and fast exploring the high-dimensional material parameter space, towards designing highly conductive SPE materials. Here we develop a coarse-grained molecular dynamics (CGMD) model with parameters calibrated by full atomistic simulations. For maximizing the ionic conductivity of composite electrolyte, one ideal structure is vertically aligned ceramic particles in the polymer matrix. Here we develop a coarse-grained molecular dynamics (CGMD) model with parameters calibrated by full atomistic simulations. The model captures both the ion motion and the polymer conformational evolution during the transport process, from which the conductivity and transference number are extracted. Adopting the Bayesian optimization (BO) algorithm, conductivity optimization is conducted by automated CGMD simulations in iterations, for screening influential factors, such as the size of molecules and the strength of intermolecular interactions, on the conduction of the polymer-salt system. This research sheds light on the mechanisms of ionic transport in polymers, and provides useful guidance for designing innovative SPE materials.

9:00 AM ET01.06.05
Examining the Low Voltage Stability of Li₇La₃Zr₂O₁₂ (LLZO) Regina Garcia-Mendez and Jeff Sakamoto; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

The band gap of bulk Li₇La₃Zr₂O₁₂ (LLZO) was reported to be 5.87 eV with its band edges positioned above and below the electrochemical potential of Li metal and high voltage cathodes (~5 V), respectively. From a quantum mechanical perspective, this unprecedented wide stability window could enable a paradigm shift in secondary Li batteries whereby the electrolyte does not decompose against the anode and cathode. However, it has been observed that the Li-LLZO interface is destabilized at high Li plating current densities resulting in Li metal penetration. In this study, we hypothesize for the first time that Li metal penetration could result from a quantum mechanical instability rather than an electrochemical or mechanical instability. To analyze this phenomenon, all-solid-state cells consisting of separate working and reference electrodes were used to measure the stability of the Li-LLZO interface at and below 0 V vs Li/Li⁺. Unlike typical tests that vary the current and measure the resulting potential, this study controls the potential and measures the current. At low underpotentials, the Li-LLZO interface exhibits Ohmic behavior. However, at greater underpotentials, deviation from Ohmic behavior is observed, which we believe it is an indicator of a threshold voltage; above which the Li Fermi level is above the conduction band minimum and below which the Li Fermi level is pushed into the conduction band. This study will analyze and interpret the consequences of the latter. Furthermore, galvanostatic tests were conducted in three electrode Li-Li symmetric cells, in which current densities were increased from 0.1 to 2 mA cm⁻² on the Li plating side. It was found that the current density of 0.5±0.1 mA cm⁻² at which the drop in voltage was observed in galvanostatic conditions is comparable to the 0.6±0.1 mA cm⁻² current density at which the threshold voltage occurs in the voltage sweep tests. At this macroscopic scale, no electric field dependence was observed. In this study, we propose a hypothesis to explain why relative soft Li metal can penetrate a relatively hard ceramic electrolyte. The mechanism could be governed by quantum mechanical aspects; an explanation that has not been considered before. The results of this work could help better understand Li-solid electrolyte interface and how to increase the rate at which solid-state batteries are cycled.


9:30 AM ET01.06.06

Solid polymer electrolytes (SPEs) are considered as promising building blocks for the next-generation lithium-ion batteries. However, current SPEs have yet to be incorporated into real-world applications, due to their low ionic conductivity. This motivates the development of advanced computational models, for better understanding the ionic transport mechanisms and fast exploring the high-dimensional material parameter space, towards designing highly conductive SPE materials. Here we develop a coarse-grained molecular dynamics (CGMD) model with parameters calibrated by full atomistic simulations. The model captures both the ion motion and the polymer conformational evolution during the transport process, from which the conductivity and transference number are extracted. Adopting the Bayesian optimization (BO) algorithm, conductivity optimization is conducted by automated CGMD simulations in iterations, for screening influential factors, such as the size of molecules and the strength of intermolecular interactions, on the conduction of the polymer-salt system. This research sheds light on the mechanisms of ionic transport in polymers, and provides useful guidance for designing innovative SPE materials.

9:45 AM ET01.06.07
Amorphous Li₅₋ₓLaₓTiO₃ (LLTO) has been proved to be a promising candidate for electrolyte in All-Solid-State-Battery (SSB), amorphous LLTO thin films were also synthesized by sol-gel process in our previous work. The ionic conductivities of amorphous LLTO thin films were 4.5*10⁻⁸, 6.9*10⁻⁸, 1.3*10⁻⁷, and 3.8*10⁻⁷ S/cm at 30°C, 50°C, 70°C, and 90°C, respectively. However, the inner relationship among the ionic conductivity, structure and mechanism of Li ion transfer is still unexplored. In this study, we successfully prepared amorphous LLTO thin film and amorphous LLTO powder via similar sol-gel procedure, moreover, differences were introduced during the sintering process. XRD and SEM were applied to demonstrate the morphology change with different annealing conditions. In addition, the ionic conductivities of the thin film prepared were measured sequentially. With the accumulation of annealing time, the ionic conductivity of LLTO thin film raised from 2.3*10⁻⁸ S/cm to 9.0*10⁻⁸ S/cm, then dropped back to 1.65*10⁻⁹ S/cm at 30°C. Whereas the activation energy of lithium ion transferring is approximately constant, from which proved the lithium ion transfer in LLTO is dynamic-controlled. It gave us an optimized synthesis condition of LLTO thin film in the meantime for future investigation.

10:00 AM BREAK

10:30 AM ET01.06.08

All-solid state Li-ion batteries (SSBs) have emerged as very attractive alternatives to conventional liquid electrolyte cells for automotive transportation, owing to their enhanced safety and higher energy densities. Similarly, low-cost solid state Na-ion batteries may prove an excellent alternative for grid storage. SSBs are founded on high-performance fast-ion conducting electrolytes, and in the important search for new materials, alkali thio phosphates are a particularly promising class of materials owing to their ductility and good mechanical properties. This presentation will focus on several new alkali fast ion conductors within this class recently developed in our laboratory, and the understanding of superionic conductivity in these materials using a combination of structural elucidation via single crystal X-ray/powder neutron diffraction, ion conductivity via impedance studies, and ab initio molecular dynamics simulations. We correlate crystal structure with ionic conductivity in a range of our newly developed fast ion Li and Na conductors to understand how changes in composition and vacancy population affect the conductivity and activation energy. These considerations lead to an overarching understanding of the relative importance of interstitial alkali ion site occupation for ion migration, and the factors that govern thermodynamic (meta)stability.

11:00 AM ET01.06.09
Li Transport Induced Phase Transitions in Epitaxial LiCoO2 Thin Films Yingge Du, Zhenzhong Yang, Phuong-Vu Ong, Le Wang and Peter V. Sushko; Pacific Northwest National Laboratory, Richland, Washington, United States.

Structurally ordered materials exhibit a broad range of structural, physical, and ion transport properties, which can be further tuned or even drastically transformed by means of judicious elemental doping, strain, and defect engineering. This talk will highlight our most recent effort aiming to modify LiCoO₂ through heteroepitaxy for tunable Li transport, which have profound implications in energy conversion and storage devices. We will present the epitaxial growth and in situ TEM studies of LiCoO₂ with or without overlayers to understand the Li transport processes across the epitaxial interfaces, and device failure mechanisms. We show that while orienting Li containing planes of LiCoO₂ can effectively tune the Li ion transport characteristics, allowing Li incorporation into the overlayers across the interface, it does not modify its stability against Li metal (mimicking a Li dendrite), which preferentially attack the LiCoO₂ crystal structure along the [001] direction, enabling to Li propagation across Li-containing planes.

11:15 AM ET01.06.10
Lithium-Metal Anode Protection—From Liquid to Solid-State Batteries Chunjpeng Yang and Liangbing Hu; University of Maryland at College Park, College Park, Maryland, United States.

High-energy lithium metal batteries are among the most promising candidates for next-generation energy storage systems. With a high specific capacity and a low reduction potential, the Li metal anode has attracted extensive interest for decades. Dendritic Li formation, uncontrolled interfacial reactions, and huge volume effect are major hurdles to the commercial application of the Li metal anodes. In this talk, I will introduce our approaches to protect Li metal anodes from liquid batteries to solid-state batteries. We designed advanced host structures with nanoseconded nucleation sites for Li anode, ion-conductive protecting layers for Li metal anode, and so on. The strategies in liquid batteries improve the performance and safety of Li metal anodes in liquid electrolytes significantly. Superior to the liquid electrolytes, solid-state electrolytes are considered able to inhibit problematic Li dendrites and build safe solid Li metal batteries, but their utilization is mainly hindered by the poor interface between the solid electrolyte and electrodes. We introduce a solid-state Li anode hosted in a 3D garnet-type ion-conductive framework with bottom-deposited Cu. The Li anode is plated within the solid garnet framework from the bottom Cu layer and shows a dendrite-free deposition behavior, effectively averting the dendrite penetration issue. Owing to the 3D ion-conductive host, the volume change and interface contact problem of the Li anode have been significantly mitigated, realizing a high-capacity and safe Li metal anode for solid-state high-energy-density batteries.

11:30 AM ET01.06.11
Dominating Factors Controlling The Ion Conductivity of Na-β''-Alumina Ceramic Electrolytes Marie-Claude Bay¹,², Meike V. Heinz², Nicola Zanon³, Ulrich F. Vogl² and Corsin Battaglia¹; ¹Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; ²Albert-Ludwigs-Universität Freiburg, Freiburg i. Breisgau, Germany; ³FZJ/Nick SA, Stabio, Switzerland.

Ceramic Na-β''-alumina is a fast solid-state sodium-ion conductor at elevated temperature (0.2 S/cm at 300 °C) and thus favored as electrolyte in high-temperature batteries (Na/NiCl₂, Na/S) [1]. Furthermore it is gaining attention as interesting candidate for all-solid-state batteries (1 mS/cm at room temperature) [2]. Although known since the 1970s, processing of Na-β''-alumina into a dense material with high ion conductivity is challenging, in particular due to significant Na loss during sintering. Ion conductivity values reported in the literature vary by a factor of 100 [3]. While these variations are largely accounted for by Archie’s law and results in lower conductivity down to 0.04 S/cm at 68 % density. The overall Na content remains constant within experimental uncertainties. However, we observe evidence in X-ray diffraction that the local sodium concentration inside the grains increases with increasing sintering temperature. We present a model to predict the influence of grain size on the ionic conductivity and effective activation energies of grain and grain-boundary phases. Our insights into microstructural factors controlling ionic conductivity such as grain size and density are instrumental for the
successful integration of Na-b' alumina ceramic electrolytes into next-generation batteries.

References:
3. X. Lu, G. Xia, J. P. Lemmon, Z. Yang, J. Power Sources, 195 (2010), 2431-2442

11:45 AM ET01.06.12
Kinetische Monte Carlo Simulations of Solid State Battery Materials
Steffen P. Grieshammer1,2; Helmholtz-Institut Muenster, Forschungszentrum Juelich GmbH, Muenster, Germany; 2Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany.

Ionic conductivities of solid state battery materials are of crucial importance for the efficiency of solid state batteries. Quantum chemical methods, such as density functional theory (DFT), have become a useful tool to predict structural and electronic properties of solid state materials as well as the migration paths of the ionic charge carriers. In ideal materials with dilute concentration of defects the macroscopic ionic conductivity can be derived analytically from the microscopic energy barrier of ion motion. However, at non-dilute concentration of defects, the motion of ions is correlated and depends on the local environment due to the interactions of the defects. In this case the ionic conductivity is determined by the inhomogeneous energy landscape of ion migration and can be simulated by the Kinetic Monte Carlo (KMC) method.

In this talk, the simulation of the ionic conductivity of solid state materials for battery applications is presented. DFT calculations are performed to derive migration energies and defect interaction energies, which are used to model the energy landscape for the migrating ions. The energy models are applied in an in-house KMC code to simulate the ionic conductivity depending on composition and temperature.

Simulations are performed for oxygen ion conductors like doped ceria and melilitic structured oxides, which are potential electrolytes in rechargeable oxide batteries. In doped ceria, the conductivity is influenced by the interaction of oxygen vacancies with dopant ions leading to a ‘trapping’ next to the dopant ions and ‘blocking’ of the migration paths. In melilitic structured oxides, different migration paths with different energies exist for oxygen interstitials and migration energies are additionally shifted depending on the local arrangement of cations. The effects of these local environments on the conductivity are investigated here.

Simulations are extended to lithium ion conducting materials for application in solid state Li-ion batteries including both electrolytes and electrodes. In particular, the ionic conductivity of Li-intercalation electrodes changes with the charge state of the battery and the advantages and challenges of the KMC method to predict these changes are discussed with regard to selected examples.

1:30 PM ET01.07.01
The Structural and Compositional Factors that Control the Li-Ion Conductivity in LiPON Electrolytes
Valentina Lacivita1, Nongnuch Artrith1 and Gerbrand Ceder1,2; 1Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Amorphous or glassy materials are ubiquitous in rechargeable battery devices. Therefore, understanding the structural and chemical factors affecting the ionic transport in such materials is key for battery technology. However, the complexity of amorphous systems makes this task very challenging. We addressed this question using ab initio computational methods. Specifically, in this presentation we report atomistic-level insight into the mechanisms underlying the mobility of Li+ in amorphous LiPON (lithium phosphorus oxynitride) thin-film electrolytes. These materials have been known for more than twenty years for their outstanding electrochemical performance which combines good ionic conductivity at room-temperature (around 2-3 μS/cm) and compatibility with Li metal anode. Despite the importance of LiPON electrolytes, no conclusive explanation has yet been given for their electrochemical behavior. Our work fits in this context revealing for the first time how structure and chemistry interplay to influence the Li-ion mobility in amorphous LiPON. We show that the conductivity benefits from both amorphization of the phosphate framework and nitrogen doping. In particular, the N doping involves 1(N):1(O) substitutions (apical N) as well as 1(N):2(O) substitutions promoting the condensation between phosphate units (bridging N). We find that the ratio between apical and bridging N changes with the Li:P content, correlating with the conductivity trends experimentally observed and also well reproduced by our models. This detailed understanding of the structural mechanisms that affect Li+ mobility should be useful in optimizing the conductivity of LiPON and other amorphous Li-ion conductors. This work was supported by the ARPA-E IONICS program, U.S. Department of Energy, award DE-AR0000775.

1:45 PM ET01.07.02
Fabrication of All-Solid-State Lithium-Ion Battery Using Inorganic-Organic Hybrid Solid Electrolyte
Jong Heon Kim and Hyun-suk Kim; Chungnam National University, Daejeon, Korea (the Republic of).

Lithium ion battery is considered to be the most promising battery technology currently available because it exhibits relatively high energy density compared to other chemical batteries. Normally, conventional lithium ion battery using organic liquid electrolyte exhibits relatively high ionic conductivity, but has some disadvantages such as safety problem, short lifetime, high cost and low power density. All-solid-state thin film battery is one of the ways to solve these problems, and safety is improved by using non-flammable solid electrolyte. It also has long lifetime, high energy density and less requirements on packaging. However, in spite of these many advantages, the low ionic conductivity of the material itself and the interfacial resistance between the electrode and the solid electrolyte are major problems to overcome for commercial application.

In this work, we studied inorganic-organic hybrid electrolyte with polyethylene oxide (PEO) based polymer and lithium phosphorous oxynitride (LiPON) of oxide based ceramics to reduce the interfacial resistance between the solid electrolyte and the electrodes. LiNi0.5Mn1.5O4 and Li4Ti5O12 were used for cathode and anode, respectively, and all the layers were fabricated on a stainless steel substrate as a thin film. Polymer electrolytes were fabricated by
electrospinning system and all other thin films were fabricated by sputtering system. The thickness, microstructure and surface morphology were examined using transmission electron microscopy and scanning electron microscopy. The crystal structure was identified by X-ray diffraction. The ion-conductivity was measured by an AC impedance method. The electrochemical properties were studied with charge-discharge cycling test and cyclic voltammetry.

2:00 PM ET01.07.03
On Applications of Li-Garnets in Energy Storage and Sensing Devices
Michal Struzik1, 2, Reto Pfenninger1, 2 and Jennifer L. Rupp3, 4; 1Warsaw University of Technology, Warszawa, Poland; 2DMSE, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Materials, ETH Zürich, Zurich, Switzerland; 4ECSS, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Technological and social advancement stimulates a need for clean and sustainable production of energy, its storage and efficient utilization, that will ensure energetic safety of the society of tomorrow. Most popular, nowadays, energy storage technology, based on components consist of lithium conducting polymers and liquids, suffer from limited power densities available, limited miniaturization potential and safety, due to dendrites growth of Li pathways in the electrolyte. New possibilities for safe energy storage devices arise with a development of new generation of highly conducting Li⁺ electrolytes, such as Li-La-Zr-O system, showing pure ionic conductivity of ca. 10⁻³ S/cm² at room temperature, good structural, thermal and chemical stability and compatibility with many of high capacity electrode materials. Li⁺ conducting ceramics can be employed not only as the electrolytes for batteries, but also can be utilized as electrolytes for potentiometric gas sensors for i.e. CO₂ detection and monitoring. The flexibility of applications and perspectives of functionalization of one electrolyte material with different sets of electrodes to define multiple functionalities is in focus of this work.

We discuss on the ceramic processing of Li-La-Zr-O; based solid electrolytes and their structural and electrical properties by the means of X-ray Diffraction, Raman Spectroscopy and Impedance Spectroscopy. Further, we employ Li-garnet electrolytes in all-solid-state battery cells and discuss their performance with emphasis on the interfacial effects. Further we turn on to gas sensing of Li-garnets. We report on the fabrication of potentiometric gas sensor for CO₂ levels monitoring and we perform an experimental evaluation of its performance in a simulated environment. We discover quick response times of ca. 60 s at working temperatures of ca. 300°C, which is faster than similar systems based on NASICON electrolytes.

2:30 PM BREAK

3:30 PM ET01.07.04
Grain Boundary and Dopant Engineered Ultra-Dense Garnet Towards Stable High Current Cycling
Lei Zhang, Chengwei Wang, Dennis McOwen, Jack Gritton, Liangbing Hu and Eric D. Wachsmann; University of Maryland, College Park, Maryland, United States.

High capacity and high rate are the two major requirements for the next generation Li ion batteries. Among all candidates, solid state Li metal battery utilizing solid electrolyte is promising. Garnet type Li ion conductor has been the most widely studied material system due to its high conductivity and stability with Li metal. Aside from high capacity, the high rate cycling with Li garnet solid electrolyte is hard to achieve. Previous reports on cycling failure pointed out Li dendrite growth at grain boundaries. However, a close examination at those reports reveals that the microstructure in their ceramics is not satisfactory. Small grain, clean grain boundary and high relative density are the three key factors that guarantee ceramics to have good mechanical properties. Herein, an ultra-dense garnet pellet was fabricated by controlling grain size and grain boundary phase. The high relative density (>99%) grants the pellet to be translucent. Nano indentation results show the improved mechanical property of ultra-dense garnet to conventional pressed-sintered garnet. Besides good mechanical property, electrochemical stability of dopants in Li garnet is another requirement. Nb, Ta and Al doped garnet were compared. It is found that Ta doped garnet has the best electrochemical stability. Nb doped garnet can be reduced upon Li metal coating. Al doped garnet is venerable to Li dendrite formation. Together with the grain boundary engineering and dopant engineering, stable long-term high-current cycling was proved to be achievable.

3:45 PM ET01.07.05
New Insights into the Most Promising Solid Electrolytes
Daniel Rotterwander1, 2, Gänther Redhammer1 and Martin Wilkening1, 2; 1Institute for Chemistry and Technology of Materials, Technical University of Graz, Graz, Austria; 2Christian Doppler Laboratory for Lithium Batteries, Technical University of Graz, Graz, Austria; 3Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria.

Much scientific attention is devoted to the development of all-solid state batteries (ASSB) as important and superior alternative to electrochemical cells relying on aprotic liquid electrolytes. Among promising solid electrolytes Li-garnets, NASICON (Na-ion Super Ionic CONductor), and LiRAP (Li-Rich Anti-Peroxides) attracted most attention having the potential to realize those future energy storage technologies, due to there extremely high ionic conductivities and exceptional high stability versus low or high voltage electrode material. Despite all the research already performed, however, many questions remain unanswered. In particular, these include the fundamental ones concerning structure, stability, Li ionic conductivity and diffusivity. Herein, we will show, e.g., that (i) the acentric cubic garnet structure is the thermodynamically favored modification of Ga-stabilized LLZO at room temperature with improved chemical and electrochemical properties, (ii) the variation in the phase behavior and ionic transport reported for “NASICON”-based solid electrolytes is related to the preparation history, and (iii) that Liₓ(OH)Cl and variants of Liₓ₋₀.1(OH)⁺Cl⁻ with x > 0, are so far the only thermodynamically stable LiRAPs having experimental proof.

4:00 PM ET01.07.06
Discovery of New Oxide and Sulfide Compounds as Electrolytes for All-Solid-State Li-Ion Batteries
Shan Xiong1, Xingfeng He2, Zhantao Liu1, Zhenhong Ren1, Shuo Chen1, Yifei Mo3 and Hailong Chen1; 1Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 3Physics, University of Houston, Houston, Texas, United States.

All-solid-state batteries (ASSBs) are considered as a promising alternative to conventional Li-ion batteries owing to their good safety properties and potentially higher volumetric energy density. Multiple challenges now exist in the development of ASSBs, including the lack of good solid electrolytes with high conductivity, good electrochemical stability and mechanical compatibility. Here we report recent progresses in our research group in the design and discovery of new oxide and sulfide based lithium ion conductors. Lithium tantalum oxosilicate was identified through a computation assisted search and screening with using ab initio molecular dynamics (AIMD). While the stoichiometric compound is expected to be an ionic insulator, a number of different ion doped compounds were predicted to have very high Li⁺ conductivities. A group of zirconia doped lithium tantalum oxosilicate were successfully synthesized and tested. The 12.5% Zr doped 3 samples showed encouraging ionic conductivity of 5×10⁻⁵ mS/cm at room temperature. Meanwhile, a group of lithium chloro-thiophosphate compounds were also experimentally identified assisted by in situ X-ray diffraction investigations. The new compounds have a novel crystal structure that have never been reported previously. The structure of both sulfides and oxides new compounds were characterized with using synchrotron X-ray diffraction and neutron diffraction. The conduction mechanisms were investigated combing AIMD computation, electrochemical impedance spectroscopy and solid state NMR experiments.

4:15 PM ET01.07.07
Resolving the Amorphous Structure of Lithium Phosphorus Oxynitride (Lipon) Andrew S. Westover1, Valentina Lacivita2, Andrew Kercher1, Nathan Phillips1, Guang Yang1, Gabriel Veith1, Gerbrand Ceder1, 2 and Nancy J. Dudney1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Material Science, University of California, Berkeley, California, United States.

Lithium phosphorus oxynitride or Lipon solid-state electrolytes are at the center of the search for solid-state Li metal batteries. Key to the performance of Lipon is a combination of high Li content, amorphous structure, and the incorporation of N into the structure. Despite the material’s importance, our work presents the first study to fully resolve the structure of Lipon. In order to resolve the structure structural models were first developed using a combination of ab initio molecular dynamics. In this presentation we compare simulated neutron pair distribution functions (PDF), and infrared spectroscopy (IR) of the Lipon with the experimental PDF and IR data. For both techniques we see exceptional agreement between the simulated and experimental results.

Although details of the modeling efforts will be presented in a separate talk, some of the key findings show that N forms both bridges between two phosphate units and non-bridging or apical N. The model further shows that as the Li content is increased the ratio of bridging to apical N shifts from being predominantly bridging at Li contents around 2.5:1 Li:P to only apical N at higher Li contents of 3.38:1 Li:P. Furthermore, the simulations show that Li hopping events are faster in the vicinity of bridging N. This crossover from bridging to apical N appears to directly correlate and explain both the increase in ionic conductivity with the incorporation of N and the ionic conductivity trends found in our own experimental results and across the literature.

This work was supported by the ARPA-E IONICS program, U.S. Department of Energy, award DE-AR0000775.

4:30 PM ET01.07.08
Vertically-Aligned and Continuous Ceramic-Polymer Interfaces in Composite Solid Polymer Electrolytes for Enhanced Ionic Conductivity Xiaokun Zhang1, Yong Xiang1 and Yi Cui2; 1University of Electronic Science and Technology, Chengdu, China; 2Stanford University, Stanford, California, United States.

Among all solid electrolytes, composite solid polymer electrolytes, comprised of polymer matrix and ceramic fillers, garner great interest due to the enhancement of ionic conductivity and mechanical properties derived from ceramic-polymer interactions. Here, we report a composite electrolyte with densely-packed, vertically-aligned, and continuous ceramic-polymer interfaces, using surface-modified anodized aluminum oxide as the ceramic scaffold and polyethylene oxide as the polymer matrix. The fast Li transport along the ceramic-polymer interfaces was proven experimentally for the first time, and an interfacial ionic conductivity higher than 10^-3 S/cm at 0 °C was predicted. The presented composite solid electrolyte achieved an ionic conductivity as high as 5.82×10^-4 S/cm at the electrode level. The vertically-aligned interfacial structure in the composite electrolytes enables the viable application of the composite solid electrolyte with superior ionic conductivity and high hardness, allowing Li-Li cells to be cycled at a small polarization without Li dendrite penetration.

SESSION ET01.08: Poster Session II
Session Chairs: Jennifer Rupp and Venkataraman Thangadurai
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET01.08.01
Role of Lattice Polarization and Rotation on Lithium Diffusion in Li10GeP2S12 (LGPS), β-Li3PS4 (LPS), and Li10GeP2O12 (LGPO) Solid Electrolytes from Ab Initio Molecular Dynamics Alex T. Hall1, Nicole Adelstein1, Nima Leclerc2, Joel B. Varley3 and Leonid Kahl4; 1San Francisco State University, San Francisco, California, United States; 2Cornell University, Ithaca, New York, United States; 3Lawrence Livermore National Laboratory, Livermore, California, United States; 4Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The search for a solid electrolyte in order to create a safe, long-lasting, all-solid battery has been extensive, but the fundamentals of lithium diffusion are still not completely understood. One of the fastest conducting electrolytes that has been identified is Li10GeP2S12 (LGPS), though this electrolyte faces challenges to incorporation in batteries due to instability with the electrode interface. While significant computational research has been done on LGPS, nuances of the mechanisms governing ion diffusion are still unknown. Insight into the extraordinary conductivity of LGPS will enable the engineering and search for new electrolyte materials. Polarization of anions and (P/Ge)S4 tetrahedra as well as rotation of tetrahedra were studied in order to elucidate the difference in conductivity between the LGPS, β-Li3PS4 (LPS), and Li10GeP2O12 (LGPO) solid electrolytes. Experimentally, LGPS has orders of magnitude lower ionic conductivity than LGPS, but a very similar composition and structure. These analyses allow quantification of the effects of electronic structure (polarization) and rotation on lithium diffusion. Polarization and rotation events were extracted from Density Functional Theory Molecular Dynamics (DFT-MD) simulations. Detailed analysis of the DFT-MD simulations revealed correlation of both tetrahedral rotation and polarization with lithium ion diffusion. Expansion of the unit cell in LGPS was found to facilitate the rotation of PS4 tetrahedra in addition to increasing lithium ion diffusion. In constrast, expansion of the LPS unit cell did not affect tetrahedral rotation in a meaningful way. Anion polarization was found to correlate with lower lithium ion diffusion in LPS. The polarization of oxygen in LGPO, a structural isomer of LGPS, is calculated to study the effect of anion polarizability.

ET01.08.02
Microstructural Characterization of Cathodes in Sulfide-Based All-Solid-State Batteries via Tomographic Techniques Sungjun Choi, Wo Dumn Jung, Ji-Su Kim, Hyoungeul Kim, Byeung-Kook Kim and Hae-Weon Lee; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

The all-solid-state lithium-ion batteries (LIBs) have drawn increasing interests and demands as the next-generation rechargeable batteries for electric vehicles and energy storage devices since they have much more potentials (e.g., higher safety, reliability, power density, and design flexibility) than conventional LIBs. However, we all know that any further advances in all-solid-state LIBs are not possible without solving the current raising issues of all-solid-state LIBs, such as low lithium-ion conductivity, structural instability, and high resistance of electrode/electrolyte interface. Recently, sulfide-based all-solid-state LIBs are exhibiting the best performance approaching to the commercialization stage with various material advantages (e.g., excellent lithium-ion conductivity, room-temperature formability, and so on). Despite the comprehensive studies to develop high-performance sulfide-based all-solid-state LIBs, the fundamental understanding of crystallographic structure and elemental distribution for materials used in sulfide-based all-solid-state LIBs has been lacking.

Here we present the recent advances of structural and elemental analysis in sulfide-based all-solid-state LIBs using vacuum-transferred transmission electron microscopy (TEM) and 3-D tomography techniques. According to the high-speed energy dispersive X-ray spectroscopy and selected area penetration.
Lithium ion batteries have shown great promise in electrical energy storage with enhanced energy density, capacity, and cycling lifetimes. However commercial liquid electrolytes consisting of lithium salts dissolved in organic solvents are toxic, corrosive or flammable. Solid electrolytes with superionic conductivity can avoid those shortcomings, so that for safe application. Meanwhile, the mechanical property of solid electrolyte enable it to prevent the risk of lithium dendrites, thereby to achieve high energy density. Here we present a novel class of solid electrolyte materials with three-dimensional conducting pathways based on lithium-rich anti-perovskites (LiRAP). Our previous work shows its high ionic conductivity, low activation energy, and high stability with lithium metal. LiRAP also serves as solid electrolyte functionally in a half battery with LTO and lithium metal, running at elevated temperature. The new LiRAP materials can be readily manipulated via chemical, electronic, and structural means to boost ionic conductivity and serve as high-performance solid electrolytes. Furthermore, by transition metal doping, as TM-LiRAP, this material can serve as cathode in lithium battery. This creative idea is promoted by the fact that the solid-solid interface is a critical issue in solid batteries. Therefore a seamless interface with bi-layered LiRAP electrolyte and TM-LiRAP cathode is designed, and preliminary test evidenced this concept. The enhanced compatibility between LiRAP based electrolyte and cathode, in the aspects of crystal lattices, chemical compositions, thermal evaporation coefficient and volume change during cycling, could improve the solid state interface and hence the battery performance. These results could be quite helpful for the R&D of solid state lithium batteries.

Enhanced Performance of Dopamine Modified Li₆.4La₃Zr₁.4Ta₀.6O₁₂/PEO Composite Electrolyte for Solid-State Battery Huang Zeya and Chang-An Wang; Tsinghua University, Beijing, China. Solid state electrolyte with high ionic conductivity and low interfacial resistance as well good stability is essential for the application of solid state battery. The Ta doped garnet-type solid state electrolyte - Li₆.4La₃Zr₁.4Ta₀.6O₁₂ (LLZTO) has high ionic conductivity and wide electrical window. However, it is not easy to be assembled into batteries due to lack of flexibility. Polymer electrolytes such as poly(oxycetylene) (PEO) have good flexibility, but the room temperature conductivity is low. The PEO has relative narrow electrochemical window and poor thermal stability. The composite electrolyte where the LLZTO particles are dispersed in the PEO has enhanced electronic conductivity, electrochemical stability, thermal stability, and good processability. The addition amount of LLZTO is an important factor affecting the performance of the composite electrolyte. A high ceramic/polymer ratio will significantly increase the proportion of high-speed channel for ion transport in the composite electrolyte and thus achieve better electrical performance. However, the increase in the proportion of ceramics will bring about problems of particle agglomeration, uneven dispersion, and deterioration of mechanical properties. These problems are caused by the incompatible of polymer and ceramic due to their difference in surface energy. In this paper, LLZTO was modified by dopamine to improve the wettability of LLZTO and PEO, so that more than 80wt% of LLZTO can be uniformly dispersed in 20% of PEO/LiTFSI polymer electrolyte. Because of the wetting nature of dopamine, the composite electrolyte has good adhesion with both positive and negative electrodes, which will improve the interfacial contact and thus decrease the resistance. The composite electrolyte with 80wt% LLZTO coated with dopamine in PEO was synthesized by solvent casting method. Electrochemical performance tests showed that after dopamine modification, the conductivity at room temperature (20 °C) increased from 2x10⁻⁸ S/cm to 4x10⁻⁵ S/cm, and the interface resistance between the composite electrolyte and metallic lithium decreased from 490 Ω·cm² to 191 Ω·cm². The thermal stability and electrochemical stability of the composite electrolyte have also been improved. These results showed that the performance of PEO-LLZTO composite electrolyte can be improved by dopamine modification.

Combined DFT and Semi-Continuum Modelling of Space-Charge Regions in Li₃OCl Solid Electrolytes Georgina Wellock, James A. Dawson, Pieremannue Canepa, Saiful Islam and Benjamin J. Morgan; University of Bath, Bath, United Kingdom. Over recent decades, lithium-ion batteries have become the dominant power source for portable devices due to their high energy densities and low self-discharge rates. However, this success, there are safety concerns regarding the use of lithium ion batteries in applications such as electric vehicles and grid scale storage, due to their use of flammable organic liquid electrolytes. Lithium rich anti-perovskites, such as Li₃Oₓ, where X is a halide ion, are a promising family of solid electrolytes with the potential for improved safety in commercial lithium-ion batteries. In polycrystalline Li₃Oₓ, the presence of grain boundaries can strongly affect the transport of lithium ions, due to local changes in atomic structure and associated electrostatic potentials, and therefore affect measured ionic conductivities. Although there has been recent work investigating the effect of grain boundaries on lithium transport in Li₃Oₓ anti-perovskites, this is still not fully understood. A key mechanism by which grain boundaries affect ionic transport is through the formation of space-charge regions. Charged defects, such as lithium vacancies, are expected to segregate to, or from, grain boundaries, which produces a net local charge. This charge interacts with the surrounding crystal regions, where the bulk defects are depleted or accumulated in so-called “space-charge” regions to restore equilibrium. Because these space-charge regions can have defect concentrations that strongly differ from the bulk crystal, they can strongly enhance or decrease the ionic conductivity of the sample. Grain boundary effects on space charge formation and ionic conductivity in Li₃Oₓ and many other lithium-ion solid electrolytes, are not fully understood, especially on the atomic scale. Considering Li₃OCl as a model polycrystalline electrolyte, we have calculated explicit defect segregation and conduction using density functional theory. We have then used these positions and segregation energies to perform self-consistent semi-continuum 1D Poisson-Boltzmann calculations, to predict equilibrium defect concentrations, electrostatic potentials, and resistivities at grain boundaries and their adjacent space-charge regions.

Compared to current commercial available lithium ion batteries, solid-state batteries are emerging as an attractive energy storage device because of their high safety, reliability and high energy density when paired with lithium metal anode. Rigid ceramic electrolytes have a high ion conductivity, but exhibit a very high interfacial resistance due to the discrete contact with electrodes. Soft polymer electrolytes enable a good contact with electrodes with a low interfacial resistance, but their conductivity is too low. Incorporating rigid ceramic electrolytes into soft polymer electrolytes matrix simultaneously enhances ionic conductivity and reduces the interfacial resistance between electrodes and electrolytes. Here we demonstrated a PEO/NASICON composite electrolyte with a high conductivity of $10^{-3}$ S cm$^{-1}$ at 60 °C. When used as a solid electrolyte in Li symmetric cell, the as-prepared PEO/NASICON composite membrane exhibits a very low interfacial resistance. Surface analyses were carried out to prove the mechanism of the low interfacial resistance. Our results show that an interphase was formed between the lithium metal anode and the composite electrolyte, which may account for symmetric cells with low resistance and high stability. Furthermore, a LFP/PEO-NASICON/Li cell was assembled to demonstrate its feasibility for practical applications.

ET01.08.07
TEM Single-Particle Analysis of Solid-State Electrolyte with Mobile Biasing Probe
Nikhilendra Singh$^1$, Timothy S. Arthur$^2$, Julio A. Rodriguez Manzo$^1$, Daan H. Alsøn$^1$ and Norman Salmon$^1$; $^1$Hummingbird Scientific, Lacey, Washington, United States; $^2$Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

Solid-state electrolytes are an alternative to liquid-based electrolytes, when it comes to improving the safety of batteries and their energy density. However, large impedances at solid-state electrolyte-electrode interfaces remain a challenge.

Obtaining reliable electrochemical information from individual solid-state particles is difficult; particles can have nanoscale dimensions and ionic current paths cannot be confined to a single particle unless the electrodes are touching only the particle of interest. However, understanding single-particle effects is paramount to optimize the functionality of assemblies—ion insertion rates can vary at subparticle length scales [1]. This challenging characterization need, however, can be addressed with a purpose-designed in-situ transmission electron microscope (TEM) sample holder with biasing capabilities and a mobile electrode probe. With this TEM platform, a static sample can be approached with a biasing sharpened probe—usually a few tens of nanometers in diameter—to create an electrical circuit, where the contact point can be chosen with high spatial resolution. With the right control electronics, ionic currents in the order of picoamps can be measured while, simultaneously, all TEM-related characterization techniques (high-resolution imaging, electron-based spectroscopy, electron diffraction, etc.) can be applied to study the particle and its interfaces. This approach has been used to investigate, for example, the switching of oxide resistive memories [2], anode materials for batteries [3,4], and the conductance through rows of atoms [5,6].

Here, we present an in-situ TEM study of solid-state electrolyte particles under load. Micron-sized particles were contacted with a mobile probe and cyclic voltammograms were obtained. Ionic currents in the order of picoamps were measured and, simultaneously, electrochemical induced structural changes—within particles and at interfaces—were imaged. Our results show clear correlations between gathered electrochemical data and structural transformations. This approach can be used to study any solid-state electrolyte-electrode configuration, provided that the electron irradiation-induced effects are taken into consideration.


ET01.08.08
Analyzing the Role of Li Transport in Achieving High Critical Current Densities in Li$_7$La$_3$Zr$_2$O$_{12}$: Michael Wang and Jeff Sakamoto; University of Michigan, Ann Arbor, Michigan, United States.

The development of cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) for physically stabilizing the Li-electrolyte interface has shown potential for safe, high energy-density Li-ion batteries in recent years. Despite its high elastic modulus and hardness, it has been observed that Li metal filaments can propagate through LLZO above a certain critical current density (CCD). Currently, reported values for CCD are still well below the current density regimes relevant to electric vehicles, and therefore, there is a need to increase the CCD and understand the mechanisms of Li propagation in LLZO. This study utilizes a combination of recently developed processing methods from the literature in order to achieve low Li-LLZO interface resistance and consistently high CCDs close to 1mA/cm$^2$ at room temperature in Al-stabilized LLZO. The relationship between CCD and temperature is examined. By analyzing the flux of Li$^+$ at the Li-electrolyte symmetric cell, the as-prepared Li$_7$La$_3$Zr$_2$O$_{12}$ symmetric cell exhibits a very low interfacial resistance. Surface analyses were carried out to prove the mechanism of the low interfacial resistance. Our results show that an interphase was formed between the lithium metal anode and the composite electrolyte, which may account for symmetric cells with low resistance and high stability. Furthermore, a LFP/PEO-NASICON/Li cell was assembled to demonstrate its feasibility for practical applications.

ET01.08.09
Mechanochemical Assembly of 3D Mesoporous Conducting-Polymer Aerogels for High Performance Hybrid Electrochemical Energy Storage: Luhua Cheng$^1$, Xiaosong Du$^1$, Yadong Jiang$^1$ and Alexandru Vlad$^1$; $^1$State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China (UESTC), Chengdu, China; $^2$Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Louvain-la-Neuve, Belgium.

Functional and structural tailoring of three-dimensional (3D) conducting polymer nanoarchitectures is a promising route but remains challenging to develop high-performance electrodes for electrochemical energy storage. Herein, we design poly(3, 4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) 3D mesoporous aerogel electrodes through a simple and original one-pot mechanochemical processing route. The hierarchical structure of neat PEDOT:PSS aerogel displays a highly interpenetrated porous conductive network with a record high active surface area of 470$^2$ g$^{-1}$ amongst the class of conducting polymer architectures. Robust structural and electrochemical performances are achieved with high gravimetric, areal and volumetric capacitance metrics of 120 F/g, 2.5 F cm$^{-2}$, and 124 F cm$^{-3}$, respectively, as the result of a mixed hybrid faradic - capacitive charge storage mechanism. Moreover, these performances are attained in organic based electrolytes, reported so far to be incompatible or hinder the electrochemical activity of PEDOT:PSS. We undermine the fundamentals of the electrochemical operation in these electrodes and show that the electrolyte chemistry and the aerogel morphology particularly impact the charge storage performances demonstrating the superiority of the mesoporous architecture for charge transfer and ion exchange. Asymmetric cells are built having a specific capacitance of 40 F/g based on the total mass of electrodes and a good cyclic stability with 90%
A new memory device that can be switched between high and low open-circuit voltages, Vol-RAM, has recently been proposed [1]. Vol-RAM has a laminated structure of Li, amorphous solid electrolyte Li3PO4 and Au, and may be able to achieve higher performance than other memory devices in terms of power consumption and integration. Elucidation of microscopic elementary processes during its operation is strongly desired for practical application. Since it has already been found that the Li ion distribution in Li3PO4 and Li3PO4/Au interface differs between the two voltage states, the next important issue that should be clarified is the behavior of Li ions in Li3PO4 under applied voltages, in other words, under electric fields. First-principles molecular dynamics (MD) simulations would be powerful to study this, but are computationally expensive. On the other hand, the computational cost of MD simulations using empirical potentials is cheap, but determination of their functional forms and parameters to achieve sufficient reliability is extremely difficult. Considering this situation, we have been trying to tackle with this issue using the high-dimensional Neural Network (NN) potential [2], which is expected to achieve high reliability and low computational cost simultaneously. Since the NN potential of Li3PO4 has already been constructed in our previous study [3], we focus on the inclusion of the effects of voltage application in the NN potential in the present study. Using simulations within the density functional theory with VASP package, we examined the dependence of the forces acting on atoms on the structure and applied electric field, and found the followings. First, the change in the force acting on the atom is proportional to the electric field. Second, the proportional coefficient shows a strong correlation with Born effective charge. Third, the Born effective charge correlates with the features of the local atomic structure. These results suggest that NN to predict the Born effective charge from the atomic arrangement information can be constructed, and the NN potential taking account of the effect of applied electric fields can be constructed using the NN for the Born effective charge. We have already constructed a preliminary NN for the Born effective charge, though its accuracy is insufficient. Its improvement is in progress.


SESSION ET01.09: Session VII
Session Chairs: Eric Wachsman and Bilge Yildiz
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 310

8:00 AM ET01.09.01 Microstructural Exploration of Solid-State Electrolytes for Dendrite Suppression—Towards a Reliable Mechanical and Electrochemical Performance Xiaomei Zeng1, Andrew J. Martinolich2, Kimberly A. See2 and Katherine T. Faber1, 1Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States; 2Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States.

The garnet-type oxide Li$_2$La$_{2/3}$Zr$_2$O$_7$ (LLZO) is one of the most promising candidates as a solid-state electrolyte in lithium ion batteries, due to its unique combination of high ionic conductivity (up to ~1.8 mS/cm), and good chemical and electrochemical stability with lithium metal or lithium-containing compounds. The high mechanical strength and shear modulus of LLZO were believed to be adequate for suppressing the formation of lithium dendrites, which is a major challenge in lithium ion battery design. However, recent research reported that the flaws in the polycrystalline microstructure, such as the grain boundaries and interconnected pores, still serve as pathways for lithium dendrite formation and lead to short-circuit in the battery. These boundaries and pores produce dendrite nucleation sites at the electrode/electrolyte interface and their propagation within the electrolyte. Though numerous studies have been conducted to modify the electrode/electrolyte interface to achieve uniform current distribution and suppress the nucleation of dendrites, limited effort has been devoted to optimizing the LLZO microstructure to obtain a robust electrolyte. In this work, we systematically explored the parameters controlling densification and grain growth of LLZO during synthesis. It was discovered that particle agglomeration is responsible for the formation of large cavities and interconnected pores along grain boundaries. The grain size was found to be limited by powder size and moisture content on the powder surface. Through high energy ball milling and freeze drying, nanoscale powders without agglomeration were successfully obtained, which sinter into dense LLZO electrolyte with a relative density > 97% and a grain size > 200 μm. This combination of large grain size and strong grain boundary without interconnected pores significantly enhances the mechanical and electrochemical reliability of the electrolyte. As a result, lithium dendrites were effectively suppressed under high current density > 0.5 mA/cm$^2$. This type of robust electrolyte is critical for the development of all-solid-state batteries to have reliable cyclic performance.

8:15 AM ET01.09.02 Probing the H$^+$ and Li$^+$ Ion Mobility in (Li$_{2/3}$H$_{0.25}$Al$_{0.25}$)La$_{2}$Zr$_2$O$_7$: Through Comprehensive Neutron Scattering and Advanced Electron Microscopy Xiaoming Liu1, Yan Chen1, Cheng Ma1, Zachary D. Hood1, Bui Wang1, Ke An2, Jeff Sakamoto2, Yongjiang Cheng1, Niina Jalarvo1 and Miaofang Chi1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2University of Science and Technology of China, Heifei, China; 3University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Though liquid-based lithium-ion batteries are ubiquitous to our daily life, they are reaching their theoretical limits in terms of their energy and power densities. New battery configurations are urgently needed to meet the requirements for large-scale applications, especially in applications where the power densities are relatively high (e.g. electric vehicles, grid energy storage systems, etc.). Aqueous lithium batteries are considered to be one of the most promising solutions due to their low cost, high rate capability, and their prospect in utilizing metallic lithium, the solid-state anode with highest theoretical capacity and lowest electrochemical potential. Recently, it was reported that the garnet-based Li$_{0.25}$Al$_{0.25}$La$_{2}$Zr$_2$O$_7$ (LLZO) shows excellent structural stability towards exposure to aqueous solutions with a large range of pH value, with Li$^+$ ions being partially substituted by H$^+$, demonstrating its promise to be used as a separator to stabilizing Li metal in aqueous lithium batteries. However, the mobility of Li$^+$ and H$^+$ ions in protonated LLZO (H$_x$-LLZO), that critically determines the performance of LLZO, has yet to be investigated. This work is largely due to the challenges in differentiating the diffusion of
the two ions. In this work, we successfully reveal not only the structural evolution after ion exchange in Hx-LLZO, but also the mobility of H+ and Li+ ions by combining high-resolution scanning transmission electron microscopy (STEM), neutron diffraction, and electron energy loss spectroscopy. Our results show that the H+ ions in Hx-LLZO are largely immobile at temperatures less than 200 °C while the Li+ ions remains mobile in the structure. The activation energy of Li+ ions in protonated LLZO is about 20.08 kJ/mol at room temperature, which is ~1.5× that of pristine LLZO, indicating a reasonable Li+ ion conductivity in Hx-LLZO. Our results highlight the potential of LLZO as a separation layer to protect metallic lithium anode in aqueous lithium batteries.

8:30 AM ET01.09.03
Direct Growth of 3D Host on Cu Foil for Stable Lithium Metal Anode Xiaogang Han¹, Fei Shen¹ and Xuchun Gui²; ¹Xi'an Jiaotong University, Xi'an, China; ²Sun Yat-sen University, Guangzhou, China.

Due to light-weight and high specific capacity, lithium (Li) metal anode has been regarded as the “Holy Graal” for lithium-ion based batteries. However, the issues of mossy and dendritic Li formation and infinite volume expansion, leading to low Coulombic efficiency and poor cycling performance, retards Li metal anode application in practice. Effort should be done to address the issues in order to the application of Li metal anode. In this study, we report a novel design to stabilize Li metal anode by growing porous carbon nanotube (CNT) sponge directly on Cu foil, (C-host@Cu), where CNT sponge as host and Cu foil as current collector. The intrinsic porous feature of CNT sponge meets the requirements for an outstanding Li host: 1) high porosity to accommodate infinite volume change of Li; 2) low local current density to suppress Li dendrite formation; 3) stable and electrically conductive framework for Li deposition during long-term cycles; 4) strong seamless attachment to the current collector. The as-designed 3D host Li metal anode exhibits stable cycling performance with high Coulombic efficiency ~99% at a current density of 1 mA/cm² over 250 cycles. In contrast, the bare Cu electrode presents a mossy-like morphology with a low Coulombic efficiency ~60% after 150 cycles. The results reveal that the effective confinement of Li deposition in this unique 3D host successfully suppresses the growth of Li dendrites.

9:00 AM ET01.09.04
Simulations of Ionic Transport in Disordered and Correlated Solid Polymer and Amorphous Ceramic Electrolytes Boris Kozinsky¹, ², Chris Ablitt¹, ², Mordechai Kornbluth¹, Jonathan Mailoa¹ and Nicola Molinari²; ¹Harvard University, Cambridge, Massachusetts, United States; ²Imperial College London, London, United Kingdom; ³Bosch Research, Cambridge, Massachusetts, United States.

Materials design for next-generation solid-state Li-ion batteries require atomistic-level understanding of ionic transport mechanisms and the required ingredients and design principles for enabling high ionic conductivity in solid-state materials at room temperature. Strong ion-ion interaction, geometric frustration, disorder and collective motion are emerging as common themes in recent investigations of super-ionic materials. In this talk, we present recent efforts to gain mechanistic understanding of the influence of correlation, disorder and frustration on ionic transport in solid polymer and ceramic materials. We find that ionic dynamics in polymer electrolytes is strongly influenced by the host polymer dynamics and the strong coupling between mobile component species and the host polymer. In the domain of inorganic electrolytes, the success of LiPON thin films indicates promise of amorphous materials, which are known to have different transport properties than their crystalline counterparts. Using atomistic simulations of ion dynamics, we analyze ionic transport mechanisms in the presence of disorder, using insights to develop design rules for optimizing structure and composition of glassy electrolytes.

9:30 AM ET01.09.05
Electrochemical Characterization of Ionic Liquid Electrolytes for Printed Secondary Zinc-Manganese Dioxide Batteries Bernard Kim¹, James W. Evans² and Paul K. Wright³; ¹Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States; ²Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Ionic liquids are room temperature solutions of cations and anions that have emerged as possible electrolyte materials for batteries due to their wide thermal and electrical potential stability windows relative to conventional electrolytes [1]. In the case of zinc-based batteries, their use has been shown to enable reversible cycling with traditional electrode materials, unlike cycling in aqueous electrolytes [2]. Furthermore, their extremely low vapor pressure allows for integration with a polymer to form a printable, monolithic gel polymer electrolyte which can function both as a mechanical separator as well as an ion conductor [3]. However, the vast array of possible cation and anion pairs making up each ionic liquid as well as each pair’s compatibility with supporting metal salts reveals a significant challenge in characterizing all possible combinations for optimal performance in full cells. Specifically, this work seeks to identify optimal ratios of ionic liquid, supporting metal salt, and gel polymer in order to maximize redox currents as well as mitigate losses associated with repeated cycling.

This work is conducted in two parts. The first part determines the diffusion coefficient of Zn²+ and the peak currents, solution resistance, and redox potentials of Zn/Zn²⁺ in solutions of only ionic liquid and zinc salt. The second part determines the solution resistance and characterizes the reversibility of gel polymer electrolytes with varying compositions of ionic liquid, zinc salt, and polymer binder. Cyclic voltammetry and electrochemical impedance spectroscopy are used to determine constant values and characterize material compositions.

Ionic liquids with smaller cations demonstrate higher peak currents in cyclic voltammograms, but they also exhibit narrower potential stability windows with higher rates of unwanted reactions within the Zn/Zn²⁺ redox window. Gel polymer electrolytes demonstrate good reversibility for at least 50 cycles and solution resistances comparable with the pure ionic liquids.


9:45 AM ET01.09.06
A Mechanism for Lithium Metal Penetration Through Solid Electrolytes—Atomic Simulations for Grain Boundary Softening Seungho Yu and Donald Siegel; University of Michigan--Ann Arbor, Ann Arbor, Michigan, United States.

Models based on linear elasticity suggest that a solid electrolyte with a high shear modulus will suppress ‘dendrite’ formation in batteries that use metallic...
We present a quantitative analysis of mechanical reliability of composite electrodes. We quantify the mechanical stress caused by chemical expansion and accommodate intercalation-induced deformations. Consequently, the effective ionic conductivity is expected to reduce. Second, interfacial delamination reduces internal contact and may become the kinetic link to the battery power-density. Low porosity solid-state composite electrodes are generally more prone to mechanical degradation if not designed to accommodate inhomogeneities in elastic properties arising from microstructural features.

This talk will review the concept and fabrication of all-solid-state Li-ion microbatteries using TiO$_2$nts as negative electrode [1-7]. Effects of material selection and processing on the performance and reliability are presented as a means to develop conceptual guidelines to understand and improve microbattery designs. Fundamentals such as electrode reactions, lithium ion diffusion and the conformal electrodeposition mechanism of polymer electrolytes onto the nanostructured electrodes will be presented. The fabrication of a full 3D microwell showing high electrochemical performance will be presented and the development of the next generation of 3D microbatteries will be discussed.

References

11:00 AM ET01.09.08
Li$_3$SnZr(PO$_4$)$_3$: NASICON-Type Solid Electrolyte for Lithium Batteries Sunil Kumar, Tanvi Pareek and Sushmita Dwivedi; Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Indore, India.

Safety issues associated with the high flammability and volatility of organic electrolytes used in commercial rechargeable lithium-ion batteries has led to significant attention to ceramic-based solid electrolytes. In this work, Li$_3$SnZr(PO$_4$)$_3$ (LSZP) ceramics were fabricated via a sol-gel route and were characterized for their properties using the X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and electrochemical chemical impedance spectroscopy. Rietveld refinement of synchrotron X-ray diffraction data confirmed the room temperature crystal structure of Li$_3$SnZr(PO$_4$)$_3$ as rhombohedral (R-3c space group). The Zr 3d, Sn 3d, P 2p, Li 1s and O 1s, core level X-ray photoelectron spectra associated with different valence states on the LSZP sample were deconvoluted. Surface morphology, densification, and the ionic conductivity of ceramics sintered at various temperatures were investigated. LSZP ceramics sintered at 1273 K exhibited an excellent room temperature bulk ionic conductivity of about $10^{-3}$ S cm$^{-1}$ and associated activation energy ~ 0.36 eV in the temperature range of 300 – 500 K. DC polarization study confirmed the conductivity of LSZP ceramics as predominantly ionic. Distinct relaxations observed in dielectric and modulus formalisms and the temperature dependence thereof are also discussed.

11:15 AM ET01.09.09
Fluorinated Solid Electrolyte Interphase Enables Highly Reversible Solid-State Li Metal Battery Xiulin Fan, Xiao Ji, Fudong Han, Jie Yue, Ji Chen and Chunsheng Wang; University of Maryland, College Park, College Park, Maryland, United States.

Solid-state electrolytes (SSEs) have received great interest in recent years due to the escalating demands for the next-generation high energy battery technologies. However, the facile formation of the Li dendrite in the SSEs with much lower critical current density of only 1/10 of the conventional non-aqueous electrolytes hindered the possible commercialization of the high energy SSE Li metal batteries. Herein, we describe a simple and efficient strategy to stabilize the Li metal anode in the SSE batteries by in situ forming an efficient LiF-rich solid electrolyte interphase (SEI) layer between the SSE and the Li metal. This LiF-rich SEI layer not only effectively blocks electron leakage but also efficiently facilitates Li transport along the interface and suppresses the penetration of Li dendrite into the SSE.

11:30 AM ET01.09.10
Electro-Chemo-Mechanical Stability of Solid-State Battery Interfaces Giovanna Bassì$^{1,2}$, Peter K. Hart$^{1}$, Yet-Ming Chiang$^{3}$ and Craig Carter$^{1}$; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; $^{2}$Energy Storage, Bosch, Sunnyvale, California, United States; $^{3}$Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Despite the progress in achieving high solid-electrolyte bulk conductivity, the rate capability of many all-solid-state batteries (ASSBs) remains poor. This is typically ascribed to various interfacial phenomena, including chemo-mechanical instability of composite electrodes and unstable metallic lithium interfaces. Such mechanisms are difficult to ascertain and characterize experimentally.

Fracture in solid Li-ion conductors represents a barrier for Li transport, and accelerates the decay of rate performance. Therefore, mechanical degradation is linked to the battery power density. Low porosity solid-state composite electrodes are generally more prone to mechanical degradation if not designed to accommodate intercalation-induced deformations.

We present a quantitative analysis of mechanical reliability of composite electrodes. We quantify the mechanical stress caused by chemical expansion and contraction of electrode particles and identify two main degradation mechanisms. First, the formation of micro-cracks within the solid electrolyte (SE) is expected to reduce the SE effective ionic conductivity [1, 2, 4]. Second, interfacial delamination reduces internal contact and may become the kinetic resistance.
Our analyses lead to guidelines for the engineering of particle size, volume ratio of active material, interfacial cohesion and the electrolyte mechanical properties [2-5]. The impact of mechanical degradation on an electrode's transport properties will also be discussed. In particular, we illustrate, via random-walk analysis, how micro-cracking of solid-Li-ion conductors increases the cell tortuosity, especially in densely packed microstructures [4, 5].

Finally, we explore the interplay of surface geometry and interfacial resistance in the Li-metal cells. Electric field magnification at the tip of surface defects and grain boundaries may lead to a largely non-uniform current density and localized Li-plating. Strategies for current density regularization are investigated. For instance, mechanical confinement causes pressure to rise within the Li metal filling a crack. Exploiting stress-potential coupling, such pressure can prevent further plating and divert deposition away from the crack tip. The model predicts the limiting conditions that hinder Li plating at the crack tip and prevent further electrolyte’s fracturing.

References:

1:30 PM ET01.10.01
Intrinsic Improvement of LLZO Solid-State Electrolyte to Suppress Li Dendrite Formation
Yulia Arinicheva1, Juliane F. Nonemacher2, Fadli Rohman2, Maria Meledina1, Chih-Long Tsai1, Alexander Schwedt1, Joachim Mayer1, Jürgen Malzbender2, Dina Fattakhova-Rohlfing1, Olivier Guillou1 and Martin Finistenрубucher1; 1Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research Materials Synthesis and Processing (IEK-1), Jülich, Germany; 2Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research: Microstructure and Properties of Materials (IEK-2), Jülich, Germany; 3Central Facility for Electron Microscopy, RWTH Aachen University, Aachen, Germany.

After the unexpected discovery of similar metal dendrite issues in dense ceramic electrolytes as in conventional liquid ones, the key factors governing the Li dendrite formation e.g. in LLZO are still not fully understood. Possible factors include lithium ion diffusion kinetics at grain boundaries, influenced by microstructure [1, 2] and density [3], as well as inhomogeneous contact between LLZO solid electrolyte and Li electrodes, leading to high contact resistance. Multiple strategies can be employed to reduce the contact resistance: first, the surface can be treated in order to remove LiOH/Li2CO3-contamination [4], second, the effective contact area can be increased [5] and third, surface defects can be reduced [6], and finally, the surface can be coated to increase the wettability [7-9].

To elucidate the interdependence of the various possibilities, the present work focuses on the effect of doping, microstructure, surface properties and density of the Li0.66La3Zr1.6Ta0.4O12 solid state electrolyte on its electrochemical performance, especially the resistance to dendrite penetration. Al-doped and Al-free LLZO:Ta precursor powders with larger (~5 μm) and nano-sized particles were synthesized via solid-state synthesis and solution-assisted solid-state synthesis, respectively. LLZO:Ta pellets with high density (~99% of the theoretical density), high conductivity (~10⁻⁴ S/cm ) and various grain sizes were obtained for both precursor powders by hot pressing. The grain size dependence of mechanical properties (fracture toughness, micro hardness, Young modulus), ionic conductivity, cycling stability, stability in contact with humid air on microstructure was investigated. The conductivity was separated into grain and grain boundary contributions. Activation energies of polycrystalline conductivity for the samples with larger and smaller grains were determined. Lower interfacial resistances and better cycling behaviour was found and attributed to surface quality and mechanical properties of the material.

7. Tsai, C.L. et al. ACS Appl Mater Interfaces 2016

1:45 PM ET01.10.02
Structure and Ion Transport at Polymer-Ceramic Electrolyte Interface
Xi C. Chen, Amaresh Samuthira Pandian, Xiaoming Liu, Robert Sacci, Gabriel Verith and Nancy J. Dudney; Oak Ridge National Lab, Oak Ridge, Tennessee, United States.

Composite solid electrolytes consisting of a polymer electrolyte and a ceramic electrolyte are promising in meeting the challenging requirements to stabilize lithium metal anode to achieve high energy density. The requirements include high ionic conductivity, high shear modulus, good chemical stability and adhesion with metallic lithium. When the components act synergistically, composite electrolytes may overcome the intrinsic weaknesses of single component electrolytes such as brittleness of ceramic electrolytes and low shear modulus of polymer electrolytes. However, composite electrolytes with high ceramic loadings suffer from low ionic conductivity due to a large interfacial resistance for ion transport [1, 2] The origin of this interfacial resistance is not well-understood.

This work focuses on understanding ion transport at the interface between polymer electrolyte and ceramic electrolyte. Polymer-ceramic-polymer electrolyte (trilayer) cell is constructed to study the interfacial resistance between the polymer and ceramic electrolyte. Sintered ceramic plate from Ohara corporation is sandwiched between two thin layers of polymer electrolyte (poly(ethylene oxide) + lithium triflate salt) obtained by spray coating. The interfacial resistance is determined by analyzing the impedance spectra of single layer ceramic plate, single layer polymer electrolyte and the trilayer sample. We discovered that at 30 °C, the interfacial resistance is as high as 10000 Ohm. As an effort to decrease the interfacial resistance, plasticizers such
as tetraethylene glycol dimethyl ether (TEGDME) and dimethyl carbonate (DMC) are infused into the polymer electrolyte of the trilayer cell. Both plasticizers enhance the ionic conductivity of the polymer electrolyte but have limited effects on facilitating ion transport across the polymer-ceramic interface. The structure of polymer electrolyte at the polymer-ceramic interface is examined with depth-profiling infrared spectroscopy and neutron reflectometry in order to shed light on the origin of this large interfacial resistance.

Acknowledgements:
This work was primarily supported by the U. S. Department of Energy (DOE-EERE), Vehicle Technologies Office (Advanced Battery Materials Research, Tien Du-Duong). We thank Brion Hoffman, Ohara Corporation, for supplying ceramic electrolyte powders.

References:

2:00 PM *ET01.10.03
Structure, Chemistry and Charge Transfer Resistance of the Interface Between Garnet Solid Electrolyte and Oxide Cathodes Bilge Yildiz, Gulin Vardar, Younggyu Kim and Yet-Ming Chiang, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

All-solid-state batteries promise significant safety and energy density advantages over liquid-electrolyte batteries. The interface between the cathode and the solid electrolyte is an important contributor to charge transfer resistance. Strong bonding of solid oxide electrolytes and cathodes requires sintering at elevated temperatures. Knowledge of the temperature dependence of the composition and charge transfer properties of this interface is important for determining the ideal sintering conditions. To understand the interfacial decomposition processes and their onset temperatures, model systems of LiCoO2 (LCO) thin films deposited on cubic Al-doped Li3La2Zr2O7 (LLZO) pellets were studied as a function of temperature using interface-sensitive techniques. X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and energy-dispersive X-ray spectroscopy (EDS) data indicated significant cation interdiffusion and structural changes starting at temperatures as low as 300°C. La2Zr2O7 and Li2CO3 were identified as decomposition products after annealing at 500°C by synchrotron X-ray diffraction (XRD). X-ray absorption spectroscopy (XAS) results indicate the presence of also LaCoO3, in addition to La2Zr2O7 and Li2CO3. Based on electrochemical impedance spectroscopy, and depth profiling of the Li distribution decomposition products after annealing at 500°C, the interfaces exhibited significantly increased impedance, up to 8 times that of the as-deposited samples after annealing at 500°C. This work was primarily supported by the U. S. Department of Energy (DOE-EERE), Vehicle Technologies Office (Advanced Battery Materials Research, Tien Du-Duong). We thank Brion Hoffman, Ohara Corporation, for supplying ceramic electrolyte powders.

References:

2:30 PM ET01.10.04
Fracture Toughness Improvements and Lithium Metal Penetration in Nanocomposite Ceramic Electrolytes Maria C. Ramirez, Mok Yun Jin and Brian W. Sheldon; Brown University, Providence, Rhode Island, United States.

The relatively low fracture toughness of ceramic solid oxide electrolytes can significantly limit battery performance and reliability. While small dimensions are generally needed for faster ion transport, these length scales also restrict the approaches that can be used to improve fracture resistance. Nanoscale reinforcements are thus a logical option for improving the fracture resistance of ceramic electrolytes. Graphene oxide and reduced graphene oxide have been successfully used to reinforce a variety of polymer and engineering ceramics, where significant changes in the elastic modulus and toughness have been obtained with relatively low volume fractions. In the present work, we explore the reinforcement capability of small amounts of graphene oxide added to oxide-based lithium ion conductors. Standard electrochemical measurements were used to measure ionic and electrical conductivities. Fracture toughness measurements on both large and small scale specimens were then employed, to provide detailed information about the mechanical properties of these materials.

2:45 PM ET01.10.05
Effects of Electrochemical Cycling on the Mechanical Behavior of High Purity Lithium Erik G. Herbert1, Stephen A. Hackney1, Nancy J. Dudney2 and Fereshette Mallakpour3; 1Michigan Technological University, Houghton, Michigan, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanindentation experiments have been performed in high purity vapor deposited and electrochemically cycled lithium. At a homologous temperature of 0.66, the measured hardness is found to depend significantly on the indentation depth and strain rate, and is studied as a function of cycling conditions. The experimental observations are rationalized in terms of lithium’s evolving dislocation density, Nabarro-Herring and Harper-Dorn creep and dislocation mediated flow. In well-annealed, low dislocation density lithium, it is surmised that dislocation motion is initiated by the activation of a Frank-Read source. Prior to dislocation motion, the plastic deformation is taken to be controlled by self-diffusion to the free surface and/or preexisting dislocations. Collectively, the proposed rationalizations provide a novel framework to better understand the complex relationship between electrochemical cycling, the dislocation density and the mechanisms that control pressure within submicron scale defects at the lithium/solid electrolyte interface. Moreover, the experimental observations and mechanistic rationalizations provide new insight into the mechanisms capable of causing mechanical failure of a solid electrolyte.

3:00 PM BREAK

3:30 PM *ET01.10.06
Beyond Dendrites, Cycling Li-Metal Across Garnet at High Current Densities Eric D. Wachsman; Maryland Energy Innovation Institute, University of Maryland, College Park, Maryland, United States.

Solid-state Li-batteries (SSLiBs) have the potential to be a transformational and intrinsically safe energy storage solution. However, their progress has been limited by high solid-solid interfacial impedance and numerous reports of Li-dendrites and a corresponding “critical current density”. By first modifying the garnet surface to enable Li-metal to wet it and then fabricating garnet-electrolytes into tailored tri-layer microstructures to form electrode supported dense thin-film (~10μm) solid-state electrolytes we have been able to overcome these limitations. The microstructurally tailored porous garnet scaffold support improves electrode/electrolyte interfacial area, overcoming the high impedance typical of planar geometry SSLiBs resulting in an area specific resistance (ASR) of only ~2 to 7 Ωcm² at room temperature. The unique garnet scaffold/electrolyte/scaffold structure further allows for charge/discharge of the Li-metal anode and cathode scaffolds by pore-filling, thus providing high depth of discharge ability without mechanical cycling fatigue seen with typical electrodes. Moreover, the scalable multilayer ceramic fabrication techniques, without need for dry rooms or vacuum equipment, provide for dramatically reduced manufacturing cost.

The fabrication of supported dense thin-film garnet electrolytes, their ability to cycle Li-metal at high current densities with no dendrite formation, and results for Li-metal anode/garnet-electrolyte based batteries with a number of different cathode chemistries will be presented.
Enhancing Stability Between Garnet Electrolyte and Li Metal Electrode with a Metal Carbide Coating

Fengyu Shen, Mamid Dixit, Wahid Zaman and Kelsey B. Hatzell, Vanderbilt University, Nashville, Tennessee, United States.

Overcoming large interfacial resistances at electrode/electrolyte interfaces is a major challenge facing all-solid-state batteries. To alleviate this challenge, there has been a significant push toward manufacturing and processing monolayer thin films and coatings at solid electrolyte interfaces [1, 2]. Typically, atomic layer deposition has been the manufacturing approach used within the solid electrolyte community. While effective, this process increases the cost of processing solid electrolytes [1, 3]. Herein, we explore a facile coating process where colloidal low-dimensional metal carbide materials are deposited on the solid electrolyte with a spray coater. The effects of spray coating sub-micron scale metal carbide coatings directly on Li10YS2La203-δZrO2 (LLZO) electrolytes to decrease the interfacial resistance are investigated. Electrochemical characterization reveals that the growth rate of interface resistance for the coated LLZO is almost one order of magnitude smaller than that of the bare LLZO. The wettability of Li on LLZO electrolyte is enhanced and a greater electrochemical window is obtained. The critical current density is improved 2x with the metal carbide coating at room temperature and the capacity of LiTi4S2/LLZO/Li cell is stabilized. This work demonstrates a facile and scalable way of coating ceramic electrolytes for low interfacial resistances.

References

Intercalation Induced Mechanical Failure of Olivine Compounds

Ananya Renuka Balakrishna1, Christian Henrikss2, Kai Xiang1, Dothe B. Ravnsbaek2, Ming Tang1, Craig Carter1 and Yet-Ming Chiang1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2University of Southern Denmark, Odense M, Denmark; 3Rice University, Houston, Texas, United States.

When electrodes fail mechanically, it affects a battery's capacity, rate capability and lifetime. In ion storage compounds, mechanical failure typically occurs after ion intercalation changes the electrode's volume. These volume changes increase the elastic energy stored in electrodes. Sometimes, electrodes crack to relieve this stored elastic energy. Electrode cracking can be mitigated by reducing the electrode particle size [1], by doping electrode compounds [2] and by operating at low overpotentials [3]. Our recent experiments show that when crack propagation is suppressed, olivine compounds such as NaFePO4 and NaMnFe203-P2O7 release their stored elastic energy by forming a disordered phase [4].

Here, we identify the critical particle size at which electrode cracking and amorization are suppressed. To that end, we use olivine compounds, such as LiFePO4, NaFePO4, LiMnFe203-P2O7, and NaMnFe203-P2O7, as model systems. We compute the elastic energy stored in electrodes analytically as a function of particle size and lattice constant. Furthermore, we compare the electrodes' stored energy with the energy required to form new surfaces (fracture) or a disordered phase (amorization). This analysis results in a narrow range of particle sizes at which olivine compounds neither crack nor amorize. The present research provides insight into the effects of scaling, lattice strains, and glass-former conditions on the mechanical stability of intercalation electrodes.

References

Rational Design of Nanostructures in Solid Polymer Electrolyte

Snehashis Choudhury and Lynden Archer; Cornell University, Ithaca, New York, United States.

Metal based batteries that comprise of a reactive metal anode like lithium, sodium or potassium are the future of energy storage devices because of their high volumetric and gravimetric energy density. However, these batteries fail by three distinct modes – chemical instability due to internal reactions, morphological instability due to uneven electrodeposition and hydrodynamic instability due to convective flows at the vicinity of electrode-electrolyte interface. Both liquid based, and solid-state electrolytes have their individual advantages and disadvantages in mitigating these issues. In this work, we show that solid-polymer interphases based on crosslinked polymer networks can essentially possess qualities from both of these worlds. We find that by tuning the thermodynamic interactions between the polymer network and oligomer diluents, one can control the bulk properties like ion transport and mass transfer rate. Thus, it is possible to design solid-like electrolyte-phases where the electroconvective flows can be inhibited, while maintaining high ionic conductivity. We further show that these polymer networks act as excellent interfacial layer for lithium metal electrode to inhibit dendrite growth and side reactions. On pairing with high voltage cathodes, the lithium metal battery exhibit over 250 cycles of stable operation even at high current densities.

Organic Radical Thin-Film Batteries with Solid-State Electrode

Roland Roese1, 2, Philip Zimmer1, 2, Raik Zacharias1, 2, Tina Mede1, 2, Ulrich S. Schubert1, 2 and Harald Hoppe1, 2; 1Center for Energy and Environmental Chemistry Jena (CEEC Jena), FSU Jena, Jena, Germany; 2Laboratory of Organic and Macromolecular Chemistry (IOMC), FSU Jena, Jena, Germany.

All-solid state thin film batteries with organic radical polymer electrodes, such as TEMPO (2,2,6,6-tetramethyl-4-piperidinyl-N-oxyl radical) [1] and TCAQ (tetraacyano-9,10-anthraquinonedimethane) [2] are demonstrated. These electrodes as well as the solid-state electrolyte were cast from solution respectively liquid-phase, which was enabled by use of orthogonal solvent systems. The thickness of all functional films within this device as well as the...
solid-state electrolyte were systematically varied in order to understand performance limiting factors, such as limited charge or ionic conductivity. For analysis of the same, impedance spectroscopy was applied. Finally, charging and discharging kinetics are presented and linked with an optimized device layout.


SYMPOSIUM ET02

TUTORIAL: High-Efficiency Crystalline Silicon Photovoltaics—Fabrication, Devices, and Testing
November 25 - November 25, 2018

* Invited Paper

Silicon and related thin films are applied widely in solar cells and other electronic devices. This tutorial will introduce the preparation methods, materials properties, fundamental Si surface chemistry, and device engineering. This will be followed by a review of the device physics of solar cells and the device output characteristics during testing. We shall also survey different monocrystalline Si solar cell architectures, with special emphasis on interdigitated back contact cells and the use of carrier-selective passivating contacts in advanced cell designs. Finally, we will discuss the physics of carrier lifetime and efficiency measurements in silicon solar cells and modules.

1:30 PM
Crystalline Si Growth, Surface Chemistry, and Passivation Sumit Agarwal; Colorado School of Mines

Overview of c-Si growth, converting SiO2 to c-Si wafers; single and multi-crystalline Si; effect of oxygen in p-type Si solar cells; passivated of c-Si; H-terminated silicon surfaces; and structure and properties of the c-Si/SiO2 and c-Si/Al2O3 interfaces.

2:15 PM
Device Physics of Solar Cells Ron Sinton; Sinton Instruments

Silicon solar cells are converging on high efficiency devices. For these the device physics is tremendously simplified, well described by a formalism first developed for high-efficiency n-type concentrator solar cells. This description, based on balancing photogeneration with recombination, gives simple insight into the operation of all modern solar cells, with extensions relevant to the interpretation of test data as well.

3:00 PM BREAK

3:30 PM
High-Efficiency Approaches for Monocrystalline Si Solar Cells Sumit Agarwal; Colorado School of Mines

Standard Al back surface field silicon solar cells; p-type PERC cells, light induced degradation and regeneration; methods for creating passivated contacts; interdigitated back contact Si solar cells; and HIT cells.

4:15 PM
Test and Measurement of Silicon Ingots, Wafers, Cells, and Modules Ron Sinton; Sinton Instruments

This section will focus on minority-carrier lifetime measurements as a tool for monitoring and optimizing device design and process optimization at each step in the production process. The difficulties in measuring the new generations of high-efficiency solar cells and modules will be discussed in detail.
Invited Paper

Interactions with the main R&D actors in the SHJ community, through collaborative projects. Three contributions of our group to this interesting research field will be reported: First, theoretical investigations of the current transport mechanism. Passivating contacts based on a stack of polycrystalline (poly-) Si on a thin interfacial oxide (POLO) are attracting enormous research interest in crystalline Solid State Physics, Leibniz Universität Hannover, Hannover, Germany. Moreover, intense R&D activities are focusing on new paths to further boost the efficiency, in the field of materials, integration, processes and new architectures thanks to the know-how developed at CEA in the field of organic, perovskite, microelectronics and materials and thanks to efficient interactions with the main R&D actors in the SHJ community, through collaborative projects.

SESSION ET02.01: Poly-Silicon Contacts I
Session Chair: Stefaan De Wolf
Monday Morning, November 26, 2018
Hynes, Level 3, Room 311

8:30 AM *ET02.01.01
In-Depth Study of poly-Si / Oxide / c-Si Junctions and p+ poly-Si / n+ poly-Si Tunneling Junctions for Applications in Si Single Junction and Si-Based Tandem Cells
Robby Peibst1, 2, Nils Folchert1, Felix Haase1, Christina Klamt1, 3, Yevgeniya Larionova1, Jan Krügener2, Agnes Merkle1, Byungsul Min1, Michael Rienäcker1, Udo Römer1, Sören Schäfer1, Dominic Tetzlaff2, Tobias Wietler1, 2 and Rolf Brendel1, 3; 1Institute for Solar Energy Research INES as one of the main European actors in the SHJ development.

In this work, an overview of the amorphous/crystalline (SHJ) activity performed at CEA-INES during the last 15 years will be presented. First, the ramping-up of R&D developments allowed us to unlock the path to > 21% efficiencies in 2011. These results were obtained through a core understanding of the technology to overcome its main limitations and drawbacks, from the silicon material up to metallization. Back then, this placed CEA-INER as one of the main European actors in the SHJ development.

Then (2012-2016), these developments were taken to the next level through the startup of the first pilot-line (1200 wph) that brought the devices to a mature technology. This second step got us familiar with production constraints and associated issues such as defectivity, silicon material impact, and reproducibility or tack-time constraints. A milestone was an R&D record bifacial cell >23% with median efficiencies around 21% in production, along with >300W on 60-cells modules thanks to associated module development.

The third phase (2016-present) based on the new generation of MeyerBurger tools (2400wph) is ongoing, demonstrating the potential of the technology in a ready-to-market approach. Median efficiencies >21.5% in a 4-busbar and >22.5% in a busbarless technology on bifacial devices are demonstrated. R&D record cells surpassing 23.5% efficiency are also systematically obtained (up to 23.8%) using R&D processes on top quality Cz wafers. Bifacial GG modules over 380W on a 72-cells are demonstrated and transfer is ongoing towards ENEL and others. A record-breaking 410W module was also recently achieved on a GBS configuration coupling the SwartWire technology and top efficiency SHJ cells form the production line (>23.4%). Bankability studies demonstrate also the economic potential of the technology.

Moreover, intense R&D activities are focusing on new paths to further boost the efficiency, in the field of materials, integration, processes and new architectures thanks to the know-how developed at CEA in the field of organic, perovskite, microelectronics and materials and thanks to efficient interactions with the main R&D actors in the SHJ community, through collaborative projects.

9:00 AM *ET02.01.02
Overview on the Amorphous/Crystalline Silicon Heterojunction Development at CEA-INER—From R&D Activities Up to Ready-to-Market Technology
Delfina Muñoz; France, CEA-INES, Le Bourget du Lac, France.

In this work, an overview of the amorphous/crystalline heterojunction (SHJ) activity performed at CEA-INES during the last 15 years will be presented. First, the ramping-up of R&D developments allowed us to unlock the path to > 21% efficiencies in 2011. These results were obtained through a core understanding of the technology to overcome its main limitations and drawbacks, from the silicon material up to metallization. Back then, this placed CEA-INES as one of the main European actors in the SHJ development.

Then (2012-2016), these developments were taken to the next level through the startup of the first pilot-line (1200 wph) that brought the devices to a mature SHJ product using industrial deposition equipment. This second step got us familiar with production constraints and associated issues such as defectivity, silicon material impact, and reproducibility or tack-time constraints. A milestone was an R&D record bifacial cell >23% with median efficiencies around 21% in production, along with >300W on 60-cells modules thanks to associated module development.

The third phase (2016-present) based on the new generation of MeyerBurger tools (2400wph) is ongoing, demonstrating the potential of the technology in a ready-to-market approach. Median efficiencies >21.5% in a 4-busbar and >22.5% in a busbarless technology on bifacial devices are demonstrated. R&D record cells surpassing 23.5% efficiency are also systematically obtained (up to 23.8%) using R&D processes on top quality Cz wafers. Bifacial GG modules over 380W on a 72-cells are demonstrated and transfer is ongoing towards ENEL and others. A record-breaking 410W module was also recently achieved on a GBS configuration coupling the SwartWire technology and top efficiency SHJ cells form the production line (>23.4%). Bankability studies demonstrate also the economic potential of the technology.

Moreover, intense R&D activities are focusing on new paths to further boost the efficiency, in the field of materials, integration, processes and new architectures thanks to the know-how developed at CEA in the field of organic, perovskite, microelectronics and materials and thanks to efficient interactions with the main R&D actors in the SHJ community, through collaborative projects.
Carrier selective tunnel oxide passivated contact (TOPCon) c-Si solar cell has attracted a great attention as one of potential technologies for high efficiency c-Si module production beyond the passivated emitter rear contact solar cell (PERC) structure. Currently, the highest TOPCon solar cell efficiencies have reached 25.7% and 24.4% with N-type and P-type c-Si wafers, respectively [1,2], demonstrating the potential in efficiency improvement of solar panels. In this contribution, we will report out recent progresses in the research and development of high efficiency TOPCon solar cells, including the fabrication and optimization of SiOx passivation layer, P-doped poly-Si contact layer, Al(OH)/SiNx:H emitter passivation, and metallization, with the focus on the post-crystallization treatment effect on the passivation quality and improvement of TOPCon solar cell efficiency. The ultrathin SiOx (~1.5 nm) passivation layers were grown in 68% HNO₃ acid at 60-110°C or in a mixed/concentrated acid of 68% HNO₃+H₂SO₄ at 60°C for 15 minutes on solar grade N-type c-Si wafers, following a 40-nm thick phosphorus doped hydrogenated amorphous silicon (n-a-Si:H) deposition on both sides. The double-side passivated samples were subjected to a high temperature annealing at 820°C for crystallizing the n-a-Si:H layer to form n- poly-Si layer as the electron selective contact layer. Furthermore, various post-crystallization treatments were carried out to study the hydrogen passivation effect on the TOPCon structures by measurement the minority carrier lifetime and the implied open-circuit voltage (Voc), including forming gas annealing, hydrogenated silicon nitride (a-SiNₓ:H) coating and annealing, and atomic layer deposited Al₂O₃ coating and annealing. We found that the mixed/concentrated acid at 60°C has much stronger oxidation capability and produces more fully oxidized chemical structures with better passivation quality than the 68% HNO₃ process at 90-110°C. The relatively lower temperature oxidation process in the mixed/concentrated acid is suitable for mass production. For the hydrogenation of the TOPCon structure, the most effective method is the Al₂O₃ coating with an annealing at 450°C for 30 minutes, which results in a minority carrier lifetime of 1.5 ms at 5¹⁰¹³ cm⁻³ carrier injection, saturated reverse recombination current density J₀=1.3 pA/cm², and Voc=743 mV. Using the improved hydrogenation procedure, we attained an energy conversion efficiency of 21.2% with the 4 cm² small area and 21.0% with 243 cm² large area n-TOPCon solar cells.

Amorphous silicon / crystalline silicon heterojunction (SHJ) solar cells have historically suffered from high series resistance that stems from transport across the heterojunction. We present a systematic analysis of the contributions from each layer of an a-Si:H(i)/a-Si:H(p/n)/ITO/Ag contact stacks and show that we can reproduce the measured series resistance of SHJ cells by summing the independently measured contributions. We find that contact resistance accounts for 50-80% of the series resistance and is most sensitive to the a-Si:H(i) layer thickness and ITO doping density. For example, a 2 nm increase in the a-Si:H(i) layer thickness above its baseline value will cause a 1.5% drop in fill factor, and this in turn narrows the processing windows of silicon heterojunction cell manufacturing. As one method to reduce contact resistance, we introduce a-Si:H(i)/a-Si:H(p/n)/Al contacts in which the Al begins to alloy with the doped a-Si:H but does not spike through the passivation layer. These contacts have resistances that are two orders of magnitude lower than conventional SHJ contacts, enabling partial-area contacts without appreciable fill factor loss.

Reducing the Resistance of Heterojunction Contact Stacks in Silicon Solar Cells
Zachary Holman; Arizona State University, Tempe, Arizona, United States.

Amorphous silicon / crystalline silicon heterojunction (SHJ) solar cells are one of the most promising photovoltaic technologies owing to the outstanding passivation quality ensured by the material that will be used in real production environment. Furthermore, it was demonstrated experimentally on the CEA-INES line that screen-printing layout changes could enable efficiency improvements up to 1% abs., going from four to six busbars. Finally, we will show recent progress on the fabrication and characterization of full bifacial SHJ modules.

Reducing the Resistance of Heterojunction Contact Stacks in Silicon Solar Cells
Zachary Holman; Arizona State University, Tempe, Arizona, United States.

Reducing the Resistance of Heterojunction Contact Stacks in Silicon Solar Cells
Zachary Holman; Arizona State University, Tempe, Arizona, United States.
Our research on front-back-contacted (FBC) cells reveals that the effective minority carrier collection is essential to minimize the drop from SunsVoc to Voc. Thick doped nc-SiOx:H layers can effectively shield the device precursor from the influence of ITO’s field effect and keep its overall passivation quality after ITO sputtering. Accordingly, the best FBC device performs promising SunsVoc with 727 mV and 734 mV, pseudo-Fill Factor (pFF) of 0.862 and 0.841, measured before and after metallization, respectively. Besides, we found that adding few nanometers of doped non-oxidic nc-Si:H between the nc-SiOx:H and ITO leads to critical improvement in FF from 0.56 to 0.73. Currently, our best FBC cell exhibits η of 20.4% with JSC measured from EQE, with the potential of large step improvement in short term by enhancing the FF via minimizing the cell series resistance. Finally, we developed a novel one-step patterning process for fabricating tunneling IBC-SHJ solar cells. Since the non-HF resistant behavior of the doped nc-SiOx:H layers and the excellent HF etching selectivity to intrinsic a-Si:H material, the process enables superior chemical passivation and no patterning step for emitter due to the tunneling IBC concept. With the optimized SHJ passivating contacts, the preliminary tunneling IBC device, exhibits an η of 18.2% with a Voc of 659 mV, Jsc of 41.3 mA/cm², FF of 0.67. Further optimization of the layer thicknesses and patterning process in the second run enables much higher Voc of 715 mV over 7 cells. By addressing the low η of the non-optimized (n)nc-SiOx:H, which limits the cell FF (~ 60%), a cell η over 22% is expected in short term.

1K. Yoshikawa et al. Nat. Energy 2017
2P. Procel et al. SOLMAT 2018
3A. Tomasi et al. Nat. Energy 2017
In a second part of this work, the recombination parameters (capture cross sections and position in the gap) of the LID defect are studied using transient-PCD. The defect SRH signature is shown to be the same over the 36% of the ingot affected by the defect. We found that the experimental data cannot be reproduced by SRH parameters from either BO-, Copper- or FZ-related LID. We conjecture that either several SRH centers are simultaneously at play, or that the defect here is singular and specific. Eventually, we report its “effective” SRH parameters to lie within: $0.2 \, \text{eV} < E_c - E_T < 0.84 \, \text{eV}$ and $10^{-2} < k < 4 \times 10^{-1}$.

2:15 PM ET02.03.03

Stability of Na Atoms at Stacking Faults in Si Depending on the Fermi Level

Yutaka Ohno1, Haruhiko Morito1, Kentaro Kutsukake1, Ichiro Yonenaga1, Tatsuya Yokoi2, Atsutoshi Nakamura2 and Katsuyuki Matsunaga2; 1Tohoku University, Sendai, Japan; 2Nagoya University, Nagoya, Japan.

In megawatt-scale solar power plants, high-voltage stresses are inevitably applied between each cell and its module frame, and the stresses sometimes cause a power drop in the module (a so called potential induced degradation (PID)). The key factor of the PID in p-type Si solar cells is sodium (Na) impurities in solar module encapsulation. During operation, they agglomerate at stacking faults (SFs) in Si cells [1]. Na atoms would spontaneously diffuse into SFs and create an electrically conductive layers [2], resulting in a reduction of the shunt resistance [1]. Those SFs would nucleate from microscopic defects on Si cells such as dislocations, during the PID stress under the influence of Na penetration [3]. Also, the Na penetration process would be modified depending on the doping level [4]. These results suggest that the formation energy of SFs varies depending on the Fermi level, as well as on the existence of Na atoms. In this work, we examine the stability of Na atoms at SFs in Si crystals with different Fermi levels, which determines the PID phenomena in p-type solar cells.

SF ribbons bound by pairs of partial dislocations were intentionally introduced into B-doped p-type Si ($c = 8 \times 10^{18} \, \text{cm}^{-3}$), P-doped n-type Si ($3 \times 10^{19} \, \text{cm}^{-3}$), and nominally undoped n-type Si ($3 \times 10^{17} \, \text{cm}^{-3}$), by applying a compressive stress at an elevated temperature. Each crystal and a Na sample were sealed within a stainless steel tube with Ar gas, and the crystal was doped with Na atoms by heating the tube in a furnace at 973 K for 5 h. The width of each SF ribbon $w_{SF}$ was estimated by TEM, as a function of the line orientation $u$ defined by the angle of $b$ to $u$ in which $b$ is the sum of the Burgers vectors of the dislocations and $u$ is a vector along the dislocations, and the formation energy of SFs $E_{SF}$ was calculated with $w_{SF}(u)$. In all the examined crystals, $w_{SF}(u)$ increased by Na doping, and the ratio between the $w_{SF}(u)$ before Na doping and that before doping was almost independent of $u$. Therefore, Na atoms would agglomerate at the SFs due to an attractive electronic interaction, and the interaction results in the reduction of $E_{SF}$. The degree of the energy reduction would decrease with rising the Fermi level; $E_{SF}$ was reduced by more than 10 mJ/m$^2$ in p-Si while it was barely reduced in n-Si [5]. These results indicate that Na agglomerates at SFs in p-Si are stable in comparison with in n-type one, and this is consistent with the PID phenomena in p-type solar cells. The SF formation energy depending on the Fermi level can be explained by using ab-initio calculations [5]. For comparison, the stability of Na atoms at $E_3$ [111] GBs will be discussed.

References

2:30 PM DISCUSSION TIME

2:45 PM ET02.03.05

Annealing Effects on the Layer Structure in BaSi2 Thin Films Studied by DB-PAS

Ana B. Montes1, 2, Yilei Tian1, Daan Schopmeijer1, Stephan Eijt1, Hendrik Schut1, Takashi Suemasu2, Noritaka Usami3, Joao Serra2, Olindo Isabella1 and Miro Zeman1; 1TU Delft, Delft, Netherlands; 2Universidade de Lisboa, Lisboa, Portugal; 3Nagoya University, Nagoya, Japan; 4University of Tsukuba, Tsukuba, Japan.

BaSi2 is a promising material for solar cell applications due to its elemental abundance, non-toxicity and electrical and optical properties [1,2]. Presently, heterojunction BaSi2/c-Si solar cells with efficiency reaching 9.9% have been reported [3]. As an industrially applicable technique, radio frequency (RF) sputtering was employed in this research. Doppler-Broadening Positron Annihilation Spectroscopy (DB-PAS) is applied to study the layer structure, material composition and the open volume deficiencies therein.

BaSi2 films were deposited by sputtering and subsequently crystallized by annealing treatment. Samples were analysed by DB-PAS depth profiling and Raman spectroscopy. Thus, $S$ and $W$ parameter curves vs positron implantation energy (roughly reflecting thickness of layers) were acquired. $S$ and $W$ physically represent annihilation events with low- and high-momentum electrons, respectively. $S$ and $W$ are fitted by VEPFIT software [4] with a five-layer model (oxide/oxide-BaSi2 interface/BaSi2/BaSi2-substrate interface/substrate) based on our previous research [5]. In the $S$ profiles, three regions are recognized as function of positron energy: surface, bulk and substrate. Once $S$ and $W$ are sensitive to the composition of the layer, such variations can be caused by changes either in composition or formation/presence of vacancies. According to our previous research, surface and bulk material hold different compositions. In the surface region, an increase of $S$ is observed by increasing annealing temperature ($T_a$) from 650 to 700°C. This can be caused by the oxidation enhancement with $T_a$. For $T_a = 700°C$, increasing the annealing time ($t_a$) from 1 to 5 min induces a shift to higher positron implantation energies of the oxide/BaSi2 interface, suggesting that the surface oxidation mainly occurs within the first 5 min, and subsequently saturates.

In the bulk, either a higher $T_a$ or a longer $t_a$ decreases the $S$. Higher $T_a$ enhances crystallization, which can decrease the defect concentrations. This may cause a lower $S$. A decrease in $S$ is observed within the first 5 min. This can be caused by the crystallization of BaSi2, as supported by Raman analysis. Longer $t_a$ cause a decrease in $S$ which is attributed to Ba diffusion. Further characterizations, e.g., positron lifetime studies, are needed to determine the presence/formation of vacancies. Films produced by molecular beam epitaxy and thermal evaporation as potential references are being studied, in order to benchmark the quality of sputtered BaSi2 films by normalizing of $S$ and $W$ to those of reference films. This contribution serves as a platform for material development and solar cell devices based on BaSi2.

References
Metal Oxide and Fluoride Heterocontacts for High Efficiency Silicon Solar Cells

James Bullock; University of California, Berkeley, Berkeley, California, United States.

The fast-growing terrestrial solar cell industry is currently dominated by crystalline silicon cell architectures which employ doping and direct metallization for electron/hole separation. Despite being commonplace, the use of doping and direct metallization is known to incur a range of fundamental and practical performance limitations. A new strategy to address these shortcomings is to replace such regions with surface passivating heterocontacts. One burgeoning stream of research utilizes low-temperature materials like metal oxides, fluorides, sulphones and organic molecules to form such heterocontacts. I will discuss recent breakthroughs in this research area, which demonstrate the potential of this concept to simultaneously reduce fabrication costs and remove efficiency limitations.

Post-annealing Temperature Effect on Electrical Properties of Al2O3 Films on Silicon by Atomic Layer Deposition for Solar Cell Applications

Ergi Dönerçark, Bilge Imer and Rasit Turan; The Center for Solar Energy Research and Applications (GUNAM), Middle East Technical University, Ankara, Turkey.

Silicon wafers, being the most dominant and almost inevitable material for solar cell production, require surface passivation to increase the solar cell efficiency by decreasing recombination losses. For this reason, several research groups are currently focused on the usage of thin alumina (Al2O3) as a passivation layer. The success of Tunnel Oxide Passivating CONFerence (TOPConf) solar cell, Passivated Emitter Rear Totally diffused (PERT) solar cell and Passivated Emitter Rear cell (PERC) structures demonstrate enhanced passivation quality of crystalline silicon (c-Si) solar cells with Al2O3 films.

The determining parameters for the passivation quality of Al2O3 can be summarized as interface trap states (Dit), fixed charge density (Qf) and flat band voltage (VFB). Due to enhanced field effect passivation quality of thin Al2O3 layer, high ratio Qf can be accomplished. Qf has been reported as high as 1-4x10^13 cm^-2eV^-1 in literature by several research groups and this charge density is sensitive to both deposition conditions and post-thermal treatments.

In addition to field effect passivation, Al2O3 layer also provides chemical passivation with relatively low density of Df. This context, the effect of different deposition conditions and post-annealing temperatures on Al2O3 films formed by atomic layer deposition (ALD) were investigated using conductance method to identify and clarify relation between interface properties and fixed charge densities under initial deposition conditions varying in between 160 - 200°C in combined with various post-annealing conditions (400°C to 600°C for 30 minutes). C-V and G-V measurements were done for each sample with various frequencies from 1kHz to 5MHz. From C-V measurements, the oxide capacitance and VFB values were calculated and conductance method was applied to determine Dit values. It was shown that Dit decreased when the post-thermal annealing was applied. The highest Dit was 5.13x10^13 cm^-2eV^-1 and the lowest one was 2.43x10^11 cm^-2eV^-1. Dit decreased at 400°C post-annealing temperature for different deposition temperatures. The highest Dit was 2.79x10^13 cm^-2eV^-1 and the lowest one was 2.39x10^12 cm^-2eV^-1. The lowest Dit was found at 400°C post-thermal annealing temperature under N2 ambient with 165°C prior deposition temperature. It was concluded that when Qf values increase, Dit values also increase. High variation on VFB was found where it changed in between 1.09V to 4.19V.

REFERENCES


Band Alignment at the Heterojunction Between Plasma Enhanced Atomic Layer Deposited SnO2 and N-Doped Hydrogenated Amorphous Silicon

Ganna Chistiakova, Mathias Mews and Lars Korte; Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

Tin oxide, SnO2, is a “classical” transparent conductive oxide (TCO) material used for a variety of optoelectronic devices, including thin film solar silicon cells. Its alloy with indium, ITO, is widely used for silicon heterojunction solar cells. Furthermore, the pure tin oxide material has recently been demonstrated to perform well as electron transport layer in perovskite solar cells. Thus, it can be surmised that SnO2 on silicon might also be used as part of the recombination contact in silicon/perovskite tandem solar cells.

Motivated by these applications, we study atomic layer deposition (ALD) of SnO2 on hydrogenated amorphous silicon. We use TDMASn as precursor, which is a prominent choice for SnO2 ALD due to its low temperature requirements and high uniformity. For this work plasma enhanced atomic layer deposition (PEALD) of TDMASn with an oxygen plasma as oxidizer was used. With the ALD process it is possible to monitor changes at the interface of the recombination contact in silicon-perovskite tandem solar cells.

During the ALD process no growth delay was observed, and the Sn 3d core level signal was already detectable after the first growth cycle. We find that during the first cycles an oxide interlayer is formed, which influences the valence band position, work function and the total band bending. The main cause is assumed to be the formation of a dipole at the interface, due to the oxygen rich conditions during the initial growth stages. Upon continued deposition, the dipole vanishes, and we observe a reversal of the Sn 3d band bending and the formation of a chemically clean SnO2 layer. The conduction band offset from (n)-a-Si:H to SnO2 was determined to be ~270 meV. Therefore, SnO2 could be applied as an electron contact to (n)-a-Si:H, if the formation of the strong interface dipole can be suppressed.

In the past eight years, perovskite solar cells (PSCs) have quickly evolved into a high-efficiency technology due to the excellent electronic and optical properties of perovskite absorbers. Among the two \( \text{p-i-n} \) and \( \text{n-i-p} \) configurations, the \( \text{n-i-p} \) has now reached record conversion efficiencies (PCE) close to 23\%, followed at some distance by its \( \text{p-i-n} \)-counterpart. The choice of solvent-compatible HTLs and the lack of efficient \( \text{p-type} \) metal oxides restricts the main causes hampering the rise of \( \text{p-i-n} \) PSCs, whose options were limited to hole transport polymers for several years. In this regard, nickel oxide (NiO\(_x\)) offers promising characteristics to replace the polymers, such as chemical stability, high broadband optical transparency, intrinsic \( \text{p-type} \) semiconducting nature, higher open circuit voltage (\( V_{oc} \)) and its deeper work function. Thanks to these unique properties, NiO\(_x\) has been studied widely and several successful reports have been published for solution processing such as sol-gel and combustion methods. However, these techniques require high-temperature annealing which increases the processing time and hinders its use on low-temperature stable substrates; low-temperature processing is crucial for monolithic perovskite/silicon tandem solar applications which promises very high efficiency beyond the single junction limit. The most promising silicon bottom cell for perovskite tandems is silicon heterojunction technology (SHJ) which has the highest \( V_{oc} \) and PCE for perovskite/silicon tandem applications. However, SHJ solar cells are only compatible with top cell processes up to ≈200 °C. Above this temperature, \( V_{oc} \) of the devices sharply drop because of hydrogen effusion from the amorphous silicon layers, hampering the passivation effect. Based on this limitation, we took advantage of RF sputtering deposition to fabricate amorphous NiO\(_x\) layers. RF sputtering offers room temperature processing, flexibility to control composition by simply changing the deposition parameters, and fast deposition. Moreover, RF sputtering enables conformal deposition on complex surfaces such as random-pyramid textured silicon solar cells. Besides, owing to its high transparency NiO\(_x\) is well fit as a scalable HTL for tandem applications. In this work, we employ various characterization methods and DFT analysis how the electrical and optical properties of optimized films correlate strongly with the specific defect chemistry of NiO\(_x\). For planar, \( \text{p-i-n} \) configured MAPbI\(_3\) based PSCs, RF-sputtered NiO\(_x\) at room-temperature enables PCE values of 17.6\%, which is highest achieved among the PSCs adopting sputtered NiO\(_x\) as HTL without heteroatom doping. These results pave the road for the development of the perovskite/silicon tandem solar cells on pyramidal textured surfaces.

**Effectively Transparent Contacts (ETCs) for Al-BSF and PERC Silicon Cells**

- *Marko Jost, Jochen Matthes, Michael Schmuki, Bernd Rech, Bernd Stannowski, Marko Kistler, Sascha Warta, Bernd Stoebe, Helmut Weller, Philipp Holzapfel, Steven Albrecht*
- *Helmholtz-Zentrum Berlin, Berlin, Germany; 2LPVO, University of Ljubljana, Ljubljana, Slovenia; 3Helmholtz-Zentrum Berlin, Berlin, Germany; 4University of Ljubljana, Ljubljana, Slovenia; 5Helmholtz-Zentrum Berlin, Berlin, Germany; 6University of Ljubljana, Ljubljana, Slovenia*
Towards CIGS Perovskite Tandem Cells

Jesper Jacobsen, Adam Hultqvist, Häkan Rensmo and Gerrit Boschloo;
Chemistry, Uppsala University, Uppsala, Sweden; 2Uppsala University, Uppsala, Sweden.

Perovskite solar cells will have a hard time to reach competitiveness with respect to conventional PV-technologies; unless they are integrated in tandem-architectures that possibly could outperform single junction silicon cells. One interesting potential perovskite tandem companion is CIGS, CuIn_xGa_{1-x}Se_2, which is a commercial thin film technology with record efficiencies above 22 % and a variable band gap. In this project, we strive for constructing efficient 2-terminal CIGS-perovskite tandem cells. We will here discuss progress and challenges connected to recombination layers, perovskite engineering, and transparent top contacts in CIGS-perovskite tandem architectures.

Thermal, Oxidative, and Operational Stability in Low Band Gap Tin-Lead Perovskite Solar Cells for Robust All-Perovskite Tandems

8:30 AM

Rohit Prasanna, Tomas Leijtens, Arevé Gold-Parker, Eli Wolf, James A. Raiford, Stacey F. Bent, Michael F. Toney and Michael McGehee;
Stanford University, Stanford, California, United States; 2Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Low band gap ABX_3 perovskites tin and lead at the B-site are a breakthrough that have enabled fabrication of efficient all-perovskite tandem solar cells. However, tin is susceptible to oxidation to the +4 state, a degradation pathway unique to tin-containing perovskites. Suppressing this oxidation reaction is essential to ensure that highly efficient all-perovskite tandem solar cells are also stable against long term environmental stressors.

We identify the specific chemical mechanism by which pure tin-based perovskites undergo oxidation using a combination of chemical methods including thermogravimetric analysis and solvent extraction of degradation products. We find that the oxidation reaction depends on a cooperative mechanism that involves simultaneous oxidation of multiple adjacent tin iodide octahedra. Critically, the most favorable oxidation pathway is blocked by substitution of 50% or more of the B-site with lead because this significantly lowers the chances of there being multiple adjacent tin octahedra that can facilitate the cooperative mechanism. As a result, the stability of tin perovskites toward oxidation is improved by orders of magnitude upon alloying with lead. The resulting guideline is that low band gap perovskites can be designed to have significantly enhanced oxidative stability by keeping the tin fraction at 50% or below.

We proceed to design solar cells to withstand aging under elevated temperatures in air. We probe the thermal stability of high-performing low band gap solar cells by aging at 85 C in air. Encouragingly, there is no measurable change in the bulk absorption of the perovskite absorber under thermal aging in air, indicating that the strategy of suppressing oxidation by using a mixed tin-lead perovskite successively avoids oxidative breakdown. However, the fill factor drops due to the formation of an S-kink after 100 hours of aging. We develop a treatment of the tin-lead perovskite film by exposure to methylammonium chloride vapour that results in significant grain growth and healing of cracks between grains. This post-treatment drastically improves the thermal stability of the full solar cells. Using an MACI-vapour-treated low gap perovskite with 50% tin, capped with a sputtered Indium Tin Oxide (ITO) top electrode, we successfully demonstrate a solar cell that maintains its full power conversion efficiency for 150 hours in air at 85 C, and remains above 85% of initial PCE for over 300 hours. In addition, we demonstrate stable operation of a tin-lead solar cell at maximum power point under 1-sun illumination for over 100 hours with no drop in performance. These measurements are a huge improvement upon any thermal stability results reported for tin-containing perovskites. The fact that good thermal stability in air is achieved with no encapsulation represents a major step toward proving the long-term stability of tin-low band gap perovskite solar cells, and of efficient all-perovskite tandem solar cells.

Two conflicting characteristics compete where the commercial viability of one-sun tandem solar cell is concerned: On the one hand, tandem solar cells have fundamentally higher efficiencies than single junction solar cells. On the other hand, tandem solar cells are intrinsically more complex than single junction solar cells and require more fabrication steps, which makes them more expensive. Only if the benefit from the additionally generated energy outweighs the higher fabrication cost can tandem solar cells be successful.

The question under which conditions the last sentence is true is a multilayered one. The value of efficiency is highest when considering the integrated PV system, which makes it necessary to explore system level aspects. These aspects include, among others, economic considerations as well as topics from material science; for example degradation.

In this work we attempt to provide an overview of what is needed to make tandem solar cells economically successful. Central to our findings is the concept of “marriage of equals”, which states that the sub cells in a tandem should be similar, as well as enable high efficiencies. We will take a look at different material pairings, including perovskite on silicon, III-V on silicon and thin-film on thin-film tandems and investigate how these tandems compare to single junction solar cells in various types of systems and various locations.

We find that under the right circumstances one-sun tandem solar cells can outperform single junction solar cells economically. Yet more than techno-economic considerations are needed to make these types of solar cell a wide-spread reality. As an outlook we hope to offer a perspective of future opportunities for this technology.

Designing Metal Halide Perovskites Solar Cells to be Stable for High Efficiency Tandems

Michael D. McGehee;
Department of Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

The talk will begin by showing what we have done to make perovskite on silicon tandem solar cells with 25 % efficiency and how 30 % efficiency can probably be obtained in the coming years. Then the challenge of making solar panels with metal halide perovskite semiconductors that will last for more than 25 years will be addressed. We will show that packaged solar cells can survive industry standard reliability tests such as 1000 hrs at 85°C and 85% humidity, 200 temperature cycles between -40°C and 85°C, and ultraviolet exposure. The strategies for making stable perovskite cells include choosing perovskite compositions that have higher thermal and oxidative stability, managing stress during the formation of the film to prevent buckling that makes perovskite compositions that have higher thermal and oxidative stability, managing stress during the formation of the film to prevent buckling that makes subsequent processing difficult, minimizing tensile stress in the final film since it appears to make bonds weaker, using solution processing of the top contact layer to fill in gaps at grain boundaries so that a sputtered transparent conducting oxide layer can form a super barrier layer, using polyolefin as the encapsulant since it does not chemically react with the perovskite and has an ideal elastic modulus, using butyl rubber edge seals and using glass on glass packaging.

9:30 AM BREAK

High Efficiency Perovskite/Silicon Tandem Solar Cells

Kylie Catchpole; Australian National University, Acton, Australian Capital Territory, Australia.
Combining perovskites with well-established photovoltaic materials such as silicon or CIGS is an attractive option for producing cheap, high efficiency and high voltage solar cells. Perovskite-based tandem solar cells can potentially achieve over 30% tandem efficiency. We demonstrate a 4-terminal tandem perovskite-silicon configuration in which the efficiency is as high as 26%. We also demonstrate a two-terminal monolithic tandem device with a perovskite top subcell and a high-temperature tolerant homojunction c-Si bottom subcell, with an efficiency of over 22%, and a perovskite/CIGS tandem with an efficiency of over 23%, which is the highest efficiency that has been reported for this configuration. We describe the optical and electronic factors that have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6 eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskitk in practical high efficiency tandem devices.

With open circuit voltages (Voc) above 730 mV, silicon heterojunction (SHJ) solar cells are promising candidates for the bottom cells in organic-inorganic lead halide perovskite/silicon tandem solar cells. Using simulation studies, we have shown that under realistic assumptions, power conversion efficiencies up to 30% should be achievable with such devices [1]. To attain this goal, starting from first devices with moderate stabilized efficiencies of 18.1% [2] we carefully optimized the optical and electrical properties of the device in order to achieve low parasitic absorption and reflection, photocurrent matching between the two sub-cells and lowly resistive current transport across the internal tunnel-recombination junction.

In this presentation, I will discuss how we were recently able to demonstrate certified 25% efficient perovskite/SHJ tandem cells [3] by addressing these issues. I will focus on the silicon bottom cell and contact stack optimization: Starting from a rear junction SHJ cell design on double side textured wafers with 22.6% power conversion efficiency (Jsc = 38.3 mA/cm², Voc= 731 mV, FF = 80.6 %) [4], we developed a rear side only-textured SHJ cell, which allows to process the perovskite top cell using conventional spin-coating methods. Optimizing film thicknesses at the perovskite/SHJ interface and tuning the refractive index of the nc-SiO₂:H film used as front surface field in the SHJ to an intermediate value of ~2.6 (at 800 nm) were instrumental in achieving 25% efficient cells with photocurrents above 17.8 mA/cm². On this basis, I will briefly discuss the potential to further enhance device performance using alternative deposition methods, such as plasma-enhanced ALD for tin oxide interlayers, and alternative materials such as tungsten oxide alloys for carrier selective contacts.

Progress on Si Tandems

Antia Ho-Baillie1, Hamid Mehrvarz2, Jianghui Zheng1, Fajun Ma1, Chuq Yi1, Stephen Brenner2, Shujuan Huang1, Hidenori Mizuno2 and Tyler. Grassman1,2 "Australian Centre for Advanced Photovoltaics, The University of New South Wales, Sydney, New South Wales, Australia; 2Fukushima Renewable Energy Institute, National Institute of Advanced Industrial Science and Technology, Fukushima, Japan; 3The Ohio State University, Columbus, Ohio, United States.

Tandem solar cell is a promising approach for achieving high efficiencies for photovoltaics [1]. The challenge is to find an efficient, economical and stable technology for each cell stack to realize true savings in the system’s levelised cost of energy. Nevertheless, substantial progress has been made in the demonstrations of two-terminal Si tandem cells. The advantage of 2-terminal over 4-terminal configuration is the reduced complexity in wiring and packaging [2]. The challenge lies in the integration of the cell stacks without electrical and optical losses.

Recently, a simple perovskite/Si tandem cell structure has been reported [3]. It does not require additional interface layer for the integration of perovskite and Si cells. Instead, the electron transport layer in the perovskite top cell serves as the recombination layer between the top and bottom sub cells. The lack of lateral conductivity in this recombination layer means undesirable shunts are effectively localized. Another advantage of this structure is its compatibility with homo-junction Si cells – the most common choice for incumbent commercial Si photovoltaic technology. Recent optimizations have improved cells’ performance from 20.5% to 22.7% on 4cm².

Great progress has been made on 2-terminal III-V/Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures require smooth interface negating the use of textured Si bottom cell. This means external measures are required for anti-reflection and light trapping. Strategies for improving the optical performances of InGaP/GaAs//Si tandem by SmartStack [4] and monolithic epitaxial GaAs/Si tandem [5] will be presented in this talk.

10:30 AM *ET02.05.07/ET04.04.07
Optimizing Interfacial Layers on Silicon Heterojunction Bottom Cells for Perovskite/Silicon Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond

Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Gianna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.

Great progress has been made on 2-terminal III-V//Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6 eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

11:00 AM *ET02.05.08/ET04.04.08
Progress on Si Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond

Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Gianna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.

Great progress has been made on 2-terminal III-V//Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6 eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

*ET02.05.07/ET04.04.07
Optimizing Interfacial Layers on Silicon Heterojunction Bottom Cells for Perovskite/Silicon Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond

Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Gianna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.

Great progress has been made on 2-terminal III-V//Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6 e V bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

10:30 AM *ET02.05.07/ET04.04.07
Optimizing Interfacial Layers on Silicon Heterojunction Bottom Cells for Perovskite/Silicon Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond

Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Gianna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.

Great progress has been made on 2-terminal III-V//Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6 eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

11:00 AM *ET02.05.08/ET04.04.08
Progress on Si Tandem Solar Cells with 25% Power Conversion Efficiency and Beyond

Lars Korte, Anna B. Morales-Vilches, Luana Mazzarella, Eike Köhnen, Philipp Tockhorn, Lukas Kegelmann, Gianna Chistiakova, Mathias Mews, Bernd Stannowski and Steve Albrecht; Helmholtz-Zentrum Berlin, Berlin, Germany.
that such effect is influenced by the a-Si:H thickness. In fact, increasing the thickness of a-Si:H layer to 50 nm, sample annealed at 650 °C presents similar optical properties to the bare BaSi2 film annealed at 650 °C rather than 700 °C. Thinner a-Si:H layers may suppress the formation of defective structures with >20 mA/cm2 in both the perovskite and silicon subcells (excluding metallization-induced shadow losses). Parasitic absorption was minimized thanks to the bottom cells for maximal optical performance given the reduced reflection losses and enhanced light trapping. This enabled current-matching conditions - Reaching maximal performance:

Overall, these results suggest a path in the development of monolithic perovskite/silicon tandem solar cells with realistic efficiency potential >30% on large area with enhanced stability.

We will review our recent attempt to integrate data science with experimental science, theory, and computation in order to enable a paradigm shift in development of complicated multicrystalline materials. This multidisciplinary scientific approach, “multicrystalline informatics”, is shown to be useful to realize ideal multicrystalline silicon (mc-Si) ingot for solar cells by various aspects. Photoluminescence (PL) images of mc-Si wafers with intentional partial introduction of the reflected incident laser contains information of crystal defects and microstructures. We captured PL images from mc-Si wafers produced from the same ingot, and attempted to clarify the distribution of crystal defects inside the ingot. Although the surface of mc-Si wafers sliced by diamond wires is mirror-like with one directional saw marks, image processing could successfully visualize crystal defects as dark regions and microstructures with different average luminance. By sequentially stacking PL images of mc-Si wafers from the bottom to top of the ingot, the structural variation in the ingot could be visualized. Furthermore, by extracting crystal defects with thresholding, three-dimensional distribution of crystal defects could be visualized. These revealed that crystal defects, which are most likely assigned as dislocation clusters, are generated at grain boundaries followed by propagation and annihilation. This permits to extract a hundreds of generation points of crystal defects for further analysis of underlying physics. To obtain information on orientation distribution in mc-Si, optical images of mc-Si wafers with white light illumination would be useful. We captured a series of optical images with different illumination angles, and investigated the relationship between angular variation of average luminance and crystal orientation. Machine learning would be utilized for fast prediction of orientation distribution in mc-Si.

By combining these information, physics of crystal defects in complicated mc-Si will be manifested to show the guide to realize high-quality mc-Si ingot for solar cells.

This work was supported by Japan Science and Technology Agency (JST), CREST, JPMJCR17J1.

Effects of Amorphous Si Capping Layer on Sputtered BaSi2 Film Properties Yilei Tian1, Ana B. Montes1, 2, Olindo Isabella1 and Miro Zeman1; 1Delft University of Technology, Delft, Netherlands; 2Universidade de Lisboa, Lisbon, Portugal.

BaSi2 has gained interest as a promising light-absorbing material for thin-film solar cells. BaSi2 is stable in ambient condition and possesses a suitable band gap ~1.3 eV for solar energy conversion [1]. Its potential also stems from attractive optical and electrical properties, i.e., a high absorption coefficient reaching 10^5 cm^-1 for hv > 1.5 eV [1], a long minority carrier lifetime ~27 μs [2], and essentially elemental abundance and non-toxicity. Theoretically, the attainable conversion efficiency of the BaSi2 solar cell is up to 25% [3]. However, BaSi2 is confronted with the issue of surface oxidation due to its reactivity with oxygen. The oxidation-induced structure transformation, altering the stoichiometry and degrading the film quality, has been uncovered by our previous research [4]. Hence, it is essential to develop anti-oxidation capping layer to improve BaSi2 film quality.

In this contribution, hydrogenated amorphous silicon (a-Si:H) is studied as capping layer. Effects of a-Si:H on film properties are investigated by Raman, atomic force microscopy, and spectrophotometry. BaSi2 films were deposited by RF magnetron sputtering and then capped by PECVD a-Si:H. Samples were subsequently annealed at temperatures ranging from 650 to 750 °C. Raman spectra confirm the formation of crystalline BaSi2 in annealed a-Si (10 nm)/BaSi2 films. Aside from the BaSi2 peaks, the crystalline Si peak is noticeable for films annealed at 650 °C, resulting from Si crystallization in both a-Si:H and BaSi2 layers. Only a Si peak is displayed instead in spectra of a-Si (10 nm)/BaSi2 film annealed at 700 °C. Besides, a-Si:H (10 nm)/BaSi2 annealed at 650 °C exhibits similar optical properties to those of an uncapped BaSi2 film annealed at 700 °C. The existence of a-Si:H capping can, therefore, decrease the thermal budget for crystallizing BaSi2 but we found that such effect is influenced by the a-Si:H thickness. In fact, increasing the thickness of a-Si:H layer to 50 nm, sample annealed at 650 °C presents similar optical properties to the bare BaSi2 film annealed at 650 °C rather than 700 °C. Thinner a-Si:H layers may suppress the formation of defective structures and/or metallic phases, thus altering positively the optical properties of the fabricated a-Si:H (10 nm)/BaSi2. Furthermore, a 10-nm thick capping a-Si:H layer increases sample surface roughness from 20 nm (bare BaSi2) to 47 nm.

The mechanism of tailoring BaSi2 properties via a-Si:H capping layer is being investigated by further composition and electrical characterizations.
Additionally, the in-situ fabrication of a-Si/BaSi₂ films by a multi-targets sputtering method is being investigated. These results lay the groundwork for the development of BaSi₂-based thin-film solar cells.

References

2:15 PM ET02.06.04

Status of and Pathways to Achieve Wafer Equivalent Crystalline Silicon Solar Cells on Glass by Liquid Phase Crystallization Daniel Amkreutz¹, Chamin Thi, Mártina Trahns, Klaus Jäger, Christiane Becker and Rutger Schlattmann; ¹Silicon Photovoltaics, Helmholtz Zentrum Berlin, Berlin, Germany; ²Young Investigator Group Nano-SIPPE, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany; ³IPh-comB, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

Laser- or electron-beam induced zone-melting crystallization of silicon films is a fast and scalable technology to fabricate polysilicon layers on glass with customizable thicknesses and grain sizes up to several centimeters. Liquid-phase crystallized (LPC) silicon is thus a very interesting material for large area applications. Especially for PV, but also for microelectronics, MEMS or microfluidic applications. In the past, most effort was put on the development of a suitable layer stack between glass substrate and silicon absorber. This interlayer is mandatory for surface passivation, provides an antireflective coating and prevents impurity diffusion into the silicon absorber during the LPC process. Based on the progress in interlayer development, we demonstrated open circuit voltages up to 660 mV using n-type silicon. Nevertheless, fabricating a suitable contact system is challenging, because the carrier lifetime amounts to a few microseconds resulting in bulk diffusion lengths in the range of 30 to 60 micrometers. An interdigitated-back-contact system (IBC) was developed which is compatible with the crystallization process on glass and which is well suited for these diffusion lengths. With this contact system we were able to show conversion efficiencies up to 14.2% with current densities up to 31 mA/cm² for an IBC cell, which exhibits a planar silicon-glass interface and a pyramidically textured silicon rear side. In this contribution we summarize the current status of liquid-phase crystallized silicon on glass with emphasis on the interlayer and contact system development. Future steps towards wafer-equivalent conversion efficiencies for silicon (thin-) film solar cells on glass are discussed. It is shown that the device performance is no longer governed by surface recombination at the interlayer so that the focus for further development shifts to the reduction of losses related to imperfect contact system and light trapping scheme. Aside from losses due to grain boundary recombination, the short circuit current mainly suffers from insufficiently passivated contacts. Together with optical losses, these effects result in a reduction of the theoretical short circuit current density by approximately 30%. While alternative ways to passivate the absorber contact are currently under investigation, optical losses have to be reduced using improved light trapping schemes. The main challenge is to texture the interlayer-silicon and silicon-air interfaces without sacrificing the electronic quality by disturbing the crystal growth process. It is shown that the SMART (smooth anti-reflective texture) scheme is well suited to enhance the optical absorption while enabling theoretical short circuit current densities exceeding 37 mA/cm². Based on this estimation, first IBC cells with front- and rear-side texture are evaluated.

2:30 PM ET02.06.05

Fabrication of SiGe Layer on Si Substrate by Screen-Printing Masahiro Nakahara¹,², Moeko Matsubara¹, Shota Suzuki¹, Shogo Fukami², Marwan Dhamrin² and Noritaka Usami¹; ¹Toyo Aluminum K.K., Shiga, Japan; ²Engineering, Nagoya University, Nagoya, Japan.

During the past few years, the photovoltaics market has grown rapidly and the total cumulative installations amounted to 400GW at the end of 2017, capable of producing roughly 2% of the world wide electricity demand. And crystalline silicon has continued to dominate the solar industry with over 90% of the market share. However the energy conversion efficiency of crystalline silicon solar cell is approaching its theoretical limit, Shockley-Queisser limit, of around 29%, giving the industry no choice but to search for new alternatives of solar cell structures that exceed this limit [1]. Meanwhile multi-junction solar cells, which combine multiple pn-junctions of different band gap energies to absorb the spectrum of the sun, are the state-of-the-art approach for achieving high efficiencies. However, compared with single junction silicon solar cells, the cost is still very high because it utilize Ge wafer as a bottom cell, which substrate for its best lattice match to grow Three Five films on it. Therefore substitution of Ge with low cost material, such as silicon, has a great interest to expand the Three Five solar cell market for terrestrial applications. The lattice mismatch between the epitaxially grown Three Five materials like a GaAsP and Si will result in a low open circuit voltage because of a high threading dislocation density when growing it directly on Si. There are few solutions to address this issue including wafer bonding, lift-off, sample recycling and growing sacrificial thick buffer layers of SiGe/Ge which increase the time and fabrication cost [2].

In this work, single-crystalline SixGe₁₋ₓ thick layers grown by screen-printing technique on Si substrate is investigated. Pastes with different Ge, Al, and Si contents were screen-printed on Si (100) substrate and annealed at different temperature in air and Inert gas to investigate the impact of different Ge paste deposition on the Si substrate. After annealing, the residue pastes on the surface were selectively removed by wet etching with a phosphoric acid solution (HFPO₄: CH₃COOH: HNO₃: H₂O = 16:1:1:2) at 60 degree. Then, the morphology, atomic composition, crystal orientation and crystal quality were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The SEM-EDX analysis indicated that SixGe₁₋ₓ layers with good uniformity and thickness up to 30µm were obtained. Also Ge content of more than 20% is achieved. The formed SixGe₁₋ₓ / Si wafer can be used with Ge buffer layer to fabricate high efficiency Three Five solar cells on cheap silicon substrates.

During the past few years, the photovoltaics market has grown rapidly and the total cumulative installations amounted to 400GW at the end of 2017, capable of producing roughly 2% of the world wide electricity demand. And crystalline silicon has continued to dominate the solar industry with over 90% of the market share. However the energy conversion efficiency of crystalline silicon solar cell is approaching its theoretical limit, Shockley-Queisser limit, of around 29%, giving the industry no choice but to search for new alternatives of solar cell structures that exceed this limit [1]. Meanwhile multi-junction solar cells, which combine multiple pn-junctions of different band gap energies to absorb the spectrum of the sun, are the state-of-the-art approach for achieving high efficiencies. However, compared with single junction silicon solar cells, the cost is still very high because it utilize Ge wafer as a bottom cell, which substrate for its best lattice match to grow Three Five films on it. Therefore substitution of Ge with low cost material, such as silicon, has a great interest to expand the Three Five solar cell market for terrestrial applications. The lattice mismatch between the epitaxially grown Three Five materials like a GaAsP and Si will result in a low open circuit voltage because of a high threading dislocation density when growing it directly on Si. There are few solutions to address this issue including wafer bonding, lift-off, sample recycling and growing sacrificial thick buffer layers of SiGe/Ge which increase the time and fabrication cost [2].

In this work, single-crystalline SixGe₁₋ₓ thick layers grown by screen-printing technique on Si substrate is investigated. Pastes with different Ge, Al, and Si contents were screen-printed on Si (100) substrate and annealed at different temperature in air and Inert gas to investigate the impact of different Ge paste deposition on the Si substrate. After annealing, the residue pastes on the surface were selectively removed by wet etching with a phosphoric acid solution (HFPO₄: CH₃COOH: HNO₃: H₂O = 16:1:1:2) at 60 degree. Then, the morphology, atomic composition, crystal orientation and crystal quality were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The SEM-EDX analysis indicated that SixGe₁₋ₓ layers with good uniformity and thickness up to 30µm were obtained. Also Ge content of more than 20% is achieved. From the XRD patterns, the crystalline SixGe₁₋ₓ peak has been detected in the vicinity of 2θ=66.2°=68.8 deg. The strong SiGe (400) detected peak confirms the epitaxial growth with respect to Si (100) substrate. The formed SixGe₁₋ₓ / Si wafer can be used with Ge buffer layer to fabricate high efficiency Three Five solar cells on cheap silicon substrates.


2:45 PM BREAK

3:15 PM ET02.06.06

Minority Carrier Lifetime Characterization from Silicon Bricks to Modules—Current Status and Future Opportunities Harrison Wiltsendeink, Adrienne Blum, Cassidy Sainsbury, Wes Dobson, Justin Dinger and Ronald Sinton; Sinton Instruments, Boulder, Colorado, United States.

Minority carrier lifetime characterization is integral to the design and production of silicon PV devices in both laboratory and industry settings. Since development of the quasi-steady-state photoconductance (QSSPC) technique for silicon wafers in 1994, comparable lifetime characterization methods have been extended to span the entire solar PV production chain—it is now possible to track relevant lifetime parameters from bulk material (ingots/bricks) all the way to finished solar cells and modules. Already this has enabled implementation of sophisticated quality control systems in production settings, for example: screening incoming material lifetime prior to processing, and monitoring/optimizing changes in lifetime for critical production processes—e.g., diffusion, passivation, laser ablation, nitride deposition, metallization, etc.
Applications of lifetime characterization at the finished cell and module stages have so far been largely untapped, but may prove especially insightful for high-efficiency cell designs featuring passivated emitters (PERC, PERL), rear contacts (IBC), or heterojunction interfaces (HTJ). For cell production lines, lifetime characterization allows power losses to be quantified and sorted by specific loss mechanisms—bulk recombination, emitter recombination (J_{ee}), shunt resistance, and series resistance. This advanced characterization is possible at line-speed, which then enables continuous data feedback to inform material screening criteria and process optimizations for the entire production line. For finished modules, lifetime characterization can enhance understanding of power degradation observed in the field. For degradation modes with distinct lifetime signatures, such characterization enables development of device-physics-based degradation models, which can inform accelerated degradation protocols and highlight potential cell-level solutions to degradation issues.

This presentation will present an overview of the applications of lifetime characterization across the whole silicon production chain mentioned above, with an emphasis on potential future applications.

3:45 PM ET02.06.07

Improvement of Electrical Properties of Laser-Induced Liquid-Phase-Crystallized Silicon Thin Films for Photovoltaic Application

Hiroshi Umishio, Takuya Matsui, Hitoshi Sai and Koji Matsubara; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

In crystalline silicon (c-Si) solar cells, decreasing wafer thickness is expected to be a way for reducing material cost. However, using thinner wafers has two major technical problems. First, wafer slicing creates extensive kerf loss that cannot be reduced easily when thinning the wafer. Second, manufacturing solar cells with thin wafers (<100 µm) is still technically challenging because of the high probability of wafer breakage. If the high quality c-Si thin films can be formed on cheap and strong glass substrates, one could avoid the kerf loss and the breakage risk of thin wafers. In addition, the long process chain for making wafers can be shortcut and that makes the wafer fabrication cost cheaper. Liquid-phase-crystallization (LPC) has emerged as a new technique to make high-quality poly-Si thin films with high crystallinity and large grains (several mm to a few cm in size) on glass. In LPC process, an amorphous silicon (a-Si) precursor film deposited on glass is melted and crystallized rapidly with a line-shaped laser or an electron beam. To achieve sufficient conversion efficiency using LPC-Si absorbers, the deeper understanding of the electrical properties of LPC-Si and their impact on photovoltaic performance are of importance. A factor that has a large impact on the electrical properties of LPC-Si is the grain quality such as grain size and defects present in the intra-grain and/or grain boundaries. In the fabrication process of multicrystalline silicon wafer, cooling rate of molten silicon is an important factor that determines grain size and dislocation densities. In case of LPC-Si, laser scan speed might play an important role in controlling the cooling rate of Si during crystal growth. Another important factor is the doping concentration that affects the carrier mobility and the carrier lifetime. In this study, to gain insight into the electrical properties of LPC-Si, we studied the majority carrier mobility and the minority carrier lifetime of the LPC-Si films prepared in a wide range of doping concentration and laser scan speed. In addition, test solar cells were made and their open-circuit voltage (V_{OC}) and internal quantum efficiency (IQE) were evaluated.

4:00 PM ET02.06.08

Impact of Undoped Substrates on High Performance Silicon Solar Cells

André Augusto, Apoorva Srinivasa, Richard King and Stuart G. Bowden; Arizona State University, Tempe, Arizona, United States.

We investigate the potential advantages of using undoped silicon wafers, including high resistivity n- and p-type, to manufacture high performance solar cells. As the quality of Czochralski material improves and carrier selective contact architectures deliver superior surface passivation (J_{0} < 5 fAcm^{-2}), the cell injection regime increases by a factor of 10 and Auger recombination becomes more predominant. This is particular true for substrates with Shockley-Read-Hall minority carrier lifetime over 1ms. For silicon heterojunction solar cells, high-resistivity base shows potential to increase both the V_{OC} and FF.

We experimentally investigate silicon heterojunction solar cells on substrates in a wide range of dopant concentrations (8-20000 ohm.cm), observing closely the transition from low-level to high-level injection. The idea is to understand the device physics in this regime where neither limiting case of injection is an accurate approximation. In field conditions modules experience different illumination conditions and as a result we also included in this study simulation and experimental measurements of the performance of these cells under light intensities from 0.2-1 suns. Preliminary results on solar cells using 8-20000 Ohm.cm n-type wafers shows excellent surface passivation (J_{0} < 2 fAcm^{-2}) regardless the base doping, impacting positively the pFF, FF and V_{OC}. These cells show similar performance behavior for different light intensities regardless their base resistivity. These studies have important implications for the yield fabrication of c-Si grown wafers for which dopant concentration varies along the length of the ingot, and for the effect of Fermi level position on cell and ingot manufacturing yield, silicon cell power output, and module reliability.

4:15 PM ET02.06.09

Liquid Phase Crystallized Silicon for Application in All-in-Thin-Film Perovskite/Silicon Tandem Cell

Martina Trahmel, Cham T. Trinh, Maurice Nuyts, Uwe Breuer, Uwe Zastrow, Natalie Preissler, Marko Jost, Steve Albrecht, Rutger Schlatmann and Daniel Amkreutz; 1Institute for Silicon Photovoltaics, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 2Institute of Energy and Climate Research - Photovoltaics-(IEK), Forschungszentrum Jülich GmbH, Jülich, Germany; 3Central Institute for Engineering, Electronics and Analytics (ZEA), Forschungszentrum Jülich GmbH, Jülich, Germany; 4PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 5Young Investigator Group Perovskite Tandem Solar Cells, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany.

Liquid phase crystallization (LPC) of silicon is an emerging photovoltaic technology that is based on laser-induced melting and subsequent crystallization of an amorphous or nano-crystalline Si-absorber. This technique avoids kerf loss which is typically associated with wafer processing. The absorber is deposited on glass with a thickness between 5 µm and 40 µm. During the crystallization process, a poly-crystalline Si-absorber with grain sizes in the order of cm in length and mm in width is formed. With an interdigitated back contact (IBC) system, conversion efficiencies of up to 14.2% were achieved. Another important factor that affects the carrier mobility and the carrier lifetime is the doping concentration. In this study, to gain insight into the electrical properties of LPC-Si, we studied the majority carrier mobility and the minority carrier lifetime of the LPC-Si films prepared in a wide range of doping concentration and laser scan speed. In addition, test solar cells were made and their open-circuit voltage (V_{OC}) and internal quantum efficiency (IQE) were evaluated.
within the absorber and are likely to segregate at grain boundaries. Impurities at the LPC-Si/a-Si heterojunction interface can also be responsible for a strong reduction of Voc. The SIMS results suggest that defects at the heterojunction, decorated grain boundaries as well as intra-grain defects might be responsible for the observed losses. To develop a suitable strategy for further device improvement, it is crucial to investigate which of these loss mechanisms are limiting the cell performance.

4:30 PM ET02.06.03
Watching Nanodefects Grow in Si Crystals Andreas Magerl, University of Erlangen-Nuremberg, Erlangen, Germany.

Nucleation and growth of oxygen precipitates in moderately p- ([B] ≈ 10^{15} 1/cm^3) and highly p+ ([B] ≈ 10^{18} 1/cm^3) boron doped Czochralski Si crystals has been investigated in-situ up to 1000°C to monitor continuously the evolution of the defect properties from their very early stages to the long time behavior. Thickness-dependent Pendellösung oscillations as described by the dynamical theory of X-ray diffraction are extremely sensitive to strain fields from defects in a host crystal. Based on this, we initiated a novel approach to study the precipitation kinetics of oxygen in Si. The data is interpreted within a diffusion-limited model of growing spherical precipitates, where two growth regimes are identified. An initial diffusion driven growth is followed by a long time precipitation behavior, which is interpreted as Ostwald ripening.

In addition, synchrotron-based rocking curves (ID15, ESRF, Grenoble) provide information about the size distribution and morphology of the precipitates. A quantitative analysis of the in-situ experiments during annealing at 1000 °C shows two growing particle populations differing in polydispersity and particle density.

4:45 PM ET02.06.10
Improving Sub-Bandgap Photoresponsivity in Silicon Photodiodes via Pulsed Laser Melting-Tailored Hyperdoping Philippe K. Chow1, Qi Lim2, Jim S. Williams3 and Jeffrey M. Warrrender4; 1Benet Laboratories - ARDEC, Watervliet, New York, United States; 2The Australian National University, Canberra, Australian Capital Territory, Australia.

Extending the absorption edge of silicon to harvest below-bandgap-energy photons is one route towards improving/extending the short-wave infrared (SWIR) performance capability of optoelectronic silicon devices including intermediate-band photovoltaics and photodetectors. Non-equilibrium pulsed-laser melting (PLM) and resolidification of silicon containing highly-substitutional chalcogen (e.g. sulfur) and transition metal (e.g. gold) impurities at above-solubility limit concentrations is known to enhance the room-temperature sub-bandgap absorption coefficient dramatically, to the order of ~10^4 cm^{-1} in the 1-2 micron range. However, the best demonstrated external quantum efficiencies (EQE) of photodiodes formed by a junction between the laser-doped layer and the Si substrate have been rather low, on the order of 10^{-1} - 10^{-2} %. It remains to be investigated how PLM condition-dependent material characteristics including impurity lattice location, concentration profile, microstructural homogeneity and chemistry influence photodiode EQE.

In a general effort to boost EQE, we investigate the PLM-dependent structure-property relationships as is relevant to optoelectronic material development. We report our findings from complementary material and photodiode characterization using the most well-studied hyperdoping impurities, gold and sulfur. To explain the observed photoresponsivity results, we employ Rutherford backscattering spectrometry, secondary ion-mass spectrometry, optical absorption spectroscopy and scanning electron microscopy. Among the results, we report order-of-magnitude sub-bandgap EQE enhancement in gold-doped photodiodes, which were fabricated using a recently developed physical vapor deposition-based doping technique. This work aims to unify the state-of-the-art understanding of PLM-induced material properties and of the resulting optoelectronic device performance. Our results showcase the flexibility of PLM-based methods towards their tailoring the structural and electronic properties of silicon for real device applications.

SESSION ET02.07: Poly-Silicon Contacts II
Session Chair: Robby Peibst
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 311

8:30 AM *ET02.07.01
Material Limitations for High-Efficiency Silicon Solar Cells Jan Benick; Fraunhofer ISE, Freiburg, Germany.

Passivating and carrier-selective contacts such as amorphous Si heterojunctions or TOPCon have led the way to further push the efficiency of silicon solar cells to the theoretical material limit. The replacement of partial rear contacts (PRC) by passivating contacts as a full-area rear contact for both sides contacted solar cells so far resulted in efficiencies records up to 25.8% for mono- and 22.3% for multi-crystalline silicon (20x20 mm²). Achieving highest efficiencies requires both, a technology and cell architecture as well as a silicon base material which allows such high conversion efficiencies.

In this paper we discuss the technology of our mono- and multi-crystalline n-type solar cells featuring a front side boron emitter and a rear side passivating electron contact. We further address material aspects and limitations in the cell efficiency associated with the silicon base material (e.g. resistivity and impurity contamination). Whereas the efficiency limitation caused by base material is more obvious in the case of multi-crystalline silicon, we show that even for mono-crystalline n-type silicon, which is less sensitive to common impurities than p-type silicon, even quite low impurity concentrations can be sufficient to limit the cell efficiency potential below 25%.

9:00 AM *ET02.07.02
Upscaling Passivating and Carrier Selective Contacts for Industrial Applications Ingrid Romijn, Maciej Stodolny, Paula Bronsveld, Agnes Mewe, Piero Spinelli and Kees Tool; ECN part of TNO, Petten, Netherlands.

The performance of current industrial solar cells is for a large part limited by recombination at metallic contacts. A solution to overcome this is to screen minority carriers from the metal by using so-called passivating carrier selective contacts. Using carrier selective contacts based on doped polysilicon layers combined with tunnel oxides, efficiencies well above 25% have already been reached on front and back contacted cells on laboratory scale.

In this contribution, we will first focus on upscaling of these polysilicon passivating contacts to 6" bifacial cells using industrial screen printed and fired metallization. The main challenge for such solar cells lies in keeping the contact recombination low, while applying a cost effective, industrial metallization approach. The contact mechanism of commercial silver and silver/aluminum pastes on both n+ and p+ doped polysilicon layers has been extensively studied using scanning and tunneling electron microscopy (SEM, TEM), X-ray and contact resistance (TLM) characterization and a comprehensive model has been built. Contact recombination on n+ poly-Si surfaces has been reduced down to 80 fa/cm² while keeping the contact resistance low enough to enable FFs above 79.5%. V_{oc} up to 685 mV have been obtained enabling initial cell efficiencies of 21.5%. Further optimization of the passivating polysilicon layers itself has yielded record low values for J_{sh} on textured surfaces: we present J_{sh} and implied V_{oc} measurements with best values of <1
Furthermore, results of an even more innovative type of carrier selective contacts based on transparent metal-oxides will be presented. Electron beam (E-beam) deposited molybdenum oxide (MoOx) has been investigated for its potential as a hole selective contact. The high work function of MoOx induces strong band bending in the silicon absorber, which diminishes the electron density at the e-Si surface, while allowing band-to-band transport for holes. Additionally, its high transparency, due to the wide bandgap and dopant-free hole selectivity, makes it a good candidate to replace other high-quality carrier-selective contacts based on doped layers (e.g. a-Si and polysilicon) at the sunny side of the cell or in bifacial solar cells.

By making large-area "moly-poly" cells, with a front side MoOx/aSi:H(i) passivating contact and a rear-side poly-Si/SiOx stack, we have demonstrated that MoOx based e-Si solar cell technology can be scaled to industrial 6" wafer size. Excellent surface passivation was achieved using MoOx and poly-Si, leading to implied Voc values > 725 mV, and a final cell Voc of 687 mV. Using thin PECVD poly-Si layers to avoid too high FCA losses, a 18.1% efficient 9.2×9.2 cm² moly-poly cell was made, which is to our knowledge the highest reported efficiency so far for moly-poly cells.

9:30 AM ET02.07.03
Carrier-Selective Passivating Contacts Based on polySiC for High Efficiency Si Solar Cells Luana Mazzarella1, Guangtao Yang2, Gianluca Limodio3, Paul Procel1, Arthur Weeber4,1, Olindo Isabella1 and Miro Zeman1; 1PVMD group, Delft University of Technology, Delft, Netherlands; 2Solar Energy, ECN part of TNO, Petten, Netherlands.

Carrier-selective passivating contacts (CSCPs) based on an ultra-thin SiO2 capped with doped thin Si based layers exhibit excellent surface passivation of the Si wafers by the SiO2 and selective carrier extraction thanks to the poly-SiC layers. Poly-Si material exhibits generally poor transparency, owing to high parasitic and free carrier absorption, enabling the use of those materials in an interdigitated back contacted (IBC) cell configuration1 with efficiency up to 26.1%. On the other hand, such materials can improve the passivation of the front side of the device induces current losses. Therefore some efforts have been carried out to reduce the layer’s thickness and to incorporate carbon or oxygen to improve their transparency. Recently, CSCP based on poly-Si alloyed with C4 and O1.4 demonstrated their potential on device level resulting in conversion efficiency up to 25.7% in front back contacted (FBC) cell configuration2.

In this study, we develop polyisolocarbide (poly-SiC) CSCPs with both doping polarities grown by plasma enhanced chemical vapor deposition in an initial amorphous arrangement (a-Si:C:H) on top of a chemically-grown SiO2 (<1.5 nm). We thus monitor the passivation quality during the fabrication process to obtain poly-SiC material. Firstly, we investigate the effect of C alloying, doping and layer thickness on the final material properties and passivation performances.

Furthermore, we optimize the annealing treatment varying both the temperature and time in a wide range (800-950 °C, 5-60 min) to identify the optimal conditions to crystallize the layer stack and drive-in the dopants beneath the passivating SiO2 thin film into the e-Si absorber. Contextually, we enhance the passivation quality of the CSPS stacks by using sacrificial layer schemes that act as source of hydrogen. In this respect, we test SiNx, Al2O3 and Al2O3/SiNx, in forming gas annealing atmosphere at 400 °C. Preliminary results were obtained on symmetric test samples capped with 75-nm thick SiN layer feature promising passivation quality for potential application in both FBC and IBC solar cells. We found that n-type poly-SiC ensures much higher temperature stability than the p-type counterpart with implied open circuit voltage (i-Voc) above 700 mV for the range of annealing temperature / time investigated. For the p-type, the value is limited to 653 mV, with much more margin of improvement. For a stack initially consisting of (a-SiC:H)2/a-Si:H (5 nm) 30 nm, we measure i-Voc above 710 mV, carrier lifetime of 7.5 ms and recombination current densities of 12 fA/cm².

9:45 AM ET02.07.04
Inkjet Printing as a New Method for the Preparation of POLO Contacts Fabian Kiefer1, Nadine Wehmeier1, Till Brendemühl1, Larysa Mettner1, Felix Haase1, Michael Holthausen2, Christian Daeschlein2, Christoph Mader2, Odo Wunnicke2 and Sarah Kajari-Schroder1; 1Institut für Solarenergieforschung GmbH, Emmerthal, Germany; 2Evonik Creavis GmbH, Marl, Germany.

The increase of Si solar cell efficiencies in the last years have been mainly driven by passivating contacts, either with amorphous Si (heterostructure with intrinsic thin layer, HIT) or silicon oxide (poly-Si on oxide, POLO; tunnel oxide passivating contact, TopCon) as an interface layer3-5. Intersubband contact (IBC) solar cells have demonstrated the highest efficiencies of more than 26 % at, as they combine a high voltage resulting from the passivating contacts and a higher current compared to front-contacted solar cells due to the absence of metal shading. A drawback shared by all presented techniques for the deposition of POLO contacts so far is that they cover the full area of one or both sides of the wafer6. During the process of an IBC Si solar cell, a structuring of the deposited poly-Si layer is necessary.

To overcome these hurdles, Evonik developed an inkjet printable, doped precursor (Evonik’s liquid silicon) which can be used for the direct generation of structured amorphous and polycrystalline Si layers7. As direct printing on silicon oxide layers used for POLO junctions is possible, this is a novel, unique possibility to prepare in-situ doped and in-situ structured poly-Si layers with only three process steps: Printing of the liquid Si ink onto the wafer under inert atmosphere with an inkjet printer – conversion of the liquid Si into amorphous Si on a hotplate – annealing of the layer stack in a tube furnace with break-up of the silicon oxide and conversion of the amorphous Si into poly-Si. The shape of the printed Si layer can be designed freely, the minimum structure size of the printed POLO contact is limited only by the drop size of the inkjet process.

In this work, we present the preparation and properties of phosphorous-doped inkjet-printed POLO layers. The electrical characterization of the layers includes measurements of the recombination current densities J0 via photoconductance decay and the contact resistances between aluminum and the printed Si layer and between poly-Si and substrate via transfer length method. We print the ink on one side of the wafer in quadratic fields with an area of 4×4 cm², which is a suitable size for the measurements. The rear side of the wafer is passivated with a silicon nitride passivation layer. We investigate the influence of two process parameters on the electrical properties of the POLO contacts: the thickness of the printed liquid Si layer and the thermal budget of the annealing process. For several poly-Si layer thicknesses and annealing temperatures between 900°C and 1000°C, we achieve J0 of the first P-doped inkjet-printed POLO contacts of < 20 fA/cm² with a minimum value of 14 fA/cm².

Ref:
1 doi:10.1016/j.solmat.2014.06.003
2 doi:10.1016/j.solmat.2013.09.017
3 doi:10.1016/j.solmat.2017.05.042
Recent progress in development of silicon heterojunction (SHJ) solar cells promotes this technology for mass production of future PV modules. In view of technology upscaling use of abundant materials for cell production is highly desirable. Particularly the tin-doped Indium oxide (ITO) - the transparent conductive oxide contact applied in high efficiency SHJ cells may be challenging in mass production due to indium-related supply/economic and environmental issues. One viable alternative for ITO in SHJ solar cells is more environmentally friendly, abundant and low-cost Al-doped Zinc Oxide (AZO). In our work we develop rear emitter SHJ solar cells with AZO contacts prepared at room temperature to explore the potential for reduction of thermal budget of SHJ cell preparation.

From the long lasting experience in the field of thin film silicon solar cells it is widely accepted that AZO as a window TCO forms better contact with microcrystalline or nanocrystalline Si (nc-Si:H) p-layer compared to the amorphous Si (a-Si:H) p-layer. Formation of the barrier for hole transport has been evident thermal activation of fill factor confirming presence of the carrier transport barrier in the cells with a combination of nc-Si:H p-layer and AZO contact. As for the n-type layers, both amorphous and nanocrystalline Si n-layers form proper contacts with room temperature AZO. In the rear emitter cells with n-type back the n-layer is at the front and nc Si:H is more beneficial than a-Si:H concerning transmission in short wavelength region of the solar spectrum. With combination of the a-Si:H p-layer, nc-Si:H n-layer, and room temperature AZO cell efficiency of 20.2% has been achieved.
Reducing thickness of crystalline silicon (c-Si) <100 µm is one of the keys to low-cost solar cells. On such thin c-Si, small textures are necessary to reduce c-Si losses by texturing process and to keep the robust property in fabrication processes. To obtain small textures with a size <2 µm, we already established “Microparticle-Assisted Texturizing” (MPAT) process and reported elsewhere. However, cleaning of such small texture surface is always challenging. Therefore, in this work, we aimed to develop a suitable cleaning procedure for the small texture surface. After attempted many cleaning procedures, finally we found a novel cleaning method to obtain large effective minority carrier lifetime ($\tau_{\text{eff}}$) of 7.8 ms corresponding to an extremely low surface recombination velocity (SRV) of 0.6 cm/s. In this cleaning method, we noticed an importance role of solution surface tension, hence methanol (CH$_3$OH) was mixed with the solutions to control the surface tension. It should be noted that without using methanol in the cleaning, only SRV$\approx$3.5 cm/s was obtained. We named this finding “Methanol-Assisted Cleaning (MAC)” process. We also verified that mixing methanol reduces contact angles or surface tensions of the solutions on the flat c-Si (100), flat c-Si (111), and textured c-Si (100). Owing to the low surface tension, the solution can reach even the bottom of the complicated small texture surface, leading to uniform chemical cleaning and better passivation quality. Features of the MAC process is also presented in this work, which are expected to be useful for cleaning of any kinds of Si wafers other than solar cell ones.

**11:45 AM ET02.08.05**
**Fabrication of Silicon Heterojunction Solar Cells Using PECVD-Grown 40 µm-Thick Epitaxial Silicon Wafers**

Ji-Eun Hong$^1$, Ka-Hyun Kim$^2$, Dong Suk Kim$^3$ and Soon-Ho Oh$^4$, KIER-UNIST Advanced Center for Energy, Korea Institute of Energy Research, Ulsan, Korea (the Republic of); $^1$Department of Integrated Energy and Photon Technology, Cheongju University, Cheongju, Korea (the Republic of).

Wafer cost occupies about 40 % of module cost in the crystalline silicon solar cells. Current wafering technology relies on wire sawing that produces wasteful kerf-loss and high mechanical stress, resulting in additional production cost and limited production yield. Various kerf-less wafering technologies, such as exfoliation or spalling of silicon wafer from an ingot, growth of wafers directly from a silicon melt, and chemical vapor deposition of silicon on release layer or sacrificial substrate, enables to reduce kerf-loss as reported by D. M. Powell et al. Among these, epitaxy silicon growth on mono- or multi-crystalline silicon seems to be the most promising candidate for the next generation wafering technology due to the fact that epitaxy growth also enables to fabricate built-in junction structure simultaneously during growth. In other word, epitaxy growth process can significantly reduce solar cell fabrication steps (i.e. gas-to-wafer) compared to the conventional solar cells using wire sawn wafers, as also reported by R. Hao et al. Recently, many research results were reported mentioning that epitaxial growth of Si films on c-Si substrates was achieved by Atmospheric Pressure Chemical Vapor Deposition (APCVD). However, this technology usually disassociates the gas precursors at substrate temperatures higher than $1000 \, ^\circ\text{C}$. As Kambara et al. reported in a recent paper that high temperature process is one of the most cost generating factors in mass production, necessity of such high temperature for APCVD makes the commercialization of the silicon epitaxy technology using APCVD less attractive. Compared to APCVD, Plasma Enhanced CVD(PECVD)-based epitaxy can be performed at a low substrate temperature of $\approx-200 \, ^\circ\text{C}$, leading it to the far more cost-effective alternative. Thus, in this presentation, we studied on epitaxy silicon growth at $200 \, ^\circ\text{C}$ using PECVD, and also demonstrated kerfless wafering using direct exfoliation. We succeeded in depositing 40 µm-thick silicon epitaxy layer at $200 \, ^\circ\text{C}$. Measurements showed that there were porous and H-rich interface layers, which can be utilized as a separation layer. Growth mechanism of epitaxy layer was further confirmed by ellipsometry using Bruggeman effective medium approximation (BEMA). And, cross-sectional transmission electron microscopy (TEM) images showed that there were hydrogen rich interface layers, and atomic arrangement at the interface was not disturbed. In addition, we investigated the exfoliation of epitaxy layer using metallic stress layer. Finally, we used the exfoliated 40 µm-thick free-standing epitaxial wafers to fabricate silicon heterojunction solar cells. The fabricated cell exhibited an efficiency of 11.42 % ($J_{\text{sc}} : 32.28 \, \text{mA/cm}^2$, $V_{\text{oc}} : 610 \, \text{mV}$, $\text{FF} : 58 \%$).

**SESSION ET02.09: Alternative Approaches to Contacting**

Session Chair: David L. Young

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 311

**1:30 PM ET02.09.01**
**Organic-Silicon Heterojunction Solar Cell**

Baoquan Sun; Institute of Functional Nano and Soft Materials Laboratory (FUNSOM), Soochow University, Suzhou, China.

Numerous new materials and device structures have been widely explored in order to cut the cost of photovoltaic (PV) manufacture. Organic-inorganic hybrid solar cells based on nanostructured semiconductor have built up in few years ago, which may promise the low cost and high performance. However, the device performances are relatively lower than its pristine all-inorganic PV devices, resulting from the numerous surface defect and improper organic-inorganic phase segregation. Here, we demonstrate that hybrid PVs based on organic conjugated molecular and nanostructured silicon nanowire arrays can achieve a high PCE by controlling the phase separation as well as surface passivation. An advantage of hybrid devices presents the excellent light harvest capability of nanostructured as well as simple fabrication process. Especially, hybrid composites of conjugated organic materials and nanostructured inorganic materials are potential candidates for cost-effective and efficient solar-energy harvesting devices. This device can be worked by a light-modulated field effect solar cell, which can be potentially integrated with halide perovskite. In addition, this type device can be easily integrated with other type energy device, for example, an energy harvesting structure that integrates an organic-Si heterojunction solar cell and a triboelectric nanogenerator (TENG) device is built to realize power generation from both sunlight and raindrop. In addition, a self-charging power unit based on an organic-Si heterojunction solar cell and a polypyrrole supercapacitor, which simultaneously achieved both photoelectric conversion and energy storage.


**2:00 PM ET02.09.02**
**Effect of Permanent Dipole Layers in the Electrical Characteristics of Electronic Devices and Solar Cells**

Elia Rosi¹, Zaira Barquera², Isidro Martin³, Pablo Ortega³, Cristobal Voz³, ⁴, Joaquim Puigdollers³ and Ramon Alcubilla³; ¹University of Politecnica-Catalunya, Barcelona, Spain; ²Cinvestav, Querétaro, Mexico.
In the last years, there has been a generalized tendency towards the use of novel materials for the formation of electron-selective contacts on n-type crystalline silicon (c-Si) heterojunction solar cells. Until recently transition metal oxides (TiO$_2$-open style=tint=accent color=010332@2×640px) or alkali and alkaline earth metal salt interlayers (LiF, MgF$_2$) have been mainly used. However new organic molecules with a permanent dipole moment are on the rise as promising candidates to improve the electric contact with the metallic electrode. Conceptually speaking, the dipole of the molecule induces a build-in tension on the layer that can move the effective work function of the metallic electrode at the interface with the semiconductor.

This effect is strongly dependent on the dipole package and orientation, but also the on the individual molecular dipole moment. Amino acids, are known for strong spatial charge splitting as amino group protonation yields a net positive charge and Carboxylate ionization yields a net negative charge. This accounts for many amino acids strong dipole moment. In this group we can find Glycine, as a stable and easy processable material. Amino acids, are known for strong spatial charge splitting as amino group protonation yields a net positive charge and Carboxylate ionization yields a net negative charge. This accounts for many amino acids strong dipole moment. In this group we can find Glycine, as a stable and easy processable material.

In a first approximation, we have studied the electric contact using Transfer Length Method (TLM) of n-type crystalline silicon with an Atomic Layer Deposited Al$_2$O$_3$/TiO$_2$ stack, reaching a maximum contact resistance of 0.75 Ohms cm$^2$. Furthermore, the effect of the dipole layer has been confirmed on Thin-Film Transistors (TFTs) by depositing a glycine thin-film layer (20 and 5 nm thick) between the silicon dioxide and the semiconductor. The incorporation of the glycine interlayer results in a significant increase of the threshold voltage. Variation of the threshold voltage allows to estimate the dipole moment of the interlayer. Finally, the influence of the incorporation of the glycine dipole was studied on final solar devices. In particular, low temperature dopant-free c-Si solar cells were fabricated using Glycine as a new ETL with the following structures ITO/V$_2$O$_5$/n-cSi:H/Glycine/Al and ITO/V$_2$O$_5$/n-cSi:Al$_2$O$_3$/TiO$_2$/Glycine/Al.

2:15 PM ET02.09.03

Effect of Slow-Speed Evaporation of BaSi$_2$ on the Performance of P-Type BaSi$_2$/n-Type Crystalline Si Solar Cells

Michinobu Fujiwara, Kazuma Takahashi, Yoshihiko Nakagawa, Kazuhiro Gotoh, Yasuyoshi Kurokawa and Noritaka Usami; Nagoya University, Nagoya-shi, Japan.

Alternatives to p-type amorphous Si (a-Si) for hole selective contacts in Si heterojunction (SHJ) solar cells have attracted significant attention. We have recently proposed p-type BaSi$_2$ (p-BaSi$_2$) as a promising candidate for a hole selective material, since device simulation (Afor-Het ver. 2.5) showed that p-type BaSi$_2$ improves open-circuit voltage ($V_{oc}$) of SHJ solar cells [1]. To deposit p-BaSi$_2$ on a large-area substrate, we developed a simple method to perform thermal evaporation of BaSi$_2$ on B-doped hydrogenated a-Si:H (a-Si:H) deposited by plasma enhanced chemical vapor deposition (PECVD). To realize high-quality p-BaSi$_2$/n-type crystalline Si (c-Si) heterostructures, control of the deposition rate during the evaporation is of crucial importance. In fact, we have shown that employment of a slow deposition rate at the initial stage of the evaporation improves $V_{oc}$ presumably due to the enhanced diffusion of Ba into the Si substrate [2]. In this study, we changed the time to hold slow-speed deposition of BaSi$_2$ and investigated the effect on film properties and solar cell characteristics.

B-doped a-Si:H thin film with a thickness of about 10 nm was deposited on a c-Si(111) substrate (resistivity: 3-6 Ωcm) by PECVD. The flow rates of SiH$_4$, H$_2$ and 1% B$_2$H$_6$ were 40, 40 and 40 sccm, respectively. Substrates were heated at 600°C for 3 h in the evaporation chamber. BaSi$_2$ granules with the weight of 0.008 and 0.1 g were evaporated by resistive heating. The heating current was initially held at 90 A for 0, 30, 180 and 600 s and then raised to 140 A. Rapid thermal annealing (RTA) was performed for some samples to diffuse B into the evaporated BaSi$_2$ thin films. After that, the solar cell structure (Ag/TO thickness (t): 80 nm/p-BaSi$_2$/30 nm/n-c-Si r. 280 mm/Au-Sb) was fabricated, and their J-V characteristics were measured under AM1.5G illumination. BaSi$_2$ single films were characterized by Raman spectroscopy and X-ray diffraction (XRD).

As a result of J-V characteristics, we achieved conversion efficiency of 8.37% by holding slow-speed deposition for 180 s. Changing the holding time of slow deposition from 0 to 180 s improved $V_{oc}$ as well as fill factor (F.F.) from 402 to 464 mV and from 24.1 to 60.1%, respectively. At the holding time of 600 s, the highest $V_{oc}$ of 554 mV was obtained although F.F. was degraded to 28.0%. Raman spectroscopy showed that the a-Si layer, which was found at the surface after evaporation, disappeared after RTA. XRD patterns showed that the holding time of 180 s a-axis-oriented BaSi$_2$ was the most predominant after evaporation. After RTA for the sample at the holding time of 180 and 600 s, a-axis orientation was enhanced and FWHM was reduced. These results show that the slow-speed evaporation improved the homogeneity and film quality, and led to the improvement of solar cell performance.


2:30 PM BREAK

3:30 PM ET02.09.04

Effects of Surface Doping of Si Absorbers on the Performance of Carrier-Selective Contacts

Hyunju Lee¹, Takefumi Kamioka¹, Noritaka Usami¹ and Yoshio Ohshita¹; ¹Toyota Technological Institute, Nagoya, Japan; ²Graduate School of Engineering, Nagoya University, Nagoya-shi, Japan.

Recently, a new alternative to the conventional silicon heterojunction (SHJ) solar cell concept has been suggested and intensively studied. In this new concept, a set of dopant-free carrier-selective contacts (CSCs) is employed to separate and collect photo-generated free carriers in a single cell structure [1]. One of the most promising materials for dopant-free CSCs is transition metal oxides (TMOs). TMOs were first used in organic solar cells. So far, as dopant-free n- and p-type CSC materials, amorphous titanium dioxide (TiO$_2$) and sub-stoichiometric molybdenum oxide (MoO$_x$) is the most promising material in TMO-based CSC Si solar cells, respectively [2-3]. Meanwhile, TMO-based CSCs have demonstrated significant progress in Si solar cell performance. However, the performance of TMO-based CSC Si solar cells is still inferior to that of thin tunnel SiO$_x$/phosphorus-doped hydrogenated poly silicon (n‘-poly-Si:H) stack-based CSC Si solar cells (also referred as TOPCon structured solar cells) owing to the higher level of surface recombination and contact resistance of TMO-based CSCs [2]. In particular, the higher performance of the TOPCon seems to be partially due to shielding of the tunnel oxide/Si interface recombination without appreciably introducing Auger recombination by shallow phosphorus diffusion from an n‘-poly-Si:H layer into an n-type Si absorber through an ultra-thin tunnel oxide layer during polysilicon annealing [4].

In this study, we have investigated:

- The performance of TiO$_2$ and MoO$_x$-based CSCs on shallowly doped n‘- and p‘- Si surfaces.
- The effects of various ultra-thin tunnel layers on the performance of TiO$_2$ and MoO$_x$-based CSCs.
- The stability of the fabricated TiO$_2$ and MoO$_x$-based CSCs on shallowly doped n‘- and p‘- Si surfaces under light illumination, for developing cost-effective, high-performance and stable CSC Si solar cells and elucidating the effects of the surface doping of Si absorbers and the ultra-thin tunnel layers on the performance of TiO$_2$ and MoO$_x$-based CSCs. During our presentation, we will discuss the experimental results and suggest ways to enhance the performance and stability of CSCs.

References

In the current study, a novel three-dimensional multiple-slip crystal plasticity based model and specialized finite-element formulations are used to analyze the reliability and lifetime of PV devices. Embedded Void Approach (EVA) to reduce defects at heterogeneous interfaces of thin-films by overcoming the thermal mismatches of multi-junction photovoltaic, e.g. Indium Gallium Nitride (InGaN) and deep reactive ion etching (DRIE) processes. To achieve the high efficiency of MW radial junction solar cells, we developed the high conductive and transparent top electrode to replace the conventional bus-finger electrode which has a significant shading loss. We devised a novel micro-grid top electrode which shows superior transparency (over 97%) and low sheet resistance (less than 30 Ω/□). By applying the micro-grid electrode on the top surface, the MWs solar cells showed outstanding fill factor (81.2%) and improved efficiency (16.5%).

As an efficient way to decrease the flat-top-surface reflection of the MWs and increase the light absorption property of the radial junction solar cells, a tapered-MW structure was employed using a simple wet-etching process. When a c-Si wafer with MWs is dipped in a silicon etchant (RSE-100, transene), the top part of the MWs that has a shorter diffusion path compared to the bottom part is etched more quickly. Since the diameter of the tapered MWs gradually increased from the top to the bottom, the tapered MWs can act as a buffer layer to compensate for the mismatch between the refractive indexes of air (1) and the silicon substrate (4). Thus, the surface reflection of the tapered MWs was observed to be less than 2% at a wavelength of 550 nm. The tapered MW based radial junction solar cells exhibit improved efficiency up to 18.9% thanks to the enhanced light absorption property.

As the last step for optimizing the device structure of the MWs solar cells, we used high purity doping process using acid dopant sources that showed improved minority carrier lifetime (from 79.29 µs to 272.24 µs). Accordingly, we achieved high efficiency (20.2%) MWs radial junction solar cell by applying all of the developed technologies such as the micro-grid electrode, tapered MWs, and high purity doping process. At present, we are aiming at developing an ideal passivation layer to achieve the more than 25% efficiency of the radial junction solar cells. Therefore, we believe the MW structures with the suggested technologies become a foundational technology for the highly efficient radial junction solar cells.

Saw damage removal and different pyramidal texture size on passivation characteristics of the SHJ solar cells. Furthermore, making abrupt pyramidal textured c-Si/i-a-Si:H interface is of significant importance. For example, Stefaan De Wolf et al. (J. Appl. Phys. (2007)) reported that for a-Si:H films with no crystalline component the passivation properties enhances by annealing most likely by film relaxation, which is not the case when an epitaxial layer was grown at the interface. However, there are few reports regarding combined effects of surface texturing and abruptness of c-Si/i-a-Si:H interfaces on the passivation properties and subsequent performance of SHJ solar cells.

Thus, in this presentation, we report on the combined effects of saw damage removal and different pyramidal texture size on passivation characteristics of i-a-Si:H/e-c-Si/a-Si:H structures. Transmission electron microscopy (TEM) observations showed that the peaks of the pyramids are not sharp but somewhat flat, and flat and side-wall area of pyramids exhibited different crystalline orientations ((100) and (111), respectively). Cross-sectional TEM measurements also showed that the c-Si/i-a-Si:H interface was abrupt when i-a-Si:H was deposited on the side walls (i.e. (111) side) of the pyramids whilst the sidewalls were textured in chemical solutions to make pyramidal textures at the both surfaces. Then, i-a-Si:H thin films (~10 nm thick) are deposited on top of pyramidal and thermal expansion coefficients mismatch during the growth of i-a-Si:H thin-film on c-Si substrate, both with/without embedded micro-voids. Further, a parametric study of voids aspect and volume ratios impact on dislocation evolution is studied.

Thus, in this study, we report on the combined effects of saw damage removal and different pyramidal texture size on passivation characteristics of i-a-Si:H/e-c-Si/a-Si:H structures. Transmission electron microscopy (TEM) observations showed that the peaks of the pyramids are not sharp but somewhat flat, and flat and side-wall area of pyramids exhibited different crystalline orientations ((100) and (111), respectively). Cross-sectional TEM measurements also showed that the c-Si/i-a-Si:H interface was abrupt when i-a-Si:H was deposited on the side walls (i.e. (111) side) of the pyramids whilst the sidewalls were textured in chemical solutions to make pyramidal textures at the both surfaces. Then, i-a-Si:H thin films (~10 nm thick) are deposited on top of pyramidal and thermal expansion coefficients mismatch during the growth of i-a-Si:H thin-film on c-Si substrate, both with/without embedded micro-voids. Further, a parametric study of voids aspect and volume ratios impact on dislocation evolution is studied.

Si substrate, both with/without embedded micro-voids. Further, a parametric study of voids aspect and volume ratios impact on dislocation evolution is studied.

Effects of Different Pyramidal Texture Size and Interfacial Abruptness on the Performance of Silicon Heterojunction Solar Cells

Joon-Ho Oh1, Ji-Eun Hong2, Hee-Eun Song3, Ka-Hyun Kim2 and Dong Suk Kim1; 1Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2Centre for Simulation Innovation and Advanced Manufacturing, The British University in Egypt, Cairo, Egypt.

The present study focuses on suppressing/sinking dislocations generated at the interface during the fabrication of single-junctions with high lattice and thermal mismatches of multi-junction photovoltaic, e.g. Indium Gallium Nitride (InGaN) thin-film on Silicon (Si) substrate. Such defects act as scattering centers that impact the minority carrier lifetime, reduce thermal conductivity, and form easy pathways for impurity diffusion. Thus, limit the performance, reliability, and lifetime of PV devices. Embedded Void Approach (EVA) to reduce defects at heterogeneous interfaces of thin-films by overcoming the thermal expansion coefficient mismatch and lattice mismatch between different layers is studied.

In the current study, a novel three-dimensional multiple-slip crystal plasticity based model and specialized finite-element formulations are used to address InGaN growth on Si substrates. The new formulations account for threading dislocations generation, mobility and interaction to account for lattice and thermal expansion coefficients mismatch during the growth of InGaN thin-film on Si substrate, both with/without embedded micro-voids. Further, a parametric study of voids aspect and volume ratios impact on dislocation evolution is studied.
ET02.10.03
Enhancement of Light Trapping for Thin-Film Silicon Solar Cells

Y. Sha Yi, M. Ye and D. Wu
University of Michigan, Dearborn, Michigan, United States

Next generation thin film solar cells (inorganic or organic) are generating wide interests recently as it promises to reduce the materials usage and significantly lower the cost of electricity generated by solar cells. One of the main types of thin film solar cells, with Si as the absorbing layer, presents two main challenges for further development: (1) how to achieve broadband antireflection at the front surface; (2) how to achieve broadband light trapping at the bottom surface (especially at longer wavelength) within the AM1.5 solar spectrum. With the rapid progress of nanotechnology, many nano scale photonic devices as small as 30 nm have been realized, which is very promising for achieving manipulation of photons at chip scale and having broad applications in renewable energy (photovoltaic cells, solid state lighting), telecommunications and the bio medical field. Accordingly, there are many routes to enhance the light absorption for thin film. Various methods of enhancing optical absorption have been proposed, including the use of dielectric photonic structures or plasmonic metallic nanoparticles; most of which are mainly focused on either front side antireflection film, or light trapping structures on the back side. Few works have been proposed that take into account the two challenges stated above; broadband antireflection photonic structures on the front side and light trapping photonic structures at the bottom side, as well as their correlation for enhancing the light absorption for thin film solar cells.

In this work, we have studied light trapping effects utilizing both top and bottom nanophotonic structures. We propose broadband nano scale pyramid light trapping top photonic structures to increase the absorption of thin film solar cells, especially at short wavelength; and broadband light trapping bottom omni directional photonic crystal structures to optimize the optical path length for longer wavelength, especially to increase the near bandgap wavelength absorption of thin film solar cells. The correlation between the front side and bottom side nano photonic structures suggests the importance of light trapping from both aspects.

ET02.10.04
Investigation of Metal Oxide/Amorphous Silicon Interfacial Conductivity Towards Solar Cells Based on Ultra-Sparse Metal Mesh

Qingyu Cui and L. Jay Guo
University of Michigan, Ann Arbor, Michigan, United States

In large-area optoelectronic and display industries, Indium Tin Oxide (ITO) is the most widely used transparent electrodes, because of its excellent transparency and conductivity. However, the storage of indium is becoming more and more limited, which will give rise to the increasing cost and concerns. In recent decades, researchers showed wide interests to the alternative candidates of ITO, including other cost-efficient conductive oxides, ultra-thin metal films, carbon-based electrodes, metal mesh and so on. Among them, the metal mesh is drawing extensive attentions, due to its easy fabrication, including nano-imprinting, electroplating, photo-lithography, even solution-coating of nanowires. However, it is not that desirable for solar cell or light emitting devices because of the large non-conductive holes in the metal mesh. As a result, people usually use conductive polymer to enhance the local conductivity.

Here we report on the device structure of amorphous silicon (a-Si) solar cells without such a conductive layer for metal mesh, which incorporates the dramatically increased interfacial conductivity for tungsten oxide (WOx) and a-Si.

Based on the inter-digitated Tungsten (W) electrodes, we found the film lateral conductance of 60nm a-Si deposited on 30nm WOX is at least 4 orders higher than individual a-Si or WOX films, where the obtained resistances are 677 ohm, 6.67E+6 ohm and over 1E+10 ohm for WOX / a-Si, WOX and a-Si, respectively. Probably this is due to the quantum confinement and reduced recombination site density for carriers along the WOX / a-Si interface, then resulting in the enhanced lateral carrier transportations.

Utilizing the WOX / a-Si interface, we fabricated solar cells (ITO / WOX / a-Si / Cathode) based on ITO-mesh with different size. The ITO mesh period is 420 um x 420 um, and the edge length of non-ITO window increases from 0 um to 410 um (the window ratio from 0% to 95.3%). We found that the WOX / a-Si interface is still sufficiently conductive to collect the photo-generated holes even under ultra-sparse mesh (window ratio 95.3%), without sacrificing the Photo-Conversion Efficiency (PCE), which remains around 3.5% for 60nm a-Si. Moreover, Jsc increased from 11.2 mA/cm2 to 13.2 mA/cm2, which is partly because of the increased overall transparency of ITO. Then Voc decreases from 0.60 V to 0.51 V, probably due to the reduced overall work-function of anode. The serial resistance decreased from 43 to 26 ohm*cm2 and the ambipolar diffusion length increased from 55.3 nm to 99.8 nm, possibly resulting from the increased lateral electric field, faster carrier transportation and reduced recombination site density along the WOX / a-Si interface.

The results reported here verified the lateral carrier transportation along the interfaces between different active interlayers can be well utilized to achieve simpler device designs, especially based on the metal mesh with a much higher overall transparency than ITO.

ET02.10.05
Figure-of-Merit Evaluation of Gold-Hyperdoped Silicon for Photovoltaic Applications

Senali Dissanayake1, Matthew Wilkins2, Philippe K. Chow3, Wenjie Yang4, Quentin Hudspeth1, Shao Qi Lim3, Jimmy Williams4, Jeffrey M. Warrender3, Jacob J. Krich2 and Meng-Ju Sher1

1Physics Department, Wesleyan University, Middletown, Connecticut, United States; 2Department of Physics, University of Ottawa, Ottawa, Ontario, Canada; 3U.S. Army ARDEC - Benet Labs, Watervliet, New York, United States; 4Research School of Physics and Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia.

Laser hyperdoping offers a viable method to introduce large concentrations of impurities into silicon, introducing states deep in the silicon band gap that could enable an intermediate band solar cell architecture. A previously reported quantitative figure of merit has been advanced as a heuristic for assessing the promise of a candidate silicon-hyperdopant system. The figure of merit is proportional to the product of the electron mobility, the recombination lifetime, and the square of the average sub-gap absorption coefficient.[1] For the first extensively-studied dopant, sulfur, the figure of merit was found to be fairly low at all S concentrations due to extremely short (~130 ps) carrier lifetimes.[2] Recent work has shown evidence of sub-band gap photocurrent response resulting from the introduction of transition metals in hyperdoping concentrations.[3] Ion implantation followed by melting is a well-established hyperdoping method for heavy chalcogen dopants (S, Se and Te), but incorporating transition metals at supersaturated concentrations with high crystalline quality has been challenging. One complication of working with transition metals as impurities is the incidence of cellular breakdown – a microstructure that results from instability during solidification – under some solidification conditions. In this work we optimize maximum concentrations that can be
practically synthesized for the prospect for PV device. We use time-resolved THz spectroscopy measurements to study carrier lifetime, and we compare these to the previously reported results for S. This work reports on a systematic study to experimentally determine the mobility, lifetime, and absorption coefficient for gold-hyderdoped silicon at several concentrations, and use these to compute a figure of merit for each dopant and dose.


ET02.10.06
Tunnel Oxide Passivated Contact for Crystalline Silicon Solar Cells Using Hot-Wire Chemical Vapor Deposition
Kaining Ding1, Manuel Pomaska1, Shenghao Li1, Jan Lossen1, Jan Hoss1, Maurice Nuyts1, Friedhelm Finger1 and Uwe Rau1; 1Research Center Juelich, Julich, Germany; 2ISC Konstanz, Konstanz, Germany.

In this work, hot-wire chemical vapor deposition (HWCVD) was utilized to fabricate amorphous silicon(a-Si) thin films for tunnel oxide passivated contacts of crystalline silicon n solar cells. So far low pressure chemical vapor deposition or plasma enhanced chemical vapor deposition are usually used to deposit thea-Si:H thin films on crystalline silicon covered by a thin tunnel oxide(SiO2/c-Si) to form the passivated contact, giving rise to excellent solar cell performances of up to 26.1% energy conversion efficiency. As the fabrication process of the solar cells includes several high temperature process steps of up to 900 °C, the a-Si precursor layer needs to have the property of remaining blister-free after all process steps. At the same time, the c-Si surface should be very well passivated by the a-Si/SiO2 layers at the end of all process steps. Last, the deposition rate should be high, in order to be attractive for photovoltaic mass production. We developed ex-situ as well as in-situ n-doped a-Si films for the electron selective passivated contacts. The films remain blister-free after all process steps, give rise to promising passivation qualities with implied open circuit voltages of more than 720 mV, and were deposited with rates of more than 1 mm/s. To correlate the passivation quality to the material properties of the n-doped layer, X-ray diffraction was measured before and after and every high temperature process step. Additionally, the investigation was completed by measuring the hydrogen and phosphorus concentration profiles using secondary ion mass spectrometry and by measuring the doping profiles using the electrochemical capacitance-voltage profiling technique.

ET02.10.07
Recombination Activity of Inclined Σ3{111} Grain Boundaries in High-Performance Si Ingots
Yutaka Ohno1, Kentaro Kutsukake1, Takehiro Tamaoka2, Seiji Takeda2, Yasuo Shimizu2, Naoki Ebisawa2, Koji Inoue2, Yasuoyoshi Nagai3 and Noritaka Usami4; 1MR, Tohoku University, Sendai, Japan; 2ISIR, Osaka University, Osaka, Japan; 3The Oarai Center, IMR, Tohoku University, Oarai, Japan; 4GSE, Nagoya University, Nagoya, Japan.

Grain boundaries (GBs) are inevitably introduced in polycrystalline silicon (Si) ingots for solar cells, and they have substantial influences on electronic properties such as minority carrier lifetime, via the segregation of impurity atoms. Especially, asymmetric GBs with higher-Σ value of the associated coincident site lattice (CSL) are frequently introduced in Si ingots, and they severely affect the overall material properties even when their density is very low. Therefore, a comprehensive knowledge of the recombination activity of the GBs, as well as their structural properties, is indispensable to produce cost-effective high-efficiency solar cells by controlling the formation of those detrimental GBs.

In the present study, we discuss the recombination activity of asymmetric Σ3 {111} GBs with the <110> tilt axis, whose GB planes are slightly inclined from [111], introduced frequently in high-performance Si ingots. The activity of those asymmetric GBs was high even when their inclination angle was small, while the activity of the symmetric Σ3{111} GBs was negligible. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed that, most of the parastas of the asymmetric GBs were composed of arrays of GB dislocations lying on symmetric Σ3{111} GB segments. Those dislocations were edge-type with the Burgers vector of 1/3<111> 1. Atom probe tomography (APT) revealed that oxygen atoms segregated at the atomic sites under tensile stress above about 2 GPa, which were presumably introduced along the GB plane due to the GB dislocations [1, 2]. Carbon atoms also segregated, while they would locate only nerby the dislocation cores. Small amount of metal precipitates such as iron silicides were occasionally observed on the asymmetric GBs, presumably along the GB dislocations [3, 4]. The correlation between the segregation ability of impurity atoms and the recombination activity will be discussed.


Acknowledgments: This work is partly supported by “Multicrystalline informatics toward establishment of general grain boundary physics & realization of high-quality silicon ingot with ideal microstructures” project in JST/CREST, Grant No. JMPJCR17J1 (2017-2023).

ET02.10.08
P-Type Molecular Monolayer Doping of Silicon for Photovoltaic and Semiconductor Devices
Megan E. Detwiler, Scott Humski, Jenna Doran, Scott Williams and Santosh Kurinec; Rochester Institute of Technology, Rochester, New York, United States.

P-type doping of silicon wafers using molecular monolayer deposition (MLD) will be presented. Our method minimizes additional lattice defects, allows the formation of ultra-shallow junctions, and enables doping of non-planar surfaces. This is an attractive alternative to the industry standards as the process does not induce crystalline damage, unlike ion implantation, and utilizes materials less hazardous than those involved in spin-on diffusion. Monolayers are formed with allylboronic acid pinacol ester (ABAPE) as well as other selected boron-containing molecules. The wafer was then photonicly or thermally treated to create the ultra-shallow junction with optimized sheet resistivities. The doping concentrations and profiles are evaluated using sheet resistance measurements, SIMS, DLTS, and TXRF. MLD temperature and time optimization will be discussed.

ET02.10.09
Effects of Oxidants of Atomic-Layer-Deposited Al2O3/TiO2 Films on Silicon Surface Passivation
Dongchul Suh; Division of Chemical Engineering, Hoseo University, Asan, Korea (the Republic of).

Al2O3 thin films have attracted substantial interest for their use as alternative passivation films of crystalline silicon (c-Si) solar cells because of their improved field-effect and chemical passivation. Among several methods that have been employed for the growth of Al2O3 films, atomic layer deposition (ALD) is very suitable in the sense that it is a self-limiting film growth process based on sequential surface reactions that offers excellent thickness uniformity. The most common ALD process is the deposition of Al2O3 by alternating exposures of trimethyl aluminium (TMA) and H2O, due to the broad ALD process window, but less extensively for passivation. In typical ALD of Al2O3 thin film for surface passivation, O2 plasma has been widely used as an oxygen source due to higher negative charge density, in particular for low deposition temperature. Thermal ALD using reactive O3 has also been introduced because it is easy to purge as well as reactive, enabling batch ALD process for high throughput.
In the formation of Al₂O₃ film, chemical exchange reaction is dominant between TMA and H₂O. However, growth mechanism of ALD Al₂O₃ using O₂ plasma and O₃ is not clearly established but believed that film growth is accompanied by covalent Si-OH group. Different growth mechanisms and high reactivity of the O₂ plasma and O₃ would cause different physical structures, electrical properties, and surface passivation qualities of Al₂O₃. The minimal Al₂O₃ thickness without compromising the passivation properties is 5 nm for plasma ALD Al₂O₃, whereas for thermal ALD, films >10 nm are required. In addition, even though low interface defect density of 10¹⁳ eV⁻¹ cm⁻² is obtained after annealing of Al₂O₃ made from all oxidants, field-effect passivation is dominant for O₂ plasma and O₃-based Al₂O₃ after annealing, but less prominent for H₂O-based Al₂O₃ before and after annealing. The oxidant has a significant influence on the surface passivation mechanism during atomic layer deposition. In this work, we studied the influence of different oxidants and thermal post-deposition treatments for the passivating ALD Al₂O₃ single layers and Al₂O₃/TiO₂ stacks. Al₂O₃ thin films have been deposited on crystalline silicon by atomic layer deposition using various oxygen precursors, such as H₂O and O₃. The electrical characterization of the stack layers has shown that in as-deposited states on Al₂O₃, H₂O-TiO₂ has lower saturation current density (J₀e) than H₂O/O₃-TiO₂ in which both H₂O and O₃ are used as oxidants. Annealing is beneficial for H₂O/O₃-TiO₂ to decrease J₀e, which is analogous to H₂O-Al₂O₃ vs. O₃-Al₂O₃.

ET02.10.10
The Effect of H in the Atomic and Electronic Structure of Amorphous Si and Hydrogenated Amorphous Si Reza Vatan Meidanishahi, Stuart G. Bowden and Stephen M. Goodnick; School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States.

Hydrogen incorporation in the fabrication of amorphous Si (a-Si) plays an important role in improving its electronic and optical properties. An important question is how H interacts with the a-Si atomic network, and consequently affects the electronic properties of a-Si. The common assumption is that the role of H is to passivate the dangling bonds (DBs) of the a-Si structure, which subsequently leads to a reduction in the density of midgap states and localized states within the mobility gap. In the present work, we first employ a combined molecular dynamic (MD) and density functional theory (DFT) method to create stable configurations of a-Si:H, and then analyze the atomic and electronic structure to investigate which structural defects interact with H, and how the electronic structure changes with H addition. We show that in contrast with the simple dangling bond picture, atoms bonded by highly strained bonds (SBs) are most significantly affected by the addition of H, in terms of the lowest energy configuration, with similar if not greater importance to that of dangling bonds in passivating a-Si. We find that H atoms decrease the density of mid-gap states of a-Si by bonding to the Si atoms with SBs. Our results also indicate that Si atoms with SBs creates highly localized orbitals in the mobility gap of a-Si and a-Si:H, and the bonding of H atoms to them can significantly decrease the degree of orbital localization. The results demonstrate the beneficial effects of hydrogenation of a-Si in terms of reducing the overall strain energy of the a-Si network, with commensurate reduction of mid-gap states and orbital localization.

ET02.10.11
Estimation of Voltage-Dependent Photocurrent Factor in Metal-Oxide Based Carrier-Selective Contact Silicon Solar Cell Suren Patwardhan1,2, Sandeep Maurya1 and Balasubramaniam Kavarijetti1; 1Indian Institute of Technology Bombay, Mumbai, India; 2K J Somaiya College of Engineering, Mumbai, India.

Typical heterojunction carrier-selective contact silicon (CSC-Si) solar cell has hole and electron selective layers on same or opposite faces of crystalline Si (c-Si) wafer. This is done by depositing thin films of either doped amorphous silicon (a-Si) or transition metal oxides/alkali metal fluorides. In our work, we fabricated heterojunction CSC-Si cells using molybdenum trioxide (MoO₃) as hole selective layer and titanium dioxide (TiO₂) as electron selective layer – to be called as “Test Cell”. It was made on a 280 μm thick n-type Si wafer (n-Si) of 1-5 Ω cm resistivity. MoO₃ was thermally evaporated and TiO₂ was deposited by atomic layer deposition (ALD). The control cell structure consisted of phosphorous diffused back surface field on n-Si (n/n+ BSF) and then analyzed in place of TiO₂ film. Dark and light current-voltage (I-V) measurements were taken at 1 sun simulated radiation with class AAA solar simulator. We tried to estimate the voltage-dependent photocurrent factor (n) due to TiO₂/Si interface based on our experimental data and available literature on heterojunction solar cells. All of our control cells (25) followed current superposition. On the other hand, all the test cells did not follow current superposition as their dark and light current densities crossed-over each other. They also possessed lower fill factor. The CSC-Si cell has many non-idealities such as voltage dependent photocurrent due to which, the current superposition is generally not obeyed. In our test cells, the light-generated current density (Iₗ) was higher by nearly 40% than the control cells. The average fill factor different (AFF) observed between them was 0.14. By using the equation AFF = (1 - n)ⁿVm max, where Vm max is the ideal voltage that a solar cell can deliver under one sun conditions, and Vm is the maximum power point (MPP), Here, Vm = 0 and Vm = V in voltage at maximum power and open circuit conditions respectively, (n is unity for conventional Si solar cell), n for our control cells is taken to be unity and voltage-independent as they showed current superposition. Average Jₗ for these cells at MPP was 15.95 mA/cm² while for the test cell, it reached 20.45 mA/cm². This ratio comes out to be 0.78, matching with that obtained from the equation above by assuming Jₗ for the control cell to be Jₗc (as n = 1). The cell parameters obtained from I-V measurements showed consistency over different sets of samples prepared. This voltage dependence results in loss of fill factor as it is mainly effective for voltages below Vm. Hence estimation of n is a key factor while designing heterojunction carrier selective contact types of cells.

ET02.10.12
Impurity Distribution at Si/GaAs Heterointerfaces Fabricated by Surface-Activated Bonding Analyzed by Atom Probe Tomography Yasuo Shimizu1, Naoki Ebisawa1, Yutaka Ohno1, Jianbo Liang1, Naotero Shigekawa1, Koji Inoue1 and Yasuyoshi Nagai1; 1Tohoku University, Ibaraki, Japan; 2Tohoku University, Sendai, Japan; 3Osaka City University, Osaka, Japan.

Tandem solar cells composed of Si and III-V materials have attracted considerable attention for next generation photovoltaic system towards 30% efficiency. Surface-activated bonding (SAB) is reported as a method to fabricate tough Si/III-V heterointerfaces, by creating dangling bonds under ion irradiation prior to bonding at room temperature in a high vacuum environment [1]. More recently, intrinsic microstructure of Si/GaAs heterointerface fabricated by SAB was examined by plane-view TEM and cross-sectional STEM [2]. Although the thin foils for TEM specimens were carefully prepared by mechnochanical etching, the TEM inspections revealed that Si/GaAs heterointerface fabricated at room temperature suggests a defective crystalline GaAs layer with less than 1 nm-thick and amorphous Si layer with around 3 nm-thick. For a comprehensive understanding of the electrical property at the SAB interfaces towards complete fabrication processes, distribution analysis of impurities at the SAB interface is required. Here we employ laser-assisted atom probe tomography (APT) for three-dimensional mapping of the impurity distribution, which has been proven useful to examine a specific grain boundary [3]. Quantitative analysis of the impurity concentration at the SAB interfaces by TEM is insufficient due to its lower detection limit than that by APT. In this meeting, we report on the impurity concentration at the SAB interfaces.

In this work, p-Si/n-GaAs heterointerfaces fabricated by SAB method at room temperature were utilized [1]. For comparison, p-Si/n-GaAs heterointerfaces were fabricated under the same SAB condition. For APT specimen preparation, Ga-FIB apparatus equipped with SEM (Helios APT). In this meeting, we report on the impurity concentration at the SAB interfaces.
Nanolab600i, FEI) was used. A local electrode atom probe (LEAP4000XR, CAMECA) equipped with a 355 nm wavelength pulsed laser was employed for APT analysis. Our APT reveals the existence of impurities such as Fe, Ni, and Cu at the Si/GaAs interfaces. These impurities, which may affect the electrical property, were introduced prior to bonding, even though the surface of both Si and GaAs substrates are activated by creating dangling bonds via the removal of native oxide under Ar bombardment in high vacuum. It should be noted that needle-shaped specimens for APT measurements were processed by Ga-FIB. The intermediate layer around SAB interfaces bonded at room temperatures seems to be unstable in an atomistic level under the Ga bombardment. One should take the FIB condition into account for precisely analyzing the impurity distributions. Their distributions found at the homo-interfaces will be also shown in the meeting.

This work was supported in part by JSPS KAKENHI Grant No. 15H05413 and JST/CREST Grant No. JPMJCR17J1.


ET02.10.13
Material Removal Simulation in Sawing Processes of Photovoltaic Silicon
Florian Wallburg1, 2, 3 and Stephan Schoenfelder1, 2; 1Faculty of Mechanical and Energy Engineering, Leipzig University of Applied Sciences, Leipzig, Germany; 2Fraunhofer Center for Silicon Photovoltaics CSP, Halle (Saale), Germany; 3Institute of Mechanics and Fluid Dynamics, TU Bergakademie Freiberg, Freiberg, Germany.

The mass production of wafers, the basic substrates of solar cells, is realised with the multi-wire sawing technology in which silicon wafers are sawn from high-purity silicon bricks. In crystalline photovoltaics the wafering processes and the material costs represent a considerable cost share of about 40% of the complete photovoltaic module. During wire sawing material removal mechanisms resulting from the interaction between hard cutting particles and the silicon surface play an important role regarding the reliability of the processes and products. However, it has not been possible so far to numerically model the mechanically complex process of material removal and subsurface damage as a function of the process parameters. Thus, it is absolutely essential to investigate the direct relationship between removal processes and sawing parameters concerning a reliable production of wafers that are continually getting thinner and thinner.

The investigations made here are focused on the diamond wire sawing process as it has become the major technique to slice bricks into wafers. Due to fixed abrasives the material removal mechanism is significantly defined by grinding processes. In order to analyse the cutting behaviour in fixed diamond wafering single grain scratch experiments were carried out since they can provide better insights into the complex material removal mechanism of grinding processes. By means of several scratch grooves at defined distances, interaction effects and their influence on the fracture process can furthermore be observed. Within this research work this relationship is investigated numerically as well as experimentally.

The basis of the numerical modelling is a pressure-sensitive Drucker-Prager material law with modified caps in the tensile and compressive zone. With the aid of that model phase transformation processes and thus, closely related volumetric changes of the silicon crystal can be predicted which is necessary for crack development. Considering the anisotropic mechanical properties in conjunction with a cleavage-plane illustrating cohesive network it can be shown that different crack systems can be described fundamentally and in interaction with each other – which ultimately leads to the material removal processes. Surface and subsurface damage processes, that are also experimentally investigated, can be examined consequently in more detail. From this, it is feasible in future to derive possibilities for a microstructure-based control of the wire process design, for example, via the cutting geometry shape and arrangement as well as the feed speed. It is well understood that changes to these parameters have a strong impact on the substrate strength and, as a consequence, on the breakage rate. The necessary further developments in substrate production are therefore directly connected to an increase in product quality.

ET02.10.14
Improved Al/n-Si Electron Selective Contact by Intermediate PFN Dipole Layer
Zaira Barquera1, 2, Eloi Ros1, Cristobal Voze, Pablo Ortega1, Isidro Martin1, Ramon Alcubilla1 and Joaquin Pugdollers1; 1University of Politcnica-Catalunya, Barcelona, Spain; 2-CNINVESTAV-I.P.N. Unidad Queretaro, Queretaro, Mexico.

Selective contacts used in crystalline silicon solar cells require both good surface passivation and very good carrier conductivity, i.e. low ohmic contact resistances, to reach high-efficiency solar cells. Traditionally selective contacts are made using high doped regions by thermal or laser process diffusion stages, which are expensive and high-cost energy. Alternatively a cost-effective approach to obtain good selective contacts relies on the use of electron or hole transport layers (ETL and HTL) processed at low temperatures. Carrier selectivity of these transport layers can be beneficial from the incorporation of dipole interlayer between the metal electrode and the ETL (HTL) layers. By using dipole interlayers a better energy band alignment can be achieved by reducing the work function of the electrode. In this work, we report on the use of a polymer dipole (PFN) to improve ohmic contact with n-type crystalline silicon. In particular, the following solar cell configuration Al/PFN/ETL/n-Si/V2O5/ITO/Ag were studied. Poly (9,9-bis(3’-(N,N-dimethylamino) propyl)-2,7-fluorene-alt-2,7-(9,9-dioctyfluorene)(PFN) was used as intermediate dipole. The influence of PFN interlayer dipole was studied on two different electron selective contacts: AlO3/TiO2 deposited by ALD and a-Si:H/a-Si:H deposited by PECVD. Best results were obtained by using a-a-Si:H/a-Si:H configuration, with Voc=0.67 V, Jsc=33.3 mA/cm2, FF=76.6% and a efficiency of 17.2%.

However, using dopant-free electron transport layer (TiO2-based), fabricated solar cells provided a Voc= 0.61 V, Jsc=30.5 mA/cm2, FF=76% and a efficiency of 14% conversion efficiency.

ET02.10.15
High Performance Transparent Electrodes in the Red/Infrared Range Made by Colloidal-Structured Metallic Micro-Grids
Antonio Terrasi1, 2, Giacomo Torrisi1, 2, Olalla Sanchez-Sobrado1, 2, Manuel Joao Mendes3, Hugo Aguas3, Elvira Fortunato3 and Rodrigo Martins3; 1IMM-CNR, Catania, Italy; 2Faculty of Physics and Astronomy, University of Catania, Catania, Italy; 3Cenimat-i3n, Faculdade de Ciencia e tecnologia, Caparica, Portugal.

One of the most promising approaches to produce industrial compatible Transparent Conducting Materials (TCMs) with excellent characteristics is the fabrication of TCO/metal/TCO multilayers. In this work, we report on the electro-optical properties of a particular type of TCO/metal/TCO, in which the intra-layer is a metallic grid instead of a uniform thin film. The grid is obtained by evaporation of Ag through a mask of polystyrene colloidal micro-spheres deposited by the Langmuir-Blodgett method and partially dry-etched in plasma. IZO/Ag grid/IZO with different thicknesses and size of the mesh have been fabricated, exhibiting excellent electrical characteristics and a particularly high optical transmittance in the red and infrared (IR) spectral region, as compared to planar (unstructured) TCM multilayers. This optical behaviour is of primary importance for the new generation of four-terminal mechanically-stacked tandem solar cells, such as the Perovskite-on-Si double junctions or the bi-facial Si solar cells. In the former case the red-IR light must pass through the junctions entering into the Si bottom cell, while in the latter case a consistent amount of red-IR light can be reflected by the ground and collected from the back side of the cell. Numerical simulations were also used to highlight and understand the role of the Ag mesh structure on the electrical properties of the material.
Enhancement at discrete wavelengths: (i) a guided resonance due to the Bragg attenuation length of the photonic crystal and (ii) confinement due to the presence of the a-Si:H layers incorporated into a-Si:H/c-Si and MoOx/a-Si:H/c-Si devices are dead layers that allow no carrier extraction and Jsc of the solar cells is limited by the minority carrier diffusion length and surface recombination velocity from the EQE analysis. Based on the EQE analysis results, the current loss mechanisms in various types of c-Si solar cells will be discussed.

We have developed a quite general device analysis method that allows the direct evaluation of optical and recombination losses in crystalline silicon (c-Si)-based solar cells. By applying this technique, the optical and physical limiting factors of the state-of-the-art solar cells with ~20% efficiencies have been revealed. In the established method, the current loss mechanisms are characterized from the external quantum efficiency (EQE) analysis with very low computational cost. We find that the developed method provides almost perfect fitting to EQE spectra reported for various textured c-Si solar cells, including c-Si heterojunction solar cells, a dopant-free c-Si solar cell with a MoOx layer, and a PERL solar cell. Detailed analyses show that a-Si:H layers behave as a perfect reflector exhibiting nearly 100% reflectivity in the stop bands, and by (ii) generating guided resonant modes at many discrete wavelengths.

We observe that a 3D inverse woodpile photonic crystal enhances the absorption of a thin silicon film by (i) behaving as a perfect reflector exhibiting increased by using a highly efficient back reflector that sends unabsorbed light back into the solar cell. As an interesting candidate for a back reflector, we study here a thin 3D photonic band gap crystal that forbids light within the band gap for all directions and for all polarizations. We consider a dispersive complex refractive index obtained from experiments. We find by extensive finite-element computations of the 3D time-harmonic Maxwell equations that even a very thin silicon 3D photonic band gap crystal slab reflects broadband visible light omnidirectionally for all polarizations. Our results show a nearly 2.6 times enhanced angle- and polarization-averaged absorption between 680 nm and 890 nm compared to a 2400 nm thin silicon film.

We find that the absorption is enhanced by positioning an inverse woodpile back reflector at the back side of a thin silicon film, which will keep the length of the solar cell unchanged and also reduce the mass of the thin film solar cell. For a very thin sub-wavelength absorbing layer with a photonic crystal back reflector, we identify two physical mechanisms that cause the large enhancement at discrete wavelengths: (i) a guided resonance due to the Bragg attenuation length of the photonic crystal and (ii) confinement due to the effective surface defect on the photonic crystal.

Field Effect Passivation of High Aspect Ratio Silicon Surfaces 

A high efficiency silicon solar cell combines high electrical performance with high optical performance. A common method to improve the optical performance is to utilize subwavelength, high aspect ratio structures, resulting in a surface with a graded refractive index and low reflectance throughout the wavelength spectrum. Although such high aspect ratio structures are relatively harder to passivate than conventional structures, reasonably high surface passivation quality have also been achieved by several research groups. However, surface recombination losses remain to be one of the major loss mechanisms for high efficiency silicon solar cells. One of the widespread methods to achieve high passivation performance on undiffused silicon surfaces is to use passivating dielectric layers with high density of fixed dielectric charges. The combination high aspect ratio structures and dielectric charges is commonly expected to result in an enhanced field effect passivation, resulting in less recombination losses in the textured region than what would be expected from the high surface area enhancement. Yet, despite the comprehensive experimental studies, quantitative analyses of the field effect passivation are mostly based on one-dimensional theory utilizing semi-ininitely thick structures. A detailed numerical analysis of the field effect passivation in multi-dimensional structures is still missing.

In this work, we provide numerical and analytical analyses of field effect passivation for two-dimensional and undiffused surface textures coated with dielectrics. We show that when the dielectric charge density is very large, an enhancement in field effect passivation is only very minor at surfaces upon texturing. Then, the local surface recombination rate is very similar for textured and planar surfaces with similar interfaces and surface recombination losses increase in proportion with surface area. For moderately-large dielectric charge densities, on the other hand, we show the effect of the enhanced field effect is much more significant at the surfaces and surface recombination losses increase sub-linearly with surface area. Thus, through proper material and process choice enabling moderate dielectric charge densities and high interface quality, surface recombination losses are expected to decrease further by taking full advantage the field effect.

References


Modeling of Effective Secondary Electron Emission Yield from Black Silicon

Black Silicon, a material with a small reflection over a broad wavelength range and large fraction of absorbed photons, introduces a complex surface architecture based on structured absorbers which can also significantly reduce the total effective emission of photogenerated charges. Although overall reflection of incident photons are reduced, the increased surface area from the sub-micron relief vertical formation introduces inherent losses in the collection of photogenerated charges and from the interference by low-energy, secondary charges emitted from the sides and lowermost region of the structures. An analytical model was developed to calculate both the cumulative secondary charge emission from the vertical surface of the black silicon and the resulting parasitic net loss in photogenerated charges based on parameters including height (above base), lateral size and packing density.

Modeling of Effective Secondary Electron Emission Yield from Black Silicon

Field Effect Passivation of High Aspect Ratio Silicon Surfaces

References


Presenters

Deniz Türkay, Cagil Koroglu, Selcuk Yerci, Center for Solar Energy Research and Applications (GUNAM), Ankara, Turkey; Department of Micro and Nanotechnology, Middle East Technical University, Ankara, Turkey; Department of Electrical Engineering, Stanford University, Serra Mall, California, United States; Department of Electrical and Electronics Engineering, Middle East Technical University, Ankara, Turkey.

A high efficiency silicon solar cell combines high electrical performance with high optical performance. A common method to improve the optical performance is to utilize subwavelength,high aspect ratio structures, resulting in a surface with a graded refractive index and low reflectance throughout the wavelength spectrum. Although such high aspect ratio structures are relatively harder to passivate than conventional structures, reasonably high surface passivation quality have also been achieved by several research groups. However, surface recombination losses remain to be one of the major loss mechanisms for high efficiency silicon solar cells. One of the widespread methods to achieve high passivation performance on undiffused silicon surfaces is to use passivating dielectric layers with high density of fixed dielectric charges. The combination high aspect ratio structures and dielectric charges is commonly expected to result in an enhanced field effect passivation, resulting in less recombination losses in the textured region than what would be expected from the high surface area enhancement. Yet, despite the comprehensive experimental studies, quantitative analyses of the field effect passivation are mostly based on one-dimensional theory utilizing semi-ininitely thick structures. A detailed numerical analysis of the field effect passivation in multi-dimensional structures is still missing.

In this work, we provide numerical and analytical analyses of field effect passivation for two-dimensional and undiffused surface textures coated with dielectrics. We show that when the dielectric charge density is very large, an enhancement in field effect passivation is only very minor at surfaces upon texturing. Then, the local surface recombination rate is very similar for textured and planar surfaces with similar interfaces and surface recombination losses increase in proportion with surface area. For moderately-large dielectric charge densities, on the other hand, we show the effect of the enhanced field effect is much more significant at the surfaces and surface recombination losses increase sub-linearly with surface area. Thus, through proper material and process choice enabling moderate dielectric charge densities and high interface quality, surface recombination losses are expected to decrease further by taking full advantage the field effect.

References

In the numerical simulations performed, a set of conditions were identified, which must be adhered to in order to suppress the effect of secondary charge emissions, and that these conditions are highly dependent on incident angle of photons to the surface coupled with the aspect ratio. In one case, a nearly 90% reduction in the parasitic secondary charge emission was observed for shallow angles, while almost 40% was achieved for normal incidence, compared to the flat surface. Our analysis assumes that secondary charge emission occurs only at the material surface, with no bulk effects. Although the formation of black silicon is becoming increasingly standard, analysis of a limited experimental sample set has shown while some low secondary charge emission yields were achieved from the material surface, many samples demonstrated significantly higher secondary charge emission yields either across the full sample size, or in regions. In this work we present the optimal aspect ratio (including packing density, lateral and vertical size) of the black silicon architecture which demonstrated the greatest suppression of secondary charge emission. This work may offer design improvements to the large scale development of black silicon to photovoltaics with optimised opto-electronic properties based on relatively controllable structural morphology features.

9:45 AM ET02.11.05
Multiscale Design of Disordered Porous Silicon Heterostructures for Infrared Light Control Alessio Palavicini Cruz and Chumin Wang; Instituto de Investigaciones en Materiales, Mexico City, Mexico.

Disordered multilayer heterostructures based on porous silicon are designed using a hybrid quantum-classical approach consisting of a Density Functional Theory calculation of the dielectric function of semiconductor layers. Each layer is modelled with a supercell of silicon atoms forming a crystalline structure where missing atoms characterize the porosity and these periodic pores are saturated with hydrogen and oxygen atoms. The ab-initio calculations are followed by the application of the transfer matrix method to compute the electromagnetic wave propagation along the heterostructure. Optical transmittance of the multilayer designs is verified by synthesizing freestanding samples of porous silicon multilayered films, obtained by means of electrochemical anodization of crystalline silicon wafers which allows us to etch each layer with specific porosities by varying current density, thus producing films with arbitrary dielectric function profiles. These samples are characterized through scanning electron microscope images and its transmittance is measured with a Fourier transform infrared spectrophotometer to compare theoretical and experimental results. Layer sequences with distinct types of disorder are assessed and compared with periodic ones for their performance as photonic structures such as mirrors and filters which could potentially be integrated into electronic circuits or used as elements of all-silicon photonic devices.

10:00 AM BREAK

SESSION ET02.12: ALD Processing for Silicon
Session Chair: Takuya Matsui
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 311

10:30 AM ET02.12.01
Materials for Solar Fuels—Coupling Efficient Water Splitting Catalysts and High-Performance Photovoltaics by Atomic Layer Deposition Paul C. McIntyre; Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Atomic layer deposition (ALD), a cyclic form of chemical vapor deposition that occurs via a series of self-limiting chemisorption reactions, is an increasingly important enabler of nanotechnology and advanced energy technologies. Exciting energy-related applications of ALD that have emerged in recent years include surface passivation of photovoltaics, electrode coating for advanced batteries, and catalyst synthesis. In this presentation, I will summarize recent research in which ALD has been used to promote stable photoelectrolysis of water for solar fuel synthesis. ALD-grown TiO_x layers are found to be particularly effective in inhibiting oxidative corrosion of high-quality semiconductor absorbers and in electronically coupling these semiconductors to efficient catalysts for oxygen evolution, the kinetically-limiting step in water splitting. In addition, ALD is used to alloy TiO_x with transition metal oxides that are themselves good catalysts for water oxidation and that exhibit a high work function. These layers produce high photovoltages in excess of 600 mV in n-Si Schottky MIS junction water splitting photoanodes. Such ALD-grown metal oxide alloys have the potential to become "all-in-one" catalyst/protection/hole-selective contact layers for photoelectrochemical devices. Finally, results obtained from a novel multijunction silicon photoelectrochemical cell incorporating ALD-TiO_2 protection and exhibiting > 10% solar-to-hydrogen efficiency will be described.

11:00 AM ET02.12.02
On the Passivating Contact Performance of Atomic-Layer-Deposited TiO_x for Silicon Solar Cells Jimmy Melskens1, Willem-Jan Berghuis1, Bas van de Loo2, 1, Bart Macco1, Lachlan Black1 and Wilhelmus (Erwin) Kessels1; 1Department of Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 2Temprex, Vaassen, Netherlands.

Transition metal oxides are attractive as full-area passivating contact materials for silicon solar cells due to their transparency which can be combined with good surface passivation and low contact resistivity [Melskens et al., IEEE JPV 2018]. A promising example is titanium oxide (TiO_x) fabricated by atomic layer deposition (ALD), which can form an electron-selective contact to silicon and has enabled solar cell efficiencies above 22% using a full-area rear contact involving a TiO_x/Al stack [Yang et al., SOLMAT 2016; Adv. Mater. 2016; PiP 2017]. However, there are still many open questions with respect to the passivating contact performance of TiO_x that need to be addressed. For example, when trying to exploit the TiO_x transparency by combining it with a transparent conductive oxide (TCO) in a front contact, a high open-circuit voltage has so far not been achieved [Boccard et al., IEEE PVSC 2016], contradicting simulations which indicate that this should be achievable.

We have investigated the TiO_x contact performance in terms of passivation quality and contact resistivity by conducting a systematic study and by making a careful comparison with the existing literature. We found that there are several ways to achieve state-of-the-art passivation performance with typical optimum lifetimes of 1-2 ms. First of all, good passivation results can be obtained using titanium(IV)isopropoxide (TTIP) or tetrakis(dimethylamido)titanium (TDMAT) as ALD Ti precursor, while good results have also been reported for titanium(IV)chloride (TiCl_4) [Cui et al., SOLMAT 2016]. Other experimental parameters, such as the substrate treatment prior to the TiO_x deposition, TiO_x deposition temperature, post-deposition annealing temperature, and film thickness have a much stronger impact on the contact performance. We found that ideally, the film is prepared at low temperature (50-200 °C) on HF-dipped Si such that crystallization is also avoided. The film thickness is particularly critical and we found that approximately 3 nm yields an optimal contact performance (S_{eff,max} = 11.6 cm/s, \rho_c = 10^2 Ωcm^2). This is similar to state-of-the-art results reported in the literature [Titova et al, Energy Proc. 2017].
It appears that there is a large field-effect contribution to the passivation that is induced by a net negative fixed charge, which is surprising for a material that can function as an electron-selective contact. The associated upward band bending in the silicon yields a rectifying contact, in particular when increasing the growth temperature or film thickness too much, although contacting the TiOx layer by either a TCO or Al might play an important role here. An Ohmic contact that provides excellent surface passivation is achievable after annealing when keeping the TiOx film sufficiently thin. This underlines that carefully engineering a thin TiOx layer is key both in improving the passivating contact performance and the understanding of the underlying working principles.

Recent developments have enabled experimental results and suggest ways to enhance the performance and stability of electron-selective TiOx contacts. For developing cost-effective, high-performance and stable electron-selective TiOx contacts and elucidating the effects of the level and polarity of fixed charges for developing cost-effective, high-performance and stable electron-selective TiOx contacts, the level and polarity of fixed charges and the electronic structure of tunnel layers on the performance of TiOx electron-selective contacts has not been evaluated under light illumination [2]. Meanwhile, the performance of electron-selective TiOx contacts strongly depends the thickness and electrical property of a SiOx tunnel layer between a TiOx thin layer and a Si substrate according to previous research [3].

In this study, we have investigated:
1. The performance of electron-selective TiOx contacts fabricated by ALD and e-beam evaporation and oxidation of Ti thin layers.
2. The effects of various metal oxide or nitride tunnel layers on the performance of electron-selective TiOx contacts.
3. The stability of the fabricated electron-selective TiOx contacts under light illumination.

for developing cost-effective, high-performance and stable electron-selective TiOx contacts and elucidating the effects of the level and polarity of fixed charges and the electronic structure of tunnel layers on the performance of TiOx electron-selective contacts. During our presentation, we will discuss the experimental results and suggest ways to enhance the performance and stability of electron-selective TiOx contacts.

References

SESSION ET02.13: Characterization
Session Chair: Hiroyuki Fujiwara
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 311

1:30 PM *ET02.13.01
The Challenges and Opportunities of Bifacial Passivating Contact and SHJ-Perovskite Solar Cells—A Device-to-System Perspective M. Ashraf Alam1, Raghu A. Chaval1 and Stefaan De Wolf2; 1Purdue University, West Lafayette, Indiana, United States; 2King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

A deep physical analysis – coupled with multiprobe characterization – is finally offering insights into the key factors that limit the performance and reliability of passivating contact heterojunction solar cells. These insights have encouraged generalization of the classical technology to multiple new formats: (a) new passivation contacts, (b) exploration of interdigitated back contact (IBC) and tunnel-IBC topologies, (b) optimization for bifacial performance, and (d) determination of performance limits for SHJ-Perovskite bifacial tandem cells, especially in response to location-specific diffused and albedo illumination. In this talk, I will discuss the physics and technology of the classical heterojunction solar cells, as well as the vibrant new research/technology options for the highly promising technology.

References

2:00 PM ET02.13.02
Local Evaluation of Non-Uniform Charge Distribution in Al2O3 Passivation Layers for Silicon Solar Cells Using Super-Higher-Order Scanning Nonlinear Dielectric Microscopy Kento Kakikawa1, Yuji Yamagishi1, Katsuto Tanahashi2, Hidetaka Takato1 and Yassuo Cho1; 1Tohoku University,
One of the factors that lower the efficiency of monocrystalline silicon solar cells is the recombination of carriers at the surface of bulk Si layers [1]. Aluminum oxide (Al₂O₃) is a promising candidate for the passivation of the bulk Si layers of monocrystalline silicon solar cells. It has been reported that the deposition of atomic-layer-deposited (ALD) Al₂O₃ passivation layers on the bulk Si layers effectively reduce the recombination losses. In the case of the passivation of the rear side of p-type passivated-emitter-and-rear-cell (PERC) solar cells, Al₂O₃ is reported to be as effective as thermally-grown SiO₂, which is also regarded as one of the best candidates for the passivation layers. It is widely accepted that the suppression of the carrier recombination by the Al₂O₃ passivation layers is attributed to the reduction of the density of recombination centers and consequently directly reduces the carrier recombination velocity.

The increase of the negative fixed charges is also effective to reduce the carrier recombination velocity because the fixed charges produce a local electric field at the surface and suppresses the diffusion of minority carriers to the recombination centers near the surface. While a number of studies investigate the passivation mechanism by Al₂O₃ from a macroscopic view, a microscopic knowledge on the passivation mechanism, which is also expected to be useful information on the properties of Al₂O₃/Si interfaces, is still missing.

In this study, we investigated the Al₂O₃/Si interfaces using scanning nonlinear dielectric microscopy (SNDM) [2] and super-high-order SNDM (SHO-SNDM) [3]. SNDM is a kind of capacitance microscopy with a sensitivity of as high as 2×10⁻²² F Hz⁻¹/₂ and has been used in the evaluation of a number of dielectric and semiconductor materials. SHO-SNDM is an extended technique of SNDM and is capable of obtaining local C⁻V curves over the sample surface. This ability enables to investigate distribution of local charges at oxide/semiconductor interfaces by analyzing the shift of the change of local C⁻V curves. We demonstrate that these techniques are applicable in the evaluation of non-uniform distribution of charges at Al₂O₃/Si interfaces. We also show that the scale of patterns observed in SNDM and SHO-SNDM images are changed by a post deposition annealing of the Al₂O₃/Si samples. Moreover, the increase of the areal density of negative fixed charges by the post deposition annealing was estimated by analyzing the local C⁻V curves obtained by SHO-SNDM.


For the sustained growth of the silicon PV market, a continued increase in cell efficiency, traditionally characterized at 25 °C, is noted as a prerequisite. However, the energy yield under field conditions, in which the cell temperature can deviate considerably from standard test conditions, is of primary importance. In this work, we analyze the thermal effects that contribute to cell heating, and so energy yield loss, in a variety of silicon solar cell designs. This knowledge will be of consequence for cells and modules deployed in high insolation, high temperature environments which are suitable for PV generation.

To demonstrate the significance of heat generation in silicon solar cells, we first analyze the energy loss in the ideal Shockley-Queisser limit of a single junction solar cell with a bandgap of 1.12 eV operating under the AM1.5 spectrum. Here, only ~34% energy from the solar spectrum is converted to electricity. The remaining energy is lost, either via transmission (19%), re-emission (15%), or thermalization (32%). It is the latter process which is the main source of heating, accounting for an increase in cell temperature above the ambient. In real devices, additional energy losses that decrease the cell efficiency from the theoretical limit contribute further to cell heating, e.g. resistive losses, extrinsic recombination and parasitic absorption.

In the above calculation, sub-gap photons are transmitted through the device. However, recent emissivity measurements on an aluminum back surface field (Al-BSF) cell by Riverola et al. demonstrate that over 80% of this energy is actually absorbed, further contributing to the thermal load of the cell. In this study we assess the absorption of sub-gap photons in the most prominent cell architectures – Al-BSF, passivated emitter and rear cell (PERC), mono- and bi-facial silicon heterojunction (SHJ) – via spectrophotometry measurements over the entire AM1.5 spectral range. We complement these measurements with quantum efficiency, and temperature dependent current-voltage (TD-IV), to assess both the current losses and the cell’s temperature coefficients.

While it is known that the SHJ cell’s temperature coefficient out-performs the Al-BSF and PERC devices, little is known of the relative difference in heat generation between these architectures. Our investigation extends this work by analyzing the thermal contribution from each material in the SHJ device. Spectroscopic ellipsometry is used to characterize each layer over the whole AM1.5 spectrum and optical modeling is utilized to estimate the contribution of each layer to cell heating. To this end, various TCOs, dopant-free contact layers, as well as the conventional a-Si layers are analyzed. These results enable accurate thermal simulation and optimization for minimizing heat generation and maximizing energy yield. Both the mono-facial and bi-facial cases are considered in our analysis.

Dorothee Menzel,
High work function materials such as molybdenum oxide (MoOx) [1] and tungsten oxide (WOx) [2] have recently been investigated as carrier-selective hole contacts for silicon heterojunction solar cells, where they could replace the p-type amorphous silicon layer. They provide a higher optical transparency, and due to their high work function it is expected that they can improve the cell’s fill factor due to a more efficient carrier separation [3]. However, we have found in previous studies [3] that tungsten oxide suffers from a tradeoff of rather poor conductivity for high work function films close stoichiometry, or a strongly reduced work function for more conductive, substoichiometric films. Therefore, we investigate possibilities to improve the electrical properties by combining the high work function and wide band gap of WOx with the good conductivity of indium oxide (InOx) in InWOx alloys. Recently, we have presented investigations of InWOx deposited with different ratios of indium-to-tungsten oxide by thermal evaporation, spanning the full range from pure tungsten oxide to pure indium oxide. Using in-situ (X-ray and UV) photoelectron spectroscopy, optical spectroscopy and surface photo voltage measurements, we found a pronounced decrease of the work function from $\Phi \approx 6.3$ eV for pure WOx down to $\Phi \approx 4.5$ eV for 40% of indium content in the alloy. Within the same tungsten oxide range, this was accompanied by a decrease of the band bending in the crystalline silicon substrate by 200 meV [4].

In the present study, we provide further insight into InWOx materials properties upon annealing of the layers up to 600 °C: We investigate the crystalline structure using X-Ray diffraction and find that InOx is fully crystallized at 250 °C, whereas WOx only starts to crystalize at 550 °C. For an indium content of more than 40 % the mixture remains in the indium oxide structure (also above 550 °C), while the tungsten rich layers show two different structures after crystallization, one at about 25 % InOx content (InOx2W1) and another one for even lower InOx content, which resembles the one of pure tungsten oxide. Concomitantly, optical transmission and reflection measurements show an increase in transmission for indium rich layers with increasing annealing temperature up to 400 °C, while tungsten rich layers showed a lower or even no change in transmission. We explore, whether such high-temperature annealed films yield improved performance when incorporated into devices.

**Passivating contacts as drop-in replacement of partial rear contacts**: for a “lean” process integration, we developed passivating contacts that are manufactured with the thermal processes employed in the PV-industry such as P-diffusion or firing. Boron-doped micro-crystalline silicon oxide layers (µc-SiOx(p)) enabled to withstand long annealing at high temperature (>800°C; >30min) typical of diffusion processes. For a firing-compatible passivating contact, the incorporation of C in nano-crystalline-SiCx(p) ensures a resilience to blistering, that may otherwise occur due to the fast firing (>800°C, >10s). The cell integration of the nc-SiCx(p) in a co-fired process with a Ag-paste contacting a front P-diffused emitter resulted in a conversion efficiency of 22.5% on 2x2 cm².

**Passivating contacts for front and rear contacted c-Si solar cells**: P and B doped silicon carbide layers were developed as electron and hole selective contacts, respectively. Very high degree of surface passivation on p-type planar c-Si is evidenced by $V_{oc}$ values of 735mV and 746mV for the hole and electron contacts, respectively. The performance of the SiCx layers is demonstrated at device level with a simple patterning-free and co-annealed process flow enabling high-level of current extraction and surface passivation with FF=84%, $V_{oc}=727$mV on planar cells, and efficiencies up to 22.6% with front-textured-cells. Highly-transparent P-doped microcrystalline silicon (µc-Si(n)) were developed as alternative to front SiCx(n) layer. High surface passivation with $V_{oc}$ of 729mV and 707mV were reached on planar and textured samples without post-hydrogenation, respectively. In a first attempt, solar cell characteristic include a promising $J_{sc}$ of 39.92mA/cm².

**Monolithic textured perovskite/e-Si tandem solar cells**: the SiCx-based cell architecture with passivating contacts deposited on both sides was used as bottom cell. This bottom cell had a textured front side, on which a fully conformal perovskite top cell was deposited to achieve a steady-state efficiency >24.5% (area ≥1 cm²).

**SYMPOSIUM ET03**

Application of Nanoscale Phenomena and Materials to Practical Electrochemical Energy Storage and Conversion
November 26 - November 30, 2018

**Symposium Organizers**
Weiyang Li, Dartmouth College
Nian Liu, Georgia Institute of Technology
Bin Liu, Nanyang Technological University
Karthish Manthiram, Massachusetts Institute of Technology

* Invited Paper

**SESSION ET03.01: Electrocatalysis Perspectives, Fundamentals and Case Study of Water Splitting**
Session Chairs: Bin Liu and Karthish Manthiram
Monday Morning, November 26, 2018
Hynes, Level 3, Room 302

**8:00 AM ET03.01.01**

**Enhanced Stability and Oxygen Evolution Electrocatatysis Activity of Heterostructured Anodes with Nanoscopically Thin Degenerately Doped Stannate and Titanate Epitaxial Layers**
*John D. Baniecki,1 Catalin Harnagea,2 Dan Ricinschi,2 Takashi Yamazaki,3 Yoshihiko Imanaka,4 and Hiroyuki Aso,4*
1Next Generation Materials Project, Fujitsu Laboratories, Atsugi shi, Japan; 2INRS - Energie Matériaux et Télécommunications, Varennes, Quebec, Canada; 3Innovator and Inventor Development Platform, Tokyo Institute of Technology, Yokohama, Japan; 4Digital Annealing Project, Fujitsu Laboratories Ltd., Atsugi shi, Japan; 5Fujitsu Laboratories Ltd., Atsugi shi, Japan.

Fuel produced from the electrochemical splitting of water can be used to power a wide variety of technologies including information communication technologies infrastructure. The slow kinetics of the oxygen evolution reaction (OER) is one of the performance-limiting factors for hydrogen production through electrolysis. OER catalysts are often unstable in alkaline environments exhibiting deactivation and structural transformation causing a significant challenge for use in photoelectrochemical cells and water electrolyzers. Moreover, in nanoscopically thin catalyst layers, OER activity also decreases due to inefficient charge transfer to the electrolyte-catalyst interface. Epitaxial heterostructures are promising to solve these issues, though recent attempts yielded improved stability only at the expense of greatly reduced OER activity. In this presentation, we elucidate the competing factors for deactivation of LaₙSr₁₋ₙCoO₃ (LSCO) in nanoscopically thin layers supported on conducting perovskite substrates, and demonstrate heterostructured anodes with simultaneously high activity and stability during electrochemical water splitting in alkaline environments (pH = 13).

Epitaxial thin films of Laₙ₋₂SrₓCoO₃, Ba₄₋₃La₃SnO₇, and SrₓLa₄TiO₇ were grown by pulsed laser epitaxy. Interface energetics were characterized using in situ X-ray and ultraviolet photoelectron spectroscopies. Scanning transmission electron microscopy and electron energy loss spectroscopy were used to resolve the atomic structures, and scanning nonlinear dielectric microscopy used to probe the nature of the charge carrier character on the heterostructured catalyst surface. Density functional theory calculations were used to assess the impact of the electronic structure of the heterostructured catalyst layers on the overpotential and OER catalytic activity.

While the LSCO undergoes dramatic structural and electronic changes during electrolysis, including leaching of La and Sr from the film to yield a layer of cobalt oxyhydroxide, the thickness dependence of the OER activity will be revealed to be due to inefficiency of charge carrier transport to active sites. We demonstrate engineering of depletion layers widths and chemical stability using heterostructures comprised of nanoscopically thin epitaxial layers of degenerately doped stannate and titanate perovskite structure oxides to yield low overpotentials ~300 mV at current densities (~10 mA/cm²) relevant for hydrogen production in electrolyzers and photo-electrochemical cells, at hundreds of hours operations in nanoscopically thin active layers. Implications of the results for applications of nanoscopically thin oxide heterostructures for designs of high activity and stable anodes for carbon neutral energy production via the electrochemical splitting of water will be discussed.
Acknowledgement
C.H. would like to thank the Japan Trust program of the National Institute of Information and Communication Technologies (NICT) for funding.

8:15 AM ET03.01.02
OER Catalyst Stability Investigation Using RDE Technique—A Stability Measure or an Artifact? Hanu El-Sayed, Alexandra Weiß, Lorenz Olbrich, Garin Pratomo and Hubert A. Gasteiger; Chair of Technical Electrochemistry, Technical University of Munich, Garching, Germany.

The development of OER catalysts for PEM water electrolysis requires both activity and stability testing methods. The OER catalyst activity can be estimated by using rotating disk electrode (RDE), flow-channel methods, or in an electrolyzer. The evaluation of catalyst stability is realized using accelerated tests as testing over the whole lifetime (5-10 years) under realistic conditions is not practical. 1, 2 A protocol for the OER catalyst stability using RDE was proposed by the ICP group and is now used by other researchers. In this protocol, a constant current is applied in a half-cell configuration and the change in potential is monitored until a sudden increase in potential indicates complete catalyst degradation. It was shown recently that the measured catalyst stability depends on the nature of the electrode substrate onto which the catalyst powder is being supported. Based on this, it was recommended that Au and boron-doped diamond be used as they show better stability of the catalyst under investigation, while glassy carbon and fluorine doped tin oxide electrodes were deemed unsuitable in such stability test. 2

Here we present a careful examination of the use of RDE for investigating OER catalyst stability. Although the increase in potential in an RDE St. T. is thought to be due to catalyst degradation (dissolution), our findings provide a clear evidence that the change in potential is rather due to an experimental artifact. The source of this artifact are nano- and micro-bubbles formed within the pores of the catalyst layer during the OER that cannot be removed by electrode rotation. These bubbles accumulate and block the OER active sites, resulting in a potential increase, which is mistakenly interpreted as catalyst degradation. Our findings indicate that almost no catalyst degradation takes place at the first phase of the St. T., which can last for several hours. In this phase, the bubbles accumulate and block the active sites, resulting in an artificial increase in the potential. The second phase of the St. T. starts once a threshold potential is realized, where a rapid potential increase is observed, due to catalyst dissolution at high potentials. Gas bubbles accumulation is responsible for the increase in potential, and ultimately resulting in the full degradation of the catalyst layer. A proper St. T. using RDE technique should avoid the accumulation of oxygen bubbles, which is currently under investigation and preliminary results will be also presented.


8:30 AM ET03.01.03

Modern societies face the challenge of supplying a continuously increasing energy demand. Intensive research is being conducted all around the globe to ensure that these needs can be satisfied while minimizing carbon emissions and other environmental threats. Electrochemistry holds promise to satisfy this requirement, either by using renewable energy to obtain fuels or store electricity or by converting fuels into electricity. Here catalysis research is pivotal, providing key advances in electrolyzers, fuel cells, and metal-air batteries.

Nature Catalysis, a new journal from the Nature Research group launched in January 2018, provides coverage of top research from the area of electrocatalysis, as well as all other areas of catalysis. Our broad scope, drawing from the work of scientists, engineers and researchers in industry and academia, ensures that published work reaches the widest possible audience. Nature Catalysis brings together researchers from all chemistry and related fields, publishing work on homogeneous, heterogeneous, and biocatalysis, incorporating both fundamental and applied studies that advance our knowledge and inform the development of sustainable industries and processes.

9:00 AM ET03.01.04

The need for a sustainable source of hydrogen has been widely recognized, not just as a potential transportation fueling vehicles, but to limit CO₂ production and fossil fuel consumption from existing industrial processes such as ammonia generation. Currently over 95% of hydrogen is made from fossil fuels through natural gas reforming or coal gasification. However, significant growth has occurred in recent years in water electrolysis research, especially in catalyst research for the hydrogen (HER) and oxygen (OER) evolution reactions. Proton exchange membrane (PEM)-based systems are relatively mature in that the technology has been commercialized, but further research and development can achieve significant impact; for example, order of magnitude reductions in catalyst loading. Anion exchange membranes based systems are still under development, with membrane and ionomer stability in the operating environment being a critical issue. In both the AEM and PEM case, there are complex interactions at the electrode level which need to be considered in catalyst and membrane development. First, the liquid electrolyte environment used for catalyst activity screening, where all of the catalyst surface is accessible to the reactant is often not comparable to a complex, 3-dimensional, ionomer-based electrode. Also, similar to automotive fuel cells, the operating environment is highly important and should be considered when claiming improvements over state of the art. For example, catalyst performance at very low current densities may indicate inherent activity but may not represent capability at typical device operating currents. Similarly, a membrane which cannot operate at differential pressure may be highly limited in utility even if more efficient than current commercial solutions. This talk will describe some of the complex interactions that need to be considered, typical operating requirements, and stages of development where relevant conditions should be introduced.

9:30 AM ET03.01.05

The catalytic oxygen evolution reaction (OER) to extract electrons from water molecules is important for the artificial photosynthesis to generate useful chemicals such as hydrogen and organic compounds [1, 2]. In terms of elements strategy, utilization of abundant element for OER catalysts is remarkably advantageous for future low-cost artificial photosynthetic system. Fe-based OER catalysts, based on the fourth most earth-abundant element, are attractive, but are known to suffer from low OER activity due to limited electrical conductivity and non-ideal electronic structures near the surfaces of these catalysts.
Here, we report a highly crystalline, 10 nm-sized red rust OER catalyst composed of pure β-phase FeOOH(Cl) nanorods (ca. 3 × 13 nm) doped with Ni ions (β-FeOOH(Cl):Ni) [3] and surface-modified with amorphous Ni(OH)2 (a-Ni(OH)2) at a Ni to Fe ratio of 22 at.%, which shows the highest level of performance among Fe-rich oxides and oxyhydroxides. This catalyst can be synthesized by a facile one-pot process at room temperature, and colloidal aqueous solutions of the β-FeOOH(Cl):Ni/a-Ni(OH)2 nanorods are very stable, with no apparent precipitation over a time span of at least one month. Electrochemical measurements for β-FeOOH(Cl):Ni/a-Ni(OH)2 stacked nanorod anodes deposited on carbon paper (CP) were performed in a 3-electrode configuration using a Ag/AgCl reference electrode and a Pt wire counter electrode. The overpotential during the electrochemical OER over the anodes was 170 mV, and an OER current of 10 mA/cm² was obtained at an overpotential of 430 mV(+1.66 V vs. RHE) in 0.1 M KOH (without subtracting the IR drop). It is suggested that the surface modification with the a-Ni(OH)2 lowered the OER overpotential of β-FeOOH(Cl):Ni, resulting in the very high current density at low potential compared with Fe-rich oxide and oxyhydroxide electrodes reported previously. Mössbauer spectroscopy also suggested electronic interaction between Fe and Ni species, which may be crucial evidence for the enhanced activity in the Fe-rich OER system [4]. The present cost-effective Fe-based OER catalysts can be widely applied to construct artificial photosynthetic systems for solar fuel generation by combination with CO2 reduction catalysts.

References

10:00 AM BREAK

10:30 AM *ET03.01.07
Hydroxide Exchange Membrane Electrolyzers (HEMELs) for Hydrogen Production Yushan Yan; University of Delaware, Newark, Delaware, United States.

One of the grand challenges facing humanity today is the development of an alternative energy system that is safe, clean, and sustainable and where combustion of fossil fuels no longer dominates. A distributed renewable electrochemical energy and mobility system (DREEMS) based on cheap renewable electricity could meet this challenge. At the foundation of this new energy system, we have chosen to study a number of electrochemical devices including fuel cells, electrolyzers, and flow batteries. We have been working on the development of hydroxide exchange membrane fuel cell (HEMFCS) and electrolyzers (HEMELs) which can work with nonprecious metal catalysts and inexpensive hydrocarbon polymer membranes. We have developed roadmaps for HEMFCs and HEMELs, the most chemically stable membranes, and the most active nonprecious metal catalysts. We have also studied why hydrogen oxidation and evolution reactions (HOR/HER) are slower in base than in acid for precious metal catalysts. For flow batteries we have developed novel designs, chemistries and cost models e.g., double-membrane aqueous flow batteries with high voltages (i.e., 3 V), single-element-mimic redox pairs, and user friendly physics-based analytical cost models. In this presentation, I will focus on our HEMEL work highlighting a new class of membranes, nonprecious metal catalysts and base/salt-free HEMEL cells for hydrogen production.

11:00 AM *ET03.01.08
Water Oxidation Mechanism of Assembled MnO Nanoparticles Ki Tae Nam; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Water splitting is regarded as a promising step towards environmentally sustainable energy schemes. The oxygen evolution reaction (OER) requires extremely high overpotential due to its slow reaction kinetics. The water oxidizing cluster in photosystem II, in the form of cubical Mn4CaO5 cluster, efficiently catalyzes water oxidation. Inspired by Mn4CaO5 cluster, we previously identified a new crystal structure, Mn3(PO4)2·3H2O, and demonstrated its novel designs, chemistries and cost models e.g., double-membrane aqueous flow batteries with high voltages (i.e., 3 V), single-element-mimic redox pairs, and user friendly physics-based analytical cost models. In this presentation, I will focus on our HEMEL work highlighting a new class of membranes, nonprecious metal catalysts and base/salt-free HEMEL cells for hydrogen production.

11:30 AM ET03.01.09
Ultrathin Pinhole-Free Molecular Wires-Embedded SiO2 Membrane Connecting Incompatible Redox Reactions for Scalable Artificial Photosynthesis Ween Jun Joo, Georgios Katsoukis and Heinz Frei; Lawrence Berkeley National Laboratory, Berkeley, California, United States.
Replacing fossil fuels with renewable resources to meet the global need requires a technology that is scalable to the unprecedented level of several terawatts. Natural photosynthesis is the sole existing technology that produces energy dense chemicals on the terawatt scale (~100 TW). Its key design feature is the closed cycle of H₂O oxidation and formation of the primary reduction products on the shortest possible length scale, the nanometer scale, while separating the incompatible redox environments by an ultrathin membrane. This offers the advantage of minimizing efficiency-degrading mass transport processes and unwanted side reactions.

To incorporate the key feature into artificial photosystems, we assembled ultrathin (2 nm), pinhole-free, molecular wires-embedded SiO₂ membrane on planar and nanotube constructs. This membrane system spatially separates the H₂O oxidation CO₂ reduction, but enables (photo-)electrochemical communication between the incompatible redox reactions by transmitting protons and electrons in a precisely controlled manner, while preventing O₂ transport causing unwanted reverse reactions. This unique mass-transport behavior on planar and nanotube configurations was systematically studied via cyclic voltammetry, electrochemical impedance spectroscopy, and visible light-sensitized short circuit current experiments. The embedded molecular wires’ integrity before and after the mass-transport process was confirmed by time-resolved optical spectroscopy and grazing angle ATR-FT-IR or IRRAS characterization.

11:45 AM ET03.01.10
Interesting Proton Conduction Environment within Thin Films of Fluorocarbon based Ionomers with Single or Multi-Acid Side Chains Shadipoto K. Dinhara. University of Nebraska--Lincoln, Lincoln, Nebraska, United States.

Polymer-catalyst interfaces control the energy efficiency of many energy conversion and storage devices. The interfacial polymer layers are very thin (typically less than one micron thick). Many interesting structural, mechanical and transport properties in such thin ion containing polymer (ionomer) layers evolve as a result of complex multimodal interfacial interactions, unusual hydration behavior and confinement. Especially ion conductivity at the interface can be drastically different from that in the bulk membranes and the route to this poor ion conduction behavior is not well-understood. It is thus highly needed to systematically study how the ion conduction environment and water uptake change with the change in ionomer structure and film thickness. In this work, three potential fluorocarbon based hydrogen fuel cell ionomers (Nafion, 3M PFIA, 3M PFSA) having single/multiple acids at side chain were studied in sub-micron thick films. All three ionomers have fluorocarbon (PTFE) backbones. The difference between Nafion and 3M PFSA is in the side chain structure, but both has single acid at the side chains. On the other hand, 3M PFIA has bis(sulfonfyl)imide group in addition to perfluorosulfonic acid which makes the polymer more acidic. By tracking the fluorescence response of photoacid dye HPTS incorporated within hydrated ionomer thin films, very interesting trends were obtained regarding the extent of proton transfer. The results, when combined with the information on nanoscale structure and water sorption, clearly indicated that there are many factors controlling the proton conduction behavior in thin ionomer films, in addition to water uptake.

SESSION ET03.02: Battery Fundamentals, Characterization and Modeling
Session Chairs: Weiyang Li and Nian Liu
Monday Afternoon, November 26, 2018
Hyne, Level 3, Room 302

2:00 PM ET03.02.02

Nanoscale transport and materials are critical to electrochemical energy storage, such as power density, cycling life and safety. In this talk, I will present two examples on advanced tools and fabrication to understand nanoscale transport phenomena and designing of nanoscale materials. The first one is based on an emerging Stimulated Raman Scattering Microscopy, which is three orders of magnitude faster than traditional Raman microscopy. Therefore it can clearly track ion transport in electrolyte together with lithium dendrite, to illustrate their correlations. A positive feedback mechanism has been visualized, which guide methods to suppress lithium dendrite. The second example is through designing nanoscale modification of interfaces between battery electrodes and solid electrolyte. Therefore, the stability between electrodes and electrolyte and the cycling life of corresponding full cells are significantly improved.

2:30 PM ET03.02.03

The design/discovery of layered materials for applicability in next-generation battery technologies requires a fundamental understanding of the links between the atomic-scale structure, chemistry and the mechanisms and energetics of intercalation and de-intercalation reactions, and a consideration of other solid-state reactions that might compete. The goal of our research is to design/discover layered material microstructures as alternatives to graphite using an innovative combination of atomic-scale modeling, experimental in-situ characterization of the microstructural evolution during (de)intercalation reactions. Density functional theory (DFT) simulations are carried out to investigate the structural accommodation of the layered material during insertion and exertion of the intercalating species (energy barriers, volumetric expansion, and phase transformations). The structural stability of the 2H and 1T phases of MoS₂ during lithiation suggests that a phase transformation of the 2H phase of MoS₂ to the 1T phase may occur when MoS₂ is reacted with Li; the computational study allows different dosages of Lithium ion to be assessed with the aim of testing these the validity of these models using in-situ characterization of the solid-state reactions between Li and MoS₂ in the transmission electron microscope (TEM). The mechanisms of strain relaxation and the energetics of Li intercalation-induced phase transformations in MoS₂ at the atomic scales will be presented. This work is supported by NSF grant No. 1820565.

2:45 PM ET03.02.04
Mechanistic Understanding of Lithiation in MoS₂ by Atomic Scale Characterization Shalini Tripathi2, Matthew T. Janish2, William Moyer Mook1, Katherine L. Jungjohann1, Avinash M. Dongare3, Arthur Dobley3 and C B. Carter1, 4; 1Center for Integrated Nanotechnologies (CINT), Sandia National
Understanding the structure and phase changes associated with two-dimensional (2D) layered transition metal dichalcogenides (TMDs) is critical in optimizing performance in lithium-ion batteries. The large interlayer spacing in MoS$_2$ (≈ 0.65 nm) accommodates species such as alkali metal ions (Li$^+$, Na$^+$, K$^+$) during intercalation. Intercalation is reported to change the electronic structure of the host molecule, resulting in variations in their electrical and optical properties. In this work, we examine the solid-state reactions between Li and MoS$_2$. Li$^+$ ions can be inserted into the vdW gap; the reaction is still unclear. Plan-view imaging has been extensively used, however, it is essential to visualize the process with the electron beam being parallel to the basal planes of the layer material to understand the reaction process. Lattice-fringe images have been discussed for several systems but relying on microtoming or simply using curved thin layers, the orientation of the specimen was less than ideally controlled. Here, TEM specimens are made using FIB, and oriented for detailed study of the intercalation process. This study of TMDs uses a Tecnai F30 and a Cs-image-corrected Titan equipped with a direct electron detector camera, K2. This camera has two major advantages: the electron dose can be minimized and quick changes during reactions are recorded; both instruments have EELS and XEDS capabilities. DFT calculations are used to probe the structure and bonding changes during these reactions.

Volumetric expansion, energy barriers, phase transformations and the role of doping, defects and interfaces can be modeled. The dynamics of the structural response are modeled using ab initio MD simulations. Electrochemical aspects can be monitored in situ in real-time and at atomic scale to provide understanding of lithium-ion storage mechanisms in these solid-state reactions and thus to test the modeling-based results.

In plan-view specimen, variations normal to the basal plane are not seen. Defects associated with the reactions were monitored real-time. As the reaction between MoS$_2$ and Li proceeds, white-line defects were observed under high-resolution imaging by TEM. Lower-magnification images show that the understanding of lithium-ion storage mechanisms in these solid-state reactions can be substantially improved by using nanoscale characterization techniques to elucidate the structural and chemical changes occurring in Li ion battery cathodes containing LiV$_3$O$_8$ thin film with high density of states and electronic occupation) at the electrode/electrolyte interface. We have developed a back-gated electrode structure that utilizes electrostatic charging (induced by a gate bias) to control electrochemical kinetics on ultrathin or 2D materials (5-nm-thick ZnO, monolayer MoS$_2$, and graphene). Such back-gated electrodes are fabricated with nanometer-thick semiconductors on SiO$_2$-degenerated Si substrates, analogous to the metal–oxide–semiconductor stack in the CMOS technology. Due to the extreme thinness of the electrode materials, the alignment of electronic bands as well as the electronic occupation, at the electrode/electrolyte interface, can be dramatically altered by the gate-induced charge carriers. Thus, real-time, continuous and efficient modulation of reaction kinetics can be achieved on 2D materials by varying the gate bias.

In this presentation, we will use back-gated monolayer MoS$_2$ as an example to demonstrate how the applied gate bias affects the kinetics of heterogeneous charge transfer and surface binding processes. Specifically, the standard charge transfer rate constant between MoS$_2$ and ferrocene/ferrocnium redox couple can be tuned by over two orders of magnitude and the catalytic overpotential of hydrogen evolution reaction on 2H-MoS$_2$ can be reduced by more than 150 mV. Overall, the approach introduced here is generally applicable to investigation and optimization of interfacial electrochemical phenomena in a wide range of electrochemical systems. With the ability to control the band alignment and electronic occupation independent of the electrode potential, the back-gated 2D electrodes will provide new insights to rational design of electrode materials.

References:

different initial microstructures obtained by thermal annealing. Bright-Field TEM and corresponding SIMS images (e.g. Li’ and V’ maps) from uncycled and cycled samples were obtained to investigate the underlying materials phenomena (such as vanadium dissolution) in the cycled cathodes and to correlate the nanoscale processes with macroscopic electrochemical performance [5].

References:
[5] Acknowledgments: LVO cathode samples are synthesized as part of the Center for Mesoscale Transport Properties, an Energy Frontier Research Center supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under award #DE-SC0012673.

4:00 PM ET03.02.07 Simulation of Charge Transfer Reactions at Graphite and Electrolyte Solution Interfaces with Density Functional and Implicit Solvation Theory Jun Haruyama and Minoru Otani; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Development of a stable energy-storage device is a fundamental approach to solve energy-related issues. Lithium-ion batteries (LIBs) are one of the most promising candidates because of their high energy density and long cycle life. From electrochemical impedance spectroscopic measurements, the cell resistance of conventional LIB is dominated by charge transfer resistance at electrode/electrolyte interfaces. [1,2] Therefore, we investigate the charge transfer process, i.e. Li insertion/desorption process, at the interface between a graphite anode and 1 M LiPF6 EC electrolyte. The density functional theory (DFT) with effective medium screening (ESM) method [3] combined with the reference interaction site model (RISM), called ESM-RISM, is employed to simulate the Li insertion/desorption process. [4] In this method, the graphite surface (LiC6slab and additional Li+) and liquid solution (1 M LiPF6 EC) are represented as quantum mechanical and implicit classical solution, respectively. The energy landscapes of reaction are revealed under constant electron chemical potential conditions at the interface. Across the transition state where the Li forms a half-solution shell, the reacting Li inside the electrode changes to a full solution structure in the solution accompanied by electron transfer. The activation energies at the equilibrium potentials of the charge transfer reaction are approximately 0.6 eV, [5] which is consistent with the electrochemical impedance spectroscopy measurements. In the presentation, we explain the details of the ESM-RISM simulation and introduce the energy profiles of the Li insertion/desorption path at the LiC6/EC LiPF6 interface.


4:15 PM ET03.02.08 Measurement of Mechanical Properties and Assessment of Mechanical Degradation of Solid Electrolyte Interphase (SEI) Formed with Carbonate-Based Electrolytes Insun Yoon; Brown University, Providence, Rhode Island, United States.

Rapidly increasing demand for low-cost, high energy density energy storage motivates researchers to develop advanced and reliable anode materials. Lithium alloying anodes such as Si, Sn, or Ge has three to ten times of charge capacity compared to the traditional graphite electrodes, and thus gathered enormous research interest. One of the major challenges associated with the lithium alloying anodes originates from de/lithiation-induced large volume change (~300%). Such volume change applies excessive cyclic strain on solid electrolyte interphase (SEI) to cause its mechanical failure and continued breakdown of SEI, and thus affects the reversibility of the Li alloying/demallloying reactions. Therefore, we investigate the mechanical properties of SEI and correlate them with the cycling performance of Si electrodes. Several electrolyte additives such as fluoroethylene carbonate (FEC) or vinylene carbonate (VC) have been investigated and demonstrated to improve cyclic performance of Si electrodes. Furthermore, we use molecular dynamics (AIMD) simulations to understand the deformation mechanism of SEI. With this background, we have developed an experimental approach to characterize elastic modulus, yield stress, inelastic deformation behavior, and crack density evolution of SEI formed with carbonate-based electrolytes. An SEI (~100nm) is prepared by lithium thin film - electrolyte (1.2M LiPF6 in ethylene carbonate) reactions on a rectangular free-standing polydimethylsiloxane (PDMS) membrane (~300 - 400nm in thickness). The prepared sample is subjected to bulge testing in an inert environment; various level of controlled pressure is applied to the SE/PDMS membrane and the corresponding deflection is measured by the atomic force microscopy (AFM). The plane strain elastic modulus and the yield stress of SEI are evaluated from the pressure-deflection relationship from the bulge testing. Moreover, a careful observation of SEI surface topography yields the evolution of crack density as a function of applied strain. The experiment is repeated using FEC added electrolytes to investigate the influence of the FEC additive on mechanical stability of SEI.

4:30 PM ET03.02.09 Developing an Understanding of Solid-Electrolyte Interphase Formation in Multivalent Ion Batteries Using First Principles Calculations Joshua Young and Manuel Smeu; Physics, Binghamton University, Binghamton, New York, United States.

Multivalent ion batteries (MIVB), or those utilizing Mg, Ca, Zn, and Al, are garnering increasing attention as alternatives to Li-ion batteries in applications where portability is not an issue owing to their high energy density, cost efficiency, and abundance. However, the lack of suitable electrolytes allowing for the reversible plating of metallic anodes has limited the development of MIVBs, especially those involving Ca. This is primarily due to the fact that the solid-electrolyte interphase (SEI), a passivating layer which forms between the electrolyte and anode, often does not allow for the migration of ions in the reversible plating of metallic anodes. [1,2] In this work, we develop an understanding of the SEI in MIVB systems using a computational approach combining density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations. [3] We first identify the principle components of the SEI by studying the decomposition of the solvents and salts comprising various electrolytes on Li, Ca, and Al surfaces using AIMD. Following this, we identify electrolytes which can be used with a Ca metal anode by investigating the diffusion of Ca ions through the likely inorganic compounds produced using DFT. Finally, we investigate the decomposition of these electrolytes in the presence of external electric fields to more fully understand these reactions in electrochemical systems. We anticipate the promising new electrolytes proposed in this work will help guide experimentalists in the development of rechargeable MIVBs.

J.Y. and M.S. were supported by funds from Binghamton University. DFT calculations were performed on the Spiedie cluster at Binghamton University, as well as the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by NSF Grant No. ACI-1053575, under allocations TG-DMR170127 and TG-DMR180009.

Room temperature ionic liquids (ILs) have recently emerged as highly promising electrolytes for a wide range of emerging energy technologies, including next-generation supercapacitors and ion-batteries, due to their high thermal stability, ionic conductivity and wide electrochemical windows. The chemical and structural diversity of ILs creates a vast design space that could be exploited to optimize the device performance and stability. However, many mechanistic details remain enigmatic, including the fundamental nature of the cation-anion interactions and their relevance in determining structural and electronic properties of the liquids. Having this information for the bulk liquid is a prerequisite for eventually deciphering the complexity the arises at nanostructured electrode interfaces, which are ubiquitous among energy storage devices. In this presentation, we combine high-level first-principles simulations and synchrotron X-ray characterization experiments to unravel the key structural, chemical and electronic properties of several archetypal ILs comprised of imidazolium-based ILs. In particular, we utilize extensive ab initio molecular dynamics simulations to probe the local density distribution and medium-range order of the ILs, which can be directly compared and validated by X-ray scattering measurements. Soft and tender X-ray absorption spectroscopy at the K-edge of fluorine, phosphorus, and sulfur contained on the anion also complements the chemical and electronic picture from the simulations. Our integrated theoretical and experimental approach relates these structural and chemical signatures with the intrinsic cation-anion interactions, by considering ILs with anions having significant differences in the molecular geometry, chemical composition, and charge distribution.

This work was supported by the U.S. Department of Energy at the Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
maximize the productive use of electric vehicles, it is very essential to meet up with the intermittent energy needs and variable power demands. Following the intermittent nature of energy from solar and wind, energy storage devices became the need of the hour. Therefore, the excellent catalytic activity and durability of N,P-HCNTs make them potential materials for replacing noble catalysts in both ORR and OER.

**Reference**


**ET03.03.04**

**Ionic Transports in Liquid Under Confinement**

**Yuqings Guan** and Jin Suntivich; Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

This presentation presents an ionic-transport measurement in aqueous electrolytes that are confined within the cavities of nanomeshes. Ionic transport plays an important role in electrochemical energy storage devices. Many studies have reported high ionic transport in nanomeshes, for example, in porous carbon and in metal-organic framework materials. However, very little is understood how the confinements affect ionic transport. In this presentation, we present our measurement of the ionic transport through different nanomeshes with controllable pore sizes and surface charges. We use these experimental measurements to establish the ionic transport ability and the role of electrical-double layer on ionic diffusions. These results provide insights into the elusive role of the electrical-double layer on confined ionic diffusions and a design strategy of future nanomeshes for energy storage devices.

**ET03.03.05**

**Graphene Oxide Enhanced Performance and Durability of Proton Exchange Membrane Fuel Cells (PEMFCs)**

**Likun Wang**, Yuchen Zhou, Stoyan Bliznakov, Miriam Raffalovich, Danielle Kelly, Audrey Shin and Guan Hao Chen; Stony Brook University, Stony Brook, New York, United States; 2Friends Academy, Locust Valley, New York, United States; 3Plainview Old-Bethpage JFK High School, Plainview, New York, United States; 4St. Georges High School, New York, New York, United States.

Proton exchange membrane fuel cells (PEMFCs) has attracted tremendous attentions as energy conversion device due to its high energy density, low operating temperature and environmentally friendly emission. Numerous efforts have been made to explore efficient catalysts for the reaction when GO is deposited on the Nafion membrane or into the catalysts layer. The maximum power output of the cell under H2/air atmosphere showed an enhancement over 20%. More importantly, the durability of PEMFCs was significantly improved by the GO introduction. 26.1% of maximum power degradation was observed for the cell without GO while only half amount decrease obtained for the cell with GO after 30K cycles of accelerated stress test based on DOE2020 protocol. Nearly 100% enhancement for the durability of PEMFCs can be attributed to the prohibition of H2O2 production. The promising durability promotion effect induced from low-cost GO involvement will help to accelerate the large-scale commercialization of PEMFCs.

**ET03.03.06**

**Effect of the Oxygen Vacancies and Concentration of Ce3+ Valence State on Enhanced Electrochemical Performance of One Step Solvothermally Synthesized CeO2 Nanoparticles**

**Hyeyeong-Heo Park**, Manjeet Kumar, Joondong Kim and Ju-Hyung Yun; 1Incheon National University, Incheon, Korea (the Republic of); 2Korea Advanced Nano Fab Center (KANC), Suwon, Korea (the Republic of).

Environment friendly, low-cost and high performance energy storage systems have been progressively required because of the global warming which has become an imperative and unavoidable factor. The increasing environmental setbacks along with the depletion of fossil fuels necessitate the transition of solar photovoltaic and wind power as a source of electrical energy in practice[1, 2]. But, the unavailability of power from photovoltaic systems during night time and fluctuation in wind speed of the deliverable power have directed the researchers towards the usage of energy storage devices. Moreover, to maximize the productive use of electric vehicles, it is very essential to meet up with the intermittent energy needs and variable power demands. Correspondingly, high power delivery and long cycling stability is some of the most important criterion to be fulfilled by an energy storage device.[3]. To accomplish these demands, devices which could entail huge initial power to start up and show capability of charging with quicker rate are prerequisite. Therefore, supercapacitors have been explored as an upgraded energy storage devices to replace batteries and conventional capacitors with superior features[4].

In this work, different sized CeO2 nanoparticles were synthesized using one step low-cost solvothermal method with various reaction time. Defect states were induced due to the reduction of Ce4+ into Ce3+ valence state. X-ray photoelectron spectroscopy results recommend that Ce3+ valence states and defects in the form of oxygen vacancies be present on the surface of CeO2 nanoparticles. Such availability of oxygen vacancies provided high specific capacitance up to 142.5 Fg-1 at a current density of 0.25 Ag-1 in three electrode system using 1 M Na2SO4 electrolyte. There is an increase in faradaic reactions taken place on the surface which is attributed to the high surface area, more oxygen vacancies, and increased diffusion rate. The highest energy density is obtained to be ~12.68 Wh/kg, and the stability result confirmed that the capacitance retention is ~75 % after 1000 cycles of operation indicating that well optimized CeO2 is a potential candidate as electrode materials for supercapacitor applications due to their fast mutation between Ce4+ to Ce3+ oxidation state.

**Reference**


**ET03.03.07**

**Heteroepitaxially Activated Durable [111]_{fcc}–Faceted Nickel Nanocrystals by Suppressing NiOOH Exfoliation during the Oxygen Evolution Reaction in an Alkaline Electrolyte**

**Byeongyoon Kim**, Aram Oh, Minral K. Kabirazz, Sang-II Choi and Kwangyeeol Lee; 1Korea University, Seoul, Korea (the Republic of); 2Kyungpook National University, Seoul, Korea (the Republic of).

One of the best catalyst for alkaline OER anode, nickel exist in various form of nickel oxide, hydroxide and oxyhydroxide in alkaline aqueous solution. Particularly facet-controlled surface of β-NiOOH is expected to have the best heterocatalytic performance. However, due to the great stability of layered structure of hcp crystal, Ni(OH)2 or NiOOH naturally prefer sheet-shape which is fully coordinated but difficult to form uncoordinated facet enclosure. Moreover, β-NiOOH inevitably oxidize to γ-NiOOH in alkaline OER condition. Herein, we demonstrate [111]_{fcc} facet controlled Ni nanoparticles and characteristic heteroepitaxy between [111]_{hcp} facet of rock salt NiO and layered Ni(OH)2/NiOOH during the sequential oxidation in alkaline OER. As the result, (100)_{hcp} faceted β-NiOOH surface formed on Ni octahedral nanoparticles that have resistance further oxidation. β-NiOOH/Ni octahedral
nanoparticles showed excellent electrocatalytic activity and stability for OER in an alkaline electrolyte, requiring an overpotential of 0.32 V at 10 mA cm\(^{-2}\) after 2 h of chronopotentiometric stability test. The facet-dependent heteroepitaxy of ionic crystals is responsible for the excellent electrocatalytic activity and stability.

ET03.03.08
Size-Controllable Synthesis of \(\text{Pd}_4\text{Ru}_4\) Solid-Solution NPs for Catalytic Applications

Dongshuang Wu, Kohei Kusada and Hiroshi Kitagawa; Graduate School of Science, Kyoto University, Kyoto-shi, Japan.

Pd and Ru, which are two neighbouring elements of Rh, are highly attractive for their wide applications in catalysis and energy area. However, the two metals are immiscible at the atomic level in bulk state even at the melting point of Pd. Very recently, our group synthesized PdRu non-equilibrium solid-solution nanoalloys over the whole composition range and demonstrated their applications in CO oxidation, formic acid electrooxidation and Suzuki–Miyaura cross-coupling reaction.[1-3] In view of both fundamental research and practical application, the influence of particle size on catalytic performance should be an interesting and significant subject. The surface area, electronic state and adsorption/desorption energy, which are important factors in catalysis, will change with size, especially in the sub-10 nm size range. Since Pd and Ru are immiscible metals in their bulk form, it is difficult to simultaneously control the metal composition and size of the PdRu solid-solution nanoparticles. To date, there is no report on the size effect in PdRu solid-solution system. Herein, fixing the Pd/Ru molar ratio at 1:1, we successfully synthesized \(\text{Pd}_4\text{Ru}_4\) solid-solution nanoparticles from 2 to 15 nm with narrow size distribution via a simple one-pot reaction. The relationship between size and catalytic properties is discussed.

ET03.03.09
Construction of Ternary Transition Metal Selenides Nanosheets for High-Performance Bifunctional Water Splitting

Jing Yu; Harbin Engineering University, Harbin, China.

Water electrolysis by splitting \(\text{H}_2\text{O}\) into hydrogen and oxygen is currently recognized as an attractive approach for developing regenerative hydrogen energy, which could in turn help to resolve the energy crisis and environmental pollution caused by overreliance on fossil fuels. The exploration of efficient electrocatalysts is highly desirable for reducing the energy barrier and accelerating the reaction kinetic. Transition metal selenides have drawn intense attention because of their outstanding electrocatalytic activity. However, the performance is not comparable favorably with costly noble-metal-based catalysts. Adding another metal element to binary selenides provides the opportunity to tune their crystalline and electronic structures and thus their electrocatalytic properties. In this work, we developed ternary NiCoSe\(_2\) nanosheets configuration via an electrodeposition technique. The loose accumulation of crimped nanosheets on carbon cloth creates a porous structure with large surface area, which could provide abundant active sites for electrocatalysis and good diffusion of charge and electrolyte. The interaction between bimetallic atoms leads to significant enhancement of the catalytic performance. Density functional theory (DFT) calculation reveals the intrinsically metallic behaviour of NiCoSe\(_2\), confirming good electronic conductivity. The prepared NiCoSe\(_2\) exhibited superior and durable activities toward hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), as well as full water splitting. The ternary metal selenides with tunable compositions provide a novel platform to develop low-cost and high-active catalysts for clean energy strategy.

ET03.03.10
Modifying Commercial Carbon with Trace Amounts of ZIF to Prepare Derivatives with Superior ORR Activities

Bing Ni, Chen Ouyang and Xun Wang; Tsinghua University, Beijing, China.

Efficient electro-catalysts are highly demanded in many energy conversion devices, such as proton exchange membrane fuel cell, rechargeable batteries, water splitting devices, etc. Electrocatalytic process can be seen in this way: electrons are transported to (or removed from) the catalysts under external voltage, then catalysts deliver electrons to (or attract from) the surface active sites and then to the reactants, the reactants receive (or donate) electrons and proceed the catalytic reactions. Thus the methods to enhance electrochemical activities mainly rely on four aspects: (1) enhancing the conductivity of catalysts; (2) increasing the intrinsic activities of active centers; (3) augmenting the amount or concentration of active centers; (4) optimizing the mass transfer during the reaction. Tuning one or multiple factors in these four could help to enhance the electrocatalytic activities. On the other hand, reducing costs while maintaining high activity and stability of the catalysts is also vital to applications. Guiding by the aforementioned aspects, we combined the virtue of zeolitic imidazolate frameworks (ZIFs, potential active centers) and commercial carbon black (CB, good conductor) to realize efficient and cheap oxygen reduction reaction (ORR) catalysts in alkaline solution.[1-3]. The modified CB (MBC) was prepared by sequentially soaking the CB in cations (Co\(^{2+}\) and/or Zn\(^{2+}\)) and ligand (2-methylimidazole) solutions, which was followed by a pyrolysis process. The sequential soaking process enabled a thin-layer coating of ZIF on the CB, and the amounts of ZIF were trace which could contribute to the great reduction of the costs (the total costs of the catalysts were less than 70RMB/kg). After the pyrolysis process, the obtained MBC showed large diffusion-limited current density (6.18mA/cm\(^2\)), half-wave potential (0.858V vs RHE), and no obvious decay after 20000 cyclic voltammetry cycles. The MBC also displayed high resistance to methanol poison. The combined experimental and theoretical studies illustrated that the C-O bond formed on the CB surface by the modification process was the main reason for the high activity, but not single-atom implanted carbon structures or metal oxides. The pristine CB surface had a large content of C=C double bonds or sp\(^2\) carbon, while the MBC had a larger content of C-O bonds which are more active in ORR, and the activity increased with the increasing content of C-O bonds. On the other hand, when this kind of materials is in acidic conditions, the C-O active sites would be protonated and lose activity.


ET03.03.11
Zr-Doped TiO\(_2\) Nanotubes with Rich Ti\(^{4+}\) Species for Electrochemical N\(_2\) Fixation

Na Cao and Gengfeng Zheng; Fudan University, Shanghai, China.

The production of ammonia (NH\(_3\)) by the well-known Haber-Bosch process from \(\text{N}_2\) and \(\text{H}_2\) has marked over a century success for providing > 80% nitrogen source for fertilizer and an alternative energy carrier with large energy density. In spite of the natural abundance of \(\text{N}_2\), the high bond energy of N\(_2\) (940.95 kJ mol\(^{-1}\)) prevents it as a reactive form and thus requires a significant amount of the global energy cost annually. In addition, the use of fossil fuels to produce \(\text{H}_2\) reactant also leads to a significant level of \(\text{CO}_2\) release. The electrochemical \(\text{N}_2\) reduction reaction (NRR) can be processed in ambient conditions and use inexpensive aqueous electrolytes as proton source, and thus is regarded as a promising approach. However, the development of high
selective electrocatalysts for simultaneously producing NH₃, rather than the competing hydrogen evolution reaction (HER), is still challenging. Herein, combined with activity of Ti³⁺ species of titanium oxides, and more strong N-adsatoms binding strength than H-adsatoms on the surface of Ti and Zr, we developed a type of hybrid oxide Zr-doped TiO₂ nanotubes via a facile wet-chemical process towards a NRR catalyst. N₂ and water were used as nitrogen and protons sources, respectively. The replacement of Ti⁴⁺ with larger diameter of Zr⁴⁺ leads to the formation of adjacent oxygen vacancies and the increase of Ti³⁺ concentration. In contrast, further increase of the dopant size (such as Ce⁴⁺) is not capable of incorporating dopants into the original TiO₂ lattice structure. As a result, the Zr-doped TiO₂ NTs exhibited excellent catalytic ammonia synthesis performances (NH₃ yield: 9.07 µg h⁻¹ cm⁻² cat., Faradaic efficiency: 4.83%) at -0.45 V vs. reversible hydrogen electrode (RHE) in 0.1 M KOH electrolyte at ambient conditions. This size-dependent doping strategy suggests an attractive way to tune the active catalytic centers of electrocatalysts.

ET03.03.12
The Gate-Opening Behavior of Water Insertion Toward Heterogeneous Catalysis
Chia-Shuo Hsu; Chemistry, National Taiwan University, Taipei, Taiwan.

For heterogeneous catalyst, the behavior of interphase between liquid and solid is the key for the activity of catalysis. The phase-transition step have been reported as the necessary one to improve the reaction. However, this behavior happened represent the catalyst have the interaction not only on the surface. The water should insert several layers of the structure. For the insertion undergoing, the structure need to open first and let the space enough to have water inside. But this gate-open behavior might not only happen toward the phase-transition. It would occur when the voltage applied. Therefore, We used three different kind of samples, Fe₃O₄, CoFe₂O₄, and NiFe₂O₄.In previous work, it have realized that the phase-transition occur in CoFe₂O₄ and NiFe₂O₄, Fe₃O₄ kept the original phase. By in-situ XRD, the gate-open can be observe and relate to the applied voltage. And three samples showed the same behavior. Furthermore, in-situ partial fluoresce yield can describe the change of structure during the gate-open. And by in-situ TEM, the amount of water capacity can be calculated. According to these in-situ technologies, this detail of this behavior can be seen. And this behavior should be considered to every heterogeneous catalysis between liquid and solid.

ET03.03.13
Open Hollow Co-Pt Clusters Embedded in Carbon Nanoflake Arrays for Highly Efficient Alkaline Water Splitting
Hong Zhang1, Yanyu Liu2, Haijun Wu1, Zongkui Kou1, Wei Zhou1, Wenjie Zang1, Stephen John Pennycook1, Jianping Xie1, Cao Guan1 and John Wang1; National University of Singapore, Singapore, Singapore; Beijing Institute of Technology, Beijing, China; Tianjin University, Tianjin, China.

Water splitting provides a clean and renewable way to produce high-purity hydrogen, but the slow kinetics and poor stability of electrocatalysts limit its practical application. Here we report a class of open hollow Co-Pt nanoclusters embedded in N-doped carbon nanoflake arrays aligned on carbon cloth (Co-Pt/C NAs, 2.5 wt% Pt), which display low overpotentials (50mV for hydrogen evolution, 320 mV for oxygen evolution, vs RHE) in alkaline media. The high performance arises from the unique nanostructure and the synergy of Co-Pt promoting water dissociation demonstrated by density functional theory (DFT) calculation results. It can be directly utilized as a highly efficient bifunctional electrocatalyst for overall alkaline water splitting and outperform noble-metal-based materials in terms of much lower operation voltage (1.54 V at 10 mA cm⁻²) and higher stability (no degradation at constant current or voltage up to 120 hrs.), representing a highly promising electrode for electrochemical energy conversion.

ET03.03.14
Gas-Phase Etched Platinum-Nickel Nanoframes and Their Extraordinary Activity Towards Methanol Electro-Oxidation
Yiliang Luan1, Can Li1, Shaohui Yan1, Bo Zhao2, Amar Kumbhar3, Chenyu Wang1 and Jiye Fang1; SUNY Binghamton, Binghamton, New York, United States; Texas Tech University, Lubbock, Texas, United States; University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Highly open nanoframes are a class of promising catalysts in many application fields due to their ultra large surface area and quasi-one-dimensional structure. However, the fabrications of such nanoframes is still a challenge. To date, they are usually produced by de-etching one active component from a bimetallic precursor with an inert counterpart in a solution system, using an acidic medium such as acetic acid or even nitric acid. The drawback of this de-etching method is that it could generate ill-defined structures with defect-rich surfaces, leading to severely deformed morphologies in the subsequent step of processing such as a substrate carbon loading process. Our recent achievement in the preparation of platinum(Pt)-nickel(Ni) tetrahexahedral nanoframes demonstrates that etching with carbon monoxide (CO), i.e. the Mond Process, is an efficient way to produce Pt-Ni nanoframes, in which a segregation of the Ni-component in the precursors is preferred. Here, we have synthesized a cationic Pt-Ni nanoparticles via this CO etching approach, which has never been reported. The nanoframe precursors presented via a colloidal synthesis presented a conventional concave cuboid profile. Our characterization indicated that there was a considerable segregation of the Ni-component on the solid concave cuboid precursors. The segregated Ni atoms could be easily removed through the Mond Process in CO atmosphere at an elevated temperature. According to TEM characterization, the resultant Pt-Ni nanoframes showed an apparent open frame structure with a solid metallic core. Further evaluation of these Pt-Ni nanoframes towards methanol electro-oxidation indicated that their surface specific activity is ~6.5-fold higher than that of the commercial Pt/C catalysts, suggesting an extraordinary performance.

ET03.03.15
Coupling Polyoxometalates and Carbon Dots for Photoelectrocatalysis
Antonino Madonna1, Fabrizio Messina1, Delphine Schaming1 and Souad Ammar1; 1ITODYS Laboratory, Université Paris Diderot, Paris, France; 2IDFC, Università degli Studi di Palermo, Palermo, Italy.

Nowadays the need for new energy sources required to let us overcome the intensive use of fossil fuels is more actual than ever. Some efforts have been focused on the development of a system to produce and store hydrogen in an affordable way; right now, though, this gaseous fuel is still produced by the decomposition of biomass. A strategy then been adopted by scientists is to develop new materials capable of producing hydrogen directly from the catalytic reduction of water, a process commonly known as water splitting. Being hydrogen a very powerful combustible that only produces water when burned, giving rise to a so-called hydrogen cycle, it could be the green fuel of the future.

In the field of nanotechnologies, among some of the most interesting materials studied for this very purpose are Polyoxometalates (POM), a class of polyatomic clusters with rich redox and photochemical properties that can be opportunely tuned modifying their structure and composition [1]; despite several reports confirming their ability to catalyze water decomposition, their main drawback lies in their sensitivity to light, limited only to the UV part of the spectrum. In order to make use of their appealing properties via the employment of the full solar radiation, several strategies have thus been approached. In this regard, many efforts have been made to obtain an effective coupling with different photosensitizers [2]; with this in mind, the recent discovery of Carbon Dots (CDs) opens completely new perspectives. CDs are a novel class of carbon-based nanostructures, very cheap to synthesize, often non-toxic and that usually show an intense and tunable fluorescence when excited by both UV and visible light. Also, it has been reported they possess a remarkable tendency to transfer their excitation state when coupled to other species [3]. Making use of the broad distribution of molecular moieties found on CDs outer shell which allows an electrostatic interaction, we have been able to obtain a static coupling between these two species, as shown both by steady state and time resolved spectroscopy. This nanohybrid has thus been used to prepare photoelectrodes that, studied in a common photoelectrocatalytic cell, show activity when irradiated by UV-
Two-dimensional (2D) layered transition-metal dichalcogenides has been regarded as highly promising electrode materials for fast-rate Li-ion and Na-ion batteries. Monolayer or multilayer MoS₂ nanoflakes have been employed for metal ion batteries, but the material suffers from poor cyclic stability due to damage of the layered structure in a decomposition reaction. Herein, we judiciously synthesize ultrathin MoS₂-xSex nanoflakes quasi-vertically aligned on 2D graphene-like carbon foam backbone (the obtained material is referred to as MoS₂-xSex/GF). The MoS₂-xSex/GF electrode with a Se concentration (x=0.9) exhibits enhanced rate performance with a higher reversible capacity and capacity retention compared to pure nanoflake MoS₂/GF electrodes. Quantitative analysis reveals that the improved pseudocapacitive contribution, derived from enlarged interlayer spacing by selenium substitution, is the origin of good rate performance. We also investigate the decomposition reaction of MoS₂-xSex with in-situ Raman and ex-situ XRD measurements in different potential ranges (0.01-3.0 V and 0.5-3.0 V vs. Na+/Na), which reveals that the 2D structure in MoS₂-xSex can be preserved due to Na-ion intercalation process in the potential range above 0.5 V. Discharge to 0.01 V leads to damage of the 2D structure and aggregation. So we can maintain the 2D layered structure and thus significantly improve the capacity retention by choosing appropriate potential ranges. This study sheds new light on better understanding of the metal ion storage mechanism of 2D transition metal chalcogenides that are being widely investigated.

ET03.03.18

Intercalation Na-Ion Storage in Two-Dimensional MoS₂-xSex and Capacity Enhancement by Selenium Substitution Guichong jia and Hongjun Fan; Nanyang technological University, Singapore, Singapore.

Carbon dioxide (CO₂) is one of the main greenhouse gases accumulating from fossil fuel consumption has been caused urgent energy crisis and serious global warming problem, which represent two major challenges of the world. The electrochemical reduction of CO₂ into value-added chemicals and fuels provides both an attractive strategy for industrial-scale means and a candidate for energy storage. Copper (Cu) has been known as an unique metal catalyst in its ability of directly converting CO₂ into a high quantity of fuels from the electrochemical reduction of CO₂. However, poor selectivity and activity degradation are two remaining restraints for practical application. Upon most occasions, the CO₂ molecules obtain an electron to form CO₂⁻ intermediate has been regarded as a rate-determining step. However, the CO₂⁻ intermediate is the key role to obtain deep reduction products. For instance, to formation of C₂H₄, the selectivity-determining step is the generation of the COH intermediate by protonation of CO₂⁻ and the subsequent to generate ethanol. To investigate the absorbed CO on the copper surface and discuss different reaction pathway through the CO₂⁻ intermediate. We designed facile electrochemical deposition strategy to synthesize Cu nanodendrites by carbonyl coordination to expose the adsorbed CO site. Meanwhile, the adsorbed CO severely restricts hydrogen formation and the CO₂⁻ intermediate adsorption strength can tailored by adjusting the applied potential.

ET03.03.19

Surface Tailoring Induced by Pt Modification on Mixed-Phase Manganese-Cerium Oxides—A Promising Cathode Catalyst for Direct Methanol Fuel Cells Ammar B. Younaf and Peter Kasak; Qatar University, Doha, Qatar.

Developing substituent of monometallic platinum (Pt) precious metal as promising cathode catalysts in direct methanol fuel cells (DMFCs) have attracted great interests underlying sustainable energy applications. Numerous strategies have been adopted to produce active Pt-based binary and ternary alloys to overcome the faced challenges in oxygen reduction reactions (ORR). To this end, we have introduced a facile strategy to develop an efficient electrocatalyst with enhanced ORR performance and negligible methanol crossover effect to maintain the overall cell voltage as a stable in DMFCs. Surface tailoring of mixed-phase manganese-cerium oxides were induced by fabrication of ultra-low and smaller sized Pt nanoparticles by capping agent free dry-chemistry reduction process. The geometry and structural analysis of as-obtained electrocatalyst were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). In addition, the precise surface tailoring was screened out by HAADF-STEM element mapping and atomic force microscopy (AFM). The cathode catalyst performance of Pt/Manganese-cerium oxides nanocomposite was analyzed by electro-reduction of oxygen with and without presence of methanol in alkaline medium to evaluate the negligence of methanol crossover from anode to cathode. The higher ORR performance with excellent methanol tolerance behavior compared with commercial Pt/C catalyst proved the promising nature and applications of present material in DMFCs.

ET03.03.20

Cobalt Phospide—A Stable, Non-Precious Metal Hydrogen Evolution Reaction Catalyst in a Commercial Proton Exchange Membrane Electroclyzer McKenzie A. Hubert1, Laurie King1, Chris Capuano2, Judith Manco1, Nemanja Danilovic1, Eduardo Valle1, Thomas R. Hellstern2, Katherine Ayers2 and Thomas F. Jaramillo1; 1Stanford University, Stanford, California, United States; 2Proton Onsite, Wallingford, Connecticut, United States.

Proton exchange membrane (PEM) electrolyzers are a promising route to large-scale energy storage. Platinum is the state-of-the-art hydrogen evolution reaction (HER) catalyst used in commercial PEM electrolyzers today owing to its excellent activity and stability. However, the cost and scarcity of Pt motivate research into non-platinum group (NPG) electrocatalysts. For decades, electrocatalysis research has focused on developing cheaper, efficient HER catalysts to reduce the capital cost of PEM electrolyzers1. However, a gap in this research has been demonstrating the stability of a non-platinum group (NPG) HER catalyst in a commercial-grade electrolyzer operating under conditions much different than lab-based tests.
Cobalt phospide is among the most active NPG catalysts for HER and has been well-studied and characterized in the literature. In this work, we develop a synthesis technique to prepare large batches of nanoparticulate CoP on a high surface area carbon support. In this form, we were able to directly integrate the nanomaterial into an 86 cm² commercial PEM membrane electrode assembly (MEA) electrolyzer without making significant changes to the fabrication process. This CoP PEM MEA demonstrated excellent stability by maintaining a nearly constant voltage for > 1500 hours of continuous operation at a current density of 1.86 A.cm⁻² and elevated temperature and pressure. To the best of our knowledge, this is the first demonstration of a stable NPG HER catalyst in a commercial PEM MEA electrolyzer.

For the purpose of energy storage, PEM electrolyzers will likely operate intermittently, following the flux in renewable power generation. We therefore also investigate lab-based accelerated stress tests (ASTs) to probe degradation of CoP to better understand failure mechanisms and predict catalyst performance when translated from the lab to a commercial device. Pre- and post-test characterization techniques such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and inductively coupled plasma mass spectrometry (ICP-MS) were used to observe and quantify degradation. Establishing standard lab-scale ASTs for HER catalysts is essential for benchmarking stability across a wide range of materials.

References

ET03.03.21
Vertically Aligned Nanoplatelets of Sputtered Iridium Oxide for the Oxygen Evolution Reaction David Baker, Milena B. Graziano and Brendan Hanranan; Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland, United States.

The key to efficient water electrolysis is finding a durable oxidation catalyst with a low overpotential for the four-electron oxygen evolution reaction (OER). Among known catalysts, iridium oxide (IrO₂) is often recognized as having one of the lowest overpotentials for the OER, and is found to be stable in a wide range of aqueous media. IrO₂ electrodes are readily deposited by reactive sputtering, a method that can reproducibly control the resulting thickness, chemistry, and morphology of the IrO₂ films by changing the sputtering growth parameters. Under low deposition temperatures and high O₂ flowrates, IrO₂ grains become vertically aligned nanoplatelets with a rutile crystal structure. Due to their vertical orientation the IrO₂ nanoplatelets exhibit exceptional antireflective properties not seen with other sputtered IrO₂ morphologies, and can be electrochemically probed for their performance as OER catalysts when deposited onto electrodes. The nanoplatelet IrO₂ electrodes demonstrate high activity and good durability compared with sputtered IrO₂ exhibiting planar surface morphologies. Tafel analysis shows that the structure of the nanoplatelets is also found to have a large impact on the OER kinetics beyond simply increasing the surface area. These electrodes also exhibit comparable performance in a wide range of media, ranging in pH values from 1 to 12. Anti-reflective, nanoplatelet IrO₂ coatings are high performance catalysts for solar water splitting, without the need for damaging treatments to make antireflective patterns out of highly specialized semiconductor light absorbers.

ET03.03.22

Currently considerable efforts are made to develop renewable ways to replace the fossil-based route for producing hydrogen. As a well-studied option, water photoelectrolysis is restricted by its low energy efficiency and low output. Water electrolyser are promising for producing renewable hydrogen based on acidic proton-exchange membranes (PEMs) or alkaline water electrolyser. However, the electrode materials of the PEM electrolyzers contain platinum group metals (PGMs), which are relatively scarce and expensive thus hindering mass commercialization. By contrast, both cathode and anode materials for alkaline water electrolyser can be produced from non-noble transition metal compounds, suitable for large scale production. However, the oxygen evolution reaction (OER) in alkaline solution is still sluggish and needs a high overpotential (>350 mV) to reach a current density of 10 mA.cm⁻². Developing the right materials with favorable structures and properties can help improve the OER performance of catalysts in alkaline solutions.

As reported by Chatenet group, magnetic nanoparticles generate magnetic heating under high-frequency alternating magnetic fields. The localized heating to the catalysts in an electrolyser can considerably reduce the overpotential for OER. Besides, introducing Fe into Ni-based materials may improve its conductivity and lead to an activation effect on Ni, resulting in a dramatically enhancement of the OER performance. In addition, hierarchical structures could facilitate the electrochemical catalysis process, with active sites locating at the micro- and mesopores (nanopores) and the macropores promoting facile diffusion of species towards these active sites.

Here we report a synthesis method that Fe was introduced into the oxide precursor (NiMoO₄) by an ion exchange method to form Russian blue analogues (PBA, KNiFe(CN)₆) which was further transformed into hierarchical hollow sub-microwires composed of NiFe metal nanoparticles without the need for hydrog post-treatment. The obtained hierarchical NiFe hollow sub-microwires, with a diameter of ~200 nm, had a high specific surface area (53 m²g⁻¹) which provided lots of active sites. These sub-units—NiFe nanoparticles, with a size of 3-5 nm, acted as precursors and experienced activation to form NiFe oxide in situ on the surface, favorable to OER.

This work introduces a facile and versatile way to introduce Fe into the precursor by an ion exchange method from different transition metal oxides, and also opened up new routes for synthesizing magnetic hierarchical hollow sub-microwires based on metal nanoparticles by directly annealing from their corresponding PBA precursors without introducing explosive hydrogen for heat-treatment.


ET03.03.23
Computational Design of Core/shell Nanostructured Materials for Energy Conversion and Storage Liang Zhang, Abhinav S. Raman and Aleksandra Hanrahan; Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland, United States.
Given the crucial role of catalysis science in our society, understanding how to design catalyst structures for desired catalytic activity and selectivity becomes a grand challenge. Core-shell nanostructured materials hold the promise of being active, cost-effective, and stable catalysts. I will demonstrate how we understand the structure-performance correlation at the atomic-scale level through a set of computational approaches and apply it to address the catalyst challenge in the fields of energy conversion and storages. Computationally, we designed heterostructured perovskites for electrochemical water splitting, which were experimentally synthesized, characterized and validated. This sets the stage for the future design of core-shell oxide nanoparticles and their use for chemical reactions under harsh chemical environments. I will provide an understanding of the activation mechanism of the heterostructures based on first principle simulations. Finally, I will bridge core-shell architecture oxide and transition metal systems and discuss our vision of potential design strategies.


Highly Stable Sodium Metal Anodes Enabled by Tuning the Thickness of Ultrathin Graphene Films Huan Wang, Chuanlong Wang and Weiyang Li; Dartmouth College, Hanover, New Hampshire, United States.

Effective surface protection of lithium metal anode is the enabling factor for next-generation high-energy batteries. However, the exacting requirements on the stability, mechanical properties and homogeneities of the protection layer hinder the realization of an ideal artificial interface. Among all the material choices, diamond with its renowned mechanical strength and exceptional electrochemical inertness is a prime candidate for lithium metal stabilization. Herein, by special synthetic techniques and rational design, we successfully rendered this desirable material compatible as lithium metal interface, which could strictly satisfy all the critical requirements. By fabricating high-quality nanodiamond film with long-range homogeneity but weak adhesion to the current collector, lithium can be electroplated solely underneath the film and effectively protected from parasitic reactions with liquid electrolyte. Notably, the nanodiamond interface possessed the highest modulus of all the lithium metal interfaces reported so far (>200 GPa), which can effectively arrest dendrite propagation to afford a dense deposition morphology. And the good flexibility of the thin film can accommodate the volume change of electrode during cycling. Importantly, since pinholes and mechanical damages during cycling are the main failure mechanisms of the artificial coatings developed so far, a unique double-layer nanodiamond design was proposed for the first time to enhance the defect tolerance of the nanodiamond interface, which enabled more uniform ion flux and mechanical properties as confirmed by both simulation and experimental results. Thanks to the multifold advantages of the double-layer nanodiamond interface, high Coulombic efficiency of over 99.4% can be obtained at a current density of 1 mA cm−2 and an areal capacity of 2 mAh cm−2. Moreover, with ~250% excess Li, more than 400 stable cycles can be realized in prototypical lithium-sulfur cells at a current density of 1.25 mA cm−2, corresponding to an average anode Coulombic efficiency of above 99%.

Nanostructured materials have been found to be critical in promoting the performance of energy storage and conversion devices, such as batteries. Here, Si anodes for Li-ion batteries (LIBs) and high capacity alloy anodes for Na-ion batteries (SIBs) are discussed as examples for the importance of design electrode materials at nanoscale.

For LIBs, we designed porous structured Si-C composite materials as high performance anodes. In one effort, the large mesoporous silicon sponge of tens of microns prepared have controlled porosity and pore size, which can limit the particle volume expansion at full lithiation to ~30% and prevent pulverization of bulk particles. The electrodes with the loading of 1.5 mAh per cm2 demonstrated ~92% capacity retention over 300 cycles. The composite electrodes of porous Si and graphite (~3 mAh per cm2 loading) with a specific capacity of ~650 mAh per gram demonstrate ~82% capacity retention over 450 cycles. In another effort, hierarchical structured Si-MWNT microspheres developed not only have good porous structure to accommodate the volume expansion and achieve ~30% apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to ~220 MPa pressure. The anodes deliver a high specific capacity of ~1500 mAh per gram and 85% capacity retention over 200 cycles at the areal loading of ~3 mAh per cm2.
For SIBs, yolk-shell structured Sb@C particles and pomegranate microspheres have been prepared as high capacity anodes. With well-controlled nanostructure, these materials render stable cycling performance. The Sb@C yolk-shell structures prepared by controlled reduction and selective removal of Sb2O3 from carbon coated Sb2O3 nanoparticles can accommodate the Sb swelling upon sodiation and improve the structural/electrical integrity against pulverization. It delivers a high specific capacity of ~554 mAh per gram and long cyclability with 92% capacity retention over 200 cycles. Sb@C yolk-shell microspheres by the emulsion method further improved the packing density and the cycling stability with ~99% capacity retention over 200 cycles.

9:00 AM ET03.04.04
Towards Better Electrochemical Devices—Building Effective Transport Networks for Electrons and Ions Yunfeng Lu; Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Electrochemical devices, such as batteries and fuel cells, are commonly used for energy storage and conversion. Generally, such devices are operated through the separation, translocation, and recombination of electrons and ions (e.g., protons and lithium ions) between the electrodes. Building devices with rapid and effective transport mechanisms towards improved performance and long cycling life. In this context, this presentation will discuss the design and synthesis of materials, as well as the engineering of electrode structure, towards electrochemical devices with improved performance. Three main topics will be covered, including 1) the design and synthesis of anode and cathode materials, 2) novel solid electrolytes and functional separators, and 3) novel hydrogen fuel cells with multifunctional anodes for enhanced transient power and prolonged lifetime.

9:30 AM ET03.04.05
Multi-Functional Few Layered Black Phosphorus Composite Qinyu Yan; Nanyang Technological University, Singapore, Singapore.

Delamination of black phosphorus (BP) into monolayer or few-layer, dubbed phosphorene, and manipulation of its newly discovered properties that are unattainable by its bulk structure have been a recent scientific breakthrough. As an elemental analogue of graphene, researchers intended to exploit its structural similarity to substitute graphene as anode for lithium ion batteries (LIBs) as one of the dominant power sources for portable electronic devices. In addition, for thermoelectric applications, theoretical studies have revealed that very high ZT values can be possibly achieved in BP with controlled charge carrier concentration.

We will present our recent activities on synthesis of few layered black phosphorus nanosheets through different methods and study their properties in Li/Na storage applications. We try to improve the chemical stability of phosphorene based composite by forming composite structures with the aid of spark plasma sintering (SPS) process. It shows that excellent air stability of SPS-processed black phosphorus can be achieved over the 60 days observation in maintaining its high storage properties. We also developed 0D-1D hybrid phosphorene-Ni3P structures to show enhanced Li storage properties.

10:00 AM BREAK

10:30 AM ET03.04.06
The Design of Nanomaterials for Pseudocapacitive Energy Storage Bruce S. Dunn; University of California, Los Angeles, Los Angeles, California, United States.

Battery materials exhibit high energy density by utilizing reversible redox reactions, but their slow ionic diffusion leads to long charging times. Electrochemical double layer capacitors (ELDCs) offer some advantages over batteries, including fast charging times (<1 minute) and long lifetimes (~500,000 cycles). However, ELDCs do not involve redox reactions and as a result they have lower energy densities compared to batteries. For this reason, there is widespread interest in pseudocapacitance, a faradaic process involving surface or near-surface redox reactions, that can lead to high energy density at high charge-discharge rates. In recent work, we have suggested that pseudocapacitive materials can be classified as extrinsic or intrinsic; in the latter case, pseudocapacitive behavior is dependent on particle size, as fundamental changes in redox reactions may occur in finite sized systems. This paper will review our work on identifying Li+ conducting nanoscale materials which exhibit pseudocapacitive behavior. One key feature associated with pseudocapacitance is that the rate of charge storage is determined by surface-like kinetics rather than semi-infinite diffusion as occurs with battery materials. In this regard, the presence of two-dimensional pathways in the structure of the oxide or sulfide material seems to be favorable for obtaining a pseudocapacitive response. In addition, when materials are reduced to nanoscale dimensions, they may begin to exhibit pseudocapacitive characteristics because of the large number of surface sites or because phase transitions which occur in the corresponding bulk materials are suppressed. MoO3 is a good example of this behavior as micron-sized particles exhibit battery-like properties while nanosized materials exhibit pseudocapacitive responses and operate at high charge/discharge rates without decreasing the level of charge storage. Morphology is another parameter that has been used to develop pseudocapacitive responses in a variety of systems. Mesoporous materials, which possess an interconnected pore network that provides electrolyte access to thin (<15 nm) redox-active walls, lead to a pseudocapacitive response while two-dimensional nanosheets of transition metal oxides exhibit surface-controlled kinetics indicative of pseudocapacitive behavior. The ensemble of these results suggests that we can expect an increasing number of nanoscale materials to be developed that retain high energy density at charge/discharge rates which are well above those of battery materials.

11:00 AM ET03.04.07
In Situ Formation of Sulfide Solid-State Electrolyte Protection Layer on the Surface of Metallic Li for High Performance Li Batteries Jianwen Liang, Xiaona Li and Xueliang A. Sun; University of Western Ontario, London, Ontario, Canada.

Metallic lithium (Li) has attracted extensive attentions for Li-S, Li-air and solid-state Li batteries, due to its high theoretical capacity and low redox potential [1-3]. However, several challenges substantially hinder the real application of Li anodes, such as dendrite formation and unfavorable reaction between Li and electrolyte. In fact, the real problem is originated from the unavoidably react of Li with electrolyte and the non-uniform distribution of electrochemical active sites for Li plating/stripping during cycling.

Formation of a thin and stable protection layer with uniform and high Li ion flux on the surface of Li metal may address all of the main problems of Li anode. Sulfide-based solid-state electrolyte possesses reasonably high ionic conductivity (especially for nanostructured layer, which can achieve ionic conductivities higher than 10 mS cm⁻¹ at room temperature), which is a good choice for the materials of Li metal protection layer. While, the formation of a thin sulfide-based solid-state electrolyte layer, especially for in-situ or adjustable layer with nanosize and different thickness, on the surface of Li metal is still a challenge due to the high chemical active of metallic Li and the difficult synthesized conditions of sulfide-based solid-state electrolyte. Here, we show an in-situ dispositional strategy to form a sulfide solid-state electrolyte protection layer on the surface of metallic Li to address the dynamic Li plating/stripping process. Taking adjustable Li2PS4 solid-state electrolyte layer as an example, due to the high ionic conductivity and low electrochemical activity of Li2PS4, the intimate protection layer of Li2PS4 between Li metal and liquid organic electrolyte can not only restrain the formation of Li dendrite, but also reduce the SEI formation and prevent further corrosion of Li metal during battery cycling. Thus, excellent electrochemical performance has been achieved: (1) Symmetric cells with the Li2PS4 protection layer can deliver stable Li plating/stripping for 2000 h with voltage hysteresis as low as ~10 mV; (2) Full cells assembled with the Li2PS4-protected Li exhibit two times higher capacity retention in Li-S batteries (~800 mAh g⁻¹) at 5 A g⁻¹ for over 400 cycles compared to their bare Li counterparts; (3) High rate performances can be achieved with Li-
In essence, nanocrystalline metals are promising building units to realize high-capacity anodes are enabling ever-increasing gravimetric and volumetric energy densities in lithium-ion batteries (LIBs), but their fading capacities upon both pulverization and electrical disconnection caused by large volume changes during repetitive lithiation/delithiation reactions must be remedied. Another challenge is the lack of a fast and scalable process to fabricate nanocrystalline metals into real electrodes. Herein, we report graphene pliable pockets (GPPs) remedying the limitations of nanocrystalline metals for high-performance LIBs, and Metal_encapsulated GPPs (M_GPPs) can be fabricated via the ultrafast dynamic polymerization and evaporation of specific polymers on nanocrystalline metals. This process is also shown to enable scalable mass production upon increasing the batch size.

We applied the GPP structure to silicon, a most promising but also difficult to handle electrode material. Utilizing Si GPPs with high tap densities exhibits excellent rate capability and robust cycle life. We discover that the inner graphene pliable layers allow electrical conductance to Si and the outer GPP controls formation of solid-electrolyte interface (SEI) layers, while both of them provide pliable compartments to prevent volume expansion and pulverization of Si nanocrystals during repeated lithiation/delithiation cycles. Full-cell LIBs of the Si GPP electrodes assembled with representative cathodes of LiCoO2 (LCO), LiMnO2 (LMO), and LiFePO4 (LFP) demonstrate remarkably high gravimetric and volumetric energy densities. Moreover, Si GPPs can be used as the battery-type electrodes for lithium-ion capacitors (LIC), such an attempt lead to a result in much faster charging/discharging and strikingly longer life performance while maintaining high energy densities. GPP structures are superior and feasible than other promising anode structures, thereby applicable to industries and attainable shortly.

In situ sodiation experiments were performed on the Na-Sn system to evaluate the rate capability and cycle stability of the anode material. Experiments showed that the sodiation rate of crystalline Sn (c-Sn) is 2-3 orders of magnitude faster than the lithiation rate of c-Si with the same diameters. Furthermore, the observed rates were nearly the same regardless of the orientation of c-Sn, causing the Sn anode to swell in an isotropic manner and thus mitigating pulverization. Here, using atomic simulations and advanced analysis techniques, we elucidated the mechanistic origins responsible for the ultrafast sodiation and isotropic swelling observed from for the Sn anode by clarifying the diffusion kinetics at the Na-Sn diffusion couple. It was found that both the crystalline-to-amorphous phase transformation at thin layers of c-Sn near the propagating interface and pipe diffusion through sodiation-induced dislocations are the two dominant structural features occurring during sodiation. These sodiation behaviors observed from the Na/Sn interface alleviate the rate-limiting behavior of the propagating interface, while nullifying the orientation effect of diffusion in c-Sn. This promotes the Na diffusion to c-Sn at unprecedented rates and enables isotropic swelling of c-Sn. The observed phenomena provide insight into the design of anode materials for realizing batteries with high rate performance and cycle stability.

1:30 PM ET03.05.01
Recent Developments in the Design and Synthesis of Platinum-Based Catalysts for Fuel Cell Application Younan Xia; Georgia Institute of Technology, Atlanta, Georgia, United States.

Platinum (Pt) is by far the best catalyst for the oxygen reduction reaction (ORR) occurring on the cathode of a proton exchange membrane fuel cell (PEMFC). Its low abundance, limited supply, and ever-increasing price have kept motivating researchers to minimize the loading of this precious metal in the catalyst. In this talk, I will discuss a number of strategies for greatly increasing the mass activity and durability of Pt-based ORR catalysts, including...
facet-controlled synthesis, increase of dispersion by forming a core-shell or hollow structure, manipulation of surface strain, electronic coupling through the incorporation of a second metal, and use of particles with an uniform, optimal size. These strategies have resulted in the development of advanced ORR catalysts, enabling the society to achieve a sustainable use of precious metals such as Pt in energy conversion, industrial catalysis, and related applications.

2:00 PM ET03.05.02
Extending the Limits of Pt/C Catalysts with Passivation-Gas-Incorporated Atomic Layer Deposition
Shicheng (John) Xu1, Yongmin Kim1, Joonsuk Park2, Drew Higgins3, Peter Schindler4, Dickson Thian5, J. Provine6, Jan Torgersen1, 7, Tanja Graf8, Thomas D. Schladt8, Marat Orazov3, 7
1Civil and Environmental Engineering, Stanford University, Stanford, California, United States; 2Department of Mechanical Engineering, Stanford University, Stanford, California, United States; 3Department of Chemical Engineering, Stanford University, Stanford, California, United States; 4Chemical Engineering, Stanford University, Stanford, California, United States; 5Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 6Department of Chemical Engineering, Stanford University, Stanford, California, United States; 7Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway; 8Volkswagen Group Research, Wolfsburg, Germany.

Cost and life-time are key factors in limiting the broad adoption of polymer electrolyte fuel cells for cars. In response, we have been investigating the morphology of noble metal nanoparticles during surface deposition. In particular, we explored the influence of precursor-substrate and precursor-deposit interactions. Depositions can be improved through a variety of means, including tailoring the surface energy of a substrate to improve precursor wettability, or by modifying the surface energy of the deposits themselves. Here, we show that carbon monoxide can be used as a passivation gas during atomic layer deposition to modify the surface energy of already deposited Pt nanoparticles to assist direct deposition onto a carbon catalyst support. The passivation process promotes two-dimensional growth leading to Pt nanoparticles with suppressed thicknesses and a more than 40% improvement in Pt surface-to-volume ratio. This approach to synthesizing nanoparticulate Pt/C catalysts achieved high Pt mass activities for the oxygen reduction reaction (ORR), along with excellent stability likely facilitated by strong catalyst-support interactions afforded by this synthetic technique.

2:30 PM ET03.05.03
High-Productivity Electrochemistry with Flow-Through Nanowire Electrodes
Myung Jun Kim, Feichen Yang and Benjamin Wiley; Duke University, Durham, North Carolina, United States.

The high surface area per unit volume and large mass-transfer rates offered by porous, flow-through electrodes have resulted in their use in a wide variety of electrochemical processes, including organic electroosynthesis, water electrolysis, water treatment, fuel cells, and redox flow batteries. Many types of porous electrodes are commercially available, including carbon paper, graphite felt, reticulated vitreous carbon (RVC), metal mesh, and metal foam. Metal foam offers relatively high conductivity but a low surface area, whereas carbon paper has one of the highest surface areas but lower conductivity.

This presentation will describe the characteristics of a Cu nanowire flow-through electrode that has 15 times more surface area and is 32 times more conductive than carbon paper. The improvement in surface area is due to the small diameter of the nanowires relative to carbon fibers. The higher conductivity is due to the intrinsically higher conductivity of Cu, and the fact that the metal nanowires can be sintered together. The nanowire electrode has a porosity of 94%, but its hydraulic permeability was 89 times lower than carbon paper. For Cu ion reduction, the Cu nanowire electrode can achieve the same single-pass conversion as carbon paper at flow rates 300 times greater under mass transport-limited conditions, and 10 times greater under kinetically limited conditions. We will also report the performance of the flow-through nanowire electrodes for organic electroosynthesis and for water splitting. The high-conductivity, high surface area, and high porosity that can be achieved with metal nanowire electrodes create new opportunities for improving the performance of electrochemical systems for energy storage, hydrogen production, water treatment and the production of fine chemicals.

2:45 PM ET03.05.04
Quasi-2D PdPt Alloy Nanoclams for CO2 Reduction and Proposed Application in Tandem with Microbial Communities
Andrew B. Wong1, Joseph A. Gauthier1, Frauke Kracke2, Antaeres Antoniuk-Pablant1, Christopher Hahn1, 3, Karen Chan1, 3, Alfred Spormann2, 4 and Thomas F. Jaramillo2, 4, 5, 6
1Department of Mechanical Engineering, Stanford University, Stanford, California, United States; 2Civil and Environmental Engineering, Stanford University, Stanford, California, United States; 3Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 4SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California, United States; 5SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 6Chemical Engineering, Stanford University, Stanford, California, United States.

Improving the performance of cathodes for the electrochemical CO2 reduction reaction (CO2RR) will benefit from the discovery of new materials as well as the introduction of new paradigms. This presentation focuses on the synthesis and systematic study of the CO2 reduction activity of a novel quasi-2D PdPt bimetallic ‘nanoclam’ catalyst synthesized on carbon cloth electrodes via a pulsed electrodeposition technique. These results highlight the importance of nanostructuring to improve selectivity and geometric activity for CO2 reduction in this system through the comparison of the bulk and nanostructured PdPt. In addition, we also propose that the high activity of this catalyst at low overpotential is ideal for paring with biological systems to realize a hybrid system for CO2 reduction.

The PdPt nanoclams catalysts that combine high surface area with exposure of numerous undercoordinated sites for CO2 reduction with activity exceeding that of either Pd or Pt for CO2 reduction to formate at 0.2 V vs RHE, which is a provocative result. In comparison with bulk Pd, PdPt, and Pt systems, we find that the interplay of multiple trends affects selectivity and activity:

1. Increasing Pt content shifts selectivity from formation of formate to hydrogen evolution in the bulk
2. Increasing Pt content increases overall activity and prevents catalyst deactivation by changing the energetics of hydride intercalation into PdPt
3. Nanostructured morphology of PdPt nanoclams increases selectivity to formate in PdPt nanoclams vs in bulk, planar PdPt.

In addition to this understanding, we report our initial results on the creation of a hybrid electrochemical-biological CO2 reduction system in which formate and hydrogen are produced through electrochemical CO2 reduction by PdPt nanoclams. These products are metabolized by methanogens in combination with CO2 to yield ~100% faradaic efficiency to methane. Going forward, the integration of microbial communities with these nanostructured PdPt catalysts has the potential to combine the best-of-both-worlds from electrochemical and biological systems to achieve a regenerative catalytic system with high-selectivity, high activity, and low overpotential.

3:00 PM BREAK

3:30 PM DISCUSSION TIME

3:45 PM ET03.05.06
Rational Design of Electrode-Electrolyte System for Highly Efficient Electrochemical Nitrogen Reduction Reaction
Bryan H. Suryanto2, Colin S.
Ammonia is one of the most important chemicals used in the modern society. As an essential precursor used in the fertilizer production, the supply of ammonia is strongly associated to food furnishing. Without ammonia, it is predicted that more than half of the world population would starve. However, the synthesis of ammonia is extremely challenging due to the great thermodynamic stability of the nitrogen triple bond. Currently, more than 90% of the global ammonia commodity is produced by the Haber-Bosch process which is responsible for the release of ~12 Gt (1.5% of global total greenhouse gas emissions) of CO₂ into the atmosphere, annually. Therefore, the synthesis of ammonia from atmospheric N₂ utilizing renewable energy sources with zero carbon footprint will become an important process in moving forward.

Electrochemistry provides a direct pathway for N₂ conversion into NH₃ utilizing renewable electricity. Historically, the NH₃ electro-synthesis suffers from the drawbacks of low yield rate and selectivity (<10%), mainly due to the predominating hydrogen evolution reaction (HER). In this work, an electrochemical nitrogen reduction reaction (NRR) with a significantly enhanced selectivity and yield rate of NH₃ have been obtained via both electrode and electrolyte engineering. Surface area enhanced α-Fe₃O₄ nanorods were employed as the NRR cathode in an apricot solvent – ionic liquid mixed electrolyte. Remarkably, a NH₃ yield rate of ~2.35 × 10⁻¹¹ mol s⁻¹ cm⁻² with a high selectivity of ~32% was achieved. This work reveals that the abilities to both regulate the proton availability and enhance the N₂ solubility in the engineered electrolyte are imperative in achieving highly efficient NRR at room temperature and pressure.

References:

4:00 PM ET03.05.07
Nitrogen Fixation via Electrochemical Biosynthesis Under Ambient Atmospheric Environment Shengtao Lu, Xin Guan and Chong Liu; Division of Chemistry, University of California, Los Angeles, Los Angeles, California, United States.

The hybridization of electrochemical interface and microbiological synthesis combines the high efficiency of electrochemical reactions and the catalytic capability of microbes to produce valuable chemicals. Such hybrid can be used for nitrogen fixation, which consumes renewable energy such as solar electricity, and can also drive distributed production of environmental-friendly fixed nitrogen species. However, a fundamental contradiction occurs as the crucial nitrogen fixing enzyme, nitrogenase, is incompatible with oxygen. This prevents nitrogen fixation via nitrogenase in air, the most abundant nitrogen source. Here we report a micro-structured electrochemical interface that solves this problem. Our design enables successful nitrogen fixation under ambient atmospheric conditions. We also prove that such interface is scalable, which enables potential applications.

4:15 PM ET03.05.08
The INCA (Ionomer Nc Analysis) Method, a New Approach to Study Perfluorinated Ionomers Riccardo Narducci1, 2 and Maria Luisa Di Vona1, 2; 1University of Rome Tor Vergata, Roma, Italy; 2LIA, Roma, Italy.

Both the impelling need for a constant reduction of pollution in large cities and carbon dioxide in the atmosphere, as well as the continuous increase in petrol cost, have reinforced the interest in more efficient, clean, and sustainable systems such as fuel cells (FCs) for the conversion of electrical energy.

However, the present FC technology does not give till now the wished performances and the complete assurance for a long durability in all climatic conditions. The proton conducting separators preferred by cars producers are perfluorosulfonic acid (PFSA) membranes at temperatures of about 80 °C. The main target of the use of the INCA Method (Ionomer Nc Analysis) is the study and the understanding of ionomers in the conditions of use and the improvement of ionomeric membranes under operating conditions. In this presentation we will illustrate the results obtained comparing pristine Nafion 1100, oriented Nafion 1100 prepared in our laboratory, and stabilized (crystalline) Nafion 1100 membranes treated with special annealing agents. We will propose the best taylor made annealing in order to avoid critical degradations of mechanical properties and ionic conductivity due to the formation of layered morphologies, prevalently oriented in the direction parallel to the membrane surface. Hence commercial Nafion 1100 membranes were treated with dimethylsulfoxide (DMSO) for 7 days at 140 °C, to increase the thermal stability because of the formation of semi-crystalline phase (physical crosslinking), followed by hydrothermal annealing in liquid water to obtain a suitable water Uptake (WU). The results obtained with the INCA Method will be compared with the Dynamic Mechanical Analysis (DMA) and tensile stress measurements. The INCA analysis was also used to study the effect of the presence of H-bond and/or crystallinity in un-crystallized Nafion 1100 prepared from the solution. This material, prevalently amorphous, has a melting temperature (Tm) lower of about 50 °C respect to commercial Nafion 1100, but presents a high WU in the same condition of temperature and relative humidity. At the same time we will present the effect of the variation of the equivalent weight (EW) on the Tm: the lowering of EW causes a decrease in Tm of 10 °C. The knowledge of this effect on Tm is fundamental for Aquivion membranes, which have a wide range of EW. The INCA method allowed us to evaluate the behavior of Aquivion membranes in fuel cell conditions and compare them with Nafion membranes. The results permit to suggest the most appropriate thermal/hydrothermal treatments to stabilized these ionomers, where the mechanical stability play a fundamental role.

4:30 PM ET03.05.09
Unveiling the Effect of Pt-Based L1₁ FCT Core in Core/Shell Nanoparticles for Oxygen Reduction Reaction Mingjie Liu, Huolin L. Xin and Qin Wu; Brookhaven National Laboratory, Upton, New York, United States.

Rational design of active, durable and low-cost catalysts for oxygen reduction reaction (ORR) is highly desirable in fuel cell research. Nanoparticles with a core (Pt-based alloy)/shell (few layers of Pt skin) structure have attracted much attention due to their lower cost than pure Pt and potential benefits of activity tuning afforded by careful configuration of the core alloys. Previous theoretical work studying the enhancement effects has primarily focused on core alloys with cubic structures, i.e. disordered alloy or L1₁ ordered structure. In this work, using ab initio calculations, we have systematically investigated the structure-activity relationship of a new class of PtₓMₓ₂ (M=V, Cr, Fe, Co, Ni, and Cu) core alloy that has a low-temperature tetragonal L1₁ intermetallic structure. We have calculated the adsorption energies of O₂, OH, and OOH on various Pt skins and the underlying tetragonal structured alloys. We comprehensively explore the interaction between Pt layers and host materials to acquire the best Pt thickness associated with certain host material, tuning the ORR activity toward the peak of the ORR volcano plot. We further decompose the enhancement factor into ligand, normal and shear strain effects in these systems and clarify the origin of the improved activity of this class of catalysts. Our results could facilitate future design of ordered intermetallic FCT structure in ORR applications.

4:45 PM ET03.05.10
Oxide Nanoparticles as High Performance Bifunctional Catalyst Hongmei Luo, Meng Zhou and Litao Yan; New Mexico State University, Las Cruces,
New Mexico, United States.

Developing efficient electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are vital to the new generation of electrochemical storage and conversion devices such as electrolyzer, metal-air batteries, and fuel cells. For the demand of reversible fuel cells and rechargeable metal-air batteries, the bifunctional catalyst that can be used for both ORR and OER is gathering attention. In order to address the longstanding problems with high cost and poor stability of noble metal electrocatalysts, perovskite (ABO₃) formula, where A is rare-earth or alkaline metal and B is transition metal) with low cost, high versatility in structure and potential as bifunctional catalyst is of special interest. Applying our successful and novel polymer-assisted chemical solution (PACS) method, we will present the controlled synthesis of \((La_{0.8}Sr_{0.2})_3(Mn_{1-y}B_y)O_3\) (B: Ir and Co, x=0-0.1, y=0-0.2) nanoparticles with different particle sizes, A-site nonstoichiometry, B-site doping, and oxygen vacancy, and epitaxial thin films with different crystal orientations. Structural characterizations and electrochemical analysis are utilized to investigate the correlation between their compositions, structures, and electrochemical properties.

ET03.06.01 Nono Scale Three-Dimensional Resistivity Mapping of the Lithium-Ion Battery Solid Electrolyte Interphase on Silicon Anodes Caleb Stetson¹,², Taeho Yoon³, Yanli Yin³, Steve Harvey³, Andrew Norman³, Chunmei Ban³, Chunsheng Jiang³, Steven DeCaluwe¹ and Mowafak Al-Jassim²; ¹Colorado School of Mines, Golden, Colorado, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States.

In lithium-ion batteries, the solid electrolyte interphase (SEI) is an important passivating layer formed on the anode from electrolyte decomposition products. On silicon anodes, the SEI is believed to be critical to battery reliability and performance. SEI must be both electronically insulating to prevent further electrolyte decomposition and ionically conductive to permit the flow of lithium ions. While electronic resistivity is a critical intrinsic property of SEI, characterization tools to investigate the electronic properties of this thin, reactive layer have been limited.

To advance understanding of the electronic properties of SEI, our group has developed an instrumental approach utilizing scanning spreading resistance microscopy (SSRM) to characterize electronic properties in three dimensions in the nanoscale. Resistivity vs. depth profiling results originating from this technique have shown that electronic resistivity decreases from the surface of SEI moving towards the SEI/Si interface. Moreover, total SEI thickness is readily calculated by the identification of electronically conductive silicon beneath the insulating SEI. Thickness of SEI is highly variable based on the electrolyte and the cycling conditions utilized. Additionally, two-dimensional mapping of electronic resistivity at varied depths within the SEI gives quantitative and qualitative data regarding the heterogeneity of SEI structures in the nanometer regime.

Investigation of reference materials with known electronic properties has allowed for determination of instrumental resolution. Characterization of model SEI systems with SSRM alongside transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) permits the association of electronic properties with specific SEI chemical components.

ET03.06.02 Muon Spin Spectroscopy as a Nanoscale Probe for Studying Ionic Diffusion in Electrode Materials Beth L. Johnston¹, Peter Baker² and Serena Corr¹; ¹University of Glasgow, Glasgow, United Kingdom; ²ISIS Pulsed Neutron and Muon Source, Didcot, United Kingdom.

Lithium ion batteries are ubiquitous in today’s technology: they power our phones, laptops and are finding greater use for larger scale applications such as electric vehicles. Developments in sodium ion batteries are also of great current interest for use in stationary energy storage technologies such as grid storage for renewable energy sources. The movement of Li⁺ or Na⁺ ions through the active electrode material in a battery is crucial for its electrochemical performance, yet quantifying this behaviour can be very technique dependant. For example, macroscopic ionic diffusion measurements can indicate greater activation energies for ion diffusion due to the extra impedance imparted by macroscopic grain boundaries. Here, we demonstrate the use of muon spin relaxation spectroscopy (µ⁺-SR) as a valuable local tool to probe the Li⁺ and Na⁺ diffusion dynamics in battery electrode materials. The µ⁺-SR method allows one to probe the nanoscale distribution of ions via the muon spin perturbation due to diffusing ions nearby. Developing a clearer understanding of these diffusion processes at a local scale can provide us insights into electrochemical behaviour and the opportunity to optimise and tailor performance.

We present the investigation of local ion diffusion in the polyamionic positive insertion electrode materials LiFeSO₄F and Na₂FePO₄F using µ⁺-SR for the first time. It is predicted that these structures possess multi-dimensional ionic diffusion pathways, suggesting facile ion diffusion. In addition to enhanced ionic diffusion, these compounds display high energy densities driven by the inductive effect where the presence of electronegative species such as fluoride changes the ionic-covalent nature of bonds. The results obtained from these µ⁺-SR studies indicate lower activation energies and larger diffusion coefficients at room temperature compared to values obtained by computational and bulk characterisation means. This indicates intrinsically favourable diffusion dynamics which could be accessed by improvements in, for example, engineering of materials to reduce impedance effects from grain boundaries.

ET03.06.03 In Situ Electrochemical Dilatometry Study of Capacity Fading in Nanoporous Ge-Based Na-Ion Battery Anode During Sodiation-Desodication Cycles Manni Li¹,² and Eric Detsi¹; ¹Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Materials Science & Engineering, Harbin Institute of Technology, Harbin, China.

Although the rechargeable battery industry is currently dominated by lithium-ion battery technology, sodium-ion batteries are expected to play a key role in the near future, owing to the high abundance of raw sodium resources. Achieving high energy densities in sodium-ion batteries equal to, or exceeding...
lithium-ion batteries requires alloy-type high-capacity anode materials such as Sn, Sn. P. Ge [1]. However, alloying reaction of sodium with these materials result in significant phase transformation-induced stresses and volume changes, which ultimately cause a rapid capacity fading. In this work, nanoporous germanium was made by selective alloy corrosion and used to prepare sodium-ion battery composite slurry anodes. The performance of this composite electrode for reversible sodium storage was investigated by in situ electrochemical dilatometry, during which the (de)sodiation-induced macroscopic dimensional changes were recorded simultaneously during (dis)charging cycles, and for the first 200 cycles. (De)sodiation-induced dimensional changes and capacity fading were found to be proportional [2].

References

ET03.06.04
Theoretical Investigations on the Structural and Electrochemical Properties of Silicon Nano-Particle Anode Material for Lithium-Ion Batteries
Seung Eun S. Lee1, Hyung Kyu Lim2 and Sangheon Lee3; 1Chemical Engineering and Materials Science, Ewha Womans University, Seoul, Korea (the Republic of); 2Chemical Engineering, Kangwon National University, Seoul, Korea (the Republic of).

Lithium-Ion batteries (LIBs) are one of the most predominant energy storage systems for portable to stationary electronic devices. The LIBs are indispensable to laptops, mobile phones, and electric vehicles due to their high energy/power density and long cycle life. Accordingly, there is a continuing increase in the technical demand for developing higher capacity/power LIBs. Especially, silicon (Si) has been intensively pursued as the most promising anode material for its high specific capacity (> 3500 mAh/g) and abundance. Despite its high capacity, Si suffers from fast capacity loss caused by its large volume change (> 300%), unstable solid electrolyte interphase (SEI) and physical disintegration (cracking and crumbling) of the electrode structure during lithiation/delithiation processes. Therefore, there are various research activities to control the physico-chemical stabilities of Si anode material. Currently, Si nanostructures such as nanowires and nanoparticle carbon composites are proved to be effective methods for improving capacity and cycling stability, since nano-sized Si can alleviate mechanical stresses during volume changes. In this work, we conducted a series of computational simulations to understand how the physico-chemical stabilities of nanostructured Si anodes are associated with the high surface ratio of Si nanostructures. Using Monte Carlo simulations within the first-principles based reactive force-field (ReaxFF) framework, we determined atomic structures of Si nanoparticles in terms of particle size and lithiation ratio. Then, we elucidated a unique relationship between the structure of Si nanoparticle anodes and their physico-chemical properties such as theoretical charge/discharge potentials, by using the density-functional theory (DFT) calculations. Our theoretical findings will provide future guidance for developing next-generation Si nanomaterials, which can be successfully applied to commercialization of Si anode materials.

ET03.06.05
Yongkwon Song, Seunghui Woo, Junsang Yun and Jinhan Cho; Department of Chemical and Biological Engineering, Korea University, Seoul, Korea (the Republic of).

The development of flexible and conductive electrodes is crucial for rapidly evolving flexible/wearable electronic applications. For this purpose, various Ag nanomaterials with high electrical conductivity, such as nanoparticles and nanowires, have been physically deposited onto flexible substrates, but the electrical conductivity and mechanical stability of these electrodes are still restricted. Including Ag nanomaterials, commercially available cellulose papers have received great attention as promising substrates for next-generation flexible electrodes due to their high flexibility, large specific surface area, lightweight and low cost. Herein, we introduce a highly porous paper electrode with bulk metal-like electrical conductivity using room-temperature metallic fusion-assisted layer-by-layer (LbL) assembly. The newly synthesized tetraethylammonium thiosulfate (TOAS) stabilized Ag NPs were LbL-assembled with tris(2-aminoethyl) amine (TAA), allowing the almost perfect ligand exchange reaction between bulky/insulating TOAS ligands and small TAA molecules. The introduced small TAA molecules connect between neighboring Ag NPs, significantly decreasing the interparticle distance of Ag-Ag NPs. In addition to the minimized interparticle distance of Ag-Ag NPs, the low cohesive energy of Ag NPs strongly induces metallic fusion between closely packed Ag NPs at room temperature without any additional treatments. The resultant multilayers of (TOAS-Ag NP/TAA), exhibits the bulk metal-like electrical conductivity of ~ 1.60 x 10^5 S cm^-1. When depositing the Ag NPs onto cellulose papers through our approach, the insulating papers can be converted to flexible and bulk metal-like conductive papers that can be used as 3D current collectors for high-performance energy storage devices.

ET03.06.06
Electron-Dense Ligands and Their Optoelectronic Effects on PbS Quantum Dot Photovoltaics
Daniel Gregory, Hazel Assender and Andrew Watt; University of Oxford, Oxford, United Kingdom.

Quantum dot solar cells offer a low-cost route to flexible photovoltaics, with additional effects such as the relative ease of multiple exciton generation (MEG) offering tantalising possibilities of breaking the Shockley Queisser limit in the future. However, bottlenecks in device design and fabrication currently limit this technology's record efficiencies. Chief among those problems are the mobility of charges within the quantum dot layers of the device – causing a reduction in fill factor - and the need for stronger n-doping to improve open circuit voltages. One method of suppressing these problems is through ligand passivation, or combinations thereof. Current research has focused on ever-smaller ligands, down to individual halide ion passivation with dissociating organic salts, while research into the effects of substitution groups residing beyond the coordinating groups of small molecules has waned. This research begins with the introduction of novel ligand systems using electron-dense substituents outside the coordinating functional group, and follows with an exploration of the optoelectronic properties this class of ligands can provide to PbS quantum dot films, finishing with an overview of the photovoltaic performance of these systems.

ET03.06.07
Two-Dimensional Hexagonal Indium Selenide Nanosheets for Li-Ion Battery Applications
Valeria Nicolosi, Chuanfang Zhang and Meiying Liang; Trinity College Dublin, Dublin, Ireland.

Metal chalcogenides (MCs), including metal sulfides, metal selenides and metal tellurides, have attracted tremendous attention for energy storage applications and development of rechargeable lithium-ion batteries due to their unique physicochemical properties (e.g. high electrical conductivity, good thermal stability, earth abundance, etc.). Especially, MCs possess higher theoretical specific capacities for rechargeable lithium-ion batteries compared to traditional intercalation electrode materials. In addition, metal chalcogenides tend to be more electrochemically reversible as compared to metal oxide counterparts due to their faster charge transfer kinetics.

Recently, as an alternative anode material for replacing currently commercialized graphite or carbon-based anode materials, various two dimensional (2D) MCs materials, such as 2D gallium sulfide nanosheets, are investigated because of their large theoretical capacity. However, there is still a plenty of room for the development of new efficient anode materials from 2D MCs since only a few studies are carried out for this type of materials.
In this work, hexagonal shape indium selenide (InSe) was prepared via phase-controlled synthesis method and 2D InSe nanosheets were obtained via liquid phase exfoliation approach. Then, single-wall carbon nanotube (SWCNT) was added to improve the conductivity and flexibility of the hexagonal shape 2D InSe nanosheets electrodes for lithium-ion batteries’ anodes. Compared to commercially available InSe and bulk layered InSe, the hexagonal shape 2D InSe nanosheets displays the most excellent rate capability and high specific capacity (926 mAh g⁻¹ and 595 mAh g⁻¹ at 50 mA g⁻¹ and 2 A g⁻¹, respectively). In addition, it shows exotic cycling stability. The capacity of it has increased with the increase of cycling numbers (the capacity of the battery dramatically increased in the first 100 cycles and it continuously increased until 900 cycles), which means the quality of a battery will be improved when the battery is used. This work opens up vast opportunities for InSe to be scalable processed into flexible conductive composite films with a broad range of applications such as wearable electronics, optoelectronics, and other energy storage systems.

ET03.06.08
Nickel Vanadium Layered Double Hydroxides Nanosstructures for High-Performance Flexible Supercapacitor Applications Ankita Tyagi and Raju Kumar Gupta; Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India.

In recent times, demand for portable electronic devices like mobile phones, cameras, and laptops, etc. is increasing day by day. Energy storage devices such as batteries and supercapacitors have significant importance because of their high energy density and high power density, respectively.¹ The supercapacitor is gaining a considerable amount of attention because it uses the less toxic material, offers high power density, excellent electrochemical stability, a wide range of operating temperatures and durability. Facile fabrication of low cost, efficient, stable, eco-friendly and earth-abundant electrode materials for supercapacitors is critical.² Layered double hydroxide (LDH) is a new class of material having positively charged hydroxylate-like layers, weakly bound, intercalating charge compensating anions and water molecules, has shown tremendous supercapacitive performance.³ In this work, an ionic lamellar, two-dimensional (2D) nickel-vanadium layered double hydroxide (NV LDH) nanosheets have been synthesized via facile, cost-effective and potentially scalable hydrothermal method. The as-prepared 2D NV LDH nanosheets over carbon cloth (NVL@CC) was used as the supercapacitor electrode. The electrochemical characterization techniques such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to characterize the material for its electrochemical properties, while SEM, TEM, XRD, BET, and XPS, etc. techniques have been used for their morphological, structural and physical characterization. The high specific capacitance of ~2600 F g⁻¹ at the current density of 1 A g⁻¹ was observed in a three-electrode system using KOH as an electrolyte, which remained quite high at an increased current density of 10 A g⁻¹. This work demonstrates excellent potential for NV LDH nanosheets as an electrode material for supercapacitor applications.

References

ET03.06.09
Improvement of LiCoO2 High Voltage Cycling Stability by Nanoscale Polymer Surface Engineering via Chemical Vapor Deposition Polymerization Laisuo Su and B. Reeja Jayan; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

The interface between an electrode and electrolyte is crucial to the overall performance of lithium ion batteries (LIBs). Here we demonstrate chemical vapor deposition polymerization as a novel method to improve the performance of LiCoO2 cathode electrode for LIBs, including both rate capability and high voltage (4.5 V) cycling stability. Three polymers are utilized to engineer the surface and CR2016 coin cells are fabricated to study the effect of these polymers on LIBs electrochemical performance. The three polymers are poly(3,4-ethylenedioxythiophene) (PEDOT), poly(divinylbenzene) (PDVB) and poly(divinylbenzene-co-1H,1H,2H,2H-perfluorocyclyl acrylate (PDVB-co-PFDA)). Our results show that the PEDOT improves both the rate and the high voltage cycling performance of LiCoO2 electrodes, the PDVB has little effect on the both performances, while the PDVB-co-PFDA inhibits the performances. The PEDOT coating increases 100% rate capacity by 62% (from 34 to 55 mAh/g). The high voltage cycling number is increased by 250% (from 40 to 100 times) when the capacity decreases to 50% of its initial capacity. X-ray photoelectron spectroscopy is applied to understand the improvement of cycling stability. The results suggest that chemical or coordination bonds form between Co in LiCoO2 and O and S in the PEDOT film, while there is no bonds formation from the PDVB or the PDVB-co-PFDA coatings. The bonds stabilize the surface of LiCoO2 and thus improve the high voltage cycling performance. This work introduces chemical vapor deposition polymerization as a new research tool for surface modification and interface engineering of lithium ion battery electrodes.

ET03.06.10
Mutually Embedded MOF-Derived Uniformly Dispersed CoS2 within Porous Graphitic Carbon Polyhedrons and Carbon Nanotube Sponge for Ultralong Life Lithium-Sulfur Batteries Hui Zhang; Peking University, Beijing, China.

Lithium sulfur battery represents an advanced energy storage system because of its environmental benignity, high theoretical energy density (2600 Wh kg⁻¹) and natural abundance of sulfur. However, the low conductivity of sulfur, polysulfides dissolution, and sulfur volumetric expansion during lithiation/delithiation process will decrease the reaction kinetics of polysulfides and sulfur utilization, leading to low capacity, limited rate capability and inferior cycling stability. To solve these problems, there have been intensive efforts in choosing highly conductive carbon materials to design porous or hollow structures for secure sulfur hosts. Although these materials can effectively alleviate polysulfides dissolution during short-time cycling, the weak interaction with polar polysulfides will inevitably results in increase of charge transfer and dissolution of polysulfides over long-time electrochemical reaction. Here, we first grew ZIF-67 nanoparticles (~350 nm) uniformly within a three-dimensional carbon nanotube sponge, and then carbonization and sulfuration, we finally fabricated a hybrid network with numerous carbon nanotubes penetrating hierarchically porous graphitic carbon polyhedrons uniformly dispersing CoS2 nanoparticles (from ZIF-67) to host sulfur. Co,S,has been reported to have strong affinity to polysulfides, and can act as a catalyst to accelerate the conversion of polysulfides to Li2S/LiS (insoluble discharged products), which are beneficial for improving battery cycling stability (polysulfide stabilization) and rate capability (increased reaction kinetics). In our system, highly dispersed CoS2 nanoparticles can provide sufficient sites to trap polysulfides and catalyze the conversion reaction smoothly, additionally the outer wrapping porous graphitic carbons (physical barriers) can further protect polysulfides from dissolving into the electrolyte. Moreover, the highly three-dimensional conductive CNT and graphitic carbon hybrid network acting as a self-standing electrode can not only facilitate electrolyte infiltration and charge transport, but also improve sulfur loading and utilization. As a result, our novel 3D hybrid electrodes exhibit a much superior ultralong Li-S battery performance than previously reported MOF-based electrodes in recent literature.

ET03.06.11
Photo- and Redox-Active Eumelanin on Carbon Quantum Dot Current Collectors as Sustainable Electrode Material for Solar Batteries Abdelaziz
Monika Biener1; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2University of California, Riverside, Riverside, California, United States.

Melanin is a bio-pigment found in various classes of mammals, fishes, and different species of plants. This organic bio-pigment features unique physiochemical properties such as UV-Vis near IR absorption, redox activity (hydroquinone-semiquinone-couple bonds), metal chelation and ion-electronic hybrid electrical conduction [2]. The photoredox properties of melanin combined to its capability to reversibly bind cations opens the door to explore this intriguing quinone-based material as electrode for solar batteries [3].

We here report on the use of melanin on carbon quantum dots (CQD)-based current collectors. CQDs offer high surface area to the redox active melanin and facilitate the electron transport to the back contact. Cyclic voltammetry and galvanostatic charge/discharge cycles were employed to evaluate the storage performance of the melanin-electrode materials at different pH conditions and chemical composition of the electrolyte (e.g. including cations such as H+, Na+, K+, Mg2+), under simulated solar light. We observed that the redox state of the melanin-based electrodes affects its photoreponse. Our work constitutes a relevant contribution towards (photo)electrodes for sustainable, aqueous, rechargeable solar batteries.


Comparison of Stress Evolution in Silicon and Silicon Oxide Composite Electrodes
Mok Yun Jin1, Ravi Kumar2 and Brian W. Sheldon1; 1Brown University, Providence, Rhode Island, United States; 2Ram Research Corporation, Tualatin, Oregon, United States.

Silicon has received much attention as a promising negative electrode material, owing to its greater theoretical capacity than state-of-the-art graphite negative electrodes. Silicon, however, undergoes internal microstructural changes and large volume changes that induce substantial compressive stresses inside of particle-based electrodes. These are believed to contribute to poor cycling performance.

In the present work, in-situ stress and electrochemical measurements are monitored directly to capture stress evolution in silicon and silicon oxide composite electrodes with various particle sizes. Silicon nanoparticle electrodes reveal a stress response with notable hysteresis characterized as plastic flow. When silicon oxide(SiOx) is incorporated, the cycling performance improves and the amount of stress decreases. The stress response of electrodes based on SiOx composite particles also shows more reversible and elastic behavior compared to electrodes with silicon nano particles.

High Tap-Density and Layer-by-Layer Assembled LiFePO4 Nanosheets as Advanced Cathode Materials used in High Power Li-Ion Batteries
Hajian Zhang1, 2, Ben Pei1, Lu Zhang1, Wenwu Qin2, Jun Zhang1 and Jiye Fang1; 1SUNY Binghamton, Binghamton, New York, United States; 2Lanzhou University, Lanzhou, China; 3China University of Petroleum, East China, Qingdao, China.

As a class of outstanding cathode material for lithium-ion (Li-ion) batteries, LiFePO4 has an obstacle of low rate capability due to its slow Li ionic diffusion and poor electronic conductivity as well as power density issue. To improve this, one should shorten the channels of Li-ion travelling (i.e. reduce the dimension of LiFePO4 in <010>), and enhance the particle impact on the same crystallographic orientation. According to this hypothesis, one of the proposals is to produce 2D LiFePO4 as the building block materials by exposing their {010} facets as the termination planes, and to further pack these 2D LiFePO4 along the <010> direction efficiently. Herein, we report a novel synthesis of ultrathin 2D LiFePO4 nanosheets using a modified hot organic solvent approach. The structure of the resultant LiFePO4 is precisely controlled with some unique features: the nanosheets exhibit in shape of rectangle with a thickness of as small as ~10 nm. Importantly, the exposed planes are {010}, which can maximize the channels for the travel of Li-ions. Calcination of the oleylamine/oleic acid capped LiFePO4 nanosheets resulted in densely hierarchical structures containing Layer-by-Layer stacked assemblies with a tap density as high as 1.3 g cm⁻³. In contrast, the tap density of freestanding LiFePO4 nanomaterials is usually less than 1.0 g cm⁻³. The in-situ generated carbon blacks from the pyrolysis of the capping ligands act as not only a medium conductor for the electrons but also a baffle to possibly prevent the nanosheets from fusing into larger particles during the calcination. With such an in-situ carbon coating evenly on every single nanosheet, the 2D LiFePO4/C composite nanosheets self-assembled into superstructures. The electrochemical evaluations on these LiFePO4/C assemblies show a reversible specific capacity of as high as 105 mAh g⁻¹ at 10 C, as well as an excellent rate capability and cycling performance. Both the high tap density and high-rate capability are promising for the increase of volumetric power and energy density as Li-ion cathodes. Such layer-by-layer compacted patterns, rather than an accumulation of disordered building blocks, could also effectively increase both gravimetric and volumetric power densities of LiFePO4 electrodes, paving the way for promoting high-rate capacity and minimizing the ionic diffusion issue by shortening the length of Li-ion travelling channels.

Capacitive Performance of C60-Functionalized Graphene Supercapacitors—Atomistic Origins and Implications
Tuan Anh Pham1, Cheng Zhan1, 2, Maira Raquel Ceron Hernandez1, Patrick G. Campbell1, Vedasri Vedharathinam1, Minora Otani1, De-en Jiang2, Juergen Biener1, Brandon C. Wood1 and Monika Biener1; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2University of California, Riverside, Riverside, California, United States; 3National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Controlling the electrical response at the electrode-electrolyte interface is key to the development of next-generation supercapacitors and other electrochemical storage systems. In this work, we utilize first-principles calculations to elucidate the key factors that determine the performance of C60-functionalized graphene as a promising carbon-based supercapacitor material. We show that, for the hybrid electrode, the surface morphology influences the electric double-layer (EDL) formation by affecting the charge localization character, which in turn significantly enhances the EDL contribution to the capacitance, in sharp contrast to pristine graphene. In addition, the electronic structure was found to govern not only the quantum capacitance but also the double-layer response. Our study highlights a complex interplay among surface morphology, electronic structure and functionality of the hybrid electrode, suggesting general improvement strategies for optimizing EDL and total capacitance in carbon-based supercapacitor materials.
Lithium-ion battery (LIB) is widely utilized in many modern applications as energy sources. Numerous efforts have been dedicated to increasing electrochemical performances, but improvement on battery safety remains a visible challenge. While new electrode materials have been developed, advancement in new separators for LIBs has remained relatively slow. A separator is the polymeric porous material that physically separates electrodes and allows free flow of ions through its structure. It is electrochemically inactive but essential for avoiding thermal runaway conditions. Besides its crucial functions, the separator has been known as the mechanically weakest component. Structural battery is a new approach that employs a multifunctional material concept to use LIB as a load-bearing material to minimize the weight of the complete system and maximize the efficiency. Separator materials are required to have good thermal stability, battery chemistry, and mechanical performance. This work aims at creating electrospun membranes with improved thermal resistance and structural integrity as the next generation LIB separators. The electrospinning (ES) is known as a versatile and straightforward technique to fabricate continuous fibers at nano- and micro-scale. Solution and process parameters including, type of polymer and solvent system, concentration of polymer solution, acceleration voltage, and solution feed rate have been studied to achieve the desirable membrane properties. Adding various ceramic materials to the polymers have been studied for improving the thermal shrinkage, increasing ionic conductivity and, decreasing interfacial resistance of the composite separators. In this study, nanofibrous membranes are created by the electrospinning process. Graphene oxide is used due to its high storage modulus. Synthesized, non-conductive graphene oxide and titanium dioxide nanoparticles (for comparisons) are incorporated into the polymer solutions for the electrospinning. In this presentation, we will discuss the control of electrospinning process, graphene oxide synthesis and properties of composite membranes for structural battery applications.

ET03.06.16
Facile and Cost effective Synthesis of Ultradense and Porous Nitrogen Enriched Carbon Hollow Shells for Energy Storage Application
Gihwan Kim1 and Jeung Ku Kang2, 1; 1Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea
(Republic of); 2Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea (Republic of).

Mesoporous carbon materials have received intensive attention due to their wide applications including energy storage/conversion, catalysis and adsorption applications. Herein, ultradense and porous nitrogen enriched carbon hollow shells have been synthesized by a facile and cost effective sol-gel coating method using different ratio of carbon precursor and nitrogen precursor. As-synthesized hollow shells possessed uniform size of ~120nm in diameter and ~4.5nm significantly thin, porous shells obtained from silica template that size controlled by solvent ratio. As the ratio of nitrogen precursor increased, thinner and smaller shells were synthesized. In lithium ion hybrid capacitor system, cathode electrode material is storing electrical energy through electrical double-layer capacitance mechanism of electrode surface. Based on these mechanisms, as-synthesized ultradense and porous nitrogen enriched carbon hollow shells used as a cathode material of lithium ion hybrid capacitor. It is shown remarkable electrochemical performance, delivering a high reversible capacity (~48mAh/g in 3.0V~4.5V (Li/Li+) potential range) as well as superior rate performance for long cycles in an organic solvent system. These excellent results can be attributed to two major reasons. First, hollow and porous structures could improve the properties of surface adsorption for lithium ion capacitor by facilitating the accessibility of ions. Sites from both inside and outside of carbon shell can be accessed by PF6- ions, whereas the closed window of the pore for solid sphere can offer the sites for electrostatic adsorption only on the outside surface. Second, nitrogen contents could significantly change the interaction sites and enhance the adsorption of ion towards a carbon shell framework. These effects are also shown in capacity analysis of various synthesized samples with different amounts of nitrogen precursor. As the nitrogen content increased, the capacity tended to increase. Even in the case of carbon precursor only, the capacity is less than half of that of nitrogen contained hollow shells. This simple and cost effective strategy could be extended to synthesize tunable interior architecture mesoporous carbon composites like yolk-shell structure and core-shell structure with metal, metal oxide. Also, due to the characteristic of the nitrogen-containing material, it can be applied to various ions adsorption. By applying this phenomenon, it can be utilized not only for commercial carbon material like an electric double layer capacitor (EDLC) but also for various electrochemical energy storage and conversion applications.

ET03.06.17
Electrochemical Behaviors of Room Temperature Ionic Liquids—Carbon Electrodes Interfaces
Kirti Bhardwaj and Greg Swain; Michigan State University, East Lansing, Michigan, United States.

Room temperature ionic liquids (RTILs) have great potential to replace conventional organic solvent/electrolyte systems in energy storage devices because of their remarkable properties like wide electrochemical potential window (>4V), environmentally-benign characteristics (non-volatility, non-toxicity) and excellent thermal and electrochemical stability. To optimally harness these properties and engineer RTIL-based devices, a comprehensive fundamental understanding of their electrochemical behavior is critical. Understanding the structure, distal extent, and dynamics of interfacial organization at RTIL-carbon electrodes interfaces has been the subject of both fundamental and applied research, particularly in the field of supercapacitors. Research is needed to better understand how electrode properties, like its material, microstructure, surface chemistry, affect the electrochemical behavior of RTILs. Traditional models of the electrochemical double layer based on the dilute-solution approximation may not be applicable to RTILs because of the absence of solvent, high concentration of ions (3–5 M), asymmetric charge distribution and strong interionic interactions. In this presentation, potential dependent capacitance of carbon electrodes as a function of the RTIL type, carbon electrode type and surface wettability will be reported on. 1-alkyl-3-methylimidazolium-based RTILs were studied at hydrogen- and oxygen-terminated boron-doped diamond and nitrogen-incorporated tetrahedral amorphous carbon thin-film electrodes. Comparison measurements were made in aqueous electrolytes. Cyclic voltammetry and electrochemical impedance spectroscopy were used to measure the interfacial capacitance. Our findings suggest that interfacial capacitance depends on the length of alkyl chain in the cationic component of RTIL. Capacitance-potential (C-E) trends on carbon electrodes are in stark contrast with theoretical models predicted for metallic electrodes. It is intriguing that heavily-doped diamond behaves as a metal with respect to faradic processes have characteristic interfacial behavior. This work highlights the unique C-E trends shown by carbon electrodes in RTILs and serves to progress the current understanding of interfacial organizations and the role of electrode-electrolyte interactions.

ET03.06.18
Freestanding 2D MXene/Polyaniline Pseudocapacitive Electrodes with High Mass loading and Ultrahigh Gravimetric and Volumetric Capacitances
Armin VahidMohammadi and Majid Beidaghi; Auburn University, Auburn, Alabama, United States.

Two-dimensional (2D) MXenes (i.e. Ti3C2Tx) have shown fascinating performances as electrode materials for electrochemical capacitors (ECs). However, conventional methods for fabrication of freestanding MXene films results in their self-restacking, decreasing ionic accessibility to their redox-active sites and limiting their rate-capability. These problems are more significant for thicker electrodes and, as a result, fabrication of MXene electrodes with thicknesses and mass loadings close to commercial EC electrodes is not feasible. Here, we demonstrate a strategy to fabricate hybrid electrodes of MXene and conductive polyaniline (PANI) with highly accessible surfaces and excellent electrochemical performance event at high mass-loadings and thicknesses. The freestanding and flexible films of Ti3C2Tx/PANI were fabricated through an oxidant-free in situ polymerization of aniline monomer on the surface of MXenes sheets. The fabricated hybrid electrodes delivered outstanding gravimetric and volumetric capacitances of 503 F g⁻¹ and 1682 F cm⁻³, respectively, at a scan rate of 2 mV s⁻¹. Even at electrode thicknesses close to commercial ECs, these hybrid electrodes could maintain their high specific capacitance. For instance, a 90-µm-thick electrode with a mass loading of 23.82 mg cm⁻² could deliver a specific capacitance of about 336 F g⁻¹ and 888 F cm⁻².
The best agreement is achieved by constructing a novel cluster expansion for alloy nanoparticles of varying shape and size that explicitly includes experimentally relevant sizes can be prohibitively expensive. It has been demonstrated that this problem can be addressed through the generation of cluster Density functional theory (DFT) is widely used to predict the structures and properties of materials, but its direct applications to nanomaterials of reaction (CO2RR) on Au nanowires. Nanowires with the 4H structure have shown enhanced activity relative to fcc nanowires and nanoparticles. Cluster expansion models trained by DFT. In this talk, two examples of using cluster expansions to better understand structure-property relationships in Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

In recent years, alloy anion exchange membrane fuel cells (AAEMFCs) have a rapid development due to their advantages including high electrode reaction activity, free from precious metal catalysts, low fuel permeation and so on. However, anion exchange membrane (AEM), which is a crucial component in AEMFCs, continue to perform unfavorably owing to its low conductivity and poor alkaline stability. Thus, constructing novel hydroxide-conducting materials with both high ionic conductivity and good alkaline stability for AEM has attracted wide interest. Herein, we have designed and synthesized a new hybrid membrane with high alkaline and thermal stability via combining quaternary ammonium (QA) functionalized covalent organic framework and brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO). Covalent organic framework was quaternized via in situ assembly of N,N,N’,N’-tetramethyl-1,6-hexanediamine (TMHDA) and allyl bromide within the highly ordered pores of two-dimensional imine-linked COF-LZU1, to fabricate long-range ordered one dimensional ion channels. The obtained QA@COF-LZU1 as a novel filler was then incorporated into QAPPO to fabricate hybrid anion exchange membrane for the application in AAEMFCs. Hybrid membranes were evaluated by hydroxide conductivity, alkaline stability, thermal stability, and so forth. Remarkably, the QA@COF-LZU1/PPO hybrid membranes showed high hydroxide conductivity, and alkaline and thermal stability of QA@COF-LZU1/PPO hybrid membranes were significantly enhanced.

8:15 AM ET03.07.02
Understanding Structure-Property Relationships in Nanocatalysts by Using Cluster Expansions Chenyang Li1, David Raciti2, Yuxuan Wang3, Liang Cao4, Chao Wang4 and Tim Mueller5; 1Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 2Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Density functional theory (DFT) is widely used to predict the structures and properties of materials, but its direct applications to nanomaterials of experimentally relevant sizes can be prohibitively expensive. It has been demonstrated that this problem can be addressed through the generation of cluster expansion models trained by DFT. In this talk, two examples of using cluster expansions to better understand structure-property relationships in nanocatalysts are given. In the first example, we compare predicted Pt-Cu nanoparticle structures with experimental characterization. We demonstrate that the best agreement is achieved by constructing a novel cluster expansion for alloy nanoparticles of varying shape and size that explicitly includes adsorbates, enabling the prediction of nanoparticle structure in an oxidizing environment. In the second example we present a study of the CO2 reduction reaction (CO2RR) on Au nanowires. Nanowires with the 4H structure have shown enhanced activity relative to fcc nanowires and nanoparticles. Cluster expansions are used to predict the equilibrium surface structures of fcc, 4H, and twinned nanowires. DFT calculations are then performed on the extended surfaces identified from cluster expansions to construct a free energy diagram for CO2 reduction. The enhanced CO2RR activity on 4H-Au nanowires is ascribed to the unique surface structure of the 4H phase, which could provide design principles for experimental research.

8:30 AM ET03.07.03
Nanoparticle Catalysts for Electrochemical Transformation of Carbon Dioxide to Value-Added Products Peidong Yang1, 2 and Dohyung Kim3, 4. 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Electrochemical conversion of CO2 to valuable products has gained much interest recently, as a part of the many efforts to develop sustainable practices that can support our society. Among a variety of approaches, utilizing nanoparticles as CO2 electrocatalysts have brought significant advances to the field. Here, various structural aspects of nanoparticles used as electrocatalysts, that range from the atomic scale all the way to the macroscopic length scales, are correlated with their CO2 electrocatalytic performances. Furthermore, the catalytic role of the dynamics of nanoparticles has been explored which can be utilized to promote their CO2 reduction activity. The complexity originating from the larger number of structural variables associated with nanoparticles requires a deepened understanding of their combined effects to the catalytic behavior of nanoparticles. Acknowledging this complexity and a thorough consideration of its impact will lead to further improvements of nanoparticles used as CO2 electrocatalysts.

9:00 AM ET03.07.04
Electrochemical Synthesis of Highly Concentrated C2 Product Streams Matt Kanan; Chemistry, Stanford University, Stanford, California, United States.

Electrochemical CO2 and CO conversions provide direct pathways to harness renewable electricity for chemical and fuel synthesis. This talk will describe our recent work to develop catalyst- and cell-design principles for electrochemical systems that generate concentrated C2 product streams. For the catalyst, a key issue is to identify structural features that favor CO2/CO reduction over H2O reduction at low overpotentials. We have previously shown that grain boundaries are correlated with electrocatalytic activity for CO2 reduction on Au and CO reduction on Cu electrodes, but not with H2O reduction on these materials. We will describe our recent work to uncover the structural origin of grain boundary effects. Experimental studies combining electron diffraction and spatially resolved (<1 µm) electrocatalytic measurements have revealed that grain boundary surface terminations are “hot spots” for electrocatalytic CO2 reduction on coarse-grained Au electrodes. This phenomenon may result from the accumulation of line defects in the grain boundary vicinity, which perturb the surface structure. I will discuss our efforts to test this model with nanograined materials and extend these studies to electrochemical CO2 reduction on Cu. For the cell design, electrocatalytic synthesis must simultaneously achieve high synthesis rates and high single-pass conversions of CO2/CO at low potentials to maximize the energy efficiency and minimize the separation costs. To this end, we have developed a gas-diffusion CO electrolysis cells that reach >100 mA cm–2 with >70% single-pass conversion at moderate cell potentials. With optimized electrode/membrane interfaces, the cells can simultaneously produce concentrated ethylene in the gas phase and a liquid product stream that is nearly 1 M in acetate. I will discuss the design features that are critical for generating concentrated products and efforts to optimize nanostructured catalysts for high synthesis rates.
Utilization of CO₂ as a feedstock for the production of intermediates for chemical or fuel production such is one of several approaches being explored to help reduce anthropogenic CO₂ emissions, while also reducing society’s dependence on fossil fuel reserves. A range of active electrocatalysts for the selective reduction of CO₂ to products such as formic acid, CO, ethylene, and ethanol have been reported. We have explored both Ag- and Au-based catalysts as well as micro-structured CuAg alloy films, respectively for the selective and energy efficient reduction of CO₂ to CO [1,2] and to ethylene and ethanol [3]. Partial current densities for CO exceeding 150 mA/cm² at cell overpotentials less than 1V now can be achieved readily at energetic efficiencies of 50-60%. Similarly, high surface area CuAg alloy films exhibit Faradaic efficiency for C₂H₄ and C₂H₅OH production of 60% and 25%, respectively, at a cathode potential of just ~0.7 V vs RHE and a total current density of ~300 mA/cm², the highest levels of selectivity at high activity and low applied potential reported to date. This talk will report mechanistic insights regarding CO₂ electroreduction on these different catalysts in alkaline electrolyte. E.g., the onset cathode potentials, the kinetic isotope effect, and Tafel slopes indicate that the production of CO at low overpotentials in alkaline media is the result of a pH-independent rate-determining step (i.e., electron transfer) in contrast to a pH-dependent overall process. Also, in situ Raman and electroanalysis studies suggest that the origin of the high selectivity toward C₂ products observed with CuAg alloy films results from both the enhanced stabilization of the Cu₂O overlayer and the optimal availability of the CO intermediate due to the Ag incorporated in the alloy. The talk will also provide a summary of techno-economic feasibility of CO₂ electrolysis for the production of these different intermediates.

Gold Nanoparticles on Polymer-Wrapped Carbon Nanotubes: An Efficient and Selective Catalyst for the Electroreduction of CO₂ to Ethylene and Ethanol, T.T.H. Hoang, S. Verma, M. Graetzel, and Y. Surendranath; 1Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Chemistry and Chemical Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

CO₂-derived fuels, electrochemically synthesized using renewable energy, present an attractive route towards fuel formation from sustainable energy. However, insufficient understanding of the factors controlling catalytic activity and selectivity, as well as the limited availability of selective, active and inexpensive catalyst materials remain key challenges on the way to the production of renewable carbon fuels. Copper is a particularly interesting electrocatalyst for this reaction since it can reduce CO₂ to a variety of products including carbon monoxide and hydrocarbons but rational modification of its selectivity towards a single product remains challenging. In this context, we here demonstrate the successful tuning of copper electrocatalysts towards the selective production of CO from CO₂ and we present unprecedented insight into the mechanistic pathways governing the electrochemical reduction of CO₂ to hydrocarbons on copper surfaces. Atomic Layer Deposition (ALD) is introduced as a versatile tool for the modification of electrocatalyst selectivity. By ALD modification with thin layers of SnO₂, the wide product distribution observed from CuO-derived nanowires could be narrowed to yield predominantly CO at low overpotentials, a feat which normally requires gold catalysts. The origin of this performance modification is investigated on the basis of kinetic studies, HR-STEM and gas chemisorption analysis. Operation of the SnO₂-CuO catalyst is subsequently demonstrated in an all Earth-abundant electrolysis cell using a bipolar membrane, allowing for the separation of product gases while maintaining a sustained pH gradient. Driven by a 3-junction solar cell, this device achieved long-term solar splitting of CO₂ into CO and O₂ at an efficiency of 13.4 %, constituting the current record.

10:45 AM ET03.07.07
Metal Ion Cycling of Cu Foil for Selective C–C Coupling in Electrochemical CO₂ Reduction Huotian Wang, Harvard University, Cambridge, Massachusetts, United States.

Electrocatalytic CO₂ reduction to higher-value hydrocarbons beyond C₁-products is desirable for applications in energy storage, transportation and the chemical industry. Cu catalysts have shown the potential to catalyse C–C coupling for C₂+, products, but still suffer from low selectivity in water. Here, we use density functional theory to determine the energetics of the initial C–C coupling steps on different Cu facets in CO₂ reduction, and suggest that the Cu(100) and stepped (211) facets favour C₂+ product formation over Cu(111). To demonstrate this, we report the tuning of facet exposure on Cu foil through the metal ion battery cycling method. Compared with the polished Cu foil, our 100-cycled Cu nanocube catalyst with exposed (100) facets presents a sixfold improvement in C₂+/C₁ product ratio, with a highest C₂-Faradaic efficiency of over 60% and H₂ below 20%, and a corresponding C₂+ current of more than 40 mA/cm².
Electrocatalytic reduction of carbon dioxide (CO₂) to value-added carbon-based chemical feedstocks addresses the need for long-term storage of renewable electricity and decarbonization of the transportation sector. Liquid multi-carbon alcohols such as ethanol and n-propanol are desired as renewable transportation fuels. They offer high energy densities, ease of long-range transport, and direct drop-in usage in existing internal combustion engines.

Engineering copper-based catalysts that favor high-value alcohols is desired. In the design of catalysts, much progress has been made to target deliberately the C–C coupling step; while comparatively little effort has been expended to target post-C–C coupling reaction intermediates.

Among electrocatalysts for CO₂ reduction, Cu-based materials are the most prone to reduce CO₂ to C₂ and above products, with alkenes traditionally dominating multi-carbon product formation. To develop more efficient electrocatalysts for alcohol production, it is crucial to modify the catalyst structure to promote the desired alcohol and suppress alkene electrosynthesis. Additionally, it is vital to understand the mechanisms that underlie selectivity to enable further catalyst refinement. We reasoned that—since ethylene and ethanol share a penultimate reaction intermediate (\(\text{C}_2\text{H}_3\text{O}\))—we could potentially modify a catalyst’s surface structure to target the hydrogenation of this intermediate, and thereby promote \(\text{C}_2\) liquid production. Suppressing off-produced ethylene would enhance production and selectivity towards alcohols.

Here we report a class of core/shell vacancy engineering catalysts that utilize sulfur atoms in the nanoparticle core and copper vacancies in the shell to achieve efficient electrochemical CO₂ reduction to propanol and ethanol. These catalysts shift selectivity away from the competing ethylene reaction and toward liquid alcohols. We increase the ratio of alcohol-to-ethylene by over 6x compared to bare-copper nanoparticles, highlighting an alternative approach to electroproduce alcohols instead of alkenes. We achieve a C₂+ alcohol production rate of \(126 \pm 5\) mA cm⁻² with a selectivity of \(32 \pm 1\%\) Faradaic efficiency.


11:15 AM ET03.07.09
Photoelectrochemical CO₂ Reduction with Nanoporous Au Electrodes

Mya Norman, Peter J. Reed and Robert H. Coridan; University of Arkansas, Fayetteville, Arkansas, United States.

Here we report a large-area, catalytically-active and highly stable nanoporous gold (np-Au) electrode for (photo)electrocatalytic CO₂ reduction in aqueous electrolytes. A one μm thick np-Au electrode has a 27x larger electrochemical activity than a comparable planar Au film, owing to increased surface area. The np-Au structure is fabricated via electron beam co-deposition of a gold/silver (Au/Ag) alloy of tunable elemental composition (10/90 to 30/70) and variable thickness (0.1 μm to 2 μm), followed by a chemical etch of silver with nitric acid to yield a monolithic, np-Au structure. Depending on the etching temperature, we can alter the Au feature size from 10 nm to 25 nm. The np-Au also possesses near-unity absorption throughout a broad portion of the visible spectrum from 400 nm to 600 nm. Gas chromatography indicates H₂ and CO as the main CO₂ reduction products from np-Au electrodes in a 50 mM K₂CO₃ buffer. Although produced in a similar CO₂:H₂ product ratio vs applied potential as that obtained for planar Au electrodes, the increased surface area results in significantly higher partial current densities for CO than planar Au. Chronoamperometry measurements indicate stable np-Au electrode operation over periods exceeding 24 h at a potential of ~0.5 V vs. RHE and a cathode current of ~6 mA/cm². The faradaic efficiency remains similar across different thickness and etch temperatures, although the current does increase as the surface area of the np-Au layer increases. These np-Au electrodes show a photocatalytic response marked by an increase in current density of ~1mA/cm² upon irradiation with white light at an incident power of 1.5 W/cm². Changes in the product selectivity observed from np-Au photocathodes as a function of electrolyte temperature, illumination wavelength, and incident light power will be discussed. In summary, np-Au electrodes exhibit both high electrocatalytic activity and sustained electrochemical stability, making them interesting candidates as cathodes for (photo)electrochemical CO₂ reduction.

11:30 AM ET03.07.10
Influence of Graded Mesoporosity on CO₂ Reduction Reaction on Copper

Mya Norman, Peter J. Reed and Robert H. Coridan; University of Arkansas, Fayetteville, Arkansas, United States.

Carbon dioxide reduction reaction (CO₂-RR) provides an environmental friendly way to convert readily available resources such as carbon dioxide and water to produce high-valued chemicals and energy-dense fuels to address the energy storage challenge. In this work, we compare the CO₂-RR on the planar copper electrode vs. mesoporous copper as a function of microstructure and pore sizes. The hypothesis is that mesoporous copper can recapature the intermediate(s) such as carbon monoxide for further reduction. We prepare the model graded mesoporous copper electrodes using electroless plating on the template formed by self-assembled trilobal terpolymer and control the pore sizes by tuning the phase separation. On these copper electrodes, we quantify the CO₂-RR products over a fixed potential range and compare the results to that of planar polycrystalline copper. We will discuss the product distribution as a function of pore sizes and new insights from this analysis in the context of the intermediate confinement and how they can be applied to the future design of CO₂-RR catalyst.

11:45 AM ET03.07.11
Photoelectrodes Fabricated by Selective Atomic Layer Deposition in Self-Assembled, Composite Colloidal Films

Mya Norman, Peter J. Reed and Robert H. Coridan; University of Arkansas, Fayetteville, Arkansas, United States.

Hierarchically structured materials are employed for applications that depend on the coordination of chemical and physical processes that function on disparate length scales. An example is photoelectrochemical energy conversion, where the electrode structure must optimize the balance of light absorption, carrier collection at a semiconductor-liquid junction, electron transfer, and mass transport of reactants in order to maximize the energy conversion efficiency of the system. Strategies for designing electrodes generally depend on techniques borrowed from semiconductor fabrication, which allow precise control for prototyping, but are not readily transferrable to the development of scalable materials. Here we describe the fabrication of hierarchically structured electrodes based on selective atomic layer deposition of ZnO in composite colloidal films. The distinct chemical susceptibilities of SiO₂ and polystyrene nanospheres can be used to generate hierarchically porous materials. By choice of the initial colloidal components, the characteristic length scales for light absorption, carrier collection, and mass transport can be independently engineered into a thin film electrode for photoelectrochemical applications. Optimized nanostructured conductive scaffolds can be prepared with a facile, continuously tunable, solution-phase synthesis. This approach offers a scalable route for synthesizing nanostructured photoelectrodes based on strategies developed from more complex fabrication techniques.
SESSION ET03.08: Interface and Beyond-Li Batteries
Session Chairs: Wei Li and Nian Liu
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 302

1:30 PM *ET03.08.01
Safe Li-Ion Battery Electrolytes—From Aqueous, Nonflammable Organic to Solid State Chuansheng Wang; University of Maryland, College Park, Maryland, United States.

Li-ion batteries are the critical enabling technology for the portable devices, electric vehicles (EV), and renewable energy. However, the safety of current battery still need to be improved to satisfy these requirements. We systematically investigated the electrochemical stability window of the electrolytes, interface/interphase stability and resistance between electrodes and electrolytes, reversibility and robustness of the cells using these electrolytes. The critical issues limiting these safe electrolytes will be discussed.

2:00 PM *ET03.08.02
Interface Design and Materials in Batteries—From Liquid to Solid-State Xueliang A. Sun; University of Western Ontario, London, Ontario, Canada.

The control and understanding of reactions at the electrode/electrolyte interface (EEI) is essential to develop strategies to enhance cycle life and safety of lithium batteries. The poor cell lifetimes of Li/Na batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of surface coatings to control the electrode-electrolyte interface is an important strategy to design new electrodes. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are ideal techniques to synthesize ultrathin and conformal coatings due to the self-limiting nature [1,2,3]. This talk will include three parts related to interface control:

In the first part, we will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries including coating materials on NMC cathode in Li ion batteries[4,5] and MLD coating on Li-S batteries operating at 55C [6].

In the second part, we will discuss our recent results on ALD and MLD coatings on Li metal protection and interface control between solid-state electrolyte and cathode/anode materials for solid-state batteries [7-10].

Reference:
[10] C. Wang, X. Sun et al., submitted, 2018

2:30 PM BREAK

3:30 PM ET03.08.03
Ionic Liquids and Dilute Electrolytes—The Surprising Connection Matthew A. Gebbie1 and Jacob N. Israelachvili; 1Stanford University, Stanford, California, United States; 2University of California, Santa Barbara, Santa Barbara, California, United States.

Solid-electrolyte interfaces are critical elements of many electrochemical devices. Nevertheless, key questions surround the nature of solid-electrolyte interfaces in highly concentrated electrolytes, particularly in nanoconfined environments. I will discuss using a novel technique that combines molecular force measurements with in situ electrochemical spectroscopy to characterize nanoscale ionic liquid-electrode interfaces. As single component liquids composed entirely of ions, it was thought that ionic liquids contain extremely high free ion densities. Yet, the conductivities of most ionic liquids are orders of magnitude lower than aqueous electrolytes. I will present our discovery that the electric double layers formed by ionic liquids can extend more than 20 ion diameters away from charged surfaces, indicating that greater than 99.99% of the ions actually behave as neutral pairs, in equilibrium with a small population of thermally-dissociated charges. This picture provides insight into the low conductivities of typical ionic liquids, and I will also highlight a molecular framework for designing high performance ionic liquids. More broadly, our findings suggest new ways of envisioning concentrated electrolytes in nanoconfined interfaces, with implications for understanding diverse electrochemical processes in nanoscale materials.

3:45 PM ET03.08.04
Interfacial Interaction between Chemically-Engineered Copper Host and Metallic Sodium for Facilitating Highly Stable Sodium Metal Anode Chuanlong Wang, Huan Wang, Edward Matios, Xiaofei Hu and Weiyang Li; Dartmouth College, Hanover, New Hampshire, United States.

Sodium (Na) metal is the most promising alternative for lithium metal as an anode material for the next-generation energy storage systems due to its high theoretical capacity, low cost and high natural abundance. However, huge volume change and severe dendrite growth of Na metal anode during repeated electrochemical stripping/plating cycles result in rapid electrode degradation, low Coulombic efficiency, and even the risk of explosion caused by short circuit of the batteries. The volume and morphology change of the “hostless” Na severely aggravates the growth of Na dendrites. Thus, it is essential to seek an ideal host to support Na metal so as to maintain the high integrity of the electrode. Despite the most recent research in using porous carbon or aluminum substrate as Na host, current research in Na metal is still in its infancy, and the exploration on promising matrices for Na metal anode is highly desirable. More important, a systematic and thorough understanding on the interfacial interaction between metallic Na and the host materials as well as its impact on the stability of Na metal anode is critical, but missing.

Through a facile and cost-effective surface treatment on commercially available Cu foam, a chemically engineered 3D porous copper (Cu) matrix with a cylindrical core-shell skeleton structure as a highly stable host for metallic Na anode was manufactured as a composite anode for Na-based batteries. It is noted that the unique surface characteristics of the as-obtained matrix can not only facilitate uniform impregnation and confinement of Na within the matrix pores promoted by the chemical interaction between Na and the matrix, but also can divert the Na plating from the matrix skeleton towards the Na reservoirs within the pores upon cycling. These special features significantly suppress the volume change and dendrite Na growth over repeated Na stripping-plating process. Benefiting from the delicately surface-engineered matrix as a host for Na, an excellent Na anode cycling stability in carbonate
electrolyte without any additives over 100 cycles (300 hours) at a current density up to 2 mA cm$^{-2}$ with a high cycling capacity up to 3 mAh cm$^{-2}$. A full cell made of Na$_3$V$_2$(PO$_4$)$_3$ as cathode and the as-prepared surface-treated Na composite as anode is further tested, showing superior cycling performance and high rate capability (at 5C) compared with that using bare Na metal as anode.

To fundamentally understand performance improvement, we systematically investigated the interfacial interactions between treated/un-treated Cu matrices and metallic Na to reveal how the surface property of the matrix skeleton greatly influences the electrochemical stability of Na anode. We believe that our approach provides a facile and low-cost route to the fabrication of stable Na metal anode for high-energy Na-based batteries, and could be a viable strategy for other metallic anode systems.

All-solid-state Li batteries using inorganic solid electrolytes are attracting intensive research interests due to the highest safe system and high energy densities. However, these systems are still confronted with major challenges in terms of rechargeability, cycling stability, Coulombic efficiency and rate performance, which are far from commercialization.[1]

The fatal weaknesses of all-solid-state Li batteries are poor Li$^+$ and electron transports between the electrode and the electrolyte. Unlike batteries with liquid electrolytes that can easily wet the electrodes and ensure smooth Li$^+$ transport, the Li$^+$ transport in solid-state batteries is highly limited at the electrode-electrolyte interface. Although many of sulfide-based solid-state electrolytes exhibit high Li$^+$ conductivities (10$^{-4}$ to 10$^{-3}$ S cm$^{-1}$ at room temperature),[2] the Li$^+$ transport through the interface can be lagged by several orders of magnitude. For instance, the Li$^+$ conductivity of Li-argyrodite phase Li$_2$PS$_3$Cl electrolyte is reported as high as 1.3×10$^{-3}$ S cm$^{-1}$ as a bulk, but the conductivity is dramatically reduced to 10$^{-11}$ S cm$^{-1}$ at the interface with the Li$_2$S cathode.[3]

Therefore, developing new cathode materials with compatible interface between electrode and electrolyte to achieve high Li$^+$ transport in the interface and high electronic conductivity in the electrochemical active electrode particles is one of the main point to realize the high performance all-solid-state Li batteries. Herein, all-solid-state Li-Se battery chemistry with the commercial Li$_2$PS$_3$Cl electrolyte was achieved. Apart from the high electron conductivity (1×10$^{-3}$ S cm$^{-1}$) of Se, a high Li$^+$ conductivity of 1.4×10$^{-3}$ S cm$^{-1}$ across the Se-Li$_2$PS$_3$ interface can be achieved. Such high Li$^+$ conductivity within the interface should be due to the formation of interfacial species of PS$_4$-Se$_3$ proved by in-situ Raman test. The Se cathode exhibited significantly high electrochemical kinetics process with high utilization and low polarization during cycling. All-solid-state Li-Se cell showed a high reversible capacity of 652 mAh g$^{-1}$ (96% of theoretical capacity) and good cycling stability with 585 mAh g$^{-1}$ remained after 100 cycles at room temperature. This work demonstrates all-solid-state Li-Se batteries as promising high-energy storage system and provides new insights of the solid-state electrode/electrolyte interfacial chemistry.[4]

Reference


Next-generation air-breathing cathodes in alkaline fuel cells and metal–air batteries will require discovering and formulating catalysts with higher activity for the reduction of molecular oxygen (ORR catalysis) and for the oxidation of water/hydroxide back to O$_2$ (OER catalysis). Strategies to enhance electrocatalytic activity. A single variable does not serve as a definitive predictor of catalytic performance, whether that variable is surface area, crystallite size, porosity, or some other factor. For example, the activity of catalysts can be enhanced by increasing the surface area, which can be achieved by increasing the particle size or by introducing defects into the crystal lattice. However, increasing the particle size can also lead to decreased activity due to the decreased contact area between the electrode and the electrolyte. Therefore, a balance must be achieved between the two factors.

As an energy storage system, Li-ion batteries are not safe because they use flammable organic electrolytes. A safer alternative is rechargeable Zn-based batteries with aqueous electrolytes. Among them, Zn-air batteries have high theoretical volumetric energy density (4400 Wh L$^{-1}$), which can even compete with lithium-sulfur batteries. Alkaline electrolyte is preferable for Zn-air batteries. However, the performance of Zn anodes in alkaline electrolyte is limited by passivation, dissolution and hydrogen evolution. Through SEM investigation, critical passivation size was found to be ~2 μm. Sub-micron-sized Zn anodes will not have passivation problem. As a result, we focus our research on nanoscale. However, Zn dissolution of nanosized anodes will be accelerated because of large electrode-electrolyte surface area.

Thus, anode modification and protection are needed to alleviate the dissolution. We designed a (1) Zn mesh@GO anode: GO layers on the Zn mesh surface deliver electrons across insulating ZnO and can slow down the Zn dissolution; (2) lasagna-inspired ZnO@GO anode: ZnO nanoparticles encapsulated by GO can solve simultaneously the passivation and dissolution problems; (3) core-shell ZnO@TiN nanorod anode: thin and conformal TiN coating mitigates Zn dissolution, mechanically maintains the nanostucture, and delivers electron to nanorods.

Hydrogen evolution is a competitive side reaction on the zinc anodes, which causes low efficiency of Zn based batteries. Two approaches are investigated.
to suppress hydrogen evolution, including (1) modify the anode with a hydrogen suppressive material: core-shell ZnO@TiO2 nanorod anode was made with hydrogen suppressive TiO2 coating, which solves hydrogen evolution, passivation and dissolution problems at the same time; (2) design a hydrogen evolution suppressive nanostuctured alloy anode: Zn-Ag alloy with increased standard reduction potential was used, which is more competitive compared with hydrogen evolution and more stable in aqueous electrolyte.

All of these anodes show superior performance compared with unmodified anodes. These anodes can be paired with air cathodes to make high energy Zn-air batteries. The nanoscale design principles here can potentially be applied to overcome intrinsic limitations of other battery materials.

4:45 PM ET03.08.08
Spontaneous Corrosion of Mg2Sn in APC Electrolyte Zeyu Wang1,2, Hemant Kumar1, Vivek Shenoy1 and Eric Detsi1; 1Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Materials Science & Engineering, State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, China.

Although the rechargeable battery industry is currently dominated by lithium-ion battery (LIB), there is a growing concern for the limited availability of raw lithium and cobalt resources used in commercial LIBs. The desire to keep pace with a growing market has led to intensive research of alternative rechargeable battery technologies that are safer and utilize earth-abundant elements such as magnesium-ion batteries (MIBs). Progress toward practical MIBs has been halted partly by the absence of suitable electrolytes that are compatible with magnesium (Mg) metal. In particular, most of the simple salts and/or organic solvents containing unsaturated carbon atoms yield a Mg-blocking passive film on metallic Mg. As a result, only a handful of electrolytes including all-phenyl-complex (APC) are compatible with Mg metal as the negative electrode [1]. Despite the huge success of APC for reversible Mg plating, this electrolyte has been reported to corrode current collectors and stainless support in battery cells at operating voltages above 2.2 V vs. Mg, limiting in that way the operating voltage window below 2.2 V vs. Mg. Chloride ion has been pointed out as the corroding agent in APC electrolyte, and this corrosion phenomenon has been investigated only electrochemically when the cell is under a bias voltage. On the contrary, the spontaneous corrosion (i.e. without any applied voltage) in APC of Mg metal and Mg alloys used as anodes in MIBs has been barely reported. In this talk, I will demonstrate that APC electrolyte has adverse effect on MIB anodes even in the absence of applied bias voltage. In particular, we have found experimentally that Mg spontaneously dissolves from Mg2Sn—a very promising MIB anode with in the presence of APC. We attribute this spontaneous corrosion to galvanic replacement, during which at least one of the following anions: Ph4Al-, Ph2AlCl2-, PhAlCl3 and AlCl4− present in APC electrolytes extract electrons from the Mg in Mg2Sn, resulting in Mg dissolution and aluminum metal deposition, as confirmed by X-ray photoelectron spectroscopy in our work. In addition, density functional theory (DFT) was used to determine the redox potentials of Ph4Al, Ph2AlCl2, PhAlCl3 and AlCl4−, in order to confirm that these anions are susceptible to dissolve Mg. This work raises fundamental questions regarding the origin of the relatively poor cycling longevity of alloy-type anodes in MIBs operating in APC electrolytes [2].

References
ET03.09.02
Enhanced Photoelectrochemical Properties of ZnO/Cu2O Heterostructures by Built-in Potential From p-n Cu2O Homojunction
Photovoltaics Joon-Soo Yoon, Joo-Won Lee and Yun-Mo Sung; Korea University, Seoul, Korea (the Republic of).

There have been suggestions integrating a photoelectrochemical (PEC) cell and a photovoltaic (PV) cell, known as PV-PEC cell, to further utilize the sunlight more efficiently. In this system, additional photovoltaic can be obtained from the photovoltaic cell, which makes the maximum of theoretical efficiency much higher than that of single or tandem PEC cell. Herein, we report the fabrication method for n-type Cu2O thin films using the electrodeposition of p-type Cu2O layers and the successive conductivity type transition to n-type by a simple solution treatment. The p-n homojunction was constructed by additional electrodeposition of p-type Cu2O on the n-type Cu2O layers. This approach could allow the fabrication of high-quality p-n Cu2O thin films. Au thin film was sputtered onto p-n Cu2O and ZnO NRs were hydrothermally grown on the Au thin film to complete PV-PEC cells. XRD, SEM, UV-vis spectroscopy analysis were performed to identify each components. The Mott-Schottky analysis, photoresponse measurement and linear sweep voltammetry support the enhancement of ZnO NRs/Au/p-n Cu2O compared to ZnO NRs/Au/n-Cu2O with respect to photovoltage and photocurrent. Finally, band structures are suggested to visualize the working mechanism. The built-in potential occurred spontaneously because of p-n homojunction. The built-in potential offered additional potential so that the photocurrent onset was shifted to the cathodic direction and the photocurrent was increased under illumination. Based upon the band diagram, it was clarified that z-type scheme and the buried p-n junction work effectively for our PV-PEC system. As a result, the enhancement of photocurrent density by 237% was achieved for ZnO-n-pn via the photocurrent-time measurements under 0.2 V vs. SCE.

ET03.09.03
Mesoporous Co/N-Amorphous N-Doped Carbon Nanocubes via Co[Co(CN)6]2 Nanocubes as an Efficient Electrocatalysts for the Oxygen Evolution Reaction Bonkuk Kang1, Sung Hoon Kwag2, Dong H Jeong2, Hyung Wook Cho1, Dae ho Yoon1 and Woo Seok Yang2; Sungkyunkwan University, Suwon, Korea (the Republic of); 1Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

In recent years, the water splitting process with electrocatalytic and photocatalytic, as one of the next generation energy conversion technology for producing hydrogen and oxygen molecules has been widely considered in solving energy and environmental problems. However, half reaction of oxygen evolution reaction (OER) plays a critical role in improving overall conversion efficiency of the water splitting process because the OER system encounters the bottleneck of a kinetically sluggish reaction with multistep proton-coupled electron transfer and considerable overpotential value (> thermodynamic value: 1.23 V). Precious metal and oxide materials (Pt, RuO2, and IrO2) as the superior active catalyst for OER have been used, however, high cost, poor stability, and scarcity of these metals hinder widespread practical use and technique. Hence, extensive research activities have focused on inexpensive earth-abundant metal based materials such as multi-composite transition metal (Ni, Fe, Mn, and Co etc.) compounds (nitride, oxide, and hydroxide), as well as hybrid structures with carbon-based materials (graphite, graphene, and carbon nanotubes (CNT)) as candidate catalysts for alternative developed OER electrocatalyst. Surprisingly, the suitable materials, metal nitrides, are a promising class of electrocatalysts for highly efficient oxygen evolution reaction (OER) because they exhibit superior intrinsic conductivity and have higher sustainability than oxide based materials. Herein, we report successful design and fabrication of unique mesoporous CoNi/amorphous N-doped carbon (AN-C) nanocubes (NCs) based on in-situ nitridation and calcination via Prussian blue analogue (PBA) of Co[Co(CN)6]2 NC precursors. Unique architectures (mesoporous and AN-C hybrid) could assign well dispersed pore, highly active sites, and good durability of Co3N NCs for OER. Mesoporous Co3N@AN-C NCs electrode exhibits outstanding performance of low overpotential of 280 mV at 10 mA cm-2 as well as excellent stability at 20 mA cm-2 in alkaline (1.0 KOH) solution for 24 hours.

ET03.09.04
2 Dimensional Structured Iron Nickel Nitride/Reduced Graphene Oxide Hybrid Composite as Oxygen Evolution Reaction Electrocataysts for Efficient Water Splitting Sung Hoon Kwag1, 2Bongkuk Kang and Woo Seok Yang1; Nano Materials & Components Research Center, Korea Electronics Technology Institute, Gyeonggi-do, Korea (the Republic of).

In water splitting, oxygen evolution reaction (OER) is important process because high overpotential is required to achieve the current density for the reaction. Transition-metal nitrides (TMN) used as electrocatalyst materials for OER are being recently studied because of high yield, easy operation, and excellent catalytic activity by high electrical conductivity. In particular, iron-nickel nitride has very high catalytic activity due to owing to high electro-catalytic and high stability. Reduced graphene oxide (rGO) known as 2 Dimensional (2 D) carbon materials is extensively used as supporting material owing to high conductivity, large theoretical specific surface area, and excellent stability. In this study, we successfully synthesized Fe2Ni2N/rGO hybrid composite for OER electrocatalyst material through two-step process with hydrothermal method and annealing. The morphology of precursor and Fe2Ni2N/rGO hybrid composite was analyzed by FE-SEM. The crystallinity of sample was confirmed by XRD. GO was confirmed by Raman spectroscopy. And the components of as-prepared precursor were measured by FT-IR spectra. Furthermore, we analyzed electrochemical properties of synthesized sample.

ET03.09.05
La0.6Sr0.4Co0.2Fe0.8O3-δ Decoration With CoO Nanoparticles and the Effect on Its Performance as SOFC Cathode Julian Ascolani Yael1, 2, Alejandro Montenegro-Hernandez1, Laura Baque1, Alberto Caneiro1 and Liliana Mogni2; 1CNEA - CAB, Bariloche, Argentina; 2Instituto Balseiro, Bariloche, Argentina.

Reducing fuel cells degradation and cathode polarization losses are currently two of the most important challenges in order to achieve more efficient and cost competitive SOFCs. One strategy has been to reduce operation temperatures to the range between 600 °C and 800 °C (IT-SOFC), which reduces degradation rates but increases activation over potentials as a consequence (mainly the cathode reaction overpotential, due to the high activation energy of oxygen reduction reaction –ORR–). Several approaches have been taken to counteract this problem and recently, promising results [1] have been obtained by modifying the electrodes surface using the impregnation technique. This technique consists of synthesizing catalyst nanoparticles on the electrode surface through a liquid solution-based process [2, 3]. The mechanisms through which the impregnated catalysts reduce the polarization resistance and even enhance durability are not completely well understood yet, especially when non conventional catalysts are impregnated, as the performance improvement relies upon the microstructure and coupled interactions between the materials.

In this work, a SOFC cathode surface modification by nanoparticle decoration was carried out. La0.6Sr0.4Co0.2Fe0.8O3-δ –LSCF– ceramic cathodes impregnated with cobalt oxide (Co3O4) nanoparticles were characterized by Scanning and Transmission Electron Microscopy –SEM and TEM-, X-ray diffraction –XRD– and Raman Spectroscopy. The electrochemical response as a function of temperature and oxygen partial pressure pO2 (10^-4 < pO2 < 1 atm) was evaluated by electrochemical impedance spectroscopy -EIS-. The impregnation was found to reduce the cathode polarization resistance –Rc– around 50% in the temperature range between 400°C and 700°C.
Electrodeposited Ni or Ni-Fe alloy was shown to effectively stabilize and catalyze the Si photoanode continuously for 24 h of water splitting. However, electrolytes but also poor catalytic property for the photo-drive electrolysis. Bandgap (1.12 eV) and high carrier mobility. However, the Si has not only low stability for the PEC cell due to the photo-induced corrosion in contact with metal oxides for water splitting via tailoring their optical and electronic properties. The need to extend the absorption spectrum to NIR and Visible regions of the light spectrum is crucial to enhance their characteristics as efficient photoelectrodes in photoelectrochemical water splitting. Bandgap tuning of semiconductors via induced defects is vital to control their optical and electrical properties. The EIS spectra show at least two arcs, where the pO2 dependence of each one allows to model the electrochemical response by a complex mechanism where the oxygen reduction reaction is co-limited by oxygen ion diffusion and oxygen surface exchange. 

References:

ET03.09.06
First-Principles Study of Bi-Functional Electrocatalytic Activity on Bi$_2$RuO$_4$ Pyrochlore Oxide Gwan Yeong Jung1, Joohyuk Park1-2, Sung O Park1, Jaephil Cho1 and Sang-Kyu Kwak1; 1School of Energy and Chemical Engineering, UNIST, Ulsan, Korea (the Republic of); 2Department of Materials, University of Oxford, Oxford, United Kingdom.


Searching for an effective catalyst to reduce CO$_2$ to value-added hydrocarbons has been a key challenge for CO$_2$ utilization. Here we design the Cu@Cu$_2$O catalyst by taking advantage of copper featuring a thin oxide layer on the surface under ambient conditions. Our results demonstrated that Cu(I) oxide species on Cu@Cu$_2$O surface can remain relatively stable against reduction under CO$_2$ electrode-reduction condition, and the synergism between surface Cu$^+$ and Cu$^{2+}$ in Cu@Cu$_2$O composites contributes to boosting its efficiency and selectivity towards to C$_2$ products. This Cu@Cu$_2$O catalyst achieved low onset potential (~0.8V vs RHE) as well as excellent selectivity (up to 50% at ~1.0V vs RHE) for C$_2$ (C$_2$H$_4$ and C$_2$H$_5$OH) production.

ET03.09.07
Effect of Size and Density of Ni Nanoparticles on Photoelectrochemical Water Splitting Songwoung Hong1, Hyo-Chang Lee1-2 and Ansoon Kim1-3; 1Korea Research Institute of Standards & Science, Daejeon, Korea (the Republic of); 2University of Science and Technology, Daejeon, Korea (the Republic of).

ET03.09.09
Cu@Cu$_2$O for Selective Reduction of CO$_2$ to C$_2$ Products Longmei Shang and Gengfeng Zheng; Laboratory of Advanced Materials, Fudan University, Shanghai, China.


Bandgap tuning of semiconductors via induced defects is vital to control their optical and electrical properties. The need to extend the absorption spectrum to NIR and Visible regions of the light spectrum is crucial to enhance their characteristics as efficient photoelectrodes in photoelectrochemical water splitting. However, the nature of defects, whether deep or shallow and how they influence the photoelectrochemical performance of TiO$_2$ is yet to be understood. Herein, four factors were utilized to increase the defect density, and eventually decrease the bandgap: alloying with Nb and Zr, nanostructuring in the form of multipodal nanotubes, annealing in a reducing atmosphere (H$_2$), and deposition of solvothermally prepared narrow bandgap CZTS nanoparticles on the nanotubes. Air-annealed samples were used as a reference to study the effect of reducing atmosphere. TEM images verified the formation of uniformly distributed MPNTs. XRD, XPS, and Raman Spectroscopy for the Hydrogen-annealed samples confirmed the presence of ZrTiO$_3$ in addition to Ti-Nb-Zr-O as single mixed oxide possessing an anatase crystal structure. XPS core spectra fitting verified the presence of Ti$^{4+}$. The presence of a large number of Ti$^{4+}$ defects/Oxygen vacancies justified the 4-orders of magnitude increase in the donor density exhibited when Mott-Schotky analysis was performed. These results were further confirmed by XPS valence band spectra showing the presence of valence band tail states. These tail states resulted in a decrease in the bandgap, besides forming a tail in the absorption spectra reaching NIR/Vis. region. Bare MPNTS showed a 25 times enhancement in the photocurrent compared to Air-annealed samples. Decorating the MPNTS with CZTS lead to further 6 times enhancement. However, on testing several cycles, CZTS showed a lack of stability in the alkaline electrolyte. This large current was attributed to the formation of a p-n junction with the desirable band alignment; enhancing charge separation and leading to charge carriers’ injection on the NTs/particles interface. Hence, annealing in a reducing atmosphere is capable of producing disordered and defective structures. This would stimulate an intriguing route for activating other promising metal oxides for water splitting via tailoring their optical and electronic properties.
Oxygen reduction reaction (ORR) is a sluggish process that causes significant cell voltage losses in low- and intermediate-temperature solid oxide fuel cells (SOFCs). Surface engineering of electrocatalysts and thin-film interfaces introduced between the cathode and electrolyte can mitigate the voltage losses associated with ORR on the cathode. In this presentation, we study the role of the metal oxide-based nanoscale interlayer inserted between the cathode and electrolyte in the kinetics and rate-limiting steps of ORR process through a series of electrochemical analyses and imaging techniques. Ultrathin yttria-doped ceria (YDC), yttria-stabilized zirconia (YSZ) and ceria (CeO$_2$) layers with different stoichiometry and thickness were inserted as the interlayer by atomic layer deposition (ALD) technique on a gadolinia doped ceria (GDC) layer that was screen printed on YSZ electrolyte supported cells. A series of electrochemical tests have been performed with two different cathode materials – lanthanum nickel ferrite (LNF) and lanthanum strontium cobalt ferrite (LSCF) cathodes – with different electronic and ionic conductivities to examine the interface engineering impact on ORR. $\text{pO}_2$-dependent ORR kinetics tested under different oxygen partial pressures ($\text{pO}_2$) ranging from 0.04 to 1.0 atm. The reaction order $m$, defined as the relation $R_p$ cathodic polarization resistance; $\text{pO}_2$, O$_2$, partial pressure) is a widely used indicator of the rate-limiting step in ORR. In addition to the dependency on $\text{pO}_2$, the wide variation in the dependency on temperature and overpotential suggests that the interface treatment not only changed the overall ORR kinetics but also shifted the bottleneck process of ORR. However, it was found that most of the samples are largely rate-limited by the charge transfer processes, but mostly in conjunction with chemical processes such as diffusion of electroactive species and/or dissociation processes.

### ET03.09.12

**Mesoporous CuO$_x$-Derived Nanostructured Copper Catalysts for CO$_2$ Reduction**

Giorgio Giuffredi$^{1, 2}$ and Fabio Di Fonzo$^2$

$^1$Istituto Italiano di Tecnologia, Milano, Italy; $^2$Department of Energy, Politecnico di Milano, Milano, Italy.

The electrochemical reduction of anthropogenic CO$_2$ to fuels and complex hydrocarbons represents a promising solution to reduce global CO$_2$ emissions and, at the same time, to efficiently store intermittent, renewable energies-generated electricity in the form of chemical energy of carbon-based fuels. The progress of the technology is still hindered by the unsatisfactory efficiency and stability of currently employed electrocatalysts. The thermodynamic stability of CO$_2$ requires a large overpotential to be applied for the reaction to take place at a satisfying rate. Moreover, electrocatalysts often undergo degradation after a limited operation time because of poisoning due to incorrect reduction of CO$_2$.

Copper, among the many metals tested as CO$_2$ reduction electrocatalysts, is interesting because, due to its ability to reduce CO$_2$ to complex hydrocarbons with good efficiency. However, even copper catalysts, when their structural and morphology are not nano-engineered, require high overpotentials and have limited selectivity and stability.

To overcome these problems, oxide-derived copper catalysts are being studied: they show improved CO$_2$ reduction efficiency, higher selectivity towards complex hydrocarbons and have longer stability. Morphology also plays a critical role in determining activity and selectivity of oxide-derived copper nanostructures: a controlled morphology in fact allows to maximize the exposed active sites and to increase the surface area, resulting in higher Faradaic efficiency towards CO$_2$ products and lower overpotentials.

In this contribution, we propose Copper Oxide (CuO$_x$) mesoporous nanostructures synthesized through Pulsed Laser Deposition (PLD) as oxide-derived Cu catalysts for CO$_2$ reduction. We evaluate the influence of both morphology and composition of the nanostructures on the final electrochemical performance, by carefully tuning the process gas kinetics and process gas type during the synthesis. We are thus able to fine-tune the deposit morphology and composition up to the nanoscale: we obtain films with different degrees of nanostructuractation, from compact films to porous nanostructures, and compositions ranging from Cu$_2$O to CuO. The PLD-synthesized nanostructures are composed of an amorphous matrix with embedded crystalline CuO$_x$ seeds, differently from other reported, purely crystalline oxide-derived Cu catalysts. This morphological feature allows for a higher availability of undercoordinated surface active sites which, coupled with the high surface area, can enhance the activity of the catalysts.

The nanostructures are characterized electrochemically, showing good current densities even at low overpotentials. The influence of both composition and morphology of the nanostructures on Faradaic efficiency and selectivity are evaluated.

This contribution shows the potential of a PLD-based technique for the synthesis of efficient oxide-derived Cu nanostructured catalysts with controlled morphology and composition.

### ET03.09.13

**Investigation on the Nano Size Effect of Ultra-Small Manganese Oxide Nanoparticles**

Kang Hee Cho, Sunghak Park, Hongmin Seo, Kang Gyu Lee, Yoon Ho Lee and Ki Tae Nam; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Nowadays, nanotechnology is really close to our daily lives and its applications are diverse such as energy, biomedical, sensors and foods. Especially in energy fields, rational design and synthesis of highly efficient nanocatalysts for various reactions are an important issue. And because of some characteristics such as large exposed surface area, morphology tuning at nano scale and electronic confinement effects within NPs, they show specific nano size effects.

Recently, our group newly synthesized partially oxidized sub-10 nm MnO NPs which show superior catalytic performance compared to the bulk manganese oxides. And in further study which was reported in JACS last year, we implemented various in-situ electrochemical analysis and in-situ spectroscopic tools such as XAS, UV-VIS and Raman and we found completely different mechanistic behavior of our NPs compared to the conventional Mn-based catalyst. Herein, we extend our understanding on nano-size effect to our manganese oxide NPs. For synthesis of ultra small NPs, various size-control parameters and synthesis methods were pre-screened. And very recently, we successfully synthesized average size of 4.1 nm NPs which show superior OER activity compared to sub-10 nm NPs. Using these as-synthesized NPs, applicability for chirality manganese oxide NPs formation will be explored and also we expect enhanced surface focused spectroscopic analysis for the capture of reaction intermediates. Additional studies on the relation between OER performance and the size of NPs will also proceed.


### ET03.09.14

**Nitrogen Doped Carbon Nanonions for Oxygen Reduction Reaction (ORR) Electrocatalysis in Fuel Cells for Microgravity Conditions**

Armando Pena-Duarte$^2$, S.H. Vijapur$^2$, T.D. Hall$^2$, E. Jennings Taylor$^2$ and Carlos R. Cabrera$^2$; $^2$Department of Chemistry, University of Puerto Rico at Rio Piedras, San Juan, Puerto Rico, United States; $^3$Department of Mechanical Engineering, University of California Merced, Merced, California, United States; $^4$Faraday
Nitrogen doped carbon nanostructures have been previously used as catalyst support in ORR [1,2]. A metal-free mesoporous nitrogen-doped carbon catalyst showed a high electrocatalytic activity, durability and selectivity toward peroxide by electrocatalysis of O$_2$ in a non-corrosive neutral as well as in acidic reaction medium [3,4]. Human space travel requires several technological developments that support the energy-efficient preservation of closed systems in microgravity spaceship environments. Especially, a technique for the in-situ generation of cleaning/sanitizing solutions such as H$_2$O$_2$ is needed to meet personal hygiene necessities during space missions. Accordingly, we developed an alternative post-synthesis nitrogen doping of CNOs by Chemical Vapor Deposition Method (CVD) in atmospheric pressure, using dicyandiamide as nitrogen precursor. The operational parameter conditions of the CVD reactor were a reaction temperature 700 °C, 2 mL/min of total argon gas flow, and a composition of precursors 2:1 DCDA:CNOs. The structural properties of the NCNOS were investigated using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. Our research involves increase surface area of carbon pristine source and improve its electronic structure and understanding of the nitrogen intercalation process by possible pyrolytic–nucleophilic mechanism of N–C doping reaction. NCNOS electrochemical characterization revealed higher performance than CNOs due to N doping. Nitrogen doping in the CNOs enhances the electronic conductivity and specific capacitance. An analysis of the rotating disk electrode (RDE) technique data was done to evaluate the ORR kinetics, including n-values which are related to the mechanism of oxidation, at the NCNOS, using the Koutechy-Levich (K-L) equation. The pH Effect on Oxygen Reduction Reaction over N-Doped CNOs in O$_2$ saturated 0.2 M Na$_2$SO$_4$ was evaluated by a scan rate of 10 mV/s at different rotation rates: 300, 700 1100, 1500, and 1900 rpm. Our results could be evidence that the H$_2$O$_2$ or H$_2$O selectivity, two-electrons and four-electrons transfer pathway, respectively, depend on the supporting electrolyte, i.e., pH value and nature of electrolyte, and increases to 0.2M Na$_2$SO$_4$ according to neutral (2.5 electrons) > acidic (1.4 electrons) > alkaline (3.4 electrons). Therefore, our approach would be promising to control of two-electrons route kinetics of ORR by the supporting electrolyte, through nitrogen carbon nanonion electrocatalyst systems for fuel cells in aerospace technologies.


ET03.09.15
First-Principles Studies of B-Site Doped PrCoO$_3$-d Perovskite
Jianguo Yu; Idaho National Laboratory, Idaho Falls, Idaho, United States.

Solid-oxide fuel cells (SOFC) based on proton-conducting (PC) ceramics are gaining wide interest as promising green technologies for H$_2$ production and conversion. However, its large-scale deployment has been hindered by severe limitations at electrodes, which must ensure catalytic activity, electronic conduction, and high proton diffusion rates. Perovskite oxides are highly desirable as the promising electrode candidates for SOFC. In this work, we present results of a density-functional theory (DFT+U) study of B-site doped PrCoO$_3$(PCO) perovskite. The investigation was focused on the key processes that determine proton transport, i.e., oxygen vacancy formation, water dissociative incorporation into the defective lattice, and proton transfer along the oxide sublattice. The materials are PCO and B-substituted derivatives with Ni. The effects of the crystal structural from cubic, tetragonal to orthorhombic and surface will also be discussed.

ET03.09.16
Promoting Surface Charge Utilization by Incorporating Novel Ternary ZnCoMn Layered Double Hydroxide Nanowall with Bismuth Vanadate for Efficient Photocatalytic Water Oxidation
Truong-Giang Vo, Yian Tai and Chia-Ying Chiang; National Taiwan University of Science and Technology, Taipei, Taiwan.

Strategically integrating a highly efficient oxygen evolution reaction electrocatalysts with a semiconductor film to reduce surface recombination and enhanced photocurrent is known as the bottleneck in solar-driven water splitting [1]. Herein, a novel integrated ZnCoMn layered double hydroxides (LDHs) photoanode with the high-quality interface was directly and conveniently deposited on a BiVO$_4$ to enhance photocatalytic photochemical water oxidation performance via fast and facile preoxidation coupled electrochemical method. Uniform two-dimensional LDH nanowalls with controlled composition anchoring onto the surface can be accomplished at room temperature within tens of seconds. Benefiting from efficient exposure of active sites, favorable charge transport and enhanced surface reaction kinetics, surface modification with ZnCoMn-LDH exhibits about 170% increment in photocurrent density at 1.23 V vs. RHE and a 280 mV shift in onset potential compared to bare bismuth vanadate. More interestingly, charge injection efficiency at the BiVO$_4$/electrolyte interface, which is well-known as one of the critical limiting factors in achieving efficient photocatalytic water splitting [2], reaches almost 100%. The results obtained here suggest the possibility of using ternary LDH as low-cost earth-abundant co-catalysts for solar water splitting. This work also provides a facile and cost-effective synthesis route that holds great promise for large-scale industrial manufacture and can be potentially used in energy conversion devices.


ET03.09.17
Stable GaAs Photoanode with Manganese Modified TiO$_2$ Protective Coatings for Water Oxidation
Xin Shen and Shu Hu; Chemical Engineering, Yale University, New Haven, Connecticut, United States.

Artificial photosynthesis, commonly used to refer to any scheme for capturing and storing the energy from sunlight in the chemical bonds of a fuel (a solar fuel), has long been considered as option to mitigate energy crisis and global climate change. Photoelectrochemical (PEC) water splitting converts water into hydrogen and oxygen, and is a major research topic of artificial photosynthesis. However, there are still lots of challenges in designing an efficient PEC cell to split water. Except for efficiency and cost, stability problem of efficient semiconductor/liquid interfaces like Si and GaAs has greatly hindered the development of many potential excellent photoanode materials as these material undergoes positive photo-corrosion during PEC operation. So, it is imperative that through this project we: 1 Understand typical photoanode corrosion process with a detailed description for the different corrosion stages with the help of our in-situ laser set-up; 2 Find the main factors influencing anode of our PEC water oxidation; 3 Determine an optimized condition for stable and efficient GaAs water oxidation, as our preliminary results showed the relative neutral PH condition (PH 5 to 9) is beneficial for PEC water oxidation by greatly lower electrode overpotential. Particularly, in this project we would also compare GaAs/TiMnOx/In to traditional GaAs/TiO$_2$/Ni to show the superiority of acid stable TiMnOx/In as a novel protective coating/co-catalyst system.

ET03.09.18
Preparation of Vertically Oriented Carbon-Coated Titanium Dioxide Nanorods as Alternative Catalyst Support to Carbon for Fuel Cells
Applications Naser Mohammadi and Mohamed Mohamedi; *Énergie Matériaux Télécommunications, INRS, Montreal, Quebec, Canada.

At present, catalyst supports in fuel cells are often made of carbon-based materials, such as graphite fiber brush, carbon paper, reticulated vitreous carbon, carbon nanofibers, etc. TiO₂ is one of the most attractive metal oxides used in many areas concerning solar cells, photocatalysis, sensors, supercapacitor, etc. TiO₂ has very good chemical stability, biocompatibility, and also is abundant as well as environment-friendly. These advantages are very attractive for practical fuel cell electrodes. Because of their special application in fuel cells, the growth of one-dimensional single-crystalline TiO₂ nanostructures on a flexible substrate is receiving intensive attention [1].

In this study, TiO₂ nanorods are hydrothermally grown on carbon paper (CP) and Titanium foil. Then Platinum layer deposited onto TiO₂ nanorods by pulsed laser deposition (PLD) at room temperature. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the synthesized nanorods, According to the SEM study, the synthesized particles have 200 nm in diameter. The catalyst showed the highly dense TiO₂ nanorods were directly grown on the Titanium foil and carbon Paper substrates, also the Pt-coated onto the surface of TiO₂ nanorods were uniform. Cyclic voltammotry (CV) and chronoaamperometry were employed to study the electrocatalytic properties and durability of thus synthesized TiO₂-Pt and CP/TiO₂-Pt samples towards ethanol electro-oxidation, the reaction that is of fundamental significance to direct ethanol fuel cells (DEFCs). The Ti/TiO₂-Pt and CP/TiO₂-Pt electrocatalysts have a larger active surface area as compared to the Ti/Pt and CP/Pt electrocatalysts. Meanwhile, the Ti/TiO₂-Pt and CP/TiO₂-Pt electrocatalysts display much better catalytic activity and higher stability for the ethanol electrooxidation in acidic than the Pt/C and Pr/Ti electrocatalysts as a result of the synergistic effect of Pt and the TiO₂ support. Thus, the prepared electrode with low platinum loading and high stability is a promising material for fuel cells and TiO₂ nanorods substrate is a potential alternative to carbon paper substrate for fuel cell technology.


8:00 AM  ET03.10.01 Directional Flow-Aided Sonochemistry Yields Graphene with Tunable Defects to Provide Fundamental Insight on Sodium Metal Plating Behavior David Miltin1 and Wei Liu; 1Chemical and Biomolecular Engineering and Mechanical Engineering, Clarkson University, Potsdam, New York, United States; 2Institute of New-Energy and Low-Carbon Technology, Sichuan University, Sichuan, China.

This is the first report of a novel directional flow-aided sonochemistry (FAS) exfoliation method to synthesize graphene with nearly ideal structure. The FAS treatment allows for control of graphene structural order and chemical uniformity not possible through prior top-down wet methods. Graphite is exfoliated into single-nm scale thickness graphene that is nearly defect free (at-edge sonication graphene "AES-G") or is highly defective (in-plane sonication graphene "IPS-G"). The AES-G has a Raman G/D band intensity ratio of 14.3 and an XPS derived oxygen content of 1.3 at.%, while the IPS-G has IₓOᵧ of 1.6 and oxygen content of 6.2 at.%. Graphene and related carbons are widely employed as templates and protection layers to improve metal plating behavior in sodium and lithium metal battery (SMBs, LMBs) anodes. We then use AES-G and IPS-G to examine the role of structure and chemistry of graphene supports in promoting efficient Na metal cycling. The graphene serves a dual role in stabilizing the Na metal anode, being a nucleation template and serving as a protective layer to keep the metal from severely reacting with the electrolyte. We are the first to demonstrate that graphene defects are actually quite deleterious for efficient Na plating and stripping. AES-G yields state-of-the-art Na performance, with stable cycling at 2 mA/cm² at 100% Coulombic efficiency (CE), and an areal capacity of 1 mAh/cm². Meanwhile IPS-G performs on-par with the baseline Cu support in terms of severe charging instability. The explanation is that the defective graphene demonstrates much more copious SEI formation due to its defects and oxygen groups being catalytic. A thicker SEI results in a larger overpotential and worse CE loss during subsequent Na plating/stripping, manifesting in severe mossy metal dendrite growth and periodic electrical shorts. We therefore propose the following design rule for next-generation supports for Na metal: An ideal architecture will not only possess a large surface area for copious preferred heterogenous nucleation, but itself will be non-catalytic for SEI formation.

8:30 AM  ET03.10.02 Nanostructured Graphene-Coated Cathodes for High-Performance Lithium-Ion Batteries Mark C. Hersam; Northwestern University, Evanston, Illinois, United States.

Efficient energy storage systems based on lithium-ion batteries represent a critical technology across many sectors including consumer electronics, electrified transportation, and a smart grid accommodating intermittent renewable energy sources. Nanostructured electrode materials present compelling opportunities for high-performance lithium-ion batteries, but inherent problems related to the high surface area to volume ratios at the nanometer-scale have impeded their adoption for commercial applications. Here, we demonstrate a scalable materials and processing platform that realizes high-performance nanostructured lithium manganese oxide (nano-LMO) spinel cathodes with conformal graphene coatings as a conductive additive. Graphene coatings provide a chemically stable interface between the electrode and electrolyte, which minimizes the formation of the solid-electrolyte interphase and mitigates electrode chemical instabilities such as manganese dissolution [1]. The resulting nanostructured composite cathodes concurrently resolve multiple problems that have plagued nanoparticle-based lithium-ion battery electrodes including low packing density, high additive content, and poor cycling stability [2]. Moreover, this strategy enhances the intrinsic advantages of nano-LMO, resulting in extraordinary rate capability and low temperature performance. With 75% capacity retention at a 20C cycling rate at room temperature and nearly full capacity retention at temperatures as low as -20 °C, this work advances lithium-ion battery technology into unprecedented regimes of operation.


Electrochemical capacitors (ECs) with high-power capabilities and stable cycling can effectively improve the state of the art in power delivery and energy storage. In this study, we investigate reactively sputtered titanium nitride (TiN) electrodes on three-dimensional (3D) substrates with various electrolytes and high-rate cycling conditions. These electrodes exhibit cycling stability with negligible capacitance fading after thousands of cycles and a great rate capability, allowing the (dis)charge rate to extend from 0.1 to 10 V s⁻¹ and retaining nearly 50% of the capacitance in a three-electrode system. Symmetric devices made with TiN/Ti electrodes are capable of working at scan rates up to 100 V s⁻¹, yielding a remarkable power density. To further maximize the energy density, the aqueous electrolyte can be replaced with an organic one. Despite not having energy density of carbon-based supercapacitors, other aspects of TiN-based systems are very attractive for future applications. Strategies for further maximizing the performance of this system will be discussed, as well as synthesis and device processing options suggest that 3D TiN structures can enable a new class of high-power ECs with enhanced stability compared to their carbon- and pseudo- counterparts.

Energy Storage Mechanisms in Niobium Oxides with Different Electrolytes Jiahe Zhang and Haitao Zhang; Chinese Academy of Sciences, Beijing, China.

Electrical energy storage and conversion devices, electrochemical capacitors and batteries, are attracting broad interests due to their advantageous features of high round-trip efficiency, long cycle life. Among of different compounds, niobium oxides are pursued drastically owing to their high specific capacitance. Numerous nanocarbons are being utilized to modify these electron insulating niobium oxides to fully manifest their high specific capacitance. In addition, these compounds are also excellent candidate anodes for solid state devices. Therefore, the energy storage processes become more complicated once solid state and formulated electrolytes are employed. Generally, there are two storage behaviors involved, surface behavior and bulk charge behavior. Here we are going to present our recent results related to the energy storage mechanisms in niobium based oxides with ionic liquids based electrolytes. (1) Qualitative analysis, the contribution of the capacitive and diffusion-limited elements are separated in different environments by using the b value. The ionic liquid system that has the highest b value can deliver the biggest capacitive contribution than organic and gel systems. (2) Quantitative analysis, we calculated the capacitive contributions at various scan rates in three systems. The highest capacitative ration exists in inorganic liquid system at all scan rates. The ionic liquid system’s capacitive contribution increased gradually with increasing scan rate. (3) Effect of temperature on the mechanisms was evaluated to optimize the formula. We found that the capacitive ratio increased gradually and ionic liquid system could achieve maximum ratio with increasing temperatures. Our finding suggests that the liquid systems could offer more capacitive contribution and regulate the storage mechanism.

Solvent-Driven Morphology Controls of Nanomaterials for High Performance Supercapacitors Jae-Jin Shim, Debananda Mohapatra, Marjorie Baynosa, Van Quang Nguyen and Ganesh Dhakal; Yeungnam University, Gyeongsan, Korea (the Republic of).

Energy storage is essential for steady supply of renewable energy such as solar energy and wind energy. A supercapacitor is an important energy storage device together with rechargeable battery. Numerous researchers have been developing novel materials for electrochemical energy storage. Graphene and carbon nanotubes have been used to enhance conductivity of active electrode materials such as metal oxides, sulfides, or hydroxides. In addition, 3-D nanostructures have been used to increase the surface area and pore sizes for a better charge collection and transfer. In this study, the morphology of nanomaterials has been successfully controlled by using different reaction medium and by use of microwave and ultrasound. Several different morphologies will be shown and their synthesis processes will be discussed. Some of them show excellent energy storage performances. The materials synthesized by these new methods may be used for energy storage devices, sensors, and photocatalysts in the near future.

Titanium Nitride Films as Electrodes for High Power Electrochemical Capacitors Tianye Zheng, Mohammad H. Tahmasebi and Steven T. Boley; Hong Kong Polytechnic University, Kowloon, Hong Kong.

As electronic technology advances, the need in safe and long-lasting energy storage devices that occupy minimum volume arises. Short charging times of several seconds to minutes, with energy densities comparable to those of batteries, can be achieved in electrochemical capacitors (supercapacitors), in particular pseudocapacitors, which utilize fast redox reactions to store charge and, thus, feature high energy densities. However, metal oxides that are currently used in energy storage technologies have certain limitations. Due to low intrinsic electrical conductivity they might suffer from poor cyclability and deterioration of electrochemical performance for thick electrodes. As an alternative, conductive materials with build-in redox centers pose particular interest. Herein, we report on the new family of the conductive 2D porous metal organic frameworks and we investigated their potential for electrochemical capacitors. A perspective of usage of the metal organic frameworks for the energy storage is particularly appealing since it can enable energy-efficient way of the room temperature synthesis of the electrode materials. Our evaluation demonstrated impressive gravimetric capacitance up to 500 F/g coupled with high volumetric capacitances up to 760 F/cm³. Moreover, we demonstrate excellent scalability of the electrochemical performance for this system: upon increase in electrode thickness up to 350 um, the areal capacitance did not plateau and reached a value over 20 F/cm². This demonstrates that redox-active conductive MOFs can potentially outperform other traditional materials in energy storage applications. We also discuss charge storage mechanism and factors affecting electrochemical performance of the conductive MOFs.

Nanoscale Ostwald Ripening—Characterizations and Effects on Realizing Fast Charging Capability of Electrochemical Capacitors with Abundant Manganese Dioxide Tianyu Lui, Yu Song, Xiaoxia Liu and Yat Li; 1Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California, United States; 2Department of Chemistry, Northeastern University, Shenyang, China.

We recently discovered that, nanoscale Ostwald ripening of a thick layer of manganese dioxide (MnO₂) nanosheets could be induced by a facile hydrothermal treatment. This nanoscale process coalesced the surface nanosheets into a highly crystalline and porous coating layer, forming a well-resolved core-shell structure. The presence of this crystalline coating was capable of substantially facilitating both ion diffusion and electron transport throughout the thick MnO₂ film, which was desirable for practical electrochemical capacitors with high mass loading of active materials. The core-shell structure, when deployed as a pseudocapacitive electrode with 9 mg cm⁻² of MnO₂, achieved a geometric areal capacitance of 618 mF cm⁻² at a fast scan rate of 200 mV s⁻¹. The MnO₂ mass loading could further be promoted to as remarkably high as 23.5 mg cm⁻² without greatly compromising its fast charge-
Nano-Sized Structurally Disordered Metal Oxide Composite Aerogels as High-Power Anodes in Hybrid Supercapacitors

Huijian Huang, Xing Wang \textsuperscript{1,3}, Elena Tervoort, Guebo Zeng \textsuperscript{1}, Tian Liu, Xi Chen \textsuperscript{1}, Alla Sologubenko \textsuperscript{1} and Markus Niederberger \textsuperscript{2}; \textsuperscript{1}ETH Zurich, Zurich, Switzerland; \textsuperscript{2}University of California, Berkeley, Berkeley, California, United States; \textsuperscript{3}Paul Scherrer Institute, Zurich, Switzerland.

With rechargeable battery technology moving to an era of medium/large-scale applications, the development of next-generation energy storage devices offering not only high-energy density but also high-power density becomes more and more imperative. Rechargeable lithium-ion batteries usually have high energy density, whereas their power density and cycle life are far from satisfactory. Alternatively, supercapacitors exhibit rapid power delivery, but are limited by low charge storage capacity. To integrate both high-power delivery, lithium-ion hybrid supercapacitors (Li-HSCs) have been explored in recent years. One of the main challenges on the way to fabricating high-performance Li-HSCs is the development of high-power Faradaic anodes to solve the kinetic imbalance between the sluggish Faradaic anode and the capacitive cathode.

In this work, we developed a general method for synthesizing nano-sized metal oxide nanoparticles with highly disordered crystal structure and their processing into stable aqueous dispersions.\textsuperscript{1} With these structurally disordered nanoparticles as building blocks, a series of nanoparticles @ reduced graphene oxide (rGO) composite aerogels are fabricated and used as binder-free high-power anodes for lithium-ion hybrid supercapacitors (Li-HSCs). To clarify the effect of the degree of disorder, control samples of crystalline nanomaterials with similar particle size are prepared. The results indicate that the structurally disordered samples show a significantly enhanced electrochemical performance compared to the crystalline counterparts. In particular, structurally disordered Ni\textsubscript{1,4}Fe\textsubscript{0,6}O\textsubscript{4}@rGO delivers a capacity of 388 mAh g\textsuperscript{-1} at 5 A g\textsuperscript{-1}, which is 6 times that of the crystalline sample. The volumetric capacitances of more than 1200 F cm\textsuperscript{-3}, maintain gravimetric capacitances in excess of 200 F g\textsuperscript{-1} at extremely high charging rates of over 100 A g\textsuperscript{-1}, and provide life cycle and capacitance retention that excel those of Ti\textsubscript{3}C\textsubscript{2}Tx. The research findings summarized in this presentation will provide a path toward high-power Faradaic anodes for Li-HSCs.

developed to potentially serve as the electrode platform component in a novel textile capacitor. This research will advance the fundamental understanding of the relationship between high surface area and the use of redox reactive nanoparticles on electrochemical charge storage mechanisms.

11:30 AM ET03.10.11
Electrochemical Intercalation of MoS2 Composites for Supercapacitor Electrodes Using Non-Hydrated Cations Pawin Iamprasertkum1,2, Wisit Hirunpinyopad1,2, Mark A. Bissett3 and Robert A. Dryfe1,2; 1School of Chemistry, University of Manchester, Manchester, United Kingdom; 2National Graphene Institute, University of Manchester, Manchester, United Kingdom; 3School of Materials, University of Manchester, Manchester, United Kingdom.

Nanochannels can be spontaneously fabricated by forming "membranes" of two-dimensional materials. MoS2 has attracted attention in this respect for fundamental studies and due to its superior properties in energy storage applications [1]. However, the charge storage mechanism, including surface ion adsorption and intercalation, are not yet fully understood. In this work, free-standing MoS2 composite electrodes are prepared and studied via the intercalation of non-hydrated cations (without hydration shell). It is found that tetramethylammonium chloride (TMACl) provides double the capacitance compared to tetraethylammonium chloride (TEACl) and tetratetrapropylammonium chloride (TPACl). This is because MoS2 provides an interlayer spacing of 0.615 nm, which is greater than the crystallographic diameter of TMA+ (0.558 nm). In contrast, the crystallographic diameter of TEA+ (0.674 nm) and TPA+ (0.758 nm) are greater than that of MoS2. This can lead to storage of the charge only on the surface of the materials, through ion adsorption. Moreover, we have found that using the TPA+ ion that is larger than that interlayer spacing of MoS2 leads to the partial re-exfoliation of the as-prepared materials, which can enhance the capacitance retention during cycling. These results improve the understanding of charge storage mechanism of layered 2D materials.

1:30 PM ET03.11.01
Carbon-Based Metal-Free Electrocatalysis for Efficient Energy Conversion and Storage Liming Dai; Case Western Reserve University, Cleveland, Ohio, United States.

Green and renewable energy technologies, such as fuel cells, batteries, and water-splitting systems, hold great promise to solve current energy and environmental challenges. However, noble metal catalysts (e.g., Pt, Pd, RuO2, IrO2) are generally needed to promote the hydrogen evolution reaction (HER) for hydrogen fuel generation from photo-electrochemical water-splitting, oxygen reduction reaction (ORR) in fuel cells for energy conversion, and oxygen evolution reaction (OER) in metal-air batteries for energy storage. The high cost of precious metal-based catalysts and their limited reserve have precluded these renewable energy technologies from large-scale applications. Along with the recent intensive research efforts in non-noble metal based ORR catalysts, we have previously demonstrated that vertically-aligned nitrogen-doped carbon nanotubes could actively catalyze ORR via a four-electron process free from the CO poisoning effects with a 3-time higher electrocatalytic activity and better long-term durability than that of commercial Pt/C catalysts. The improved catalytic performance was attributed to the doping-induced charge transfer from carbon atoms adjacent to the nitrogen atoms to change the chemisorption mode of O2 and to readily attract electrons from the anode for facilitating the ORR.

Subsequently, it was demonstrated that various graphitic carbon materials, doped with heteroatoms of different electronegativities from that of carbon atom, physically adsorbed with certain polyelectrolytes, and even without any apparent dopant or physically adsorbed polyelectrolyte, could also exhibit good ORR performance. More recent studies have further demonstrated that certain heteroatom-doped carbon nanomaterials could act as metal-free bifunctional catalysts for O2/R on metal-air batteries for energy storage, and even O2/R/ORR/HER trifunctional catalysts for self-powered water-splitting to generate hydrogen fuel and oxygen gas from water.

In this talk, I will summarize some of our work on the metal-free catalysts based on carbon nanomaterials for various energy-related reactions, along with an overview on the recent advances and perspectives in this exciting field.

2:00 PM ET03.11.02
Electrochemically Driven High Hydrogen Concentrations into Palladium via Aqueous and Solid Electrolytes Yet-Ming Chiang1, Jesse D. Benck1, Ariel Jackson1, David Young1 and Daniel Rettenwander2; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2TU Graz, Graz, Austria.

Metal hydrides are critical materials in numerous energy technologies including hydrogen storage, gas separation, and electrocatalysis. Here, using Pd-H as a model metal hydride, we perform electrochemical insertion studies of hydrogen via liquid and solid state electrolytes at 1 atm ambient pressure, and achieve H2/Pd ratios near unity, the theoretical solubility limit, in nanometer-scale films. We show that the compositions achieved result from a dynamic balance between the rate of hydrogen insertion and evolution from the Pd lattice, the combined kinetics of which are sufficiently rapid to enable accurate quantification of the composition of electrochemically synthesized PdHx. Furthermore, we show that the achievable hydrogen concentration is severely limited by electrochomechanical damage to the palladium and/or substrate. The understanding embodied in these results helps to establish new design rules for achieving high hydrogen concentrations in metal hydrides.

2:30 PM ET03.11.03
Computational Study of Nanoscale Active Sites in PGM-Free Electrocatalysts for Proton Exchange Membrane Fuel Cells Kexi Liu, Boyang Li, Zhenyu Liu and Guofeng Wang; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Proton exchange membrane fuel cells (PEMFCs) can covert chemical energy stored in hydrogen fuels to electricity and produce environmentally benign product water. However, the commercialization of PEMFCs is hindered by the present requirement of expensive Pt group metals (PGM) as their electrocatalysts. To advance PEMFC technology, it is of great interest to develop earth-abundant, non-precious metal based catalysts in replacement of Pt,
especially for oxygen reduction reaction (ORR) occurring at the cathode of PEMFCs. Recently, non-precious transition metal/nitrogen doped carbon (TM-N-C) catalysts have been shown much attention as a promising PGM-free ORR electrocatalyst due to its ORR activity approaching to Pt. However, the chemical structure of the active sites in these TM-N-C catalysts and their catalytic mechanism for ORR have not been fully understood. To gain insight into the nature of the nanoscale active sites in the TM-N-C catalysts, we have performed density functional theory (DFT) calculations to investigate the progression of ORR on various types of TM-Nx (TM = Fe, Co) moiety substituted embeddingly into a graphene plane. On each possible TM-Nx active site, we calculated the adsorption energies of all the relevant chemical species, namely, O2, O, OH, OHOO, and H2O, and the activation energies for O-O dissociation reactions involved in ORR using the DFT method. On FeNx and/or CoNx embedded in an intact graphene plane, our DFT calculations predicted that the ORR could happen through 4e- associative pathway on the FeNx site, whereas follow a 2e- pathway on the CoNx site due to high activation energy for O-O bond splitting and extremely weak adsorption of H2O on the CoNx site. These theoretical results are in agreement with experimental observations. In addition, we studied the ORR on a FeNx moiety bridging two adjacent armchair like graphene edges as well as a FeNx moiety bridging two adjacent zigzag graphene edges with a porphyric architectural. Among the three FeNx moieties, the porphyric-like FeNx moiety was predicted to catalyze ORR with the highest onset potential. Moreover, we found that the O-O bond scission had lower activation energy on the FeNx moieties bridging graphene edges than on the FeNx moiety embedded in an intact graphene layer. Consequently, our computation results suggest that introduction of micropores in the TM-Nx catalysts would enhance their catalytic activity for ORR through improving not only the specific area but also the intrinsic activity of the active sites.

2:45 PM ET03.11.04
Design of Cathode Materials for Solid Oxide Fuel Cells—A Mechanistic Approach
M. Ali Haider and Uzma Anjum; IIT Delhi, New Delhi, India.

Molecular Dynamics (MD) simulations were utilized to calculate the oxygen anion diffusivity (D) in the lattice of the LnBa2SrCo2Fe2O8 (LnBSCF, Ln = Gd, Pr) double perovskite structure. Oxygen anion diffusion coefficient for the PrBaCoO3.4 (PBCO) material was calculated to be 3 x 10^-2 cm^2 s^-1 at 873 K in the a-b (Pr-O and Co-O) direction, which was observed to be higher than in the Ba-O plane (D = 8x10^-7 cm^2 s^-1 at 873 K). On doping, the A-site of PBCO with Sr and B-site with Fe, the resultant PrBa1.8Sr0.2CoFe2O8 (PBCF) structure was calculated to show an order of magnitude higher diffusivity (D = 1.1x10^-2 cm^2 s^-1 at 873 K) as compared to PBCO. Calculated diffusivity coefficients compared well with the measured electrocatalytic activity of the material. The electrochemical measurements were performed on a geometrically well-defined nanostructured thin-film electrode, fabricated as a symmetric cell using a spray pyrolysis deposition method. In combination with density functional theory (DFT) and MD simulations, experiments provided an insight into the operating mechanism. Following the hypothesis of a characteristic thickness (Lc) below which the performance is expected to be predominately controlled by surface reactivity, the Lc for layered perovskite LnBSCF at 973 K was calculated to be well above 1000 nm. Interestingly, a dense thin-film electrode of PBCSF (1 to 3 μm thick) deposited using the spray pyrolysis method showed a thickness dependent electrochemical performance suggesting bulk diffusion limitation. To understand the origin of this diffusion limited electrochemical performance, DFT calculations were utilized to calculate the surface energy (γ) and oxygen vacancy (Eov) formation energies. For example, the Eov in the Gd plane (98.4 kJ/mol) of GdBaCoO3.4 (GBCO) was calculated to be lower than that of Ba plane (Eov = 266.3 kJ/mol). However, the surface energy of the Ba plane was calculated to be minimum (γ = 7.2 kJ/mol), which makes it the most exposed surface, while it is least diffusive. GBCO nanoparticles of reduced size were expected to expose higher energetic Gd plane, which may enhance diffusivity at the surface. The particle size of GBCO was reduced to 20 nm using a bio-milling approach, wherein the chemically synthesized particles were subjected to fungus Saccharomyces Cerevisiae, for 72 hours. The measured impedance of the electrode made up of bio-milled nanoparticles was improved by 20% as compared to the chemically synthesized material. MD simulation on the GBCO nanoparticles indicated two distinct regimes of diffusion; one corresponding to the surface and other to the bulk region of the nanoparticle. The diffusivity of the shell regime (D = 6.8x10^-11 cm^2 s^-1 at 1073 K) was calculated similar to that of core (D = 5.7x10^-11 cm^2 s^-1 at 1073 K). Thus, nanoparticles showed improved electrochemical performance as compared to the bulk electrode, likely due to the disruption of the Ba-plane at the surface.

3:00 PM BREAK

3:15 PM ET03.11.04.5
How Strain Affects Reactivity at the Nanoscale
Andrew A. Peterson, Shubham Sharma, Cheng Zeng and Alireza Khorsheid; Brown University, Providence, Rhode Island, United States.

The reactivity of nanoscale surfaces drives the functional nature of materials such as catalysts, electrocatalysts, sensors, and batteries. This reactivity is known to be a function of the strain applied to the material. Here, we present a new way to rationalize such strain effects via an eigenstress model, which at the nanoscale manifests itself in simple force-displacement terms. We show how this can quantitatively rationalize such effects, and can lead to new designs at the nanoscale, such as anistropic strain, which can break conventional constrains of amterials design (such as the adsorbate scaling relations).

3:45 PM ET03.11.05
Theoretical Insights into the Effects of Transition Metal Doping on the Structure and Enhanced Stability of Pt-Ni Nanoparticles
Liang Cao and Tim Mueller; Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

We present the use of ab-initio calculations and the kinetic Monte Carlo method to develop atomic-scale structure-stability relationships for Pt-Ni nanoparticles, promising catalysts for the oxygen reduction reaction (ORR). Although the practical use of Pt-Ni catalysts is limited by Ni dissolution under cell operating conditions, it has recently been shown that it is possible to stabilize octahedral Pt-Ni nanoparticles by alloying them with transition metals (e.g. Mo, Cu, and Rh). We discuss two examples of alloyed Pt-Ni nanoparticles: Mo-Pt-Ni and Cu-Pt-Ni. Using a newly developed kinetic Monte Carlo (KMC) model based on cluster expansions, we demonstrate that Mo atoms are preferentially located on the vertex and edge sites of Mo-Pt-Ni in the form of oxides which are stable within the wide potential window of the electrochemical cycle. These surface Mo oxides help protect Ni in sub-surface layers against acid dissolution. KMC simulations reveal that the enhanced stability of Cu-Pt-Ni is likely due to the reduction of the number of Ni and Cu atoms on the surface during synthesis, reducing the opportunity for Ni and Cu atoms in sub-surface layers to move to the surface and dissolve.

4:00 PM ET03.11.06
Ionomer Distribution Control in Fuel Cell Catalyst Layer via Pt Surface Modification
Gisu Doo, Seongmin Yuk, Sungyu Choi, Dong-Hyun Lee, Dong Wook Lee and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

An universal structure of catalyst layer for polymer electrolyte membrane fuel cell is a mixture of proton conducting ionomer and carbon supported Pt nanoparticle catalyst. Such structure is commonly used because of its large catalyst surface area with abundant multiscale pores for gas diffusion. But, since the membrane is fabricated just by a vigorous mixing process, it has a limitation on the uncontrollabe distribution of ionomer on catalyst particles. And because of the high polar-polar attraction between Pt and ionomer, the ionomer generally tends to distribute to Pt surface, forming few nanometer film. The ionomer films on Pt surface retard the oxygen transfer for the oxygen reduction reaction and adversely affect the power performance especially at a low Pt content in cathode. In this sense, nano-scale ionomer distribution modification toward the ionomer film reduction is needed for the enhancement of
Anion-Exchange Membrane Fuel Cells with Improved CO₂-Tolerance—Impact of Chemically Induced Bicarbonate Ion Consumption

Yu Katayama1,2,3, Kosuke Yamazaki1, Kohei Hayashi1, Takeou Okamishi1, Hiroki Muroya1, Toshiaki Matsui1, Yuuki Kikkawa1, Takayuki Negishi1, Shin Watanabe1, Takenori Isomura1 and Koichi Eguchi1, 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Yamaguchi University, Ube, Japan; 3Kyoto University, Kyoto, Japan; 4Tokuyama Corporation, Tsukuba, Japan.

Over the last few decades, owing to the significant development of anion exchange membranes, increasing efforts have been devoted to the realization of anion exchange membrane fuel cells (AEMFCs) that operate with the supply of hydrogen generated on-site. In this work, ammonia was selected as a hydrogen source, following which the effect of conceivable impurities, unreacted NH₃ and atmospheric CO₂, on the performance of AEMFCs was established. In situ surface enhanced infrared absorption spectroscopy (SEIRAS) revealed that the degradation of the cell performance was primarily due to the inhibition of the hydrogen oxidation reaction (HOR). This is attributed to the active site occupation by CO-related adsorbates derived from bicarbonate adsorbates. The degradation in the HOR activity is suppressed in the presence of both NH₃ and HCO₃⁻ due to the bicarbonate ion consumption reaction induced by the existence of NH₃. A fuel cell test was conducted by using the practical AEMFC with the supply of NH₃-contained H₂ gas to the anode and ambient air to the cathode. The coexistence of NH₃ and HCO₃⁻ improved CO₂-tolerance of AEMFCs, the cell performance was nearly 95% of that without any impurity in the fuels. These results clearly show the impact of the chemically induced bicarbonate ion consumption reaction on the realization of highly CO₂-tolerant AEMFCs.

Mapping Lattice Distortions with Sub-Nanometer Resolution in Strained Core-Shell Nanoparticle Fuel Cell Catalysts

Elliot Padgett1, Megan E. Holtz1, Paul Cueva1, Anusorn Kongkanand2, Venkata Yarlagadda2 and David Muller1,3, 1Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; 2Global Fuel Cell Business, General Motors, Pontiac, Michigan, United States; 3Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York, United States.

Strain and lattice distortions play an important role in a variety of electrochemical energy materials, such as enhancing activity in catalytic nanoparticles and driving fracturing in lithium ion battery materials. However, detailed understanding of strain in many real nanoscale systems has remained elusive because of challenges for effective strain characterization. Localizing strain in nanomaterials requires spatial resolution unavailable in conventional diffraction, while sample instabilities and random crystallite orientations frequently hinder strain characterization by conventional high-resolution direct imaging techniques. With a new generation of fast, high-dynamic range electron cameras, scanning nanobeam diffraction provides a powerful approach to mapping lattice structure and distortions across a variety of length scales, from multi-micrometer battery particles to nanometer-sized core-shell nanoparticles.

Here we apply this approach to Pt-Co nanoparticle fuel cell catalysts, where a Pt-Co alloy core exerts a compressive strain on the surrounding Pt shell. This compressive strain is believed to enhance the oxygen reduction activity by modifying the electronic structure and oxygen binding strength at the catalyst surface. However, the relationship between activity and the structure of the nanoparticle and shell, as well as mechanisms by which strain may be relaxed, remain poorly understood. Using scanning nanobeam diffraction with new algorithms, we map lattice distortions with pico-meter precision and sub-nanometer spatial resolution. In combination with composition mapping by electron energy loss spectroscopy, this allows us to establish the connection between the nanoparticle structure, composition, and strain distribution. We examine the impact of variable Pt shell thickness on the surface strain, including unique strain relaxation effects due to the geometry of core-shell nanoparticles, and investigate the implications for catalyst activity. We also explore the mechanisms of strain loss after electrochemical aging in fuel cell membrane electrode assemblies leading to catalyst activity losses.

Scale up of Advanced Fuel Cell Catalysts


A recently discovered Pt₃Ni(111) catalyst exhibits 90-fold improvement of catalytic activity compared to commercial Pt/C catalyst toward oxygen reduction reaction (ORR). Following this exciting development a variety of Pt alloy nanostructures with controlled size, morphology, composition, and surface arrangements have been synthesized using wet chemistry methods. Significant performance improvement has been observed in rotating disk electrode (RDE) measurements for many of the new materials. However, their performance in membrane electrode assembly (MEA) have been rarely tested because of the difficulty of producing larger quantity of uniform, high quality nanoparticles. One of Argonne’s Materials Engineering Research Facility (MERF) programs is devoted to investigate the chemistry and processes that govern the reproducibility and scalability of nanomaterials synthesis. The aim of this program is to develop scalable processes for making large quantity of materials without sacrificing performance and to eliminate batch-to-batch variation in order to accelerate the transition of new discoveries from lab to industrial applications. In this presentation, I will talk about our recent efforts in scaling up advanced fuel cell catalysts. A multi-layer Pt-skinned PtNi nanoparticles have been successfully scaled up from tens of milligrams to several grams per batch with improved ORR activity in RDE measurement which is a 10-fold improvement over commercial Pt/C catalyst. The material was synthesized in a sufficient amount to enable MEA tests to be carried out. The results revealed significant performance improvements compared to commercial Pt/C catalyst. Our recent effort to remove restraints associated with batch processes lead us to develop a continuous flow synthesis platform. Our approach to gain fundamental understanding of the particle formation mechanism in microfluidic reactors will also be discussed.
Light-Weight 3D Co-N-Doping Hollow Carbon Spheres as Efficient Electrocatalyst for Rechargeable Zinc-Air Battery  Shengmei Chen; City University of Hong Kong, Hong Kong, Hong Kong.

Rational design of cost-effective, nonprecious metal-based catalysts with desirable oxygen reduction reaction (ORR) performance by simple and economic synthesis route is a great challenge for future fuel cell and metal air batteries commercialization. Herein, the light-weight 3D Co-N-doped hollow carbon spheres (Co-NHCSs) has been fabricated via a facile emulsion approach followed by carbonization. The prepared 0.1-Co-NHCS catalyst with suitable Co doping content exhibits favorable ORR catalytic activity (onset potential of 0.99 V and half-wave potential of 0.81 V vs. RHE), comparable to that of the commercial Pt-C (onset potential of 1.02 V and half-wave potential of 0.83 V vs. RHE) and rivals that of Pt-C with better cycling stability. The excellent performance of the catalyst is attributed to the synergetic effect of Co and N doping with high total ratio of active sites, high surface area and good conductivity of the material. More impressively, the assembled rechargeable zinc-air batteries based on the 0.1-Co-NHCS catalyst outperforms those afforded by commercial Pt-C. The progress represented by this reported work is of great importance in the development of outstanding non-noble metal based electrocatalyst for the fuel cell and metal air battery industry.

ET03.12.02 Hierarchical SbMoO6 Hollow Microspheres with Distinctive Capability of Self-Constructing Conductive Buffer Matrix for Sodium-Ion Batteries Xuan Lu1, 2; Hongkang Wang1 and Weiyang Li2; 1Electrical Engineering, Xian Jiaotong University, Xi'an, China; 2Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, United States.

In order to solve the capacity degradation problem caused by the severe volume expansion in alloy-type Sb anode materials, we report a simple and efficient microwave-assisted hydrothermal method of hierarchical Sb\textsubscript{6}Mo\textsubscript{2}O\textsubscript{6} hollow microspheres (denoted as h-SMO-hms) assembled by one-dimensional (1D) nanobelts without use of any surfactants, as well as a special conductive Na\textsubscript{10}Mo\textsubscript{5}O\textsubscript{26}, NaMoO\textsubscript{4} buffer matrix is firstly proposed. When used as an anode material for sodium-ion batteries (SIBs), it delivers large reversible discharge capacities of ~637.3~/~498.7 mA h/g at current densities of 200/1000 mA/g after 100 cycles, respectively, and an exceptional rate capability with ~429.1 mA h/g retained at 5A/g. By means of ex-situ XRD, XPS, (HR)TEM, STEM-EDS mappings and results of the first-principles calculations, such superior electrochemical performances can be attributed to their distinctive capability of self-constructing conductive Na\textsubscript{10}Mo\textsubscript{5}O\textsubscript{26}, NaMoO\textsubscript{4} buffer matrix during the discharge/charge process, which not only efficiently buffer the volume expansion of the Na-Sb alloying-dealloying upon cycling, but also provide good electronic conductivity to facilitate electron transfer. More importantly, the novel Sb\textsubscript{6}MoO\textsubscript{26} anode materials can achieve excellent electrochemical behaviors without the need to hybridize with any carbonaceous materials (ex. carbon nanotubes, graphene and carbon nanofibers) in contrast to those of Sb-C composites. This kind of materials may offer new strategies for researchers to design high-performance energy storage devices.

ET03.12.03 Single-Site Active Iron-Based Bi-Functional Oxygen Catalyst for a Compressible and Rechargeable Zinc-Air Battery Longtao Ma; Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

With the ever-increasing energy demands for portable electronic equipment, numerous researches have been done to develop related functional (e.g., stretchable, compressible, bendable/flexible, self-healing) electrochemical energy storage and conversion devices. Zinc-air battery, which is typically comprised of air electrode containing a catalyst painted on gas diffusion layer, alkaline electrolyte and metallic zinc electrode to provide a high theoretical energy density (1370 Wh/Kg), is a promising energy storage appliance for next-generation portable electronics. For rechargeable zinc-air battery, a high-efficient, low-cost and stable non-noble metal-based catalyst with oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) simultaneously, as air electrode material is significantly crucial. Moreover, the compressible flexibility of a battery is the prerequisite of wearable or/and portable electronics.

Herein, we present a strategy via single-site dispersing Fe-N\textsubscript{x} species on a two dimensional (2D) highly-graphitic porous nitrogen-doped carbon layer to implement superior catalytic activity toward ORR/OER (with a half-wave potential of 0.86 V for ORR and an over-potential of 390 mV at 10 mA/cm\textsuperscript{2}} for OER) in alkaline medium. Furthermore, an elastic polyacrylamide (PAM) hydrogel based electrolyte with the capability to retain great elasticity even under highly corrosive alkaline environment, is utilized to develop a solid-state compressible and rechargeable zinc-air battery. The creatively developed battery performs a low charge-discharge voltage gap (0.78 V at 5 mA/cm\textsuperscript{2}) and large power density (118 mW/cm\textsuperscript{2}) largely and bended up to 90° without charge/discharge performance and output power degradation. Our results reveal that single-site dispersing catalytic active sites on porous support for bi-functional oxygen catalyst as cathode integrating specially designed elastic electrolyte are feasible strategies for fabricating efficient compressible and rechargeable zinc-air batteries, which could enlighten the design and development of other functional electronic devices.

ET03.12.04 Silicon Nanoparticles in Lithium-Ion Batteries—Influence of Size and Morphology Samson Y. Lai1, Thomas J. Prestor2, Hallgeir Klette2, Trygve T. Mongstad2, Jan Petter Mehlen2 and Alexey Y. Koposov2; 1Neutron Materials Characterization Department, Institut For Energiteknikk, Kjeller, Norway; 2Battery Technology Department, Institutt For Energiteknikk, Kjeller, Norway.

Silicon as a negative electrode material attracts significant research and development attention for next-generation lithium-ion batteries (LIBs). To counteract the high volume expansion associated with lithiation, silicon nanoparticles are materials designed to extend cycle life. However, silicon nanoparticles can be synthesized using different routes that result in variations in particle size, size distribution, and morphology, which then influence the overall electrochemical performance. The optimal size of the particles is still disputed in the literature. Correlating morphology and size with battery properties is needed to apply the diverse knowledge of these different approaches toward understandable behavior of silicon nanoparticles in LIBs.

In the present work, we examine silicon nanoparticles synthesized by pyrolysis of silane gas and correlate morphological characteristics with battery performance. We demonstrate that temperature and silane concentration during synthesis influence the size and morphology of the silicon nanoparticles. For example, relatively low temperatures typically produce a mixture of small and large round particles with smooth surfaces while relatively high temperatures produce particles with rougher surfaces with a narrower size distribution. These differences are correlated to crack formation and propagation in the electrode during formation cycles, as evidenced by post-mortem analysis. Furthermore, although charge-discharge capacities and Coulombic efficiencies of half cells made with these particles are initially high, the degradation rate of particles with rougher surfaces is noticeably worse, suggesting a synergistic mechanism in action. Thus, although nanoparticle smaller than a widely cited 200 nm size may resist cracking individually, the size and morphology of the nanoparticles appears to influence macro-scale crack formation in the electrode and consequently, electrochemical performance. As silicon nanostructures become more defined and controlled through synthesis, understanding the relationship between structure and properties of silicon nanoparticles is important in order to take full advantage of this promising approach in LIBs.

ET03.12.05 LiNi0.5Mn0.3Co0.2O2/Au Nanocomposite Thin-Film Cathode with Enhanced Electrochemical Properties Zhimin Qi1, Jie Jian1, Jijie Huang1, Jialiang

University of Hong Kong, Hong Kong, Hong Kong.

Efficient microwave-assisted hydrothermal method of hierarchical Sb\textsubscript{6}Mo\textsubscript{2}O\textsubscript{6} hollow microspheres (denoted as h-SMO-hms) assembled by one-dimensional (1D) nanobelts without use of any surfactants, as well as a special conductive Na\textsubscript{10}Mo\textsubscript{5}O\textsubscript{26}, NaMoO\textsubscript{4} buffer matrix is firstly proposed. When used as an anode material for sodium-ion batteries (SIBs), it delivers large reversible discharge capacities of ~637.3~/~498.7 mA h/g at current densities of 200/1000 mA/g after 100 cycles, respectively, and an exceptional rate capability with ~429.1 mA h/g retained at 5A/g. By means of ex-situ XRD, XPS, (HR)TEM, STEM-EDS mappings and results of the first-principles calculations, such superior electrochemical performances can be attributed to their distinctive capability of self-constructing conductive Na\textsubscript{10}Mo\textsubscript{5}O\textsubscript{26}, NaMoO\textsubscript{4} buffer matrix during the discharge/charge process, which not only efficiently buffer the volume expansion of the Na-Sb alloying-dealloying upon cycling, but also provide good electronic conductivity to facilitate electron transfer. More importantly, the novel Sb\textsubscript{6}MoO\textsubscript{26} anode materials can achieve excellent electrochemical behaviors without the need to hybridize with any carbonaceous materials (ex. carbon nanotubes, graphene and carbon nanofibers) in contrast to those of Sb-C composites. This kind of materials may offer new strategies for researchers to design high-performance energy storage devices.
Silicon (Si) is regarded as a most promising anode material because of its high energy density, the earth-abundant, and low toxic nature. However, the electrochemical reversibility of Si degrades upon cycling; mainly due to huge volume changes and crack formation during lithiation and delithiation.

Recent work has investigated the cracking formation mechanism and the impact of capping layer on the mechanical deformation behavior. Here, we will demonstrate the agreement between experiments and simulation.

Li(Ni0.5Mn0.3Co0.2)O2 (NMC) is considered as one of the most promising cathode materials for Li-ion batteries. Highly textured LiNi0.5Mn0.3Co0.2O2 (NMC532) thin films with well dispersed Au nanoparticles (~5 nm in average diameter) were deposited by pulsed laser deposition. Microstructure studies reveal the epitaxial nature of the Au nanoparticles and NMC matrix, and their lattice matching relationships. The Au nanoparticles are uniformly distributed and form faceted interfaces with NMC matrix. NMC with 2 at.% Au shows the highest volumetric capacity, best initial columbic efficiency, highest cycling performance, best rate capability and highest capacity retention among all the samples, due to alteration of chemical environment of transition metal while keeping high crystallinity. Moreover, the electrochemical impedance spectroscopy shows that the incorporation of the Au nanoparticles also reduces charge transfer resistance compared to the pure NMC. The results suggest that appropriate Au nanoparticle incorporation enhances the volumetric capacity and promotes the charge transfer process, and thus could lead to enhanced battery performance.[1]

Keywords: Au nanoparticles; NMC; Nanocomposite; Lithium ion battery; Cathode


ET03.12.06
The Initial Stages of Polaron Formation in Energy Materials Shuaishuai Yuan, Zi Wang and Kirk H. Bevan; McGill University, Montreal, Quebec, Canada.

Polaron transport severely limits the conduction properties of most transition metal oxides utilized electrochemical energy storage and conversion applications. Thus, to improve the charge performance of such energy devices, it is essential to delve more deeply and understand the fundamental stages of polaron formation. To this end, we have conducted extensive first-principles studies of polaron evolution in the peroxide family of materials: lithium peroxide (Li2O2), sodium peroxide (Na2O2) and potassium peroxide (K2O2). Our analysis points to competing lattice and electronic realization phenomena driving the rapid localization of polarons very early on in the relaxation process. They also indicate that the formation of polarons may be mitigated by suitably engineering the electronic structure response to lattice distortions, through a delayed electronic relaxation mechanism. Overall, these results point towards a systematic bottom-up approach for engineering the conductivity and overall electrochemical rate performance of metal oxide energy materials.

ET03.12.07
Novel Application of Magnetite Nanospheres as Supercapacitors—Synthesis, Magnetic, and Electrocapactive Study Dipesh Neupane, Deepa Guragain, Sanjay R Mishra and Ram Gupta; Pittsburg State University, Pittsburg, Kansas, United States.

Among various morphologies of nanomaterials, hollow spheres are of great interest because of their high ratio of surface to volume, large pore volume and low density, which could be exploited for applications in controlled encapsulation-release of drugs and medical diagnostic, energy storage and conversion, photocatalysis, chemical sensors, and photonic crystals. In the context of magnetism, magnetic hollow spheres can show unique physical properties compared to those of flat thin films and their solid counterparts of the same sizes, due to their confined hollow geometry and curved surfaces. It is known, that coercivity is dependent on domain-wall motion and the barrier to domain-wall propagation along a curved surface is larger than that of a flat surface. Due to growing application of nanoscale magnetic hollow spheres in biomedical and energy fields it remains important to understand the influence of growth parameters to prepare Fe3O4 with highly homogeneous features in terms of size and shape.

In this work, effect of hydrolyzing agents such as urea, ammonium bicarbonate (ABC), dodecylamine (DDA) on morphology, size and electrochemical activity of Fe3O4 nanospheres was investigated. For comparison, Fe3O4 nanospheres were also synthesized without hydrolyzing agent. The structural and morphological assessment of the synthesized Fe3O4 nanopowder was performed using x-ray diffraction, scanning electron microscopy and surface area analysis. The room temperature magnetic properties were studied via vibrating sample magnetometer. The scanning electron microscopy images showed nanospheres of Fe3O4 with a range of sizes (150-330 nm) which depend on hydrolyzing agents used. All the synthesized samples were crystalline in structure with distinct signature of maghemite phase. The surface area analysis indicated that these particles were mesoporous in nature. VSM measurement show that Fe3O4 prepared via hydrolyzing agent display high magnetization ~85 emu/g with average coercivity in the range of 150 Oe. Different hydrolyzing agents were observed to have minimum influence on the magnetic property of Fe3O4 hollow spheres. Electrochemical characteristics were investigated using cyclic voltammetry and galvanostatic measurements. Cyclic voltammetry measurements were performed in three different electrolytes viz. KOH, NaOH, and LiOH and observed that specific capacitance of the synthesized Fe3O4 depend on electrolyte used. Relatively high specific capacitance of 173.8 F/g was observed for Fe3O4 prepared using DDA in 3M KOH electrolyte. Fe3O4-DDA also showed excellent cyclic stability as well, retaining 107% of specific capacitance value at up to 5,000 cycles measured. The study clearly elucidates the effect of hydrolyzing agent on physical and morphological properties of Fe3O4. In addition, through electrochemical testing the study illustrates the choice of aqueous electrolyte in optimizing the electrocapactive performance of Fe3O4 nanospheres.

ET03.12.08
Population Dynamics of Driven Reactive Mixtures Applied to Li-Ion Battery Electrodes Hongbo Zhao and Martin Bazant; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Li-ion batteries manifest intriguing asymmetric autocatalytic or autoinhibitory reaction kinetics during charge or discharge through experimental techniques such as X-ray imaging or diffraction performed on lithium iron phosphate and LiNi0.5Mn0.3Co0.2O2 (NMC). We use a population-dynamics approach to model such asymmetry, as the phenomenon arises from an assemble of particles that consist of the electrode. We study the collective dynamics of such systems with thermodynamically consistent nonequilibrium kinetics. When chemical driven, autocatalytic or autoinhibitory reactions lead to broadening or narrowing of the population distribution in terms of the state of subsystems compared to the intrinsic variance due to thermodynamic fluctuations and system noises. As an application, we obtain the inherent reaction kinetics from XRD and electrochemical experiments performed on NMC and demonstrate the agreement between experiments and simulation.

ET03.12.09
Current Density Dependency of Crack Formation in Si Wafer Electrode Taeho Yoon, Chuanshiao Xiao, Jun Liu, Seoung-Bum Son and Chunmei Ban; National Renewal Energy Laboratory, Lakewood, Colorado, United States.

Silicon (Si) is regarded as a most promising anode material because of its high energy density, the earth-abundant, and low toxic nature. However, the electrochemical reversibility of Si degrades upon cycling; mainly due to huge volume changes and crack formation during lithiation and delithiation.

Recent work has investigated the cracking formation mechanism and the impact of capping layer on the mechanical deformation behavior. Here, we will...
focus on the effects of current density on crack formations and propagation. The information from this research is essential to develop high-capacity and high-power Si electrode materials for high-performance lithium-ion batteries. Si (0.1 μm wafer) has been used as a model electrode to establish a systematic understanding of cracking behavior as a function of lithiation/delithiation rate. Moreover, the internal strain energy developed at the high current density and the strategies to mitigate cracking formation and propagation will be discussed in this work.

ET03.12.10 Effect of Graphene Oxide on Electrochemical Behavior of MnO2 Super capacitor Rahul Singhal1, Justin Fagnoni2, David Thorne1 and Mani Maniannthanavan2; 1Central Connecticut State University, New Britain, Connecticut, United States; 2Global Pragmatic Materials, Morgantown, Virginia, United States.

Super-capacitors have received a lot of attention due to their high-power performance, long cycle life, and low maintenance, for applications in hybrid electric vehicles, portable electronic devices, and power back-up devices [1-3]. Various researchers studied MnO2 cathode materials for application in electrochemical capacitors, because of its low cost and natural abundance [2, 3]. However, MnO2 has limited electrochemical performance because of its poor conductivity and low surface area. To improve the electrochemical performances of MnO2, we have synthesized MnO2/graphene oxide (GO) nanocomposite with varying concentration of GO (0.4 mg/ml and 0.8 mg/ml).

GO/MnO2 nanocomposite was synthesized by adding KMnO4 in a solution of water and ethanol (3:1), containing desired amount of GO. The brown precipitates were obtained after a continuous stirring for 1 hr. The precipitate was washed and dried to obtain the GO/MnO2 nanocomposites. The electrodes were prepared by spreading a slurry of GO/MnO2 powder, carbon black, PTFE binder (80:15:5 weight ratio) onto Ni mesh. The electrochemical characterizations were carried out in an aqueous solution of 1M Na2SO4. The charge discharge studies were carried out between 100 mA/g to 5A/g current range. The discharge capacities were found to be 227 F/g and 90 F/g at a current of 100 mA/g and 5A/g, respectively for 0.4 mg/ml GO. These results will be presented and discussed at the meeting.

References:

ET03.12.11 Sub-5 nm Graphene Oxide Nanofilm with Exceptionally High H+/V Selectivity for Vanadium Redox Flow Battery Seul Chan Park, Moon G. Hyoen, ByungSu Kim and Yong Soo Kang; Energy Engineering, Hanyang University, Seoul, Korea (the Republic of).

Highly H+/V selective membranes are desirable in high-performance vanadium redox flow batteries (VRFBs) to overcome the cross-over phenomena of vanadium species. Herein, we first demonstrated that the molecular-sieving nanochannels (~0.84 nm) formed inside a graphene oxide (GO) laminate (~5 μm) efficiently blocked the transport of vanadium ions, while allowing the transport of H+. Furthermore, a ultrathin (sub-5 nm) and highly-selective GO nanofilm was successfully coated on a porous substrate to increase the H+ flux using a facile spin-coating method. The GO-coated thin-film composite (TFC) membrane showed much higher H+ flux, along with an exceptionally high H+/V selectivity (up to 850), due to the molecular-sieving nanochannels inside the GO nanofilm, leading to a much more enhanced VRFB performance in terms of the energy efficiency (EE: ~84%), compared to the benchmark Nafion membrane (EE: 69.2%). The GO-coated thin-film composite membrane was successfully coated on a porous substrate to increase the H+ flux using a facile spin-coating method. The GO-coated thin-film composite (TFC) membrane showed much higher H+ flux, along with an exceptionally high H+/V selectivity (up to 850), due to the molecular-sieving nanochannels inside the GO nanofilm, leading to a much more enhanced VRFB performance in terms of the energy efficiency (EE: ~84%), compared to the benchmark Nafion membrane (EE: 69.2%).

ET03.12.12 Lattice Strain and Phase Transition Induced by Li Migration in Cyclic NCM111 (LiNi0.5Co0.2Mn0.3O2) Young-Woon Byeon1, 2, Jun-Dong Kim1 and Jaeyoung Ahn1; 1Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Matier Science and Engineering, Korea University, Seoul, Korea, (the Republic of).

The phase transformation of LiNi0.5Co0.2Mn0.3O2 (NMC) cathode materials during charging and discharging Li-ion batteries was evaluated by lattice strain measured by nano-beam diffraction (NBD) equipped in transmission electron microscopy (TEM). Here we propose a relationship between lattice strain determined by Li contents and phase transition. When Li site in NCM lattice was emptied below 1% by the delithiation during charging, the surface of NCM particles has high strain over 3% and the correlated phase transition also occurred from rhombohedral to spinel structure. The continued Li release in NCM led to the expansion of the spinel region from surface. Most of the strain and phase transition occurred near the side planes of NCM, not prism planes. On the Li insertion during discharging, on the other hand, the lattice strain of NCM recovered up to the level, below 0.8%, of pristine NCM due to the reverse phase transition from spinel to rhombohedral structure. However, NCM that had cycled under the harsh condition of 60 cycles at 60°C showed irreversible phase transition to rhombohedral phase, which acted as a reason of a direct degradation. We propose a design rule that can prevent the capacity decrease of batteries by clarifying the relationship between the lattice strain and phase transition, which act as a direct cause of the deterioration phenomenon of NCM.

ET03.12.13 Fabrication and Characterization of the Microporous Foam Thick Electrodes Based on LiFePO4/Carbon Nanotube Composites Tawaddod S. Alkindi, 1Rahmat Susantyoko1, Saif Al Mheiri1, Daniel Choi1, Sultan N. Al Dahmani1 and Hamed Fadad1, 1Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates; 2United Arab Emirates Space Agency, Abu Dhabi, United Arab Emirates.

Although Li-ion batteries are very promising, their areal capacity is quite low (2.09 mAh cm-2 for conventional LiFePO4 on aluminum foil). The aim of this work is to create CNT/LiFePO4 composite thick cathode via Freeze-casting method to enhance the areal capacity of LiFePO4 cathode. The CNTs form electrically conductive networks that also result in enhancing the charge transport of Li-ions. Conventional Li-ion batteries consist of multiple stacks of electrodes with aluminum and copper separator between them. This cell configuration increases the size of the battery, which increases battery weight, waste of the material, thus, yields to high cost. Using thick electrodes that will provide a favorable electrode to current collector ratio per stack volume, will increase the interface area between electrode and electrolyte, and fewer cutting and stapling steps. However, mechanical stability is a main challenge in thick electrodes that are synthesized by this method. Various amount of polyvinylidene difluoride (PVDF) additives is added to the CNT/LiFePO4 mixture to study their effect on the mechanical stability along with the battery performance. After determining the optimum thickness and composition, batteries with thick electrodes will be assembled and characterized (CV, charge-discharge, EIS) using battery tester and potentialstat/galvanostat. Investigation of the multi-layered CNT/LiFePO4 sheets by scanning electron microscopy, Raman scattering spectroscopy and X-ray diffraction is also in progress. Preliminary result shows 125 mAh g-1 for 3.14 mm thickness cathode of CNT/LiFePO4/PVDF (3% PVDF) which is very close to that from the conventional 2.03 mm thick conventional CNT/LiFePO4 electrode (0% PVDF). Mechanical compression results show that we can sacrifice the small decrease in specific capacity for the enhancement in the mechanical stability where CNT/LiFePO4/PVDF (3% PVDF) exhibited stress values of 0.83752
MPa, while CNT/LiFePO4 electrode (0% PVDF) exhibited a value of 0.05685036 MPa. Further increased thicknesses of electrodes with improved mechanical and thermal properties are to be pursued in future work. Such thick CNT/LiFePO4 electrodes are very promising candidate for applications which is very sensitive to weight but not sensitive to size, such as space applications and electrical truck/bus.

ET03.12.14

The electrochemical reduction of oxygen is a critical process for many energy storage and conversion technologies including metal-air batteries and fuel cells. For these technologies, the energy output is proportional to the oxygen reduction reaction (ORR) potential. Although the theoretical potential of the ORR reaction in alkaline media is 0.3 volts vs. Hg/HgO, most electrodes are far below 0.3 volts vs. Hg/HgO due to the slow ORR kinetics. In this abstract, we use surfactant-modified dealloying to synthesize (100) rich nanoporous gold (100-np-Au) electrodes which increased the ORR potential from -0.01 to 0.18 V vs. Hg/HgO when compared to nanoporous Au (np-Au) synthesized without surfactant. The 100-np-Au had a higher reduction potential than conventional np-Au because Au (100) is the most active ORR facet of gold in alkaline solution. Density functional theory simulations show that Au (100) activity exceeds platinum in alkaline solution.1 We observe a similar trend experimentally as the 100-np-Au electrodes (2.1 mg/cm2) had a 2.8% improved ORR potential vs. Hg/HgO when compared to nanoporous gold Au (np-Au) synthesized without surfactant. The 100-np-Au had a higher reduction potential than conventional np-Au because Au (100) is the most active ORR facet of gold in alkaline solution.1

The ORR potential vs. Hg/HgO compared to high performance commercial platinum coated electrodes with double the mass loading density (4 mg/cm²). When integrated into aluminum-air batteries, the 2.1 mg/cm² 100-np-Au increased the cell energy density to 4256 mWh/g-AI compared to 3575 mWh/g-AI for 2.1 mg/cm² np-Au and 4060 mWh/g-AI for 4mg/cm² Pt/C cathodes by improving both the extracted capacity, through improved activity, and output voltage. The 100-np-Au Al-air battery achieved a 2800 mAh/g capacity at 50 mA/cm² and a peak power density of 176 mW/cm². We synthesized 100-np-Au by adding sodium citrate to a nitric acid dealloying bath. The stronger binding energy between the citrate ligand and Au (100) surface reduced the (100) facets. This technique could be extended to the design and synthesis of various nanoporous catalysts with specific facets for energy storage and conversion.


ET03.12.15
Vertically Integrated Method For The Development of Nano-Structured Electrodes for Flow Battery Application Eugenio Rovera1,2, Francesco Funagalli1, Matteo Zago1, Andrea Casalegno1 and Fabio Di Fonzo1,2; CNST@Polimi, Milano, Italy; 2Energy, Politecnico di Milano, Milan, Italy.

Hollow particles are regarded as a class of promising anode materials for lithium-ion batteries since they benefit from their shorter Li-ion and electron diffusion paths, an increased amount of electrochemically active sites created by more electrode/electrolyte interfaces, and the ability to better accommodate the strain induced by volume changes during cycling. In this work, we developed a facile and low-cost process for fabricating hierarchical hollow and dense submicrospheres assembled from SnS nanosheets and protected with a uniform layer of nitrogen-doped carbon. In the synthesis, oleic acid is utilized to form micro-droplets in ethylene glycol as soft templates. We found that by manipulating the precursor concentration and the number of template droplets, the nuclei process is confined to take place either inside the droplet or merely on the surface, leading either to dense or hollow particles. High-resolution transmission electron microscopy showed that the particles are built up by nanosheets with 4-6 atomic layers, wrapped in a uniform carbon shell of 4-5 nm. By using focus ion beam technique, we cut the particles and observe the cross-section by scanning electron microscopy, confirming that the desired morphologies are obtained. The fact that the two hierarchical particles with the same composition and building block dimension only differ in the internal morphology, we got a good opportunity to show the electrochemical merits from the hollow structure. The lithium-ion storage capacities of the hollow and dense spheres were tested and compared as anodes in lithium-ion battery half cells. The hollow microspheres showed low internal charge transfer resistance, good buffering of volume changes during lithiation and delithiation and good rate and cycling performance. After 1000 cycles, the hollow SnS composite still delivered a capacity of 420 mAh g⁻¹ at 1.0 A/g, which is 2.5 times higher than that of the dense spheres. The capacity retention from the second cycle on was 84% and 75%, respectively. Due to the enhanced overall electrical conductivity from the carbon shell and the hierarchical hollow structure, 40% to 70% capacities are contributed from pseudocapacitive behaviors at different cyclic voltammetry scan rates, explaining the good
Abstracts and Discussions:

ET03.12.17  Enhanced Cycling Stability of Macroporous Bulk Antimony-Based Sodium-Ion Battery Anodes Enabled through Active/Inactive Composites

Olivia Ruiz, Mark Cochrane, Yan Yan, Ke Ma, Jintao Fu, Sarah Tolbert, Vivek Shenoy and Eric Detsi

Engineering approaches based on ‘nanostructuring’ and ‘active/inactive composites’ have been used to improve the performance of alkali-ion battery electrodes. In this talk it will be shown that a combination of both approaches yields an anode material with high cycle life. Specifically, we show that the use of a macroporous Sb/MgF2 active/inactive composite material creates a high-performance Na-ion battery anode. This composite consists of a porous Sb phase as the electrochemically active component, with pore size in the sub-micrometer range, and a dense MgF2 phase as the electrochemically inactive component. This high performance is attributed to the "porous active/inactive" configuration. In such a configuration the dense inactive phase absorbs a part of the phase transformation-induced stresses, while porosity in the active phase helps to accommodate part of the phase transformation-induced volume expansions generated in this active phase. Porosity is also expected to help facilitate the electrolyte transfer into the bulk of this composite. This new strategy could be used to improve the performance of high-capacity materials for next generation alkali-ion battery anodes [1, 2].

References:
[1] Eric Detsi, Olivia Ruiz, and Mark Cochrane: "Porous Active/Inactive Composites for High-Performing Alkali and Alkaline-Earth Ion Battery Anodes" PENN Invention Disclosure #18-8677
[2] Olivia Ruiz, Mark Cochrane, Yan Yan, Ke Ma, Jintao Fu, Sarah H. Tolbert, Vivek B. Shenoy and Eric Detsi: "Enhanced Cycling Stability of Macroporous Bulk Antimony-Based Sodium-Ion Battery Anodes Enabled through Active/Inactive Composites" (Under review)

ET03.12.18  Influence of the Carbon Material Structure on the MoS2 Charge Storage Mechanism

Basant A. Ali, Ossama I. Metwali, Asmaa M. Omar, Ahmed S. Khalil and Nagham K. Alamm

Developing materials for energy storage that can maintain both high energy density and high power density is becoming a mandatory demand in our modern society. Supercapacitors can store energy in the electrical double layer (EDL), especially when carbon-based materials are used that store energy in the form of accumulated ions at their surfaces. The other mechanism of charge storage is the pseudocapacitors “faradic materials” in which the material undergoes redox reaction. In order to benefit from both the faradic materials and the carbon materials, hybrid materials are usually used. However, the charge storage and delivery mechanisms are not very well understood for those hybrid materials. MoS2 has proved to be a good material that undergoes both redox and EDL capacitance mechanisms. Unfortunately, the 2H semiconductor phase of the MoS2 has a low capacitance but much more stable than the 1T conductor phase.

In this study, flower-shaped MoS2 was mixed with two different structures of carbon materials in different ratios in order to investigate the effect of the shape of the carbon material and its amount on the charge storage mechanism and the energy density, power density and capacitance. Our results showed that mixing MoS2 with graphene nanoflakes (GNF) or 8 nm-diameter carbon nanotubes (CNT) increased the capacitance linearly with increasing their amount. However, CNT showed higher capacitance than the GNF mixtures. A mixture of equal weights of MoS2, CNT and GNF (MCG) showed the highest capacitance among all mixtures and increased the capacitance of the MoS2 by 111%. The small diameter of the CNT allowed to interfere with the flower shaped MoS2 and surround it from outside and inside. On the other hand, the GNF sandwiched the MoS2 flowers between its layers. These different shapes of the carbon material affected the mechanism of charge storage and the origin of capacitance. From Tafel plots, all the materials studied originate current due to electric faradic mechanism. The contribution of current to the faradic mechanism was larger for the MoS2 alone and with increasing the ratio of carbon materials, the contribution of current towards the EDL mechanism increased. The contribution of current towards the EDL changed from 11.2 % to 28 % in the MoS2 and the MCG mixture, respectively. For the capacitance value origin, it was found that more than 98% of the capacitance of the studied materials was diffusion controlled and the carbon materials enhanced the diffusion capacitance of the MoS2 up to 97.8%.

SESSION ET03.13: Li/Na Battery Cathodes and Thermal Energy

Friday Morning, November 30, 2018
Hynes, Level 3, Room 302

8:15 AM ET03.13.01  Metallic Carbon and Its Applications in Lithium-Ion Batteries

Qian Wang; Peking University, Beijing, China.

Due to the special electronic configuration, small atomic size and flexible bonding features, carbon exhibits many phases with very different physical and chemical properties. In this talk, I will focus my discussion on our recently identified metallic carbon phases, including 3D metallic T6-C4, Hex-C182 and a 2D metallic ψ-graphene2, and their applications as potential anode materials in lithium-ion batteries (LIBs). These new carbon allotropes are not only dynamically, thermally and mechanically stable, but also metallic. Due to their unique atomic configurations and metallicity, they provide the basis for the storage and transportation of Li ions with good conductivity. For instance, Hex-C18 exhibits exceptional properties such as a large heat capacity, high Debye stiffness, and anisotropic elasticity, while ψ-graphene shows robust metallicity against external strain during the adsorption of Li-ions. We demonstrated that both Hex-C18 and ψ-graphene have promising applications as effective anode materials in LIBs.

References
A new metallic carbon allotrope with high stability and potential for lithium ion battery anode material Nano Energy 38, 263(2017).
ψ-Graphene: A new metallic allotrope of planar carbon with potential applications as anode materials for lithium-ion batteries
8:30 AM ET03.13.02
Novel Design of Hollow \(g\)-C\(_3\)N\(_4\) Nanofibers Decorated with MoS\(_2\) and S, N-Doped Graphene for Stable Electrochemical Hydrogen Evolution Reaction
Suhee Kang, Joonyoung Jang and Caroline S. Lee; Hanyang University, Ansan, Korea (the Republic of).

Recently, depletion of fossil fuels and contamination of environmental issues leading to the energy crisis is making renewable energy productions extremely important. Among the sustainable energy, hydrogen is considered as one of the most important alternative fuel and the ways to obtain this gas have been widely studied during the past few years. Many catalysts have been developed for hydrogen production but still, its activity is limited owing to wide band gap energy and long-term stability problems. Therefore, electrocatalysts should be proposed to design innovative structures with superior performance.

Graphitic carbon nitride (g-C\(_3\)N\(_4\)), a non-metallic semiconductor having a bandgap of 2.6 eV, has been attracting much attention due to its easiness to manufacture as well as its environmentally benign and high thermal stability. However, g-C\(_3\)N\(_4\) suffers from high recombination rate of charge carriers and low surface area. To overcome these drawbacks, one-dimensional (1-D) structured nanofiber can be considered to be an effective accelerator of the electrons as well as separators of the electron-hole pairs. Moreover, decorated MoS\(_2\) onto g-C\(_3\)N\(_4\) nanofibers can be properly matched to band levels and accelerate the electron pathways. Sulfur/nitrogen-doped graphene (SNG) is again applied onto g-C\(_3\)N\(_4\)/MoS\(_2\) nanostuctures to improve charge transportation by increasing its entire surface area. In the present work, hollow g-C\(_3\)N\(_4\) nanofibers (HGCNF) were prepared by electrospinning followed by thermal condensation methods. The prepared hollow g-C\(_3\)N\(_4\) nanofibers decorated with MoS\(_2\)/SNG are synthesized in-situ by a hydrothermal process at relatively low temperature. The morphologies by SEM and TEM analysis were used to characterize this fabricated sample. XPS analysis was measured to distinguish its chemical compositions according to their properties. Finally, HGCNF/SNG/MoS\(_2\) showed the lowest Tafel slope of 83 mV/dec as well as the lowest impedance value among those of all prepared samples. This structures also showed the lowest overpotential of 282 mV at 10 mA/cm\(^2\) from hydrogen evolution reaction among all prepared samples with stable current density at applied potential under 48 hours. Therefore, the optimized heterostructures were proven to be efficient electrocatalytic materials which can be applied to various fields including CO\(_2\) reduction, artificial photosynthesis, solar cell, bio-application and Li-ion battery cell.

8:45 AM ET03.13.03
Nanostructured Conjugated Polymers as Promising Electrodes for Li-Ion Batteries
Qichun Zhang; Nanyang Tech University, Singapore, Singapore.

Electrode materials play a critical role in approaching high energy density and long cycle life lithium-ion batteries (LIBs). The increasing concern about the traditional inorganic electrode materials on resources and environmental issues has strongly inspired scientists to switch on searching green energy electrodes. Organic compounds are potentially sustainable and renewable materials as many of them can be obtained from natural products and biomass. Additionally, the properties of organic compounds can be tuned through the modification of the structures as well as the introduction of functional groups. In this talk, I will present our recent progress on the preparation of novel conjugated polymers and their application in Li-ion batteries.

9:15 AM ET03.13.04
Measuring Surface Phonon Vibrations on the (010) Surface of LiFePO\(_4\) Platelet Particles
Peter Benedek¹, Nuri Yazdani¹, Hungru Chen², Nils Wenzler¹, Fanni Juranyi³, Martin Månsson⁴, Saiful Islam⁴ and Vanessa Wood⁴; ¹ETH Zürich, Zürich, Switzerland, ²University of Bath, Bath, United Kingdom; ³Paul Scherrer Institut, Villigen, Switzerland; ⁴Royal Institute of Technology, Stockholm, Sweden.

LiFePO\(_4\) (LFP) is a commercial cathode material often used for high power applications. Typically, nanoparticles of LFP are used due to the shorter path-length for lithium ions in the [010] transport direction. However, since nanoparticles have a large surface area to volume ratio compared to larger micron-sized particles, the question of how the surface influences ion diffusion and transfer becomes relevant. Here, we report on how surface vibrational modes at the surface of LFP differ from those in the bulk of the LFP particle and how different surface treatments change the vibrational structure at the surface of LFP. To systematically measure the influence of surface, we prepare platelet-shaped LFP particles of different sizes, where the number of atoms at the (010) surface changes from less than 1% of the total number of atoms in the particle to more than 10%. On these different samples, we measure the phonon density of states via inelastic neutron scattering (INS) and find that Li-O bond changes at the (010) surface. Combining our technique with other analytical techniques such as FTIR and XRD as well as density functional theory (DFT) simulations, we find that carbon coating, for example, can be used to influence the Li-O bonding at the LFP surface.

9:30 AM ET03.13.05
Mesoscopic Phase Transition Kinetics in Secondary Particles of Battery Electrode Materials
Kai Xiang², Kaiqi Yang¹, Craig Carter², Ming Tang¹ and Yet-Ming Chiang²; ¹Rice University, Houston, Texas, United States; ²Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Many battery compounds undergo first-order phase transformations upon composition swing during charge and discharge. While such phase transformations are often studied using single crystalline particles as model systems, real battery electrodes are typically composed of mesoscopic assemblies of nanocrystallites, of which the phase transformation behavior is still not well understood. Here we report systematic measurements of the phase transition kinetics under potentiostatic conditions in secondary particles of several representative intercalation compounds including LiFePO\(_4\), LiMn\(_2\)O\(_4\), FePO\(_4\) and Li\(_2\)Ti\(_2\)O\(_7\). We find that the measurement results, which are obtained over a wide range of overpotential, composition, primary particle size and temperature, can be self-consistently interpreted in the framework of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model for nucleation and growth kinetics. This finding suggests that the interfaces between primary particles do not impede the propagation of phase transformation in a secondary particle. Interestingly, the JMAK analysis suggests that the phase growth appears to be predominantly one-dimensional in nature in the systems studied regardless of the lithium diffusion anisotropy, which can be explained by a hybrid growth model in which rapid surface propagation is followed by slower growth into particles.

9:45 AM ET03.13.06
Size-Dependence of Li-Mediated Phase Transformation in Roxhyte Nano-Disks
Yuan Yao and Richard D. Robinson; Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

Nanostructuring is one of the best strategies to improve the existing electrode materials due to the decrease in diffusion length and the higher surface area for accessibility of reactions. However, there are many outstanding questions fundamental mechanism behind the size-dependent electrochemical behavior. The Cu\(_{2-x}\)S system have been studied extensively as a cathode material for lithium ion batteries due to its high theoretical capacity and ionic conductivity, and low material costs. However, the exact mechanism for the first discharge plateau is still under debate (lithium intercalation versus lithium-induced phase transformation). Within the nanoscience community Cu\(_{2-x}\)S nanosynthethic chemistry has progressed to the degree that a high level of size control and
size dispersion has been achieved. This makes Cu2−xS a good system for studying the relationship between nanoparticle size and electrochemical properties. Using high concentration synthesis methods, we synthesize a series of roxbyte (Cu2S) hexagonal nanodisks ranging from 10 nm to 27 nm. A size-dependent discharge plateau behavior is found on the first discharge plateau: as the size of the particle decreases, the discharge plateau decreases, resulting in lower capacities. As a result, the discharge curve for smallest nanoparticles resemble a supercapacitor, meaning the capacity has a linear relationship with the potential. To understand the reaction mechanism on the first plateau, we use XRD and UV-Vis spectroscopy to study the phase evolution and plasmonic peak change before and after discharge. The reaction mechanism is confirmed to be a lithium-induced phase transformation from Cu2S to CuS. Through XRD and HRTEM we find that lithium ions react laterally, through the side (16 0 0) of the nanodisk, and, the extent of the phase transformation reaction is limited for smaller size particle. We find the surface of the nanoparticle is dominated by Cu2+, and the core is mainly composed of Cu1+. As a result, the surface of the particle has a lower reaction potential, and, smaller size particles contain more Cu2+. This leads to the size-dependent electrochemical behavior. Based on these information, we build a model to simulate the discharge curve. The model successfully captures the size-dependent capacity and plateau length.

10:00 AM BREAK

10:30 AM ET03.13.07
Controlled Nanoscale Morphology of Sodium Rhodizonate Ionic Crystal Realizing Reversible Four-Sodium Ion Storage Minah Lee1, Yi Cui2 and Zhenan Bao1; 1Chemical Engineering, Stanford University, Stanford, California, United States; 2Materials Science & Engineering, Stanford University, Stanford, California, United States.

Sodium ion batteries (SIB) for grid-scale applications need active materials that combine a high energy density with sustainability. Organic compounds which can be obtained from natural biomass with minimum energy consumption are an attractive low-cost and sustainable choice for battery electrode materials, provided a high energy density and long cycling stability can be obtained. Given the earth abundance and high theoretical specific capacity of 501 mAh g−1, disodium rhodizonate (Na2C6O6) is one of the most promising cathodes for SIB. However, substantially lower reversible capacities have been obtained compared to the theoretical value while the origin of such discrepancy remains unanswered. Here, we reveal the origin of the limited electrochemical performance of Na2C6O6 and provide an effective path to achieve reversible four-sodium storage. By controlling of nanoscale morphology, we reveal that phase transformation of Na2C6O6 is kinetically limited during the desodiation process, being the origin of deteriorating redox activity of Na2C6O6. The reversible phase transformation of Na2C6O6 accompanied with spontaneous nanostructuring of active particles is achieved by decreasing active particle sizes and selecting proper electrolytes, which provides a mechanism to realize efficient four-sodium ion storage with a specific capacity of 484 mAh g−1. Our work highlights the importance of understanding redox mechanisms at nanoscale, which opens up new opportunities to build a high performance and sustainable energy storage system.

Reference

10:45 AM ET03.13.08
Study of Anisotropic Charge Storage Behaviour of LiNi0.5Mn0.3Co0.2O2 Using Pulse Laser Deposited Epitaxial Thin Films Rohit Satish, Yang Zhou, Rodney Chua Yong Sheng and Madhavi Srinivasan; Nanyang Technological University, Singapore, Singapore.

To realise future demands of energy storage, enhancements in terms of performance need to be made across the table in all the components of a battery including the Cathode, anode, separator and the electrolyte. A cursory examination of literature would indicate that anode chemistries are already able to store much more energy when compared to their cathode counterparts. This is largely due to the formation of an anode/electrolyte interface which passivates the anode and allow s for facile Li migration through it. Unlike its anodic counterpart the cathode/electrolyte interface is one of the least investigated and one of the least understood aspects of Li-ion battery design. It is thus of high impact to develop an understanding of the charge storage process at the surface of the cathode. In this study we observe the surface of epitaxially grown layered LiNi0.5Mn0.3Co0.2O2 with an aim to understand the dependence of the cathode/electrolyte interface, material stability and charge storage mechanism, on the direction of Lithium diffusion. Epitaxial LiNi0.5Mn0.3Co0.2O2 with restricted lattice parameters are grown on single crystal SrTiO3 substrates oriented along 110,111 and 100 directions with SRO as conductive buffer layer. The samples oriented along 100, 110 and 111 were probed using Cyclic Voltammetry, Impedance Spectroscopy coupled with X-ray Diffraction and ex-situ X-ray reflectivity measurements and ex-situ STEM measurements. Initial testing indicated we have been able to grow perfectly epitaxial films with negligible amount of lattice mismatch. Electrochemical studies surprisingly indicate different storage and failure mechanism for each of the samples. Reversible intercalation was observed only along the 110 direction with indication of a stable Ni2+ to Ni3+ transition coupled with an Co3+/4+ transition. A combination of X-ray reflectometry measurements carried at specific potentials coupled with ex-situ STEM micrographs indicate that for samples grown along the 111 and 100 directions there is a greater tendency towards cation disorder, and loss of the overall layered structure during cycling but in the case of the samples grown along the 110 direction stable structure accompanied with the formation of a thin organic layer on the surface is observed. The SEI layer formed is expected to passivate the electrode at higher potentials and prevent any capacity decay. The results of the study can potentially open the doors for the widespread application of high energy density Ni rich layered structures as cathodes of the future.

11:00 AM ET03.13.09
Towards Three-Dimensionally Interdigitated Energy Storage Nanoarchitectures—A Bottom-Up Battery Synthesis Joerg Werner1, Gabriel G. Rodriguez-Calero2, Héctor D. Abruña2 and Ulrich Wiesner2; 1Harvard University, Cambridge, Massachusetts, United States; 2Cornell University, Ithaca, New York, United States.

The traditional design of two-dimensionally layered anode-electrolyte/separator-cathode assemblies has persisted over centuries as the dominating battery architecture for its advantage of separated manufacturing of each component and ease of subsequent assembly. In common batteries these layers 100s of microns thick, soaked with liquid electrolyte for ion transport. The need for energy storage systems that exhibit high energy storage capacity coupled with fast accessibility of the energy manifested by high power output, demands architectures that increase the kinetics of batteries. A major hurdle for fast battery kinetics are ionic transport and solid-state reactions in nanodimensions are fast, porous nanostructured electrode materials have enabled much higher power densities of batteries over the past decades. However, the high porosity of nanostructured electrode materials comes at the price of reduced energy density due to a lower volumetric loading of the energy storing material. To overcome these limitations, intriguing 3-D architectures for batteries have been proposed over 15 years ago. In such 3-D designs, the porosity of one nano- or micro-structured electrode is coated and filled with the electrolyte and second electrode materials, respectively. The design principle of 3-D batteries conceptually enables fast diffusion and reaction kinetics due to small electrode dimensions and distances without sacrificing space for porosity. To obtain such intricate architectures with nanoscale dimensions, the battery components have to be synthesized within each other from the bottom up. The difficulties of compatibility and spatial
precision in such nanoconfined synthesis of functional materials have significantly held back the development of nano-interdigitated 3-D batteries. Here we present a step-wise bottom-up strategy to such nanoarchitectures with all functional phases synthesized and integrated within a triblock terpolymer derived core-shell double gyroid morphology. Our 3-D interdigitated design comprises a gyroidal carbon anode network that is electrochemically coated with an ultrathin polymer electrolyte in a self-limiting and self-correcting process. The 3-D continuously nanoporous anode-electrolyte monolith is in turn filled with an inorganic-polymer hybrid cathode that is synthesized in the confinement of the nanoporous network. All three-dimensionally networked phases are less than 20 nm in their layer dimensions and integrated throughout a macroscopic monolith. Despite the small separation distances, the solid-state nano-3-D energy storage system exhibits battery-like characteristics and can be cycled numerous times.

11:15 AM ET03.13.10
Hybrid Aqueous Electrochemical System of Lithium Manganese Oxide and Prussian Blue Analogue for Low-Grade Thermal Energy Harvesting Yezhou Liu, Caitian Gao, Soojin Sim, Moobum Kim and Seok Woo Lee; Nanyang Technological University, Singapore, Singapore.

Low-cost and high-efficiency systems are in urgent demand to harvest abundant but mostly wasted low-grade heat sources (<100°C). Existing technologies like thermoelectric for heat-to-electricity conversion shows limited efficiency due to relatively low figure of merit at low temperature differential. Thermally regenerative electrochemical cycle (TREC) is a promising candidate to harvest heat by using dependence of electrode potential on temperature. By varying the temperature in a TREC cycle, the electrochemical cell is charged at a lower voltage and discharged at higher voltage, therefore, converting heat to electricity. Most previous TREC studies focused on materials with negative temperature coefficient (α), such as Prussian Blue Analogs (PBAs). Combining negative-α material with positive-α material without ion-exchange membrane could improve the efficient and reduce the cost. Exploring suitable positive-α material is necessary and urgent for further development of TREC low-grade heat harvesting system. Here we report lithium manganese oxide, a widely-used lithium-ion battery cathode material, showing positive-α of 0.617 mV K⁻¹ and stable performance in aqueous electrolyte. An electrochemical cell consists of lithium manganese oxide (LMO) cathode and copper hexacyanoferrate (CuHCF) anode. The electrochemical system is operated in Li⁺ and K⁺ hybrid aqueous electrolyte without ion exchange membrane. The temperature coefficient of the full cell is 1.161 mV K⁻¹ and the relative conversion efficiency of heat-to-electricity convert can reach 3.8% in TREC cycling between 10 and 50 °C without heat recuperation. This new application of LMO may open the opportunities for positive α material and lead to an affordable and simple-structure low-grade heat harvesting electrochemical system.

11:30 AM ET03.13.11
From Thermopower Waves to Asymmetric Chemical Doping—New Concepts in Energy Storage and Generation Using Molecular Interactions with Single-Walled Carbon Nanotubes Albert T. Liu, Yuichiro Kunai and Michael Strano; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

There is a pressing need to find alternatives to conventional energy generation techniques, specifically those that rely on elements in finite global supply. Thermopower wave (TPW) devices, which convert chemical to electrical energy by means of self-propagating reaction waves guided along nanostructured thermal conduits, have the potential to address this demand. We show that conversion efficiency can be increased significantly by selecting molecules such as sodium azide or sucrose with potassium nitrate to offset the inherent penalty in chemical potential imposed by strongly p-doping chemicals, a validation of the predictions of Excess Thermopower theory. Such chemical-potential-gradient-induced-electricity can be further exploited in a more direct manner, decoupled completely from the combustion reactions, affording another novel energy generation scheme using only molecular interactions, and subsequent charge transfers, with single-walled carbon nanotubes. Specifically, we demonstrate that chemically-modified carbon nanotube fibers enable unique power sources driven entirely by a chemical potential gradient. Short circuit electrical current (11.9 μA mg⁻¹) and open circuit potential (525 mV) are reversibly produced by localized acetoniitride doping under ambient conditions. An inverse length-scaling of the maximum power as L⁻¹.⁰ three to four orders of magnitude larger than previously reported, this work could open new avenues for the exploitation of nanoscale energy harvesting.

11:45 AM ET03.13.12
Thermal Transport Crossover from Crystalline to Partial-Crystalline Partial-Liquid State in Li-S Batteries Ming Hu1 and Yanguang Zhou; 1University of South Carolina, Columbia, South Carolina, United States; 2University of California Los Angeles, Los Angeles, California, United States.

Phase change materials (crystalline at low temperature and partial-crystalline partial-liquid state at high temperature) are widely used as thermoelectrics (Cu2Se [Phys. Rev. Lett. 118, 145901 (2017), Proc. Natl. Acad. Sci. 111, 15031 (2014) and Nature Mater. 11, 422 (2012)] and Ag2Te [Nanotech. 26, 25702 (2014)]) and battery electrodes (Li2S [Sci. Rep. 7, 5873 (2017)] and LiSi [Nano Energy 18, 89 (2015)]) due to their low thermal conductivity and high ionic conductivity, respectively. Both thermoelectrics and Li batteries are energy related subjects and the relevant researches are hot topics in physics, chemistry and materials fields today. The scientific challenge resides in that, the well-developed computational methods such as anharmonic lattice dynamics coupled with Boltzmann transport equation (ALD/BTE) cannot be straightforwardly used to study such partial-crystalline partial-liquid systems. By performing systematic first-principles and reaxFF molecular dynamics simulations, for the first time we give a robust and detailed explanation of the thermal transport behavior in phase change material (i. e., Li2S). At the temperature range in which the system can be regarded as a solid, the large hopping of Li is found to be the reason for phonon thermal conductivity’s deviation from the traditional 1/T relationship. At the high temperature range (T > 1000 K), the contribution of convection and across increase significantly due to the fluidization of Li ions. The effective mean free path of the crystalline part shows that, at high temperature (e. g., 1300 K), the diffusions, which transport heat via overlap of ions’ trajectories, can contribute as much as 44% of the total thermal conductivity, which leads to the unusual increase of k waived at temperature above 1200 K. These results offer useful guidance for the development of phase change material based thermoelectrics (such as Cu2Se and Ag2Te based thermoelectrics), where low thermal conductivity is required to maximize the efficiency, and also suggest a strategy to solve the overheating problem in LIBs. This work will not only be of interest to the thermoelectrics and Li battery community, and the revealed thermal transport mechanism will also have large impact in the nanoscale thermal transport community.

SYMPOSIUM ET04
While perovskite solar cells (PVSCs) have drawn intense attention due to their high solar-to-power conversion efficiency (PCE), their practical application is hampered by the poor long-term stability against moisture. Although strategies have been reported to solve this issue, they are introduced during core-device fabrication processes which will increase the risk of introducing unexpected impurities during the fabrication.

In this work, we propose a new scheme of ligand-induced post-device (LPD) modification of perovskite on completely fabricated devices at room temperature to simultaneously improve the performance and stability of PVSCs [1]. The ligand vapors will induce chemical modification in the selected lateral regions particularly that of perovskite layer which prevent the diffusion of water molecules into the protected active perovskite region for enhancing PVSC stability. This post-device treatment could also passivate the surface defects of perovskites in active region for improving the PVSC performance. Interestingly, this LPD modification strategy shows a special ‘stitching effect’, namely repairing the as-fabricated ‘poor devices’ by healing the defects of perovskite in the operation region and significantly improve PCE by over 900%. The work greatly improves the production yield of PVSCs and their performance of perovskite solar cells via off-the-shelf post-device ligand treatment”, Energy & Environmental Science, 2018, DOI: 10.1039/C8EE00580J.

conversion efficiency, particularly for large-area cells, is the tradeoff between the optical and electrical performance of the top contact. Because perovskite absorbers are not used in traditional electrode materials, they provide a little lateral conductivity for current collection; a transparent conduction oxide (TCO) such as indium tin oxide (ITO) must be used for the front contact. However, TCOs offer a tradeoff between transparency and conductivity, resulting in cells that slightly compromise both their short-circuit current density due to optical losses, and their fill factor due to resistive losses. A solution is to increase the density of the grid fingers such that thicker TCOs can be used; however, this increases the shading losses.

Recently, a method to produce effectively transparent front contact grids has been described (Adv. Optical Mater. 4 (10), 1470-1474 (2016); Photovoltaic Specialists Conference (PVSC) IEEE 43rd, 3612-3615, (2016); Sustainable Energy and Fuels, 1 (3), 593-598, (2017)). This approach yields a relatively dense array of high-aspect-ratio, triangular-shaped front contact fingers, in which light striking the metal is reflected towards the cell. We previously described the application of this technique to produce effectively transparent superstrates for perovskite solar cells, which based on optical absorption measurements, is expected to increase the short-circuit current density of perovskite solar cells by ~1 mA/cm² (R. Saive, et al., PVSC 2018).

In the present work, we describe our efforts to integrate the effectively transparent superstrates with functional perovskite solar cells to realize the benefits of effectively transparent contacts (ETCs). We have investigated various combinations of perovskite absorbers and selective contact materials, and will report the results of our fabrication efforts. We are also investigating other approaches to integrate ETC technology with perovskite solar cells, including directly printing or transferring ETCs onto substrate-based perovskite cells topped with optimally thickned ITO layers.

9:00 AM ET04.01.04
Highly Efficient Thermally-Stable Perovskite Solar Cells via Cs-NiOx/CuSCN Double Inorganic Hole Extraction Layer Interface Engineering
Sawanta S. Mali and Chang Kook Hong; Chonnam National Univ, Gwangju, Korea (the Republic of).

Obtaining long-term thermally stable via low-cost inorganic-hole extraction layer (i-HEL) is the best choice towards the commercialization of thermally stable, low-cost perovskite solar cells (PSCs). In the present investigation we have developed a simple method for p-type cesium doped NiOx (CsNiOx) an active interfacial layer between perovskite and CuSCN i-HEL towards thermally stable low-cost PSCs. CsNiOx nanoparticles were synthesized by simple solution method followed by spin-coating between perovskite and CuSCN interface for mesoscopic regular (n-i-p) type PSCs. The developed method is not only protecting perovskite layer from poor diethyl sulfide solvent but also extract holes efficiently. The best efficiency based on CsNiOxCuSCN double i-HEL devices exhibited 18.42% with >95% thermal stability over 1000 hours at 60 degree Celsius. Interestingly, NiOx/CuSCN and CsNiOxCuSCN double i-HEL based devices are much stable either conventional spiro-MeOTAD or single i-HEL based PSCs due to perfect isolation of the perovskite layer from polar solvent.

9:15 AM ET04.01.05
Progress on Device Stability Enhancement of Perovskite Solar Cells via High Mobility P-Type Buffer Layer or Phthalocyanine Derivative with Long Carrier Lifetime
Xiaoli Zheng1, Yulong Wang2, Hongwei Lei1, Guang Yang1, Zongxiang Xu2 and Guojia Fang1; 1School of Physics and Technology, Wuhan University, Wuhan, China; 2Department of Chemistry, South University of Science and Technology of China, Shenzhen, China.

Organo-lead halide perovskite solar cells (PSCs) have attracted tremendous attention owing to their superior photovoltaic properties. However, despite the excellent power conversion efficiencies (PCEs) that have recently been achieved, the device stabilities are still a challenge for the commercialization of PSCs. Spiro-OMeTAD is a widely used hole transport layer (HTL) in conventional n-i-p type PSCs, which has been reported to suffer degradation from the permeate of moisture due to the hydrophobic additive and the presence of pinholes. To fix the relatively low device stability of PSCs based on spiro-OMeTAD, numerous strategies have been developed and used in PSCs. One approach to diminishing these adverse effects introduced by the moisture permeate and ion migration is to insert a buffer layer. To avoid decreasing the device performance while improving the stability, this p-type semiconductor needs possess high conductivity and superior hole mobility besides hydrophobicity. Lead sulphide (PbS) is a traditional direct bandgap semiconductor with high hole mobility. We found that when inserting a thin layer of PbS between the metal electrode and spiro-OMeTAD, the PSCs with PbS buffer layer exhibited a better photovoltaic performance and significantly enhanced stability with respect to the reference cells. The superior hole mobility of spiro-OMeTAD/PbS bilayer was considered to be the dominant origin of the device performance improvement. And the hydrophobic nature and dense morphology of PbS enable it to provide an efficient permeation barrier against moisture and metal migration. The champion cell with PbS buffer layer displayed a PCE of 19.58% and maintained almost 100% of its initial PCE after 1000 h stored in ambient air. While in this structure the spiro-OMeTAD is still requisite. Metallophthalocyanine (MPC) compounds that consist of an 18-electron conjugated macrocycle skeletal structure are potential candidates for stable HTLs in PSCs. We reported a novel heavy metal Pb derivative, octamethyl-substituted palladium(II) phthalocyanine(PPm2Pc), which shows promise as an HTL in PSCs. The introduction of the heavy Pd atom endows the material with a long carrier lifetime and without dramatically reducing its mobility. This PdMPC exhibited a long carrier diffusion length (LD) which is benefit to reducing the charge recombination. As a result, the devices based on PdMPC displayed a relatively high PCE of 16.28% and good long-term stability.

9:30 AM ET04.01.06
Environmental-Induced Luminescence Hysteresis in Cs-FA Perovskites
John M. Howard1,2, Elizabeth Tennyson1,2, Sabayasachi Barik2,3, Rodrigo Szostak1, Edo Waks4, Michael F. Toney5, Ana F. Nogueira5, 3, Bernardo Neves2, 6 and Marina S. Leite1, 2; 1Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 2Institute of Chemistry, University of Campinas, Campinas, Brazil; 3Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland, United States; 3Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 4Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Brazil; 5Department of Physics, University of Maryland, College Park, Maryland, United States.

Metal halide perovskites show great potential for a wide variety of optoelectronic devices, ranging from light-emitting diodes to photocatalysts. While the prototypical MAPbI3 has relatively poor stability under ambient conditions, the addition of small amounts of Cs (10-20%) to FAPbI3 has been shown to enhance thermal, optical, and structural stability across the entire range of possible IBr ratios. However, the influence of moisture, oxygen, and temperature on the optoelectronic properties of these Cs-FA perovskites remains unknown. To explore the individual and combined contributions of each of these parameters onto perovskites' optical behavior, we use micro-photoluminescence (micro-PL) with in situ environmental control on four relevant Cs,FAPbI3,(1-x)PbBrx compositions [1,2]. We subject each sample to temporally identical humidity loops (< 5%, 15%, 35%, 55%, and < 5%RH) and identify that humidity levels up to 55%RH increase the PL emission of all compositions considered by removing surface trap states. By contrast, we find that 55%RH reduces the overall PL emission for 38%-Br films, but sustains the PL enhancement from the prior 35%RH soak for the 17%-Br perovskites. The same 38%-Br films also show an appreciable and partially reversible red shift in their PL peak, correlated with the relative humidity level. Finally, upon completion of the humidity loop, all compositions except Cs-17%-Br-38% exhibit luminescence hysteresis; the extent of hysteresis is predominantly influenced by the Cs-Br ratio. We attribute this PL hysteresis to surface-limited degradation occurring throughout the 55%-RH condition, where sufficient intercalation of the water into the perovskite lattice leads to the formation of FAI,FABr,PbI and PbBr. This degradation process leads to the
formation of new sites for nonradiative recombination. Our environmental micro-PL method can be expanded to a range of emerging perovskite compositions and extended to include additional degradation factors. Finally, we will discuss how the control of each environmental parameter on perovskites degradation and recovery can be tackled by a machine-learning paradigm [3].


9:45 AM BREAK

10:15 AM ET04.01.07
Charge Injection from Excited CsPbBr3 Nanocrystals into TiO2 in Perovskite and Its Role in the Degradation of Perovskite Layer in Visible Light Prashant Kamat, Rebecca A. Scheidt and Elisabeth Kerns; University of Notre Dame, Notre Dame, Indiana, United States.

The role of TiO2 as an electron transport layer (ETL) that captures electrons from excited CsPbBr3 seems to play an important role in delivering superior device performance. However, its role in perovskite solar cell is yet to be understood fully. By anchoring CsPbBr3 nanocrystals onto mesoscopic TiO2 film, we have probed the charge injection from excited perovskite into mesoscopic TiO2 and other semiconductor oxides. The electron transfer rate constant in all these case was found to be >10^11 s^-1. When subjected to steady state irradiation with visible light in air, the injected electrons are scavenged away from the TiO2, thus inducing oxidation of CsPbBr3 nanocrystals. No such degradation is seen when CsPbBr3 nanocrystals are coated on an inert support such as ZrO2. We have also probed the charge recombination process in CsPbBr3 deposited on FTO/TiO2 films at different applied electrochemical bias and investigate the influence of electron charging effect in TiO2 layer. Steady state and luminescence measurements that elucidate the role of TiO2 in the solar cell operation will be discussed.

10:30 AM ET04.01.08
Exploring Bulk and Interfacial Degradation Effects in Perovskite and Perovskite-Inspired Absorbers for Solar Cells Azat Akbulatov2, Lyubov Frolova1,2, Olga Yamilova1, Sergey Luchkin1, Moneim Elshobaki1, Sergey Tsarev1, Alexandra Sveshnikova1, Keith Stevenson1 and Pavel Troshin1,2; Skoltech, Moscow, Russian Federation; 1IPCP RAS, Moscow, Russian Federation.

The emerging perovskite solar cells have demonstrated impressive power conversion efficiencies exceeding 22%, while their practical application is restricted mainly by poor operation stability. We have reported recently that hybrid MAPbX3 (X=I, Br, I+Br, I+Cl) perovskites undergo facile thermal and photochemical degradation even under anoxic conditions without exposure to oxygen and moisture, while their all-inorganic counterparts CsPbX3 proved to be significantly more stable [1]. Here we will discuss our most recent results coming from a systematic study of the intrinsic stability of a broad range of materials represented by various lead-based perovskites as well as lead-free complex halides of tin, germanium, bismuth and antimony. The revealed pathways of thermal, photochemical and electrochemical degradation processes will be presented and a conclusion on the potential of different groups of materials for practical application in PV technology will be drawn.

We will also analyze the interface degradation effects occurring between the electrodes, charge transport layer materials and the photactive layer induced by electric field, elevated temperatures, solar light or a combination of these stress factors [2-3]. Finally, it will be shown that any commercially interesting operation lifetimes for perovskite solar cells requires a considerable shift from the currently used device design paradigms as well as a comprehensive multiparametric optimization of all used materials and functional components.


10:45 AM ET04.01.09
Transport Layers Limit the Efficiency of Perovskite Solar Cells—An Experimental and Theoretical Study Vincent Le corre1, Lorena Perdigón Toro1, Markus Feuerstein1, Martin Stolterfoht2, Dieter Neher2 and Lambert Jan Anton Koster1; 1Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands; 2Institute of Physics and Astronomy, Universität Potsdam, Potsdam, Germany.

Perovskite solar cells (PSCs) are the current rockstar of photovoltaic research attracting more and more attention. With efficiency now reaching up to 23% PSCs are on the way of catching up with classical inorganic solar cells. However, PSCs have not reached their full potential yet. In fact, their efficiency is limited, on the one hand, by non-radiative recombination, mainly via trap states located either at the grain boundaries or at the interface between the perovskite and the transport layers. On the other hand, it is limited by losses due to the poor transport properties of the commonly used transport layers. Indeed, state-of-the-art transport layers (e.g. TiO2, PCBM and Spiro-OMeTAD…) suffer from rather low mobilities, typically within 10^-4 – 10^-2 cm^2 V^-1 s^-1, measured when compared to the high mobilities, 1 – 10 cm^2 V^-1 s^-1, measured for perovskite using field-effect transistors or space-charge-limited-current measurement.

In this work, the effect of the mobility, thickness and doping density of the transport layers was investigated by means of a combined experimental and modeling analysis. For the experiment, two sets of devices made of a triple-cation perovskite were studied, including n-i-p and p-i-n structures demonstrating efficiencies of up to 20%. For the two structures, the thickness and doping density of one of the transport layers were varied in order to understand their effect on the performance and especially on the FF. In addition, we performed a transient extraction experiment to look at the influence of the transport layers properties on the rate of extraction. The experimental results were then reproduced using drift-diffusion simulations to explain how and by how much every single parameter influences the extraction and the performance. A new and simple formula was also introduced to easily calculate the amount of doping necessary to counterbalance the low mobility of the transport layer.

In conclusion, this work presents a comprehensive analysis of the effects of the different properties of a transport layer on the efficiency of PSCs. We also present general guidelines on how to optimize a transport layer to avoid losses.

11:00 AM ET04.01.10
Strategically Construct Bilayer SnO2 as Electron Transport Layer in Perovskite Solar Cells Liuangyou Lin1,2, Jacob Tse-Wei Wang1, Timothy Jones1 and Gregory J. Wilson1; 1CSIRO Energy, Newcastle, New South Wales, Australia; 2Huazhong University of Science and Technology, Wuhan, China.

The highly diverse and adaptable architectures of the PSCs is also one of the key steps that leading PSCs to the forefront of the emerging PV technologies.
Among various device configurations, the “n-i-p” planar structure without secondary mesoporous layers has attracted lots of attention due to its simple device fabrication process where n-type metal oxides have been widely applied as the first layer on top of the FTO or ITO. TiO2 is the most commonly used electron transport material in the PSCs due to its mature development in the field of DSSCs, however, several studies have pointed out that TiO2 may not be the best candidate to carry PSCs toward commercialization due to its unfavorable properties, including UV instability, high-temperature sintering process, large energy level offset, etc. On the contrary, SrTiO3 emerged as an ideal n-type layer for PSCs recently, with advantages of higher electron mobility, low-temperature process, and UV-stabilized properties. However, SrTiO3 behaves quite differently while prepared by different methods. In this work we devised a facile strategy to combine the strength of two different SrTiO3. Interestingly, we found the bilayer displays better energy level alignment with perovskite, faster charge extraction, and lower trap-density. As a result, the photovoltaic devices based on this electron transport layers demonstrate a superior power conversion efficiency up to 20.5% with Voc close to 1.2 V and negligible J-V hysteresis in the device.

ARGON PLASMA TREATMENT TO TUNE PEROVSKITE SURFACE COMPOSITION FOR HIGH EFFICIENCY SOLAR CELLS AND FAST PHOTODETECTORS

Xun Xiao1, Chunxiong Bao, Yannian Fang, Jun Dai, Benjamin R. Ecker, Yue Li1, Shi Tang, Ye Li2, Yehao Deng1, Xiaopeng Zheng1, Yongli Gao1, Xiao Cheng Zeng1 and Jinsong Huang1,2

1University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 2Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, United States. 1Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 2Department of Physics and Astronomy, University of Rochester, Rochester, New York, United States.

The surface composition of perovskite films is very flexible in film process and can deviate from optimal, which generates unfavorable defects and results in efficiency loss in solar cells and slow response speed in photodetectors. An argon plasma treatment is introduced to modify the surface composition by tuning the ratio of organic and inorganic component ratio as well as defects type before deposition of passivating layer and form an ultra-thin n-type self-doping layer. It efficiently enhanced the charge collection over the perovskite-electrode interface by suppressing charge recombination. Therefore, perovskite solar cells with argon plasma treatment yield enhanced efficiency to 20.4% and perovskite photodetectors can reach their fastest respond speed which is solely limited by the carrier mobility.

FROM THIN-FILM TO SINGLE CRYSTALS—PROBING THE INTRINSIC ANISOTROPY AND INSTABILITY IN CUBIC LEAD PEROVSKITES

Qing Sun1, Federico Brivio1, Fengxia Wei1, Yue Wu2, Zeyu Deng1, Gregor Kieslich2, Paul D. Bristowe1, Pietro Buonassisi1 and Anthony K. Cheetham2,3

1University of Cambridge, Cambridge, United Kingdom; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Technische Universität München, Munich, Germany; 4A*Star, Singapore, Singapore; 5National University of Singapore, Singapore, Singapore.

The commercialization of perovskite solar cells (PSCs) have been hindered by their chemical, structural and thermal instability. There is an increasing interest in compositional tuning of perovskites to improve their intrinsic stability. In this study, extrinsic and intrinsic strain in cubic perovskites, methylammonium lead iodide (MAPbI3) and formamidinium (FA) lead bromide were examined in thin-film, powder and single crystal forms to investigate the role of A-site cations on the structural-property relationships. Based on laboratory and synchrotron X-ray diffraction and density functional theory (DFT), our quantitative analysis reveal the presence of anisotropic strain in the cubic perovskites, where the lattice strain is the highest on {111} and lowest on {100}. Comparative studies on FA(PbI3)2 and MAPbBr3 showed that the cation dynamics and hydrogen bonding of FA contributes to the higher strain as well as more compliant bulk properties. Our results shed light on the rational perovskite compositional design to minimize strain induced decomposition.

THERMALLY DRIVEN EVOLUTION OF FERROELECTRIC DOMAINS IN PEROVSKITE SOLAR CELLS

Holger Röhm, Tobias Leonhard, Alexander Schulz, Michael J. Hoffmann and Alexander Comlmann, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Every perovskite solar cell undergoes changes in temperature during operation and most fabrication routes include one or more thermal annealing steps. For methylammonium lead iodide (MAPbI3), the archetype of metal halide perovskite solar cells, both the formation and growth of the crystals are strongly interlinked with the phase transition temperature at 328 K. At this temperature, the crystal changes from a polar tetragonal to a non-polar centrosymmetric cubic structure. To date, the majority of research related to the thermal treatment of perovskite solar cells focuses on the growth of crystals from precursor chemicals during layer formation or the thermal decomposition at elevated temperatures. So far, the influence of temperature on the formation of the microstructure within perovskite grains such as formation and evolution of polar domains remains unclear. Here, we study the effects of annealing temperature and duration on the formation and transformation of ferroelectric domains and show the influence of domain patterns on the optoelectronic microstructure and macroscopic device performance of solar cells. Annealing of MAPbI3 layers at 100°C yields flat grains with an average diameter of > 1 μm. After fast grain growth in the first few minutes, further annealing does not change the layer morphology anymore. However, ferroelectric domains as revealed by piezoresponse force microscopy (PFM) show vastly different orientations and domain shapes during this thermal treatment. The investigation of the corresponding solar cells elucidates the influence of changes in the sub-grain microstructure on the JV-characteristics, power conversion efficiencies and the hysteretic behavior of solar cells.
charge carriers largely contributes to the outstanding optoelectronic properties of lead-halide perovskites.

References:

2:00 PM *ET04.02.02
Perovskite Material and Solar Cell Research by Surface Science and Advanced Characterization Yabing Qi; Okinawa Institute of Science and Technology, Okinawa, Japan.

Perovskite solar cell research has been continuously advancing in various fronts. To fabricate high performance stable perovskite solar cells, it is of paramount importance to obtain a better understanding of fundamental aspects with the help of surface science and advanced characterization. My group at OIST is making concerted efforts to investigate these materials and devices and to develop innovative strategies to improve their performance. In this talk, I will present our research progress on the improvement of perovskite solar cell stability and development of upscalable processes to fabricate perovskite solar cells and modules.

2:30 PM ET04.02.03
Perovskite Solar Cells—The Role of Ions, Density of States and Device Structure Nir Tessler1 and Yana Vaynzof; 1Technion-Israel Institute of Technology, Haifa, Israel; 2Universität Heidelberg, Heidelberg, Germany.

Preventing hysteresis and enhancing stability remain key challenges that could be resolved with the aid of judicious device design. We report numerical study of a solar cell model system that is based on a mixed electron-ion conducting perovskite active layer having various device configurations. In the full picture we allow for both mobile ions and the polarizability due to the easy-rotational methylammonium (MA). We then compare with cells where the MA rotation is frozen and/or the ions are non-existing. Several insights, resulting from these detailed simulations, will be presented.

For example: Even when there is no indication of hysteresis and the device’s characteristics can be modelled using ionic free model, the actual electron and hole distributions may be vastly different to the predictions by ionic free model. The low effective DOS promotes higher Voc but makes it more difficult to overcome energy level mismatch. These are related to the fact that the ionic motion is not only causing the hysteresis, it also allows for large deviations between electron and hole densities. Also, when a large energy mismatch exists between the BL and the perovskite the charge density distribution self-adapt to create an effective dipole at the interface. Such self-induced dipole can compensate for 0.4eV mismatch and thus prevent any loss in Voc. In this context formamidinium is preferred to MA.

We also found that while the use of doped BLs is effective to reduce serial resistance and potential S shapes it also results in a relatively pronounced ionic motion. We note that even in hysteresis-free cells the ions still redistribute as a function of bias. We show that by keeping a certain level of resistivity, as in undoped BL, the ionic motion is significantly reduced. We expect this to have significant impact on device long term stability.

2:45 PM ET04.02.04
Structural Origins of Light-Induced Phase Segregation in Organic-Inorganic Halide Perovskite Photovoltaic Materials Rachel E. Beal1, 2, Hans Steinrueck2, Nanna Zhou Hangström2, Michael F. Toney2 and Ana F. Nogueira1; 1Stanford University, Stanford, California, United States; 2Materials Sciences Division, Stanford Synchrotron Radiation Lightsource, Stanford, California, United States; 3Institute of Chemistry, University of Campinas, Campinas, Brazil; 4Stockholm University, Stockholm, Sweden.

Organic-inorganic perovskite materials offer a promising route to reducing the dollars-per-watt cost of solar energy due to their ease of deposition and favorable optoelectronic properties. A wide range of perovskite compositions can be solution processed with relative ease where changing the stoichiometry of the material allows for the preparation of materials with bandgaps tailor-made for specific tandem and single-junction applications. Early work showed that varying the Br:I ratio in (CH3NH3)Pb(Br1-xIx)3 tunes the bandgap between 2.3 and 1.6 eV, but photo-induced phase segregation leads to the formation and I-enriched regions in materials with x ≥ 0.2 that trap carriers and pin the voltage of photovoltaic devices. Materials with a combination of formamidinium (FA) and cesium of the A-site in the general ABX3 stoichiometric formyla have demonstrated improved stability to this phenomenon, but the fundamental and mechanistic underpinnings of photo-induced phase segregation are not well understood. We have studied the structural origins of photo-induced phase segregation by coupling synchrotron X-ray diffraction with photoluminescence experiments. We examine materials with a range of FA:Cs and Br:I ratios and show that optical stability is observed at the phase boundary between Br-poor cubic and Br-rich tetragonal compositions, with material compositions farther from the boundary demonstrating a greater extent of segregation. Ours is the first study to examine materials in the FA:Cs phase space with bandgaps relevant for high-efficiency device applications. By mapping out the phase boundary, we provide a roadmap for compositional selection for photostable devices.

3:00 PM BREAK

3:30 PM *ET04.02.05
'The Life' of Halide Perovskite—Evolution From the Solution and Degradation in the Environment Yuanyuan Zhou; Brown University, Providence, Rhode Island, United States.

Halide perovskites have recently emerged as a new family of semiconducting materials that are revolutionizing the field of photovoltaics. The rapid development of perovskite-based solar cells is being led by advances in microstructural/compositional engineering of perovskite thin films. In this context, understanding the 'life' of halide perovskite: evolution/crystallization from the solution and degradation in the environment, and developing new strategies for the 'life-lengthening' (stabilization) of perovskites are becoming the most significant research directions.

In this talk, first, I will look at fundamental phenomena pertaining to nucleation & grain growth and grain-boundary evolution involved in the thin-film crystallization of perovskitites from a materials-science perspective. Established scientific principles that govern these phenomena will be invoked in the context of specific examples of perovskite thin films. Based on these fundamentals, I will present a set of new synthetic strategies that have been recently developed in our group for scalable processing of high-performance large-area perovskite thin films and devices. Second, I will discuss the key role of
grain boundaries in the degradation processes of perovskites, and show our recent progress in the grain-boundary tailoring of perovskite thin films that enable perovskites with new functionalities and enhances the perovskite stability. Finally, I will discuss the challenges and opportunities in the advanced characterization (high-resolution and in-situ/operando TEM, etc.) of perovskites for not only gaining a deep understanding of defects/microstructures, but also elucidating classical and non-classical phenomena pertaining to the crystalization, degradation, and stabilization of perovskites. The overall goal is to gain a deterministic control over the perovskite thin films with engineered microstructures/compositions for efficient PSCs that are also highly durable under environmental (heat/moisture/light) stresses.

How Does the Chemical Reactivity of Mobile Ions Trigger Reversible Performance Losses at Reverse Bias in Lead Halide Perovskite Solar Cells? Luca Bertolazzi, 1 Kevin A. Bush, 1 Rohit Prasanna, 1 Brian O'Regan, 1 and Michael D. McGehee; 2 Stanford University, Stanford, California, United States; 3Sunlight Scientific, Berkeley, California, United States; 4Department of Chemical Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Enhancing the stability of perovskite solar cells is currently one of the main preoccupations of the perovskite research community. Environmental degradation triggered by moisture, oxygen, UV light and termal stress, is being efficiently tackled by the concomitant engineering of the device architecture and encapsulation. 1 However, multiple groups have pointed out that different conditions of light and applied voltage can also lead to partially reversible efficiency losses. We recently reported partially reversible performance losses caused by reverse bias. 2 Other groups remarked that devices placed outdoor loose part of their efficiency during the day and partially recover during the night. 3 Finally, since these processes are not fully reversible, it is important to understand and stop them for reliability reasons.

Mobile ions within the active material have been suspected to trigger these processes. We have recently proposed a drift-diffusion model to examine the role of such ions at reverse bias. 2 We concluded that while ion migration can explain the reverse bias leakage current, ionic transport alone cannot explain the reversible performance losses we measured. Instead, we suggested that a reversible electrochemical reaction involving these ions is likely to take place. In a different study, Maier and coworkers showed that iodide vacancies can be created under prolonged illumination due to the oxidation of iodide into iodine, which subsequently migrate to interstitial sites. 4 While growing evidence suggests that ionic chemistry is triggering partially reversible losses, it is crucial to understand and stop ionic reactivity. In this talk, we will discuss the nature of the ionic reaction triggered by prolonged reverse bias by resorting to different electrochemical techniques for strategically chosen perovskite compositions and contacts. In addition, we use a drift-diffusion model to explain a mechanism for how such a reaction can lead to partially reversible performance losses.

Deposition of Halide Perovskite Thin Films and Solar Cells Using the RIR-MAPLE Technique

Wiley A. Dunlap-Shohl, 1 E. T. Barraza, 2 Andrew Barrette, 3 David J. Dirkes, 4 Wei You, 1 Kenan Gundogdu, 1 Adrienne D. Stiff-Roberts 2 and David Mitzi 1, 5

1Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; 2Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; 3Physics, North Carolina State University, Raleigh, North Carolina, United States; 4Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 5Chemistry, Duke University, Durham, North Carolina, United States.

Although many techniques have been developed for the deposition of high-quality halide perovskite thin films, the dominant solution- and vapor-deposition methods often possess some undesirable attributes, such as the challenges associated with drenching potentially sensitive substrates in solvents, or with controlling fluxes of volatile and thermally unstable organic salts. These obstacles constrain the range of possible device architectures used in halide perovskite optoelectronics. Thus, it is desirable to explore novel perovskite thin film deposition methods that might help to circumvent these challenges. In this work, we use the resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) technique, wherein a frozen solution of the precursors is evaporated by a laser whose energy is resonant with chemical bonds in the solvent, to deposit various hybrid halide perovskite thin films and explore their morphological, compositional, and optoelectronic characteristics. 1 We demonstrate, for the first time, perovskite solar cells with absorber deposited by RIR-MAPLE, which reach stabilized power conversion efficiency of over 12%. 2 The technique is also extended to consider layered or two-dimensional perovskites with more complex organic structure.


4:15 PM ET04.02.07

Deposition of Halide Perovskite Thin Films and Solar Cells Using the RIR-MAPLE Technique

Wiley A. Dunlap-Shohl, 1 E. T. Barraza, 2 Andrew Barrette, 3 David J. Dirkes, 4 Wei You, 1 Kenan Gundogdu, 1 Adrienne D. Stiff-Roberts 2 and David Mitzi 1, 5

1Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; 2Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; 3Physics, North Carolina State University, Raleigh, North Carolina, United States; 4Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 5Chemistry, Duke University, Durham, North Carolina, United States.

Although many techniques have been developed for the deposition of high-quality halide perovskite thin films, the dominant solution- and vapor-deposition methods often possess some undesirable attributes, such as the challenges associated with drenching potentially sensitive substrates in solvents, or with controlling fluxes of volatile and thermally unstable organic salts. These obstacles constrain the range of possible device architectures used in halide perovskite optoelectronics. Thus, it is desirable to explore novel perovskite thin film deposition methods that might help to circumvent these challenges. In this work, we use the resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE) technique, wherein a frozen solution of the precursors is evaporated by a laser whose energy is resonant with chemical bonds in the solvent, to deposit various hybrid halide perovskite thin films and explore their morphological, compositional, and optoelectronic characteristics. 1 We demonstrate, for the first time, perovskite solar cells with absorber deposited by RIR-MAPLE, which reach stabilized power conversion efficiency of over 12%. 2 The technique is also extended to consider layered or two-dimensional perovskites with more complex organic structure.


4:30 PM ET04.02.08

Trapped-Charges as the Core Origin for Degradation of Perovskite Crystals

Namyoung Ahn, Min-chuel Kim, Kwisung Kwak and Mansoo Choi;

Seoul National University, Seoul, Korea (the Republic of).

Jacob Tse-Wei Wang1, Liangyou Lin1, Timothy Jones1, Mihaela Grigore1, Andre Cook1, Dane deQuilettes3, Roberto Brezes1, Benjamin Duck1, Kenrick Anderson1, Noel W. Duff2, Vladimir Bulovic1, Jian Pu2, Jian Li3, Bo Chi3 and Gregory J. Wilson2

CSIRO Energy, Newcastle Energy Centre, Mayfield West, New South Wales, Australia; Center for Fuel Cell Innovation, School of Materials Science and Engineering, Huazhong University of Science & Technology, Wuhan, China; Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; CSIRO Energy Clayton Laboratories, Clayton, Victoria, Australia.

The state-of-the-art PSCs use mixed-cation and mixed-halide perovskite compositions due to the superior qualities over the archetypal MAPbI3. Adding Cs+ to perovskites has been shown to improve qualities including thermal stability, reproducibility; and suppression of phase segregation. In general, controlling the precise stoichiometry in a perovskite is critical for meeting its desired properties. However, it has been found purposely introduced excess PbI2 in the perovskite causes significant influence on the intrinsic perovskite qualities. The few percent excess PbI2 predominantly resides at grain boundaries, providing benefits of prolonged carrier lifetime, enhanced charge carrier injection, suppressed ion migrations and hysteresis, leading to improved overall device performance. Theories have been proposed to explain these beneficial effects, including the better energy level alignments, grain boundary passivation, and superior crystal quality and crystallinity. Nevertheless, there are also reports showing the residual PbI2 can lead to degradation and fragile film structure with long-term device stability concerns. Nonetheless, with most of the best performing cells still incorporating slight excess PbI2, it is important to investigate this indefinite property function for further improving device performance and stability.

In this study, we use the Cs0.05(FA0.85MA0.15)0.95Pb(Br0.15I0.85)3 stoichiometric perovskite structure as a platform to demonstrate a simple yet effective recrystallization method for PbI2-rich perovskite crystals with a series of recrystallization agents. Surprisingly, for the first time, through the Grazing Incidence X-ray Diffraction (GIXRD), we found not only the excess PbI2 in the film can be successfully removed, the perovskite had a profound recrystallization throughout the bulk, showing enhanced PL emission/lifetime, charge collection efficiency, reduced defects at grain boundaries (GBs) as well as superior device performance over 20% PCE.

High crystallinity and compactness of the active layer is essential for metal-halide perovskite solar cells. Here, a simple pseudohalide (NH4SCN)-induced film retreatment technology is developed as the passivation for preformed perovskite film. It is found that the retreatment process yields a controllable decomposition-to-recrystallization evolution of the perovskite film. Correspondingly, it remarkably enlarges the grain size of the film in all directions, as well as improving the crystallinity and hindering the trap density. Meanwhile, owing to an intermediate catalytic effect of the pseudohalide compound (NH4SCN), no crystal orientation changing and no impurity introduction in the modified film. By integrating the modified perovskite film into the planar heterojunction solar cells, a champion power conversion efficiency of 19.44% with a stabilized output efficiency of 19.02% under 1 sun illumination is obtained, exhibiting a negligible current density–voltage hysteresis. Moreover, such a facile and low-temperature film retreatment approach guarantees the application in flexible devices, showing a best power conversion efficiency of 17.04%.


Jacob Tse-Wei Wang1, Liangyou Lin1, Timothy Jones1, Mihaela Grigore1, Andre Cook1, Dane deQuilettes3, Roberto Brezes1, Benjamin Duck1, Kenrick Anderson1, Noel W. Duff2, Vladimir Bulovic1, Jian Pu2, Jian Li3, Bo Chi3 and Gregory J. Wilson2

CSIRO Energy, Newcastle Energy Centre, Mayfield West, New South Wales, Australia; Center for Fuel Cell Innovation, School of Materials Science and Engineering, Huazhong University of Science & Technology, Wuhan, China; Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; CSIRO Energy Clayton Laboratories, Clayton, Victoria, Australia.

In our work, an inorganic-organic bilayer hole transport layer (B-HTL) was designed and utilized in planer perovskite solar cells. Here the B-HTL consist of the inorganic V2O5 matrix and copper phthalocyanine (CuPc) buffer layer, providing the excellent resistance of moisture as well as the alignment of the interfacial energy level. Benefiting from this typical HTL, enlarged built-in potential and charge extraction can be achieved in PSCs simultaneously. Correspondingly a champion device with B-HTL shows a 16.85% efficiency with negligible hysteresis, which is superior to the PSC based on PEDOT:PSS HTL. Meanwhile, significantly prolonged stability of the PSCs with B-HTL can be observed, exhibiting an only 10% efficiency loss after 350 hours in the ambient air. Moreover, such an entire low-temperature (~560C) fabrication process of this typical PSCs exhibits its successful application in flexible devices.

Inorganic-organic bilayer hole transport layer: the B-HTL is consist of the inorganic V2O5 matrix and copper phthalocyanine (CuPc) buffer layer, with excellent resistance of moisture as well as the alignment of the interfacial energy level.

Considerable improvement of the PCE: nearly 20% PCE enhancement of the PSCs based on B-HTL compared with the device with PEDOT:PSS HTL. Meanwhile, significantly prolonged stability of the PSCs with B-HTL can be observed, exhibiting an only 10% efficiency loss after 350 hours in the ambient air. Moreover, such an entire low-temperature (~560C) fabrication process of this typical PSCs exhibits its successful application in flexible devices.

Inorganic-organic bilayer hole transport layer: the B-HTL is consist of the inorganic V2O5 matrix and copper phthalocyanine (CuPc) buffer layer, with excellent resistance of moisture as well as the alignment of the interfacial energy level.

Considerable improvement of the PCE: nearly 20% PCE enhancement of the PSCs based on B-HTL compared with the device with PEDOT:PSS HTL. Meanwhile, significantly prolonged stability of the PSCs with B-HTL can be observed, exhibiting an only 10% efficiency loss after 350 hours in the ambient air. Moreover, such an entire low-temperature (~560C) fabrication process of this typical PSCs exhibits its successful application in flexible devices.

Inorganic-organic bilayer hole transport layer: the B-HTL is consist of the inorganic V2O5 matrix and copper phthalocyanine (CuPc) buffer layer, with excellent resistance of moisture as well as the alignment of the interfacial energy level.

Considerable improvement of the PCE: nearly 20% PCE enhancement of the PSCs based on B-HTL compared with the device with PEDOT:PSS HTL. Meanwhile, significantly prolonged stability of the PSCs with B-HTL can be observed, exhibiting an only 10% efficiency loss after 350 hours in the ambient air. Moreover, such an entire low-temperature (~560C) fabrication process of this typical PSCs exhibits its successful application in flexible devices.
Organic-inorganic hybrid lead-based perovskite solar cells have shown tremendous growth in power conversion efficiency (PCE) over recent years. Despite remarkable strides in performance, one of the biggest barriers to commercialization is the toxicity of lead. Therefore, there has been a growing interest in implementing high performance solar cells based on lead-free perovskites with lower toxicity and outstanding optoelectronic properties. In this regard, tin-based perovskite solar cells have been spotlighted because they show suitable optical band gap, high absorption coefficient and high charge carrier mobility. However, self-p-doping by the oxidation of Sn2+ to Sn4+ in tin-based perovskite solar cells has been a critical issue for achieving high performance tin-based perovskite solar cells. Therefore, essential strategies that take into account tin chemistry are required to mitigate the intrinsic instability and improve the performance of tin-based perovskite solar cells. Based on the chemical nature of tin, N-, S-, O-based electron donors can coordinate with tin halides (SnX3, X = halide anions) by donating a lone pair electron to the empty orbital in the valence shell of divalent tin. Accordingly, it is expected that coordination between Sn2+ ions and appropriate ligands could block the reaction of Sn2+ ions with oxygen, resulting in effective suppression of the oxidation of Sn2+ to Sn4+. Taking this into account, herein we fabricated quasi-two-dimensional (quasi-2D) tin-based perovskite solar cells with greatly enhanced performance and stability compared to conventional three-dimensional (3D) formamidinium tin iodide (FASnI3) perovskite solar cells, by employing an additional formamidinium thiocyanate (FASCN) additive into the quasi-2D tin-based perovskites. The incorporation of the FASCN additive greatly prevented quasi-2D tin-based perovskites from oxidation during film formation, through the strong chemical interactions with tin component (Sn2+). Moreover, it resulted in a coarser perovskite grain and a higher degree of crystallinity in the out-of-plane direction, leading to enhanced optoelectronic performance of the quasi-2D tin-based perovskites. As a result, we achieved reproducible high-performance tin-based perovskite solar cells with improved stability, reaching the highest PCE up to 8.17% compared to that of 3D FASnI3 device (1.84%), and retaining over 90% of its initial efficiency after 1000 hours aging in a nitrogen-filled glove box. These results demonstrate a versatile, yet simple methodology that can be applied to other lead-free perovskites suffering from poor oxidative stability.

ET04.03.04
Plasmonic Enhancement for High Efficient and Stable Perovskite Solar Cells by Employing ”Hot Spots” Au Nanobipyramids
Feifei Wei, Hua Dong, Jie Xu, Ting Lei and Zhaoxin Wu; Xi’an Jiaotong University, Xi’an, China.

Metal plasmonic effect is one promising way for improving the performance and stability of the perovskite solar cells via optical-electrical behalves, and the ability is in proportion to the enhanced local electromagnetic fields induced by metal nanostructures. In our work, unique gold nanobipyramids (Au NBs) structures were explored and incorporated in the hole transport layer of planar heterojunction PSCs. This typical “bipyramid-like” metal nanostructure with sharp tips has the multiple and strong plasmonic absorption properties from visible to the NIR, exhibiting high plasmonic-induced probability. In addition, generated “hot spots” around Au NBs provided much stronger EM fields enhancements than conventional Au nanoparticles, hence enhanced light harvesting and improved interfacial charge dynamic process can be achieved simultaneously. As for the further investigation of the electrical property, hot holes injection induced by Au NBs effectively filled in the interfacial traps under operation condition, contributing to the improvement of the open circuit voltage, the elimination of the hysteresis effect and the long-term stability. Accordingly, the best PSC incorporated with Au NBs showed the PCE of 18.84% whereas the reference device just showed the PCE of 16.02%. Our work demonstrated that plasmonic metal nanostructures possessing the feature of “hot spots” offered a great potential to further expand the performance limitation and operation tolerance of the PSCs.

ET04.03.05
Theoretical Investigation of Water-Resistant Halide Perovskites
Hiromitsu Takaba, Tatsuya Hongo and Junna Takahashi; Kogakuin Univ, Tokyo, Japan.

Organic / inorganic perovskite compound is capable of highly efficient energy conversion and halide perovskites are important issue for its practical application in a solar cells. However most perovskite of APbI3 has a problem that the structure is distorted and degraded by invasion or diffusion of water molecules or the existence of defect in the crystal. Therefore, it is necessary to search for structures having energetically stable and high water resistance. In this study, energetically stable and water resistance for various virtual halide perovskites containing fluoride in A-ion site were investigated by density functional theory and molecular dynamics. Dynamics of bond dissociation or water adsorption as well as the electronic structure, e.g. band gas and light adsorption spectrum, of various compounds were systematically investigated and then the novel composition for durable halide perovskite was theoretically suggested. Our simulation results indicate that fluoride halide perovskite is stable and a little bit wide band gap compared to CH3NH3PbI3 (MAPbI3) perovskite. The calculated adsorption energy of water molecule on the surface of fluoride halide perovskite is smaller than that on MAPbI3. The reaction barrier for 2(Pb-I) + H2O = PbO + 2HI was estimated and it is confirmed the presence of fluoride molecule at A-ion site prevent from the reaction showing higer reaction barrier than that for MAPbI3. This would be due to the interaction with negatively charged atoms of F. We also investigated the combination of fluoride and other A-ion to tune the band gap suitable for the application to solar cell.


ET04.03.06
Highly Efficient and Stable Tandem Solar Cells Based on Halide Perovskites
Ik Jae Park, Jaey Hoon Park, Su Geun Ji, Min Ah Park and Jin Young Kim; Seoul National University, Seoul, Korea (the Republic of).

The tandem configuration consisting of two or more solar cells is practically the only approach to overcome the Shockley-Queisser limit. From theoretical calculation shows that the combination of a top cell with a large bandgap energy (1.5~1.7 eV) and a bottom cell with a low bandgap energy (1.0~1.1 eV) can lead to a conversion efficiency higher than 30%. Given that the bandgap energy of most commercial single junction solar cells is around 1.1 eV, the perovskite solar cell with a bandgap energy around 1.6 eV must be a very promising candidate for the top cell of tandem solar cells. In this presentation, I will discuss the essential requirements for preparing highly performing perovskite top cells of tandem solar cells. Firstly, the strategies for improving the performance of the p-i-n type planar perovskite solar cell will be introduced. After a series of interfacial engineering procedures to the charge extraction layers, a conversion efficiency as high as 19% could be achieved. Secondly, strategies for fabricating transparent perovskite solar cells with a TCO top electrode layer will be discussed. Finally, some of the recent results on the highly efficient (> 23%) tandem solar cells incorporating the transparent perovskite top cell will be introduced.
Enhancing Stability for Organic-Inorganic Perovskite Solar Cells by Atomic Layer Deposited Al2O3 Encapsulation Eun Young Choi1, Jinhook Kim1, Seun Lim1, Ekyu Han1, Anita Ho-Bailie1 and Nochang Park1; 1University of New South Wales, Sydney, New South Wales, Australia; 2Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

In this work, we employed atomic layer deposition (ALD) to form Al2O3 layer as an encapsulant for perovskite solar cells (PSCs). Al2O3 layer deposited at temperature as low as 95°C achieved excellent water vapour transmission rate (WVTR) of 1.84 x 10⁻² g/m²/day at 45°C-100 %RH when thermal ALD (Th-ALD) was used. In order to test the moisture barrier capability of Al2O3 layer for PSCs, mesoporous perovskite devices, with spiro-OMeTAD or PTAA as hole transport layer (HTM) encapsulated by 50 nm Al2O3 film, were exposed to 65°C-85 %RH for 350 hours and their stabilities were monitored. We found that the colour of perovskite did not change after 350 hours of exposure regardless of the type of HTM used. With regards to Th-ALD encapsulated devices, PTAA based PSCs experienced a smaller power conversion efficiency (PCE) drop than spiro-OMeTAD based PSCs after thermal stress at 65°C. This is due to the presence of pinholes within spiro-OMeTAD layer after thermal stress which were not observed in PTAA. Finally, we have successfully achieved excellent durability test results for mesoporous (HC(NH2)2PbI3)x(CH3NH3PbBr3)1-x/PTAA devices encapsulated by 50nm Al2O3 with less than 4% drop in PCE after 7500 hours (>10 months) of exposure to 50 %RH under room temperature.

Planar Perovskite Solar Cells with High Open-Circuit Voltage Containing a Supramolecular Iron Complex as Hole Transport Material Dopant Yasemin Saygili1, Silver-Hamill Turren-Cruz1, 2, Selina Olthof1, Iknar Bayrak Pehlivan1, Michael Saliba1, Klaus Meierholz2, Tomas Edvinsson4, Shaik Mohammed Zakeeruddin1, Silver-Hamill Turren-Cruz1, 2, Juan-Pablo Correa-Baena1, Anders Hagfeldt1, Marina Freitag2 and Wolfgang Tress1; 1Institute of Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; 2Benemerita Universidad Autonoma de Puebla, Puebla, Mexico; 3Department of Chemistry, University of Cologne, Cologne, Germany; 4Department of Engineering Sciences, Solid State Physics, Uppsala University, Uppsala, Sweden; 5Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 6Department of Chemistry Angstrom Laboratory, Uppsala University, Uppsala, Sweden; 7Adolphe Merkle Institute, Fribourg, Switzerland.

In perovskite solar cells (PSCs), the most commonly used hole transport material (HTM) is spiro-OMeTAD, which is typically doped by metalorganic complexes, for example, based on Co, to improve charge transport properties and thereby enhance the photovoltaic performance of the device. In this study, we report a new hemicage-structured iron complex, 1,3,5-tris(5'-methyl-2,2'-bipyridin-5-yl)ethylbenzene Fe(III)-tris(bis(trifluoromethylsulfonyl)imide), as a p-type dopant for spiro-OMeTAD. The formal redox potential of this compound was measured as 1.29 V vs. the standard hydrogen electrode, which is slightly (20 mV) more positive than that of the commercial cobalt dopant FK209. Photoelectron spectroscopy measurements confirm that the iron complex acts as an efficient p-dopant, as evidenced in an increase of the spiro-OMeTAD work function. When fabricating planar PSCs with the HTM spiro-OMeTAD doped by 5 mol % of the iron complex, a power conversion efficiency of 19.5 % (AM 1.5G, 100 mW cm⁻²) is achieved, compared to 19.3 % for reference devices with spiro-OMeTAD with 20% Co dopant.

Two-Dimensional Perovskites with Short Interlayer Distance for High Performance Solar Cell Chunqing Ma, Dong Shen, Yuhui Ma and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

Two-dimensional (2D) perovskites have emerged as one of the most promising photovoltaic materials owing to their excellent stability compared to their three-dimensional (3D) counterparts. However, in typical 2D perovskites, the highly conductive inorganic layers are isolated by large organic cations leading to quantum confinement and thus inferior electrical conductivity across layers. To address this issue, the large organic cations are replaced with small propane-1,3-diammonium (PDA) cations to reduce distance between the inorganic perovskite layers. As shown by optical characterizations, quantum confinement is no longer dominating in the PDA-based 2D perovskites. This leads to considerable enhancement of charge transport as confirmed with electrochemical impedance spectroscopy, time-resolved photoluminescence and mobility measurements. The improved electric properties of the interlayer-engineered 2D perovskites yield a power conversion efficiency (PCE) of 13.0%. Furthermore, environmental stabilities of the PDA-based 2D perovskites are improved. PDA-based 2D perovskite solar cells (PSCs) encapsulated can retain over 90% of their efficiency upon storage for over 1,000 h and PSCs without encapsulation can maintain their initial efficiency at 70°C for over 100 h, which exhibit promising stabilities. These results reveal excellent optoelectronic properties and intrinsic stabilities of the layered perovskites with reduced interlayer distance.

Direct Observation of Cation-Exchange in Liquid-to-Solid Phase Transformation in FAx-MAxPbI3 Based Perovskite Solar Cells Yue Min Xie, Xiwen Xu, Menglin Li, Yuhui Ma and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

As one of the emerging photovoltaic technologies, the high performance and ease of fabrication of organometal halide perovskite based solar cells (PVSCs) draw tremendous attention in the photovoltaic community. Recently, formamidinium (FA) dominating mixed-organic-cation FAx-MAxPbI3 perovskites are attracting intensive attention for their extended optical absorption range (reduced optical bandgap) and high photovoltaic performance. However, FAx-MAxPbI3 based perovskite usually has undesired yellow colour non-perovskite phase (δ-phase) leading to a compromised efficiency, and a facile strategy to achieve pure-phase FAx-MAxPbI3 is rarely reported. Here, we demonstrate a facile approach to form δ-phase free FAx-MAxPbI3 using non-stoichiometric precursor solution. It is found that even a small amount of excessive methylammonium iodide (MAI) added in the precursor solution has a profound effect on perovskite crystallization during the liquid-to-solid phase transformation. In contrast to previous reports, using an in-situ photoluminescence spectroscopy measurement, it is directly observed that the organic-cation-exchange process is in fact occurred in the early stage of film formation during the liquid-to-solid phase transition, which can promote the formation of FAx-MAxPbI3 and pure-phase perovskite film can be achieved. By controlling the amount of cation ratio in the precursor solution optimized pure-phase FAx-MAxPbI3 is achieved. The champion perovskite solar cell exhibits an encouraging power conversion efficiency (PCE) of 17.40%. This study demonstrates a facile method to achieve high performance FAx-MAxPbI3 dominating mixed-organic-cation perovskite devices while providing insight into the ion-exchange process during perovskite crystallization.

Publication: Direct observation of cation-exchange in liquid-to-solid phase transformation in FA1-xMAxPbI3 based perovskite solar cells, Yue-Min Xie et al., J. Mater. Chem. A, 2018, 6, 9081-9088.
Organolead halide perovskite devices are reported to be susceptible to thermal degradation, which is resulted from heat-induced fast ion diffusion and structural decomposition. In this work, it is found that perovskite solar cells fabricated in humid air (RH: 70%) can achieve a power conversion efficiency (PCE) of 19.1% when the controlled devices have a VOC of 1.07 V and a PCE of 18.0%. To the best of our knowledge, up to now, this is the highest VOC obtained by using an inorganic electron transport layer for pure CH3NH3PbI3-based P-PSCs. Moreover, a higher EFF and ECBM of ETL are believed to drive a larger VOC and a better PCE. These indicate that it is a very significant method to achieve a higher VOC for P-PSCs by matching ETLS with a higher EFF and ECBM.

**ET04.03.12**

High-Performance MA0.96FA0.04PbI3 Perovskite Solar Cells Made in a Humid Air with a Relative Humidity of 70% Xiuwen Xu, Yuenin Xie, Menglin Li, Yuhui Ma and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

Understanding air-processing limitations and developing facile strategies to fabricate high-performance air-processed perovskite solar cell (PSC) is appealing yet challenging for the low-cost industrial deployment. Here, we demonstrate that besides the general wisdom of the moisture effect, oxygen induces a de-wetting behavior during the spin-coating of PbI2 precursor solution, both of which leads to the failure of desirable PbI2 deposition in air. Interestingly, by simply preheating the substrate and PbI2 solution, uniform PbI2 films can be deposited in air with a relative humidity (RH) of 70%. This is probably due to the rapid solvent evaporation at high temperature, reducing the ingress of oxygen and moisture. With the preheating approach, PSCs based on MA0.96FA0.04PbI3 achieves an encouraging power conversion efficiency (PCE) of 18.11%. More importantly, it is found that the combination of preheating and a PbI2(Cs)0.15(FAPbI3)0.85 intermediate complex can unlock the processing limitation and facilitate the growth of high-quality FA based perovskite films in humid air (RH: 70%). With the coupled method, a low-temperature air-processed planar Cs0.15FA0.85PbI3 PSCs achieves a high PCE of 15.56% with superior thermal-stability and photo-durability. Our work not only reveals the origin of the detrimental effects on perovskite formation in humid air, but also provides practical strategies for high-efficiency air-processed MA or FA based PSCs for future commercialization.

**References**


**ET04.03.13**

ZnO/SnO2 Double Electron Transport Layer Guides Improved Open Circuit Voltage for Highly Efficient CH3NH3PbI3-Based Planar Perovskite Solar Cells Duo Wang; School of Physics, Peking University, Beijing, China.

The electron transport layer (ETL) is a very important component of planar perovskite solar cells (P-PSCs), and it can effectively extract photon-generated electron from perovskites and convey them to the cathode. By this token, its properties directly determine the photovoltaic performances of P-PSCs. Herein, we developed ZnO/SnO2 as a double electron transport layer for CH3NH3PbI3-based P-PSCs, achieving a high open circuit voltage (VOC) of 1.15 V with the power conversion efficiency (PCE) of 19.1% when the controlled devices have a VOC of 1.07 V and a PCE of 18.0%. To the best of our knowledge, up to now, this is the highest VOC obtained by using an inorganic electron transport layer for pure CH3NH3PbI3-based P-PSCs. Moreover, a higher EFF and ECBM of ETL are believed to drive a larger VOC and a better PCE. These indicate that it is a very significant method to achieve a higher VOC for P-PSCs by matching ETLS with a higher EFF and ECBM.

**ET04.03.14**

High Crystallization of Perovskite Film by a Fast Electric Current Annealing Process Wei Luo; School of Physics, Peking University, Beijing, China.

High efficiency organic–inorganic hybrid perovskite solar cells have experienced rapid development and attracted significant attention in recent years. Crystal growth as an important factor would significantly influence the quality of perovskite films and ultimately the device performance, which usually requires thermal annealing for 10 min or more. We demonstrate a new method to get high crystallization of perovskite film by electric current annealing for just 5 s. Two strip electrodes were clipped onto the opposite sides of the FTO/SnO2 coated perovskite film, and subsequently applied with a direct voltage of 30 V for 5 s. The coated perovskite film was annealed quickly by the joule heat current flowing through the FTO layer. In contrast to conventional thermal annealing, a homogeneous perovskite film was grown on large grains and fewer pinholes, leading to a better performance of the device with higher open-circuit voltage and fill factor. The average PCE consequently improved to 17.02% from 16.05% with the conventional thermal annealing (100 °C for 10 min). In addition, the annealing time is significantly shortened to a few seconds and the heating area is relatively concentrated to the only film. This facile electric current annealing process with less energy loss and time consumption shows great potential in the industrial mass production of photovoltaic devices.

**ET04.03.15**

Solution-Processed Cu9Sn5 as Hole Transport Doping Layer for Efficient and Stable Perovskite Solar Cells Dong Han; School of Physics, Peking University, Beijing, China.

In recent years, perovskite solar cells have drawn widespread attention. We believe that investigation of long-term stability of perovskite solar cells is a critical issue and necessary to solve for its commercialization. As a hole transport material (HTM), Cu9Sn5 is widely used in n-i-p perovskite solar cells (PVSs). However, it suffers from a severe degradation from the penetration of moisture due to the doping of lithium bis(trifluoromethyl)sulfonyl)amide (Li-TFSI), which has strong hygroscopicity. In this paper, we propose a method which offers a new way to reduce the hysteresis and improve the stability of n-i-p perovskite solar cells by employing nitrogen-doped SnO2 (N:SnO2) electron transport layer (ETL) and Spiro-OMeTAD/Cu9Sn5 hole transport layer (HTL) without Li-TFSI doping. Cu9Sn5 is a p-type transport material with favorable energy level matching with Spiro-OMeTAD. Furthermore, since there is no Li-TFSI doping in HTL, it can avoid devices suffering a severe degradation from the permeation of moisture. In the meantime, the LUMO of SnO2 can be tuned from -4.33 eV to -3.91 eV by implanting nitrogen ions into the SnO2, which exactly match the LUMO of CH3NH3PbI3 (-3.90 eV) and thus help to reduce the hysteresis. The modified n-i-p perovskite solar cells achieve maximum PCE of 17.10% and remain about 96 % of PCE after 1200 hours stability test in air environment with no encapsulation.

**ET04.03.16**

Impact of SnF2 and Pyrazine Additives in Formamidinium Tin Iodide Perovskite Solar Cells Simon Sanders1, Dominik Stümmeler1, Pascal Pfieffier1, Florian Schinkant1, Peter Baumann2, Gintautas Simkus1, 3, Michael Heuken1, 3, Andrei Vescan1 and Holger Kalisch1; 1Compound Semiconductor Technology, RWTH Aachen University, Aachen, Germany; 2APEVA SE, Herzogenrath, Germany; 3AIXTRON SE, Herzogenrath, Germany.

Due to a steep rise in efficiency, organic-inorganic halide perovskite solar cells have attracted wider research interest in the past few years. The achievement of a power conversion efficiency (PCE) of 22.7 % in 2017 using a lead halide perovskite makes these devices a promising alternative to the established

**References**

thin-film and wafer-based solar cell technologies. Nevertheless, the toxicity of Pb remains as a major issue for the commercialization of perovskite photovoltaics. So far, Sn-based perovskites showed the most promising results in Pb-free perovskite solar cells with efficiencies up to 9.0 %. However, Sn-based perovskite layers typically suffer from poor layer quality (coverage and homogeneity issues) and fast degradation caused by the instability of the Sn2+ ion which easily oxidizes to Sn4+.

In this work, we present formamidinium tin iodide (FASnI3) perovskite solar cells which are processed by spin-coating under inert nitrogen atmosphere, employing a standard non-inverted stack composed of compact and mesoporous TiO2, the perovskite layer and Spiro-MeOTAD sandwiched between fluorine-doped tin oxide (FTO) and evaporated gold contacts. Morphological and structural characterization of processed layers and devices is carried out by scanning electron microscopy. Photovoltaic measurements are performed in nitrogen atmosphere under simulated AM1.5 sunlight of 100 mW/cm² illumination. Absorption spectra measurements are conducted in the wavelength range of 300 - 1000 nm. To increase the area covered with the perovskite film, we examine the influence of using different amounts of toluene as anti-solvent initiating a rapid crystallization. It was determined that 1 ml of toluene is sufficient for 80 µl perovskite solution to produce closed films. To suppress Sn2+ oxidation and to obtain smooth perovskite films, pyrazine and SnF2 were added into the perovskite precursor solution. By varying the ratio of additives in this solution, their impact on layer morphology and on cell performance are investigated. A pyrazine/SnF2 ratio of 0.2 M / 0.1 M has proven to be the optimum leading to smooth layers and a maximum PCE of 2.1 %. We highlight that layers with higher concentrations of additives suffer from delayed crystallization and therefore reduced coverage. However, we found that these layers exhibit additional light absorption for wavelengths above 650 nm and still provide reasonable photocurrents.

ET04.03.17
High Efficiency Perovskite Solar Cells with Molecular Passivated NiOx Charge Extraction Layer
Menglin Li; Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

Developing low cost and stable metal oxide charge extraction layer is attractive yet challenging for fabricating long-term stable high-performance perovskite solar cells (PSCs). Here, it is found that the solution processed NiOx based PSCs surface suffers from strong recombination with interfacial defects. We have found that continuous light soaking is required in the NiOx based PSCs to recover the built-in potential and consequently open-circuit voltage ( VOC ). Interestingly, we have found that n-butylamine molecular monolayer can effectively passivate those defects in the NiOx layer. The device power conversion efficiency (PCE) with molecular passivated NiOx as the hole transport layer is increased from 13.5% to 18.0%. Further molecular dynamic simulation reveals auto-decomposition process at as-prepared NiOx/MAPbI3 interface, which can be eliminated by surface passivation.

ET04.03.18
Understanding the Crucial Design of Amorphous Hole Transport Materials in Perovskite Solar Cell
Kun-Han Lin, Antonio Prlj and Clémence Corminboeuf; Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland.

Within the last nine years, the power conversion efficiency of perovskite solar cell (PSC) has soared to 22.7% [1]. Among recently proposed high-performance PSCs, hole transport layers have proved to be essential components for these devices [2]. A promising HTM should possess a suitable ionization potential (IP) to enlarge the open-circuit voltage (Voc); meanwhile, it should transport charge carriers efficiently from the perovskite/HTM interface to the electrode [3]. In contrast to this well-known design principle, a comprehensive understanding of the structure-property relationship remains lacking, especially for the challenging relationship between molecular structure and mobility. The discrepancy of knowledge in these two aspects hampers the discovery pace of promising HTMs. As a result, investigating the non-trivial structure-mobility relation with the aid of computer simulations at a molecular level would be beneficial. Our recent work on a prototype HTM, TPAC-3M [4], demonstrated that increasing the number of “carbazole side arms” (mono- to tri- arm) attached to a triphenylamine (TPA) core enhances the mobility by approximately 5 times by lowering the reorganization energy and the energetic disorder. Further optimization of the IP of the high-mobility tri-arm HTM by substituting methoxy groups with various other electron-withdrawing groups results in HTMs with desirable energy alignments with the perovskite materials. Care should be taken, however, as an enormous molecular dipole moment can result from IP-tuning, which magnifies the energetic disorder and leads to a mobility loss of more than one order of magnitude. After a thorough investigation, we propose a new tri-arm molecule containing pyridine substitutions, that possesses enhanced hole mobility and a suitable IP. Moreover, the pyridine moiety can also serve as a Lewis base that passivates the surface defects of perovskite, which reduces charge recombination at the perovskite/HTM interface [5].

ET04.03.21
Thermal Stability of Polycrystalline Hybrid Perovskite Thin Films Demonstrated by Grain Boundary Ruihan Yang, Yaefe Wang and Shibin Li; University Of Electronic Science And Technology Of China, Chengdu, China.

Perovskite solar cells (PSCs) have been developed rapidly with power conversion efficiencies (PCE) rushing from 3.8% to a certified 22.1%. Accompanied with the improvement of PCE, the stability of perovskite has become a focus recently. Thermal instability of hybrid perovskite thin films is one of the important issues that must be overcome on the way to commercialization of PSCs, and then its essence to deeply understand the degradation mechanism of perovskite thin films caused by thermal instability. In this work, we studied the dependence of thermal stability of CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) crystals on grain size. We fabricated MAPbI$_3$ films by anti-solvent one-step deposition method and increased the grain size by IPA solvent annealing. According to the SEM, XRD and UV-Vis absorption measurements, it was demonstrated the thermal stability of polycrystalline hybrid perovskite thin films dominated by grain boundaries (GBs). The grain size plays a key role in the thermal degradation of the MAPbI$_3$. It was found that degradation rates of MAPbI$_3$ films in thermal environment are sensitive to the grain size and temperature. MAPbI$_3$ films with larger grain sizes and less GBs have a better resistance to heat-transfer. To further understand the thermal degradation mechanism of perovskite crystals, a molecular model was put forward. The dangling bonds in GBs were considered to promote the process of thermal decomposition. Thus MAPbI$_3$ films with less GBs exhibit higher thermal stability. Meanwhile, solar cell devices with a structure of FTO/TiO$_2$/meso-TiO$_2$/MAPbI$_3$/PTAA/Au were fabricated and J-V curves of PSCs were measured to compare the photovoltaic performance of PSCs. The highest efficiency of PSCs increased from 16.87% to 18.56% with the increase of grain size. The results indicate that the reduction of GBs of perovskite is a feasible way to improve the thermal stability of PSCs.

ET04.03.22
Multi-Layered Thin Film Encapsulation for Perovskite Solar Cells via Low-Temperature Plasma-Enhanced Atomic Layer Deposition Seong Hyun Lee1, Jung Wook Lim1,2, Gayoung Kim1,2 and Man Gu Kang1,2; 1ICT Material Research Group, Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); 2Department of Advanced Device Engineering, University of Science and Technology (UST), Daejeon, Korea (the Republic of).

The performance of perovskite solar cells (PSCs) has dramatically improved over half a decade, and a record efficiency of 22.7% for a cell with an active area of less than 0.1 cm$^2$ has been achieved. However, the stability against moisture is essential for viability in the commercial market. Many efforts have been devoted to modifying the stability of either the perovskite material itself or the electron and hole transport layers but the fundamental solutions have not been found to date. Therefore, the encapsulation technologies have received a considerable amount of attention for the long-term stability of PSCs. In this study, we investigated the thermal stability of perovskite thin films deposited by low-temperature plasma-enhanced atomic layer deposition (PEALD). The multi-layered encapsulation films consist of Al$_2$O$_3$ and SiO$_2$ layer which have high moisture barrier properties. We optimized the thickness of each layers and the number of layer interfaces of the encapsulation layers to reduce the water vapor transmission rate (WVTR). Through the MOCON test, it was demonstrated that the WVTR of Al$_2$O$_3$/SiO$_2$ multi-layered encapsulation film with a 100 nm-thick is lower than that of Al$_2$O$_3$ and SiO$_2$ single-layered encapsulation film with the 100 nm-thick. And, in the case of multi-layered encapsulation, it was indicated that the number of Al$_2$O$_3$/SiO$_2$ interfaces strongly affects the values of WVTR. Based on above results, we applied the multi-layered encapsulation to PSCs and investigated the moisture stability of the PSCs with respect to the process temperature, film thickness and process sequences of the multi-layered encapsulation thin films. And we explored the effect of plasma damage on the performance and moisture stability of the PSCs during the PEALD process. Furthermore, we will discuss the performance degradation of large-scale PSC modules with the Al$_2$O$_3$/SiO$_2$ multi-layered encapsulation under damp heat conditions consisting in 85 °C and 85% relative humidity, during a period of 1000 hours. This work would pave the way for the commercialization of the practical PSC modules in the near future.

ET04.03.23
Interconnection Optimizations for Efficient Perovskite Solar Modules Zhen Li1,2, Mengjin Yang1, Donghoo Kim1, Talsya Klein2, Maikel van Hest1 and Kai Zhu1; 1Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, Colorado, United States; 2State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shannxi Joint Laboratory of Graphene (NPU), Xi’an, China; 3Materials Science Center, National Renewable Energy Laboratory, Golden, Colorado, United States.

Small area perovskite solar cells (PSCs) have achieved power conversion efficiency (PCE) comparable to other thin film solar cells. Pushing PSC technology toward commercialization requires developing large-area perovskite solar modules with fully scalable deposition approaches. A fully scalable deposition scheme for perovskite module fabrication was demonstrated using spray coating for TiO$_2$ electron transport layer (ETL) and blade coating for both perovskite absorber layer and spiro-OMeTAD hole transport layer (HTL). It is found that the interconnections between sub-cells in the PSC modules are important for achieving high performance and reliability. Due to the difficulty of removing TiO$_2$ layer by scribing, the interconnection between sub-cells contains a TiO$_2$/metal junction. The TiO$_2$/metal junction shows a schottky diode or ohmic contact behavior, depending on the thickness of the TiO$_2$ layer. Optimization of the interconnection contact achieves better module performance, mainly contributed from improved fill factor. Finally, we demonstrated a highly efficient 4-cell MA$_0.7$FA$_{0.3}$PbI$_3$ perovskite module with a stabilized PCE of 15.6% measured from an aperture area of ~10.36 cm$^2$, corresponding to an active-area PCE of 17.9% with a geometric fill factor of ~87.3%.

ET04.03.24
The Abnormal Synergetic Effect of Organic and Halide Ions on the Stability and Optoelectronic Properties of Mixed Perovskite via In Situ Characterizations Minzhu Long, Tiankai Zhang and Jianbin Xu; Chinese University of Hong Kong, Hong Kong, China.

The mixed cation lead mixed halide perovskite (MLMP) Cs$_x$FA$_{1-x}$PbI$_3$Br$_y$ is one of the most promising candidates for both single-junction and tandem solar cells applications due to its high efficiency and remarkable stability. However, the composition effect on thermal stability and photovoltaic performances has not yet been comprehensively investigated. Therefore, the interplay between composition, crystal structure, morphology and optoelectronic properties under heat stress, were systematically elucidated here through a series of in situ characterizations. It is revealed for the first time that the FA and Br-spin span style="font-size:10.8333px">-would release synchronously at first even under mild annealing. This release leads to serious
Methylammonium lead halide perovskites suffer from a high degradation rate of \(<0.1\% \text{ h}^{-1}\). Some of this degradation is extrinsic, e.g. exposure to humidity, which can be minimized via device encapsulation. However, perovskite is also intrinsically unstable, even in completely encapsulated conditions hybrid perovskite degrade at the temperatures \(>80\, ^\circ\text{C}\), mainly due to the organic component i.e., methyl ammonium ion (MA). In this work, we report a novel mixed-cation perovskite with 40% acetamidinium (AA) cation in the MAPbI\(_3\) matrix. Unlike MA cation, the AA cation has a restricted C-N bond rotation due to delocalized n-electron cloud over N-C-N bond. This results in stronger hydrogen bonding that enhances the intrinsic stability of the lattice. MA\(_x\)AA\(_{1-x}\)PbI\(_3\) thin-films with 5%, 10%, 20% and 40% AA are synthesized in the same manner as MAPbI\(_3\), with AAI precursor added to the precursor solution in the stoichiometric ratio. Spin-coated films are annealed at 100°C to obtain black coloured MA\(_x\)AA\(_{1-x}\)PbI\(_3\) films. The XRD pattern shows a monotonic shift in 29 peak from 14.24 to 14.02 when we increase the AA% in perovskite matrix from 0 to 20%, however, we see the presence of some other secondary phases like AAAPbI\(_3\) when AA% is \(>10\%\). Further, post-treatment of the as deposited film with methylamine vapor suppresses the secondary phases. In addition, it also improves the grain sizes from about 200 nm needles to 1-2 \(\mu\text{m}\) grains with complete surface coverage in accordance with a literature. The improvement in the film quality also reflects in the increase in the carrier lifetimes to 37 \(\mu\text{s}\) for 10% AA substituted films compared to 25 \(\mu\text{s}\) for the standard MAPbI\(_3\) films. Further, 12 devices with FTO/c-TiO\(_2\)/m-TiO\(_2\)/MA\(_x\)AA\(_{1-x}\)PbI\(_3\)/Spiro-OMeTAD structure were fabricated. An increase in the open-circuit voltage was observed for the AA substituted devices having \(V_{oc}\) in the range of 1.04–1.08 V against 0.96–1.01 V of the standard MAPbI\(_3\) devices. Also, the fill-factors of the AA cells increased to 0.73–0.75 against 0.67–0.69 of the MAPbI\(_3\) devices. But the short-circuit currents of the AA devices fell to 15–19 mA/cm\(^2\) from 21–22.5 mA/cm\(^2\) of the standard devices. The thicknesses and absorption spectra of the films are currently under investigation to account for the decrease in the \(J_{sc}\). The overall PCE of the AA devices came out to be 13.2% against 14.53% of the standard devices. Increasing the thickness of the AA substituted films will increase the \(J_{sc}\) of the devices possibly without affecting the \(V_{oc}\) owing to their higher carrier lifetimes, thus providing scope for higher PCE’s. Also, thermal degradation measurement shows that as expected, AA substituted films are more stable than pure MAPbI\(_3\) films. While pure films lose their color and luster in just 32 hours at 120 °C, MA\(_x\)AA\(_{1-x}\)PbI\(_3\) films retain the black phase. The thermal stability measurements of the fabricated devices are underway.

**References:**


---

**8:15 AM ET04.04.02/ET02.05.02**

**Towards CIGS Perovskite Tandem Cells**

**Jesper Jacobsen**, Adam Hultqvist, Håkan Rensmo and Gerrit Boschloo; 1Chemistry, Uppsala University, Uppsala, Sweden; 2Uppsala University, Uppsala, Sweden.

Perovskite solar cells will have a hard time to reach competitiveness with respect to conventional PV-technologies; unless they are integrated in tandem-architectures that possibly could outperform single junction silicon cells. One interesting potential perovskite tandem companion is CIGS, CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\), which is a commercial thin film technology with record efficiencies above 22 % and a variable band gap. In this project, we strive for constructing efficient 2-terminal CIGS-perovskite tandem cells. We will here discuss progress and challenges connected to recombination layers, perovskite engineering, and transparent top contacts in CIGS-perovskite tandem architectures.
Low gap ABX₃ perovskites tin and lead at the B-site are a breakthrough that has enabled fabrication of efficient all-perovskite tandem solar cells. However, tin is susceptible to oxidation to the 4⁺ state, a degradation pathway unique to tin-containing perovskites. Suppressing this oxidation reaction is essential to ensure that highly efficient all-perovskite tandem solar cells are also stable against long term environmental stressors.

We identify the specific chemical mechanism by which pure tin-based perovskites undergo oxidation using a combination of chemical methods including thermogravimetric analysis and solvent extraction of degradation products. We find that the oxidation reaction depends on a cooperative mechanism that involves simultaneous oxidation of multiple adjacent tin iodide octahedra. Critically, the most favorable oxidation pathway is blocked by substitution of 50% or more of the B-site with lead because this significantly lowers the chances of there being multiple adjacent tin octahedra that can facilitate the cooperative mechanism. As a result, the stability of tin perovskites toward oxidation is improved by orders of magnitude upon alloying with lead. The resulting guideline is that low band gap perovskites can be designed to have significantly enhanced oxidative stability by keeping the tin fraction at 50% or below.

We proceed to design solar cells to withstand aging under elevated temperatures in air. We probe the thermal stability of high-performing low band gap solar cells by aging at 85°C in air. Encouragingly, there is no measurable change in the bulk absorption of the perovskite absorber under thermal aging in air, indicating that the strategy of suppressing oxidation by using a mixed tin-lead perovskite successively avoids oxidative breakdown. However, the fill factor drops due to the formation of an S-kink after 100 hours of aging. We develop a treatment of the tin-lead perovskite film by exposure to methylammonium chloride vapour that results in significant grain growth and healing of cracks between grains. This post-treatment dramatically improves the thermal stability of the full solar cells. Using an MAC1-vapour-treated low gap perovskite with 50% tin, capped with a sputtered Indium Tin Oxide (ITO) top electrode, we successfully demonstrate a solar cell that maintains its full power conversion efficiency for 150 hours in air at 85°C, and remains above 85% of initial PCE for over 300 hours. In addition, we demonstrate stable operation of a tin-lead solar cell at maximum power point under 1-sun illumination for over 100 hours with no drop in performance. These measurements are a huge improvement upon any thermal stability results reported for tin-containing perovskites. The fact that good thermal stability in air is achieved with no encapsulation represents a major step toward proving the long-term stability of tin-lead low band gap perovskite solar cells, and of efficient all-perovskite tandem solar cells.

Two conflicting characteristics compete where the commercial viability of one-sun tandem solar cell is concerned: On the one hand, tandem solar cells have fundamentally higher efficiencies than single junction solar cells. On the other hand, tandem solar cells are intrinsically more complex than single junction solar cells and require more fabrication steps, which makes them more expensive. Only if the benefit from the additionally generated energy outweighs the higher fabrication cost can tandem solar cells be successful.

The question under which conditions the last sentence is true is a multilayered one. The value of efficiency is highest when considering the integrated PV system, which makes it necessary to explore system level aspects. These aspects include, among others, economic considerations as well as topics from material science; for example degradation.

In this work we attempt to provide an overview of what is needed to make tandem solar cells economically successful. Central to our findings is the material science; for example degradation.

The talk will begin by showing what we have done to make perovskite on silicon tandem solar cells with 25% efficiency and how 30% efficiency can probably be obtained in the coming years. Then the challenge of making solar panels with metal halide perovskite semiconductors that will last for more than 25 years will be addressed. We will show that packaged solar cells can survive industry standard reliability tests such as 1000 hrs at 85°C and 85% humidity, 200 temperature cycles between -40°C and 85°C, and ultraviolet exposure. The strategies for making stable perovskite cells include choosing perovskite compositions that have higher thermal and oxidative stability, managing stress during the formation of the film to prevent buckling that makes subsequent processing difficult, minimizing tensile stress in the final film since it appears to make bonds weaker, using solution processing of the top contact layer to fill in gaps at grain boundaries so that a sputtered transparent conducting oxide layer can form a superb barrier layer, using polyolefin as the encapsulant since it does not chemically react with the perovskite and has an ideal elastic modulus, using butyl rubber edge seals and using glass on glass packaging.

Combining perovskites with well-established photovoltaic materials such as silicon or CIGS is an attractive option for producing cheap, high efficiency and high voltage solar cells. Perovskite-based tandem solar cells can potentially achieve over 30% tandem efficiency. We demonstrate a 4-terminal tandem perovskite-silicon configuration in which the efficiency is as high as 26%. We also demonstrate a two-terminal monolithic tandem device with a perovskite top subcell and a high-temperature tolerant homojunction c-Si bottom subcell, with an efficiency of over 22%, and a perovskite/CIGS tandem with an efficiency of over 23%, which is the highest efficiency that has been reported for this configuration. We describe the optical and electronic factors that have been instrumental in reaching these efficiencies. We also show that interface passivation can lead to open circuit voltages over 1.2V for a 1.6eV bandgap perovskite, and that semi-transparent cells can achieve high stability under combined heat and light. These results show the clear potential of perovskites in practical high efficiency tandem devices.

With open circuit voltages (V_{oc}) above 730 mV, silicon heterojunction (SHJ) solar cells are promising candidates for the bottom cells in organic-inorganic lead halide perovskite/silicon tandem solar cells. Using simulation studies, we have shown that under realistic assumptions, power conversion efficiencies up to 30% should be achievable with such devices [1]. To attain this goal, starting from first devices with moderate stabilized efficiencies of 18.1% [2] we carefully optimized the optical and electrical properties of the device in order to achieve low parasitic absorption and reflection, photorecurrent matching between the two sub-cells and lowly resistive current transport across the internal tunnel-recombination junction. In this presentation, I will discuss how we were recently able to demonstrate certified 25% efficient perovskite/SHJ tandem cells [3] by addressing these issues. I will focus on the silicon bottom cell and contact stack optimization: Starting from a rear junction SHJ cell design on double side textured wafers with 22.6% power conversion efficiency (J_{sc} = 38.3 mA/cm², V_{oc} = 731 mV, FF = 80.6 %) [4], we developed a rear side only-textured SHJ cell, which allows to process the perovskite top cell using conventional spin-coating methods. Optimizing film thicknesses at the perovskite/SHJ interface and tuning the refractive index of the nc-SiO_{x}:H film used as front surface field in the SHJ to an intermediate value of ~2.6 (at 800 nm) were instrumental in achieving 25% efficient cells with photocurrents above 17.8 mA/cm². On this basis, I will briefly discuss the potential to further enhance device performance using alternative deposition methods, such as plasma-enhanced ALD for tin oxide interlayers, and alternative materials such as tungsten oxide alloys for carrier selective contacts.

References:
3. E. Köhnen, S. Albrecht et al., to be submitted

Progress on Si Tandems [Anita Ho-Baillie1, Hamid Mehrvarz1, Jianghui Zheng1, Faqun Ma2, Chuo Y1, Stephen Brenner1, Shujuan Huang2, Hidenori Mizuno2 and Tyler J. Grassman3;1Australian Centre for Advanced Photovoltaics, The University of New South Wales, Sydney, New South Wales, Australia; 2Fukushima Renewable Energy Institute, National Institute of Advanced Industrial Science and Technology, Fukushima, Japan; 3The Ohio State University, Columbus, Ohio, United States.

Tandem solar cell is a promising approach for achieving high efficiencies for photovoltaics [1]. The challenge is to find an efficient, economical and stable technology for each cell stack to realize true savings in the system’s levelised cost of energy. Nevertheless, substantial progress has been made in the demonstrations of two-terminal Si tandem cells. The advantage of 2-terminal over 4-terminal configuration is the reduced complexity in wiring and packaging [2]. The challenge lies in the integration of the cell stacks without electrical and optical losses. Recently, a simple perovskite/Si tandem cell structure has been reported [3]. It does not require additional interface layer for the integration of perovskite and Si cells. Instead, the electron transport layer in the perovskite top cell serves as the recombination layer between the top and bottom sub cells. The lack of lateral conductivity in this recombination layer means undesirable shunts are effectively localized. Another advantage of this structure is its compatibility with homo-junction Si cells – the most common choice for incumbent commercial Si photovoltaic technology. Recent optimizations have improved cells’ performance from 20.5% to 22.7% on 4cm². Great progress has been made on 2-terminal III-V/Si and III-V/Si tandems via wafer bonding and direct growth. Many of these tandem cell structures require smooth interface negating the use of textured Si bottom cell. This means external measures are required for anti-reflection and light trapping. Strategies for improving the optical performances of InGaP/GaAs/InP tandem by SmartStack [4] and monolithic epitaxial GaAsP/Si tandem [5] will be presented in this talk.

References:

Textured Monolithic Perovskite/Crystalline Silicon Tandem Solar Cells with >25% Power Conversion Efficiency [Jeremie Werner1, Florent Sahli1, Brett Kamino2, Matthias Brüning2, Raphael Mond1, Giszem Nogy1, Philippe Wyss1, Andrea Ingenito1, Bertrand Paviot-Salomon2, Loris Barnaud1, Laura Ding2, Juan Diaz Leon2, Gianluca Cattaneo1, Arnaud Walter1, Soo-Jin Moon2, Terry Chien-Jen Yang1, Peter Fiala1, Fan Fu1, Mathieu Boccard1, Matthias Despeisse1, Bjorn Niesen2, Sylvain Nicoloy2, Quentin Jeangros1 and Christophe Ballif1;1PV-Lab, Ecole Polytechnique Fédérale de Lausanne (EPFL), Neuchâtel, Switzerland; 2PV-Centre, CSEM, Neuchâtel, Switzerland.

As crystalline silicon (c-Si) solar cells are approaching their efficiency limit of 29%, novel solutions must be found to increase the competitiveness of Si photovoltaics compared to conventional energy sources. One of the most promising approaches lies in combining c-Si solar cells with a low-cost wide-bandgap top cell to form a tandem device. Organic-inorganic halide perovskite solar cells are particularly attractive candidates for top cells, showing high efficiencies with simple and potentially cost-effective device fabrication. Calculations have shown that the practical efficiency potential of perovskite/c-Si tandem solar cells is beyond 30%.

Here, we present perovskite/silicon tandem devices featuring fully textured bottom cells, through a careful control of the top cell deposition conditions and hence of the optoelectronic properties and interfaces of the different materials. These cells were employed as a platform to address the most crucial questions for tandem development: - Reaching maximal performance: fully conformal perovskite top cells were developed and optimized, enabling the usage of industrially viable textured bottom cells for maximal optical performance given the reduced reflection losses and enhanced light trapping. This enabled current-matching conditions with >20 mA/cm² in both the perovskite and silicon subcells (excluding metallization-induced shadow losses). Parasitic absorption was minimized thanks to the development of highly transparent charge transport layers and electrodes. This optical optimization of the tandems led to a certified steady-state
efficiency of 25.2% for an aperture area of >1 cm².
- **Up-scaling:** A nanocrystalline silicon intermediate recombination layer was developed to increase the shunt resistance and enable large-area tandem devices, achieving 13-cm² cells with a steady-state efficiency above 20%.
- **Silicon bottom cell technology:** We tested our process with different bottom-cell technologies (silicon heterojunction or tunnel oxide passivated contact) and reached >25% efficiencies on both cell types for an aperture area of >1 cm².
- **Industrially viable metallization:** A screen-printed silver (Ag) metallization method was developed for the front grid. It employs a low-temperature Ag paste that can be cured without affecting the perovskite properties.
- **Encapsulation and cell reliability:** An encapsulation process involving a glass/glass configuration with a butyl rubber edge sealant was developed. Encapsulated tandems were subjected to standard reliability testing conditions, including damp heat at 85 °C/85%RH and light soaking for 1000 hours. Overall, these results suggest a path in the development of monolithic perovskite/silicon tandem solar cells with realistic efficiency potential >30% on large area with enhanced stability.

SESSION ET04.05/ET05.05: Joint Session: The Past, Present and Future of Halide Perovskites
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room Ballroom B

1:30 PM *ET04.05.01/ET05.05.01
**Hybrid Halide Perovskite Semiconductors—An Historical Perspective**

David B. Mitzi
Duke University, Durham, North Carolina, United States.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable structures/band gaps, relatively benign defects and grain boundaries, and facile processing for systems based on Group 14 metals (e.g., Ge, Sn, and Pb). Most recently, these materials have enabled unprecedented rapid improvement in performance within single junction photovoltaic (PV) devices, from an initial demonstration in 2009 [2] to levels with >20% power conversion efficiency and open circuit voltages >1V [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility, semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures [4,5]. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.


2:00 PM *ET04.05.02/ET05.05.02
**Photovoltaics of Halide Perovskites and Perspectives of Extensive Applications from the Ground to the Universe**

Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Lead halide perovskite absorbers have achieved high photovoltaic performance exceeding the efficiency of CIGS and CdTe and their long term stability against heat, moisture, and light are being improved by compositional engineering of perovskite and surrounding carrier transport materials. For industrial applications, thermal stability of perovskites and carrier transport materials is a critical issue in comparison with thermally highly strong inorganic solar cell (Si, CdTe, etc.). Metal oxide electron transport layers (ETLs) generally have advantage in higher thermal stability than organic ETLs. We have been working with TiO₂ ETL-based cation perovskite cells, which yielded efficiency over 21% by ambient air solution processes. Light intensity dependence of Voc shows ideality factor low enough (n<1.4) for the perovskite solar cell to work as a high voltage power source even under weak light. Such merit meets a requirement in solar cell application to space satellite missions, which needs high photovoltaic performance even under very weak sunlight (Mars and Jupiter). We have examined the durability of perovskite solar cells which have thermally stable compositions comprising FA-based perovskites, TiO₂ ETL, and P3HT as hole transport layer (HTL). These cells exhibit good stability against thermal impact between temperature range between ~80°C and +100°C. We also confirmed very poor thermal stability of spiro-OmeTAD as a reference HTL. On exposure to high energy electron and proton radiations as accelerated conditions simulating long term space irradiations, the perovskite cells demonstrated high stability and tolerance, which are superior to those of Si and GaAs solar cells. Space applications also require fabrication of lightweight flexible devices. Thin film substrate-based perovskite solar cells were fabricated by low-temperature multilayer coating methods using amorphous TiO₂ as ETL, which yield efficiency up to 18%. Future perspectives of industrialization of perovskite photovoltaic devices will be discussed focusing on the durable composition of perovskite devices and advantage of lightweight thin film device.

References


2:30 PM BREAK

3:00 PM *ET04.05.03/ET05.05.03
**Perovskite Photovoltaics—History, Progress and Perspective**

Nam-Gyu Park; Sungkyunkwan University, Suwon, Korea (the Republic of).

Since the first report on the high efficiency, stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 22.7% in 2017. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches about 9,000 as of May, 2018, which is indicative of a paradigm shift in photovoltaics. Although high photovoltaic performance was achieved, current-voltage hysteresis has been issued because it is related
to stability of PSC. In this talk, methodologies to remove hysteresis are described. Interlayers at heterojunction are found to play important role in reducing hysteresis and improving stability. Manipulation of Frenkel defect is a universal approach toward hysteresis-free PSC. We have discovered novel methods for large-area perovskite coating and phase transformation in perovskite, which will be discussed in detail. In addition to photovoltaics, perovskite can be used to other applications. Long charge diffusion length and high energy stability of organic-inorganic halide perovskite are suitable for low-dose, high resolution X-ray imaging. We demonstrated X-ray image using millimeter thick perovskite film based on multicrystalline perovskite crystal with single-crystal-like optoelectronic properties. For heading toward Shockley–Queisser limit, research direction in PSC is proposed in this talk.

3:30 PM  *ET04.05.04/ET05.05.04*  
Compositional Engineering for Efficient and Durable Perovskite Solar Cells  
Anders Haasefeldt, Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 20% with a mixed composition of iodide/bromide and methyl ammonium/formamidinium [1]. For cells larger than 1 cm\(^2\) we have obtained 19.6% [2], replacing the anti-solvent step in the perovskite film formation with a vacuum flash treatment. With the use of SnO\(_2\) compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20% [3]. The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/Ma as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example with a hysteresis free efficiency above 20% [3]. The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/Ma as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example with a hysteresis free efficiency above 20% [3].

The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/Ma as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example with a hysteresis free efficiency above 20% [3]. At the meeting we will discuss our follow up works [3] and present our champion data; up to 22% efficiency with an external electroluminescence of 4%, and an outstanding open-circuit voltage of 1.24 V at a band gap of 1.63 eV entailing one of the smallest loss-in-potential of 0.39 V ever measured for any solar cell material. Furthermore, we will report promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (during which 95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests [6].

**Keywords:** Perovskite, composition, stability

**References**

[1] Bi et al., Science Advance, DOI: 10.1126/sciadv.1501170
[2] X. Li et al., Science, DOI:10.1126/science.aaf8060

4:00 PM  *ET04.05.05/ET05.05.05*  
Perovskite Solar Cells—The Path to a Printable Terawatt-Scale Technology  
Kai Zhu; National Renewable Energy Laboratory, Golden, Colorado, United States.

Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching to about 23%. Uniquely, PSCs have the highest efficiencies when they are solution processed, so one can envision solar cells printed in a similar manner and scale as newspapers. In addition, the bandgap tunability through perovskite composition engineering can enable high-efficiency multijunction devices, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). Thus, PSCs are suited to helping address the challenge of terawatt-scale, PV-based electricity production that can power the future world. In this talk, I will discuss our recent progress in two areas: (1) scalable fabrication of high-efficiency, large-area perovskite solar cells and modules; (2) development of perovskite-based tandem devices. I will discuss our recent studies toward better control of film formation across the device stack at large scales by improving the precursor chemistry to better match the processing methods. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. The challenges associated with perovskite solar module fabrication will be discussed. I will show the impact of interconnections on the performance of perovskite solar modules fabricated by scalable depositions. Toward perovskite-based tandem device development, I will discuss our recent effort on improving the optoelectronic properties of wide-bandgap as well as low-bandgap perovskite absorbers through solution chemistry engineering. Challenges and progress on perovskite-based tandem devices will also be discussed. These results demonstrate a promising path towards commercialization of the perovskite photovoltaic technology.

4:30 PM  **DISCUSSION PANEL: UNSOLVED PEROVSKITE PROBLEMS—OPPORTUNITIES AND CHALLENGES - DISCUSSION**  
LEADER: IVÁN MORA-SERÓ

**SESSION ET04.06: Poster Session II**  
Tuesday Afternoon, November 27, 2018  
8:00 PM - 10:00 PM  
Hynes, Level 1, Hall B

**ET04.06.01**  
Understanding the Doping Effect on NiO—Toward High-Performance Inverted Perovskite Solar Cells  
Wei Chen\(^1\), Yinghui Wu\(^1\), Aleksandra B. Djurišić\(^1\) and Zhubing He\(^1\); \(^1\)Southern University of Science and Technology, Shenzhen, China; \(^2\)Physics, The University of Hong Kong, Hong Kong, Hong Kong.

Metal organic halide perovskite solar cells (PSCs) are emerging photovoltaic technology of significant interest due to their high power conversion efficiency (PCE), with record efficiency exceeding 22%. The use of inorganic hole transport layers (HTLs) in PSCs has been attracting increasing attention to improve the stability of the devices. Among various inorganic hole extraction/hole transport materials, NiO is of particular interest for PSC application. However, low intrinsic conductivity of NiO is a significant drawback, since it can result in hole accumulation near the perovskite interface, increasing the chance of recombination and reducing the charge collection. Therefore, considerable efforts have been made to improve the charge collection by improving the quality of deposited NiO and/or doping the NiO to improve conductivity and charge collection.

In this abstract, we synthesized high-quality copper doped nickel oxide (Cu: NiO) nanoparticle as hole transport layers in inverted perovskite solar cells at room temperature without further processing. In agreement with theoretical calculations predicting that Cu doping results in acceptor energy levels closer to the valence band maximum compared to gap states of nickel vacancies in undoped NiO, an increase in the conductivity in Cu: NiO films compared to
high performance of hybrid perovskite solar cells via organic fullerene doping and interfacial modification

High Performance of Hybrid Perovskite Solar Cells via Organic Fullerene Doping and Interfacial Modification

Yuchen Zhou1, Likun Wang1, Yifan Yin1, Zhenhua Yang1, Chang-Yong Nam2, and Miriam Rafailovich3; 1Stony Brook University, Stony Brook, New York, United States; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

The metal halide perovskite solar cells (PSCs) with remarkable power conversion efficiency (PCE) have been unprecedentedly popular in the research community in past several years. The state-of-art PSCs require a smooth and pinhole-free perovskite layer. It has been proved that key characters of high-quality perovskites can be obtained through optimizing the kinetics of nucleation and growth of perovskite crystals. Despite of several successful practices of modifying the crystal formation process, the lack of precise controls over the structure makes these methods less repeatable. In this study, we utilized a simple but effective doping method by firstly introducing a small amount of insulating polymer of poly (lactic acid) (PLA) into the perovskite layer as a dopant. The benefits of doping PLA polymer comes in 2-folds: 1) the PLA additive can serve as heterogenous nucleus for preferential formation and growth of perovskite crystals. 2) PLA can also introduce PbI2 passivation via the bonding of electron donor-acceptor pairs between C=O and Pbl6− ions. The bonds induced precipitation of PbI2 would preferentially assemble at grain boundaries of perovskites during the process. It is believed that the passivation of PbI2 by PLA at the boundaries can largely reduce the defects and trap states and benefit the overall cell efficiency. Characterizations based on x-rays diffraction and scattering (XRD and GIWAXS), microscopies (scanning electron microscopy and atomic force microscopy) and spectrometers (photoluminescence emission and lifetime decay spectrometer) were carried out to prove the morphology, structure and optical variation of the doped/passivated perovskites. Do so, we were able to confirm the increase of crystal grain size, the presence of PbI2 passivations and the extended carrier lifetime, etc. of our passivated perovskites. Finally, as compared with the original counterparts, the non-encapsulated devices of passivated perovskites were able to maintain 20% power conversion efficiency under the ambient condition, with the best PCE exceeding 18%.

Improving Uniformity and Reproducibility of Hybrid Perovskite Solar Cells via a Low-Temperature, Vacuum Deposition Process for NiOx Hole Transport Layers

Seong Ryal Paek, Segi Byun, Jekyung Kim, Min Kyu Kim, and Byungha Shin; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).  

Recently, the trend in inverted hybrid perovskite solar cells (PVSCs) has been to utilize NiOx as hole transport layers. However, the majority of reported solution-processed NiOx films require a high-temperature thermal annealing process which is unfavorable for large-scale manufacturing and suffers from lack of uniformity. We report, for the first time, e-beam evaporation as a low-temperature, vacuum process for the deposition of NiOx, hole transport layers for PVSCs. Device characterization shows that efficiency is on par with solution-processed methods; the highest efficiency exceeding 15.4% with no obvious hysteresis. Differences are found to be due to the presence of more Ni3+ in e-beam evaporated NiOx which are responsible for a lower transmittance but higher conductivity. Most importantly, e-beam evaporated NiOx-based PVSCs show greater uniformity and reproducibility compared to those of spin-coated NiOx-based PVSCs. Finally, e-beam evaporated NiOx has the additional advantage of being a low-temperature deposition process and being applicable over large areas. This work, therefore, represents a significant step towards large-area PVSCs where e-beam evaporation can be used for the low-temperature, uniform deposition of charge transport layers such as NiOx.
Perovskite solar cells are especially promising when considering the technology lifespan. The advantages of using perovskite for the active layer include but are not limited to broad a light absorption spectrum, tunable band gaps, long charge carrier diffusion, and low fabrication cost. The current project involves the design and simulation of different configurations of Methyl Ammonium Bismuth Iodide active layer based lead-free perovskite solar cell. The goal of the project is to develop a configuration that is non-toxic as well as stable in natural open air environments with a specific resistance to moisture. This design incorporates the use of organic and inorganic materials, as well as the efficient use of the perovskite crystalline structure that is produced by using the properties of Bismuth (III). The project also includes opto-electronic simulations of a variety of different configurations using two software packages. The configurations include perovskite layers using low toxicity alternatives of Pb: Bi and Mn. Different halide species has also been explored to evaluate the impacts on opto-electronics, and photon-to-current conversion efficiencies. The stacking structure is further modulated within the cell by progressively including a recombination-inhibiting thin TiO2 of a ZnO layer with the FTO, followed by an electron-transport layer (various oxides). The aim of these studies is to delineate the sources and quantify the impacts of efficiency-limiting process such as recombination. This work is intended to build up to a broader project of selecting the most optimal low-toxicity perovskite cell to stack onto a Si or FTO bottom cell for tandem configurations.

ET04.06.06


Owing to their remarkable photovoltaic performance, hybrid organic-inorganic perovskite solar cells have attracted tremendous research interest. The high efficiencies are enabled by the outstanding electronic properties of the hybrid perovskite materials. On the other hand, the design of the device structure, including the selection of electron- and hole- transport materials, determines how efficiently the photo-excited charge carriers can be selectively extracted from the perovskite absorber, ultimately influencing the energy conversion efficiency. The use of alternative metal oxide charge-transport layers is a strategy to improving device reliability for large-scale fabrication and long-term applications.

Here we demonstrate solution-processed perovskite solar cells employing nickel oxide hole-extraction layers produced in situ using an atmospheric pressure spatial atomic layer deposition (AP-SALD) system, which is compatible with high-throughput processing of electronic devices from solution. Our sub-nanometer-thick (average roughness < 0.6 nm) oxide films enable efficient collection of holes and the formation of perovskite absorbers with high electronic quality. Highly uniform, sub-nm smooth AP-SALD NiOx films also improve the reproducibility of perovskite optoelectronic devices. Initial solar cell experiments show a power-conversion efficiency of 17%, near-unity ideality factor, and a fill factor of >80% with negligible hysteresis. Transient measurements reveal that a key contributor to this performance is the reduced luminescence quenching trap density in the perovskite/nickel oxide structure. We also present perovskite green light-emitting diodes(LEDs) adopting AP-SALD NiOx with an EQE > 8% and luminance over 10000 cd m-2. Further improvements are possible through the optimization of AP-SALD NiOx growth.

ET04.06.07

Impact of Grain Size on Photovoltaic Performance in Halide Perovskite Solar Cells Ekyu Han1, Dohyung Kim1, Jincheol Kim1 and Jae Sung Yun2 1 School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, New South Wales, Australia; 2 Korea Electronics Technology Institute, Seongnam, Korea (the Republic of); 3 Materials Science and Engineering, University of New South Wales, Kensington, New South Wales, Australia.

The past two years have seen the uniquely rapid emergence of a new class of solar cell based on mixed organic-inorganic halide perovskite. Organic-inorganic hybrid materials have been demonstrated to be excellent photovoltaic materials having a large absorption coefficient, high carrier mobility, high carrier diffusion length, and direct band gap. Conversion efficiencies have increased from 3.8% in 22.7%. Despite a rapid increase in the performance, there are still many unknown fundamental properties that requires further investigation. The perovskite film consists of large amount of grain boundaries due to its polycrystalline nature. There have been contradicting reports on the role of the grain boundaries in photovoltaic performance. Although it is originally known that the grain boundaries limit the effective diffusion length of the solar cells, recent studies performed by Kelvin Probe Force Microscopy showed that the grain boundaries have benign or even beneficial properties. In this work, we measure average grain size of halide perovskite films that has been reported in the literatures and plot with each photovoltaic parameter, i.e, Voc, Jsc, FF, and efficiency. We provide a mathematical model to examine the relevance between grain size and photovoltaic parameter and discuss its influence. Our findings suggest that the size of grain is not a key factor for improving the solar cell performance. Rather, specific chemical species exist at the grain boundaries tunes their properties which could enhance the macroscopic cell performance.

ET04.06.08

A Green Fabrication Route Avoiding the Usage of Toxic Solvents in Perovskite Solar Cells Liming Zhao1,2, Xianyong Zhou1, Deng Wang3, Jian Wen1 and Baomin Xu1 1 Southern University of Science and Technology, Shenzhen, China; 2 University of California Irvine, Irvine, California, United States.

In recent years, organic-inorganic hybrid perovskite solar cells have attracted extensive attention, the photovoltaic conversion efficiency (PCE) of which rose rapidly from 3.8% [1] to 22.7%, due to their impressive PCE, low cost and the ease of making flexible solar cells. However, most perovskite solar cells require the usage of toxic organic solvents during the manufacturing process, such as N,N-Dimethylformamide (DMF) [2]. Dimethyl sulfoxide (DMSO) [3][4] and Chlorobenzene (CB) [2][4], which are prohibited in the commercialized production. Thus, how to avoid using these toxic solvents is a problem that needs to be solved urgently. Aimed at this problem, we developed a novel route to fabricate invert “p-i-n” perovskite solar cells without any toxic solvents. The structure of the perovskite solar cells is FTO/PEDOT.PSS/CH3NH3PbI3/C60/Cs2/Ag. The perovskite layer was synthesized via two-step method by lead acetate trihydrate and methylamine iodine. We found a new eco-friendly solvent, glycerol [5] and 1-butanol component solvent, to dissolve lead acetate trihydrate, and methylamine iodine was dissolved in isopropanol. PEDOT.PSS and Cs2 served as the hole transport layer and electron transport layer, respectively. C60, BCP and Ag electrode were sequentially thermally deposited on the top of solar cells. The J-V test shows that the PCE of the solar cells with 0.1mm2 reaches 4.84%. The XRD indicates that the CH3NH3PbI3synthesized by this route possesses a high purity. The FTIR shows that glycerol and 1-butanol can be removed just at low temperature, 110°C, which means that this method can be applied in flexible devices. The AFM images reveal that both lead acetate and perovskite layers obtained by this route have low roughness. It can be expected that this preparation technique offering a safe and non-toxic environment has a great potential to fabricate perovskite solar cells in the industrial assembly lines, such as roll-to-roll production.

Reference:
Ultrafast Room-Temperature Reactive Ion Etching Process for High-Efficiency Flexible Perovskite Solar Cells

ET04.06.09 Light-Assisted Size- and Dimension-Control of Perovskite Nanocrystals and Their Optoelectronic Devices Qingsong Dong; Jilin University, Changchun, China.

Perovskite Nanocrystal (NCs) offer simply solution synthesis and low-cost film forming process, which take advantages of quantum confinement effect and controlled size distribution, and show higher photoluminescence quantum yield (PL QY) and higher open circuit voltage in photovoltaic devices than perovskite thin film. Here, we developed lead halide perovskite NCs with controllable crystal structures and semiconductor properties by light soaking. The dimension and the size of perovskite NCs correlate with a soaking duration. Light soaking change the crystallization environment, inducing the formation of differently perovskites CsPbBr3, CsPbBr3, or CsPbBr3 assembled in CsPbBr3. Bright perovskite mixture (CsPbBr3@CsPbBr3) with the PL QY reaching 90% were employed for fabrication of light-emitting diodes (LEDs), with the peak external quantum yield of 8% and current efficiency of 20 cd A−1. Since CsPbBr3 is insensitive to the atmosphere, the optical stability of the CsPbBr3 within the CsPbBr3 was greatly improved, and thus the storage and operational stability, the enhanced stability also enable efficient photovoltaic devices with high environment stability.

ET04.06.10 Enhanced Performance and Mechanical Durability of a Flexible Perovskite Solar Cell from the Dry Transfer of PEDOT:PSS with Polymer Nanoparticles Jonghwa Lee1, Jin Hyuck Heo2, Sang Hyuk Im2 and O Ok Park1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Department of Chemical and Biological Engineering, Korea University, Seoul, Korea (the Republic of).

Stamping transfer has been considered as an alternative process because of its various advantages such as a simple, flexible, and repeatable process, which is suitable for large area fabrication. In this research, Inverted-type CH3NH3PbI3 flexible perovskite solar cells with enhanced cell performance and mechanical durability were fabricated by performing a simple dry transfer of a poly(3,4-ethylenedioxyxophirole): poly(styrenesulfonate) (PEDOT:PSS) hole transport layer (HTL) with polystyrene nanoparticles (PS NPs). In order to ensure the stable flexibility of these flexible solar cells, the cross-linked PS NPs synthesized with a size of 70nm were introduced to the PEDOT:PSS HTL. The transfer of the PEDOT:PSS layer with PS NPs onto the polymer electrode (PH1000) was performed completely via stamping transfer with polyurethane acrylate stamp. The power conversion efficiency of flexible perovskite solar cells prepared by the transfer of PEDOT:PSS with PS NPs was 16.8%, which was significantly higher than that of the spin-cast device. The charge transport from the active layer to the PEDOT:PSS HTL was improved by the tuned morphology of the PEDOT:PSS achieved through transfer and the increased surface area of the PEDOT-PSS resulting from the corrugated structure provided by the protruding PS NPs. This in turn resulted in an enhanced short-circuit current density. In addition, the introduced PS NPs significantly improved the mechanical stability of these flexible devices, allowing the devices prepared by the transfer of PEDOT:PSS with PS NPs to tolerate more cycles of strain in the bending test. The introduced PS NPs enhanced the mechanical strength of PEDOT:PSS by acting as not only binders within PEDOT:PSS, but also as interfacial modifiers which can improve the interfacial adhesion between the active layer and PEDOT:PSS HTL. Thus, the transfer of a PEDOT:PSS layer with PS NPs will contribute to the long-term operation of flexible solar devices with enhanced device performance and mechanical durability.

ET04.06.11 Metal Oxides Charge Transport Layers and Interface Tailoring for Highly Stable Perovskite Solar Cells Chao Zhao1, Jia Zhang2, Meng Li3, Adam Pockett1 and Matt Carmie1; 1Swansea University, Swansea, United Kingdom; 2Harbin Institute of Technology, Harbin, China; 3Soochow University, Suzhou, China.

Solvothermal processed hybrid organic–inorganic perovskite solar cells (PSCs) have recently attracted tremendous attention due to their ease of fabrication and excellent photovoltaic performance. However, challenges of long-term working stability under normal conditions of PSCs (i.e., perovskite material and/or the charge transport layers (CTLs)) are still existed. In this work, we achieved reasonable improved PSC stability with good performance by applying an interlayer (ionic-liquid and/or graphene based 2-dimensional (2D) material) as either CTL modifying interlayer. Correlations between performance characteristics of the PSCs and interlayers will be investigated. Performance of PSCs and their relation between carrier dynamics and material properties will be studied based on measurements of current density–voltage, quantum efficiency and transient. The initial study indicated that the interlayers/composite of the interlayer used in the devices will be a promising way to enhance stability and suppress carrier recombination in the whole PSCs, facilitate carrier injection into the carrier transport layers, and maintain a good carrier extraction at the electrodes, thus resulting a good performance.

ET04.06.12 Ultrafast Room-Temperature Reactive Ion Etching Process for High-Efficiency Flexible Perovskite Solar Cells Byoung Jo Kim1, Dong Geon Lee1, Gill Sang Han1, Sangwook Lee2 and Hyun Suk Jung3; 1School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon-Si, Korea (the Republic of); 2School of Materials Science and Engineering, Kyungpook National University, Daegu, Korea (the Republic of).

Perovskite solar cells (PSCs), which have surprisingly emerged in recent years, are now aiming at commercialisation. Rapid, low-temperature, and continuous fabrication processes that can produce high-efficiency PSCs with a reduced fabrication cost and shortened energy payback time are important challenges on the way to commercialisation. Herein, we report a reactive ion etching (RIE) method, which is an ultrafast room-temperature technique, to fabricate mesoporous TiO2 (mp-TiO2) as an electron transport layer for high-efficiency PSCs. Replacing the conventional high-temperature annealing process [A1] by RIE, reduces the total processing time for fabricating 20 PSCs by 40%. Additionally, the RIE-processed mp-TiO2 exhibits enhanced electron extraction, whereupon the optimized RIE-mp-TiO2-based PSC exhibits a power conversion efficiency (PCE) of 19.60% without J-V hysteresis. Finally, a flexible PSC employing the RIE-mp-TiO2 is demonstrated with 17.29% PCE. Considering that the RIE process has been actively used in the semiconductor industry, including for the fabrication of silicon photovoltaic modules, the process developed in this work could be easily applied towards faster, simpler, and cheaper manufacturing of PSC modules.

ET04.06.13 Interface Engineering of Solution Processed Hybrid Organohalide Perovskite Solar Cells Shanshan Zhang; University of Queensland, Brisbane, New South Wales, Australia.

Rapid progress has been achieved in improving the power conversion efficiency (PCE) of organohalide perovskite solar cells (PVSCs), which have now reached 22.1%. Engineering the interlayers between the junction and electrodes has enabled enhancement of charge extraction efficiency and open-circuit
The efficiency of ~10%.

We attribute these results to the oxygen content present in the Nb2O5 films which could have influence on the charge transfer properties. Here, we present coatings that can potentially enhance the efficiency of solar cell devices, increasing the open circuit voltage and photoconversion efficiency. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films.

This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.

Metal-halide perovskite solar cells are considered as one of leading candidates for next-generation photovoltaics, exhibiting the excellent performance over 22% PCE (power conversion efficiency) in spite of its simple and low-cost solution process. Despite their excellence in PCE, the development of large-area coating technology is demanding to replace the spin coating for maximizing the benefits of solution-processed perovskite solar cells. Therefore, it is critical to find out other processes which replace spin coating and enable roll-to-roll (R2R) and continuous processes. Our prior studies presented that the sheet coating process can be an efficient way to produce large-scale perovskite layers and the formation of smooth interface and surface is quite relevant to achieve higher device performance. Anti-solvent treatment is commonly adopted to make smooth perovskite films for the spin-coating process. However, anti-solvent cannot be adopted for R2R processes so that the solution engineering becomes essential to produce high-quality perovskite films. This study presents that the crystallization rate control of perovskite films is a crucial factor to realize the smooth surface film formation. We fabricate perovskite films by controlling the ratio of additives and substrate temperature, and then confirm the film roughness and existence of additive particles in the grain. The Solution engineering can control the perovskite crystallization kinetics. The effects of additives and the composition of precursor solution on crystallization kinetics during sheet coating will be presented.
Potassium niobate (KNbO₃) is known to be an important eco-friendly lead-free ferroelectric material that possess excellent physical properties such as large electro-optical coefficients, electromechanical coupling constant, and nonlinear optical coefficients for several photonic device and electronic applications. The physical properties of KNbO₃ can be modified by substituting isovalent or heterovalent cations into K and/or Nb sites. Herein, we present systematic investigations carried out on structural, optical, dielectric, charge transport and ferroelectric properties of a solid solution [KNbO₃]ₓ[BaNi₁/₂Nb₁/₂O₃₋ₓ]. The electro-ceramics were prepared by standard solid-state reaction method using K₂CO₃ (99.9%), BaCO₃ (99.95%), Nb₂O₅ (99.9%), and NiO (99.9%) as starting reagents. Formation of ferroelectric-ferroelectric (FE-FE) phase of the as-synthesized sample was confirmed using x-ray diffractometry. Temperature dependent Raman spectra measured from liquid nitrogen temperature to 800 K and analyzed using damped harmonic oscillator model; provides valuable information about phonon behaviors and suggests absence of any structural phase transition. A direct optical band gap E_g of 3.16 eV was estimated from Kubelka-Munk analyses of the diffuse reflectance spectra. Investigations on dielectric behaviors on a metal-KBNNO ferroelectric-metal capacitor in the T range 80–500 K with the frequencies range 10⁻¹⁰–10² Hz suggests a broad peak with discernible dispersive features with frequencies indicating its relaxor-like behavior. A slim P-E loop measured up to 1800 V corroborates its relaxor behaviors. The frequency dependence of ac conductivity showed typical features of universal dynamic response and satisfy the known power law, \( \sigma (\omega) \propto \omega^\alpha \). The \( I-V \) characteristic curves measured in between ±600 V at several temperatures (100-500 K) suggest a typical Schottky-type (diode) behavior. The vibrating sample magnetometer results at room temperature show a linear magnetization curve with negative slope suggesting its diamagnetic behavior. Our experimental results establish the fundamental physics and materials science of the KBNNO compound and its potential for ferroelectric device applications.

ET04.06.19
Spatially-Resolved Ion Migration in Mixed Cation Lead Hybrid Perovskite

This study is spatially-resolved emission measurements, we directly monitor cation migration in triple cation (FA, MA and Cs) lead hybrid perovskite. We show, that under applied voltage cations segregates and form single cation perovskite phases. This leads to degradation and decreasing of photovoltaic performance of solar cells devices. Next, by tuning the composition of cations we show improved stability against cation migration in perovskite solar cell devices.

ET04.06.20
Ultra-High Vacuum Investigations of Methylammonium Lead Tribromide Single Crystals Perovskites—Sample Stability and Photo-Carrier Recombination

Methylammonium lead tribromide (CH₃NH₃PbBr₃) single crystals are studied under Ultra High Vacuum (UHV) by non-contact Atomic Force Microscopy (nc-AFM) and Kelvin Probe Force Microscopy (KPFM). [1, 2] We demonstrate that when exposed to ambient atmosphere, the sample exhibit important surface degradations. Even when sample is cleaved in air and exposed shortly (around few minutes) to ambient conditions, it reveals surface nanometric droplets (<100 nm). We demonstrate that such surface modifications can be avoided by UHV sample cleavage. The sample prepared and analyzed under UHV does not exhibit surface modifications even under illumination with laser power of few tens of mW per mm².

Furthermore, we perform time-resolved measurement by KPFM on this UHV-cleaved sample. While most of the experimental approaches developed so far consist in studying recollection by techniques such as: transient photovoltage or charge extraction, these techniques average sample properties over macroscopic scales, making them unsuitable for directly assessing the impact of local heterogeneity on the recombination process. Recently, we showed that it is possible to measure the photo carrier lifetime with nanometric spatial resolution by photo-modulated techniques based on KPFM over organic and inorganic solar cells. [3, 4, 5] We will present the principle of this original method based on the nanometrically resolved measurement of the surface potential by KPFM under a modulated illumination. Finally, we apply this protocol to measure nanometric resolved images of photo-carrier dynamics on CH₃NH₃PbBr₃. During this talk, we will show results of lifetime mapping as a function of laser power.

This work was supported by the French “Recherche Technologique de Base” Program.

1. S. Pouch et al. RSC Advances 6, 6782 (2016).

ET04.06.21
Investigating the Effects of Functionalized Benzylphosphonic Acid SAMs on Triple Cation Lead Halide Perovskite Based Solar Cells

The modification of interfaces with self-assembled monolayers (SAMs) are an interesting approach for enhancing the performance of perovskite solar cells. [1, 2, 3] Recently, Wang et al. outlined the importance of the dipole moment by modifying nickel oxide (NiOₓ) hole transport layers in perovskite solar cells with differently functionalized benzoic acid SAMs. [4] In this work, we investigate the influence of para-functionalized benzylphosphonic acid (R-BPA) SAMs on CsxFA/MA based triple cation perovskite solar cells prepared in inverted architecture using NiOₓ as hole and PC60BM as electron transport layer. The phosphonic acid groups act as an anchor to the NiOₓ hole transport layer and besides the dipole moment of the molecules, the functional groups (we investigated: -Br, -F, -NH₂, -NO₂ and -OCH₃) can also act like a seed layer influencing the perovskite crystallization. The presence of R-BPA SAMs on the NiOₓ films was confirmed by contact angle measurements and X-ray photoelectron spectroscopy (XPS). Further, the influence of the SAM modifications on the perovskite layer modification was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. The SAM images reveal smaller grain sizes and narrower grain size distributions for (4-nitrobenzyl) phosphonic acid and (4-methoxybenzyl) phosphonic acid based solar cells compared to the reference (without SAM modification) and other R-BPA SAM based solar cells. The introduction of (4-bromobenzenyl) phosphonic acid led to solar cells with an improved power conversion efficiency of 16.5% (reference 12.3%). Similarly, (4-fluorobenzenyl) phosphonic acid SAM based solar cells exhibited an improved open circuit voltage (V_OC) of 1.087 V (reference 0.977 V). On the contrary, a reduction of the V_OC was observed for solar cells modified with a (4-aminobenzyl) phosphonic acid SAM.


SESSION ET04.07: Interfaces II
Session Chairs: Henk Bolink and Laura Herz
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room Ballroom C

8:00 AM *ET04.07.01
Radiative and Non-Radiative Excited State Decay in Lead Halide Perovskites Richard H. Friend; University of Cambridge, Cambridge, United Kingdom.

Lead halide perovskite materials can show very high internal luminescence efficiencies, and this has enabled the fabrication of LEDs with high external quantum efficiencies, approaching 20%. High luminescence yield is also critical for efficient solar cell operation. I will discuss recent approaches to eliminate non-radiative decay channels within the bulk and at also at charge injection/extraction interfaces. I will also discuss how recycling of internally-generated photons, both within LEDs and also in solar cells, affects device performance and design.

8:30 AM *ET04.07.02
Long-Range Hot Carrier Transport in Hybrid Perovskites Visualized by Ultrafast Microscopy Libai Huang; Purdue University, West Lafayette, Indiana, United States.

The Shockley-Queisser limit for solar cell efficiency of ~ 33% can be overcome if hot carriers can be harvested before they thermalize. Recently, carrier cooling time up to 100 picoseconds was observed in hybrid organic-inorganic lead halide perovskites, but it is unclear whether these long-lived hot carriers can migrate long distance for efficient collection. Here we report direct visualization of hot carrier migration in CH3NH3PbI3 thin films by ultrafast transient absorption microscopy, demonstrating three distinct transport regimes. Quasi-ballistic transport was observed to correlate with excess kinetic energy, resulting in up to 230 nanometers transport distance in 300 fs that could overcome grain boundaries. The nonequilibrium transport persisted over tens of picoseconds and ~ 600 nanometers before reaching the diffusive transport limit. These results suggest potential applications of hot carrier devices based on hybrid perovskites.

9:00 AM ET04.07.03
Perovskite—A Wonder Material for High Efficiency Solar Cells and Optoelectronic Applications Shengzhong Liu1,2; 1Dalian Institute of Chemical Physics, Dalian, China; 2Shaanxi Normal University, Xi'an, China.

The organic lead halide perovskites have been demonstrated as a group of wonder materials for their excellent optical absorption, long range charge-carrier diffusion and apparent tolerance to defects. In just a few years, the efficiency of these perovskite solar cells has been improved from 3.8% to 23%. We have developed a few dry deposition processes without using any solvent to fabricate high efficiency perovskite solar cells with high stability. The new deposition processes allow us to relax the strict deposition monitoring and control measures, while realizing superior uniformity in film morphology, surface coverage and smoothness, together with crystalline phase purity, leading to high efficiency solar cells. Our current status for the rigid thin film cell efficiency is over 21.5% (Newport certified) and that for the flexible device over 18.3%, both are the highest for their respective categories. Meanwhile, the devices show very good stability over long term exposure in ambient with very low degradation. After a representative cell was exposed in ambient lab condition for more than two years, its final cell efficiency is as high as ~90% of its initial efficiency with its degradation accounts for only ~10%. Further analysis on the stability of the perovskite solar cells will be discussed. We have also developed a series of single-crystalline perovskites with superior stability and optoelectronic performance.

9:15 AM ET04.07.04
One Step High-Throughput Deposition for Flexible Perovskite Solar Cells Tae-Youl Yang1, Young Yun Kim1, Rikka Suhonen2 and Jangwon Seo1; 1Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2VTT, Oulu, Finland.

Despite a high efficiency in the perovskite solar cells (PSCs) of over 22%, the large-area fabrication of PSCs is another issue that is receiving growing attention. The large-area PSCs requires more reliability than lab-scale devices for precisely controlling the crystallization behavior of perovskites. In order to transfer these technologies from laboratory scale to industrial-scale, large-area PSC manufacturing using scalable coating and printing processes have been evolved. The key advantage of printing in comparison to coating is the possibility of direct patterning on substrates. Printing provides a large degree of freedom for module design in arbitrary shapes and sizes.

In this presentation, we demonstrate one step fabrication of perovskite film via gravure printing. SnO2 nanoparticles layer as an electron transport layer, CH3NH3PbI3 as a photoactive layer, and Spiro-OMeTAD as a hole transport layer were sequentially printed on ITO-PET substrate. We optimized properties of each solution and drying process conditions to deposit uniform films. The resulting devices showed the power conversion efficiency of up to 15 %, which is significantly higher than most conventional perovskite solar cells. This study illuminates the possibility of the fabrication of high-performed PSCs using gravure printing which is a high throughput production technologies that enables more cost-effective industrial production.

9:30 AM ET04.07.05
Effective Passivation of Perovskite Film for Highly Efficient and Stable Solar Cell Using Adamantanes Mohammad Mahdi Tavakoli1,2; 1Materials Science and Engineering, Sharif University of Technology, Tehran, Iran (the Islamic Republic of); 2Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Passivation of electronic defects is an effective strategy to boost the performance and operational stability of perovskite solar cells (PSCs). Identifying molecular materials that achieve this purpose is a key target of current research efforts. Here, adamantane (AD) and adamantylamine (ADA) are introduced...
as molecular modulators to abate electronic defects present within the bulk and at the perovskite–hole conductor interface. To this effect, the modulator is added either into the antisolvent (AS) to precipitate it together with the perovskite (AS method) or they are spin coated (SC) onto its surface (SC method). Time resolved photoluminescence measurements show substantially longer lifetimes for perovskite films treated with AD and ADA compared to the reference sample. In line with this observation, it is found that the presence of AD and ADA molecules at the interface between the perovskite film and the hole conductor increases all photovoltaic metrics, in particular the open circuit photovoltage ($V_{oc}$) as well as the operational stability of the PSC.

9:45 AM BREAK

10:15 AM ET04.07.06
Synthesis and Ionic Conductivity Measurements of Highly Efficient Perovskites from Blade Coated and Non-Toxic Solvents Antonio Guerrero;
Institute of Advanced Materials (INAM), Castellón de la Plana, Spain.

Understanding crystallization of lead halide perovskites by industrially relevant techniques is a topic that needs development as large area crystallization processes lead to inhomogeneous films, extremely large perovskite thickness or presence of pinholes. In this work, we show that efficient one-step perovskite solar cells can be obtained by doctor blade by controlling the coordination chemistry with non-toxic solvents via Spherulitic growth mechanism. This method results in highly crystalline perovskite films with preferential crystal orientation and spherulitic growth. Optical and electrical measurements indicates that generated chemical defects are confined at the boundary of spherulites and these do not have a negative effect on the extracted photocurrent. Strikingly, spherulitic formation leads to better photovoltaic performance in hybrid perovskite films with record efficiencies of 18.0% for MAPbI₃, for doctor bladed processing using one-step and non-toxic solvents. Alternatively, ionic conductivity plays a key role in perovskites during photovoltaic device operation and degradation. In this presentation it is also described how to characterize the ionic properties of lead halide perovskites by electrical (impedance spectroscopy) and optical techniques (PL confocal microscopy). Approaches to minimize the electronic contribution to the measured current are used so the ionic current can be probed.

References

10:45 AM ET04.07.07
Interfacial Modification for Highly Stable and Efficient SnO₂ Based Planar Perovskite Solar Cells Kyoungwoon Choi, Hong Il Kim, Minjun Kim, Hyuntae Choo and Talho Park; POSTECH, Pohang, Korea (the Republic of).

We report a facile and effective interface modification for highly stable and efficient planar perovskite solar cells (P-PSCs) by employing a zwitterion-modified SnO₂ electron transport layer (ETL). A 3-(1-pyridinio)-1-propanesulfonate is used to modify the SnO₂/perovskite interface. The zwitterion plays a few important roles in P-PSCs: (1) Shifting the work function of the SnO₂ to a more suitable energy level for charge extraction. (2) Pulling electrons from perovskite toward the ETL/perovskite interface. (3) Suppressing backward transport of electrons from SnO₂ to the perovskite layers. (4) Passivating halide-induced deep traps and improving thermal stability of devices. With these desirable properties, the efficiency of devices and thermal stability increase remarkably. Therefore, P-PSCs with the modified SnO₂ ETL showed reduced hysteresis owing to effective electron extraction and reduced recombination. The best device achieved a power conversion efficiency (PCE) of 21.43% in reverse scans. Accordingly, newly developed interface engineering is a promising method for fabricating efficient and hysteresis-less P-PSCs with high thermal stability.

11:00 AM ET04.07.08
Crystalline Metal Oxide Contact Layers in Organic and Hybrid Photovoltaics Mehraad Ahmadpour1, André Cauduro2, Mina Mirsafaei1, John Lundsgaard Hansen1, Brian Julsgaard2, Horst-Günter Rubahn3, Peter Balling1, Nadine Witkowski4, Andreas K. Schmid2 and Morten Madsen1; 1Mads Clausen Institute, SDU NanoSYD, University of Southern Denmark, Sonderborg, Denmark; 2The Molecular Foundry, LBNL Berkeley, National Center for Electron Microscopy, Berkeley, California, United States; 3Department of Physics and Astronomy and iNano, Aarhus University, Aarhus, Denmark; 4Institut des Nanosciences de Paris (INSP), Sorbonne Universités, UPMC Univ Paris 06, Paris, France.

Thin metal oxide films have attracted a lot of attention in the past years due to their unique ability to act as electrode contact layers in novel electronic and optoelectronic devices. Prominent examples are molybdenum oxide (MoO₃) and titanium oxide (TiO₂) thin films used as hole and electrode contact layers, respectively, in organic and hybrid photovoltaics. Amongst many different methods used for fabrication of these films, reactive sputtering remains as a promising technique, due to the unique composition tuning and industrial scale processing possibilities. In the work presented here, crystalline MoO₃ and TiO₂ layers are developed from reactive sputtering and vacuum annealing, and implemented as contact layers in organic and hybrid solar cells.

The film composition is characterized using X-Ray Photoelectron Spectroscopy (XPS), work function using Low Energy Electron Microscopy (LEEM) and Ultraviolet Photoelectron Spectroscopy (UPS), structure using Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD), morphology using Atomic Force Microscopy (AFM) and optical properties using UV-VIS spectroscopy. Importantly, we find that both the structure and work function of the developed thin films can be tuned by the annealing process, spanning an almost 2eV tuning range in the case of MoO₂. Furthermore, due to the formation of the crystalline films with a low defect density, made possible via the reactive sputtering method, more efficient and stable contact layers for photovoltaic devices are developed. Non-encapsulated DBP/C₆₀ solar cell devices based on the sputtered MoO₃ are demonstrated to remain with impressive 80% of the initial performance after 240 hours of light soaking under 1 sun (1000W/m²) at ~60°C, which is superior to similar devices based on conventional thermally evaporated MoO₃ layers. Fabricated PTB7/PCBM solar cells devices based on the sputtered TiO₂ are demonstrated to lead to shape-free high performing devices, otherwise typically appearing when employing TiO₂ as contact layers. Integration of the crystalline metal-oxide interlayers in perovskite solar cells is furthermore investigated and discussed. The underlying film properties leading to these appealing device properties are evaluated based on the extensive surface and film characterization performed.

The work thus demonstrates a viable method for tuning the electronic and optoelectronic properties of metal oxide thin films, which can be applied in combination with a wide range of materials in e.g. organic and hybrid photovoltaics.

Organic-inorganic metal halide perovskites have gained considerable attention for next-generation photovoltaic cells due to rapid improvement in power conversion efficiencies. Even though there have been immense efforts towards fabricating high performance solar cells, fundamental understanding of underlying mechanisms related to light and bias induced effects at the nanoscale is still required. In this study, structural variations of the perovskites induced by light and bias are systematically investigated using scanning probe microscopy techniques. We show that periodically striped ferroelastic domains, spacing between 40 nm to 350 nm, exist within grains and can be modulated significantly under illumination as well as by electric bias. Williamson-Hall analysis of X-ray diffraction results shows that strain disorder is induced by these applied external stimuli. We show evidence that the structural emergence of domains can provide transfer pathways for holes to a hole transport layer (HTM) with positive bias, whereas negative bias attracts organic cations to the surface, which can induce structural damage to the perovskite-HTM interface. Our findings point to potential origins of I-V hysteresis in halide perovskite solar cells and provide fresh microscopic insight into external stimuli-induced structural disorder governing the superior performance of the metal halide perovskites solar cells.

11:30 AM ET04.07.10
Hydrophobic Self-Assembling Monolayers for Stable Perovskite Solar Cells Laura Cani1 and Antonio Abate; Helmholtz Zentrum Berlin, Berlin, Germany.

With a power conversion efficiency over 22%, perovskite solar cells (PSCs) are considered a rising star in the solar energy field. Nevertheless, the device long-term stability under working condition remains a big challenge. In particular, most of the halide perovskite compositions are highly sensitive to moisture. Indeed, the initial device performances degrade abruptly in only a few days of air exposure.

Our strategy to enhance the moisture stability of PSCs is to functionalize the interface between the perovskite and the charge selective contacts within the device. We make use of specific molecule-to-substrate interaction to self-assembly perfluorinated small molecules on the perovskite surface. The formation of a nanometer thick perfluorinated layer results in hydrophobicity and potentially in super-hydrophobicity of the perovskite surface, which prevents the ingress of water from the atmosphere. Notably, such a functionalization can be done through scalable solution processing methods, which are compatible with fast output production including roll-to-roll and inject printing. We investigate the impact of the functionalization on material and device stability, providing data from lab-scale devices aged in real working conditions – under light and voltage load. Our results show that the interface functionalization with perfluorinated molecules is an effective new approach to enhance PSCs lifetime.

11:45 AM ET04.07.11
Hole Transport Bilayer for Improved Photocurrent and Stability in Perovskite Solar Cells for 2-Terminal Tandems James A. Raiford1, Rebecca A. Belisle2, Kevin A. Bush2, Axel F. Palmstrom2,3, Rohit Prasanna2, Michael D. McGehee2,4 and Stacey F. Bent1; 1Chemical Engineering, Stanford University, Stanford, California, United States; 2Materials Science & Engineering, Stanford University, Stanford, California, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Perovskite solar cells used in tandem with existing silicon cell technology is a promising pathway towards achieving next-generation, high efficiency devices at a lower cost. To date, the highest efficiency monolithic perovskite/silicon tandem are fabricated in the inverted p-i-n architecture, despite the fact that the best single-junction devices have been reported in the standard n-i-p orientation. The primary source of performance loss in the standard architecture, 2-terminal tandem is optical losses associated with replacing an opaque contact with a transparent one. Common hole transport and window layers like doped spiro-OMeTAD and molybdenum oxide, respectively, parasitically absorb significant amounts of light before it can reach the perovskite and be converted to useful photocurrent. Additionally, these hole contact layers have been shown to be sources of chemical instability, leading to long-term degradation of device performance. In this work, we present an alternative hole contact bilayer, consisting of a thin, undoped organic small molecule and an air-stable vanadium oxide (VOx) buffer layer deposited via atomic layer deposition (ALD). This novel bilayer allows for the subsequent sputtering of a transparent indium tin oxide top electrode. Its minimal absorption in the ultra-violet and visible regions of the solar spectrum result in the fabrication of a semi-transparent perovskite cell with 2.3 mA/cm² more photocurrent than its spiro-OMeTAD counterpart without a loss in cell voltage. Our design also leverages the conformal, compact nature of the ALD buffer layer to help slow the thermal degradation of mixed cation, mixed halide perovskite films. Unlike molybdenum oxide, we show that our VOx ALD buffer layer is inert to the perovskite material by demonstrating stable device performance after 1000 hours of thermal aging at 85°C in an inert N₂ atmosphere. Lastly, we will discuss the implications of this work as they relate to the fabrication of more efficient 2-terminal perovskite/silicon tandems.

SESSION ET04.08: Stability and Testing
Session Chair: Michael McGehee
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room Ballroom C

1:45 PM ET04.08.01
Firing up Perovskite Solar Modules Bert Conings, Aslıhan Babayigit and Hans-Gerd Boyen; Materials Research Institute, Hasselt University, Diepenbeek, Belgium.

All metal halide perovskite solar cells with decent efficiencies so far contain lead (Pb). Since the rapidly evolving perovskite photovoltaic technology is on the cusp of commercialization, the existence and gravity of hazardous components as a consequence of its Pb content is a growing point of debate. Probably the most likely scenario for an uncontrolled exposure to the enclosed Pb-containing chemicals and related reaction products — that can fuel this debate— is that where perovskite PV installations in structure fires, the latter statistically representing a significant risk. To shed light on the potential impact of such an event, a careful assessment of the fire safety of perovskite-containing PV mini-modules is presented. A balanced discussion is provided comparing the hazard originating from an encapsulation failure of a perovskite-based rooftop installation (worst case scenario) and that associated with the burning of common materials found in buildings. In addition, a rough atmospheric dispersion model is used to estimate the heavy metal concentrations downwind of a typical structure fire.
Hybrid organic-inorganic lead halide perovskite solar cells have surpassed other commercialized thin-film solar cell technologies in record efficiency, but they have yet to demonstrate excellent stability that precludes commercialization. While moisture exposure can be mitigated through careful encapsulation, the thermal stability of the cell is intrinsic to operation and must be improved.

We show that thermal stability of semitransparent perovskite solar cells in the inverted (p-i-n) architecture (ITO/NiOx/FA0.83Cs0.17Pb(I0.83Br0.17)3/evaporated Cs60/SnO2/TTO(metal)) at 85°C in a nitrogen environment is limited by reaction with metal contacts, regardless of whether Ag, Cu, or Au is used. We found similar results with MAPbI3 and FA0.83Cs0.17Pb(I0.83Br0.17)3 devices. We used x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) depth profiling to show that Ag not only creates a driving force for iodine migration from the perovskite, but also surprisingly has the potential to diffuse through a sputtered tin-doped indium oxide (ITO) window layer, an atomic layer deposited (ALD) tin oxide layer, and an evaporated fullerene electron transport layer into the perovskite, harming the performance of the perovskite solar cell.

We found using scanning electron microscopy (SEM) that the poor barrier quality of the transparent conducting oxide (TCO) is due largely to diffusion channels created by a proliferation of the existing rough perovskite morphology. This also occurs when the crystalline ITO is replaced with amorphous indium zinc oxide (IZO).

We found that the key to creating a good barrier layer to prevent metal degradation and escape of volatile halide species is by (1) adding a planarizing layer (such as a conformal layer of indium tin oxide or ZnO) and (2) including a thin planarizing layer of indium zinc oxide (IZO) between the TCO and the perovskite.

The stability of perovskite solar cells is considered poor compared to other solar cells. One reason for this is thought to be the volatile organic methylammonium (MA) cation. At the same time, small amounts of MA are used for practically all highest performing solar cells with efficiencies beyond 20%. These compositions have also shown some of the best reported stabilities indicating that MA might not be as unstable as previously assumed. This raises the question of whether excluding MA for the sake of stability has been concluded prematurely. Interestingly, MA instability was mainly concluded from thin film studies that differ strongly from full devices. Therefore, the degradation behaviour on complete MA containing devices is crucial to quantify the long-term stability of MA. Only then, it is possible to determine at which timescales MA is unstable and if it must be categorically excluded from future compositions. Without such assessment, valuable time may be lost due to false prioritisation that is not justified by actual data. Here, we use weakest link devices, i.e. MAPbI3, to study the stability under light and different temperatures.

Organic Gelators as Growth Control Agents for Stable and Reproducible Hybrid Perovskite-Based Solar Cells

Natalie Stingelin; Georgia Institute of Technology, Atlanta, Georgia, United States.

Low-molecular-weight organic gelators are widely used to influence the solidification of polymers, with applications ranging from packaging items, food containers to organic electronic devices, including organic photovoltaics. Here, I discuss how this concept can be extended to hybrid halide perovskite-based materials. In situ time-resolved grazing incidence wide-angle X-ray scattering measurements performed during spin coating reveal that organic gelators beneficially influence the nucleation and growth of the perovskite precursor phase. This can be exploited for the fabrication of planar n-i-p heterojunction devices with MAPbI3 (MA = CH3NH3+) that display a performance that not only is enhanced by ~25% compared to solar cells where the active layer is produced without the use of a gelator but that also features a higher stability to moisture and a reduced hysteresis. Most importantly, the presented approach is straightforward and simple, and it provides a general method to render the film formation of hybrid perovskite more reliable and robust, analogous to the control that is afforded by these additives in the processing of commodity “plastics.”

Efficient and Stable of Inorganic Perovskite Solar Cells

Jingbi You; Chinese Academy of Sciences, Beijing, China.

Inorganic halide perovskites such as cesium lead halide have attracted great attentions due to their excellent thermal stability. Cesium lead iodide (CsPbI3) has a bandgap of 1.73 eV and is very suitable for making efficient tandem solar cells, either with low bandgap perovskite or silicon. However, the phase instability is hindering the further optimization of the device performance. Here, we show that high quality and stable black-phase CsPbI3 film is obtained via solvent-controlled growth of the precursor film in dry environment. A 15.7% power conversion efficiency of CsPbI3 solar cells is achieved, which is the highest efficiency reported so far for inorganic perovskite solar cells. And more importantly, the devices can tolerate continuous light soaking for more than 500 hours without efficiency drop. Recently, we have pushed the efficiency of inorganic perovskite solar cells to 17%.

References


Enhanced Photovoltaic Performance and Stability of Tin-Based Perovskites by Forming 3D Hollow Structure with Diamonium Dichloride

Weijun Ke, Constantinos Stoumpos, Ioannis Spanopoulos, Lingling Mao, Oleg Kondetski, Michelle Chen, Michael R. Wasielewski and Mercouri G. Kanatzidis; Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

The stability of perovskite solar cells is considered poor compared to other solar cells. One reason for this is thought to be the volatile organic methylammonium (MA) cation. At the same time, small amounts of MA are used for practically all highest performing solar cells with efficiencies beyond 20%. These compositions have also shown some of the best reported stabilities indicating that MA might not be as unstable as previously assumed. This raises the question of whether excluding MA for the sake of stability has been concluded prematurely. Interestingly, MA instability was mainly concluded from thin film studies that differ strongly from full devices. Therefore, the degradation behaviour on complete MA containing devices is crucial to quantify the long-term stability of MA. Only then, it is possible to determine at which timescales MA is unstable and if it must be categorically excluded from future compositions. Without such assessment, valuable time may be lost due to false prioritisation that is not justified by actual data. Here, we use weakest link devices, i.e. MAPbI3, to study the stability under light and different temperatures.
The power conversion efficiency of perovskite solar cells has increased from 3.8 to above 22% within a few years.[1] Currently, the highest-efficiency perovskite solar cells are made on lead-based light absorbers; however, the toxicity of lead constitutes a serious issue which hinders the commercialization attempts of the perovskite solar cells technology. It is therefore imperative to reduce or altogether eliminate Pb from these devices and replace them with other less toxic elements. Sn is an especially attractive candidate because its perovskite analogs have similar or even superior optical and electronic characteristics compared to those of Pb. However, the efficiency of the Sn-based perovskite solar cells is low and the stability of Sn-based perovskite solar cells is usually very poor in air. In this work, we demonstrate a new type of tin-based perovskite absorber that incorporates both ethylenediammonium (en) and formamidinium (FA)/methylammonium (MA) forming new materials of the type [en]FASnI3/[en]MASnI3.[2,3] We show that the use of Sn can serve as a new A dication capable of achieving dramatic increases in bandgap without the need of solid solutions. The en introduces a new bandgap tuning mechanism that arises from massive Schottky style defects. Our best-performing [en]FASnI3 and [en]MASnI3 solar cells have the highest efficiency of 7.23% and 6.65%, respectively. Most importantly, the stability of tin-based perovskite solar cells is significantly enhanced by the incorporation of en dication in the structure. Recently, we also found two other new diaminonium cations of propylenediammonium (PN) and trimethylenediammonium (TN) which have slightly larger size but can still be incorporated into 3D FASnI3 structure. A similar efficiency enhancement was also observed for the {PN}FASnI3 and {TN}FASnI3 solar cells. Our results suggest that developing tin-based perovskites with suitable diaminonium cations such as en, TN, and PN in their structure is a new promising approach for fabricating high-performance tin-based perovskite solar cells.

References

4:30 PM ET 04.08.07
Outdoor Analysis of the Active Layer Temperature in Perovskite Photovoltaic Modules Robert Gehlhaar, Tamara Merckx and Weiming Qiu; imec, Leuven, Belgium.

Perovskite solar cells have seen an enormous improvement in the relevant photovoltaic parameters of power conversion efficiency and device lifetime. Within less than a decade of development, efficiencies exceeded 22% and lifetimes increased from a couple of seconds to more than 10000 hours. A various number of device configurations is showing the potential to improve the performance to industrial relevant levels. Leaving the level of research from lab environment, the temperature of a perovskite solar cell can have a serious effect on the performance. The power conversion efficiency as well as the stability can be drastically influenced and reduced by increasing the device temperature.

We report on the temperature of perovskite modules under outdoor conditions and the modeling of the temperature fluctuations in dependence in the influential parameters. The report provides insights into the exact temperature evolution of the photoactive layer over a wide range of solar irradiance and various ambient temperatures. The provided model allows for an accurate prediction of the module temperature beyond the measured range of the parameters.

The evolution of the device temperature of a perovskite module of 225 cm² area has been recorded during a period of 25 days under central European conditions. The temperature of the glass–glass packaged perovskite solar module was directly measured at the back contact by a thermocouple. The device was exposed to ambient temperatures from 3 °C to 34 °C up to solar irradiation levels of 1300 W m⁻² resulting in a maximum module temperature of 61 °C. Under strong fluctuations of the global solar irradiance, temperature gradients of more than 3 K min⁻¹ with total changes of more than 20 K are measured. Based on the experimental data, a dynamic iterative model is presented for the module temperature evolution in dependence on ambient temperature and solar irradiation. Furthermore, specific thermal device properties that enable an extrapolation of the module response beyond the measured parameter space can be determined.

The presented set of data and analysis gives an insight in the expected device temperature in real world applications. This knowledge is essential to design future experiments to bring the perovskite PV technology to the next level. The analysis of temperature coefficients for power conversion efficiency, stability and hysteresis are going to be benefited from the provided measurements and model of the exact layer temperature.

4:45 PM ET 04.08.08
Stability Studies of Perovskite PV Devices Using Natural and Concentrated Sunlight Iris Visoly-Fisher1, Eugene A. Kat1, Mark V. Khemkin1, K.M. Anoop1, Yulia Galagan2, Francesco Di Giacomo3, Morten Madsen1, Bhushan R. Patil4, Golnaz Sherafatipour5 and Vida Turkovic6; 1Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion, Israel; 2Holst Centre – Solliance, Eindhoven, Netherlands; 3SDU NanoSYD, Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark.

Standard, outdoor operation under natural sunlight includes diurnal light/ dark cycling. Both reversible improvement and reversible degradation of perovskite solar cell efficiency were observed under illumination-darkness cycling.[1] Quantifying the performance and stability of cells exhibiting significant diurnal performance variation is challenging, and we suggest that its figures of merit should be reconsidered.[2]

Concentrated sunlight allows accelerated stability studies and separating the effect of light on material and cell stability from other factors. We recently demonstrated an experimental methodology with independent control of sunlight intensity, the sample temperature, bias and environment during the exposure. Studies of perovskite devices as a function of sunlight concentration were aimed at determining which degradation factors are more dominant: light and spectrum, bias or their combination? Preliminary results of studies of ITO/SnO2/Cs0.07(FA0.83(NH3)3)0.83Pb0.78Sn0.22I3/Spiro-OMeTAD/Au cells show a monotonic dependence of the PCE degradation kinetics on sunlight concentration, as expected. This dependence on intensity was significantly stronger than the degradation dependence on the illumination dose (in sun*hours).[3] Significant effect of UV- and IR- filtering on the cell's degradation rate was also noted. Possible underlying degradation mechanisms will be discussed.

In the last few years a new type of solar cell, the lead-halide perovskite solar cell, CH₃NH₃PbI₃, has gained interest in photovoltaic community due to its high efficiency and low cost compared with the well-known silicon solar cells. In spite of incredible efficiencies as high as 22.1% that it have presented, it faces a problem concerning the commercial use due to its lead content and poor stability. In this way, new lead-free materials have been studied in the last few years. One of it is the lead - free perovskite-like material (CH₃NH₃)ₓBiₓBrₙ₋₅ that can act as the absorption material in solar cells and has a better stability than CH₃NH₃PbI₃ [1]. In spite of the good stability, the efficiencies this type of solar cell has achieved are still very low. In this work we combined this two semiconductors, CH₃NH₃PbI₃ and (CH₃NH₃)ₓBiₓBrₙ₋₅, by the addition of small amounts (1% to 25%) of Bi in the lead-perovskite in order to observe if this would affect the stability of the final perovskite, inspired in a similar study where one has inserted tin in CH₃NH₃PbI₃ [2]. The films were made by one-step, mixing suitable amounts of PbI₂, MAI (methylammonium iodide) and BiI₃ in dimethylformamide. The films were obtained by spin coating this solution in glass substrates. After deposition we monitored the degradation of the films exposed to light and humidity for 16 days through X-ray Diffraction and Ultraviolet-Visible Spectroscopy measurements as well as photographs of the films. The last ones indicate that the lead-perovskite (dark gray) degrades to PbI₂ (yellow) faster than the ones where small amounts of Bi were inserted, indicating that the material stability was increased through the bismuth-doping. X-ray diffraction measurements of as-deposited films indicate that the crystal structure of all films, including the Bi-doped ones, have the crystal structure of lead-perovskite. The results indicate that with the implantation of small amounts of Bi (~25%) does not affect the crystal structure of the lead-perovskite and increases the stability of the material.

Acknowledgements: CNPq, Capes, Fapesp, Lamult Unicamp.

References:
Perovskite solar cells are an important photovoltaic technology with high efficiencies exceeding 20% due to their optimal band gap, large absorption coefficient, and high charge mobilities. One of these challenges is the understanding and control of their defect structures because perovskite compounds are relatively soft ionic crystals and ions are migrating in the crystals relatively low activation energy. In this study, we have investigated the effect of low energy ion irradiations to both all inorganic and organic-inorganic lead halide perovskite films on the structure, morphology optical and electronic properties systematically. Several kinds of halogen ion beam irradiations on the perovskite thin film was performed by using a tandem type ion accelerator with changing acceleration voltages and irradiation time. Incorporation of ions in perovskite crystals by irradiations were confirmed under several conditions. Detailed experimental results on the structure, optical properties, electronic properties and photovoltaic properties by ion irradiations will be reported on the conference.

ET04.09.06
Solvant-Engineering Method to Deposit Compact Bismuth-Based Thin Films—Mechanism and Application to Solar Cells Seong Sik Shin1, 2 and Tonio Buonassassi3; 1Korea Research Institute of Chemical Technology, Cambridge, Massachusetts, United States; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Bismuth-based materials have been investigated as an alternative to lead-based perovskite materials for photovoltaic applications. However, inferior film quality has limited device performance. Here, we propose a one-step solvent evaporation method for deposition of various bismuth-based films. Through this one-step method, we obtain compact films of methylammonium bismuth iodide (MBI), cesium bismuth iodide (CSI), and formamidinium bismuth iodide (FDI). On the basis of film growth theory and experimental analyses, we propose a possible mechanism of film formation. Additionally, we demonstrate that the resultant compact MBI film is more suitable to fabricate efficient and stable photovoltaic devices, compared to baseline MBI films with pinholes. We further employ a new hole-transporting material to reduce the valence-band offset with the MBI. The best-performing photovoltaic device exhibits an open-circuit voltage of 0.85 V and fill factor of 73%, and a power conversion efficiency of 0.71%.

ET04.09.07
Tuneable Silver Bismuth Sulphoiodide Solar Cells Narendra Pari1, Jianfeng Lu1, Phillip C. Andrews1, Yi-Bing Cheng1, Udo Bach2 and Alexandr N. Simonov3; 1Chemistry, Monash University, Clayton, Victoria, Australia; 2Chemical Engineering, ARC Centre of Excellence in Exciton Science, Monash University, Clayton, Victoria, Australia; 3Materials Science and Engineering, ARC Centre of Excellence in Exciton Science, Melbourne, Victoria, Australia; 4Chemistry, ARC Centre of Excellence for Electromaterials Science, Monash University, Melbourne, Victoria, Australia.

Organolead halide perovskite solar cells have recently emerged as a solar energy technology with immense potential for large-scale generation of renewable electricity. However, the hazardous nature of lead and intrinsic instability of perovskites has driven the search for simpler and more robust light-absorbing materials. From this perspective, cheap, abundant and non-toxic bismuth-based systems with favourable optoelectronic properties are attracting a growing interest. Unfortunately, bismuth-based perovskites provide incompability lower photovoltaic performance than the lead counterparts due to poor interfacial charge extraction and wide indirect band gap. Viable alternatives are silver(I) and copper(I) iodobismuthates that have been recently found to exhibit promising photovoltaic performance. However, their relatively wide band gaps (Eg) of 1.8-1.9 eV and downshifted valence band edges (EvB) limit the charge transfer through conventional charge transport materials and the photocurrent density. Interestingly, silver bismuth sulfoiodides, which are also currently explored as photovoltaic materials, have an excessively positive EvB and too narrow Eg of 1.2-1.4 eV. Herein, silver bismuth sulfoiodides are introduced, for the first time, as a new class of light harvesting materials that balance out the unfavourable optoelectronic properties of iodides and sulfoiodides. We demonstrate a facile and efficient strategy to tune the optoelectronic properties of silver bismuth iodobismuthates by varying the sulphide: iodide ratio. A consistent narrowing of the bandgap by 0.1 eV and an upshift of the valence band edge by 0.1-0.3 eV upon modification with small amounts of sulphide is demonstrated for thermodynamically stable Ag5Bi4I16−xSx compositions. Photovoltaic devices based on new silver bismuth sulfoiodide light absorbers embedded into a mesoporous TiO2 electron transporting scaffold and covered with PTAA hole transporting layer outperform control solar cells based on sulphide-free materials, in full agreement with changes in the optoelectronic properties. An enhanced power conversion efficiency of 5.44 ± 0.07 % under 1 sun AM 1.5G irradiation and over a month stability under ambient conditions for photovoltaic devices based on Ag5Bi4I16−xSx is demonstrated.

ET04.09.08
Low-Temperature SnO2-Based Planar Perovskite Solar Cells—Interface Engineering, Large-Scale Manufacturing and High Performance Achievement Junjie Ma, Guojia Fang, Zhiliang Chen and Xiaolu Zheng; Wuhan University, Wuhan, China.

Perovskite solar cells (PSCs) have attracted considerable research interest because of their excellent photovoltaic performance and simple fabrication process. Tin oxide (SnO2) has emerged as a promising candidate for electron transfer layer (ETL), which shows much higher electron mobility, good antireflection, low-temperature process. Herein, we report a simple and efficient interfacial engineering method for achieving highly efficient Low-temperature SnO2-based PSCs. An ultrathin wide bandgap dielectric MgO nanolayer is incorporated between electrode and SnO2 ETL, realizing enhanced electron transporting and hole blocking properties. A power conversion efficiency (PCE) of 18.82% is demonstrated. On the other hand, systematic exploration of commercialized application in SnO2-based PSCs is conducted. We prepared SnO2 ETL through the electron beam evaporation (e-beam) technology, realizing large-scale, low-cost and uniform manufacture which would be available for industrial deployment. A Cs-containing blended perovskite absorber layer was introduced into the PSCs to effectively enhance the ambient stability. As a result, PSCs exhibit a high efficiency of 18.2% without any interface modification, and remarkable long-term stability, which remained 97% of its initial PCE after been stored over 34 days. Our result demonstrated the great potential of the PSCs based on SnO2 ETL towards commercially viable.

ET04.09.09
Single-Step CVD Approaches for Producing Thin-Film Perovskites Andrew J. Clayton, Arthur Connell, Rosie V. Anthony, Leo W. Furnell, Eurg W. Jones, Stuart J. Irvine and Peter J. Hoffiman; Swansea University, St. Asaph, United Kingdom.

Chemical vapor deposition (CVD) is a proven method [1-4] for depositing organic-inorganic metal halides, such as methylammonium lead iodide (MAPI)1, 2 and cesium lead iodide (CsPbI3)3, including Pb-free perovskite materials [4] for thin film photovoltaics (PV). The CVD process can be used in conjunction with other processes (hybrid) [1] or as a single step process [2-4]. The latter offers a simpler approach with reduced processing time. CVD is a controllable process with consistent results, also negating the requirement for solvents and limiting moisture incorporation.

Effect of Ion Irradiation on the Properties of Perovskite Solar Cells Hironori Ogata, Tomoaki Nishimura, Hiroya Kiuchi, Kazunori Ito, Toshiya Kobayashi and Yuki Fukazawa; Hosei University, Tokyo, Japan.

Perovskite solar cells are an important photovoltaic technology with high efficiencies exceeding 20% due to their optimal band gap, large absorption coefficient, and high charge mobilities. One of these challenges is the understanding and control of their defect structures because perovskite compounds are relatively soft ionic crystals and ions are migrating in the crystals relatively low activation energy. In this study, we have investigated the effect of low energy ion irradiations to both all inorganic and organic-inorganic lead halide perovskite films on the structure, morphology optical and electronic properties systematically. Several kinds of halogen ion beam irradiations on the perovskite thin film was performed by using a tandem type ion accelerator with changing acceleration voltages and irradiation time. Incorporation of ions in perovskite crystals by irradiations were confirmed under several conditions. Detailed experimental results on the structure, optical properties, electronic properties and photovoltaic properties by ion irradiations will be reported on the conference.
In this present study, different single step CVD approaches have been investigated for effective deposition of thin film MAPbI₃ and CsPbI₃. A CVD growth chamber with simple quartz tube design and two separately controlled temperature zones has been employed. The first zone was operated at high temperature (HT) to evaporate the precursor materials and sublime the chemical vapor in a low temperature (LT) zone on to a substrate. This was positioned on an angled graphite susceptor to counteract gas phase depletion and improve thickness uniformity.

Temperature control was achieved using K-type thermocouples inserted into the chamber from each end to measure and control the HT and LT zones. A small quartz tube was attached to the growth chamber, in which a thermocouple was inserted to at different sections along the tube to profile the temperature across the two zones. Both reactor tube and attached thermocouple tube were enclosed in a furnace encompassing both ceramic heaters for each temperature zone. A nitrogen (N₂) gas carrier was used to carry the chemical vapor downstream to the substrate in the growth zone. The N₂ carrier was dried by molecular sieves as it entered the CVD gas delivery system and a hygrometer was used to measure the dew point of the gas.

Two approaches were used to deliver the precursor chemical vapor to the substrate; firstly, a graphite crucible with two precursor positions was used, transporting the precursors in the same carrier flow [2, 3]; secondly, an additional inner tube was inserted into the main reactor tube to independently transport the lead iodide (PbI₂) to the substrate. The methylammonium iodide (MAI) or cesium iodide (CsI) were sublimed from a graphite crucible further upstream with vapor transported outside of the inserted tube carrying the PbI₂. Both approaches were to ensure sufficient reaction on the substrate in the LT growth zone. The different approaches were assessed to identify the best method for producing the perovskite films. Thin film solar cells will be prepared utilising the preferred CVD approach for the perovskite films and PV performances presented.

References

ET04.09.10 Interaction of Oxygen with Halide Perovskites Alessandro Senocaro1, 2, Tolga Acartuerk3, Goe Yeong Kim1, Rotraud Merkle1, Ulrich Starke1, Michael Graetzel1-2 and Joachim Maier1; 1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

The significance of degradation processes involving halide perovskite materials and devices is widely recognized, as it jeopardizes their practical application. Among the various degrading agents, oxygen has been shown to be extremely problematic, [1-3] and to even pose a severe threat to the technology as it is ubiquitous. On the other hand, oxygen exposure can also be beneficial for the materials, since it greatly improves their photoluminescence response. [4-5] For these reasons, it is highly important to understand the interaction of oxygen with halide perovskites from a mechanistic point of view. Here, we investigate the consequences of oxygen exposure on the stability and transport properties of halide perovskites, focusing on methylammonium lead iodide. Thermodynamic considerations show that the material is unstable against O₂, and this decomposition reaction is indeed observed, but only under illumination. In contrast, in the dark a sluggish surface reaction kinetics maintains the material metastable. Light accelerates the interaction kinetics, resulting in a quick and significant O₂ dissolution in the material lattice (directly observed through O¹ incorporation experiments), that can ultimately lead to degradation. Remarkably, this accelerated incorporation (in conditions that precede degradation) can significantly alter the electronic and ionic transport properties of the material in a way that conforms to acceptor doping. [7] We discuss these issues quantitatively on the basis of point defect chemistry, and extend these considerations to mixed-cation and mixed-anion compositions, as these are applied in state-of-the-art devices. While some compositions show a higher kinetic stability, the degradation tendency is still observed. [5]

ET04.09.11 Applications of Fused-Ring Electron Acceptor ITIC-Th in Perovskite Solar Cells Minchao Qin and Xinhui Lu; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Solution-processed perovskite solar cells offer a great potential of low-cost roll-to-roll fabrication. However, the degradation of aged precursor solutions will become a critical obstacle to mass production. In this report, we employ a small molecule (ITIC-Th) to stabilize the perovskite precursor solution containing mixed cations and halides. We find that ITIC-Th can effectively suppress the formation of yellow δ-phase in the films made from aged precursor solutions. Consequently, the devices fabricated from the aged precursor solution with ITIC-Th experience much less efficiency drop with the increase of the precursor aging time - from 19.20% (fresh) to 16.55% (39 days), compared with the devices made from conventional precursor solutions dropping from 18.07% (fresh) to 1.76% (39 days). The characteristics suggest that ITIC-Th is beneficial for MA cations to be incorporated into the crystal structure, facilitating the formation of perovskite phase. Furthermore, the presence of ITIC-Th in the perovskite thin film gives rise to additional photocurrent as well as improved fill factor due to the well-matched energy levels, the passivation of defects and the complementary absorption spectra, suggesting a new route towards future high-efficiency solar cells - incorporating organic non-fullerene acceptors and halide perovskite materials into the same active layer.

ET04.09.12 In Situ X-Ray Observation of Lead Iodide Perovskite Films Prepared by a Gas Blowing Method Yoshihiko Nishihara1, 2, Tetsuhiko Miyadera2, Masayuki Chikamatsu2 and Yuji Yoshida1, 2; 1University of Tsukuba, Tsukuba, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

The lead iodide perovskite solar cells have an energy conversion efficiency about 22%, and the bottleneck for practical use is the stability, and the large area fabrication process. The conventional antisolvent method has poor yield and is not suitable for large area. Thus, a combination of a coating method and a gas blowing method has attracted attention. However, its control technique has not been established and it is necessary to elucidate the formation mechanism. In this study, we introduced an in situ observation system including synchrotron based grazing incident X-ray diffraction for the film formation process by coating and gas blowing methods, and compared with a nitrogen drying process. A simple bar coater was used as a coating method, and nitrogen gas was blowing from a nozzle set onto the coating film.
After drying process, perovskite crystals were overgrown and the film surface was roughened, preparing it unsuitable for solar cells. As shown in the X-ray diffraction images of the precursor films before formation of perovskite, many bright spots showing random growth of large crystals were observed. However, in the case of gas blowing, the ring patterns indicates uniform film formation, and 020+002 diffractions oriented normal to the film surface. It is considered that the orientation of the precursor crystal contributes to the formation of a flat thin film having a large crystalline domain and hence improvement of the photovoltaic performance.

ET04.09.13
Understanding the Effects of Oxygen on Light-Induced Degradation of Perovskite Solar Cells to Achieve Long-Term Operational Stability
Tae-Youl Yang1, Nam Joong Jeon2, Hee-Won Shin2, Seong Sik Shin2, Young Yun Kim1 and Jangwon Seo1; 1Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea (the Republic of); 2Sungkyunkwan University, Suwon, Korea (the Republic of).

Perovskite solar cells (PSCs) in which organometal halides act as photoactive materials have achieved power conversion efficiency (PCE) of approximately 23 % by improving perovskite materials and fabrication process. Nowadays the substantial progress in long-term stability have been also achieved to commercialize PSCs based on such as high PCE with developing durable perovskite composition, interlayers, and encapsulation. It has been known that the degradation of PSCs is induced by stress conditions such as light (UV), heat, moisture, and oxygen. Even though the degradation mechanisms for heat and moisture was clearly explained, that for light soaking has not been clarified yet. In practice, because the protocols to test long-term operational stability of PSC is not standardized, the results of light soaking tests have been reported in a number of combinations of stress conditions. We reason that the operational stability under light soaking correlates with the stress factors from the atmosphere because the stability of PSCs depends on encapsulations or the testing atmosphere.

In this work, we systemically investigate the effects of oxygen on the degradation of PSCs under illumination. When PSCs were exposed to oxygen and light simultaneously, the devices were degraded quickly within an hour despite the perovskite material, (FAxPb1-x)0.93(MAPbBr3)0.07, was stable in the same condition. While most of discussions focus on the degradation at the interface between electron transport layers such as TiO2 and perovskite, here we present the degradation of the interface between perovskite and hole-transporting layer (HTL). We found that oxygen and light induce iodine diffusion from perovskite to HTLs, and reveal that charge transport from the perovskite to the HTM becomes ineffective before the degradation of bulk perovskite. Based on this understanding we demonstrated the long-term operational stability over 1000h of high-efficient mp-TiO2 used PSCs even under light including UV by preventing the iodine migration and oxygen ingress.

ET04.09.14
Morphology Mapping of Hybrid Perovskite Coated with Solution Shearing
Min Kyu Kim1, Hyeon Seok Lee1, Seong Ryeol Paé1, Issam Gereige2, Steve Park1 and Byungha Shin1; 1KAIST, Daejeon, Korea (the Republic of); 2Saudi Aramco Research & Development Center, Dhahran, Saudi Arabia.

Large area scaling of hybrid perovskite is essential to bring the technology into commercialization. Various large-scale printing techniques have been successfully employed to fabricate high performance perovskite solar cell. In particular, solution shearing is a versatile technique in which many processing parameters can be tuned in order to produce films with desired structure and morphology. In this study, we have examined the impacts of substrate temperature and coating speed (i.e., how fast the blade is moving), two of the most influential process parameters, on morphology of the resultant perovskite films. Four distinct phases are identified and a morphology-phase map is constructed with the aforementioned parameters. Through optical analysis, an optimal phase window is chosen and the device performance with the chosen condition exhibits power conversion efficiency over 15%, which is comparable to a reference device prepared by the conventional spin-coating process. A uniform perovskite film of an area > 55 cm2 is prepared with solution shearing. Several small-area devices from different locations of the large-area films shows uniform efficiencies within 5% deviation, illustrating the good uniformity achievable with our solution shearing techniques.

ET04.09.15
High-Efficient Perovskite Solar Cells Using Selectively Grown TiO2 Nanorod-Patterned Substrates
Daihong Huh1, Minjin Kim1−2, Wonjoong Kim1, Kwan Kim1, Minseo Byun1, Dong Suk Kim1 and Heon Lee1; 1Korea University, Seoul, Korea (the Republic of); 2Advanced Center for Energy, Korea Institute of Energy Research, Ulsan, Korea (the Republic of).

Organic–inorganic hybrid perovskite solar cells (PSCs) are attracting tremendous attention for new-generation photovoltaic devices because of their excellent power conversion efficiency and simple fabrication process. One of the various approaches to increase the efficiency of PSCs is to change the morphology of the carrier transport layer. Here, optically long and electrically short structural concept is proposed to enhance the characteristics of a PSC by employing selectively grown single crystalline TiO2 nanorods. The approach has the merit of increasing the electron-hole separation effectively and makes a thicker active layer to be coated without electrical loss by using TiO2 nanorod as an electron pathway. Moreover, selectively grown TiO2 nanorods increase the optical path of the incident light via scattering effects and enable a smooth coating of the active layer. Nanoimprint lithography and hydrothermal growth were employed to selectively grown TiO2 nanorod substrates. The efficiency of fabricated PSCs have about 20 % higher than that of planar-type devices. The fabricated PSCs exhibits an efficiency of 19.86% with a current density, open-circuit voltage, and fill factor of 23.13 mA cm−2, 1.120 V, and 76.69%, respectively. Time-resolved photoluminescence, UV-Vis spectroscopy, and the incident photon to current efficiency (IPCE) analysis were conducted to understand the factors responsible for the improvement in characteristics of the fabricated PSCs.
The influence of the film formation and morphology of perovskite top solar cells prepared on textured silicon bottom solar cells was investigated by modeling the deposition process and the optics of the perovskite/silicon tandem solar cells. An efficient photon management is required to realize perovskite/silicon tandem device with energy conversion efficiency exceeding the efficiency of crystalline silicon single junction solar cells. The perovskite solar cell has to be deposited on a textured crystalline silicon solar cell to allow for an efficient incoupling of light in the low refractive index top and the high refractive index bottom solar cell [1]. A recently developed fully textured perovskite/silicon tandem solar cell exhibits the record efficiency of 25.2% [2]. The formation of films on textured surfaces varies from the non-conformal deposition, which is typically observed for physical deposition techniques (e.g. PVD), to conformally prepared films obtained for some chemical deposition techniques (e.g. CVD, ALD). A 3D morphological algorithm was used to model the film formation [3]. The investigation is carried out for a wide range of pyramidal textured surfaces with a constant period to height ratio. A hybrid approach is used to investigate the optics by combining a three-dimensional (3D) finite-difference time-domain simulations with experimental measurements. Short-circuit current densities exceeding 20 mA/cm² were obtained for non-conformally and conformally grown perovskite films. A comparison of non-conformally and conformally deposition shows that short circuit current densities of 20 mA/cm² can be reached for distinctly thinner conformally deposited films. On the other hand, the roughness of the underlying silicon bottom solar cells has to be larger in the case of the conformally deposited films. Guidelines will be provided on how to achieve high short circuit currents for non-conformal and conformally prepared perovskite films.

Acknowledgement: This work is financially supported by the The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

References:

ET04.09.17
Influence of Perovskite Film Formation and Morphology on Textured Perovskite/Silicon Tandem Solar Cells Md Waseh Qarony1, Mohammad I. Hossain2, Vladislav Jovanov2, Dietmar Knipp3 and Yuen H. Tsang3; 1Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

The influence of the film formation and morphology of perovskite top solar cells prepared on textured silicon bottom solar cells was investigated by modeling the deposition process and the optics of the perovskite/silicon tandem solar cells. An efficient photon management is required to realize perovskite/silicon tandem device with energy conversion efficiency exceeding the efficiency of crystalline silicon single junction solar cells. The perovskite solar cell has to be deposited on a textured crystalline silicon solar cell to allow for an efficient incoupling of light in the low refractive index top and the high refractive index bottom solar cell [1]. A recently developed fully textured perovskite/silicon tandem solar cell exhibits the record efficiency of 25.2% [2]. The formation of films on textured surfaces varies from the non-conformal deposition, which is typically observed for physical deposition techniques (e.g. PVD), to conformally prepared films obtained for some chemical deposition techniques (e.g. CVD, ALD). A 3D morphological algorithm was used to model the film formation [3]. The investigation is carried out for a wide range of pyramidal textured surfaces with a constant period to height ratio. A hybrid approach is used to investigate the optics by combining a three-dimensional (3D) finite-difference time-domain simulations with experimental measurements. Short-circuit current densities exceeding 20 mA/cm² were obtained for non-conformally and conformally grown perovskite films. A comparison of non-conformally and conformally deposition shows that short circuit current densities of 20 mA/cm² can be reached for distinctly thinner conformally deposited films. On the other hand, the roughness of the underlying silicon bottom solar cells has to be larger in the case of the conformally deposited films. Guidelines will be provided on how to achieve high short circuit currents for non-conformal and conformally prepared perovskite films.

Acknowledgement: This work is financially supported by the The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

References:

ET04.09.18
Spin Coated Copper (I) Thiocyanate as a Hole Transport Layer for Perovskite Solar Cells Utku Er1,2, Kerem Cagatay Icili1,2 and Ahmet Macit Ozenbas1,2; 1Orta Dogu Teknik University, Ankara, Turkey; 2GUNAM, Ankara, Turkey.

Application of a low cost and efficient p-type inorganic hole-transporting material, copper thiocyanate (CuSCN), on mesoporous n-i-p configurated perovskite based devices was conducted in this study. Diethyldisulfide was chosen for the preparation of precursor solution in order to deposit CuSCN layer on perovskite without degrading it. Topographical, elemental and electrical characterizations of spin coated CuSCN layers were performed using XRD, AFM, SEM, XPS, UPS, and UV-Vis studies. A power conversion efficiency exceeding 11.02 % with an open circuit voltage of 0.83 V was succeeded in the perovskite solar cells under full sun illumination. Low-temperature solution process used for the deposition of CuSCN and a fast solvent removal method allowed the creation of compact, highly conformal CuSCN layers that facilitate rapid carrier extraction and collection. The differences in series and recombination resistances for CuSCN free and CuSCN containing cells were also determined using impedance spectroscopy (IS) analysis. Moreover, the effect of TiO₂ layer thickness on the cell performance was studied where these TiO₂ layers were used not only for electron extraction and transportation but also as hole blocking layer in perovskite solar cells. The impedance spectroscopy results were also consistent with the differentially configured cell performances. This work shows a well defined n-i-p configurated perovskite cell with optimized layers which utilizes low cost and abundant material for photovoltaic applications.

ET04.09.19
Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucia Rakocevic1,2, Laura Mund1, Robert Gehlhaar1, Tamara Merckx1, Tom Aernouts1, Martin Schubert3, Stefan Glunz2 and Jef Poortmans1, 2; 1TFPV, imec, Leuven, Belgium; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Organometallic halide perovskites are effective low-cost photovoltaic materials that require low energy fabrication processes. Perovskite thin film PV modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the coating technique. We will apply lessons learned to further optimize module performance.

ET04.09.19
Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucia Rakocevic1,2, Laura Mund1, Robert Gehlhaar1, Tamara Merckx1, Tom Aernouts1, Martin Schubert3, Stefan Glunz2 and Jef Poortmans1, 2; 1TFPV, imec, Leuven, Belgium; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Organometallic halide perovskites are effective low-cost photovoltaic materials that require low energy fabrication processes. Perovskite thin film PV modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the coating technique. We will apply lessons learned to further optimize module performance.

ET04.09.19
Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucia Rakocevic1,2, Laura Mund1, Robert Gehlhaar1, Tamara Merckx1, Tom Aernouts1, Martin Schubert3, Stefan Glunz2 and Jef Poortmans1, 2; 1TFPV, imec, Leuven, Belgium; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Organometallic halide perovskites are effective low-cost photovoltaic materials that require low energy fabrication processes. Perovskite thin film PV modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the coating technique. We will apply lessons learned to further optimize module performance.

ET04.09.19
Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucia Rakocevic1,2, Laura Mund1, Robert Gehlhaar1, Tamara Merckx1, Tom Aernouts1, Martin Schubert3, Stefan Glunz2 and Jef Poortmans1, 2; 1TFPV, imec, Leuven, Belgium; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Organometallic halide perovskites are effective low-cost photovoltaic materials that require low energy fabrication processes. Perovskite thin film PV modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the coating technique. We will apply lessons learned to further optimize module performance.

ET04.09.19
Area Loss Analysis in Perovskite Modules Using Dark Lock-In Thermography and Luminescence Imaging Lucia Rakocevic1,2, Laura Mund1, Robert Gehlhaar1, Tamara Merckx1, Tom Aernouts1, Martin Schubert3, Stefan Glunz2 and Jef Poortmans1, 2; 1TFPV, imec, Leuven, Belgium; 2Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany; 3Geballe Laboratory for Advanced Materials, Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Organometallic halide perovskites are effective low-cost photovoltaic materials that require low energy fabrication processes. Perovskite thin film PV modules. Current processing techniques result in 12-15 % power conversion efficiency for 16 cm² aperture area modules, depending on the coating technique. We will apply lessons learned to further optimize module performance.
Industrial Case of Perovskite Solar Cells

Konrad Wojciechowski; Saule Technologies, Wroclaw, Poland.

Metal halide perovskites constitute a very attractive class of materials for optoelectronic applications, such as solar cells, light emitting diodes, lasers and photodetectors. Most notably, solid-state photovoltaic devices based on these materials have reached power conversion efficiencies (PCEs) of 22% after just five years of academic research.

Perovskite solar cells have a great commercial potential, but there still remain few challenges, which need to be resolved to prove the viability of the technology. Some of the well-known issues include material stability. Furthermore, cost-effective, reliable fabrication process capable of delivering highly efficient, large-area perovskite modules is yet to be demonstrated.

This talk will outline the industrial challenges of perovskite solar cells including legislative hurdles as well as the potential impact on the solar industry. Moreover, we will present fully scalable ink-jet printing process of the perovskite PV stack and fabrication of perovskite printable mini-modules of areas up to A4 size, complemented with a robust encapsulation methodology.

Metal halide perovskites constitute a very attractive class of materials for optoelectronic applications, such as solar cells, light emitting diodes, lasers and photodetectors. Most notably, solid-state photovoltaic devices based on these materials have reached power conversion efficiencies (PCEs) of 22% after just five years of academic research.

Perovskite solar cells have a great commercial potential, but there still remain few challenges, which need to be resolved to prove the viability of the technology. Some of the well-known issues include material stability. Furthermore, cost-effective, reliable fabrication process capable of delivering highly efficient, large-area perovskite modules is yet to be demonstrated.

This talk will outline the industrial challenges of perovskite solar cells including legislative hurdles as well as the potential impact on the solar industry. Moreover, we will present fully scalable ink-jet printing process of the perovskite PV stack and fabrication of perovskite printable mini-modules of areas up to A4 size, complemented with a robust encapsulation methodology.

Metal halide perovskites constitute a very attractive class of materials for optoelectronic applications, such as solar cells, light emitting diodes, lasers and photodetectors. Most notably, solid-state photovoltaic devices based on these materials have reached power conversion efficiencies (PCEs) of 22% after just five years of academic research.

Perovskite solar cells have a great commercial potential, but there still remain few challenges, which need to be resolved to prove the viability of the technology. Some of the well-known issues include material stability. Furthermore, cost-effective, reliable fabrication process capable of delivering highly efficient, large-area perovskite modules is yet to be demonstrated.

This talk will outline the industrial challenges of perovskite solar cells including legislative hurdles as well as the potential impact on the solar industry. Moreover, we will present fully scalable ink-jet printing process of the perovskite PV stack and fabrication of perovskite printable mini-modules of areas up to A4 size, complemented with a robust encapsulation methodology.
9:15 AM ET04.10.05
Upscaled Roll-to-Roll Manufacturing of Perovskite Based Solar Cells Pim Groen1,2; 1Holst Centre, Eindhoven, Netherlands; 2Aerospace Engineering, Delft University of Technology, Delft, Netherlands.

Metal-halide based perovskites are promising novel materials for thin-film photovoltaics, exhibiting high power conversion efficiencies. A number of challenges still need to be addressed before PSCs can enter the PV market. One of these challenges is the development of industry-relevant technologies for scaling up the perovskite module manufacturing. The feasibility of upsaling the perovskite solar cells technologies to high volume production using Roll-to-Roll (R2R) slot die coating is demonstrated in this talk. Perovskite solar cells were produced by R2R slot die coating on flexible PET/ITO substrates with the width of 30 cm. Roll-to-Roll deposition of electron transport layer (ETL) and perovskite is performed at ambient atmosphere from non-toxic solvents compatible with industrial manufacturing. The average stabilized power conversion efficiency of the devices made from the foils randomly cut from different places was 12%, with the best value of 13.5%. The demonstrated achievement is an important milestone and a big solid step towards future commercialization of perovskite-based solar cells technologies.

9:30 AM ET04.10.06
R2R Compatible High-Speed Coating of Perovskite Solar Cell Henning Doerr, David T. Moore, Kai Zhu and Maikel van Hest; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

High efficiency combined with transformative roll-to-roll (R2R) printability makes metal halide perovskite (MHP)-based solar cells the most promising solar technology to address the terawatt challenge of the future energy demand. However, translation from lab-scale deposition techniques to large-scale R2R methods has typically led to reduced photovoltaic performance. Here, we demonstrate an MHP ink that allows R2R compatible high-speed (>2.5 m min⁻¹) one-step blade coating. MHP solar cells from the developed ink can produce power conversion efficiency over 19% in the ambient environment, without any addition of antisolvent, gas blow, vacuum treatment or high-temperature stage temperature. This report on one-step antisolvent (or similar process)-treatment-free blade coating technique paves the way for the R2R production of high-efficiency MHP solar cells.

9:45 AM BREAK

10:00 AM ET04.10.08
Vacuum Deposited Single and Double Junction Perovskite Solar Cells Henk J. Bolink, Ana Igual Munoz, Benedikt Daenekamp, Jorge Ávila, Daniel Pérez del Rey, Michele Sensolo and Pablo P. Boix; University of Valencia, Paterna, Spain.

We will report on the progress on vapor phase deposited perovskites, including low bandgap Pb-Sn and wider bandgap multiple cation versions. The performance of these materials in both single and double junction solar cells will be reported. The influence of the use of thin organic charge extraction layers, using strong dopants, ionic compounds and conjugated polymers will be described.

10:30 AM ET04.10.09
Coevaporated p-i-n Perovskite Solar Cells Deposited at Elevated Substrate Temperature—Process Optimization and Photo Stability Ranith Kottokkaran, Harshavardhan A Gomnikar, Hisham A. Abbas, Max Noack and Vikram L. Dalal; Microelectronics Research Center, Iowa State University of Science and Technology, Ames, Iowa, United States.

Thin-film photovoltaics represents the next generation of promising photovoltaics technology. Exhibiting a verified efficiency of over 22%, perovskite solar cells are the fastest growing solar material to date. Lead tri-halide perovskites (MAPbX₃) are a new and exciting technology among perovskite solar cells. Solution process-based fabrication of perovskite solar cells have known problems of reproducibility, whereas vacuum deposition, which involves sequential or co-evaporation of lead halide and methyl ammonium iodide (MAI), is a much more reproducible technique. Devoid of any organic solvents, vapor deposited perovskite solar cells show superior photo stability.

In this work, we report on co-evaporated MAPbI₃ perovskite deposited at various substrate temperatures using a multi-source thermal evaporator. The central challenge involved with the deposition process is precise control of the MAI pressure during the deposition process. A p-i-n device architecture of FTO/ PTAA/ MAPbI₃/ PCBM/ Al with power conversion efficiency of >17.5% was achieved by maintaining the MAI pressure between 5.5-6 x10⁻⁵ Torr for a room temperature deposition. Further, we also carried out co-evaporation of MAPbI₃ perovskite at higher substrate temperatures of 50 °C and 75 °C. Here, elevating the MAI pressures (9-9.5x10⁻⁵ Torr and 1.2-1.3x10⁻⁴ Torr respectively) is essential to achieve efficiencies of >16%. SEM micrographs show grain enhancement for films deposited at higher temperatures. Photo degradation studies show that perovskite devices deposited at 75 °C show superior photo-stability, with less than 1% degradation in the short circuit current for over 100 hours of light exposure.

10:45 AM ET04.10.10
A Novel Cryo-Controlled Growth Technique for High Efficiency Organometal Halide Perovskite Solar Cells Annie Ng1, Zhiwei Ren2, Qian Shen2, Sin Hang Cheung2, Aleksandra B. Dijarić4, Shu Kong Su4, Gang Li5 and Charles Surya1; 1Nazarbayev University, Astana, Kazakhstan; 2Hong Kong Polytechnic University, Hong Kong, China; 3Hong Kong Baptist University, Hong Kong, China; 4The University of Hong Kong, Hong Kong, China.

Perovskites with multi-components have demonstrated significant potential for the development of high performance photovoltaic cells with better device efficiency and stability. Optimization of perovskite growth techniques are crucial for acquiring mixed halide perovskite films with precise stoichiometry, desirable morphology and low defect density. Reports on growth processes involving the formation of Lewis acid–base adduct in precursor films and the application of anti-solvent dripping process have become the mainstream for preparing solution based mixed halide perovskites. However, a number of limitations are found for using anti-solvent techniques to prepare large-scale samples. The resultant morphology of the perovskite films is significantly affected by many factors such as the anti-solvent dripping time, volume and location on the samples. Furthermore, the anti-solvent technique commonly works together with the spin-coating process and it would be difficult to apply on other large-scale solution processing techniques.

We report a novel cryo-controlled growth technique for the growth of mixed halide perovskites. The abrupt decrease in the ambient temperature results in a supersaturation condition in the as-casted precursor films, leading to the formation of uniform nucleation sites for subsequent crystal growth. A blow dry process is introduced subsequently to facilitate the removal of residual solvents from the films before thermal annealing. Our proposed strategy can effectively retard the pre-nucleation crystallization of the perovskites and, thereby, decoupling the pre-nucleation and crystallization phases. This material growth approach can be applied to different types of mixed halide perovskites, ensuring excellent uniformity of the nucleation layers and, subsequently, higher quality perovskite films. A power conversion efficiency (PCE) of 21.4 % with a fill factor of 80 % for the champion PSC is achieved using the proposed perovskite growth technique without utilizing any anti-solvents.

11:00 AM ET04.10.11
Chemical Vapor Deposition for 10 cm × 10 cm Large-Array Perovskite Solar Modules Longbin Qiu, Yan Jiang, Zonghao Liu, Luis K. Ono, Dae-Yong
Perovskite solar cells have shown efficiency approaching silicon photovoltaic counterparts, but mostly achieved on a small area. To commercialize this low cost technology, scalable fabrication is one of the main challenges to be addressed [1]. For large-area, uniform and high quality film deposition, we have employed industry compatible chemical vapor deposition to deposit MAPbI$_3$, FAPbI$_3$, and Cs$_x$FA$_{1-x}$PbI$_3$ films with high quality for solar cells/modules [2-5]. In this work, fully scalable perovskite solar modules with high-geometric fill factor have been fabricated by a further optimized chemical vapor deposition process. Upon increasing of device area, device performance decreases only gently. 10 cm x 10 cm solar modules showed an aperture efficiency approaching 10% with a geometric fill factor greater than 90%. We show that chemical vapor deposition is compatible for large-area, uniform and high quality perovskite films and solar modules.


11:15 AM ET04.10.12
Towards Completely Inkjet-Printed Perovskite Solar Cells Aron J. Huckaba, Yonghui Lee, Andreas Lesh, Hubert Girault and Mohammad K. Nazeeruddin, Ecole Polytechnique Federale deLausanne, Sion, Switzerland.

In the past ten years, the efficiencies of perovskite solar cells have risen from 3.8% to > 22% power conversion efficiency (PCE). The highest performing devices typically have small areas (<1 cm$^2$) and are fabricated by spin-coating deposition of most of the active layers. While spin-coating works well for small area substrates, it is not industrially applicable due to the high percentage of material loss and substrate size limitation. Reports of perovskite absorber layer deposition by industrially relevant techniques such as slot-die coating, evaporation, and inkjet printing are becoming more frequent. Inkjet printing is a digital, mask-less and contact-less fabrication technique that allows the direct deposition of miniscule ink volumes onto substrates with full pattern control, where the pattern resolution is limited by the droplet volume (generally below 100 pl) and the spreading diameter of the droplet on the substrate. Complete Organic Light Emitting Diodes (OLEDs), Field Effect Transistors (FETs), and Organic Photovoltaic (OPV) devices have been fabricated using inkjet printing, but this has not yet been achieved with perovskite solar cells. Herein, efforts towards the fabrication of completely inkjet-printed perovskite solar cells by bottom-up layer construction are described. Optimization studies of each active layer will be discussed, as well as the inclusion of inkjet-printed active layers in high-efficiency perovskite solar cells.

11:30 AM ET04.10.13
A Vacuum-Free Plasma Enhanced Ultrasonic Spray Deposition Process for Highly Efficiency Large-Area Perovskite Solar Cells Dimitry Lopatin2, Oleg Baranov2, Elizaveta Kozhova1, Bogdan Bragin2 and Vinay Gupta1, 1Advanced Materials and Devices Division, National Physical Laboratory, New Delhi, India; 2Kuban State University, Krasnodar, Russian Federation; 1University of Franche-Comté, Besançon, France.

The photovoltaic performance of Metal halide perovskite solar cells (PSCs) has reached beyond 20% on a small device area (≤0.1cm$^2$) and shown potential to overtake silicon solar cells. However, the researchers are still grappling with maintaining high efficiency over large device area due to the current technological barrier. Here we have achieved a single cell efficiency of ~14% over an area of 10 x 10 cm$^2$ by inventing a disruptive vacuum-free plasma enhanced ultrasonic spray deposition (PEUSD) technology and obtained uniform and high-quality perovskite film over large area. The PEUSD is a vacuum free technology that can print all the layers of a PSC i.e. Ni$_x$NiO$_{1-x}$/CH$_3$NH$_3$PbI$_3$/Cs$_x$TiO$_2$/Cu-NWs/ITO including metal contacts. This technology would enable low-cost architecture for the commercialization of PSCs and can potentially replace current vacuum-based coating technologies for thin film deposition.

11:45 AM ET04.10.14
Pulsed Flash Infrared Annealing for Efficient and Stable Perovskite Inorganic Solar Cell Sandy Sanchez1, Michael Saliba1 and Antonio Abate2, 1Adolphe Merkle Institute, Fribourg, Switzerland; 2Helmholtz-Zentrum Berlin, Berlin, Germany.

Organic-inorganic perovskite solar cells have achieved impressive power conversion efficiency over the past years, yet operational stability remains the key concern. One strategy to improve long-term stability is to replace the thermally unstable organic with inorganic cations comprising the perovskite lattice. Here, for the first time, we make use of pulsed infrared light to drive the crystallisation of inorganic mixed halide Cs$_x$Pb$_{1-x}$Br$_2$ perovskite films in solar cells with a power conversion efficiency exceeding 10%. By varying the iodide-bromine ratio systematically, we found that to keep the inorganic perovskite black phase stable at the room temperature we need to limit the iodine content to lower than 60% - bromine content higher than 40%. Our finding revises previous reports claiming stable compositions with higher iodine content, which was systematically exploited to reduce the perovskite bandgap with the aim to enlarge the light absorption spectra and thus to boost the device efficiency. We demonstrate that the newly defined stable compositional range enables devices that retain 90% of the initial efficiency after stressing the perovskite at 200°C for one hour. This result is a key finding for the application of perovskite in concentrated photovoltaic.
A Strategy for Architecture Design of Crystalline Perovskite Light-Emitting Diodes with High Performance and Stability

Our fabrication approach is fully reproducible and is a technological base for mass-fabrication of active optoelectronic circuits with hybrid perovskite. Measured devices. The lasing thresholds are in the order of 5 µJcm⁻² which outperforms most unpatterned single crystal perovskite lasing techniques can be applied enabling the usage of the material in commercial systems; i.e. optoelectronic circuits with monolithically integrated lasers. We paves the way to more complicated circuits and structures enabling electrically pumped perovskite laser in the near future. High-throughput fabrication technologies for reproducible on-chip devices with low device-to-device variations and low sample-to-sample variation with almost emission linewidths (to below 40nm, and maximize their photoluminescence quantum efficiencies (up to 89%) and phase/chemical stabilities [3]. Detailed structural analysis revealed that the CsxFA₁₋ₓPb(Br₁₋ᵣIʳ)₃ NCs adopt a cubic perovskite structure of FAPbI₃, with iodide anions partially substituted by bromide ions. Most importantly, we demonstrate the excellent transference of reaction parameters from microfluidics to a conventional flask-based process enabling up-scaling thereby further implementing CsxFA₁₋ₓPb(Br₁₋ᵣIʳ)₃ NCs with an emission maximum at 735 nm were integrated into light-emitting diodes, exhibiting high external quantum efficiency of 5.9% and very narrow electroluminescence spectral bandwidth of 27 nm [3].

Monolithically Integrated On-Chip Lasers Based on Perovskite Optoelectronics

Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

We demonstrate latest achievements of integrated perovskite devices on a silicon nitride photonic platform. Perovskite as a class of solution processed semiconductors with a direct bandgap offering a variety of interesting emission wavelengths for on-chip photonics. Spin-coating enables a possibility of direct integration of the lasing material as a counterpart to epitaxial growth with is not applicable on amorphous substrates such as silicon nitride. We report on methylammonium lead iodide (MAPbI₃) perovskite micro-disc and microring lasers which are monolithically integrated into silicon nitride photonic integrated circuits showing low lasing thresholds at room temperature. The perovskite micro-discs are placed in the vicinity of a single mode silicon nitride waveguides so that the generated laser light can be directly used by a photonic circuitry. A top-down lithographic structuring approach has been developed to pattern perovskite micro-discs without degenerating the active material. This method paves the way to more complicated circuits and structures enabling electrically pumped perovskite laser in the near future. High-throughput fabrication techniques can be applied enabling the usage of the material in commercial systems; i.e. optoelectronic circuits with monolithically integrated lasers. We report on fabrication technologies for reproducable on-chip devices with low device-to-device variations and low sample-to-sample variation with almost 100 measured devices. The lasing thresholds are in the order of 5 µJcm⁻² which outperforms most unpatterned single crystal perovskite lasing demonstrations. The laser emission lies at ~785 nm and is narrow in linewidth (~1 nm). The micro-discs were optically pumped at room temperature in ambient conditions with 120 fs laser pulses with 250 kHz repetition rate at 630 nm wavelength. X-ray diffraction crystallography has been performed prior to processing the perovskite and on the final device showing only small changes in the material after the patterning process. Device performance is confirmed by simulations (Finite Difference Time Domain, FDTD).

Our fabrication approach is fully reproducible and is a technological base for mass-fabrication of active optoelectronic circuits with hybrid perovskite-dielectric waveguide materials.

A Strategy for Architecture Design of Crystalline Perovskite Light-Emitting Diodes with High Performance and Stability

Zhaoxin Wu, Yifei Shi, Hua Dong, Chenchin Ran, Jinfei Dai, Fang Yuan, Bo Jiao and Xin Hou; School of Electronic and Information Engineering, Xi’an Jiaotong University, Xi’an, China.

Hybrid halide perovskites have recently emerged as new promising semiconductors for both photovoltaic and optoelectronic applications. Given the rapid rise in performance of perovskite solar cells, the demonstration of high photoluminescence quantum efficiency and optical gain in these hybrid perovskites suggests that these materials should also be potential light emitters for light emitting diodes and lasers. Here, we introduce a new design strategy and conception, “Insulator-Perovskite-Insulator” (IPI) architecture tailored to perovskite light-emitting diodes (PeLEDs). We experimentally show that the IPI structure effectively induces charge carriers into perovskite crystals, blocks leakage currents via pinholes in the perovskite film, avoids exciton quenching simultaneously. Consequently, as for FAPbBr₃, a 30-fold enhancement in the current efficiency of IPI-structured PeLEDs compared to a control device was achieved - from 0.64 cd/A to 20.3 cd/A. As the example of CsPbBr₃, compared with the control device, both current efficiency and lifetime of IPI-structured PeLEDs were obviously improved [1]. In addition, we also demonstrate tin (Sn) based PeLEDs with all-inorganic heterostructure fabricated by the vapor-deposition process. The all-inorganic hetero-structured PeLEDs exhibited a maximum EQE of ~0.34%, and withstood current density up to 915 A/cm² with small emission zone of 0.01 mm². Besides, low threshold (7 µJ/cm²) amplified spontaneous emission was presented from the extremely smooth and uniform cesium tin halide perovskite films. These characteristics demonstrate the great potential of using them as gain media for electrically pumped lasers [2,3].

References

Space Based Perovskite Photovoltaics

Samuel Loke, Nina Vaidya, Pilar Espinet Gonzalez, Michael Kelzenberg, Qin Yang, Emily C. Warmann and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Organo-lead halide perovskite solar cells are an exciting candidate for future space based photovoltaics. Perovskites have potential for significantly higher specific power (power generated per unit mass) compared to other photovoltaic technologies, since intrinsic radiation hardness may potentially enable radiation shielding to be omitted as a cell component. This creates an opportunity for perovskites to be a leading photovoltaics technology for space power, where the cost per kg is a demanding metric owing to high payload launch costs, provided radiation robustness and environmental stability can be
validates. It is thus imperative to study how perovskites respond to thermal and radiative loads in space. We have demonstrated methylammonium lead iodide (MAPbI3) based solar cells to be resistant to 30, 50 and 350 keV proton irradiation at 10^{11} p/cm^2 fluence, and 1 MeV electron irradiation at 10^{15} e^-/cm^2 fluence. In order to deepen our understanding of the space performance of perovskite solar cell devices, we fabricate several perovskite device structures, with various hole transport layer (HTL) materials and electron transport layer (ETL) materials, and characterize their performance in simulated space environments with respect to radiation stability, under air mass 0 (AM0) illumination in vacuum and under thermal cycling. Finally, we examine the feasibility of fabricating perovskites on various flexible substrates that will allow for even lower areal mass density as well as easier payload storage. For this study, we examine the perovskite materials MAPbI_3, formamidinium lead iodide (FAPbI_3), as well as efficient mixed cation perovskites. For our tests, we examine the perovskites on various flexible substrates that will allow for even lower areal mass density as well as easier payload storage. For this study, we examine the perovskite materials MAPbI_3, formamidinium lead iodide (FAPbI_3), as well as efficient mixed cation perovskites.

Despite significant advances in simulation and theory, progress toward identifying lead-free perovskite materials has been limited by low experimental throughput and reproducibility. For early-stage materials, characterization tools are often slow or are too imprecise in pinpointing the bulk or interface property that limits efficiency and/or reliability. Lack of proper diagnosis makes the process-optimization feedback loop more open ended, and driven by intuition rather than the scientific method.

In this talk, we present progress toward a closed-loop, automated experimental system for novel photovoltaic materials discovery. We present advances in rapid diagnosis, enabled by a combination of machine learning and non-destructive electrical testing. The closed-loop feedback loop enables more rapid process optimization to occur. We discuss prospects of using this improved experimental loop for new materials discovery, and the realization in thin-film form of materials that previously had only been synthesized in bulk (e.g., certain double perovskites).

The identification of suitable lead-free perovskites is crucial for their envisioned applications in photovoltaics. Homovalent substitution of lead with Sn- and Ge-based compounds are under intense investigation as potential alternatives, but suffer from instability issues, for example, due to the susceptibility of these ions toward the 4+ oxidation state. Mixed compositions, with two or more possible ions for each lattice position, have been proposed for overcoming these issues and enhancing performance [1, 2]. However, as it is computationally and experimentally prohibitive to measure the vast configuration space available to the mixed perovskites, statistical learning techniques are needed to find a more efficient mapping of mixing parameters to the properties of interest.

Efficient and accurate vetting of perovskites for a range of properties has recently been accomplished in high-throughput Density Functional Theory (DFT) studies of compounds by use of Kernel Ridge Regression (KRR) [3, 4]. Crucial to their success is the determination of adequate material fingerprints which uniquely define the materials and capture the property of interest. Here we demonstrate how one such important screening parameter, the fundamental bandgap, can be predicted for a family of inorganic mixed halide perovskites using novel globally valid material fingerprints based solely on the atomic configurations of arbitrary unit cells. The Partial Radial Distribution Function method [5] is expanded upon to include densities for a variety of elemental properties, enabling us to define a more robust material fingerprint while illuminating the underlying drivers of target properties in a chemically intuitive manner. The results are supplemented with thermodynamic and geometric data to identify the best compositions and the features responsible for them.

References


4:15PM ET04.11.07

Halide Perovskites—A Platform for ‘Defect-Tolerance’ and ‘Self-Healing’ Yevgeny Rakita, Davide R. Ceratti, Gary Hodes and David Cahen; Weizmann Institute of Science, Rehovot, Israel.

In recent years, halide perovskites (HaPs) have taken a unique place among functional semiconductors, surpassing expectations, and surprising many materials researchers. An often-asked question is: what may be the reason(s) that HaPs performance gets close to that of high-quality optoelectronic semiconductors, although their fabrication is similar to that of the organic electronic materials which, though, are of considerably lower semiconductor quality? As ‘quality’ refers (here) to ‘low density of defects/traps that are optical or electronically active’ (the defect density of HaPs is ~10^{10} cm^{-3} in single crystals and <10^{10} cm^{-3} in polycrystalline films), ‘defect-tolerance’ and ‘self-healing’ have been proposed as possible explanations. Although these two properties may seem to be related, ‘defect-tolerance’ is a property that does not exclude the presence of structural defects, but only their impact on the charge carrier dynamics and optical absorption and emission. This will give rise to an effectively reduced optoelectronically relevant defect density. ‘Self-healing’, however, is the property of elimination of structural defects over time by a driving force within the structure (likely to reduce the system’s free energy). To support the ‘defect tolerance’ and ‘self-healing’ hypothesis, I will present experimental evidence that strongly supports the idea that HaPs (not limited to the commonly used APbI_3) are a platform for both ‘defect tolerance’ and ‘self-healing’, physically as well as chemically. The ‘physical’ part includes experimental analysis of the ‘deformation potential’, which makes ‘defect tolerance’ very probable, both due to its absolute value and algebraic sign. The ‘chemical’ part includes assembly of evidence that support recyclability of degradation products back to the starting material, which means a path for ‘self-
Fully inorganic chalcogenide perovskite photoabsorbers are a relatively unexplored class of materials that could potentially overcome the stability issues of hybrid perovskites. However, only few chalcogenide perovskites have been synthesized to date, and no reports of solar cell devices based on chalcogenide perovskite absorbers exist to the best of our knowledge. Chalcogenide perovskites have recently been the subject of a few computational screening studies, including the one carried out by our group and focusing on sulfide (ABS₃) perovskites [1]. Among the 705 ABS₃ compounds that were screened, 15 of them were identified as promising. One of the new compounds that passed all the screening rounds (LaYS₃) was successfully synthesized in thin film form in our group, confirming the theoretically predicted crystal structure and band gap [1].

The main challenge in fabricating LaYS₃ solar cells is the relatively high temperature needed to crystallize the material. As a consequence, we were only able to fabricate prototype LaYS₃ solar cells using back contact materials with high temperature resistance. At the present stage, those devices exhibit diode-like rectification but no photocurrent. Nevertheless, we believe this is the first solar cell fabrication attempt using a sulfide perovskite photoabsorber, and one of the first examples of a solar cell fully inspired by computational screening. In this contribution, we will present the updated status of LaYS₃ solar cell performance, as well as the main challenges encountered in this project and possible future directions.


ET04.11.08 Solar Cells with LaYS₃ Perovskite-Like Absorber Discovered by Computational Screening Andrea Crovetto, Rasmus Nielsen, Brian J. Seger, Ole Hansen, Peter Vesborg and Ib Chorkendorff, Technical University of Denmark, Kgs. Lyngby, Denmark.


The open-circuit voltages ($V_{OC}$) of hybrid perovskite (HP) solar cells do not increase sufficiently with increasing bandgap (for $E_g > 1.70$ eV). We study the impact of A⁺ size mismatch induced lattice distortions (in ABX₃ structure) on the optoelectronic quality of high-bandgap HPs and find that the highest quality films have high A⁺ site size-mismatch, where large guanidinium (GA) compensates for small Cs to keep the tolerance factor in the range for the perovskite structure. Specifically, we find that 1.84 eV bandgap (FA$_{0.33}$GA$_{0.67}$Cs$_{0.80}$)$_2$Pb(I$_{0.13}$Br$_{0.87}$)$_{3.24}$ and 1.75 eV bandgap (FA$_{0.33}$GA$_{0.67}$Cs$_{0.80}$)$_2$Pb(I$_{0.13}$Br$_{0.87}$)$_{3.24}$ attain quasi-Fermi level splitting of 1.43 eV and 1.35 eV, respectively, which is >91% of the Shockley-Queisser limit for both cases. To study the optoelectronic quality of perovskite films and understand device losses, we employ absolute intensity photoluminescence and compare device $V_{OC}$ with absorber quasi-Fermi level splitting for perovskite films with bandgaps spanning from 1.35 to 1.85 eV. Further, we employ wide-field photoluminescence imaging to identify interface recombination in our device stack and explore various interlayer alternatives to ultimately achieve high $V_{OC}$. Films of 1.75 eV bandgap (FA,GA,Cs)Pb(I,Br) are then used to fabricate p-i-n photovoltaic devices that have a $V_{OC}$ of 1.24 V. This $V_{OC}$ is among the highest $V_{OC}$ reported for any HPs with similar bandgap (1.7 to 1.8 eV) and a substantial improvement for the p-i-n architecture, which is desirable for two-terminal tandems with Si, CIGS, or a low-bandgap HP. Methods to improve high-bandgap device $V_{OC}$ further using passivation and controlled crystallization are also explored and discussed. Collectively, our results show that non-radiative recombination rates are reduced in (FA,GA,Cs)Pb(I,Br) films and prove that FA-GA-Cs alloying is a viable route to attain high $V_{OC}$ in high-bandgap HP solar cells.

References


ET04.12.01 Micro Lasers by Scalable Lithography of Metal-Halide Perovskites Ofer Bar-On1, Philipp Brenner2, Uli Lemmer2 and Jacob Scheuer2; 1Tel Aviv University, Tel Aviv, Israel; 2Karlsruhe Institute of Technology, Karlsruhe, Germany.

Metal-halide perovskites have emerged in recent years as a powerful material system in the field of photonics. Due to their promising electronic and optical properties, tremendous progress has been made in the performance of perovskites solar cells. Rapid progress was also demonstrated in the field of light emitting diodes and lasers. As the field advances, new approaches for patterning perovskite films are becoming essential. More specifically, a lithographic approach that can define desired perovskite patterns is highly needed in order to utilize these materials for the realization of integrated perovskite photon devices.

During the past few years, several attempts have been made in order to address this challenge. Nevertheless, many of the attempts were only partially successful, being unable to remove completely the perovskite from the undesired area, or necessitating slow and serial fabrication techniques which are not...
compatible with mass production. Hence, a complete, efficient and scalable lithographic approach for the patterning of metal halide perovskite films is still highly needed and sought for. Here, we demonstrate a complete lithographic scheme for thin metal halide perovskite films, and utilize it for the realization of perovskite micro lasers. The process consists of nano imprint lithography followed by ion beam milling. The approach is simple, fast, scalable, and exhibits sub-micron resolution. Lines with critical dimensions of <250nm are realized, followed by complete removal of the perovskites in the non-protected areas. The optical properties of the perovskite films are obtained by employing analytical tools as well as by characterizing distributed feedback laser fabricated from these films. It is shown that the material properties are not impaired by the lithographic process. Using this approach, on chip, micro lasers are fabricated. The experimental characterization of these lasers shows that they exhibit low threshold levels and single-mode lasing. To the best of our knowledge this is the first demonstration of complete, high-resolution lithography of perovskite films exhibiting the smallest perovskite features realized using a top-down lithography technique. This process offers a scalable approach for patterning large areas of perovskites devices with tens of nanometers resolution. This is an important tool towards integrated perovskite photonics and is highly applicable also for the fields of photovoltaics, meta-surfaces, electronics and other promising applications.

ET04.12.02
Temperature-Dependent Chemical-Structural Correlation in CHNHPbI3
Yongtao Liu1, Anton V. Jevlev2, Liam Collins2, Miaosheng Wang1, Jong K. Keum1, Alex Belianinov2, Stephen Jesse, Scott Retterer, Kai Xiao, Mahshid Ahmadi1, Bobby G. Sumpter1, Sergei V. Kalinin1, Bin Hu2 and Olga Ovchinnikova2; 1Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Hybrid organic-inorganic perovskites (HOIPs) have been demonstrated as a promising candidate for photovoltaic applications. For efficient and stable photovoltaic devices, it is critical to understand the effects of environment on the material. In this work, we investigate the evolution of chemical distribution as a function of temperature and its correlation to lattice distortion. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS), we reveal the chemical gradient of CHNHI; and Pb into the bulk at room temperature. As temperature increases, the CHNHI; distributes uniformly and PbI2 gradient does not change. These results prompted a further crystal structure study as our earlier investigations revealed a strong interaction between ion segregation and lattice strain. We performed grazing incidence X-ray diffraction (GIXRD) to explore the lattice change in the direction normal to the sample surface by adjusting grazing incidence angle. As expected, the GIXRD results indicate lattice expansion in (110) and compression in (002) directions with the grazing incidence angle increase corresponding to depth increases. Moreover, both chemical and lattice strain gradients decrease as temperature increases. DFT simulations corroborate these results, suggesting a coupling between temperature, lattice distortion, and chemical distribution. Finally, we demonstrated that temperature, lattice distortion, and chemical distribution simultaneously alter photovoltaic performance. These measurements and results offer an in-depth understanding of the extrinsic and intrinsic chemical effects on device performance.

ET04.12.03
ALD of Tin Oxide on Metal Halide Perovskite Photovoltaics
Axel F. Palmstrom1, James A. Raitford2, Rohit Prasanna2, Kevin A. Bush3, Jinhai Tong1, Kai Zhu1, Joseph J. Berry1, Michael D. McGhee1 and Stacey F. Bent1; 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Chemical Engineering, Stanford University, Stanford, California, United States; 3Materials Science and Engineering, Stanford University, Stanford, California, United States.

Metal halide perovskites offer a wide and tunable bandgap, making them promising candidates for top-cell absorbers in tandem photovoltaics. Atomic layer deposition (ALD) is becoming an increasingly prevalent technique for the conformal deposition of metal oxides in perovskite devices, including on top of perovskite materials for improved moisture stability and inorganic carrier selective contacts. We recently reported tin oxide by ALD on top of metal halide perovskites as a dual-purpose layer to achieve electron selectivity and stiffer protection with high optical transmission; this layer was critical to achieving a 23.6% record-efficient monolithic perovskite-silicon tandem devices. Engineering of an ALD charge extraction layer on top of perovskite materials is non-trivial due to interfacial degradation and energy band alignment.

In this work, we aim to understand the ALD precursor-perovskite interactions of the tin oxide ALD system and the role of organic fullerenes at the perovskite-tin oxide interface while establishing a framework for developing alternative perovskite-compatible ALD processes in the future. We show, in the case of tin oxide ALD growth with tetrakis(dimethylamino)tin(IV) and water on FA0.83Cs0.17Pb(I0.83Br0.17)3 perovskite, that perovskite stability is most sensitive to metal organic exposure at elevated temperatures with an onset near 110 °C, resulting in removal of the formamidinium (FA) cation. Transitioning from ALD to pulsed-chemical vapor deposition (pulsed-CVD) tin oxide growth can minimize the degradation effects. Investigation of fullerenes at the perovskite interface shows that thin fullerene layers offer minor improvements to perovskite stability under ALD conditions, but significant enhancement in carrier extraction. We report high efficiency semi-transparent perovskite devices utilizing fullerene materials, however, fullerenes are undesirable due to fabrication cost and poor mechanical stability. Compositional tuning of the perovskite material can improve the fullerene-free device performance. We demonstrate this method with a bromine-rich perovskite phase to enable an 8.2% efficient perovskite device with all-inorganic charge extraction layers.

ET04.12.04
Role of Domain Walls in Halide Perovskite Solar Cells
Jae Sang Yun1, Dohyung Kim2, Da Seul Lee1, Pankaj K. Sharma2, Jincheol Kim1, Anita Houbail1, Martin Green1 and Jan Seidel2; 1School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, New South Wales, Australia; 2Materials Science and Engineering, University of New South Wales, Kensington, New South Wales, Australia.

Organometal halide perovskite solar cells have shown a tremendous improvement in the photoconversion efficiency from 3.8% to 22.7% in recent years. Self-assembling organic-inorganic hybrid materials have been demonstrated to be excellent photovoltaic materials with several superior properties such as high optical coefficient, tuneable bandgap, long carrier diffusion length, and high ambipolar charge carrier mobility. Despite the enormous interest in these materials, many fundamental material properties still remains elusive. Here, we report role of domain walls in halide perovskite film which is systematically investigated using Scanning Probe Microscopy (SPM) techniques. Ion migration is found to be playing a significant role at the domain walls. We examined effect of domains in terms of photovoltaic properties using Kelvin Probe Force Microscopy (KPFM) and conductive AFM (C-AFM). Our findings suggest that these domains walls play a critical role in PV performance. These findings of domain properties can provide a new possibility to understand effect of domains and domain walls in solar cell device.

ET04.12.05
Manipulation of Metal Oxide-Based Electrodes for Semi-Transparent Perovskite Solar Cells
Kai Zhu1, Joseph J. Berry1, Michael D. McGehee3 and Stacey F. Bent2; 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Chemical Engineering, Stanford University, Stanford, California, United States; 3Materials Science and Engineering, Stanford University, Stanford, California, United States.

Due to their high transparency and large bandgaps, transition metal oxides have been widely used in optoelectronic devices, such as light-emitting diodes...
and solar cells, including semi-transparent devices, tandem solar cells, and building-integrated photovoltaics (BIPV). Thermally evaporated molybdenum oxide (MoO₃) has been commonly used as the sputtering buffer material to protect the organic hole transporting layer from damage due to sputtering of the transparent conducting oxide. However, MoO₃ has strong extinction coefficient in the infrared and has detrimental impact on the fill factor, along with uncertain long-term stability. In this talk, we address a bilayer architecture approach for tunable metal oxide-based transparent electrodes through capping the transition metal oxide with a more stable material and possibly altering the electronic properties through a doping effect. Incorporation of this transparent electrode technique to the protective buffer layer significantly enhanced the fill factor from 70.4% to 79.6%, resulting in power conversion efficiencies over 18% for semi-transparent perovskite solar cells. Effects on the morphology, optical and electrical properties, and performance of working devices will be addressed, and the mechanisms involved in the enhanced performance will also be discussed in this presentation.

ET04.12.06
Integration of Electrospun Fibers into Perovskite Solar Cells
Cavit Eyovge; Mesoscale Chemical Systems, MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

Extensive studies performed in the past 5 years showed that power conversion efficiency values over 20% can be reached with perovskite solar cells. This achievement also led researchers to look for different cell architectures, not only for increasing the efficiency but also for extending application area. Electrospinning in that sense can be regarded as a promising method for flexible perovskite solar cell production. It is highly possible to use stacked fibers to form cell layers if one can control the fiber characteristics and deposition pattern. In this study, a modified electrospinning system was used to fabricate electron transport layer for perovskite solar cells, namely ZnO and TiO₂. Linearly aligned fibers of semiconducting oxides were electrospun with 1 kV/cm field strength in between the nozzle and parallel plate structure serving as a collector. Annealing was performed at 500 °C under ambient atmosphere for conversion into oxide. Physicochemical structure and morphology of the fibers were investigated with SEM and XRD. Applicability of the method for all-electrospin perovskite solar cells was also discussed.

ET04.12.07
In Situ Investigation of the Effect of the Lead Film Precursor States and Their Influence on the Conversion to MAPbI₃ Hybrid Perovskite Layers for Solar Cell Applications
Dounya Barrit1, Peirui Cheng2, Ming-Chun Tang1, Hoang X. Dang1, Kai Wang1, Detlef-M. Smilgies1, Kui Zhao2, Thomas Anthopoulos1 and Aram Amassian1; 1King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, China; 3Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York, United States.

Due to their low-cost fabrication, the use of abundant materials and their high power conversion efficiency of 22.1%, metal halide perovskite solar cells are currently attracting tremendous attention as a prime alternative to incumbent photovoltaic technologies. In this work, we use the two-step conversion process to produce high-quality layers of the prototypical hybrid organic-inorganic perovskite MAPbI₃. The processes is simple and involves the reaction of a solution deposited PbI₂ solid layer with MAI to produce the targeted MAPbI₃ film. Particular emphasis is placed on investigating the ink-to-solid conversion during the two-step solution process of PbI₂ from DMF solution by performing in situ grazing incidence wide angle X-ray scattering (GIWAXS) measurements. Obtained results reveal an elaborate sol–gel process involving three PbI₂-DMF solvate complexes—including disordered and ordered ones—prior to PbI₂ formation. The ordered solvates appear to be metastable as they transform into the PbI₂ phase in air within minutes without annealing. Complementary measurements including optical reflectance and absorbance and quartz crystal microbalance with dissipation monitoring (QCM-D) were further used to monitor the solution thinning behavior, changes in optical absorbance and structural, viscoelastic properties during the PbI₂ film formation and its conversion to perovskite film. Results indicate that the conversion of PbI₂ to perovskite is largely dictated by the state of the PbI₂ precursor film in terms of its solvated state which have implications on solar cell manufacturing and overall performance.

ET04.12.08
Analysis for Efficiency Potential of Perovskite Solar Cells
Masafumi Yamaguchi, Kan-Hua Lee, Kenji Aekaki and Nobuaki Kojima; Toyota Technological Inst, Nagoya, Japan.

Remarkable recent advances in perovskite solar cells with efficiencies of over 22% have drawn world-wide as high-efficiency and low-cost solar cells. However, there are some problems to be solved in perovskite solar cells. In addition to improvements in stability, developments in high-efficiency large-area perovskite solar cell modules are very important. Therefore, understanding and reducing non-radiative recombination losses in those materials and solar cells and resistance losses in order to realize higher efficiency perovskite solar cells and modules. In this paper, efficiency potential of perovskite solar cells is discussed based on external radiative efficiency (ERE), open-circuit voltage loss and fill factor loss and non-radiative recombination losses..

One of problems to attain the higher efficiency perovskite solar cells is to reduce non-radiative recombination loss. The open-circuit voltage drop compared to bandgap energy (Eg-Voc) is dependent upon non-radiative voltage loss (Voc, rad) that is expressed by external radiative efficiency (ERE). Open-circuit voltage is expressed by Voc = Voc,rad + (KT/q)ln(ERE), (1) where the second term shows non-radiative voltage loss, and is radiative open-circuit voltage and 0.28V was used as the A value. Voc, rad = Eg/q · Voc,rad value for perovskite solar cells in this study. Correlation between Voc values for perovskite solar cells in the references estimated by eqs. (1) suggests that perovskite solar cells have still non-radiative loss and further improvements in efficiency are thought to be possible by improving minority-carrier lifetime. In addition, reduction in resistance loss is suggested to be decreased. The perovskite solar cells have efficiency potential of 25% by improving ERE from around 0.3%-1% to 20%. Progress steps for efficiency of perovskite solar cells are analyzed. As a result of high quality thin film growth with large grain size and annealing, ERE have been improved from 8 x 10^-10 % to 0.3-1%. By decrease in series resistance and increase in shunt resistance, resistance losses have been reduced from 0.65 to 0.12 with low normalized resistance, rₛ/τₑ. As a result of increases in open-circuit voltage Voc and fill factor FF, conversion efficiency for perovskite solar cells has been improved from 3.8% to 22.7%. However, because perovskite solar cells have still higher non-radiative recombination losses compared to GaAs and crystalline Si solar cells, further improvements in efficiency are thought to be possible by improving minority-carrier lifetime due to reduction in recombination losses and by decreasing resistance losses. Importance of non-radiative recombination loss and resistance loss is also discussed.

ET04.12.09
Doping TiO₂: Electron Transport Layers in Halide Perovskite PV Cells by Combinatorial Material Science
Anat Itzhak1, Adi Kama1, Shalom Avadayev1, Adam Ginsburg1, Hannah Noa Barad1, David A. Keller1, Simcha Meir1, Arie Zaban1 and David Cahen1; 1Chemistry, Bar Ilan University, Ramat-Gan, Israel; 2Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

The optical properties, stability, wide band gap, and a conduction band just a bit deeper than the conduction band of Pb-based halide perovskites (HaP), makes TiO₂ a very good electron transport layer (ETL) in PV solar cells, based on these HaPs. As a result, TiO₂ is the most commonly used ETL in
perovskite (n-i-p structure) solar cells. Here we report on results obtained, from combinatorial materials science, CMS, experiments to optimize the TiO2 ETL layer by doping with other metals, to explore more efficient and stable HaP solar cells. To dope TiO2 with other cations we use CMS, together with high-throughput characterization techniques to examine the effects of different metal cations on the TiO2 ETL layer and, subsequently, on the HaP PV performance. Each measurement is conducted on a ~ 50 cm2 FTO-coated glass, divided into a matrix of 13 x 13 measurement areas (a library), thus measuring 169 different compositions and or thicknesses, to look for trends in the properties. Different ETL mixtures were deposited on a substrate, using a custom-made spray pyrolysis deposition system[1], combining TiO2 with cations, such as Zr4+ or Sr2+. This method of preparation assures a gradient of concentrations across the library. We used scanning EDX to verify the cation concentration at each examined point, and follow the changes in the library. As high-throughput characterization tools we used scanning optical spectroscopy, Kelvin probe, and XRD, to understand the influence of the different cations and their varying concentrations on the doped TiO2 layer. To see how the changes in the ETL affect HaP PV performance, we fabricated complete MA-Pb-trihalide solar cells and used an additional high-throughput method, scanning I-V measurements, to monitor the changes as a function of the type and density of the doping cation.

We will in the presentation report on, and trends how and with which different cations affect the properties of the TiO2 ETL layers and the PV performance of cells made with them.

Reference

ET04.12.10
All Vacuum Processed Large Area Perovskite Solar Cells Using Sputtered NiOx as Hole Transport Layer Wiria Soltanpool1; 2, Gence Bektas1; 2, Mehmet C. Sahiner1; 3, Hava Z. Kaya1, Esra Bag1; 4, Gorkem Gunbas1; 4, 5 and Selen Yerci; 1; 2, 5 1Center for Solar Energy Research and Applications (GÜNAM), Middle East Technical University, Ankara, Turkey; 2Micro and Nanotechnology, Middle East Technical University, Ankara, Turkey; 3Electrical and Electronics Engineering, Middle East Technical University, Ankara, Turkey; 4Polymer Science and Technology, Middle East Technical University, Ankara, Turkey; 5Chemistry, Middle East Technical University, Ankara, Turkey.

Metal halide perovskite solar cells have proven to be an inexpensive yet easy to manufacture photovoltaic technology in the last few years. This is due to numerous reasons including tunable optoelectronic properties along with high power conversion efficiencies beyond 22%. The planar configuration of perovskite solar cells has been especially popular due to its versatile use in tandem devices and over flexible substrates. However, in order to grant large scale fabrication of such devices, they need to be uniform, hysteresis free, viable with large areas, and have acceptable stability. Recently, NiOx has been a favored hole transport layer providing more stable perovskite solar cells. Furthermore, NiOx can be deposited via sputtering to form uniform, compact layer without high temperature treatments. In this study, sputtering power and Ar-pressure were shown to play the key role in suppressing the hysteresis and in achieving high power conversion efficiencies. As Ar-pressure increased, the transparency of NiOx improved while reducing its conductivity. According to our experiments, 16 mTorr of Ar-pressure at an RF-power of 150 W resulted in the best performing devices. A uniform CH3NH3PbI3-XClX layer was deposited via co-evaporation on top of NiOx-coated ITO substrates. The electron transport layer (C60) and BCP/Ag were also evaporated on perovskite lamination at various temperatures is probed. The application of this technique to a mixed-cation and -anion perovskite composition shows the viability of the approach. Currently, solid state perovskite solar cells have achieved 24% efficiency[1] and, as such, large area perovskite devices are currently under the development.

ET04.12.11
Perovskite/Perovskite Lamination of Complex Compositions to Obtain Alternate Phase Spaces Armani Alfaiat1; 3, 4, Sean Dunfield1; 2, Joseph J. Berry1, Matthew O. Rees1, Maikel van Hest1 and Davor Balzar1; 1University of Denver, Denver, Colorado, United States; 2University of Colorado Boulder, Boulder, Colorado, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4Taif University, Taif, Saudi Arabia.

Hybrid perovskites’ low temperature solution processing, extreme tolerance to defects, high absorption coefficients, and long carrier diffusion lengths have drawn much attention from the photovoltaic community, leading to a rapid advance in efficiency from just 3.8% in 2009 to 22.6% today. Despite having many benefits, the standard layer-by-layer solution process commonly used in fabrication creates several limitations in solvent compatibility and thermal budgeting that have prevented the implementation of various device material layer combinations. In order to overcome the aforementioned limitations while maintaining the advantages of the cost-effective solution processing, we recently developed a procedure to create perovskite devices by first fabricating two transparent conductive oxide/transport material/perovskite half stacks and then laminating them together at the perovskite/perovskite interface. Using various techniques, we show that the developed process largely improves the electronic structure, reduces the number of defects, increases the crystallinity, and enhances the properties of MAPbI3. Moreover, we show that the results in a self-encapsulated device format which permits processing above the temperatures allowed in standard fabrication due to its decoupling of the positive effects of annealing with the negative effects of normally-seen thermal degradation. E.g., MAPbI3 films laminated together at 150 °C for 5 days kept black interiors rather than turning yellow, indicating no significant decomposition to Pb2. While shown to work on a standard ABX3 perovskite composition containing methylammonium, the original work forgoes applying the method to more complicated compositions containing multiple chemical constituents at any given site. This work builds off said study, improving the uniformity of pressure and temperature obtained in the lamination process and implementing the process on a more advanced perovskite, [Cs0.85MA0.15FAS1.93]0.85PbI3.5-xBr0.5-xIy] at various temperatures to explore the newly afforded phase space for processing. Through ultraviolet–visible absorption spectroscopy, X-ray diffraction, and time-resolved photoluminescence spectroscopy, the effect of lamination at various temperatures is probed. The application of this technique to a mixed-cation and -anion perovskite composition shows the viability of the process on perovskites prone to phase segregation. Future work will focus on utilizing the procedure to explore compositions and defect-passivating elements not obtainable by traditional solution processing routes.

ET04.12.12
Enhanced Photovoltaic Performance of Perovskite Solar Cells via Defect Passivation by Incorporating the Physisorbed Small Organic Molecule Shivan Smajl1, Sudip Chakaborty1, K. L. Narasimhan2, Parag Bhardwaj3 and Dinesh Kabra1; 1Department of Physics, Indian Institute of Technology Bombay, Mumbai, India; 2Department of Electrical Engineering, Indian Institute of Technology Bombay, Mumbai, India; 3Department of Metallurgical Engineering and Material Science, Indian Institute of Technology Bombay, Mumbai, India; 4Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden.

Perovskite semiconductors are known to have dynamic disorder[2] which is known to affect its recombination dynamics. These defects seem to be created and removed via various processing conditions in literature. Here, we studied the role of small organic molecule, bathocuproine (BCP), as an additive in the CH3NH3PbI3 thin film based photovoltaic devices using optoelectronic measurements and first principle calculation. A solar cell with power conversion efficiency of 16% and fill-factor of 82% with no significant hysteresis is achieved, where BCP not only passivates the bulk and interfacial defects but also shows highly improved electroluminescence efficiency. Addition of BCP into perovskite precursor does not cause any structural change in the 3D structure of perovskite, which is confirmed using time-delayed emission spectroscopy and first principle electronic structure calculations. Furthermore, calculations suggest that a physisorption type of interaction has been found in between MAPI and BCP with an average distance of 2.9 Å. Hence, hydrophobic organic molecule plays an important role in defect passivation to achieve very high fill factor and improving the film

Reference
quality for efficient perovskite solar cells. This study has also shown to work for LED application, hence can be utilized for wider bandgap semiconductors LED application and/or triple cation based 3D perovskite solar cells.

**Keywords:** MAP, Solar cells, Defect Passivation, Physiosorption, Electroluminescence, Moisture Stability.

**Reference:**

**ET04.12.13**
**Double Perovskite Cs2AgBiBr6 Film for Optoelectronic Devices**
**Cuncun Wu; Peking University, Beijing, China.**

Recently, lead-free double perovskites have emerged as a promising environment-friendly photovoltaic material for their intrinsic thermodynamic stability, appropriate band gaps, small carrier effective masses, as well as low exciton binding energies. Herein, we report a first lead-free double perovskite planar heterojunction solar cell with high quality Cs2AgBiBr6, film, fabricated by low-pressure assisted (LPA) solution processing under ambient conditions. The device presents a best power conversion efficiency (PCE) of 1.44%. The preliminary efficiency, the high stability under ambient condition without encapsulation, together with the high film quality with simple processing, show a glimmer of hope for the lead free perovskite solar cell. Hole transport layer free planar heterojunction device based on this film was fabricated for photodetector application. The device is self-powered with two responsivity peaks at 350 nm and 435 nm, which is suitable for ultraviolet-A (320-400 nm) and deep-blue light detecting. A high responsivity of 0.11 A/W at 350 nm and a quick response time of less than 3 ms were obtained, which is significantly higher than other semiconductor oxide heterojunction based UV-detectors.

**ET04.12.14**
**Controllable and Reproducible Doping of Spiro-OMeTAD in the Absence of LiTFSI and Air—Spiro-OMeTAD(TFSI)2 in Perovskite Solar Cells**

**with PCEs Exceeding 19%**

**Boer Tan1, 2 and Udo Bach1, 2, 3; 1Chemical Engineering, Monash University, Melbourne, Victoria, Australia; 2Manufacturing, Commonwealth Scientific and Industrial Research Organisation, Melbourne, Victoria, Australia; 3Melbourne Center for Nano Fabrication, Melbourne, Victoria, Australia.

2,7,7′-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobi fluorene (spiro-OMeTAD) is the dominant hole transporting material (HTM) in high efficiency perovskite solar cells (PSCs). To achieve better photovoltaic performances, the conductivity of pristine spiro-OMeTAD needs to be improved through the addition of dopants. Conventional doping methods use redox inactive ionic compounds, in particular lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and chemical p-dopants, such as tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) (FK209). However, the power conversion efficiency (PCE) and the reproducibility of device performance are contingent on a combination of factors, such as light exposure, ambient air conditions and the concentration of LiTFSI/ FK209. Therefore, the reproducibility of these devices is typically problematic.

In this study, spiro-OMeTAD(TFSI)2 is implemented as a p-dopant in spiro-OMeTAD to reproducibly control the doping level without the need for air exposure and LiTFSI addition. Device performances comparable with conventional LiTFSI doping have been obtained by simply mixing the dopant with spiro-OMeTAD during precursor solution preparation. Unlike the conventional doping method, device performance is less influenced by the environment (oxygen and light). Furthermore, good device performances can be obtained without hygroscopic LiTFSI, which potentially introduces a source of instability in the perovskite device. Remarkably, the reproducibility is strongly enhanced with minimal variation in PCE at the optimized doping concentration. A maximum PCE of 19.3% is achieved in reverse scan with minor hysteresis observed in forward scan with a PCE of 18.1%, performing a stabilized power output of 18.5%. Our comprehensive study of the hole transfer process and device performance enables us to determine the optimum doping concentration and also confirm the influence of the spiro-OMeTAD doping level on device performance. These are critical to highly efficient and reproducible perovskite solar cells.

**ET04.12.15**
**A Machine Learning Algorithm for Analyzing the Crystal Morphology of Perovskite Solar Cells**
**Thomas Chen1; Yi fan Yin2 and Yuchen Zhou; 1Mission San Jose High School, Fremont, California, United States; 2Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States.

Perovskite solar cells (PSCs) are a rapidly evolving photovoltaic technology where performance and crystal grain size are highly correlated. Therefore, there is a constant need to analyze crystal size distributions in SEM images of the perovskite layer of PSCs. This research attempts to automate this process using both machine learning (ML) and non-ML approaches to edge detection. Once the edges of the crystal grains are located, a flood-fill algorithm can be used to find the area distribution. The ML based edge detection uses GNU Octave Programming Software[1] to run a regularized logistic regression algorithm that classifies each pixel of an input image as part of an edge or not part of an edge. The features used for the algorithm are each pixel’s grayscale intensity, its Sobel derivative[2], and second order combinations. Training data is obtained by using non-ML Canny Edge Detection[2] to annotate the edges on a 100X100 pixel SEM image of a PSC modified with 16,000 amu Polyactic Acid at 0.3 mg/mL. The classifier exhibits an 85.2% accuracy, though it has difficulty with edge pixels with a low Sobel derivative. A macro for ImageJ Fiji Software was created to automate a non-ML approach using Sobel edge detection. A Gaussian blur with radius 2 pixels is applied to the 16K 0.3mg/mL image and Sobel edge detection is run. The resultant image is then thresholded to differentiate the brightest 50% of pixels and darkest 50%. Area distributions are found with ImageJ’s particle analyzer. Edge detection was highly accurate, and the macro exhibited high automation. Both approaches offer a quick and automated way to analyze the crystal distributions of perovskite SEM images. The non-ML method exhibits better edge detection and immediate usefulness, but the ML based method requires far fewer operations than its counterpart, making it more efficient in the long run despite the initial time required for training. [1] GNU Octave. (n.d.). Retrieved from https://www.gnu.org/software/octave/ [2] Savant, Shubhashree, (2014). A Review on Edge Detection Techniques for Image Segmentation. International Journal of Computer Science and Information Technologies. 4.

**Acknowledgments:** Funding from the NSF- Inspire Program Grant No. 1344267 and the Morin Foundation Trust is gratefully acknowledged.
Towards Efficient and Stable Mixed Sn-Pb Perovskite Solar Cells

Yanfa Yan; University of Toledo, Toledo, Ohio, United States.

Mixed Sn-Pb perovskite absorber materials have attracted extensive attentions because they offer opportunities to reduce the usage of toxic Pb, tune the bandgap to be more suitable for efficient single-junction solar cell applications, and enable the realization of all-perovskite tandem solar cells. Though significant progress has been made in the past several years, the record powder conversion efficiency (PCE) of mixed Sn-Pb perovskite solar cells is still significantly lower than the theoretical maximum PCE. Furthermore, the study of stability of mixed Sn-Pb perovskite solar cells is rarely reported. In this talk, we will present detailed analysis of the possible factors that limit the PCEs of mixed Sn-Pb perovskite solar cells and discuss possible solutions for overcoming the limitations. Furthermore, we will discuss the stability issues that mixed Sn-Pb perovskite solar cells may encounter.

New Materials, Systems and Applications with Halide Perovskites

Ivan Mora-Sero; Institute of Advanced Materials (INAM), Universitat Jaume I, Castello de la Plana, Spain.

Halide perovskite have demonstrated an outstanding performance for the development of photovoltaic devices. This excellent behavior is based, among others, in a benign defect physics producing low non-radiative recombination, making halide perovskite also enormously appealing for the development of other optoelectronic devices as LEDs or lasers. While first studies focused just in conventional hybrid halide perovskite materials with general formula ABX₃, (where A=methylammonium, formamidinium, Cs, X-Pb, Sn, X-I, Br, Cl) and just in photovoltaic devices, the current interest has been extended. A broader range of material compositions are now investigated and not just with 3D structure but also layered perovskites or as nanoparticles. These systems also are awaking a great interest as very high photoluminescence quantum yield can be obtained with relative easy synthesis processes. In addition, multiple materials are also analyzed as selecting contact layers. In this talk, I present non-conventional perovskite materials and contacts for photovoltaics and optoelectronic applications. The structural, chemical, electric and optical properties of materials and devices have been systematically characterized, highlighting the interest of these new systems for further development of perovskite technology. A new hole selective contact based on a fullerene derivative a new family of 2D/3D perovskites using conjugated anilinium as long organic cation will be introduced. The development of optical amplifiers based on halide perovskites and the use of the perovskite nanoparticles for the development of optoelectronic devices will be also discussed.

Estimating Oxidised Sn⁴⁺ Species at the Precursor Stage—On the Effect of Reducing Agents in Sn-Based Perovskites

Muhammad Akmal Kamarudin1, Kohei Nishimura1, Daisuke Hirotani1, Qiang Shen2, Taro Toyoda1, Satoshi Ikubo1, Takashi Minamoto3, Kenji Yoshino3 and Shuji Hayase3; 1Kyushu Institute of Technology, Kitakyushu, Japan; 2The University of Electro-Communications, Chofu, Japan; 3Ritsumeikan University, Kusatsu, Japan.

The poor opto-electronic properties often associated with tin (Sn) halide perovskites are usually ascribed to the oxidation of Sn⁰ to Sn⁴⁺. Due to the generation of Sn⁰ vacancies upon oxidation that limit the electron and hole diffusion lengths to 30 nm by acting as scattering centres, it remains challenging to obtain highly efficient Sn-based perovskite solar cells in planar as well as mesoporous device architectures. Theoretical calculations corroborate that reducing the background hole concentration by suppressing oxidation could allow favourable opto-electronic properties for these materials with diffusion lengths approaching 1 micron. Nevertheless, innovative approaches based on reducing agents remain rather limited as only inadequate fractions of these compounds are tolerated in the formation of the desired efficient absorbers. Hence, it remains particularly challenging to maintain a stoichiometric solution for the development of highly efficient Sn-based perovskite solar cells.

Having demonstrated vast potential as a narrow bandgap rear-cell in perovskite-perovskite tandems, the optimisation of Sn (and thereby Pb-Sn mixed) perovskites is of particular relevance as currently all-perovskite multi-junction solar cells are being envisioned— with reports of theoretical performances surpassing 45%. To that end, this work focuses on the extent of oxidation present in supposedly pristine precursor solutions—an aspect currently not profoundly professed in literature. Based on observed changes in morphology, crystallinity and optoelectronic properties of films obtained from corresponding solutions, an efficient method is discussed to estimate the early-on degradation induced at the precursor stage. The quantification can be used as an effective tool to characterise and extend the effect of reducing agents, and thereby assist in enhancing the performance of Sn-based solar cells.

Towards Efficient and Stable Mixed Sn-Pb Perovskite Solar Cells

Muhammad Akmal Kamarudin1, Kohei Nishimura1, Daisuke Hirotani1, Qiang Shen2, Taro Toyoda1, Satoshi Ikubo1, Takashi Minamoto3, Kenji Yoshino3 and Shuji Hayase3; 1Kyushu Institute of Technology, Kitakyushu, Japan; 2The University of Electro-Communications, Chofu, Japan; 3Ritsumeikan University, Kusatsu, Japan.

The low performance of tin-based perovskite solar cells is attributed to the tendency of Sn²⁺ to oxidize to Sn⁴⁺ resulting in higher charge carrier concentration. This oxidation process also leads to the degradation of the perovskite solar cell over time even in N₂ atmosphere and much so in ambient atmosphere. To this effect, we have successfully employed GeBr₃ as passivation layer which could extend the lifetime of PSCs in air, in addition to reducing the charge carrier concentration. The performance of GeBr₃-doped perovskite solar cell achieved a high efficiency of 4.2 % compared to 2.9 % for FASnI₃Ma₂SnI₉ when measured in air. The increased in efficiency comes from the significant increase of short circuit current due to the reduction of charge carrier concentration. The reduction of trap states upon addition of GeBr₃ has also been confirmed by thermally stimulated current measurement. The formation of monolayer GeO₂ reduced the surface oxidation of the perovskite and helped to improve the air stability of the perovskite solar cell even without encapsulation. This work provides a platform of fabricating air stable tin perovskite solar cells with high efficiency.

Towards Efficient and Stable Mixed Sn-Pb Perovskite Solar Cells

Muhammad Akmal Kamarudin1, Kohei Nishimura1, Daisuke Hirotani1, Qiang Shen2, Taro Toyoda1, Satoshi Ikubo1, Takashi Minamoto3, Kenji Yoshino3 and Shuji Hayase3; 1Kyushu Institute of Technology, Kitakyushu, Japan; 2The University of Electro-Communications, Chofu, Japan; 3Ritsumeikan University, Kusatsu, Japan.

The low performance of tin-based perovskite solar cells is attributed to the tendency of Sn²⁺ to oxidize to Sn⁴⁺ resulting in higher charge carrier concentration. This oxidation process also leads to the degradation of the perovskite solar cell over time even in N₂ atmosphere and much so in ambient atmosphere. To this effect, we have successfully employed GeBr₃ as passivation layer which could extend the lifetime of PSCs in air, in addition to reducing the charge carrier concentration. The performance of GeBr₃-doped perovskite solar cell achieved a high efficiency of 4.2 % compared to 2.9 % for FASnI₃Ma₂SnI₉ when measured in air. The increased in efficiency comes from the significant increase of short circuit current due to the reduction of charge carrier concentration. The reduction of trap states upon addition of GeBr₃ has also been confirmed by thermally stimulated current measurement. The formation of monolayer GeO₂ reduced the surface oxidation of the perovskite and helped to improve the air stability of the perovskite solar cell even without encapsulation. This work provides a platform of fabricating air stable tin perovskite solar cells with high efficiency.
layered 2D Ruddlesden-Popper perovskites, as shown from the investigation of both thin films and small exfoliated single crystals. Wannier exciton at room temperature. However, solar cells or LED device efficiencies are related to internal exciton dissociation through edge states in activation energy calculated to be 0.4 eV (in the range of many literature values for iodide migration). However, it takes place at a much slower rate due to the carbon devices the exceptionally slow dynamic behaviour observed at room temperature has a similar origin linked to the effects of ion migration – structure-device measurements are critical for understanding optoelectronic transport and determine the design principles for operation of perovskite-based to discover new emergent functionalities. Therefore, a basic principle on the interplay between structure, light and electrical field with in-situ correlated

The improvement in stability is easily understood: 2D perovskite consists of inorganic blocks separated by bulky organic cations. These organic cations act 2D Ruddlesden-Popper perovskites have improved the stability of fabricated solar cells, but their efficiency is reduced compared to 3D bulk perovskite. We show that the inhibited ion migration is the dominant affect rather than the AVA having a direct impact at the TiO2 interface by adsorption via the carboxylic acid group. This inhibition of iodide migration is also linked to the increased stability demonstrated for these devices.

Negative transient was shown to diminish over time as ions in the perovskite redistributed, leading to a reduction in the recombination rate. We show that in the TiO2 surface. The cells undergo a slow light soaking effect during which time the JV performance of the device is vastly improved. They also show promise for scale-up and wide spread implementation. To improve these devices and begin to challenge inorganic PV record efficiencies a deeper understanding of their operation, and in particular sources of performance loss, is needed.

In my talk, I will focus on understanding these complex behaviors arising from the interaction between structure, light and electric field in both 3D and 2D hybrid perovskite systems by using different device platforms such as photovoltaics, field-effect transistors and light emitting diodes to understand these correlations. Our studies are aimed toward utilizing this fundamental understanding to develop new behaviors and device concepts using perovskite materials.

In the past five years, solution-processed organometallic perovskite based solar cells have emerged as a promising thin-film photovoltaic technology. Presently, the intended optoelectronic applications of this class of 3D materials are in the realm of conventional semiconductors. The presentation will present recent theoretical, spectroscopy and diffraction results on monocrytals of halide perovskites, colloidal nanocrystals or thin-films. Related 2D multilayered phases, composed of perovskites multilayers sandwiched between two layers of large organic cations, have recently demonstrated improved solar cells photostability under standard illumination as well as humidity resistance over 2000 hours, leading to a conversion efficiency of 12.5 %. In this case, intrinsic quantum and dielectric carrier conﬁnements are afforded by the organic inner barriers, which lead to a stable Wannier exciton at room temperature. However, solar cells or LED device efficiencies are related to internal exciton dissociation through edge states in layered 2D Ruddlesden-Popper perovskites, as shown from the investigation of both thin films and small exfoliated single crystals.

In carbon based cells the phenomena is observed at room temperature and is very slow to disappear under continued illumination. For the planar devices the negative transient was shown to diminish over time as ions in the perovskite redistributed, leading to a reduction in the recombination rate. We show that in the carbon devices the exceptionally slow dynamic behaviour observed at room temperature has a similar origin linked to the effects of ion migration – activation energy calculated to be 0.4 eV (in the range of many literature values for iodide migration). However, it takes place at a much slower rate due to the 2D AVA based perovskite hindering iodide ion migration – attempt frequency reduced by several orders of magnitude compared to pure MAPI devices. We show that the inhibited ion migration is the dominant affect rather than the AVA having a direct impact at the TiO2 interface by adsorption via the carboxylic acid group. This inhibition of iodide migration is also linked to the increased stability demonstrated for these devices.

Charge Transport Mechanisms in Vertically Stacked 2D Ruddlesden-Popper Perovskite Solar Cells—Theory and Experiments Reza Asadpour, Hsinhan Tsa1,2, Wanyi Nie2, Aditya D. Mohite2, M.Ashraf Alam2; 1Purdue University, West Lafayette, Indiana, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Material Science and Nano Engineering, Rice University, Houston, Texas, United States.

2D Ruddlesden-Popper perovskites have improved the stability of fabricated solar cells, but their efficiency is reduced compared to 3D bulk perovskite. The improvement in stability is easily understood: 2D perovskite consists of inorganic blocks separated by bulky organic cations. These organic cations act
as intrinsic passivation and prevent moisture ingress hence higher stability [1]. Unfortunately, these cations also lead to localized quantum confinement effects that influence the optical and electrical behavior of the material [2]. In this talk, we will discuss how we quantified the transport of conduction electrons, holes, and photons by interpreting the thickness-, temperature-, and illumination-dependent efficiencies of these 2D solar cells. The detailed understanding of optoelectronic and charge transport mechanisms in these structures will guide the future efforts in creating perovskite solar cells that are simultaneously highly efficient and highly stable.

References:

11:15 AM ET04.13.09
Two-Dimensional Tin-Based Hybrid Halide Perovskites for Photovoltaics Zhenyu Wang1, 2, Alex M. Ganose2, 3, Chunming Niu4 and David O. Scanlan2, 3, 4.
1School of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China; 2Department of Chemistry, University College London, London, United Kingdom; 3Thomas Young Centre, University College London, London, United Kingdom; 4Diamond Light Source Ltd., Diamond House, Oxfordshire, United Kingdom.

The drive towards reduced costs, higher conversion efficiencies and environmentally friendly solutions to current photovoltaic technologies is immensely important in the search to relieve the world’s reliance on fossil fuels and promote sustainable economic development. Since the first reports of solid-state hybrid perovskite solar cells in 2012, power conversion efficiencies (PCEs) have increased dramatically up to 22.7%. Despite the rapid rise in efficiencies of the hybrid lead perovskite such as CH3NH3PbI3 (MAPbI3), their poor long-term stability and the toxicity of water-soluble lead compounds, necessitates the development of alternative lead-free halide perovskite materials with improved moisture tolerance.

Although 2D hybrid halide perovskites have been known since they were first synthesized by Mitzi et al. in 1994, they were not investigated as solar cell absorbers until Smith et al. found the 2D perovskites to be more resistant to moisture than their 3D analogues. Additionally, environmental concerns can be addressed by replacing Pb with less toxic elements, such as Sn and Ge. The band gaps of the 2D series generally decrease monotonically with increasing perovskite-like layer thickness, finally tending to that of corresponding 3D perovskite. In this way, the 2D hybrid perovskites have attracted increasing attention and witnessed a sharp rise in efficiency over the past two years, with champion devices (containing (PEA)2(MA)59Pb60I181) showing efficiencies of 15.3%. For the reasons, 2D perovskites are promising candidates for solar cell absorbers.

In this work, we investigate the geometrical, electronic and optical properties of the semiconductor 2D tin-based perovskites (CH3(CH2)3NH3)3(CH3NH3)2SnI6+1-x (n = 1, 2, 3), using relativistic hybrid density functional theory calculations. We demonstrate that the band gaps of the series decrease with increasing perovskite-like layer thickness, from 1.85 eV (n = 1) to 1.38 eV (n = 3). We find strong and broad optical absorption across the series, in addition to highly effective masses of electrons and holes in the laminar plane. The low n tin-based 2D perovskites should possess the best of both worlds, with optimal band gaps but improved moisture stability. Particularly, the n = 3 composition displays a high spectroscopic limited maximum efficiency (SLME) of 24.6%. Our results indicate this series of homologous 2D tin halide perovskites are a promising class of stable and efficient light-absorbing materials for photovoltaics.

Organic–inorganic lead-based halide hybrid perovskites have attracted immense attention because of their extraordinary optoelectronic properties. Beyond the traditional low bandgap hybrid perovskite solar cells, namely MAPbI₃, the wide bandgap MAPbBr₃₋ₓClₓ perovskite is demonstrated to realize a wide and tunable bandgap ranging from 2.3 eV to 3.1 eV (x = 0 to 3), leading it suitable not only for semitransparent and transparent perovskite solar cells, but also blue and ultraviolet light emitting diode and photodetector applications. In this contribution, we compare and contrast the crystallization kinetics and growth behaviors of wide and tunable bandgap MAPbBr₃₋ₓClₓ to conventional MAPbI₃ from precursor inks to solid-state thin films using the one-step spin coating approach. We employ a multi-probe in situ investigation method consisting in grazing incidence wide-angle x-ray scattering (GIWAXS) and time-resolved UV-Vis absorbance complemented with ex situ characterization of wide and tunable bandgap hybrid perovskite thin film morphology and solar cell performance. Obtained results reveal that the tunable and wide-bandgap MAPbBr₃₋ₓClₓ perovskite phase forms directly from disordered solvate during solution processing, while MAPbI₃:ink tends to form intermediate ordered phases requiring further thermal annealing to form perovskite phase. Furthermore, we disclose the role of anti-solvent dripping is to not only benefit the morphology of perovskite thin film but also pre-nucleate and promote wide-bandgap MAPbBr₃₋ₓClₓ perovskite phase formation. We use this insight to develop a solvent engineering protocol suitable for depositing fully cover and pin-hole-free high-quality MAPbBr₃₋ₓClₓ hybrid perovskite thin films and present working single junction photovoltaics with high open circuit voltage > 1.6 V and promising future for transparent hybrid perovskite solar cells.
Organic-inorganic halide perovskite solar cells (PSCs) have been considered a viable member of next generation photovoltaics, which can address the scalability changes with a low-cost solution process. The perovskite layer is the main source of photogenerated electron-hole pairs in PSCs. The energetic loss in the hybrid system has been approved to be principally caused by traps at grain boundaries and surfaces as well as point defects such as interstitial defects or vacancies in the perovskite compounds crystal lattice. Therefore, the first concern in PSCs is constructing a highly crystallized and defect-free perovskite thin film with full surface coverage, smooth, and ordered crystallography with big crystal grains. In this study, we observe a significantly enhancement in power conversion efficiency (PCE) of photovoltaic device by incorporating a small amount of polycaprolactone (PCL) into the perovskite layer. The long-chain PCL polymer can serve as an efficient passivating agent in the bulk film, due to the formation of weak coordination bonds between Pb\(^{2+}\) and the O in the ester group of PCL. Furthermore, the PCL polymer with small volume can participate in the nucleation step as heterogeneous nucleus and help reduce interfacial energy, which eventually promotes the growth of each crystal grain. As evidenced from the surface scanning electron microscopy (SEM) images, the average crystal grain size of the perovskite layer with PCL addition increases significantly, as compared with the PCL free sample. The enhanced absorption intensity from UV-vis spectra after the incorporation of PCL indicates the increase of film thickness as well as the light absorption ability. X-ray diffraction (XRD) results prove the purity and high crystallinity of tetragonal (14 mm) MAPb\(_x\) perovskite phase of the PCL passivated perovskites with no sign of PbI\(_2\) peaks, while signal of trace amount PbI\(_2\) are seen on the PCL free perovskite layers. Moreover, provided by steady-state and time-resolved photoluminescence (TRPL) results, addition of PCL increases the emission intensity and prolongs the charge carrier lifetime of the perovskite layer, which largely results from reduced surface/boundary defects/traps as well as minimized corresponding non-radiative recombinations due to the passivation of the crystal grains by PCL. As a result, the perovskite thin films with proper amount of PCL addition exhibits superb device performance with PCE of the champion device surpassing 18%, indicating a more than 20% enhancement to the original devices. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

SnO\(_2\) Quantum Dot Electron-Selective Layer for High-Performance Perovskite Solar Cells

Zhiliang Chen, Guang Yang and Guojia Fang; Wuhan University, Wuhan, China.

The carrier concentration of the electron-selective layer (ESL) and hole-selective layer can significantly affect the performance of organic-inorganic lead halide perovskite solar cells (PSCs). Herein, a facile yet effective two-step method, i.e., room-temperature colloidal synthesis and low-temperature removal of additive (thiourea), to control the carrier concentration of SnO\(_2\) quantum dot (QD) ESLs to achieve high-performance PSCs is developed. By optimizing the electron density of SnO\(_2\) QD ESLs, a champion stabilized power output of 20.32% for the planar PSCs using triple cation perovskite absorber and 19.73% for those using CH\(_3\)NH\(_3\)PbI\(_3\) absorber is achieved. The superior uniformity of low-temperature processed SnO\(_2\) QD ESLs also enables the fabrication of \( \approx \)19% efficiency PSCs with an aperture area of 1.0 cm\(^2\) and 16.97% efficiency flexible device. The results demonstrate the promise of carrier-concentration-controlled SnO\(_2\) QD ESLs for fabricating stable, efficient, reproducible, large-scale, and flexible planar PSCs.

Photovoltaic Efficiency of CsPbI\(_3\) QDs-Based Solar Cell Exceeding 13%

Yuwei Liu; State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China.

The emergence of organic-inorganic hybrid lead halide perovskites has received the impressive power conversion efficiency (PCE) over 22% within a few years [1]. However, the long-term stabilities of perovskite materials, including the durability under humid, thermal, UV radiation and other environmental conditions, are still poor due to the organic components, which are becoming to be the major challenges for their commercialization [2]. α-CsPbI\(_{3}\), as an all-inorganic lead halide, has been reported recently and exhibited excellent optoelectronic property and good stability, which is regarded as an outstanding alternative to organic-inorganic hybrid lead halide perovskites and a promising light-harvesting absorber for solar cell application [3]. Quantum dot-induced phase stabilization is believed to be an effective procedure to get α-CsPbI\(_{3}\) and suppress the formation of orthorhombic phase (α-CsPbI\(_{3}\)). Protesescu et al. have provided a hot-injection method for the preparation of high quality α-CsPbI\(_{3}\) quantum dots (QDs) [4]. α-CsPbI\(_{3}\) QDs based solar cells are reported by Luther and co-workers subsequently, which receive a high PCE over 13% [5]. However, the short-circuit current density (JSC) is still low at present, which restrains the performance of CsPbI\(_{3}\)-based solar cells. In the work, α-CsPbI\(_{3}\) QDs were prepared by hot-injection method, and high performance inorganic perovskite quantum dot-based solar cells over 13.78% was fabricated, and the optimized device achieved a highly reproducible champion PCE of 13.05% with a high short-circuit current density (18.68 mA cm\(^{-2}\)). This work provides an effective strategy for boosting high performance for all-inorganic lead halide PSCs.

References

Hydroscopic Polymer Passivation Improving Durability of Perovskite Solar Cells

Min Kim, Min Kim, Silvia G. Motti, Roberto Sorrentino and Annamaria Petrozza; \(^{1}\)Physics, Politecnico di Milano, Milan, Italy; \(^{2}\)CNST, Istituto Italiano di Tecnologia, Milan, Italy.

Long-term device instability is one of the most critical issues that impede perovskite solar cell commercialization. Here we show that a thin layer of a functional hydroscopic polymer on top of the perovskite thin film can make perovskite-based solar cells highly stable under illumination and in a humid atmosphere. We prove that the oxygen atoms in hydroscopic polymer chemically interact with lead atoms on the perovskite surface, thus passivate undercoordinated defect sites. Importantly, the defect healing effect leads to an improved photo-voltage and photo-stability. Overall, such interface engineering leads to highly durable perovskite solar cell, which, in the presence of polymer passivation, retained more than 95% of initial power conversion efficiency over 15-h illumination, under load, in the ambient atmosphere without encapsulation. Our findings experimentally reveal the role of defects in
triggering the instability of perovskite materials and propose a general approach for improving the reliability of perovskite-based optoelectronic devices.

3:00 PM BREAK

3:30 PM ET04.14.07

A Simple Molecular Reactive Force Field and Its Application to Perovskite Nucleation

Henry C. Herbol¹, Gregory Casee², Oluwaseun Romiluyi², Wang Guo¹, Jace Chaudhuri¹ and Paulette Clancy²; ¹Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²Chemical Engineering, Cornell University, Ithaca, New York, United States.

In recent years, research into Hybrid Organic-Inorganic Perovskites (HOIPs) has led to numerous experimental and computational insight into the effects of composition, stoichiometry, and solution processing on the overall Photo Conversion Efficiency (PCE) and stability of HOIP thin-films. Computationally, effort has been primarily focused towards time-intensive Density Functional Theory (DFT) simulations: due to the lack of Force Fields for Molecular Dynamics (MD) studies. As such, some of the benefits of a computational approach, such as atomic scale revelations on nucleation, have been hindered. An easy to parameterize reactive force field would empower computationalists to probe these nucleation mechanisms, and help validate/guide experiments; however, as of yet none exists.

In this talk, we present updates to the Simple Molecular Reactive Force Field (SMRFF), and demonstrate initial capabilities as applied to Nanoparticle nucleation (PSN). Further, we illustrate the ease of use, parameterization procedure, and how the force field can be extended. SMRFF takes the idea of hybridizing force fields to the next step, and elaborates on how to smoothly transition between force fields based on interatomic distances. Further, it allows for as many transitions as possible, implying a fully extensible and customizable approach to force field development. A pair style, written to work in the popular LAMMPS codebase, implements the procedure, and an accompanying python script automates the process of developing new parameters.

3:45 PM ET04.14.08

Tandem Hybrid Organic-Inorganic Photocathode-Perovskite Solar Cell for Unassisted Solar Fuel Production

Antonio Alfano1, 2, Alessandro Mezzetti¹, Francesco Fumagalli¹, Chen Tao¹, Maria Rosa Antognazza¹, Annamaria Petrozza¹ and Fabio Di Fonzo¹; 1Istituto Italiano di Tecnologia, Milano, Italy; 2Physics, Politecnico di Milano, Milan, Italy.

Molecular hydrogen produced via solar energy is emerging as a prominent way to convert and store the copious energy that the Sun daily irradiates on Earth. Hybrid Organic photoelectrochemical (HOPEC) water splitting is gaining momentum in this field, and various approaches are currently being developed to realize hybrid tandem systems to perform unbiased water splitting. By taking advantage of the organic semiconductors properties such as low cost, stability, tuneable electronic properties and ease of large area production, these materials can help overcoming the limitations of standard inorganic photoelectrochemical water splitting. The potential of hybrid organic systems has been proven by our previous works. Indeed, excellent photocurrent performances or extended operational lifetime have been obtained through careful optimization of hybrid photocathodes (PC) architecture. Good results have also been achieved investigating novel materials belonging to the family of transition metal dichalcogenides which fit for hole selective layers (HSL) application, allowing to deliver good performances both on stability and photocurrent.

Our main interest is now to tune the properties of hybrid organic PC acting on their photoactive layer, taking advantage of the latest advancements in the field of organic photovoltaic (OPV). Promising materials from OPV are, among many, the high-performance photo-absorbers PCE11 and PCDTBT, and the non-fullerene acceptors IDTBR and IDFBIR, which were found to be responsible of a sharp increase in the open circuit voltage in OPV devices. Their improved electronic properties and optimized band gap are here exploited to realize hybrid PC specifically designed to be coupled in a tandem configuration with a high performing perovskite, realizing a full water-splitting system with cheap, easily processable and suitable for large area production materials. By modifying the hybrid PC, it was possible to extend the absorption range of the stack. Taking advantage of the high Voc of the perovskite and the additional photovoltage coming from the PC, the system efficiently performs the full water splitting reaction without the application of any external bias. The results clearly indicate that the Solar To Hydrogen (STH) efficiency of the system increases sensitively when proper design of the tandem system is achieved, with STH above 2% for the best performing case. These results prove that a tandem hybrid organic perovskite-photocathode stack can be used to realize efficient photoelectrochemical systems for solar fuels production, unlocking a new field of application for these excellent performing class of materials.


4:00 PM ET04.14.09

Copper Complexes Redox Couple as Solid-State Hole Transporting Material for Perovskite Solar Cells

Jacopo Benespori, Hannes Michaels and Marina Freitag; Institutionen för kemi - Ångström, Uppsala University, Uppsala, Sweden.

Perovskite solar cells (PSCs) have been extensively studied in the past six years. The development of effective deposition methods for this material have lead to devices rivaling in efficiency – at least at the laboratory scale – with silicon-based solar cells, at a fraction of the cost. The introduction in recent years of mixed cation perovskite materials has also started to address what is nowadays the main issue of this technology: long-term stability. While there has been an evolution of the perovskite layer in the past lustrum, the same cannot be said about another essential layer in PSCs – the hole transporting one. Spiro-OMeTAD, first introduced in solid-state dye-sensitized solar cells (DSSCs) and then employed at the beginning of the solid-state PSCs era is, in fact, still considered the material of choice for this particular component of a device. This fact is not due to a lack of research effort. In the past four years almost two hundred new hole transporting materials (HTMs) have been developed for PSCs and, despite the fact that some were claimed to perform better than spiro-OMeTAD itself, none managed to become widely employed by the larger research community. Although spiro-OMeTAD’s successor has not been found yet, its replacement is paramount for PSC commercialization. Spiro-OMeTAD is known to be very expensive, which in part nullifies the inexpensive nature of the perovskite material. More importantly, however, spiro-OMeTAD is known to introduce stability issues inside PSC devices, greatly reducing their life. This is in part due to spiro-OMeTAD’s properties themselves, in part due to all the additives and dopants embedded in the spiro-OMeTAD film to improve its poor conductivity and film-forming properties.

To date, little research has been focused on transition metal coordination complexes, and especially metal complex redox couples, as HTM for PSCs. Metal complexes are known to be generally conductive and stable compounds, with their energy level easily tuned by changing the metal center or by applying small modifications to the organic ligand. They have been shown to perform very well in liquid DSSCs and they have recently been successfully employed in solid-state DSSCs. A proof of concept, with mixed results, has also been demonstrated for PSCs. Here, we employ a copper(I/II) complexes redox couple in devices featuring a mixed cation perovskite light absorber. These copper complexes feature good energy alignment with the perovskite material.
and good conductivity.


4:15 PM ET04.14.10
Hole Extraction from Lead Halide Perovskite to PDPP-3T Probed by Ultrafast Transient Absorption Spectroscopy
Jafar I. Khan1, Esma Ugur1, Erkan Aydin1, Mindaugas Kirkus1, Marios Neophytou1, Iain McCulloch1,2, Stefan De Wolf1 and Frédéric Laquai1; 1King Abdullah University of Science and Technology, Jeddah, Saudi Arabia; 2Imperial College London, London, United Kingdom.

Solution-processed metal-halide perovskite solar cells (PSCs) have received immense attention in the field of photovoltaics due to their high power conversion efficiency (PCE) of now more than 22% reached in a relative short time. Today, various electron and hole transport layers (HTLs) have been implemented to further enhance the device performance and stability. State-of-the-art PSCs use spiro-OMeTAD as HTL in n-i-p device structures, however, doping with both tBP and Li-TFSI is required to increase the hole mobility and conductivity of the HTL and achieve optimum performance. Long-term stability of devices is severely limited by Li-TFSI doping because of its hygroscopic nature. Here, as an alternative to spiro-OMeTAD, we used the high molecular weight solution-processed polymer PDPPP-3T and demonstrate comparable performance to spiro-OMeTAD. Furthermore, we are interested in the dynamics of hole extraction from the perovskite to the HTL and interfacial recombination of charge carriers at the perovskite/HTL interface, which we studied by ultrafast transient spectroscopy. We show that the ground state bleach of the polymer allows direct optical probing of the carrier extraction and recombination dynamics. Hole transfer takes place from the perovskite to the HTL in tens of nanoseconds when the sample is excited from the perovskite side. By varying the perovskite film thickness from 170 nm to 570 nm, we investigate the diffusion of holes in the perovskite absorber layer, when PDPPP-3T is used as HTL. Finally, we discuss the dynamics of carrier recombination at the PDPPP-3T/perovskite interface.

4:30 PM ET04.14.11
Modification of TiO2/CH3NH3PbI3 Interface with KCl, KI, or KBr in Planar Perovskite Solar Cells
Amrita Yasin, Adam Pockett, James McGetrnick, Stoichko Dimitrov, Catherine S. De Castro, Matthew Davies, Matt Carnie, Trystan Watson and Cecile Charbonneau; Swansea University, Cardiff, United Kingdom.

This work showcases our research on modification of compact TiO2 electron transport layers (ETLs) at the TiO2/CH3NH3PbI3 interface for application in planar lead halide perovskite solar cells. Compact TiO2 ETLs were formed via spraying of a commercially available titanium diisopropoxide bis(acetylacetonate) precursor on fluorine-doped tin oxide (FTO) glass followed by annealing at 550 °C. These layers were subsequently spin coated with aqueous solutions of 10 mM and 40 mM of KX (X = Cl-, I-, Br-, prior to CH3NH3PbI3 deposition. Presence of potassium and the X- ions on the TiO2 surface is evident via X-ray photoelectron spectroscopy (XPS) analysis, and individual crystals can be seen on the modified TiO2 films. The absorbance and photoluminescence spectra of TiO2/KX/CH3NH3PbI3 films do not show significant difference, however the work function of the modified TiO2 film decreases. Against a stabilized power conversion efficiency of 8.25% in the reverse direction for unmodified planar devices, KI modified devices reach up to 5.13%, followed by KBr at 4.82%, and finally KCl at 3.89%. The change in efficiency can be correlated with a change in work function of the modified films.

4:45 PM ET04.14.12
Gas-Solid Reaction Based over 1 μm Thick High-Quality Stable Perovskite Films for Efficient Solar Cells and Modules with High Reproducibility
Zonghao Liu1, Longbin Qiu1, Emilio J. Juarez-Perez1, Zafer Hawash1, Taehoon Kim1, Yan Jiang1, Zhifang Wu1, Sonia R. Raga1, Luis K. Ono1, Shengzhong Liu1 and Yabing Qi1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Shaanxi Normal University, Xi’an, China.

Organic-inorganic halide perovskite solar cells (PSCs) have drawn a great deal of attention in the photovoltaic research community due to their high efficiency over 23%. Besides high efficiency, the stability and reproducibility of PSCs are also key for their commercialization.1 Here, we report a simple perovskite formation method to fabricate perovskite films with thickness over one micrometer in ambient condition on the basis of the fast gas-solid reaction of chlorine incorporated hydrogen lead triiodide and methylamine gas. The comprehensive characterization results reveal that with the synergistic effect of methylamine gas and partial substitution of iodine ions by chorine ions, the resultant perovskite films with a thickness over one micrometer and low thickness variation exhibit excellent film quality. The resultant PSCs gave an average power conversion efficiency (PCE) of 19.1% and low PCE standard deviation (+ 0.4%), which indicates the excellent reproducibility of this method. Meanwhile, this method enables a best active-area PCE of 15.3% for 5 cm × 5 cm solar modules and good reproducibility (13.6 ± 0.8%). Besides, the un-encapsulated PSCs exhibit an excellent T80 lifetime exceeding 1600 h under continuous operation conditions in dry N2 environment. Our study not only provides a highly reproducible method to fabricate PSCs and modules with enhanced efficiency, reproducibility and stability, but also offers the in-depth understanding for the underlying mechanisms responsible for device stability improvement. The encouraging results in this work points out a promising direction, i.e., use of thick absorber films to realize PSCs and modules with high efficiency, reproducibility and stability.2

References

SYMPOSIUM ET05

Fundamental Aspects of Halide Perovskite (Opto)electronics and Beyond
November 26 - November 30, 2018

Symposium Organizers
Ivan Mora-Sero, Universitat Jaume I
Unsolved Mysteries of Halide Perovskites
Aron Walsh; Imperial College London, London, United Kingdom.

Perovskites are the wonder compounds of materials science, with examples of dielectrics, semiconductors, metals, and superconductors. This talk will address the chemical and physical properties that make halide perovskites unique. Following six years of intensive research, there has been a number of breakthroughs in understanding, but many challenges and opportunities remain.

These organic-inorganic semiconductors satisfy the optoelectronic criteria for an active photovoltaic layer, i.e. spectral response in the visible range combined with light electron and hole effective masses. In addition, they are structurally and compositionally flexible with large dielectric constants, and the ability to alloy on each of the lattice sites. To understand the success of methylammonium lead iodide photovoltaics, we have been applying materials theory and simulation across multiple length scales [1-5].

I will discuss issues ranging from disorder associated with molecular rotations and tilting of the inorganic network, to macroscopic polarisation arising from charged defect formation and diffusion. A number of unsolved mysteries will be outlined including self-healing effects, apparent ferroelectricity, light-enhanced ion transport, and ultimately, the origin of their high performance in optoelectronic devices.

This research has been supported by the Royal Society and a wide collaboration network with contributions from current and former group members including Federico Brivio, Keith Butler, Jarvist Frost, Jonathan Skelton, Katrine Svane, Ruoxi Yang, Lucy Whalley, Youngkwang Jung, Jacob Wilson, and Samantha Hood.

Halide Perovskites, HaPs, may be mostly normal (inorganic) semiconductors and, indeed, we should be careful to describe them with concepts from organic electronics. HOWEVER, it is remarkable that a material with over-all high quality optoelectronic properties can result from fast, low temperature, solution preparation. This suggests that there may also be issues with using some concepts from “classical” semiconductors. Now we can ask if minor revisions will do or if major ones are needed (rejection is not an option; HaPs exist...).

For that we need to define and understand what remains special about HaPs and what is/are the reason(s) for what, if anything, remains special. Being able to do so may help answer the nagging question if this is all because Pb is so unique, or if we can generalize to find other materials like these. I will consider the general question and, as things look now, 5.5 months before the talk, consider the relevance of mechanical, in conjunction with other properties, to challenge what we think we know about defects in HaPs, note a confusing semantic issue and more, to arrive at an answer, to guide us in future work.

Work done with Gary Hodes (Weizmann), with input from many others, whom I will credit in my talk.

10:00 AM BREAK

10:30 AM ET05.01.04
Theory and Modeling of Correlated Ionic and Electronic Motions in Hybrid Organic-Inorganic Perovskites
Matthew Mayers1, Liang Z. Tan1, David A. Egger1, Andrew M. Rappe1 and David Reichman1; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Chemistry, Columbia University, New York, New York, United States; 3University of Regensburg, Regensburg, Germany.

The perovskite crystal structure hosts a wealth of intriguing properties, and the renaissance of interest in halide (and hybrid organic-inorganic) perovskites (HOIPs) has further broadened the palette of exciting physical phenomena. Breakthroughs in HOIP synthesis, characterization, and solar cell design have led to remarkable increases in reported photovoltaic efficiency.

However, the observed long carrier lifetime and PV performance have eluded comprehensive physical justification. The hybrid perovskites serve as an enigmatic crossroads of physics. Concepts from crystalline band theory, molecular physics, liquids, and phase transitions have been applied with some success, but the observations of HOIPs make it clear that none of these conceptual frameworks completely fits. In this talk, recent theoretical progress in understanding HOIPs will be reviewed and integrated with experimental findings. The large amplitude motions of HOIPs will be highlighted, including ionic diffusion, anharmonic phonons, and dynamic incipient order on various length and time scales. The intricate relationships between correlated structural fluctuations, polar order, and excited charge carrier dynamics will also be discussed.

11:00 AM ET05.01.05
Low Charge Mobility in SOFT Polar Crystals is Fundamental! The Case of Halide Perovskites
Yevgeny Rakita, Gary Hodes and David Cahen; Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

The combination of properties halide perovskites (HaPs) possesses (e.g., high absorption coefficient, low effective mass, low exciton binding energy, low carrier recombination lifetimes, etc.) should (and does) allow high-performing optoelectronic devices. However, there is one fundamental property that does not fit the expected prognosis coming from the superior material’s properties – its carrier mobility.

When comparing mobility values of HaPs (~1-100 cm2V-1s-1) with those polar semiconductors, such as GaAs or CdTe (~103-105 cm2V-1s-1), a significant difference is revealed. Mobility temperature dependence, which points on the scattering mechanism, is found in HaPs, GaAs, CdTe and other polar semiconductors to be similar and suggest scattering by polar optical phonon. Low defect density, as found for HaPs (~1016 cm-3 in single crystals) as well as for other high-quality polar semiconductors (e.g., GaAs and CdTe), make scattering by defects insignificant (at temperatures > ~100 K). Therefore, the origin of charge scattering and, thus, their mobility, probably relate to more intrinsic properties of these polar semiconductors. So what makes the mobility in HaP to be so different from that in other polar semiconductors? Correlation of experimentally-derived physical values from semiconductors, including HaPs, reveals a clear correlation between the mechanical properties (or what is called a ‘deformation potential’) and the charge mobility. In fact, the softer the material, the lower its mobility. In my talk, I will explain the origins for such relation, which suggest that in a soft material such as HaPs mobility will never reach values as high as in GaAs.


11:15 AM ET05.01.06
The Polar Liquid Sublattice in Single Crystal Perovskite CH3NH3PbBr3(001)
Prescott E. Evans1, Marin Pink2, Ayan Zhmukhenov3, Guanghua Hao1, Yaroslav Lozovyy1, Osman M. Bakr1, Peter Dowben1 and Andrew J. Yost1; 1University of Nebraska-Lincoln, Lincoln, Nebraska, United States; 2Italian University, Bloomington, Indiana, United States; 3King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The dynamic motion, within the lattice of single crystal CH3NH3PbBr3(001) hybrid halide perovskite, was investigated using powder and single crystal x-ray diffraction, and x-ray photoemission spectroscopy. Single crystal x-ray diffraction studies indicate the methylammonium adopts multiple orientations within the crystal, at room temperature, evidence of a soft and disordered methylammonium sublattice within a stiff and ordered PbBr3 matrix lattice. Temperature dependent x-ray photoemission spectroscopy for bromine and lead core level peaks near the cubic to tetragonal I phase transition tend to support the characterization of methylammonium as a lattice polar liquid within the CH3NH3PbBr3 crystal. The Br 3d3/2 core level Debye-Waller factor plots exhibited a temperature dependence indicative of an effective Debye temperature of 160±81K, while the Pb 4f7/2 core-level Debye-Waller factor plots show little temperature dependence, indicative of a very stiff lattice along the <001> direction. MAPbBr3 satisfies the criteria for a lattice polar liquid and does not meet the criteria required for a ferroelectric material.

11:30 AM ET05.01.07
Impact of Crystallographic Orientation Disorders on Electronic Heterogeneities in Metal Halide Perovskite Thin Films
Benjamin Foley1, Seung-Hun Lee2, Kai Xiao1, Benjamin Doughty1, Yingzhong Ma2 and Joshua Chou1; 1University of Virginia, Charlottesville, Virginia, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Metal halide perovskite thin films have achieved remarkable performance in optoelectronic devices, but suffer from spatial heterogeneity in their electronic properties. To achieve higher device performance and reliability needed for wide-spread commercial deployment, spatial heterogeneity of optoelectronic properties in the perovskite thin film needs to be understood and controlled. Clear identification of the causes underlying this heterogeneity, most importantly the spatial heterogeneity in charge trapping behavior, has remained elusive. Here, a multimodal imaging approach consisting of
photoluminescence, optical transmission, and atomic force microscopy is utilized to separate electronic heterogeneity from morphology variations in perovskite thin films. By comparing highly oriented and randomly oriented polycrystalline perovskite thin film samples, we reveal that disorders in the crystallographic orientation of the grains play a dominant role in determining charge trapping and electronic heterogeneity. This work also demonstrates a polycrystalline thin film with uniform charge trapping behavior by minimizing crystallographic orientation disorder. These results suggest that single crystals may not be required for perovskite thin film based optoelectronic devices to reach their full potential.

11:45 AM ET05.01.08
Thermodynamic Stability of Perovskites—From Empirical Tolerance Factor to Machine Learning Wanjian Yin; Soochow Institute for Energy and Materials Innovations (SIEMIS), Soochow University, Suzhou, China.

Perovskite stability is of the core importance and difficulty in current research and application of perovskite solar cells. Nevertheless, over the past century, the formability and stability of perovskite still relied on simplified factor based on human knowledge, such as the commonly used tolerance factor t. Instead of t, we proposed a new factor (μ+η), where μ and η are the octahedral factor and the atomic packing fraction respectively. As a stability descriptor (μ+η) is able to predict the relative stability among any two perovskites with the accuracy ~90%, much better than ~70% of t [1,2].

We further combined machine learning (ML) with first-principles density functional calculations, proposed a strategy to calculate the decomposition energies, considered to be closely related to thermodynamic stability, of 354 kinds halide perovskites, established the machine learning relationship between decomposition energy and compositional ionic radius and investigated the stability of 14100 halide double perovskites. The ML model, which was trained based on the theoretical data, has been validated by experimental results of a series of rare earth metal halide perovskites (up to ~10^3 kinds), performs much better than descriptors such as tolerance factor t and (μ+η) and further provides elemental and concentration suggestion for improving the stability of mixed perovskite [3].


SESSION ET05.02: Defects, Ion Motion and Polarization
Session Chairs: Saiful Islam and Yabing Qi
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room Ballroom B

1:30 PM ET05.02.01
Ionic Transport, Defects and Electrooptical Response of Perovskite Solar Cells Juan Bisquert; Institute of Advanced Materials, Universitat Jaume I, Castello, Spain.

The development of organic-inorganic lead halide perovskites with very large efficiency requires us to understand the operation of the solar cell. This class of semiconductors presents remarkable bulk electronic and optical properties, but the contacts to the device are a key aspect of the operation and show important dynamic interactions. We describe the results of analysis of kinetic phenomena using frequency modulated techniques. First with impedance spectroscopy we provide an interpretation of capacitances as a function of frequency both in dark and under light, and we discuss the meaning of resistances and how they are primarily related to the operation of contacts in many cases. The capacitance reveals a very large charge accumulation at the electron contact, which has a great impact in the cell measurements, both in photovoltage decays, recombination, and hysteresis. We also shows the identification of the impedance of ionic diffusion by measuring single crystal samples. Working in samples with lateral contacts, we can identify the effect of ionic drift on changes of photoluminescence, by the creation of recombination centers in defects of the structure. We also address new methods of characterization of the optical response by means of light modulated spectroscopy. The IMPs is able to provide important influence on the measured photocurrent. We describe important insights to the measurement of EQE in frequency modulated conditions, which that showed the quantum efficiency can be variable at very low frequencies.

References


2:00 PM ET05.02.02
From MAPbI3 to Mixed-Cation Perovskites—Atomic-Scale Insights into Defects, Diffusion and Degradation Saiful Islam; University of Bath, Bath, United Kingdom.

Further breakthroughs in perovskite solar cells require advances in new compositions and underpinning materials science. Indeed, a greater fundamental understanding of perovskite materials requires atomic-scale characterization of their underlying structural, defect and transport behaviour. In this context, combined modelling-experimental work is now a powerful approach for investigating these properties at the atomistic level. This presentation will describe such studies on hybrid perovskites [1-3] in two related areas: (i) the defect and ion transport properties of methylammonium lead iodide (MAPbI3) in relation to atmospheric effects and degradation; (ii) the molecular cation dynamics and octahedral distortion of halide perovskites with mixed A-cations (MA, FA, Cs) in relation to their improved stability and photovoltaic performance.

Perovskite semiconductors are a new class of semiconductors, significantly different from organic and also inorganic semiconductors. We have applied thermally stimulated current measurements to study the polarization processes of the organic cation in MAPbI$_3$, thin films across the orthohombic to tetragonal phase transition. The nature of the cation polarization within the orthorhombic phase was found to be highly repeatable, with a separation of 20 K between polarization and depolarization processes, and was investigated with respect to its extrinsic polarizability by external electric fields. Our results show that the polarization of organic cations is correlated with a sudden improvement in solar cell performance and has impact on the working mechanisms of perovskite solar cells.

Huge Enhancement of Ion Conduction and Implications for Photo-Decomposition in Hybrid Organic-Inorganic Lead Halides Perovskite

Gee Yeong Kim$^1$, Alessandro Senocrate$^1$, Tae-Youl Yang$^1$, Giuliano Gregori$^2$, Michael Graetzel$^2$ and Joachim Maier$^1$; $^1$Max Planck Institute for Solid State Research, Stuttgart, Germany; $^2$Swiss Federal Institute of Technology in Lausanne, Lausanne, Switzerland.

Methylammonium lead iodide (MAPI) is the archetype material of the class of halide perovskites that are currently in the focus of photovoltaic research because of high conversion efficiencies. MAPI exhibits some anomalies properties such as a huge apparent low frequency dielectric constant and severe hysteretic current-voltage behavior. In order to investigate the key features of its performance, not only electronic, but also ionic transport properties need to be considered [1,2]. Here we report on huge photo effects on ion conductivity in MAPI. To measure and separate both transport contributions not only in the dark, but also under illumination, we carried out a variety of tailored electrochemical studies. In this way, an enhancement of ionic conductivity by as much as two orders of magnitude in MAPI by light illumination can be unambiguously demonstrated [3]. The mechanism of ion conduction under light is proposed to rely on a translation of a great fraction of the generated holes into iodine vacancies which are the ionic charge carriers. Localized holes correspond to neutral iodine which can -owing to site and poly-anionic stabilization- occupy interstitial sites leaving vacant iodine sites that are causing the ionic conductivity. This process is reversible under homogeneous conditions. If, however, iodine is irreversibly removed under illumination, photo-decomposition occurs. This unexpected finding does not only give rise to a decomposition path for metal halide perovskites, it also allows one to tune ion transport by light.

References
A pertinent investigation of the exceptional photoelectrochemical properties of halide perovskites has to consider the significant ion transport present in these materials. Such transport gives rise to bulk and boundary ionization phenomena during operation, and it is also relevant for the degradation kinetics of halide perovskites materials and related photovoltaic devices. In this contribution we analyze the nature of the ionic conductivity in methylammonium lead iodide, the archetype hybrid halide perovskite, by means of various electrical, electrochemical and nuclear magnetic techniques. Under equilibrium conditions, iodine vacancies are unambiguously shown to be the dominant ionic carriers, while electron holes dominate the electronic conductivity at high (and excess electrons at low) iodine activities. The contributions of methylammonium and lead ions, instead, are small (upper limits are given). As a follow-up, we discuss the changes of the various charge carrier concentrations as a function of the decisive control parameters (stoichiometry and doping content). Based on these equilibrium considerations, we can also discuss the charge carrier chemistry under illumination where not only electronic, but also ionic conductivity are largely enhanced.

References

4:30 PM ET05.02.08
Highly Stable Perovskite Solar Cells via Controlling Ions/Charges/Molecules Diffusion Xudong Yang1, 2; Han Chen1 and Liyuan Han*; 1State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai, China; 2Research Network and Facility Services Division, National Institute for Materials Science, Tsukuba, Japan.

Organic-inorganic hybrid perovskite solar cells (PSCs) are promising low-cost photovoltaic technology owing to the high energy conversion efficiency. However, the device stability has a large gap to the ideal level for future application. Here I would like to introduce our recent approaches in achieving highly stable PSCs. We proposed a strategy to control the diffusion of ions/charges/molecules by developing nano-carbon electron transporting layer in p-i-n structure perovskite solar cells. It successfully enabled better stability because the diffusion of iodide within the device was hindered before it induced corrosion of the metal electrode while the diffusion of electrons was improved. We further control the ions/charges/molecules diffusion within n-i-p structure perovskite solar cells. The ions diffusion was reduced to decrease the charge trap states when the device was aging. This helped to obtain device with excellent stability and high efficiency. The device performance was certified by a public test center with the record of certified stabilized power output.


4:45 PM ET05.02.09
Impact of Thin-Film Perovskite Composition on Sub-Band Gap Absorption Due to Defect States Biwas Subedi, Chongwen Li, Cong Chen, Maxwell Junda, Dewei Zhao, Yanfa Yan and Nikolas Podraza; Physics and Astronomy, University of Toledo, Toledo, Ohio, United States.

Organic-inorganic halide ABX3 (A: methylammonium—MA, formamidinium—FA, Cs; B: Pb, Sn; X: I, Br) perovskites currently serve as absorber materials in highly efficient solar cells. Preparation of films which are highly crystalline; defect free; stable against heat, light, and moisture; and with desired optoelectronic properties are present challenges. Cationic and anionic alloying / doping has been shown to improve phase stability, increase grain size and uniformity, and reduce sub-bandgap absorption and recombination due to defects to improve solar cell performance. A combination of photothermal deflection spectroscopy, spectroscopic ellipsometry, and unpolarized transmittance measurements of solution processed perovskite thin films prepared with mixed cation/anion composition are used to study the impact of these variations on sub-bandgap absorption due to defects. In particular, Urbach energies from sub-bandgap absorption are correlated with structural, electrical, above band gap optical properties, and device performance. As an example of A-cation substitution, replacing 0.4 FA with MA in x = 0.15 FA0.6MA0.4Sn0.6Pb0.4I1-xBrx reduces Urbach energies from 53 to 26 meV and is accompanied by increased grain size, reduced defect density, and improved electronic properties. For anion substitution, I to Br ratios in FA0.6MA0.4Sn0.6Pb0.4I1-xBrx (x ≤ 0.15) show materials prepared with x ≤ 0.04 having the lower Urbach energy than higher Br content. In FA0.8Cs0.2PbI3-xBrx, Urbach energies are reduced from lead thiocyanate (Pb(SCN)2) treatment and solvent annealing preparation. Links will be established between the particular cation/anion composition configurations currently used in solar cell device grade perovskite films, structural and electrical properties, and the associated sub-bandgap absorption characteristics. Further expansion of these studies will help to more fundamentally understand the defect states present in particular compositions and to identify practical pathways to improvements in stability and electronic quality for experimentally produced perovskite thin films used as solar cell absorbers.

SESSION ET05.03: Poster Session I: Fundamentals of Halide Perovskite Optoelectronics
Session Chair: Wolfgang Tress
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET05.03.01
Interface Engineering to Improve Efficiency and Operational Lifetime of Perovskite Solar Cells Longbin Qiao, Luis K. Ono, Yan Jiang, Matthew R. Leyden, Sonia R. Raga, Shenghao Wang and Yabing Qi; Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), Okinawa, Japan.

Operational lifetime is one of the main challenges for perovskite solar cells towards commercialization [1]. Other than the stability of perovskite materials...
General Nondestructive Post-Treatment to Passivate Perovskite Solar Cells with Enhanced Stability and Performance

Shencheng Xie, Han Wang, Jianbin Xu and Keyou Yan; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Hybrid perovskite thin films have many vacancies at surface and interface during the film formation, which degrade the stability and photovoltaic performance. Passivation via post-treatment can enhance the film quality, but present methods are slightly destructive to three-dimensional perovskite (3DP) due to the solvent effect, which hinders fabrication reproducibility. Herein, we demonstrate that 4-fluoroaniline (FAL) is an effective antisolvent candidate for surface/interface passivation and thus nondestructive during the fabrication. Density functional theory (DFT) calculation reveals that the antisolvent and non-destructive properties are attributed to the conjugated amine in aromatic ring. Hot vapor assisted colloidal process (HVACP) is employed for the post-treatment. The molecular passivation yields an ultrathin protection layer with hydrophobic fluorine tail and thus enhances the stability and optoelectronic properties. FAL perovskite solar cell (PSC) delivers 20.48% power conversion efficiency (PCE) in the ambient condition. Moreover, PPA-capped MAPbBr3 QDs films show high electronic conductivity, which carrier transport are adopted to increase the film conductivity of QDs, but still didn’t break the dilemma of the trade-off between the film conductivity and colloidal stability. Herein, a uniform and large grain size of max approx. 3 µm is demonstrated for two steps solution process of MAPbI3 perovskites at 100°C using a simple annealing method. The annealing time duration varies from 1 hour to 24 hours long, while the grain size gradually increases with the prolongation of the annealing time. However, the grain size remains almost constant when the annealing time longer than 12 hours. Furthermore, a distinctly larger grain size of about 6 µm is also exhibited for the same perovskite film deposited on a PbI2 seed layer prepared by chemical vapor deposition method. An optical measurement is being carried on with some initial promising results to characterize the photocurrent loss and recombination center on the grain boundaries, intra-grain, and inter-grain scale of perovskites using femtosecond laser of confocal microscope. The investigations on such microcrystalline perovskites with large grains are highly essential for conducting electronic and optical measurements to enhance the performance of perovskite devices.

Acknowledgement: This work was financially supported by a grant from Shenzhen Municipal Science and Technology projects (Grant No. 201605313001154) and The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

Reference:

Enlarging the Grain in Low-Temperature Solution Processed Perovskite Films Using Simple Annealing Method

Md Wayesh Qarony1, Saiman Ma1, Mohammad I. Hossain1, Chu Tung Yip2 and Yuen H. Tsang1; 1Department of Applied Physics and Material Research Center, The Hong Kong Polytechnic University, Kowloon, Hong Kong; 2Department of Physics, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, China.

Perovskites have recently attained great attention owing to its excellent electronic and optical properties. The optoelectronic properties can be further tailored according to the needs of applications. It is demonstrated that perovskites photovoltaic devices with a theoretical energy conversion efficiency limit of 31% can be realized if large grain size with uniform intra-grain and inter-grain crystallinity are ensured [1-2]. However, achieving a good crystallinity along with larger grain using the low-temperature solution processed organic-inorganic halide polycrystalline perovskites (MAPbI3) remains a challenging task. Herein, a uniform and large grain size of max approx. 3 µm is demonstrated for two steps solution process of MAPbI3 perovskites at 100°C using a simple annealing method. The annealing time duration varies from 1 hour to 24 hours long, while the grain size gradually increases with the prolongation of the annealing time. However, the grain size remains almost constant when the annealing time longer than 12 hours. Furthermore, a distinctly larger grain size of about 6 µm is also exhibited for the same perovskite film deposited on a PbI2 seed layer prepared by chemical vapor deposition method. An optical measurement is being carried on with some initial promising results to characterize the photocurrent loss and recombination center on the grain boundaries, intra-grain, and inter-grain scale of perovskites using femtosecond laser of confocal microscope. The investigations on such microcrystalline perovskites with large grains are highly essential for conducting electronic and optical measurements to enhance the performance of perovskite devices.

Conventional colloidal quantum dot solutions (QDs), long hydrocarbon chains capping ligands such as n-octylamine (OA) are indispensable. However, the commonly used long hydrocarbon capping ligands are always insulator and block efficient carrier transport between QDs, leading to inferior performance of light-emitting diode (LED), and other optoelectronic devices. Until now, ligand exchange, reducing ligand chain length and ligand density control are adopted to increase the film conductivity of QDs, but still didn’t break the dilemma of the trade-off between the film conductivity and colloidal stability of QDs. In this work, for the first time, we overcame this dilemma, successfully synthesized methyleneimine lead bromide (MAPbBr3) QDs with an unsaturated conjugated alkyl-amine, 3-Phenyl-2-propen-1-amine (PPA), as ligand. Owing to the denser electron cloud overlapping and delocalization effect of conjugated molecules, PPA effectively improves the conductivity of QDs film without compromising its colloidal stability. With analogous quantum photoluminescence yield and stability of OA-capped MAPbBr3 QDs, films of PPA-capped MAPbBr3 QDs show high electronic conductivity, which carrier mobility has increased nearly 22 times of that of OA-capped MAPbBr3 QDs films. As an example of application in LEDs, the QD-LED based on PPA-capped MAPbBr3 QDs exhibited a maximum luminance of 9052 cd m⁻² and an maximum current efficiency of 9.08 cd A⁻¹, which is eight times of that of QD-LED based on OA-capped MAPbBr3 QDs (1.14 cd A⁻¹). This work provides critical solution for the poor conductivity of QDs in applications of energy-related devices.

Conformational Ligands Assisted Charge Transport Between Coupling Colloidal Perovskite Quantum Dots

Jinfei Dai, Yifei Shiy, Jie Xu, Lin Zhang and Xiaowin Wu; Xi’an Jiaotong University, Xi’an, China.

Conventionally, in preparing stable colloidal quantum dots (QDs), long hydrocarbon chains capping ligands such as n-octylamine (OA) are indispensable. However, the commonly used long hydrocarbon capping ligands are always insulator and block efficient carrier transport between QDs, leading to inferior performance of light-emitting diode (LED), and other optoelectronic devices. Until now, ligand exchange, reducing ligand chain length and ligand density control are adopted to increase the film conductivity of QDs, but still didn’t break the dilemma of the trade-off between the film conductivity and colloidal stability of QDs. In this work, for the first time, we overcame this dilemma, successfully synthesized methyleneimine lead bromide (MAPbBr3) QDs with an unsaturated conjugated alkyl-amine, 3-Phenyl-2-propen-1-amine (PPA), as ligand. Owing to the denser electron cloud overlapping and delocalization effect of conjugated molecules, PPA effectively improves the conductivity of QDs film without compromising its colloidal stability. With analogous quantum photoluminescence yield and stability of OA-capped MAPbBr3 QDs, films of PPA-capped MAPbBr3 QDs show high electronic conductivity, which carrier mobility has increased nearly 22 times of that of OA-capped MAPbBr3 QDs films. As an example of application in LEDs, the QD-LED based on PPA-capped MAPbBr3 QDs exhibited a maximum luminance of 9052 cd m⁻² and an maximum current efficiency of 9.08 cd A⁻¹, which is eight times of that of QD-LED based on OA-capped MAPbBr3 QDs (1.14 cd A⁻¹). This work provides critical solution for the poor conductivity of QDs in applications of energy-related devices.

DO : 10.1002/anie.201801780

Nondestructive Post-Treatment to Passivate Perovskite Solar Cells with Enhanced Stability and Performance

Shencheng Xie, Han Wang, Jianbin Xu and Keyou Yan; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Hybrid perovskite thin films have many vacancies at surface and interface during the film formation, which degrade the stability and photovoltaic performance. Passivation via post-treatment can enhance the film quality, but present methods are slightly destructive to three-dimensional perovskite (3DP) due to the solvent effect, which hinders fabrication reproducibility. Herein, we demonstrate that 4-fluoroaniline (FAL) is an effective antisolvent candidate for surface/interface passivation and thus nondestructive during the fabrication. Density functional theory (DFT) calculation reveals that the antisolvent and non-destructive properties are attributed to the conjugated amine in aromatic ring. Hot vapor assisted colloidal process (HVACP) is employed for the post-treatment. The molecular passivation yields an ultrathin protection layer with hydrophobic fluorine tail and thus enhances the stability and optoelectronic properties. FAL perovskite solar cell (PSC) delivers 20.48% power conversion efficiency (PCE) in the ambient condition. Moreover, PPA-capped MAPbBr3 QDs films show high electronic conductivity, which carrier transport are adopted to increase the film conductivity of QDs, but still didn’t break the dilemma of the trade-off between the film conductivity and colloidal stability. Herein, a uniform and large grain size of max approx. 3 µm is demonstrated for two steps solution process of MAPbI3 perovskites at 100°C using a simple annealing method. The annealing time duration varies from 1 hour to 24 hours long, while the grain size gradually increases with the prolongation of the annealing time. However, the grain size remains almost constant when the annealing time longer than 12 hours. Furthermore, a distinctly larger grain size of about 6 µm is also exhibited for the same perovskite film deposited on a PbI2 seed layer prepared by chemical vapor deposition method. An optical measurement is being carried on with some initial promising results to characterize the photocurrent loss and recombination center on the grain boundaries, intra-grain, and inter-grain scale of perovskites using femtosecond laser of confocal microscope. The investigations on such microcrystalline perovskites with large grains are highly essential for conducting electronic and optical measurements to enhance the performance of perovskite devices.

Acknowledgement: This work was financially supported by a grant from Shenzhen Municipal Science and Technology projects (Grant No. 201605313001154) and The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

Reference:
Bulk Heterojunction Quasi-Two-Dimensional Perovskite Solar Cell with 1.18 V High Photovoltage Han Wang, Jiangsheng Xie, Shenghe Zhao, Jianbin Xu and Keyou Yan; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Multicomponent quasi-two-dimensional perovskites (Q-2DPs) have efficient luminescence and improved stability, which are highly desirable for light-emitting diode (LED) and perovskite solar cell (PSC). However, the lack of radiative recombination at room temperature is still not well understood and the performance of PSC is not good enough as well. The open-circuit voltage ($V_{oc}$) is even lower than that of 3D PSC with narrower band gap. In this work, we study the energy transfer of excitons between their multiple components by time-resolved photoluminescence (TRPL) and find that charge transfer from high energy states to low energy state is greatly suppressed at elevated temperature due to increasing trap-mediated recombination. This may reveal the bottleneck of luminescence at room temperature in Q-2DPs, leading to large photovoltaic loss in PSC. Therefore, we develop a p-i-n bulk heterojunction (BJH) structure to reduce the nonradiative recombination. We obtain high $V_{oc}$ of 1.18 V for (PMA)$_2$MA$_n$Pb$_{3n}$Cl$_{3n}$(N = 5) in PSC, much higher than the planar counterparts. The enhanced efficiency is attributed to the improved exciton dissociation via BHJ interface. Our results provide an important step towards high $V_{oc}$ and stable 2D PSCs, which could be used for tandem solar cell and coloreful photovoltaic windows.

ET05.03.06

Two-Dimensional Hybrid Dion-Jacobson Perovskite for Solar Cell Application Lingling Mao$^1$, Weijun Ke$^1$, Laurent Pedesseau$^2$, Claudine Katano$^3$, Jacky Even$^4$, Constantinos Stoumpos$^4$ and Mercouri G. Kanatzidis$^5$; 1Chemistry, Northwestern University, Evanston, Illinois, United States; 2Institute for Photon Science and Technology, The University of Tokyo, Tokyo, Japan; 3Physics, The University of Tokyo, Rennes, France.

Hybrid organic-inorganic perovskite material has emerged as one of the most promising semiconducting materials for optoelectronic applications. The power conversion efficiency (PCE) of the three-dimensional (3D) perovskite based solar cell has achieved 22%. With a higher flexibility in structural engineering, the two-dimensional (2D) perovskite not only allows for property tuning in a broader sense, but also demonstrates higher stability in devices compared to the 3D perovskite. Here, we present the first complete series of the Dion-Jacobson phases in the halide perovskite family, incorporating the 3-(ammoniomethyl)pyridinium (3AMP) or 4-(ammoniomethyl)pyridinium (4AMP) as spacing cations. The general formula for the DJ perovskite is A$^+$, $\text{Pb}_n\text{X}_m$(A$^+$ = 3AMP or 4AMP, A$^+$ = methylammonium (MA$^+$)). Compared with the Ruddlesden–Popper (RP) phases, the DJ perovskite only has one sheet of organic cations in between the layers, resulting in much closer interlayer distance (~4 Å). The inorganic layers in the DJ phases are stacking perfectly on top of each other with no displacement. With a slight modification on the organic cation (3AMP vs. 4AMP), the optical properties are heavily influenced by the distortion of the inorganic layers, as the 3AMP series (less distorted) has narrower band gaps than the 4AMP series (more distorted). We further demonstrate their difference in solar cell devices, as the (3AMP)(MA$^+$)$_2$Pb$_3$I$_9$ has the best PCE of 7.3%, much higher than the corresponding (4AMP)(MA$^+$)$_2$Pb$_3$I$_9$. With compositional engineering on the existing system, we optimize the device performance of (3AMP)(MA$^+$)$_2$F$_2$Pb$_3$I$_9$ (FA$^+$ = formamidinium) to 12.0%. The new DJ system highlights the crucial role of functional organic cations in the 2D hybrid perovskite, where they influence the overall property of the material by interactions with the inorganic framework, which ultimately affect the device performance.

ET05.03.07

Unveiling the Room Temperature Low-Threshold Amplified Spontaneous Emission in All-Inorganic Perovskite Thin Films by Dual Source Thermal Evaporation Lin Zhang, Zhaoxin Wu, Hua Dong, Jinfei Dai and Xiaoyun Liu; Xi’an Jiaotong University, Xi’an, China.

Recent years have witnessed rapid development of halide perovskite as a new class of optical-gain media for lasing applications. Driven by the rapidly increased research on organic-inorganic perovskite CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I) (Science, 356, 1376 (2017)), inorganic perovskite CsPbX$_3$ has also attracted high attention because it shows increased air-stability (Nat. Commun. 8, 15640 (2017), Nat. Photon. 11, 108 (2017)). For achieving amplification spontaneous emission (ASE) with low threshold from perovskite thin films, ultra-compact grains and smooth morphology are prerequisites. Meanwhile, the prepared perovskite thin films have good photo and environmental stability under ambient conditions is also paramount. However, the solution-processed thin films generally difficult to control crystal perovskite crystallization and film quality due to low solubility of the cesium bromide (CsBr) precursor, result in inevitable large pinholes and poor surface coverage (Nat. Commun. 6, 8056 (2015)). Such defects may result in reduced optical confinement effect and poor ASE from the perovskite films, seriously affecting their lasing performance. To solve these issues, herein, we demonstrate that by dual source thermal evaporation which enables the attainment of nearly pinhole-free thin films, inorganic perovskite (such as CsPbBr$_3$ or CsSnI$_3$) films exhibit enhanced crystallization, improved photoluminescence (PL) uniformity and intensity, and long-term reliability. The ASE with improved emission intensity and reduced threshold from evaporated thin film were demonstrated in our previous works (J. Phys. Chem. C, 28, 1211(2017); PSS RRL, 5, 12, (2018)). Notably, the unannealed CsPbBr$_3$ thin films fabricated by thermal evaporation exhibit ultralow ASE threshold of ~ 3.3 μJ/cm$^2$, enhanced crystallization, improved surface morphology and gain coefficient above 300 cm$^{-1}$. Stable ASE intensity without degradation for at least 7 hours is observed under continuous excitation under ambient conditions. Meanwhile, a Fabry-Perot (F-P) cavity layer based on unannealed CsPbBr$_3$ thin film, featuring ultralow threshold and directional output is also realized. Our works advocate that the perovskite thin films possess excellent film morphology and excellent long-term stability which prove to be critical to enhance ASE and lasing performance, as well as highlights the feasibility of evaporated CsPbBr$_3$ thin films as practical optical gain media for the further light-emitting applications.

ET05.03.08

First Principle Polaron Modeling in Hybrid Perovskites Using the GGA+U Method Eric W. Welsh$^1$, Amanda J. Neukirch$^2$, 3, Sergei Tretiak$^2$, Petr Obraztsov$^4$, 5, Dmitry Lyashenko$^1$, Pavel Chizhov$^1$, Kuniaki Konishi$^6$, Natsuki Nemoto$^6$, Makoto Kuwata-Gonokami$^7$, Petr Obraztsov$^4$, 5 and Alex Zakhidov$^4$, 5; 1Material Science, Texas State University, San Marcos, Texas, United States; 2T-Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Institute for Photon Science and Technology, The University of Tokyo, Tokyo, Japan; 4Physics, The University of Tokyo, Tokyo, Japan; 5General Physics Institute, Russian Academy of Sciences, Moscow, Russian Federation; 6Physics and Mathematics, University of Eastern Finland, Joensuu, Finland; 7Physics, Lomonosov Moscow State University, Moscow, Russian Federation; 8Physics, Texas State University, San Marcos, Texas, United States.

Organohalide lead hybrid perovskites (HPs) have become the benchmark, state-of-the-art materials in third generation, perovskite solar cell devices, achieving a power conversion efficiency of over 22%. Yet, the underlying photo-physical properties of HPs are still under debate. Here we use density functional theory within the generalized gradient approximation with a Hubbard correction (GGA+U) to study structural properties, band structures, charge carrier dynamics and electron-phonon coupling in HPs with different compositions. Our preliminary DFT+U simulations reveal the formation of light-induced self-trapped hole polarons in HPs with different halides, which may have profound implications on charge transport, recombination, and experimentally observed device instability under illumination. Moreover, we argue that polaron induced loss of exciton symmetry and enhanced Rasha splitting might be responsible for our recent experimentally observed room-temperature ultrafast photocurrent and free-space terahertz emission generation from unbiased CH$_3$NH$_3$PbI$_3$ benchmark HPs. Polarization dependence of the observed responsese is consistent with the Bulk Photovoltaic Effect caused by a combination of injection and shift currents. Ballistic by nature, these photocurrents may enable next generation perovskite solar cells with efficiency that can theoretically exceed the Shockley–Queisser limit. We also developed a computational method that allows estimating the polaron size, while minimizing self-interaction errors, as well as the overall computational requirement of each calculation.
Surface functionalization of nanoscale materials has significant impacts on their properties due to their large surface-to-volume ratio. In this work, we studied temperature dependent crystal phase transitions in CH$_3$NH$_3$PbI$_3$ (P-OABr-stabilized FAPbI$_3$) films. ASE from MABr-stabilized FAPbI$_3$ films was also achieved, with an ultralow threshold of about 1.6 μJ/cm$^2$. More importantly, upon continuous operation under pulsed laser for several hours, the ASE intensity in the MAPbI$_3$ film decreased to 9% of the initial value, while it was maintained above 90% in the FAPbI$_3$ film. The low trap density, smooth film morphology, high thermal stability, and the excitonic emission in nature of the FAPbI$_3$ film are expected to contribute to its low lasing threshold and high stability, demonstrating a strong potential for applications in continuouswave pumped lasers and electrically driven lasers.

ET05.03.11 High Stability and Ultralow Threshold Amplified Spontaneous Emission from Formamidinium Lead Halide Perovskite Films Xiaoyun Liu; Xi’an Jiaotong University, Xi’an, China.

The opportunity of lasing from organolead halide perovskite materials has recently attracted extensive attention in order to realize electrically driven lasers. So far, for devices with planar structure, most reports focus on CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) films, which are unstable when in operation due to phase transitions and elemental redistribution. Therefore, we have demonstrated highly stable amplified spontaneous emission (ASE) with ultralow threshold from formamidinium-based perovskite CH$_3$NH$_3$PbI$_3$(FAPbI$_3$) films. ASE from MABr-stabilized FAPbI$_3$ films was also achieved, with an ultralow threshold of about 1.6 μJ/cm$^2$. More importantly, upon continuous operation under pulsed laser for several hours, the ASE intensity in the MAPbI$_3$ film decreased to 9% of the initial value, while it was maintained above 90% in the FAPbI$_3$ film. The low trap density, smooth film morphology, high thermal stability, and the excitonic emission in nature of the FAPbI$_3$ film are expected to contribute to its low lasing threshold and high stability, demonstrating a strong potential for applications in continuouswave pumped lasers and electrically driven lasers.

ET05.03.12 A Novel Series of Quasi-2D Ruddlesden-Popper Perovskites Based on Short-Chained Spacer Cation for Enhanced Photodetection Dong Ruoting, Changyong Lan, Xiwen Xu and Johnny Ho; City University of Hong Kong, Hong Kong, Hong Kong.

Quasi two-dimensional (2D) layered organic-inorganic perovskite materials (e.g. (BA)$_2$(MA)$_n$PbnI$_{3n+1}$; BA = butylamine; MA = methylamine), have recently attracted a wide attention due to their superior moisture stability as compared with three-dimensional counterparts. Inevitably, hydrophobic yet insulating long-chained organic cations improve the stability at the cost of hindering charge transport, leading to the unsatisfying performance of subsequently fabricated devices. Here, we report the synthesis of Quasi-2D (iBA)$_2$(MA)$_{n-1}$PbnI$_{3n+1}$ perovskites, where the relatively pure phase (iBA)$_2$PbI$_4$ and (iBA)$_2$MA$_n$PbnI$_{3n+1}$ films can be obtained. Because of the shorter branched-chain of iBA as compared with that of its linear equivalent (n-butylamine, BA), the resulting (iBA)$_2$(MA)$_{n-1}$PbnI$_{3n+1}$ perovskites exhibit much enhanced photodetection properties without sacrificing their excellent stability. Through hot-casting, the optimized (iBA)$_2$(MA)$_{n-1}$PbnI$_{3n+1}$ perovskite films with $n=4$ give significantly improved crystallinity, demonstrating the high responsivity of 117.09 mA/W, large on-off ratio of 4.0×10$^2$ and fast response speed (rise and decay time of 16 ms and 15 ms, respectively). These figure-of-merits are comparable or even better than those of state-of-the-art Quasi-2D perovskites-based photodetectors reported to date. Our work not only paves a practical way for future perovskite photodetector fabrication via modulation of their intrinsic material properties, but also provides a direction for further performance enhancement of other perovskite optoelectronics.

ET05.03.13 Hybrid Organic-Inorganic Lead Halide Perovskites Investigated by Modulated Surface Photovoltage Spectroscopy Celine A. Omondi; Katrin Hirslandt* and Eva Unger; Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Berlin, Germany; Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Young Investigator Group Hybrid Materials Formation and Scaling, Berlin, Germany.

Hybrid organic-inorganic lead halide perovskites have emerged as a new group of materials for highly efficient solar cells (SCs) based on earth abundant elements which can be processed from solutions at low temperature. CH$_3$NH$_3$PbI$_3$(1-x)Br$_x$ perovskite films were studied since it belongs to the materials which are of great interest for top SCs in tandem SCs with c-Si bottom SCs due to its tunable band gap. Electronic properties of CH$_3$NH$_3$PbI$_3$(1-x)Br$_x$ perovskite films sensitively depend on crystallization and defect formation and are crucial for the performance and stability of SCs. The band gap ($E_g$), exponential tail states ($E_T$) and the diffusion length ($L$) are decisive parameters for absorbers in SCs since they give principle limitations for photo-generation and Fermi-level splitting. In CH$_3$NH$_3$PbI$_3$(1-x)Br$_x$ perovskites, $E_T$, $E_g$, and $L$ are not necessarily constant and can depend, for example, on the preparation conditions and degradation. Therefore, $E_T$, $E_g$, and $L$ of CH$_3$NH$_3$PbI$_3$(1-x)Br$_x$ perovskites were studied with respect to stoichiometry, interfaces, degradation and temperature. Modulated SPV spectroscopy allows for the contactless and very sensitive characterization of $E_T$, $E_g$, direction of charge separation and $L$ (after Goodman) without the requirement of the preparation of contacts after or during different stages of layer preparation, light soaking
etc. Vegard’s law was applied to obtain the composition of CH$_3$NH$_3$Pb$_{1-x}$Br$_x$ films. The $E_g$ of CH$_3$NH$_3$PbI$_3$ films varied between 1.59 eV to 2.30 eV depending on the stoichiometry whereas the bowing parameter was 0.36 eV. The influence of the substrate on the band gap $E_g$ of CH$_3$NH$_3$PbI$_3$ was investigated. It has been found, for example, that $E_g$ and $E_s$ of CH$_3$NH$_3$PbBr$_3$ sensitively depend on the substrate and on soaking in nitrogen atmosphere and that light soaking has strong influence on the direction of modulated charge separation. CH$_3$NH$_3$PbI$_3$ deposited on double layers of TiO$_2$/PCBM and SnO$_2$/PCBM showed a constant band gap of 1.58 eV and a low scatter in $E_s$. This was attributed to the modification of the TiO$_2$ or SnO$_2$/CH$_3$NH$_3$PbI$_3$ interfaces by PCBM allowing for efficient charge separation and transfer and well reproducible conditions for the layer formation. A decrease of $L$ with light soaking was observed and can be attributed to light induced degradation due to charging and discharging of trap states and formation of defects at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface. Furthermore, $E_g$ and $E_s$ of CH$_3$NH$_3$PbI$_3$ stabilized with PMMA increased with increasing temperature, i.e. thermal expansion gives the predominant contribution to $E_g$ of CH$_3$NH$_3$PbI$_3$ whereas dynamic disorder was limited by phonons. A jump-like increase of $E_s$ in the region of phase transition was attributed to the phase transition from the tetragonal to the cubic phases.

ET05.03.14

In Situ Grain Encapsulation for Stable Formamidinium-Based Perovskite Solar Cells

Tianhao Liu$^{1,2}$, Yuanyuan Zhou$^1$, Nitin Padure$^1$, Kai Zhu$^2$, Rui Zhu$^2$ and Deying Luo$^2$; $^1$Brown University, Providence, Rhode Island, United States; $^2$School of Physics, Peking University, Beijing, China; $^3$National Renewable Energy Laboratory, Golden, Colorado, United States.

Owing to the wide absorption range and high thermal stability, formamidinium (FA) based lead iodide perovskites have recently emerged as the most promising light-absorber materials for photovoltaics. However, they suffer from fast degradation to undesirable non-perovskite polymorphs in the ambient atmosphere, which retards the real-world application of FA-based PSCs. Herein, a new strategy of in situ grain encapsulation is demonstrated to address this issue. This strategy is realized by co-addition of tetraethylrhodisilicate (TEOS) and H$_2$O into the perovskite precursor solution. The hydrolysis of TEOS produces silica oligomers in the precursor solution. Driven by the perovskite crystallization, silica fills in the grain boundaries and covers the surfaces of perovskite grains, forming encapsulating layers at the “grain”-scale. Silica protects perovskite grains from the ambient air, thus improving the stability. Furthermore, SiO$_2$ passivates defects and reduces the recombination, enhancing the photovoltaic performance. Using the in situ grain encapsulation strategy, FA-based PSCs can exhibit a power conversion efficiency of 19.5% and keep stable for 1000 h in the ambient atmosphere.

ET05.03.15

Modification of Excitonic Properties of Halide and Mix-Halide Hybrid Perovskite Thin Films Using Interface Engineering

Katerina Nikolaidou$^1$, Som Sarang$^1$, Denzal Martin$^1$, Vincent Tung$^1$, Jennifer Lu$^1$ and Sayantani Ghosh$^1$; $^1$Physics, University of California, Merced, Merced, California, United States; $^2$Materials Science and Engineering, University of California, Merced, Merced, California, United States.

Zinc oxide (ZnO) substrates of varying morphologies, including single crystalline (SC), micro-structured (MS) and nanostructured (NS) substrates, are interfaced with pure (CH$_3$NH$_3$PbI$_3$) and mixed (CH$_3$NH$_3$PbI$_3$xCl$_x$) halide hybrid perovskite thin films. The perovskite/ZnO interfaces are characterized by means of electron microscopy correlated with charge transfer properties that are probed by temperature, power and time-resolved photoluminescence (PL) spectroscopy. SC-ZnO acts as an effective electron extraction layer as evidenced by PL quenching, reduced exciton density and recombination lifetime in the perovskite thin film. On the other hand, MS-ZnO is observed to result in a mild increase of the PL intensity of the perovskite film at room temperature, and NS-ZnO further results in PL intensity enhancement by up to a factor of thousand and increase of recombination rates by 50%. These trends vary with temperature, and our results demonstrate the critical role played by morphology of the underlying substrates in charge dissociation and extraction in perovskite thin films. We conclude that while SC-ZnO can be implemented as an electron extraction layer in photovoltaic devices, MS- and NS-ZnO can be incorporated as scaffold in optical devices that require high quantum yield.

ET05.03.16

Discovery of the 2D Mixed Halide Perovskites A$^3$Bi$_2$I$_6$Cl$_3$ (A = Cs, Rb)—Exploring the Limits of the Defect Perovskite Structure

Kyle M. McCall, Grant C. Alexander, Oleg Kontsevoi, Bruce Wessels and Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

Halide perovskites have remarkable optoelectronic properties which enabled their success as solar cells, with device efficiencies quickly rising above 22%. Perovskites have the formula A$^3$MX$_6$, where A is a large cation occupying voids between a corner-connected framework of MX$_6$ octahedra. Much of this work is based on the organic-inorganic CH$_3$NH$_3$PbI$_3$ and HC(NH$_2$)$_2$PbI$_3$, however these hybrid perovskites are limited by stability issues which have led researchers to pursue all-inorganic compositions. The tolerance factor of the 3D structure limits the number of such compounds, prompting the extension of the perovskite structure to other main group metals such as Bi$^+$ and Sb$^+$ which retain the n$^0$ lone pair that plays an important role in the halide perovskite electronic structure.

One structure family that maintains a corner-connected MX$_4$ octahedral framework with trivalent M$^+$ are the defect perovskites A$^3$M$_2$X$_6$. We have been investigating the optoelectronic properties of the iodide defect perovskites A$^3$M$_2$X$_6$ (A = Cs, Rb; M = Sb, Bi), finding that these four compounds have strong electron-phonon coupling that results in self-trapped exciton photoluminescence (PL). They also show promise as semiconductor radiation detectors, with each responding to alpha particle irradiation. However, the A$^3$M$_2$X$_6$ are not entirely isostructural. The archetypical structure is a trigonal 2D bilayer that can be viewed as a (111) slicing of the AMX$_3$ structure, caused by an ordered vacancy on every third M site. In contrast, Cs$_3$Bi$_2$I$_6$ has a 3D dimer structure of isolated Bi$_3$I$_9$ octahedra, while Cs$_3$Sb$_2$I$_6$ can form either of these structures depending on preparation method. Even the 2D Rb$_3$M$_2$I$_6$ compounds have distorted octahedra which lower the symmetry to monoclinic. To evaluate the size requirements that govern structure in this family, we modified these 2D and 0D structures using mixed halides.

We found that addition of Cl in a 1:2 ratio with I induced the trigonal 2D structure from the 0D Cs$_3$Bi$_2$I$_6$, resulting in the novel 2D defect perovskite Cs$_3$Bi$_2$I$_6$Cl$_3$ with I atoms on the terminal sites while the Cl atoms take the bridging sites that bind the octahedral bilayers. Cs$_3$Bi$_2$I$_6$Cl$_3$ shows a bandgap of 2.04 eV which is remarkably similar to 2.06 eV bandgap of the 0D parent compound Cs$_3$Bi$_2$I$_6$. Beyond inducing the 0D to 2D transformation, the addition of Cl also converts the monoclinic Rb$_3$Bi$_2$I$_6$ to the higher-symmetry trigonal 2D structure, forming the new compound Rb$_3$Bi$_2$I$_6$Cl$_3$ with a band gap of 2.01 eV. Furthermore, the PL of Cs$_3$Bi$_2$I$_6$Cl$_3$ is nearly identical to that of Cs$_3$Sb$_2$I$_6$, showing that the self-trapped exciton emission is retained even though the inter-octahedral connections consist of Bi-CI bonding. This remarkable finding imparts a greater flexibility to the defect perovskites, as similar optoelectronic properties can be obtained in higher-dimensional structures. These results will guide tuning of these compounds towards functional inorganic perovskites.

ET05.03.17

Achieving Full Solubility—The Hidden Role of Oleic Acid in Cs Oleate Precursor Preparation for Perovskite Synthesis

Chang Lu, Marcus Wright, Xiao Ma, Hui Li, Dominique S. Itanze, Corey Hewitt, David L. Carroll and Scott M. Geyer; Wake Forest University, Winston Salem, North Carolina, United States.
In the colloidal synthesis of inorganic perovskite materials, cesium oleate (CsOl) is the most commonly used Cs precursor. This precursor is synthesized by combining cesium carbonate (Cs2CO3) or cesium acetate (CsOAc), and the long alkyl chain of CsOl is expected to impart solubility in the non-polar solvents used in synthesis, similar to Pb(oleate). However, despite its ubiquitous use in literature, CsOl has been found to be insoluble at room temperature and leads to surprisingly inconsistent results in perovskite nanocrystal synthesis depending on the Cs salt from which the precursor is derived. We show that under the conditions used in most reports, the amount of oleic acid (OA) added, while stoichiometrically sufficient, still leads to incomplete conversion of the Cs salts to CsOl. This results in a mixture of Cs sources being present during the reaction, causing decreased homogeneity and reproducibility. When a proper Cs:OA ratio is used, complete conversion is readily obtained even under mild conditions, resulting in a precursor solution that is soluble at room temperature and yields identical synthetic results regardless of the initial Cs source. Further, 1H NMR of solutions prepared using varying Cs:OA ratios confirms that the maximum ratio of Cs:OA obtainable in solution, with any excess Cs present in the precipitate. The super-stoichiometric ratio observed is attributed to the monovalent nature of the Cs cation which leads to a permanent dipole moment in Cs oleate, reducing solubility compared to commonly used divalent oleate complexes such as Pb(oleate). Dynamic light scattering reveals that the addition of Cs yields a reverse micelle-like structure with a diameter of 3.1 nm, consistent with the excess oleic acid complexing with the CsOl in the nonpolar solvent. Careful control of the ligand ratio yields a fully soluble precursor, which is shown to enable facile, reproducible, and scalable synthesis via the slow addition of precursors, with the notable ability to control particle morphology through injection rate.

ET05.03.18
TDDFT Investigation of Hybrid Organic Inorganic Perovskite—CH3NH3PbCl3
Ganesh Subramanian Alwarappan1, Aashik Padmanabhachary1, MD Raiyan Alam2, Aashka Bhundari3, Walid M. Hassani4, Mohamed F. Shihb5, Sunil Patel6, Jeyakumar Ramanujam7, Reza Nekovei7 and Amit Verma1;
1Department of Electrical Engineering and Computer Science, Texas A&M University-Kingsville, Kingsville, Texas, United States; 2Physics of Energy Harvesting Division, National Physical Laboratory, New Delhi, India; 3Indian Institute of Science Education & Research Mohali, Mohali, India; 4Department of Chemistry and Earth Sciences, Qatar University, Doha, Qatar; 5Gas Processing Center, Qatar University, Doha, Qatar.

Hybrid organic-inorganic metal perovskites (chemical formula: ABX3, A-organic cation, B-metal ion, X-halide) are the latest advancements for increasing efficiency in thin-film solar cells or Dye solar cells (DSC). They have become the fastest growing technology in solar cells, rising in efficiency from 3% to 20% in less than a decade. This work focuses on a time-dependent density-functional theory (TDDFT) study of CH3NH3PbCl3 - methylammonium lead chloride - a perovskite material of potential and current research interest.

Both the cubic and tetragonal phases are investigated. The cubic phase for CH3NH3PbCl3 is the room temperature phase for this configuration of the perovskite and it crystallizes in the Pm3m space group, while the tetragonal phase crystallizes in P4mm space group. The cubic structure has an outer PbCl6 octahedra and a central organic methylammonium cation (CH3NH3+). Each Pb is bonded to three CI atoms. The organic cation is not connected to the metal or halide atoms and it exists as a sub-molecule inside the metallic halide cage structure.

All the calculations were performed using Gaussian 16 software package. VESTA is used for building the crystal structures. Cam-B3LYP functional with LanL2dz basis set is used to optimize the structures. The cubic and tetragonal structures are assigned with singlet multiplicity and the net charge of the structures are -3 and -36, respectively, as calculated from the formula ABX3, (A = CH3NH3+; B = Pb 2+; and X = Cl-). Once optimized, frequency calculations and TDDFT calculations are performed at the same level of theory. Electronic and optical properties, including transition energy, band gap, and vibrational frequencies are examined.

The Density of States (DOS) spectrum, IR and UV-VIS spectra as well as the Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) values are computed. It is observed that the cubic phase of CH3NH3PbCl3 shows responsivity for optical excitation between wavelength ranges from 180 nm to 350 nm, with the peak observed at 240 nm. This work will help significantly to understand charge transport and optical properties, and design optimized solar cells involving these materials.

ET05.03.19
Enhanced Performance of Highly Efficient Formamidinium-Based Perovskite Light-Emitting Diodes via Rubidium Incorporation Yifei Shi,
Zhaoxin Wu, Jinfie Dai, Jie Xu and Ting Lei, Xi'an Jiaotong University, Xi'an, China.

Recently, organometal halide perovskites as promising candidates for light-emitting diodes have been studied greatly. However, for light-emitting application, the low photoluminescence quantum yield (PLQY) of OHPs film is critical to hinder the efficiency improvement of OHP film based light emitting diodes (PeLEDs). Although OHPs exhibit high photoluminescence quantum yield (PLQY~90%) in solution for nanocrystals or quantum dots, PLQY of OHPs is rather low in film state, which is a fatal limit for the high performance of PeLEDs.

To improve the PLQY of perovskite film, low dimensional perovskites were proposed to achieve high PLQY perovskite film. Nevertheless, the long-chain alkyl halides are indispensable to form quasi-2D structure, in which the insulative ligands will restrict the conduction of perovskite films and hamper the movement of carriers. In addition, partial substitution of A-site (ABX3) cations is an effective method to stabilize the crystal lattice and improve the PLQY. It is reported that Cs introduction to perovskite leads to improved PLQY and better stability of device, for example, device efficiency increased form 2.76cd/A to 10.09cd/A. While CsBr exhibits low solubility in solvent which leads to the difficulty in preparation for Cs-doping provskite film, to pursue other better suitable A-site substitute cations is desirable for the higher performance of PeLEDs.

Owing to RbBr exhibits higher solubility than CsBr in solvent, we select RbBr as dopant to incorporate into FAfPbBr3 perovskite film. The optimal precursor is derived. We show that under the conditions used in most reports, the amount of oleic acid (OA) added, while stoichiometrically sufficient, still leads to incomplete conversion of the Cs salts to CsOl. This results in a mixture of Cs sources being present during the reaction, causing decreased homogeneity and reproducibility. When a proper Cs:OA ratio is used, complete conversion is readily obtained even under mild conditions, resulting in a precursor solution that is soluble at room temperature and yields identical synthetic results regardless of the initial Cs source. Further, 1H NMR of solutions prepared using varying Cs:OA ratios confirms that the maximum ratio of Cs:OA obtainable in solution, with any excess Cs present in the precipitate. The super-stoichiometric ratio observed is attributed to the monovalent nature of the Cs cation which leads to a permanent dipole moment in Cs oleate, reducing solubility compared to commonly used divalent oleate complexes such as Pb(oleate). Dynamic light scattering reveals that the addition of Cs yields a reverse micelle-like structure with a diameter of 3.1 nm, consistent with the excess oleic acid complexing with the CsOl in the nonpolar solvent. Careful control of the ligand ratio yields a fully soluble precursor, which is shown to enable facile, reproducible, and scalable synthesis via the slow addition of precursors, with the notable ability to control particle morphology through injection rate.

DOI: 10.1021/acsami.8b00079

ET05.03.20
Two-Dimensional (2D) Halide Perovskites Incorporating Straight Chain Alkylidiammonium Cations, (NH(C4H9)3)2(CH3NH3)PbBr2Cl (m = 4-9; n=1-4) Xiaotong Li1, Justin Hoffman1, Weijun Ke1, Michelle Chen1, Hisinah Tsai2, Mikael Kepenekian3, Constantinos Stoumpos4 and Mercouri G. Kanatzidis5; 1Department of Chemistry, Northwestern University, Evanston, Illinois, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Institut des Sciences Chimiques de Rennes, Rennes, France.

Low-dimensional halide perovskites have recently attracted intense interest as alternatives to the three-dimensional (3D) perovskites because of their greater tunability and higher environmental stability. Herein, we present the new homologous two-dimensional (2D) series (NH(C4H9)3)2(CH3NH3)PbBr2Cl, (m = 4-9; n=1-4), where m represents the carbon-chain number and n equals layer-thickness number. Multilayer (n > 4) 2D perovskites incorporating diammonium cations were successfully synthesized by solid state grinding method for m = 4 and 6, and by solution method for m = 7-9. Structural characterization by single-crystal X-ray diffraction for the m = 8 and m = 9 series (n=1 - 4) reveals that these compounds adopt the space group.
of $C_c$ for even $n$ members and $P_r$ for odd $n$ members. The optical bandgaps are 2.15 eV for two-layer ($n=2$), 2.01 eV for three-layer ($n=3$) and 1.90 eV for four-layer ($n=4$), all behaving as direct bandgap semiconductor, also confirmed by DFT calculations. The materials exhibit excellent solution processability and casting the materials of $n=3$ into thin-films was successfully accomplished. The films show a clear tendency for the higher-$n$ members to have preferred orientation on the substrate, with $m = 8$ exhibiting almost perfect vertical layer orientation and $m = 9$ displaying both vertical and parallel layer orientation, as confirmed by GIWAXS measurements. The vertical layer orientation for the (NH$_4$C$_8$H$_2$NH$_3$)(CH$_3$NH$_3$)$_3$PbI$_{10}$ member results in the best thermal, light and air stability within this series, thus showing excellent potential for solar cell applications.

References.

ET05.03.22

Temperature-Dependence of Perovskite Solar Cell Efficiency Revealed by Electron Spin Resonance and Photocurrents
Nam Joong Jeon, Jangwon Seo, S. H. Kim, J. M. Cho and Jung-Keun Lee; 1Chonbuk National Univ, Jeonju, Korea (the Republic of); 2Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 3Korea Basic Science Institute, Seoul, Korea (the Republic of); 4Research Institute, TOpenCo., Ltd., Daejeon, Korea (the Republic of).

We have investigated the temperature-dependence of light-induced electron spin resonance (LESR) and photocurrents in perovskite solar cells. The perovskite layer was (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$. PCBM and doped-PTAA (poly-triarylamine) layer was used as an electron transport layer (ETL) and hole transport layer (HTL), respectively. The temperature-dependence of LESR suggested the existence of an interfacial thermal barrier and charge accumulation between the perovskite and the HTL. The temperature-dependence of the photocurrents reflected that most of the photocurrents are temperature-independent and ESR silent. However, part of the currents experience thermal barrier, passing through the interfacial states, and also are detected by ESR.

ET05.03.23

Surface Modification of Mesoporous TiO$_2$ Layer with Self-Assembled Monolayers for the Fabrication of High Efficiency Perovskite Solar Cells
Seid Yimer Abate$^{1,2}$ and Yu-Tai Tao$^3$; 1Institute of Chemistry, Academia Sinica, Taipei, Taiwan; 2Taiwan International Graduate Program (TIGP), Sustainable Chemical Science and Technology (SCST), Academia Sinica, Taipei, Taiwan; 3Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

Hybrid organic-inorganic halide perovskite solar cells attract enormous attentions due to their excellent photovoltaic properties which can compete with that of the crystalline silicon solar cells. However, there are some issues in perovskite solar cell that need to be fully understood and solved before its commercialization. These include the operation mechanism, device stability, environment impact, and so on. In this study, charge extraction characteristics at the perovskite/TiO$_2$ interface is studied by interface engineering. So that self-assembled monolayer of phosphonic acids with different chain length (spacer group) and functional (tail) group were adsorbed on mp-TiO$_2$ at -4.19 eV. A correlation of charge mobility, charge extraction and transport with respect to the energy alignment of mp-TiO$_2$ was demonstrated. The work function of the SAM-modified mp-TiO$_2$ varied from -3.80 eV to -4.87 eV, with that of the crystalline silicon solar cells. However, there are some issues in perovskite solar cell that need to be fully understood and solved before its commercialization.

ET05.03.24

Highly Luminescent and Stable Bromide Perovskites via the Formation of Low Dimensional Architectures
Mingue Shin$^1$, Joonyun Kim$^1$, Young-Kwang Jung$^2$, Tero-petri Ruoko$^3$, Arri Primagi$^2$, Aron Walsh$^{+3}$ and Byungha Shin$^1$; 1KAIST, Daejeon, Korea (the Republic of); 3Korea Basic Science Institute, Seoul, Korea (the Republic of); 4Research Institute, TopnC Co., Ltd., Daejeon, Korea (the Republic of).

Organic-inorganic halide perovskites have been attracting attention as materials for light-emitting diodes (LEDs) due to unique emission properties, which include high color purity with a very narrow emission and tuning the emission wavelength easily through the adjustment of the halide components, covering the entire range of visible light. However, one roadblock to LED application is the low exciton binding energies, which results in low luminous efficiencies. One of the proposed strategies to enhance the exciton binding energy is reduction of the dimensionality of the perovskite crystal structure. Here, we report highly luminescent thin films of formamidinium (FA) lead bromide perovskite (photoluminescence quantum yield, PLQY = 35.7%) via the formation of low dimensional architectures. A mixture of 3D FAPbBr$_3$ and a new type of 2D perovskite FA$_2$PbBr$_4$, intercalated with dimethyl sulfoxide (DMSO) was formed by controlling the molar ratio of FABr/PbBr$_3$ in the precursor solutions and annealing condition. A type I band alignment between the lower bandgap 3D FAPbBr$_3$ and the higher bandgap 2D FA$_2$PbBr$_4$ was supported by density functional theory (DFT) calculations, which results in exciton confinement in the 3D phase and a substantial increase in PLQY. The composite films also exhibited excellent air and thermal stability. Details of analysis will be presented and discussed.
ET05.03.25
Ultra-High Purity, Monocrystalline Quality Hybrid Perovskite Thin Sheets for Radiation Detectors

Hisato Yamauchi, Fangze Liu, Hsinhan Tsai, Michael D. Yoho, Aditya D. Mohite, Sergei Tretiak, Duc T. Vo and Wanyi Nie; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Halide perovskite materials synthesized via cost-effective solution process recently emerged as a promising candidate for detection of X-ray and gamma-ray. This is because of their high radiation absorption cross section in presence of heavy elements in the lattice, long mobility-lifetime product, balanced carrier mobility, which leads to high detectivity and energy resolutions. The current challenge is to synthesize large-scale high quality single crystals with minimal structural defects in both of bulk and surface. In this study, we report high quality Methylammonium Lead Bromide (MAPbBr3) single crystals that are prepared via modified inverted temperature crystallization (ITC) approach from precursor solution. With balanced crystalline-rate and proper choice of growth volume, we obtain mono-crystal with well controlled thickness from 400 nm up to 10 µm. Obtained mono-crystals demonstrate high material quality by the narrow peak width of X-ray diffraction (XRD) spectra that is comparable to the values reported for its bulk single crystals via ITC. In addition, the surface roughness is an order of magnitude lower compared to the bulk counterpart with homogeneous surface charge distribution. Our high quality crystals with smooth surface are further fabricated into diodes with PIN junction by sandwiching them in between p-type and n-type electrodes. The dark current noise of the two terminal devices is as low as 50 pA/V, several orders of magnitude lower compared to our bulk crystals via ITC. Such crystals are ideal for extracting ultra-low density of carrier with radiation excitations.

ET05.03.27
A Comprehensive Approach to Measuring and Understanding the Electronic Structure of Lead-Halide Perovskite Materials

Alexandra Ramadan1, Maryline Ralaiarisoa2, Fengshuo Zu2, Jonathan Warby1, Norbert Koch1 and Henry Snaith1; 1Department of Physics, University of Oxford, Oxford, United Kingdom; 2Humboldt-Universität zu Berlin, Berlin, Germany.

Perovskite-based photovoltaics are an emerging solar technology, with device efficiencies exceeding 22 % and significant steps are being made towards their commercialisation. In spite of the impressive strides made in device performance and stability, fundamental characterisation of these materials is still severely lacking. Studies of the electronic structure of perovskite materials have resulted in a broad range of values reported for the electronic energy levels and the instability and complex nature of these systems has resulted in a lack of consensus in the electronic properties of these materials. To tackle this ambiguity we have developed a new comprehensive approach to understanding the electronic structure of a perovskite.

In this work the all inorganic perovskite cesium lead bromide (CsPbBr3) is used as a model system. This material was selected as it demonstrates a high stability of both the perovskite material and its non-volatile precursors. We begin by probing the electronic structure of CsBr and PbBr2, we investigate the electronic structure and their contribution to the overall electronic structure of our CsPbBr3. Films prepared with varying concentrations of the precursor materials up to the full perovskite structures have been investigated using x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and inverted photoemission spectroscopy (IPES). The surface chemistry of the films, as determined from UPS and IPES, will be presented. This information is then correlated with morphological and structural data, provided by atomic force microscopy (AFM) and x-ray diffraction (XRD). These techniques enable a full picture of the electronic structure of these systems to be developed and provides a method through which the structure of other perovskite materials can be investigated.

ET05.03.28
Thermodynamic Stability of Halide Perovskites

Alessandro Senocra1,2, Gee Yeoong Kim1 and Joachim Maier1; 1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2École Polytechnique Fédérative de Lausanne, Lausanne, Switzerland.

Hybrid halide perovskites (HOIPs) have been extensively studied in recent years due to their potential use as light-harvester in photovoltaic devices. While the efficiencies of such devices pose no limitation to commercial applications, the severe lack of stability of the materials remains an important issue to be overcome. Indeed, HOIPs are known to easily degrade under moderate thermal stress[1] or upon oxygen[2] and/or light exposure.[3] Notably, recent calorimetric studies even suggested that some HOIPs (MAPbI3 in particular and MAPbBr3 to a minor extent) could be thermodynamically unstable,[4] in agreement with DFT calculations.[5] In contrast, other studies indicate the materials to be intrinsically stable.[6] Obviously these questions need to be unambiguously answered. In this contribution, we discuss the underlying thermodynamics of HOIPs both intrinsically (i.e., with respect to temperature) and extrinsically (against oxygen exposure and/or light). Intrinsically, we find the materials to be stable (albeit, in the case of MAPbI3, only slightly) under standard conditions, and we also can assess the most favorable degradation path upon heating. Extrinsically, our considerations reveal a large tendency towards degradation of HOIPs in the presence of oxygen, especially under real conditions. Notably, light itself can activate a relevant photodecomposition pathway.[7] We discuss these issues on a quantitative level, in conjunction with experimental observations of the degradation phenomena.

References

ET05.03.29
Enhanced Photoresponse in Hybrid Perovskite Thin Film via Integrating with MoS2

Jingfeng Song1, Dawei Li1, Bo Chen2, Zhiyong Xiao1, Yongfeng Lu1, Jinsong Huang2 and Xia Hong1; 1University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 2University of North Carolina-Chapel Hill, Chapel Hill, North Carolina, United States.

Over the past five years, the organolead trihalide perovskites such as CH3NH3PbI3 (MAPbI3) have gained significant research interests with a rapid rise of power conversion efficiency of up to 22%. Integrating MAPbI3 with the two dimensional transition metal dichalcogenides such as MoS2 has the potential of achieving enhanced photosensitivity and broadened absorption bandwidth. In this work, we have integrated MAPbI3 polycrystalline thin film with few-layer MoS2 and demonstrated up to two orders of magnitude enhancement of the photoresponse in the heterostructure compared with the single layer MAPbI3 and MoS2. We mechanically exfoliated few-layer MoS2 flake and transferred it onto the SiO2/Si substrate. The sample was fabricated into 2 point device, on top of which we spincoated uniformly 500 nm MAPbI3 film. Between the two parallel Au electrodes, half of the area contains the MoS2-MAPbI3 hybrid structure, while the other half contains only single layer MAPbI3. We performed high-resolution photocurrent mapping within those two channels, and observed that the MoS2-MAPbI3 region had up to two orders of magnitude higher photocurrent than single layer MAPbI3. The enhancement
is attributed to the charge transfer between these two materials due to band alignment, which facilitated photo-carrier separation. The MoS2-MAPbI3 hybrid device showed faster transient photoresponse of 200-300 μs, which makes it promising for constructing high performance photo-detectors.

*This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award No. DE-SC0016153, NSF Grant No. OIA-1538893, and NSF Nebraska Materials Research Science and Engineering Center (MRSEC) Grant No. DMR-1420645.

**ET05.03.30**

**Perovskite LEDs using ZnMgO Interfacial Layer**

Hua Wu1, Yu Zhang2 and William Yu3; 1Louisiana State University Shreveport, Shreveport, Louisiana, United States; 2Jilin University, Changchun, China.

Perovskite quantum dots are promising optoelectronic materials but are very sensitive to oxygen and water. Here, we report a highly efficient and stable light emitting device (LED) by applying solution-processed Mg-doped ZnO (MZO) nanocrystals (NCs) as an interfacial layer. We investigated the effect of Mg doping on the optical and electronic properties of NCs. We demonstrated that the air stability of perovskite NC film was significantly enhanced because of the decreased oxygen vacancy surface sites of MZO NCs. Incorporation of a MZO layer with favorable electronic energy level to form a suitable band alignment promoted electron injection and enhanced the LED performance. Compared to the device without MZO, the LED showed 3059 cd/m² of luminance, with 1.9 times enhanced current efficiency and 2 times increased external quantum efficiency. In addition, the device with MZO also exhibited better operation and storage stability. This research provides a potential strategy for realizing stable and efficient perovskite LEDs.

**ET05.03.31**

**Efficient and Stable White LEDs Using Silica-Coated Perovskite Quantum Dots**

Chun Sun1, Yu Zhang2 and William Yu1; 1Louisiana State University Shreveport, Shreveport, Louisiana, United States; 2Jilin University, Changchun, China.

Inorganic perovskite QDs (CsPbX3), with narrow size distribution, narrow emission line width, as well as high PL QY without surface shelling, have broad applications. Their emission lights cover the entire visible spectral region and can be easily adjusted. However, their instability and the anion-exchange reaction between different halide QD particles when used together are still the major issues that obstruct their practical applications. In this work, (3-amino(prop)|trithiophosyilane (APTES) was chosen as both the capping agent for inorganic perovskite QDs and the precursor for a silica matrix. All chemicals were mixed in a water-free synthesis system to form perovskite QDs, then the system was open to the air and the trace water vapor was captured and reacted with APTES for its hydrolysis for the matrix before contacting the QD surface. In this way, a silica matrix was slowly formed but the delicate perovskite QDs were protected. This is an easy one-pot operation and can be done with large quantities. The as-prepared QD/silica composites possesses high PL QY. Most importantly, the composites exhibited extremely high stability in air and the anion-exchange reactions were not observed between different perovskite QDs, which are beneficial to fabricating the white LEDs. By combining the green and red QD/silica composites with a blue LED chip, a white LED with CIE color coordinates of (0.33, 0.33) and a power efficiency of 61.2 lm/W was obtained, demonstrating their application potentials in such as white lighting.

**ET05.03.32**

**Material Preparation and Emission Properties of Pure and Pr3+ Doped CsPbCl3 Perovskite Crystals for Photonics and Radiation Detection**

Uwe Hermersch1, Lianjah Flagg1, Al Amin Kabir1, Altha Bluets1, Sudhir Trivedi2, Clayton S. Yang3 and Feng Jin1; 1Hampton Univ, Hampton, Virginia, United States; 2Chemistry, Geology, and Physics, Elizabeth City State University, Elizabeth City, North Carolina, United States; 3Brimrose Technology Corporation, Sparks Glencoe, Maryland, United States.

We report on the material preparation and emission properties of pure CsPbCl3 and Pr3+ doped CsPbCl3 perovskite crystals for possible applications in multi-wavelength photonics and nuclear radiation detection. The material properties of lead halide perovskites continue to be of great current for optoelectronic applications such as solar cells, light emitting diodes, lasers, and radiation detectors. In this work, we prepared pure and Pr3+ doped CsPbCl3 bulk crystals in an effort to further extend its functionality. The investigated materials were synthesized from purified precursors of PbCl2, CsCl, and PrCl3 followed by melt growth in a vertical Bridgman station. Purification steps included directional freezing and multi-pass unidirectional translation in a zone-melting system. The pure CsPbCl3 crystal exhibited a light yellow color, whereas the Pr: CsPbCl3 crystal was light green indicating the incorporation of Pr3+ ions into the host lattice. Under UV optical pumping (340 nm) the pure CsPbCl3 samples showed bandedge related emission centered at ~410 nm and a broad defect-related emission band extending to ~600 nm. The Pr: CsPbCl3 samples exhibited a bright red emission under resonant intra-4f excitation of Pr3+ ions at 450 nm, with strongest lines peaking at 492 nm, 621 nm, 647 nm, and 732 nm. Furthermore, the Pr: CsPbCl3 sample also exhibited IR emission bands centered at ~1.6 μm, ~2.5 μm and ~4.5 μm under optical pumping at ~1500 nm. The observation of IR emission at room temperature reflects on the low maximum phonon energy of chloride crystals (< 250 cm⁻¹), which reduced non-radiative decay though multiphonon relaxations of Pr3+ ions. More details of the material preparation, emission properties of pure and Pr3+ doped CsPbCl3 crystals as well as initial studies for nuclear radiation detection will be presented at the conference.

**ET05.03.33**

**Super-Resolution Infrared Imaging of Mixed Cation Perovskites—Local Compositional Heterogeneities**

Ilija M. Pavlovec1, Rusha Chatterjee, Kyle Aleshire, Gregory Hartland and Masaru Kuno; Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States.

Hybrid organic-inorganic lead halide perovskites such as MAPbI3 or FAPbI3 (MA=CH3NH3+ and FA=CH(NH2)2+) and their mixed cation analogues represent one of the most promising alternatives to conventional Si based solar photovoltaics. Intriguing aspects include tunable band gap depending on composition, large optical absorption coefficients, and certified power conversion efficiencies (PCEs) that now exceed 22%. Additionally, composition-based tunable band gap makes these systems ideal candidates for multi-junction solar cells. Unfortunately, there has been relatively little work done to explore perovskites compositional cation uniformity. Variation in cation stoichiometry may represent an important limiting factor for these devices as bandgaps – and by immediate extension open circuit voltages – are exquisitely sensitive to local cation composition. Although reports already exist, suggesting cation compositional heterogeneity across perovskite films, this is the first direct study of this phenomenon. Here, we provide the first direct evidence for intrafilm cation heterogeneities within mixed cation FA0.8MA0.2PbI3 films using a spatially-resolved, super-resolution infrared photothermal heterodyne imaging (IR-PHI) technique. We establish that these films exhibit large compositional spatial heterogeneities with cation distributions varying on the order of ~20%, with some areas exceed stoichiometric differences that exceed thrice the expected ideal stoichiometry. The impact of these cation heterogeneities is further corroborated by emission measurements showing intrafilm emission energies differing by over 30meV directly correlated to local stoichiometry. These measurements thus reveal, for the first time, cation stoichiometric heterogeneities and their direct impact on local photovoltaic response-determining optical properties of mixed cation perovskites.
ET05.03.34 Highly Efficient and Hysteresis-Less Planar Perovskite Solar Cell with Enhanced Open Circuit Voltage and Stability Mohammad Mahdi Tavakoli1, Punkaj Yadav2, Roudollah Tavakol1 and Jing Kong1; 1Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Solar, Pandit Deendayal Petroleum University, Gujarat, India; 3Sharif University of Technology, Tehran, Iran (the Islamic Republic of).

Interfacial studies and band alignment engineering on electron transport layer (ETL) play a key role for fabrication of high performance perovskite solar cells (PSCs). Here, we inserted an amorphous layer of SnO2 (a-SnO2) between the TiO2 ETL and the perovskite absorber and studied on the charge transport properties of the device. The double-layer structure of TiO2-compact layer (c-TiO2) and a-SnO2 ETL leads to modification of interface energetics, resulting in improved charge collection and decreased carrier recombination in PSCs. The optimized device based on a-SnO2/c-TiO2 ETL shows a maximum power conversion efficiency (PCE) of 21.4% as compared to 19.33% for c-TiO2 based device. Moreover, the modified device demonstrates a maximum open circuit voltage ($V_{oc}$) of 1.223 V with 387 mV loss in potential, which is among the highest value reported for PSCs. In addition, the optimized PSC depicts a negligible hysteresis, and stabilized performance measured under continuous light (AM 1.5G) and UV light illumination. The stability results show that the device on c-TiO2/a-SnO2 retains about 91% of its initial PCE value after 500 h light illumination, which is higher than that pure c-TiO2 (67%) based devices. Interestingly, using a-SnO2/c-TiO2 ETL the PCE loss was only 10% of initial value under continuous UV light illumination after 30 h, which is higher than that of c-TiO2 based device (28% PCE).

ET05.03.35 Prediction of Novel $p$-Type Transparent Conductors in Layered Double Perovskites—A First-Principles Study Jian Xu1,2, Jian-Bo Liu1, Bai-Xin Liu1 and Bing Huang1; 1Tsinghua University, Beijing, China; 2Beijing Computational Science Research Center, Beijing, China.

The development of high-performance transparent conducting oxides (TCOs) is critical to various technologies from transparent electronics to solar cells. Whereas $n$-type TCOs have been extensively applied in many electronic devices, their $p$-type counterparts have not been largely commercialized due to the lack of ideal materials. Combining atomic replacement and first-principles calculations, we have identified 7 stable layered double perovskites, i.e., CsCuSbCl$_{12}$-like Cs$_{2}$M$^{2+}$B$^{3+}$X$_{12}$ compounds as promising $p$-type TCOs with sufficiently large bandgaps, delocalized wavefunction distribution with s-orbital components in valence band maximum (VBM) and the antibonding character of VBM to ensure their optical transparency, light hole effective masses and intrinsic good $p$-type conductivities, respectively. Taking CsCuSbCl$_{12}$ as a representative example, we demonstrate that under Cd-poor (Cl-rich) conditions, Cs$_{2}$Sb$_{5}$Cl$_{12}$ could exhibit excellent $p$-type conductivity with high hole concentration, contributed by the intrinsic shallow-acceptor C$_{do}$ with extremely low formation energy. Generally, the other 6 Cs$_{2}$M$^{2+}$B$^{3+}$X$_{12}$ compounds exhibit similar intrinsic $p$-type defect properties as CsCuSbCl$_{12}$, which could rank them as the top $p$-type TCOs discovered or predicted until now.

ET05.03.36 Direct observation of deep defects in wide bandgap Halide Perovskites Jialin Levine1, Giovanni Corcione2, Nano Garcia Verar, Michael Kulbak1, Carolin Rehermann2, Eva L. Ungerechts3, Gary Hodes3, Isaac Balberg3, David Cahen3 and Thomas Dittrich3; 1Weizmann Inst of Science, Rehovot, Israel; 2Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany; 3The Hebrew University of Jerusalem, Jerusalem, Israel.

Lead Bromide-based perovskites (HPs) are of interest as parent composition for wide bandgap (> 1.75 eV) absorbers for low-cost solar spectrum splitting to boost solar-to-electrical energy conversion efficiency/area by adding them to c-Si or CIGS PV cells, and for photoelectrochemical solar fuel synthesis. Deep in-gap electronic states in solar cell absorbers serve as recombination centers and are detrimental for the cell’s photovoltaic performance, especially the open circuit voltage ($V_{oc}$) of the cell. However, since several studies showed that the concentration of defects in the HPs is relatively low (< 10$^{14}$ cm$^{-3}$), there is a general difficulty to observe deep in-gap states by direct optical absorption of sub-band gap photons in the HPs. Here we use modulated Surface PhotoVoltage (SPV) measurements, a non-destructive contactless technique that relies on direct sub-gap band gap absorption, with exponentially higher sensitivity than photocurrent-based measurements. SPV can show the existence of in-gap states and their relative positions with respect to the band edges both within the bulk semiconductor band gap, as well as at the interfaces of the HP with the Electron Transport Layer (ETL) or the Hole Transport Layer (HTL).

For the first time, we reveal that three different, deep, defect levels exist in the bulk of the mix- Cation Lead Tribromide layers. Two of the levels are close to midgap, and the third lies ~0.8 eV below the Conduction Band Maximum (CBM). We also find that aging in inert atmosphere, as well as light soaking, increases the defect concentration. Furthermore, by performing photoconductivity measurements over a wide excitation intensity range, we show that under steady-state 1-sun equivalent conditions, this sub-band gap defect levels play an active role as non-radiative recombination centers.

ET05.03.37 Composition Engineering and Microspectroscopic Study for Efficient and Spectrally Stable Mixed Halide Perovskite LEDs Yongheng Jia, Yuwei Guo, Yang Zhou and Ni Zhao; EE, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Quickly following the development of perovskite solar cells, the field of perovskite light-emitting diodes (LEDs) has proceeded rapidly, with some devices already showing comparable efficiencies with those of the state-of-the-art organic LEDs. Perovskite LEDs offer tunable emission wavelength from visible to near-infrared; however, in certain temperature range the device performance is highly unstable. Taking red-emitting perovskite LEDs as an example, since the devices often rely on a mixed bromide-iodide perovskite for light emission, the typical light-induced phase segregation behavior of the material system results in a rapid red-shift of the electroluminescence (EL) peak, leading to a color change of the LEDs. In this presentation, we will introduce our recent endeavors on composition engineering and optical microspectroscopy to address the aforementioned stability problem of perovskite LEDs. We show that by simultaneously introducing lead thiocyanate and organoiodine additives in the perovskite precursors one can obtain a stable perovskite phase with high photoluminescence quantum yield (PLQE). The corresponding LEDs exhibit stable spectral emission and good performances (e.g., irradiance of 400 W sr$^{-1}$ m$^{-1}$, maximum external quantum efficiency (EQE) of 14.5% and maintained at 12.0% at a high current density of 500 mA/cm$^2$), despite the fact that perovskite film is discontinuous. The material strategy has been examined in the wavelength range from 630nm to 700nm. To better understand the morphology-performance correlation, we apply charge-modulation microspectroscopy (CMM) to investigate the electric-field inhomogeneity in the perovskite film, the impact of electron- (or hole-) transport layer on the LED EL properties, as well as the spatially resolved degradation processes in the electrode-covered and –uncovered regions. The findings provide some guidelines to the design of perovskite LED structures.

ET05.03.38 Highly Luminescent 0D Organic Metal Halide Hybrids with Tunable Colors Chenkun Zhou1, Haoran Lin1, Michael Worku1, Jennifer Neu1, Yan Zhou1, Yu Tian1, Peter I. Djurovich3, Theo Siegrist3 and Biwu Ma1; 1Florida State University, Tallahassee, Florida, United States; 2University of Southern California, Los Angeles, California, United States; 3FAMU-FSU College of Engineering, Tallahassee, Florida, United States.

Organic-inorganic metal halide hybrids, consisting of a great variety of inorganic metal halide anions and organic cations, are an emerging class of functional crystalline materials with exceptional structural tunability. By choosing appropriate organic and inorganic components, the crystallographic
structures can be finely engineered with the inorganic metal halides forming three-dimensional (3D) networks, two-dimensional (2D) planar or corrugated layers, one-dimensional (1D) chains or tubes as well as zero-dimensional (0D) structures. The structural versatility of this class of materials suggests there is a vast parameter space to explore novel crystal structures exhibiting properties obeying non-obvious trends.

In this talk, I will present our recent efforts in developing and studying new classes of 0D metal halide hybrids. By choosing appropriate organic and inorganic components, the emitting species in 0D structure can be tuned from MX₃ octahedra to MX₅ pyramids, MX₆ seass structure, and metal halide clusters. Due to the structural reorganization and efficient ionic system cross the on the excited states, highly luminescent broadband emissions with large Stokes shift have been achieved for these 0D metal halide hybrids. Our findings show the molecular nature of small metal halide species in the 0D structure and allow us to relate the emission from either structure reorganization or localized excitons in metal halides to molecular phosphorescence. The application of these 0D materials as down converter in optically pumped white light emitting diodes will also be discussed.

ET05.03.39
Solvent Effects on the Thin-Film Quality and Photovoltaic Performance of Metal Halide Perovskites Yuchen Zhou¹, Yifan Yin¹, Chang-Yong Nam¹ and Miriam Rafailovich¹; Stony Brook University, Stony Brook, New York, United States; ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

The metal halide perovskite solar cells (PSCs) has become one of the most popular types of photovoltaic devices in past 6 years. High power-conversion efficiency (PCE), panchromatic light absorptions and long carrier diffusion length, etc, makes the PSCs significantly competitive among the thin film solar cells. However, optimal function and performance of the PSCs usually require high quality of a perovskite film with full coverage, low roughness, big grain size and proper thickness, etc. Numerous methods have been applied to make high quality perovskite film, among which, the solution-based spin casting is one of the most widely used methods. Although different groups have succeeded in making perovskite film using the spin casting, specific conditions such as solvent type, thermal treatment etc, varies largely. Lack of rational comparisons and instructive guidance on the deposition condition selection result in huge difficulty in performing repeatable experiments. Herein, we compare the effect of solvents, co-solvents and their ratios on the quality of the perovskite thin films. DMF and/or GBL are used as major solvents, while DMSO is applied as the co-solvent. Several ratios of DMF/GBL to DMSO from 10:0, 9:1 to 7:3 have been tried to prepare the perovskite precursor solutions. Interestingly, we observe significant differences on crystallinity, morphology and thickness of the thin film made by different types and combination of solvents. For instance, 1) From the XRD data, perovskite deposited from DMF based solution exhibits 10 times stronger crystallinity as compared with samples made from GBL. 2) SEM images indicate that DMF based solution guarantees compact and 2 times thicker films than the GBL ones, while the surface of DMF made layer shows much higher roughness. 3) Reducing the amount of the DMSO in the solution can promote the smoothness of the surface but result in the decrease of the film thickness. 4) Crystals with smaller grain size are observed in samples made from solution without DMSO, while excessive of DMSO content leads to vacancies inside the films. 5) Films deposited from the combined solvents of 90% DMF and 10% DMSO presents best compactness, thickness, smoothness and crystallinity among all other solvent combinations, showing 1.5-2 times longer charge carrier lifetime and superb PCE with the best device exceeding 17%. We attribute the better quality of the DMF deposited layers to higher PbI₂ solubility and lower boiling point of the DMF, as compared with GBL. The addition of DMSO slows down the crystal growth rate of perovskite by forming MAI-DMSO-PbI₂ intermediate, guaranteeing larger crystal grain size. While excessive DMSO, which does not participate in the formation of the intermediates, remains in the supersaturated film (before annealing) and causes rupture and vacancies in the film during the vigorous annealing process. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

ET05.03.42
Effect of Chromium Doping on the Electronic Structure of CH₃NH₃PbI₃ Perovskite Mapeng Nam1, Christopher McCleese2, David Stewart1, 2, Tod Grusenmeyer1, Thomas M. Cooper1 and Joy Haley1; 1Air Force Research Laboratory, Dayton, Ohio, United States; 2General Dynamics Information Technology, Dayton, Ohio, United States.

Organic-inorganic lead halide perovskites (mainly CH₃NH₃PbI₃) are being extensively studied because their excellent photovoltaic properties, such as small bandgap, high optical absorption and long carrier lifetime. To explain the large recombination time, the hypothesis that the formation of ferroelectric domains can separate the diffusion pathways of electrons and holes, has been proposed. We have found that a two-dimensional hole confinement in CH₃NH₃PbI₃ is possible under room temperature conditions.

In this work, we explore the possibility of increasing their photovoltaic efficiency through additional sub-bandgap absorption. This would result in the creation of extra electron-hole pairs and in an increase in photocurrent without a decrease in open-circuit voltage. We assess the formation of a new band in the gap as well as its effect on the absorption features of hybrid halide perovskites CH₃NH₃PbI₃ (MAPI). This approach has been widely studied to improve the efficiency of common semiconductors with photovoltaic performance such as GaP, CuInS₂, thiospinels, SnS₂ or Sn. We report here the electronic structure of new CH₃NH₃PbI₃ perovskite derivatives, in which narrow band is obtained by replacing Pb atoms by Cr atoms. To deal with the bandgap underestimation problem of common DFT methods, quasiparticle calculations have been applied via the GW approximation. The investigation of the electronic structure of new CH₃NH₃PbI₃ perovskites suggests that the presence of point defects play an important role in the coupling of two low energy photons to achieve a higher energy electron excitation (like in the Z-scheme of photosynthesis), which would maximize the photovoltaic performance.

G. García, P. Palacios, et al. Scientific Reports, 2018, 8, 2511

ET05.03.43
Monitoring Nonradiative Charge Carrier Recombination and Extending the Excited State Lifetimes in Methylammonium Lead Bromide Perovskite Nanocrystals Christopher McCleese¹, David Stewart¹, ², Tod Grusenmeyer¹, Thomas M. Cooper¹ and Joy Haley¹; ¹Air Force Research Laboratory, Dayton, Ohio, United States; ²General Dynamics Information Technology, Dayton, Ohio, United States.

Lead halide perovskites have applications in the fields of photovoltaics, light emitting diodes, and lasers. Their success results from their high absorption coefficients, low exciton binding energy, long charge carrier diffusion lengths, and high photoluminescence quantum yields. In order to optimize these devices to their full potential, it is important to understand their fundamental photophysical properties and how processing conditions affect their optical and electronic properties. Currently in the literature, the majority of time-resolved optical studies on perovskite nanocrystals utilize time-resolved photoluminescence to determine the excited state lifetimes. However, the nonradiative recombination processes should be further investigated due to the fact that they can have drastically different charge carrier recombination rates. Here, steady state and time-resolved optical spectroscopy is used to study the photophysical properties of hybrid organic-inorganic methylammonium lead bromide nanocrystals. Time-resolved spectroscopy measurements show that the band edge bleach decay dynamics are longer compared to the photoluminescence decay. These results indicate that dark carrier recombination is the primary mechanism leading to the long lived excited state lifetime of perovskite nanocrystals. Additionally, the effect of the precursor starting material purity on the excited state lifetimes is investigated.

ET05.03.44
Mapping the Inter-Diffusion of A-Site Cations in Metal Halide Perovskites Sarthak Jariwala, Irika Sinha, Kathryn N. Guye and David S. Ginger;
Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 21%. We discuss the fundamental photophysical processes that have enabled these materials to be such efficient light-harvesters and charge collectors.

As photovoltaic power conversion efficiencies of single-junction cells approach the Shockley-Queisser limit, the recombination and mobility of charge-carriers will be limited only by intrinsic properties. We demonstrate that at the intrinsic limit, the mobility of charge-carriers is predominantly governed by interaction of carriers with optical vibrations of the lead halide lattice (Fröhlich interaction)\(^1\). Therefore, predictions of maximum attainable mobilities can be made from easily accessible parameters, such as LO phonon frequencies and limits of the dielectric function.\(^2\)

In the absence of trap-mediated charge recombination, bi-molecular (band-to-band) recombination will dominate the charge-carrier losses near the Shockley-Queisser limit. We show that in methylammonium lead triiodide perovskite, such processes can be fully explained as the inverse of the radiative recombination processes is a critical factor determining device efficiency. We demonstrate that at the intrinsic limit, the mobility of charge-carriers is predominantly governed by interaction of carriers with optical vibrations of the lead halide lattice (Fröhlich interaction)\(^1\). Therefore, predictions of maximum attainable mobilities can be made from easily accessible parameters, such as LO phonon frequencies and limits of the dielectric function.\(^2\)

Finally, we examine the prospect of such highly performing hybrid lead iodide perovskites in solar concentrator environments.\(^3\) We demonstrate that in the absence of degradation, perovskite solar cells can fundamentally exhibit appreciably higher energy-conversion efficiencies under solar concentration, where they should be able to exceed the Shockley-Queisser limit and exhibit strongly elevated open-circuit voltages.

9:00 AM ET05.04.04
Impact of the Rashba Effect on Radiative Recombination in Hybrid Perovskites Xie Zhang, Jimmy-Xuan Shen, Wennie Wang and Chris G. Van de Walle; University of California, Santa Barbara, Santa Barbara, California, United States.

Hybrid perovskites exhibit pronounced momentum splitting at band edges due to a strong Rashba spin-orbit coupling effect. This effect was invoked by a number of groups to explain the high efficiency of hybrid perovskite solar cells. It was argued that the Rashba-induced splitting effectively suppresses the radiative recombination by mismatched spins and momenta between photogenerated electrons and holes. In the present study, we perform first-principles calculations to explicitly examine the impact of the Rashba effect on the radiative recombination coefficient in the archetypical hybrid perovskite, CH$_3$NH$_3$PbI$_3$. We demonstrate that the band extrema have consistent spin orientation and the momentum mismatch affects the radiative recombination coefficient by less than a factor of two. The computed radiative recombination coefficients are as high as in typical direct-gap semiconductors. Our insights establish a solid basis for accurate modeling of hybrid perovskites.

9:15 AM ET05.04.05

Recently, 2-dimensional (2D) Ruddlesden-Popper lead-halide based perovskite layered systems are attracting attention. Compared to their 3D counterpart, 2D systems offer greater tunability and stability, making them candidates for high-performance optoelectronic applications. Here we report the charge carrier recombination rate and spin depolarization times in single crystals of 2D perovskites PEA$_2$PbI$_3$ and (PEA$_2$PbI$_3$)$_n$ (PEA, phenethylammonium; MA, methylammonium; n = 1, 2, 3, 4). Layer thickness dependent charge carrier recombination rates were observed with the fastest rates for n = 1 due to the large exciton binding energy. Interestingly the slowest recombination rates occurred for the n = 2 sample and not n = 4. Room temperature spin-decoherence times also show a nonlinear layer thickness dependence with an increasing spin-coherence lifetime with increasing layer thickness from n = 1 to n = 4, followed by a decrease in lifetime from n = 4 to n = ∞. The longest decoherence time of ~7 ps is observed in the n = 4 sample. Our results are consistent with two contributions; Rashba-splitting increases the spin-coherence time going from the n = ∞ to the layered systems, while phonon-scattering which increases for smaller layers decreases the spin-coherence time. The interplay between these two factors contributes to the layer thickness dependent spin-coherence lifetimes. To correlate we monitored the LO and TO phonon frequency and phonon linewidth. For thinner layers the phonon frequencies decrease and broaden substantially indicating a large electron-phonon coupling.

9:30 AM ET05.04.06
Charge Carrier Dynamics in Metal Halide Perovskite Solar Cells Change after Exposure to Humidity and Light Esma Ugur, Jafar I. Khan, Erkki Alarousu, Sandra P. Gonzalez-Lopez and Frédéric Laqhai; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

In a very short time span, the power conversion efficiency (PCE) of metal halide perovskite solar cells (PSCs) has reached 23%, a massive improvement for solution-processed photovoltaic devices. Towards this end, both surface and bulk recombination of photogenerated charge carriers in the perovskite absorber layer are the major efficiency-limiting factors. [1] In this respect, controlling the growth and crystallization of the perovskite thin film is crucial for the performance of the perovskite solar cells as the crystal growth dynamics are very susceptible to the processing conditions [2]. Interestingly, some studies report a beneficial effect from water inclusion during processing, while others claim an adverse effect. Moreover, the effect of humidity and light exposure on the performance of PSCs is still debated. In this study, we fabricated, using a two-step protocol, MAPbI$_3$ perovskite solar cells with SnO$_2$ electron transport layers to study how the device performance and photophysics change upon exposure to humidity and light. Reference devices, not exposed to humidity and light, exhibit 18.4% PCE with 22.5 mA/cm$^2$ short-circuit current density ($J_{sc}$) and 1.12 V open circuit voltage ($V_{oc}$). After exposing the perovskite absorber layer to 55% relative humidity under 1-sun illumination prior to completing the device fabrication, a reduction in $V_{oc}$ to 1.09 V was observed. We study the influence of excess lead iodide (PbI$_2$), which is commonly believed to be passivating the PSCs, on the humidity resistance of MAPbI$_3$ devices. While the $V_{oc}$ value of samples with excess-PbI$_2$ was lowered to 1.10 V, we did not observe any change in $J_{sc}$. Since $V_{oc}$ losses can be attributed to non-radiative recombination, we performed time-resolved photoluminescence (TR-PL) spectroscopy before and after humid air exposure of perovskite thin films under 1-sun illumination. We will discuss in detail how the exposure to humid air under illumination alters the surface structure of the perovskite samples, affects the device performance, and the photophysical processes.

References

9:45 AM BREAK

10:15 AM ET05.04.07
Ferroelectric Large Polaron in Lead Halide Perovskites Xiaoyang Zhu; Columbia University, New York, New York, United States.

A major puzzle from recent studies on LHPs is that optoelectronic performances suggest nearly perfect semiconductors despite the unavoidable presence of defects from room temperature and solution processing. Here we explain the essential physics in this class of materials based on their disordered phonon dynamics and dielectric functions. We show that the dielectric function of a hybrid organic-inorganic lead halide perovskite (LHP) possesses combined characteristics of a polar liquid and a ferroelectric material. The latter response in the THz region may lead to dynamic and local ordering of polar nano domains by an extra electron or hole, resulting a quasiparticle which we call a ferroelectric large polaron. Compared to a conventional large polaron, the collective nature of polarization in a ferroelectric large polaron may give rise to order(s)-of-magnitude larger reduction in the Coulomb potential and introduce potential barriers to charge carrier scattering. The ferroelectric large polaron may explain the defect tolerance, low recombination rates, and slow cooling of charge carriers in lead halide perovskites, as well as providing a design principle for high performance semiconductors from nano, molecular, and hybrid materials.

10:45 AM ET05.04.08
Loss Mechanisms in Perovskite Solar Cells—Initially and During Aging Wolfgang Tress; LSPM, EPFL, Lausanne, Switzerland.
Solar cells based on lead halide perovskites have recently emerged showing a tremendous increase of power-conversion efficiency which exceeded 22%. In this contribution, the device physics of perovskite solar cells is addressed. The focus is on recombination of charge carriers because this process is ultimately limiting the efficiency. Furthermore, the performance and changes thereof during light-soaking and operation under real weather conditions are addressed.

The origin of the open-circuit voltage is discussed based on the reciprocity relation between electroluminescence and photovoltaic quantum efficiency. Sharp absorption onset and high radiative recombination yield due to an extraordinary defect tolerance are identified as reasons for the outstanding optoelectronic properties of perovskites. Furthermore, the role of defect and surface recombination are addressed by employing a detailed analysis of the diode ideality factor. Upon deliberately introducing defects in a controlled way it is found that the defect tolerance does not span to any kind of extrinsic defect.

The current-voltage curve of perovskite solar cells yields different results dependent on the initial voltage and scan rate of the voltage sweep. The resulting hysteresis is related to recombination as well. These results are explained based on the mixed ionic and electronic conductivity of the material, where displaced ions change interface and defect recombination rates. Reversible effects are observed on timescales of hours and their origins distinguished from irreversible degradation. The interplay of all these processes is analyzed for long-term operation under real weather conditions, where a better low-light performance and a low temperature coefficient result in relatively higher energy yields compared to a silicon solar cell.

An outlook is given on strategies aiming for a further improvement of open-circuit voltage and performance of perovskite solar cells toward their thermodynamic limit.

References

11:15 AM ET05.04.09
Imaging the Inhomogeneous Trap State Distribution in Hybrid Organic-Inorganic Perovskite Films
Andrew J. Winchester1, Christopher Petoukhoff1, Mojtaba Abdi Jalebi1, Zahra Andaji-Garmaroudi2, Vivek Pareek1, E Laine Wong1, Julien Mado1, Michael K. L. Man1, Samuel D. Stranks2 and Keshav Dani1; 1Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom. 2Chimie des Matériaux Nouveaux, Université de Mons, Mons, Belgium; 3Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland.

Hybrid organic-inorganic perovskite semiconductors have recently emerged as high performance thin-film photovoltaic materials. Their combination of good optoelectronic properties and low-cost synthesis processes has led to an unprecedented rate of development in perovskite-based solar cell devices over several years. Despite this development, however, there are still ongoing efforts to reduce unwanted non-radiative carrier loss and further push solar conversion efficiencies towards theoretical limits. One of the phenomenological observations highlighting the efficiency limits is the non-uniform radiative emission seen in photoluminescence (PL) microscopy, suggesting that there is an underlying nanoscale variation in the carrier trapping centers in solution processed perovskite films.

Here, we utilize time resolved photoemission electron microscopy (TR-PEEM) to view directly the nanoscale electronic variation and its effect on photo-excited carriers in mixed cation perovskite films. We investigate regions with different PL efficiency and find an increased number of nanoscale trap centers in low PL efficiency regions. We show that these traps are due to occupied mid gap states and probe the corresponding ultrafast hole trapping dynamics at these nanoscale locations. Our work gives a direct view at the nanoscale distribution of trap centers in perovskite materials and their connection to macroscale carrier recombination.

11:30 AM ET05.04.10
Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy
Xiaoqing Chen, Yasuhiro Shira1, Masatoshi Yanagida and Kenjiro Miyano; National Institute for Materials Science, Tsukuba, Japan.

In intensity-modulated photovoltage spectroscopy (IMVS) and impedance spectroscopy (IS) experiments of perovskite solar cells (PSCs), two features with different power dependences are observed to coexist corresponding to two relaxation routes. The relaxation rate of the slower feature is independent of light power while that of the faster one is proportional to the light power. Similar power dependence is observed in PSCs with various hole transport layers. Apparently, understanding the slower process will be helpful in optimizing the electric hysteresis in PSCs. In addition, because previous report assigns the faster process to the recombination of free carriers, understanding the faster feature will be helpful in minimizing the photocarrier loss in PSCs.

We notice that the recombination mechanisms involving only free carriers (e.g., band-to-band recombination) yield sublinear power dependence. Therefore at least two kinds of carrier species should be considered to explain the linear power dependence of the faster feature. Consequently, the next question is what this second carrier species other than free carriers is. We think it could be either accumulated carriers involved in the surface polarization model or the mobile ions/vacancies. In order to convincingly assign it, various photoelectric measurements are performed to provide additional information to these carriers. Our results indicate that these carriers should 1) be photogenerated with fixed lifetime (regardless of light power) so that its number is proportional to light power, 2) readily migrate along the electrode/perovskite surface so that it could uniformly distribute the device area (0.26 cm²), 3) be thermally activated before it could recombine with the free carriers, 4) be directly relevant to the slower IMVS or IS feature.

11:45 AM ET05.04.11
Origin of High Photoluminescence in Mixed-Cation Perovskites—Energetic Disorder Leads to Charge Localization
Sascha Feldmann1, Stuart Macpherson1, Jasmine Rivet1, Mojtaba Abdi Jalebi1, Satyaprasad P. Senanayak1, Guangjun Nan2, David Beljonne2, Michael Saliba2, Samuel D. Stranks1 and Felix Deschler1; 1Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 2Chimie des Matériaux Nouveaux, Université de Mons, Mons, Belgium; 3Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland.

Metal-halide perovskites have demonstrated exceptional optoelectronic properties for next generation photovoltaics and light-emitting diodes. Recently, cation substitution has been reported to generate luminescence very efficiently, yet the underlying photo-physics are poorly understood. Here, we study the origin of this increased brightness by combining transient absorption and photoluminescence (PL) spectroscopy to track charge carrier dynamics in perovskite thin films. Unexpectedly, we find the recombination mechanism to change from the previously-reported second to a first order regime dynamically within tens of nanoseconds after excitation, in line with fluence-dependent PLQE measurements. In temperature-dependent PL we find a redshift of the luminescence with decreasing temperature, directly mapping localized shallow traps. Supported by DFT calculations and transistor measurements we propose that energetic disorder in the distribution of electronic states leads to spatial accumulation of charges, creating n- and p-type doped regions,
explaining the PLQE observations. Our results indicate that strong luminescence can be achieved in mixed-cation perovskites even at low carrier densities and thereby provides a roadmap for highly efficient LEDs.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable structures/band gaps, relatively benign defects and grain boundaries, and facile processing for systems based on Group 14 metals (e.g., Ge, Sn and Pb). Most recently, these materials have enabled unprecedented rapid improvement in performance within single junction photovoltaic (PV) devices, from an initial demonstration in 2009 [2] to levels with >20% power conversion efficiency and open circuit voltages >1V [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite solar cells, including discussion of crystal structure flexibility, semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures [4,5]. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.

1:30 PM *ET05.05.01/ET04.05.01
Hybrid Halide Perovskite Semiconductors—An Historical Perspective David B. Mitzi; Duke University, Durham, North Carolina, United States.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable structures/band gaps, relatively benign defects and grain boundaries, and facile processing for systems based on Group 14 metals (e.g., Ge, Sn and Pb). Most recently, these materials have enabled unprecedented rapid improvement in performance within single junction photovoltaic (PV) devices, from an initial demonstration in 2009 [2] to levels with >20% power conversion efficiency and open circuit voltages >1V [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite solar cells, including discussion of crystal structure flexibility, semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures [4,5]. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.

References

2:00 PM *ET05.05.02/ET04.05.02
Photovoltaics of Halide Perovskites and Perspectives of Extensive Applications from the Ground to the Universe Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Lead halide perovskite absorbers have achieved high photovoltaic performance exceeding the efficiency of CIGS and CdTe and their long term stability against heat, moisture, and light are being improved by combined engineering of perovskite and surrounding carrier transport materials. For industrial applications, thermal stability of perovskites and carrier transport materials is a critical issue in comparison with thermally highly stable inorganic solar cell (Si, CdTe, etc.). Metal oxide electron transport layers (ETLs) generally have advantage in higher thermal stability than organic ETLs. We have been working with TiO2 ETL-based multi-cation perovskite cells, which yielded efficiency over 21% by ambient air solution processes.1 Light intensity dependence of Voc shows ideality factor low enough (n<1.4) for the perovskite solar cell to work as a high voltage power source even under weak light. Such merit meets a requirement in solar cell application to space satellite missions, which needs high photovoltaic performance even under very weak sunlight (Mars and Jupiter). We have examined the durability of perovskite solar cells which have thermally stable compositions comprising FA-based perovskites, TiO2 ETL, and P3HT as hole transport layer (HTL). These cells exhibit good stability against thermal impact between temperature range between -80°C and +100°C. We also confirmed very poor thermal stability of spiro-OMeTAD as a reference HTL. On exposure to high energy electron and proton radiations as accelerated conditions simulating long term space irradiations, the perovskite cells demonstrated high stability and tolerance, which are superior to those of Si and GaAs solar cells.2 Space applications also require fabrication of lightweight flexible devices. Thin film substrate-based perovskite solar cells were fabricated by low-temperature multilayer coating methods using amorphous TiO2 as ETL, which yield efficiency up to 18%. Future perspectives of industrialization of perovskite photovoltaic devices will be discussed focusing on the durable composition of perovskite devices and advantage of lightweight thin film device.

References

2:30 PM BREAK

3:00 PM *ET05.05.03/ET04.05.03
Perovskite Photovoltaics—History, Progress and Perspective Nam-Gyu Park; Sungkyunkwan University, Suwon, Korea (the Republic of).

Since the first report on the high efficiency, stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 22.7% in 2017. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches about 9,000 as of May, 2018, which is indicative of a paradigm shift in photovoltaics. Although high photovoltaic performance was achieved, current-voltage hysteresis has been issued because it is related to stability of PSC. In this talk, methodologies to remove hysteresis are described. Interlayers at heterojunction are found to play important role in reducing hysteresis and improving stability. Manipulation of Frenkel defect is a universal approach toward hysteresis-free PSC. We have discovered novel methods for large-area perovskite coating and shape transformation in perovskite, which will be discussed in detail. In addition to photovoltaics, perovskite can be used to other applications. Long charge diffusion length and high energy stability of organic-inorganic halide perovskite are suitable for low-dose, high resolution X-ray imaging. We demonstrated X-ray image using millimeter thick perovskite film based on multicrystalline perovskite crystal with single-crystal-like optoelectronic properties. For heading toward Shockley–Queisser limit, research direction in PSC is proposed in this talk.

3:30 PM *ET05.05.04/ET04.05.04
Compositional Engineering for Efficient and Durable Perovskite Solar Cells Anders Hasfelfdt; Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.
In our work on perovskite solar cells (PSC) we have achieved efficiencies above 20% with a mixed composition of iodide/bromide and methyl ammonium/formamidinium [1]. For cells larger than 1 cm² we have obtained 19.6% [2], replacing the anti-solvent step in the perovskite film formation with a vacuum flash treatment. With the use of SnO₂ compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20% [3]. The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. CsFA/Ma as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example reproducibility and device stability are improved [4]. At the meeting we will discuss our follow up works [5] and present our champion data; up to 22% efficiency with an external electroluminescence of 4%, and an outstanding open-circuit voltage of 1.24 V at a band gap of 1.63 eV entailing one of the smallest loss-in-potential of 0.39 V ever measured for any solar cell material. Furthermore, we will report promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (during which 95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests [6].

Keywords: Perovskite, composition, stability

References
[1] Bi et al., Science Advance, DOI: 10.1126/sciadv.1501170
[2] X. Li et al., Science, DOI:10.1126/science.aaq8060

4:00 PM *ET05.05.05/ET04.05.05

Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching to about 23%. Uniquely, PSCs have the highest efficiencies when they are solution processed, so one can envision solar cells printed in a similar manner and scale as newspapers. In addition, the bandgap tunability through perovskite composition engineering can enable high-efficiency multijunction devices, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). Thus, PSCs are suited to helping address the challenge of terawatt-scale, PV-based electricity production that can power the future world. In this talk, I will discuss our recent progress in two areas: (1) scalable fabrication of high-efficiency, large-area perovskite solar cells and modules; (2) development of perovskite-based tandem devices. I will discuss our recent studies toward better control of film formation across the device stack at large scales by improving the precursor chemistry to better match the processing methods. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. The challenges associated with perovskite solar module fabrication will be discussed. I will show the impact of interconnections on the performance of perovskite solar modules fabricated by scalable depositions. Toward perovskite-based tandem device development, I will discuss our recent effort on improving the optoelectronic properties of wide-bandgap as well as low-bandgap perovskite absorbers through solution chemistry engineering. Challenges and progress on perovskite-based tandem devices will also be discussed. These results demonstrate a promising path towards commercialization of the perovskite photovoltaic technology.

4:30 PM DISCUSSION PANEL: UNSOLVED PEROVSKITE PROBLEMS—OPPORTUNITIES AND CHALLENGES - DISCUSSION
LEADER: IVÁN MORA-SERó

SESSION ET05.06: Poster Session II: Fundamentals of Halide Perovskite Optoelectronics
Session Chair: Philip Schulz
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET05.06.01
Photobleaching and Recovery of Photoluminescence of CsPbBr₃ Perovskite Quantum Dot Yoshiki Iso, Koji Kidokoro and Tetsuhiko Isobe; Keio Univ, Yokohama, Japan.

CsPbX₃ (X = Cl, Br, I) perovskite quantum dots (QDs) have attracted many attentions because of their excellent photoluminescence (PL) properties such as high quantum yields, narrow PL peak widths, and emission color tunability by elemental composition of the halide ions. CsPbBr₃ QD, which exhibit highly-pure green emission under blue and UV light irradiation, is a good candidate for applications to wide-color gamut displays. However, photodegradation of the CsPbBr₃ QD under excitation is a significant problem to be solved for their practical use. Herein, we found recovery of photodegraded CsPbBr₃ QD after continuous blue light excitation. In this work, the photobleaching and recovery phenomena of the CsPbBr₃ QD are investigated by evaluation of their optical properties. CsPbBr₃ QD was synthesized by a conventional hot-injection method. Cs₂CO₃ was added into a mixture of 1-octadecene and oleic acid. The mixture was dried at 120 °C for 1 h, and then dissolved at 150 °C under Ar. Next, a mixture of 1-octadecene and PbBr₂ was vacuum-dried at 120 °C for 1 h, and then purged with Ar. Oleylamine and oleic acid were added to the solution. After complete dissolution of PbBr₂, the solution was heated to 180 °C. The solution of cesium oleate kept at 100 °C was injected into the PbBr₂ solution, and, 5 s later, the mixture was cooled in an ice-water bath. Synthesized CsPbBr₃ QD was precipitated by addition of tert-butyl alcohol, and then collected by centrifugation. After vacuum-drying for 1 day, yellow sample was obtained. For photobleaching test, the dried sample in a sample holder was placed on a plane light source of 468-nm blue LEDs with ~50 W m⁻² at room temperature; its absorption and PL spectra were measured at designated duration during and after 72-h irradiation using UV-vis and fluorescence spectrometers. According to transmission electron microscopy, the obtained sample was cubic particles with an average size of 8 nm. CsPbBr₃ QD with the structure was verified from the X-ray diffraction pattern. A narrow PL peak was observed at ~520 nm under 468-nm excitation. During the continuous blue light irradiation, the sample color changed from yellow to black. Actually, its absorbance at 700 nm, in which CsPbBr₃ QD had no light absorption, increased as the irradiation duration prolonged. The PL intensity decreased to 20% of the initial intensity after 72-h irradiation, revealing photodegradation of CsPbBr₃ QD. During storage in the dark at room temperature after 72-h irradiation, body color of the degraded sample returned to yellow from black. This phenomenon was consistent with a change in absorption spectra. At the same time, recovery of PL intensity was observed. After storage for 18 days, the final PL intensity reached up to 90% to the initial intensity. Such recovery of degraded CsPbBr₃ QD gives us a hint to solve the photobleaching problem. In
Minimizing Non-Radiative Losses Through Rational Defect Passivation for High Performance Perovskite Light-Emitting Diodes

ET05.06.02

Understanding Grain Boundary Effects in Methyliammonium Lead Bromide Films Using Electron Backscatter Diffraction (EBSD) Gede Adhyaksa1, Sarah Brittain1, Haralds Abolins1, Andries Loë1, Yueying Li2, Joel D. Keelor3, Yanqi Luo4, Teodor Duevski5, Ron M. Heeren1, Shane Ellis1, David P. Fenning1 and Erik Garnett1; 1AMOLF, Amsterdam, Netherlands; 2University of California, San Diego, San Diego, California, United States; 3Maastricht University, Maastricht, Netherlands.

Grain boundaries play a key role in the performance of thin-film optoelectronic devices, yet their effects in halide perovskite materials are still not understood. The biggest factor limiting progress is the inability to identify grain boundaries. Non-crystallographic techniques can misidentify grain boundaries, leading to conflicting literature reports about their influence; however, the gold standard – electron backscatter diffraction (EBSD) – destroys halide perovskite thin films. We solve this problem by using a solid-state EBSD detector with 6,000 times higher sensitivity than the traditional phosphor screen and camera. Correlating true grain size with photoluminescence lifetime, carrier diffusion length and mobility, shows that grain boundaries are not benign but have a recombination velocity of 1670 cm/s, comparable to that of crystalline silicon. We also observe amorphous grain boundaries that give rise to locally brighter photoluminescence intensity and longer lifetimes. This anomalous grain boundary character offers a possible explanation for the mysteriously long lifetime and record efficiency achieved in small-grained halide perovskite thin films. It also suggests a new approach for passivating grain boundaries to lead to even better performance in optoelectronic devices.

ET05.06.03


Hybrid organic-inorganic halide perovskites have emerged as a new family of optoelectronic materials because of their wide tunability in structural and optoelectronic properties via varying the compositions in A, B and X sites of the formula ABX3. While the primary structural and optoelectronic properties of hybrid organic-inorganic halide perovskites are dominated by transient metal divalent cations in the B-site and halide anions in the X-site, recent research has shown the impact of A-site monovalent cations on phase and device stability and the additional tunability in structural and optoelectronic properties. In this work, we focused on the investigation of A-site cations on the structural and optoelectronic properties of perovskites with a formula Aₓ(MA₁₋ₓFAₓ)₁₋ₓPb₁₋ₓSnₓ(I₁₋ₓBrₓ)₃, where A are Cs⁺, Rb⁺, and guanidinium (GA⁺), or Cs⁺–GA⁺ and Rb⁺–GA⁺ with x = 0 – 0.2, and y = 0 – 1.0. Because of the smaller ionic radii of Cs⁺ (1.8 Å) and Rb⁺ (1.52 Å) than methylammonium (MA⁺, 2.16 Å) and formamidinium (FA⁺, 2.53 Å) and GA⁺ (2.78 Å), adding Cs⁺ and Rb⁺ pushes the Goldschmidt tolerance factor into the cubic perovskite phase regime for each Sn composition while adding GA⁺ leads to an opposite direction. We prepared densely-packed, pinhole-free perovskite films with one-step solution process with mixed solvents plus anti-solvent wash method followed by thermal annealing. X-ray diffraction (XRD) patterns show pure cubic phase for all composition perovskites. The lattice parameter of these perovskites show non-linear lattice parameter versus Sn composition for each A composition with alloyed Pb-Sn having larger lattice parameters than those of pure Pb or Sn perovskites. However, a linear decrease or increase of lattice parameter versus A composition with each fixed Sn composition. The bandgaps deduced from the UV-Vis absorption spectra edges show that the bandgaps decrease with the increasing of Sn to the minima around 75% Sn and then increased to pure Sn. In Pb-rich perovskites, adding Cs⁺ or Rb⁺ increases the bandgaps for each fixed Sn composition, while in Sn-rich perovskites, it causes the decrease of bandgaps. The mechanism of A-site cations on the structural and optoelectronic properties of Pb-Sn and pure Sn perovskites will be discussed based on their impacts on B-X orbital overlap, BX₆ octahedral tilting, and strain tolerance. In addition, we also fabricated solar cells with the p-i-n structure and achieved a record maximum PCE of 9.61% for a low band gap (1.26 eV) perovskite of Cs₀.₁₀(MA₀.₁₇FA₀.₈₃)₀.₉Pb₀.₂₅Sn₀.₇₅(I₀.₈₃Br₀.₁₇)₃. Moreover, this 75% Sn device can retain 80% of initial PCE after 30 days storage in inert condition followed by over 100 hours in ambient condition. Overall, this study demonstrated the impact of A-site cations on structural and optoelectronic properties of Pb-Sn and pure Sn double halide perovskites and provides a route to enhance phase and device stability for high Sn or pure Sn perovskite solar cells.

ET05.06.04

Minimizing Non-Radiative Losses Through Rational Defect Passivation for High Performance Perovskite Light-Emitting Diodes Weidong Xu1,2 and Feng Gao1; 1The Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden; 2Institution of Advanced Materials (IAM), Nanjing Tech University, Nanjing, China.

Minimizing defect-mediated non-radiative recombination is crucial for the fabrication of high-performance perovskite optoelectronic applications, e.g. perovskite light-emitting diodes (PeLEDs). We demonstrate a rational defect engineering strategy for substantial mitigation of non-radiative losses, including both molecular design and passivating agents (PAs), and a modified passivation technique. With using the optimal PA, the well defect-engineered perovskite films enable the preparation of high performance PeLEDs with a high maximum external quantum efficiency (EQEₓₑₓ) of 18.9% and a large radius of 316 W m⁻². Importantly, our research reveals the key factor in determining the passivation effect, and provides a useful guideline for promoting passivation effects.

ET05.06.05

Electrode Polarization and Role of Polaron States at Methylammonium Lead Halide Perovskite Interfaces Mahshid Ahmadi1, Maximilian Heres3, Emmanuel Mapesa1, Eric Lukos1, Juan Bisquert2, Joshua Sangor1 and Bin Hu1; 1Joint Institute for Advanced Materials, University of Tennessee, Knoxville, Tennessee, United States; 2Institute of Advanced Materials, Universitat Jaume I, Castello, Spain; 3Chemical and Biomolecular Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Electrode polarization is a universal phenomenon taking place at the interface between a metallic electrode and an ionic/electronic semiconductor which needs to be studied in detail for organometallic halide perovskite (OMHP) devices. In general, interfaces between hybrid perovskite and electrode or charge transport layers are gaining more attention as studies showed that interfaces can significantly control the operation of hybrid perovskite devices as well as long term performance stability. Previously, the increase of dielectric permittivity in low frequencies <100 kHz in thin films of OMHP was attributed to the ionic migration and accumulation at the interface and space charge polarization enhanced along grain boundaries1. It was suggested that long range ion diffusion under external field would be the governing mechanism at low frequencies. In order to gain insight on the origin of dielectric permittivity at low frequency regime here, we study single crystals of MAPbI₃ excluding polarization enhanced through grain boundaries effect. This study is done using broadband dielectric spectroscopy (BDS) in dark condition by varying temperatures and external biases. Generally, there are three sources contributing to the conduction in OMHPs including ions, electrons and holes and polarons. So far, the atomistic origin of slow dynamic process in OMHPs was explained by the transport of ionic species and the drift and/or diffusion of polarons was totally overlooked. In our ac conductivity measurements, we observed that the conductivity decreases with decreasing frequency and temperatures. The accumulation of ions at the interface usually block the carriers from conduction and conductivity is expected to drop at this region. In this study we found that at low frequencies, there is a plateau in ac conductivity. This conductivity is only dropped if a large bias is applied. The polaronic nature of charge carriers in OMHPs has been demonstrated but the transport, migration

the presentation, the observed photobleaching and recovery will be discussed with further analyses.

ET05.06.06

Understanding Grain Boundary Effects in Methyliammonium Lead Bromide Films Using Electron Backscatter Diffraction (EBSD) Gede Adhyaksa1, Sarah Brittain1, Haralds Abolins1, Andries Loë1, Yueying Li2, Joel D. Keelor3, Yanqi Luo4, Teodor Duevski5, Ron M. Heeren1, Shane Ellis1, David P. Fenning1 and Erik Garnett1; 1AMOLF, Amsterdam, Netherlands; 2University of California, San Diego, San Diego, California, United States; 3Maastricht University, Maastricht, Netherlands.

Grain boundaries play a key role in the performance of thin-film optoelectronic devices, yet their effects in halide perovskite materials are still not understood. The biggest factor limiting progress is the inability to identify grain boundaries. Non-crystallographic techniques can misidentify grain boundaries, leading to conflicting literature reports about their influence; however, the gold standard – electron backscatter diffraction (EBSD) – destroys halide perovskite thin films. We solve this problem by using a solid-state EBSD detector with 6,000 times higher sensitivity than the traditional phosphor screen and camera. Correlating true grain size with photoluminescence lifetime, carrier diffusion length and mobility, shows that grain boundaries are not benign but have a recombination velocity of 1670 cm/s, comparable to that of crystalline silicon. We also observe amorphous grain boundaries that give rise to locally brighter photoluminescence intensity and longer lifetimes. This anomalous grain boundary character offers a possible explanation for the mysteriously long lifetime and record efficiency achieved in small-grained halide perovskite thin films. It also suggests a new approach for passivating grain boundaries to lead to even better performance in optoelectronic devices.
and accumulation of polarons at the interfaces was not explored. It was suggested that small polarons which transfer through hopping mechanism may not directly contribute to the overall carrier mobility unlike large polarons but they can form charge accumulations states\(^2\). Here, we conclude that ion migration and accumulation is not solely responsible for giant dielectric constant at low frequency in OMHPs but also there is an effective role from polarons. Indeed, polarons can migrate and accumulate at the interface first. This study opens a way for better understanding of a key aspect in the operation of highly efficient OMHP devices.

**References:**


**ET05.06.07**

Tuning the Electronic and Defect Properties of Methylammonium Lead Bromide via Composition Engineering

Arun Kumar Manndi Kanakkithodi, Ji-Sang Park, Duyen H. Cao, Nari Jeon, Alex Martinson and Maria K. Chan; Argonne National Laboratory, Lemont, Illinois, United States.

Methylammonium lead bromide (MAPbBr\(_3\)) has grown in prominence as an attractive photovoltaic (PV) absorber owing to its higher stability compared to MAPbI\(_3\), and its desirable electronic, absorption and defect properties which can be further tailored by composition engineering. Inspired by recent work on partial substitution of Pb in MAPbBr\(_3\) by Cobalt to yield additional energy states within the semiconductor band gap leading to intermediate band photovoltaics (IBPVs)\(^3\),\(^4\), we explore the possibility of substituting Pb by various other elements selected from across the periodic table in a high-throughput fashion. Using state-of-the-art density functional theory (DFT) computations, we study the crystalline and electronic structure as well as the energetics of 1/8th substitution of Pb in a MAPbBr\(_3\) supercell by all cationic elements from periods 2, 3, 4, 5 and 6. Both the density of states and the calculated charge transition levels are used to probe the energy states created by the substituent atom in the electronic structure of MAPbBr\(_3\), revealing several substituents that create mid-gap states while retaining the parent band gap (~2 eV at the PBE level of theory). Formation energies of substituent defects are calculated in various charged states\(^3\),\(^4\) and compared with the energetics of dominant intrinsic defects, established as the vacancy defects V\(_{\text{MA}}\) (dominant acceptor) and V\(_{\text{MB}}\) (dominant donor)\(^4\). It is observed that depending on the chemical potential of relevant species, transition metals Zr, Hf, Nb and Sc, and group V element Sb create low formation energy defects that compensate for the dominant intrinsic defects and shift the equilibrium Fermi level closer to the conduction band minimum, making the semiconductor conductivity more n-type. The relative stability of these substitution defects coupled with the fact that they produce mid-gap energy levels not only makes them promising candidates for IBPV's but raises the possibility of these impurities creating deep trap states in the MAPbBr\(_3\) band gap that can cause harmful non-radiative charge carrier recombination and reduce the PV efficiencies. Further, many of the promising substituents thus identified were experimentally synthesized and characterized, and the measured absorption coefficients compared favorably with the computed spectra. Lastly, machine learning techniques were applied on the high-throughput computational data to yield simple predictive models for the substituent transition levels as a function of structural and electronic features derived from a significantly cheaper unit cell calculation on a completely Pb-substituted hybrid perovskite.

**REFERENCES**


**ET05.06.08**

Light-Induced Dynamic Chemical and Structural Disorder in Mixed Halide Hybrid Perovskites

Tim W. van de Goor, Sian E. Dutton and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

Mixed halide hybrid perovskites are highly efficient semiconductors with promising applications in optoelectronics. Defects and disorder dictate the properties of this material. Structural disorder can be defined as local variations in the crystal structure, whereas chemical disorder refers to local inhomogeneities in material composition. Both types of disorder are highly dynamic and are likely responsible for the favourable (e.g. long carrier lifetimes\(^1\) and unfavourable (e.g. the Hoke effect\(^2\)) properties observed in this material. In the rapidly maturing field of hybrid perovskite optoelectronics, where the hunt is now on for the best performing material composition, little attention is given to the fundamental role of disorder. Here we aim to elucidate the relevant time- and length- scales for both types of dynamic disorder in this material, with the aim of gaining a better understanding of their relation to the optoelectronic properties. In particular, we use a combination of structural and thermodynamic techniques to investigate transitions in the prototypical mixed halide hybrid perovskite CH\(_3\)NH\(_3\)PbBr\(_3\)I\(_3\)). We use temperature dependent powder X-ray diffraction and heat capacity measurements under illumination to quantify the nature of— and energy associated with light-induced order/disorder transitions.

**References**


**ET05.06.09**

Controlled Nucleation and Growth for Optimum Perovskite Film Morphology at Liquid-Electrolyte Interface—A Study by Electrochemical Impedance Spectroscopy

Prva Srivastava and Monojit Bag; Indian Institute of Technology Roorkee, Roorkee, India.

Perovskite Solar Cells (PSCs) have already attracted considerable attention attributed to its intriguing properties, showing a tremendous jump in efficiency from 3.8%\(^6\) to 22.1%\(^6\) by Yang et al. (2017). A lot of research has been done on the efficiency improvement of PSCs by optimization of the film morphology at the interfaces in the device. Analyzing these interfaces by various characterization techniques including electrochemical impedance spectroscopy (EIS) in a solid state active device geometry\(^7\) is not only difficult to decipher but sometime is misleading as well since there may be multiple processes occurring at similar time scale at multiple interfaces.

To simplify the analysis of the perovskite films EIS should be carried out in perovskite-liquid electrolyte interface. Recently, Li et al. have measured the flat band potential, charge carrier density and type of charge carrier accumulation at the perovskite-liquid interface from Mott-Schottky plot for spin coated and spray coated films of methylammonium lead tri-iodide (MAPbI\(_3\)) perovskite.\(^8\) In this work, MAPbI\(_3\) perovskite has been synthesized by one step spin coating of lead acetate-trihydrate and methylammonium iodide precursor on pre-heated substrate. Significant difference in film morphology has been observed as the substrate temperature (T\(_{\text{subt}}\)) varied from room temperature to 120 °C prior to spin coating. Nucleation and growth mechanism is revisited to find out the optimum T\(_{\text{subt}}\) for fabricating uniform perovskite films and is
attributed to the fast homogenous nucleation followed by delayed growth. We confirmed that if the transformation temperature is just below the equilibrium melting point of the material, the nucleation is more homogeneous and hence more uniform and compact films are formed. EIS measurement at perovskite-liquid electrolyte interface reveals the impact of film morphology on the anomalous diffusion behaviour observed at low frequency regime and on the open circuit voltage ($\text{V}_{\text{OC}}$) of the device. More uniform and compact films show less degree of diffusion across the interface as compare to the rough ones. Also the $\text{V}_{\text{OC}}$ (1.018 V) is highest for the device fabricated by more uniform and compact film (Tsubt = 120 °C) among all the devices followed by the one fabricated at Tsubt = 120 °C (0.963 V). This reveals that film morphology is an important factor in deciding the kinetics at the interface and $\text{V}_{\text{OC}}$ and hence the performance of the device.


ET05.06.10

Electrospray Perovskite Fibers – New Flexible 1D Nanocomposites for Light Harvesting Applications Christoph Bohl1, Senol Oez2, Ashish Lepcha1, Markus Schütz1, Florian Stauber3, Thomas Fischer1, Thomas Kirchartz2,3 and Sanjay Mathur1; 1Institute of Inorganic Chemistry, University of Cologne, Cologne, Germany; 2FHEF-Polyvaltak, Forschungszentrum Jülich GmbH, Jülich, Germany; 3Faculty of Engineering and CENIDE, University of Duisburg-Essen, Duisburg, Germany.

The interest in perovskite solar cells is growing rapidly due to their versatile applicability for energy harvesting systems. In a short period of time, devices already reached efficiencies up to 22%, making them comparable to established thin-film solar cells like Cu(In,Ga)Se2 or CdTe. The quantity of publications dealing with planar and rigid solar cells is growing tremendously; however, fibrous solar cells have not been in focus yet. Since the 1D structure provides a greater flexibility in comparison to planar systems, applications ranging from e-textiles/weareables to lightweight applications are feasible. Here, the single step fabrication of phase-pure organic-inorganic lead halide perovskite fibers by inert electrosprining technique is presented. Morphological, as well as optical/photonic properties have been studied and demonstrate first comprehensive data on electrospruned organic-inorganic hybrid materials. Substitution of the absorbing layer in planar heterojunction solar cells with perovskite fibers resulted in a photoelectric response under simulated sunlight conditions. These flexible 1D hybrid solar fibers are potential elements for flexible optoelectronics and mark a starting point towards competitive fibrous solar cells.

ET05.06.11

Dynamics of Trap States in Passivated Halide Perovskite Films Stuart MacPherson1, Andrew J. Winchester2, Tiarkan Doherty1, Christopher Petukhov2, Michael K. L. Man3, Keshav Dani3 and Samuel D. Stranks1; 1Department of Physics, University of Cambridge, Cambridge, United Kingdom; 2Femtosecond Spectroscopy Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa, Japan.

The photovoltaic performance of world-leading Organic-inorganic halide perovskite (OHP) solar cells remains limited by defective electronic states, which introduce non-radiative recombination pathways for charge carriers. In OHP thin films, it is emerging that surface defects are the most prevalent and thus have the largest impact on luminescence and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yields substantially but the direct impact on carrier traps has not yet been elucidated.

Here, we employ a state-of-the-art photoemission electron microscopy (PEEM) setup to map local surface defect states on triple cation, mixed-halide perovskite (CsFAMA)Pb$_x$(Br$_{1-x}$)$_3$ films with < 30 nm spatial resolution. Our results show that chemical passivation by potassium doping reduces the density of surface defects on the films. Confocal photoluminescence maps of fiducially marked sites show a clear anti-correlation between areas of high photoluminescence intensity, and regions of high trap densities based on the photoemission fingerprints.

Finally, we examine how increasing levels of potassium doping affect the local carrier trapping dynamics by integrating PEEM with time-resolved pump-probe spectroscopy. This enables us to monitor the rate and intensity of photoexcited hole trapping into these intra-band surface states. When teamed with the spatial resolution of PEEM beyond the diffraction limit, such time-resolved measurements provide a uniquely powerful tool for characterising defect states, both in local regions and across larger regions of films.

ET05.06.12

Relation Between Absorption and Electronic Properties of Organic-Inorganic Halide Perovskites Martin Ledinsky1, Tereza Schonfeldova1, Jakub Holovský1,2, Zdenka Hajkova1, Lucie Abelova1,2, Neda Neykova1, Erkan Aydin2, Stefaan De Wolf1 and Antonín Fejfar1; 1Department of thin films, Institute of Physics AS CR, Prague, Czechia; 2Faculty of Electrical Engineering, Czech Technical University in Prague, Prague, Czechia; 3KAUST Solar Center (KSC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

We have probed the temperature dependence of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) absorption spectra. We extract the Urbach energy as the reciprocal value of the slope at the band edge plotted in logarithmic scale. Its value depends on the material disorder and generally correlates well with the loss in the open-circuit voltage ($\text{V}_{\text{OC}}$) of optimized cells, compared to their bandgap [1]. When cooling CH$_3$NH$_3$PbI$_3$ film we find a strong decrease in their Urbach energy and a slow decrease of their optical band gap energy.

From the theoretical Urbach energy temperature dependence we obtain an average energy of electronically active phonon states of 110 ± 20 cm$^{-1}$, which implicates that the dynamic disorder of CH$_3$NH$_3$PbI$_3$ is mainly caused by cage vibrations [2]. This further gives evidence that the density of active static defects in perovskites is very low in comparison to other materials used for solar cells, including bulk monocystal semiconductors.

From comparing the photoconductivity and emission-based absorption spectroscopies, we find that the CH$_3$NH$_3$PbI$_3$ band structure is slightly indirect. This may be caused by spin-orbital coupling, the so-called Rashba splitting effect. Our results prove the direct nature (non-phonon assisted) of both absorption and emission in CH$_3$NH$_3$PbI$_3$. The experimentally observed long photoluminescence decay time is given by small overlap between free electrons and holes.

Finally, we found a strong correlation between the $\text{V}_{\text{OC}}$ deficiency, compared to the bandgap, of finalized solar cells and Urbach energies measured by PL spectroscopy. These results will help to establish more refined practical efficiency limits of perovskite solar cells by taking into account the Urbach energy, to be compared to the Shockley-Queisser limit, which only considers the bandgap.


ET05.06.13

Feasibility of Quantum Dot Based Lasers in Blue and Green Region Aparna S. Shinde, Anirupa A. Lohar, Richa Gahlaut and Shailaja Mahamuni; Savitribai Phule Pune University, Pune, India.
Hybrid organic-inorganic perovskites (HOIPs) formed with organoammonium iodide and lead iodide precursor solutions are remarkable absorbing layers for photovoltaic (PV) devices. HOIPs with mixed cations, specifically those comprising combinations of formamidinium, methylammonium (CH$_3$NH$_3$\(^+\)) and cesium cations, have resulted in devices with record-setting efficiencies. Troublingly, recent reports have shown that CH$_3$NH$_3$\(^+\) is consumed through annealing of the precursor solutions, suggesting that reaction of CH$_3$NH$_3$\(^+\) with DMSO produces dimethylammonium, (CH$_3$)$_2$NH$_2$\(^+\) during solution annealing. X-ray diffraction on model HOIP films formed with precursor solutions in which CH$_3$NH$_3$I is intentionally and stoichiometrically replaced with (CH$_3$)$_2$NH$_2$I confirms that substitution of CH$_3$NH$_3$\(^+\) with (CH$_3$)$_2$NH$_2$\(^+\) alters the perovskite structure. When CH$_3$NH$_3$I is the sole organoammonium iodide in the precursor solution, the formation of (CH$_3$)$_2$NH$_2$I and its subsequent incorporation in thin films produces a cubic-phase film instead of the conventionally accessed tetragonal-phase CH$_3$NH$_3$PbI$_3$. Interestingly, devices that incorporate such cubic-phase films exhibit enhanced stability towards humidity compared with devices with the more conventionally accessed tetragonal-phase CH$_3$NH$_3$PbI$_3$. Our study emphasizes the importance of precise control over the composition of the active layer as a general strategy to control the size of the nanocrystallites (<10 nm) in the strong quantum size effect region.
Photoluminescence tuning between near infrared and ultraviolet is achieved by manipulating the size of perovskite crystals through confinement in nanocrystalline perovskite (mpSnI3) [1]. Our novel method of nanocrystalline perovskites preparation within a porous oxide matrix results in device-relevant structure that requires no colloidal stabilization. Low-voltage LEDs with narrow, blue-shifted emission fabricated with perovskite nanocrystallites confined within npAAO thin films support the general concept for next-generation photonic devices. The template-controlled size of the perovskite crystals is quantified in mpSnI3 with microfocus high-energy X-ray depth profiling in transmission geometry, verifying the growth of perovskite nanocrystals throughout the entire thickness of the nanoporous films. We study in detail exciton recombination, exciton-phonon interactions and energy trap states in confined and bulk semiconductor films using low temperature photoluminescence spectroscopy down to 3.8 Kelvin. Further areas of application include photon detectors, (polarized) electroluminescent devices, single-photon sources and metasurfaces. Future developments will include increasing the efficiency of the LEDs, exploring their applications in flexible devices and in depth study of the fundamental properties of the confined structures.


ET05.06.17
Mass Transfer-Tuned Growth Pathways of Colloidal Perovskite Quantum Dots Revealed by a High-Throughput Microfluidic Strategy
Robert W. Epps, Corwin Kerr, Kameel K. Abdel-Latif, Michael Bowen and Milad Abolhasani; North Carolina State University, Raleigh, North Carolina, United States.

Since the advent of organic/inorganic metal halide perovskites and their expanding application in low cost solution-phase processing of high efficiency optoelectronics, a wide expanse of colloidal synthesis techniques have been developed. However, due to the inherent limitations of batch screening approaches, these studies struggle to effectively characterize large parameter spaces and thereby develop a complete understanding of the fundamental nucleation and growth pathways of perovskite quantum dots (QDs). Recent works in colloidal QD growth characterization have implemented rapid microfluidic screening strategies. However, similar to their flask-based predecessors, these flow studies have not accounted for the effect of reactant mixing rates which are known to significantly influence growth pathways in the controlled synthesis of perovskite nanocrystals.

Herein, we present a systematic study of the mass transfer-tuned synthesis for three different cesium-lead-tribromide perovskite nanocrystal reaction strategies using an intelligent microfluidic screening technology. The microfluidic characterization platform consists of modular heated units equipped with a unique in-situ spectral monitoring probe (UV-Vis absorption and fluorescence spectroscopy) which may translate along the 27 cm tubular microreactor reaching 68 sampling ports. Complete platform automation enables high-efficiency collection of inline photoluminescence and absorption spectra spanning four orders of magnitude in residence time (i.e. growth time), from 100ms to 17 min. The portability of the sampling probe allows us to decouple fluid velocity-controlled mass transfer from reaction time.

This microfluidic approach enables rapid discovery, screening, and optimization of colloidal QDs with desired optoelectronic properties via high-throughput screening (>10,000 experimental conditions) of the accessible synthesis parameter space. Utilizing this developed intelligent microfluidic platform, we systematically studied the effect of early mixing timescales on the QD nanocrystal size and size distribution. Varying the average fluid velocity and slug size tunes the degree of mixing within droplets containing the cesium-lead-tribromide precursors, resulting in perovskite nanocrystals with different optoelectronic properties.

ET05.06.18
Lead-Free Perovskite for Highly Sensitive Photodetectors
Chun K. Liu; Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Recently, organic-inorganic lead halide perovskites have emerged as potential light absorbing materials for high-performance photodetectors. However, the toxicity of Pb-containing perovskites significantly hinders their practical applications. Thus, it is necessary to develop lead-free alternatives while maintaining high sensitivity. Herein, we report a lead-free, low-voltage and high-performance photodetector based on a tin perovskite. The device shows broadband photoreponse from ultraviolet to near infrared with highest responsivity (R) of 1.7 x 10^4 AW^-1. After vertically heterostructuring the perovskite with an organic semiconductor, the maximum R increases to 2.1 x 10^5 A W^-1, and specific detectivity of 1.5 x 10^11 Jones as well as EQE of 3.8 x 10^-6 can be obtained. The impressive performance of the photodetector is due to the superior optoelectronic properties of the tin perovskite and photogating effect originated from the vertical heterojunction. Moreover, the device is also assembled on a flexible substrate, demonstrating both high sensitivity and outstanding bending stability. This work paves the way for realizing non-toxic, low cost and high-performance photodetectors.

ET05.06.19
Digitally Programmable Polarization Anisotropy of Perovskite Nanowire-Block Copolymer Composites
Yehonadav Bekenstein1, 2, Nanjia Zhou1, A. P. Alivisatos1 and Jennifer Lewis1; 1Chemistry, University of California, Berkeley, Berkeley, California, United States; 2Materials Science, Technion-Israel Institute of Technology, Haifa, Israel; 1School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Semiconducting nanowires possess unique anisotropic optoelectronic properties arising from quantum confinement effects, making them attractive candidates for a wide range of electronic and photonic applications. The ability to precisely pattern one-dimensional nanomaterials with controlled spatial orientation into planar and 3D structures that exhibit highly anisotropic properties would open new avenues for the integrated design and assembly of optoelectronic devices. Towards this goal, we created stable nanocomposite inks composed of brightly emitting colloidal cesium lead halide perovskite (CsPbX3, X = Cl, Br, and I) nanowires suspended in a polystyrene-polyisoprene-poly styrene block copolymer matrix. Using direct ink writing, we programmably controlled the nanowire alignment within these matrices to produce photonic nanocomposites that exhibit highly polarized absorption and emission properties. Using this approach, we created several device motifs for optical storage, encryption, sensing, and full-color displays as exemplary demonstrations. The polymer encapsulated perovskite nanowires exhibit increased stability towards air and moisture degradation process, suggesting the methods and materials we use can be implemented in future devices.

ET05.06.20
All-Solution Processed Perovskite Light-Emitting Devices
Tejun Kim1, 2, Jin-Hoon Kim1 and Jin-Woo Park1; 1Yonsei University, Seoul, Korea (the Republic of); 2Samsung Electronics, Seoul, Korea (the Republic of).
As research on perovskites has rapidly developed in recent years, various research groups have made great efforts on improving the process and characteristics of perovskite light-emitting devices (PeLEDs). Perovskite has advantages of low material cost and simple process. However, it also has technical issues like short life-time and low stability. In this study, we demonstrated large area PeLEDs that are all-solution processed under ambient condition using organic-inorganic hybrid perovskite compounds as next generation light sources. In this work, an electron transport layer (ETL) was optimized to improve the electrical characteristics, to reduce the operating bias voltage and, to improve the optical characteristics. To improve the electron injection at the interface between the cathode and the perovskite layer, a thin layer of polyethyleneimine (PEI) was spin-coated on the perovskite layer prior to the deposition of the cathode. The PEI could reduce the work function of the cathode; hence, the electron injection barrier was significantly reduced. The electron transport properties of PEI were further improved by simply doping some elements. Solution processable n-type semiconducting materials (Cs2CO3, Alq3, and CsF) were selected as n-type dopant. Also, thin layer of poly(methyl methacrylate) (PMMA) was spin-coated on the perovskite layer to reduce the pin-holes in the perovskite layers. As fabricated PeLEDs based on these solution processable materials showed extremely low turn on voltage and high maximum luminance. Also, a silicone encapsulation was used to prevent the device from degradation by moisture and oxygen. The silicone encapsulation materials for commercial LEDs were used. Liquid silicone was coated on the as-fabricated PeLEDs to passivate the devices. Based on our results, the coated liquid silicone did not affect the performance of the PeLEDs. The lifetime of the PeLEDs encapsulated with commercial silicone was good performance which was comparable to the glass-lid encapsulation. Since the silicone was flexible, these encapsulation materials could be used in flexible PeLEDs. The luminescence characteristics of green region were confirmed by using a perovskite compound of MAPbBr3 which is attracting attention as a next generation light source, and its value as a next generation light-emitting devices was confirmed by applying it to a large area flexible device.

ET05.06.21
Impact of Excess PbI2 on the Structure and the Temperature Dependent Optical Properties of Methylammonium Lead Iodide Perovskites

Fabian Panzer1,2, Tobias Meier1, Tanuja Gujar1, Andreas Schönleber3, Selina Olthof4, Klaus Meerholz5, Sander van Smalen1, Mukundan Thelakkat4 and Anna Kohler1; 1Univ of Bayreuth, Bayreuth, Germany; 2University of Cologne, Cologne, Germany.

We investigate the impact of excess PbI2 in the precursor solution on the structural and optical properties of thin films of the model hybrid perovskite methylammonium lead iodide (MAPbI3). We find that excess of PbI2 in the precursor solution results in crystalline PbI2 in the final thin film that is located at the grain boundaries. From UPS we find that this phase has no direct impact on the electronic structure of MAPbI3. In contrast to that, temperature dependent absorption measurements indicate a systematic change in the temperature dependence of the exciton binding energy in the perovskite. We also observe a decrease in the critical temperature and a concomitant smearing out of the tetragonal – orthorhombic phase transition as a function of excess PbI2. Our results help to better understand the exact role of PbI2 in the perovskite layer and pave the way for a more tailored design of perovskite solar cells.

ET05.06.22
Broadband Luminescence in Small Molecule Engineered Hybrid Perovskites

Shreyaa Krishnamurthy1,2, Rounak Naphade3, Suresh Gosavi1, Sudip Chakaborty1, Ramanathan Vadhyayanathan1 and Satishchandra Ogale2; 1Department of Physics, Indian Institute of Science Education and Research (IISER), Pune, India; 2Department of Physics, Savitribai Phule Pune University, Pune, India; 3Department of Science Education and Research (IISER) Pune, Pune, India.

The emerging class of hybrid perovskite systems has attracted immense attention recently due to their uniquely interesting properties which has led to solar cell architectures with very high conversion efficiency. These materials have also been explored for other optoelectronic device applications such as: lasers, photo-sensors, light emitting devices (LED). Lately, this class of systems is being further explored for futuristic optoelectronic devices by employing small molecule engineering. Such molecular manipulations have been shown to control the dimensionality and associated photo-physics of these systems such as the electron-hole interactions and excitonic effects. In particular, one sub-group of such hybrid perovskites has exhibited broadband emitting properties which are of great interest as potential materials for white light emitting diodes (LEDs).

The discussion of broadband luminescence in the literature has focused on the identification of the specific contributions to such emission (e.g. bound excitons, self-trapped excitons, STE) and their possible connection to the specific structural features and organic/inorganic components in the system. In this work we report the observation of broadband emission in 1D ribbon system of (H2N2CH2-CH2-NH3)2(Pb2Br5) (or as 2D corrugated system of (H2N2CH2-CH2-NH3)2(PbI4), the common amine used being ethylene diamine (En), which is the smallest amine not used thus far in this context. We have employed several techniques such as single crystal x-ray diffraction (SC-XRD), steady state photoluminescence (PL), UV-absorbance, diffused reflectance spectroscopy (DRS), time resolved photoluminescence (TRPL) and Raman spectroscopy to study and compare the structural and optical properties of the two materials as well as their respective daimmonium salts. Our studies have brought out structure-specific contributions and interplay of the molecular and STE contributions. The primary absorption process appears to be driven by the molecular component while the STE appears to be centered on the inorganic component which may involve the intrinsically heightened polarization at the organic-inorganic interface. Distortions can be important for localization but do not appear uniquely control this phenomenon.

ET05.06.23
Electronic Structure Analysis of an Organometallic Halide Perovskite via Photoemission Yield Spectroscopy in Air at Various Temperature

Around the Phase Transition Temperature

Panuice Yamashita1, Yoshiyuki Nakajima1, Satoshi Uchida1 and Hiroshi Segawa2; 1RIKEN KEK, Co., Ltd., Kasukabe, Japan; 2The University of Tokyo, Tokyo, Japan.

An open counter [1] is a unique detector that can operate in air at atmospheric pressure to detect and count a small number of low-energy photoelectrons. Therefore, photoemission yield spectroscopy in air (PYSA) can be performed by employing an open counter as the detector. Recently, PYSA measurement was performed at various temperatures [2-4], and its applicability to the analysis of temperature dependence on the change of work function was demonstrated [3, 4]. In these cases, PYSA measurement was performed as follows. UV light emitted from a deuterium lamp was monochromatized using a grating monochromator, which was then focused on the sample surface. The number of photoelectrons emitted from the sample surface was counted using an open counter. During the measurement, the sample temperature was controlled using a small heater connected to a temperature controller. This method was considered effective for the comparison of the electronic structures of materials that exhibit different properties at high temperatures. Temperature effects of CH3NH3PbI3 perovskite solar cells having simple planar architecture were reported [5]. According to this report, the obvious changes in the crystal structure which seriously affects the performance of the solar cells were found. Therefore, PYSA was applied to analyze the change in the electronic structure of CH3NH3PbI3 at various temperatures. We discussed the change in the threshold energy of photoemission, which corresponds to the first-ionization potentials, at around the phase transition temperature of the perovskite.


Although metal halide perovskites (MHPs) have emerged as exceptional materials for optoelectronics, their charge transport properties remain under scientific debate. One of the reasons for this is that most charge transport measurements are conducted on polycrystalline thin films, which adds complexity to the system and makes it difficult to interpret the results in an unambiguous way. In this work, we concentrated on surface-guided planar nanowires of CsPbBr₃, single crystals with a 1D nature, which serve as a simplified model system for charge transport measurements. The surface-guided growth of MHP nanowires on sapphire substrates in ordered and well-defined arrays, which can be easily integrated into functional devices. We studied the charge transport in these arrays as well as in individual CsPbBr₃ nanowires, all having uniform crystallographic orientation and well-defined facets. We fabricated the first field-effect transistor on a single nanowire of MHPs and measured charge transport characteristics such as field-effect mobility and charge carrier concentration. We also observed intriguing time-dependent electrical behavior in dark and under illumination, related to the dynamic nature of these soft semiconductors. Surface-guided growth of MHP nanowires enables fast, simple and efficient fabrication of multiple devices in parallel manner for fundamental research and optoelectronic applications.

ET05.06.25
Photoluminescence Spectroscopy of Halide Perovskites
Stuart Thomson
Edinburgh Instruments, Livingston, United Kingdom.

Halide perovskites are a promising new class of semiconducting materials for a wide variety of optoelectronic applications, such as photovoltaics, light emitting diodes, lasers and optical sensing. They have received widespread attention due to their many attractive synthetic and photophysical properties, namely; solution processability, high tunability, low charge carrier lifetimes and high charge carrier mobilities. Photoluminescence spectroscopy is a powerful tool for the photophysical investigation and materials optimisation of halide perovskites. Using photoluminescence spectroscopy we have investigated the photophysics of a range of halide perovskite photovoltaic absorbers and light emitters.

Methyl ammonium lead iodide (MAPI) is one of the most efficient and widely investigated perovskite absorbers for photovoltaic cells. Using time-resolved photoluminescence, the charge carrier lifetime of MAPI was measured and was found to increase with the thermal annealing duration of the perovskite layer. In addition, temperature dependent photoluminescence spectroscopy was used to monitor the change in the perovskite bandgap with temperature and determine the orthorhombic to tetragonal and tetragonal to cubic phase transition temperatures.

Photoluminescence spectroscopy is particularly well suited for the study of perovskite materials for light emitting applications. Two dimensional perovskites are a promising material for the creation of single component white light source. We investigated the two dimensional white light emitter, α-(DMEN)PbBr₄, using steady state photoluminescence to determine the chromaticity coordinates of the emission and time-resolved photoluminescence to probe the excited state lifetimes.

ET05.06.26
Elucidating Exciton-Phonon Interaction in Quasi-2D Ruddlesden-Popper Perovskites
Watercharaphol Pariromongkol, Nabeel S. Dahod, Alexia Stollmann, Shao-Liang Zheng and William Tisdale; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; Mechanical and Process Engineering, ETH Zürich, Zürich, Switzerland.

Two-dimensional lead halide perovskites (2D LHPs) are solution-processed semiconductor quantum wells with great promise for optoelectronic applications. Their properties are highly tunable, and can be modified by changing the quantum-well thickness as well as their chemical constituents. Since 2D LHPs have high exciton binding energies, understanding exciton dynamics is important for designing novel 2D LHP devices. Here, we present a study based on temperature-dependent photoluminescence to elucidate exciton-phonon interactions in these materials. Our study is based on iodide perovskites with varied quantum-well thicknesses, cations, and organic spacer lengths. The results show that tuning these parameters affects photoluminescence properties as well as phase transitions. This study provides a fundamental understanding of 2D LHP photophysics, necessary for developing novel 2D LHP optoelectronics.

ET05.06.27
Time-Resolving Ultrafast Polaron Formation Dynamics in Lead-Halide Perovskites via Terahertz Emission Spectroscopy
Burak Guzel turk1,2 and Aaron Lindenberg3; 1Stanford University, Stanford, California, United States; 2SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Recently we have revealed that poly-crystalline thin-films of hybrid lead-halide perovskites emit broadband electromagnetic radiation within the terahertz (THz) frequency window [1]. This radiation mainly arises from ultrafast electron-hole separation due to different diffusivities of photo-generated carriers (i.e., photo-Dember effect). A transient photocurrent with a rise-time shorter than the period of an optical phonon mode can coherently drive the corresponding phonon. By means of this, longitudinal optical (LO) phonons can be coherently launched via ultrafast photo-excitation and can be detected via measurement of the associated THz emission [1, 2]. In a polaron picture, a carrier alters the equilibrium position of ions within a polar semiconductor and this effectively induces a potential well for the carrier causing its "self-trapping" around the displaced ions [3]. Polaron formation proceeds through long range carrier – LO phonon coupling [4] and was lately evoked to account for the surprising opto-electronic properties of the hybrid perovskites [5]. Here we show that we can time-resolve polaron formation dynamics via monitoring of the emitted THz radiation from the coherent LO phonon mode. In MAPbI₃, we observe a strong emission peak at 1.15 THz corresponding to the lowest energy LO phonon mode of the inorganic sub-lattice. By time- and frequency-resolving this LO phonon-associated emission, we observe an intriguing dependence on the excitation photon energy. When we excite the perovskite at its band-edge (770 nm), the emission at the LO mode arises instantaneously. However, when a well-above bandgap excitation (400 nm) is used, the emission at the LO phonon mode emerges with a finite time delay (~300 fs). This suggests that hot-carriers cannot form polarons due to their excess kinetic energy. Therefore, initial carrier cooling dominates over the polaron formation. Furthermore, we observe a dynamic softening of the LO mode within the first ps suggesting that electronic charge alters the stiffness constant of the ionic bonds within the material as predicted in other polaronic systems [3].

Lead halide perovskites are promising materials for a range of applications owing to their structural uniqueness and optoelectronic properties. Understanding the relationship between the atomic/superstructures and the associated properties of perovskite materials is vital to fully utilize their potential performances. We present the detailed pressure processing of CsPbBr₃ perovskite nanocube superlattices (NC-SLs) for the first time. By using diamond anvil cell combined with in situ synchrotron-based small/wide angle X-ray scattering (SAXS and WAXS) and photoluminescence (PL) probes (shown A in the Figure), the NC-SL transformations are correlated at both atomic and superlattice levels with the PL transition through a pressure cycle of 0 ↔ 17.5 GPa. In-situ SAXS and WAXS measurements monitored its mechanical and structural changes showing that the NC-SL went through multiple phase transitions both at both atomic and superlattice levels. After the pressure process, the individual CsPbBr₃ NCs fused into two-dimensional nanoplatelets (NPLs) with a uniform thickness (~10.1 nm). The pressure-synthesized perovskite NPLs exhibited a pure single cubic crystal structure, a 1.6-fold enhanced photoluminescence quantum yield, and a longer emission lifetime than the starting NCs. These results suggest that pressure processing can provide a novel approach for the quick conversion of lead halide perovskites into structures with enhanced properties.

Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects. Metal halide perovskites have been successfully applied as optically active layers in photovoltaic and optoelectronic devices. The high efficiency of such research-scale devices hold the promise for an imminent application of perovskites in large scale energy production and lighting solutions. Intrinsic thermal and photo-physical instability of these materials pose, however, a challenge for further developments in device scale up and long-term reliability. Instabilities are manifested as light-induced ion migration and segregation, eventually leading to material degradation under prolonged exposure to light. Understanding, controlling and eventually blocking such material instabilities are fundamental steps towards large scale exploitation of perovskite in optoelectronic devices. By combining photoluminescence measurements under controlled conditions with ab initio simulations we identify photo-instabilities related to competing light-induced formation and annihilation of trap states, disclosing their characteristic length and time scales and the factors responsible for both processes. We show that short range/short time defect annihilation can prevail over defect formation, happening on longer scales, when effectively blocking undercoordinated surface sites, which act as a defect reservoir. By an effective surface passivation strategy we are thus able to stabilize the perovskite layer towards such photo-induced instabilities, leading to improved optoelectronic material quality and enhanced photo-stability in a working solar cell. The proposed strategy represents a simple solution towards longer stability perovskite thin films that could be easily implemented in large scale manufacturing.
strategy, we studied an ethyldimethylamine-containing compound that yielded an open-circuit voltage of 1.59 V.(4)

The last part elaborates on a roadmap on how to extend the multiplication to multicomponent engineering providing a series of new compounds that are highly relevant candidates for the coming years.

(1) McMeekin et al. Science (2016)
(2) Saliba et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. EES (2016)
(3) Saliba et al., Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. Science (2016)
(4) Gholidpour, ...Saliba, Globularity Selected Large Molecules for a New Generation of Multication Perovskites, Advanced Materials (2017)

9:15 AM ET05.07.04
Anisotropic Moisture Erosion and Carrier Transport in CH3NH3PbI3 Single Crystal Qianrui Lv and Qingfeng Yan; Tsinghua University, Beijing, China.

As a new semiconductor material, methyl ammonium lead iodide (CH3NH3PbI3) perovskite has attracted much attention in recent years owing to its outstanding photoelectric properties. Although CH3NH3PbI3 perovskite has achieved tremendous progress in photovoltaic devices, a deeper understanding of its intrinsic physical properties is still of great interest. The anisotropy of properties is an important feature of semiconductor materials, while limited relevant work has been reported regarding the anisotropy of CH3NH3PbI3 perovskite. In this work, we report the fast growth of high-quality CH3NH3PbI3 single crystal by using a non-seeded solution growth method. When exposed the CH3NH3PbI3 single crystal to moisture, it was found that the (001) facet exhibited more sensitive to water molecules and showed faster erosion rate compared with the (100) facet and (112) facet. We then developed a top-down strategy to prepare CH3NH3PbI3 single-crystalline thin films of tens of micrometers in thickness with different orientations, which provided the possibility of directly studying the anisotropy of conduction transport in CH3NH3PbI3 single crystals. Vertical-structured FET devices based on CH3NH3PbI3 single-crystalline thin films with different orientations were fabricated. Compared with the [100] and [112] orientation, it was found that carriers have lower mobility along the [001] orientation than along the [100] and [112] orientation. The origin of the anisotropy in moisture erosion and carrier transport was elucidated from the perspective of crystal structure. The reveal of the orientation-dependent moisture erosion and carrier transport in perovskite CH3NH3PbI3 single crystal may deepen the understanding of physical properties of the material and guide the design of stable and high-performance optoelectronic devices in the future.

9:30 AM ET05.07.05
Spiro-MeOTAD Hole Transport Layer in Perovskite-Based Solar Cells Luis K. Ono1, Zafer Hawash1, 2, Sonia R. Raga1, 3, Emilio J. Juarez-Perez4, Matthew Leyden4, 5, Yuichi Kato1, 6, Mikas Remeika1, 6, Shenghao Wang7, 8, Michael V. Lee9, 10, Andrew J. Winchester3, 11, Atsushi Gabe4, 12, Yan Jiang1, 13 and Yabing Qi1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Department of Engineering and Physics, Karlstads University, Karlstad, Sweden; 3Centre National de la Recherche Scientifique, Service de la Recherche, Laboratoire de Synthèse et Physico-Chimie des Matériaux Solides, Univ. Grenoble Alpes, CEA, INPG, CNRS, Grenoble, France; 4School of Mechanical Engineering, University of Sydney, Sydney, Australia; 5Materials Science and Technology (AIST), Tsukuba, Japan; 6Department of Applied Physics, University of Tsukuba, Tsukuba, Japan; 7Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, Arizona, United States; 8Institute of Materials Science, University of Alicante, Sant Vicent del Raspeig, Spain.

In organic-inorganic hybrid perovskite solar cells, optimization of hole transport materials (HTMs) is important for enhancing solar power conversion efficiency and improving stability [1,2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit has been making concerted efforts to study 2,2',7,7'-tetrakis[N,N-di-(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-MeOTAD), which is the most widely used HTM in perovskite solar cells [2-8]. In this talk, we will present our latest understanding of fundamental interactions between Li-bis(trifluoromethanesulfonfyl)-imide (LiTFSI), 4-tert-butylpyridine (t-BP) and spiro-MeOTAD. Also, we will show how gas exposure (e.g., exposure to O2, H2O, N2) influences electronic structures and conductivity of such HTM films. In addition, we will propose further strategies to improve perovskite solar cell performance and stability.


9:45 AM ET05.07.06
In Situ X-Ray Investigation Underpins Moderate Annealing Humidity on Improving Crystallinity of Organohalide Perovskites Zhiyuan Ma1, 4, Hun Zhou1, Wei Chen1, 2 and Zhang Jiang1; 1Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois, United States; 2Materials Science Division, Argonne National Laboratory, Lemont, Illinois, United States; 3Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, United States; 4Materials Science and Engineering, China University of Petroleum, Beijing, China.

Emerging organolead-halide-perovskite-based materials and devices have recently received tremendous attention due to their extraordinary photonic and optoelectronic performance and potential low production costs. Many physical and chemical properties beyond light harvests have erupted. Despite the rapid development of perovskite materials and devices, the impact of environmental factors on different stages of materials synthesis and device fabrication still remains unclear. Moisture or humidity is widely recognized as one of the major lethal factors in perovskite devices degrade or decompose after rapid development of perovskite materials and devices, the impact of environmental factors on different stages of materials synthesis and device fabrication still remains unclear. Moisture or humidity is widely recognized as one of the major lethal factors in perovskite devices degrade or decompose after
optoelectronic device performance. By taking advantage of synchrotron-based grazing incident wide-angle x-ray scattering (GIWAXS), we in situ monitor the transformation of organohalide perovskites from precursors to final films upon thermal annealing at different relative humidity. in situ GIWAXS reveals the formation of crystalline perovskite materials over relevant time and moisture scales to decipher the effect of humidity on both phase transition and crystal structures during annealing. These in situ measurements demonstrate that moderate humidity accelerates the formation of organohalide perovskites and improves the orientation of the film, but more than 50% relative humidity retards the formation of perovskites and destructs their crystal structures. Furthermore, the highly oriented films obtained at optimized relative humidity are observed which could be attributed to the hydration of precursors. These findings clearly elucidate the influence of moisture environment in annealing process of organohalide perovskites and, in turn, allow us to correlate the improved performance of organohalide perovskite materials and devices to structural features in terms of environmental effects.

10:00 AM BREAK

10:30 AM * ET05.07.07
Advances in Perovskite Active Layer Stability  Edward H. Sargent; University of Toronto, Toronto, Ontario, Canada.

I will discuss advances - including doping strategies and reduced-dimensional perovskites - in increasing the stability of the perovskite active layer.

11:00 AM ET05.07.08
Dipolar Cations Confer Defect Tolerance in Wide Bandgap Perovskites Haiyen Tan1,2; Fanglin Che2, Mingyang Wei2 and Ted H. Sargent2; 1University of Toronto, Toronto, Ontario, Canada.

Efficient wide-bandgap perovskite photovoltaics will enable tandem solar cells when successfully combined with low-bandgap absorbers such as crystalline silicon. However, wide-bandgap perovskite solar cell materials (PSCs) today exhibit performance far inferior to that of sub-1.6 eV bandgap PSCs. Their tendency to form a high density of deep level trap states underpins this limitation. Here we show that healing the deep traps in mixed cation-halide wide-bandgap perovskites - in effect, increasing the defect tolerance via cation engineering - could enable further performance improvements in PSCs. We achieve a stabilized power conversion efficiency (PCE) of 20.7% for 1.65-eV-bandgap PSCs by incorporating a small concentration of dipolar cation additive. The devices exhibit a high open-circuit voltage ($V_{oc}$) of 1.22 V and a fill factor (FF) that exceeds 80%. We also achieve a PCE of 19.3% for 1.1 cm$^2$ large-area devices with a $V_{oc}$ of 1.24 V. We achieved commendable improvements in 1.74-eV-bandgap PSCs, where we obtained a stabilized PCE of 19.1% together with a high $V_{oc}$ of 1.25 V and FF of over 80%. From density functional theory calculations, we find that the presence and reorientation of the dipolar cation in mixed perovskites can heal the defects that introduce deep trap states.

Our findings shed light on defect healing in perovskite materials and pave the way to further increasing the efficiency of perovskite-enabled tandem photovoltaic devices.

11:15 AM ET05.07.09
Degradation Analysis of Perovskite Films Using the Photo Thermal Induced Resonance Technique Hyang Mi Yu1, Hye Min Oh1 and Mun Seok Jeong1,2; 1Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); 2Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Suwon, Korea (the Republic of).

Organic-inorganic mixed halide perovskite (MAPbX$_3$: MA=CH$_3$NH$_3$, X=Cl, Br, or I) are extensively used as absorbing materials for solar cell due to its broad absorption range and long charge carrier diffusion length. Despite its high photovoltaic efficiency, their poor stability remains a major challenge for high performance device and their commercialization.

Perovskite films based on CH$_3$NH$_3$PbI$_3$-Cl undergo rapid degradation when exposed to oxygen and moisture. To overcome this problem, many researchers have been studied about the degradation mechanism of perovskite films. However, these results were not simultaneously obtained with structural and chemical properties of perovskite films. Thus it is not provided complete degradation mechanism of perovskite films.

In this work, we investigated the degradation mechanism of perovskite films by performing simultaneous measurement of the structural and chemical informations using the photo thermal induced resonance technique combined with atomic force microscope. Finally, this study will contribute to understanding of the mechanism of the degradation process of perovskite films and enhance the stability of perovskite optoelectronics field.

11:30 AM ET05.07.10
First Principles Modelling of Grain Boundaries in (FA/Cs)Pb(I/Br), Perovskite Solar Absorbers Keith McKeen; Univ of York, York, United Kingdom.

Mixed-cation lead mixed-halide perovskite solar absorbers such as (FA/Cs)Pb(1/Br) exhibit remarkable and tunable optoelectronic properties that make them attractive for next generation solar cell technologies [1]. In practice such materials are always polycrystalline however the role of grain boundaries (GBs) remains poorly understood and a subject of much speculation. For example, separate experimental studies suggest GBs in MAPbI$_3$ can be both act as recombination centers [2] and structural barriers to charge transport [3]. We will present our latest theoretical modeling of GBs using density functional theory, with particular focus on the electronic properties of mixed-cation mixed-halide perovskites.

In this talk, I will present our recent theoretical predictions of GBs in (FA/Cs)PbI/Br). We employ density functional theory methods similar to those we have previously applied to model extended defects in a range of other materials including CIGS, TiO$_2$ and Fe$_3$O$_4$[6,8]. We find that for the Σ3 (111) GB there is strong segregation of Br to the GB (but not Cs) and it remains electrically benign with no preferential electron or hole trapping. However, for the Σ3 (111) GB there is strong segregation of both Cs and Br and this is associated with the introduction of shallow electron trap states at the GB. We note that this may be beneficial for efficient electron/hole separation since there is no tendency for holes to trap at the GB [9]. These results highlight the point that not all GB types are equivalent and so one needs to consider a range of GBs to build a statistical picture. Importantly, mixed perovskite absorbers present the possibility of much wider compositional variations (even without intrinsic defects) and so understanding GB properties is key to understanding the behaviour of real polycrystalline materials.

[9] K. P. McKenna, manuscript in preparation
Combining and grain-boundary engineering involved in the processing of OIHP thin films for PSCs will be discussed with specific examples. Additionally, the are able to characterize and monitor fast reaction/formation of perovskite thin films immediately after the spin-coating process which is commonly used in improvements however, were mostly achieved through empirical optimization of processing conditions. Due to the fast and complex chemical reactions of devices. The field is moving towards more and more complex chemical compositions enabling dramatically improved device performances. Those materials. The overall goal of our research is to have deterministic control over scalable processing of tailored halide perovskite thin films with desired large areas is critically important. The microstructures and grain-boundary networks in the resulting polycrystalline OIHP thin films are equally important As a result, in 100% humidity at 40 °C, the 10% w/w PbSe-doped CH₃NH₃PbI₃ films exhibited >140-fold stability improvement over pristine CH₃NH₃PbI₃ films. Whilst perovskite structure of the PbSe-doped CH₃NH₃PbI₃ films reserved, a top efficiency of 10.4% with 70% retention after 700 hours aging in ambient air was achieved on an unencapsulated 10% w/w PbSe:CH₃NH₃PbI₃-based cell. Significantly, the incorporated Se²⁻ effectively suppressed iodine diffusion in solar cell, leading to enhanced chemical stability of the silver electrodes. Successful doping of divalent Se²⁻ in perovskite lattice is further confirmed by enlarged lattice spacing from X-ray diffraction patterns, asymmetric photoluminescence peaks with shoulder electronic states, and concomitantly increased electrical conductivity of 5%, 10% w/w PbSe:CH₃NH₃PbI₃ thin films. This work could advance the fundamental understanding of degradation and stabilization of hybrid perovskites in both material and device settings.

Chemical stabilities of hybrid perovskite materials demand further improvement towards long-term and large-scale photovoltaic applications. Herein, we report enhanced chemical stability of CH₃NH₃PbI₃ by doping divalent anion Se²⁻ in the form of PbSe in precursor solutions to enhance the hydrogen-bonding-like interactions between organic cation and inorganic framework, as evidenced by redshifted N-H stretch from Fourier-transform infrared spectra. As a result, in 100% humidity at 40 °C, the 10% w/w PbSe-doped CH₃NH₃PbI₃ films exhibited >140-fold stability improvement over pristine CH₃NH₃PbI₃ films. Whilst perovskite structure of the PbSe-doped CH₃NH₃PbI₃ films reserved, a top efficiency of 10.4% with 70% retention after 700 hours aging in ambient air was achieved on an unencapsulated 10% w/w PbSe:CH₃NH₃PbI₃-based cell. Significantly, the incorporated Se²⁻ effectively suppressed iodine diffusion in solar cell, leading to enhanced chemical stability of the silver electrodes. Successful doping of divalent Se²⁻ in perovskite lattice is further confirmed by enlarged lattice spacing from X-ray diffraction patterns, asymmetric photoluminescence peaks with shoulder electronic states, and concomitantly increased electrical conductivity of 5%, 10% w/w PbSe:CH₃NH₃PbI₃ thin films. This work could advance the fundamental understanding of degradation and stabilization of hybrid perovskites in both material and device settings.

In Situ Phase and Optical Characterizations to Unveil the Chemistry of CH₃NH₃PbI₃ Formation Jue Gong1, Mengjin Yang3, Dominic Rebollar1, 2, Peijun Guo2, Jordan Rucinski1, Zachary Liveris1, Richard D. Schaller2, 4, Kai Zhu1 and Tao Xu1; 1Northern Illinois University, DeKalb, Illinois, United States; 2Argonne National Laboratory, Lemont, Illinois, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4Chemistry, Northwestern University, Evanston, Illinois, United States.

Solution-processed thin-film perovskite solar cells (PSCs), where the record efficiency has rocketed from ~4% to ~23% — comparable to commercial silicon-based solar cells — in just nine years, offer unprecedented promise of low-cost, high-efficiency renewable electricity generation. Organic-inorganic halide perovskites (OIHPs) at the heart of PSCs have unique structures, which entail rotating organic cations inside inorganic cages, imparting them with desirable optical and electronic properties. To exploit these properties for PSCs application, the reliable deposition of high-quality OIH thin films over large areas is critically important. The microstructures and grain-boundary networks in the resulting polycrystalline OIH thin films are equally important as they control the PSC performance and stability. Fundamental phenomena pertaining to synthesis, crystallization, coarsening, microstructural evolution, and grain-boundary engineering involved in the processing of OIH thin films for PSCs will be discussed with specific examples. Additionally, the discovery of Pb-free, Ti-based all-inorganic halide perovskites will be presented, together with the demonstration of viable PSCs based on these new materials. The overall goal of our research is to have deterministic control over scalable processing of tailored halide perovskite thin films with desired compositions, microstructures, and grain-boundary networks for large-area, high-efficiency, and stable PSCs.

Combining In Situ Phase and Optical Characterizations to Unveil the Chemistry of CH₃NH₃PbI₃ Formation Jue Bing Song1, Faizan Motiwala1, 2, Megumi Mori1, 2, Gideon Segev1, 3, Camelia V. Stan4, Nobumichi Tamura4 and Carolin M. Sutter-Fella1; 1Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkley, California, United States; 3Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States. Over the past decade, organic-inorganic halide perovskite semiconductors have attracted substantial research attention for application in optoelectronic devices. The field is moving towards more and more complex chemical compositions enabling dramatically improved device performances. Those improvements however, were mostly achieved through empirical optimization of processing conditions. Due to the fast and complex chemical reactions of hybrid metal halide perovskites, significant variations in material properties and device performances are observed from previous reports. Therefore, in depth understanding of the fundamental film formation processes and relevant synthesis parameters is critical for the control of the final film properties and to achieve reproducible, high performance devices. Here, we establish methodical insights into the film formation process of metal halide perovskites by developing complementary in-situ characterization techniques including synchrotron diffraction, optical imaging and photoluminescence spectroscopy. These in-situ characterization techniques complement each other in providing a holistic picture of the relation between phase, optical response and morphology evolution. With our newly designed systems, we are able to characterize and monitor fast reaction/formation of perovskite thin films immediately after the spin-coating process which is commonly used in lab research. As a model system, we studied methylammonium lead iodide (CH₃NH₃PbI₃) as one of the most studied compounds among organic-inorganic halide perovskites. At relevant time scales, we demonstrate how the precursor chemistry influences phase formation, crystallization kinetics, film morphology, and optical response. We find that the perovskite film morphology is directly related to the structure of the intermediate phase and by tuning the precursor chemistry, we are able to tune the film morphology. The precursor chemistry plays the main role in the perovskite film formation and prevents the formation of needle-like morphology. In addition, using the CI chemistry, the disappearance and re-appearence of perovskite phases was observed over the course of crystallization which is distinctly different from other non-Cl chemistries. The combination of state-of-art in-situ characterization techniques could pave the way towards assessing the roles of synthesis and processing designs very efficiently thus, enables mechanistic insights and control of the film properties for high efficiency devices.

2:00 PM ET05.08.02 Adsorption Induced Anisotropic Growth—Band Gap Engineering in Gas induced Hybrid Perovskite Sayantan Sasmai1, 2, Raj Pala2, Sri Sivakumar2 and Suresh Veniyaveetil1; 1National University of Singapore, Singapore, Singapore; 2IIT Kanpur, Kanpur, India. Extremely high optical absorption, benign intrinsic defects, much longer diffusion length, a perfect synergy to achieve astonishingly high photovoltaic efficiency has made hybrid halide perovskites one of the major research fields in last few years. Additionally, facile band gap tunability make this hybrid perovskites a promising contender for double junction tandem solar cell useful to achieve much higher efficiency (theoretical efficiency limit 46.1%) than
single junction solar cell (efficiency limit 33.7%). Although several methods such as simple exchange of alkyl halides, compositional substitution, variation of precursor solution concentration, and solvent annealing as well as lattice footing induced fragmentation exists to tune the band gap of hybrid perovskite originated in solution phase, none of them applied in case of band gap tuning in recently acclaimed gas induced growth of hybrid perovskites due to less flexibility to implement all these methods in gas induced reaction impeded its use in multi junction tandem solar cell. Formation of ultra-thin film, facile quantum confinement and most importantly large area fabrication established an unsalable importance of gas induced growth process in hybrid halide perovskite field, albeit limited in use in double junction tandem solar cell due to inability to tune the band gap.

In the context of band gap tuning of methylammonium lead iodide (MAPbI₃) in gas induced growth, here we introduced a complete mechanistic detail highlighting a new synthetic route depicting selective adsorption of in situ formed hexylamine on the Pb site of growing MAPbI₃ induced anisotropic growth of MAPbI₃ leading to a unique sheet like structure of much higher band gap (2.18 eV). Moreover, gradual evaporation of in situ formed free hexylamine from the solvated intermediate and simultaneous relaxation of growth restriction on MAPbI₃ during prolonged exposure of methylamine leading to structural transformation of sheet to particle with continuous band gap engineering reflected in continuous change in emissive properties. This selective adsorption induced anisotropic growth of MAPbI₃ enable continuous shifting of conduction band of growing MAPbI₃ proved by scanning tunnelling spectra was also validated by DFT simulation points to the partial charge transfer to nonbonding p orbitals of Pb responsible for tuning of band gap of MAPbI₃. We believe this selective adsorption induced band gap tuning of MAPbI₃ will encourage to prepare new series of variant of MAPbI₃ which can be useful in tandem solar cell as well as light emitting diode and display application.

2:30 PM BREAK

3:30 PM *ET05.08.04
Material Engineering for Wide-Bandgap Perovskite Solar Cells Ni Zhao, Yang Zhou, Jie Cao and Ching-Ping Wong; Chinese University of Hong Kong, Shatin, Hong Kong.

Wide bandgap organic-inorganic hybrid perovskites with a bandgap ranging between 1.7-2.0 eV have shown great potential to improve the efficiency of single-junction silicon or thin-film solar cells by forming a tandem structure with one of these cells or with a narrow bandgap perovskite cell. However, solar cells based on this class of materials generally suffer from poor stability and a large open-circuit voltage (Voc) deficit, which is associated with the phase segregation of the materials under light illumination. In this talk I will explain how these issues can be addressed via multi-scale material modification combining composition tuning, grain engineering and surface passivation. Firstly, I will introduce a new mechanism to suppress ion migration in bulk perovskites through the interstitial incorporation of small alkali cations in the lattice of the state-of-the-art Cs/MFA triple cation perovskites. Through a combined experimental and theoretical investigation on the incorporation of extrinsic alkali cations (Rb⁺, K⁺, Na⁺, and Li⁺) in the perovskite materials, we unambiguously reveal the size-dependent interstitial occupancy of these cations in the perovskite lattice and demonstrate increased ion migration barriers in the lattice after the interstitial occupation. Secondly, I will describe how improved grain crystallization and grain boundary passivation can be achieved simultaneously through tuning of perovskite precursor composition. Using FAS0.17Cs0.83PbI3-xBrx (x=0.8, 1.2, 1.5 and 1.8) with a varied bandgap from 1.72eV to 1.93eV as the model system, we illustrate how precursor additive Pb(SCN)₂ should be matched with a proper ratio of FAX (I and Br) to realize large grains with defect-healed grain boundaries. The optimized perovskite films showed good photostability at both room-temperature and elevated temperature. Moreover, the corresponding solar cells exhibited excellent photovoltaic performances with the champion Voc/stabilized power output efficiency reaching 1.244V/18.60%, 1.284V/16.51%, 1.296V/15.01% and 1.312V/14.35% for WB-OHPPs with x=0.8, 1.2, 1.5 and 1.8, respectively.

4:00 PM *ET05.08.05
Homogeneity in Halide Perovskites—The Implications of Disorder on Stability and Advancing to a Terawatt Scale Photovoltaic Technology Joseph J. Berry; National Renewable Energy Laboratory, Golden, Colorado, United States.

Photovoltaic devices based on hybrid organic-inorganic perovskite absorbers have reached outstanding performance over the past few years, surpassing power conversion efficiency of over 22%. This talk we discuss the progress at the National Renewable Energy Lab (NREL) on the challenges in hybrid perovskite solar cells (HPSCs) and stability of HPSC devices and materials. This talk will highlight work at NREL to develop understand and enhance stability of HPSCs. Discussion will focus on efforts to more carefully understand the implications of process on stability and efficiency in the HPSC devices. Connections to aspects of material formation and processing for high-volume manufacturing will also be made. In the case of stability, an examination of different perovskite active layers their formation and resulting interfacial electronic structure with contacts in the HPSCs stack will be presented. Work at NREL indicate interface formation of the active layer with different carrier transport materials has direct implications for performance and it evolution over time in the resulting devices will be built upon. Results extending these results to additional active layers and associated interfaces studies in which photoemission, time resolved spectroscopy, structural studies and device level studies are combined indicates the importance of both processing and impacts of interface electronics and carrier dynamics. Results on the extension of existing stable architectures to mini-module devices will be presented along with performance data for these systems.

4:30 PM ET05.08.06
The Fluid Dynamics in Perovskite Scalable Coating and Its Suppression by Surfactants for Efficient Photovoltaic Modules Yehao Deng1, 2 and Jinsong Huang1, 2; University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 3University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Organic-inorganic hybrid perovskites are novel photovoltaic materials with high power conversion efficiency over 22% and low-cost solution processability. However, scaling up of perovskite fabrication remains a challenge due to the complex fluid dynamics within perovskite precursor solution when drying. Here, we show the fluid flow pattern observed by in-situ microscopy and report that surfactants additives can dramatically suppress the flow. The surfactant additives enabled the deposition of uniform, full-coverage perovskite film at a coating rate of 180 meter per hour and resulted in stabilized module efficiencies of 15.3% and 14.6% measured at aperture areas of 33.0 and 57.2 square centimeter, respectively. The result indicates that surfactants could be a kind of general additives in perovskite inks for improving perovskite film quality in scalable solution coating methods.

4:45 PM ET05.08.07

Two dimensional metal halide perovskites have demonstrated exceptional stability and performance in various optoelectronic applications. A key to higher performance is to align the insulating organic layers vertical to the substrates to avoid inhibition of charge transport. Several fabrication routes have been presented in literature but there is not yet a general strategy to orient 2D perovskite sheets vertically to the electrodes, due to lack of understanding of the crystallization process. In our research, based on our previous discovery that vertically oriented 2D perovskite crystallization can occur at liquid-air...
However, in order for perovskite compounds to reach eventually the market, some severe limitations have to be addressed. Those are not other than their (FA)x(Pb(I1-xBrx))3 channel layers to produce TFTs with significantly enhanced performance characteristics. Optimised transistors are shown to combine low mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to f...
on green emission region. In this regard, herein we tried to tailor the emission range of Br-based quasi-2D perovskite from green to blue region by integrating organic carrier spacers. As the candidates for the spacer, aromatic phenylethylammonium (PEA), benzyltrimethylammonium (BTA) and aliphatic isoproplammonium (IPA), n-propylammonium (nPA) cations were employed by controlling the relative concentration ratio. As a result, the PL intensities and the emission wavelength of the new class of quasi-2D perovskites, BTA and nPA-based perovskites, showed deep-blue emissions at 475 nm, with uniform and well-structured surface coverage. In addition, The PL intensity of the blue perovskite thin film was on par with that of the green one \((\text{PEA}_4\text{MA}_8\text{PbBr}_{30})\). By controlling the ratio of BTA and nPA, we could fine-tune the PL wavelength from 610 nm (green) to 475 nm (blue) systematically (with 7 nm intervals). Based on our dimensionally-controlled perovskites, the blue-emissive Q-2D perovskite LED showed low turn-on voltage (less than 4 V) with high-current density (42 mA/cm²). The protocol and strategy established in this study can be exploited to enhance high-level electron quantum efficiency (EQE) and lumiance.

**ET05.09.04**

Highly Efficient Perovskite Quantum-Dot Light-Emitting Device by Gel Permeation Chromatography as New Purification Process and Interfacial Engineering Using Alkyl Ammonium Salt Layer [Hinako Ebe, Yoshihito Takashashi, Jun Sato, Takayuki Chiba, Satoru Ohisa and Junji Kido.]

Lead halide perovskite (CsPbX₃, X = Cl, Br, or I) quantum dots (QDs) have recently attracted considerable interest for light-emitting device (LED) applications such as thin film displays and solid-state lighting, owing to electroluminescence emission with narrow full width at half maximum (FWHM), tunable color properties by anion exchange method, and ease of solution processability (1,2). The optical properties of perovskite QDs as ionic nanocrystals are greatly affected by highly polar washing solvent due to occurring cation- and anion-defects (3). In this work, we achieved low driving voltage and high efficiency perovskite QD-LED using Gel permeation chromatography (GPC) with nonpolar solvent to remove excess ligand such as oleic acid (OA), oleylamine (OAM) and synthesis solvent 1-octadecene (ODE). We confirmed completely remove these impurities by GPC in contrast to conventional reprecipitation process. In addition, we demonstrated the effect of interfacial layer between the hole transport layer and the perovskite QDs using alkyl ammonium salts containing the Br anion, oleylamine bromide (OAM-Br) to passivate cation- and anion-defects. The LED based on OAM-Br interfacial layer exhibited higher efficiency compare to the LED without OAM-Br layer due to the suppression of interfacial cation- and anion-defects.


**ET05.09.05**

Metal Halide Perovskite Based Optical Phase Shifter—Giant Photocarrier-Induced Refractive Index Change [Hirokazu Tahara, Tomoko Aharen, Atsushi Wakamiya and Yoshikiko Kanemitsu, Kyoto University, Uji, Japan.]

Metal halide perovskites are excellent optoelectronic materials that are quite suitable for thin-film solar cells, light-emitting diodes (LEDs), and lasers. This is because they exhibit strong optical absorption, high luminescence efficiencies, long carrier lifetimes, long diffusion lengths, and low densities of nonradiative recombination centers [1]. Recently, unique properties of halide perovskites have been discovered, e.g., photon recycling, ion migration, and local rearrangement of molecular dipoles [2-4]. These properties are expected to lead to the development of new-type optoelectronic devices. One of the most important properties of halide perovskites is that they crystallize in low-temperature solution processes. In particular, it is remarkable that large-size single crystals of halide perovskites can be grown in low-temperature solution exhibiting high optical transparency and exceptionally low surface light scattering. These optical properties are beneficial for novel optical transmittance applications in the broad spectral range from visible to infrared. In this work, we studied the photocarrier-induced refractive index change in organic-inorganic hybrid perovskites. The crystal used in this study was a methylammonium lead bromide (MAPbBr₃) single crystal. To measure the photoreflective properties of the halide perovskite, we developed an interferometric system that is synchronized with photoexcitation. The photoreflective phase shift was measured by detecting the phase shifts of the transmitted light through the perovskite single crystal mounted in the interferometric system. From the time-resolved measurements and excitation-pulse fluence dependence of the photoreflective phase shifts, we clarified that photogenerated carriers cause extremely large and long-lived changes in the refractive index. This result shows that the perovskite single crystal works as an optical phase shifter. Moreover, we demonstrated that infrared laser light is tunable to any desired polarization configuration by employing the photoreflective phase shift. Our demonstrations provide new pathways to develop optical devices with organic-inorganic hybrid perovskites leading to variable wave plates, optical switches, and phase modulators.

Part of this work was supported by JST-CREST (JPM16N3) and JSPS KAKENHI (18K13481).


**ET05.09.06**

A Device Simulation of Organohalide Perovskite Resistive Random Access Memory [Kyunghwan Min, Sungwoo Cho and Yongwoo Kwon; Hongik University, Seoul, Korea (the Republic of)].

Resistive random access memory (ReRAM) based on organohalide perovskite (OHP) shows excellent properties compared to conventional metal oxide resistive memory such as low operating voltage, high on/off ratio, and fast switching speed in several experimental demonstrations. Nevertheless, this technology is still in the premature stage. The design strategy of the active material and the device architecture must be established for the OHP ReRAM to be promoted to the stage of the commercial development. Thus, a device simulation based on finite element method is necessary to investigate the optimal device architecture on constituent materials and geometry. In this work, we will present a stochastic finite element simulation of conductive filament formation to perform reverse engineering on the material parameters of the OHP, in other words, to estimate which material parameters critically affect switching characteristics. In addition, the effects of device geometry and the nature of OHP/metall contacts were also studied.

**ET05.09.07**

First-Principles Investigations on Amotomic Origin of I-V Hysteresis in Hybrid Perovskite Solar Cell [Seong Hun Kim¹, Pli-Ryung Cha² and Donghwa Lee²; ¹Pohang University of Science and Technology, Gyeongbuk, Korea (the Republic of); ²School of Advanced Materials Engineering, Kookmin University, Seoul, Korea (the Republic of)].

In spite of the unprecedented advance of MAPbI₃-based perovskite solar cell, there are still remaining issues to be resolved for its industrial applications.
Especially, hysteresis in current-voltage (I-V) curve is one of big challenges since it can limit its potential large scale application by causing abnormal efficiency drops. Various studies have proposed different physical origins such as ferroelectric polarization, charge trapping/detrapping and ion migration, none of study has clearly explained the microscopic origin of the hysteretic behavior in MAPbI₃-based perovskite solar cell. In this study, thus we have employed first-principles density functional theory calculations to identify the atomic origin of hysteresis in MAPbI₃. Our study has found that excess electrons or holes can stabilize the formation of iodine Frenkel defect structures in MAPbI₃. Since excess charge carriers can be easily accumulated near the electrode interface, the formation of two different iodine Frenkel defects is inevitable and reversibly it can act as a charge trap in MAPbI₃-based solar cell. Thus, the hysteretic behavior of I-V curve is a result of charge trapping and detrapping during the formation of two types of iodine Frenkel defects near electrodes. Based on our understanding, we have suggested several possible ways to suppressed the hysteresis in MAPbI₃-based solar cell.

ET05.09.08

Correlation between the Charge Transporting Layers and Defect States Distribution in Perovskite Solar Cells Measured by Admittance Spectroscopy

Rashid A. Awni, Changlei Wang, Xinxing Yin, Zhaoqing Song, Corey R. Grice, Lei Guan, Xiaoming Wang and Yanfa Yan; Department of Physics and Astronomy, and The Wright Center for Photovoltaics Innovation and Commercialization (PVIC), The University of Toledo, Toledo, Ohio, United States.

In the past decade, organic-inorganic halide perovskite solar cells (PVSCs) have achieved outstanding progress in power conversion efficiency. However, solution-processed polycrystalline perovskite thin films possess a significant number of defects. Accurately probing the defect states distribution and understanding the origins of the defects are critical for further improving the device performance. Thermal admittance spectroscopy (AS) is a powerful characterization technique to determine the energetic distribution of defect states for different inorganic (e.g., CdTe, Cu(In, Ga)Se₂, etc.) and organic thin film solar cells, and has recently been used to characterize PVSCs. Interestingly, some unique trap signatures were observed in the AS measurements of PVSCs, but their origin has yet to be determined.

Here, we perform AS measurements on the PVSCs in the n-i-p planer structure to determine the impact of electron and hole transporting layers (ETL and HTL) on the trap states. We measured PVSCs with and without the SnO₂: F- coated ETL and the spiro-OMeTAD HTL as well as devices with different HTL thicknesses, doping densities, and materials. The AS measurements at different DC bias voltages are employed to identify whether the trap features are originated from the bulk or interface defects. Our results show that defect states are less dependent on the ETL but strongly affected by the HTL. Additionally, we compared the admittance spectra of the n-i-p and p-i-n devices with the same absorber but different ETLs/HTLs. The devices exhibit different capacitance signatures, indicating that defect states probed by AS are affected by the ETLs/HTLs. More importantly, we identify that the trap states that were originally attributed to perovskite absorber layer by previous studies may likely be originated from the spiro-OMeTAD HTL. Our approach provides insights on the defect state measurement using AS and the limitations of this method.

ET05.09.09

Impact of B-Site Doping on the Optical Properties of Lead Halide Perovskites

Abdeljaleel Ismail, Mahesh K. Gangishetty and Dan Congreve; Rowland Harvard University, Cambridge, Massachusetts, United States.

Lead halide perovskites (ABX₃) have been attractive materials for various applications in optoelectronics such as solar cells and light emitting diodes (LEDs). The quantum efficiency of green and red perovskite LEDs has reached over 10% within the last few years. The composition of the perovskite has been shown to play a crucial role on their optical properties. Recently, several groups including ours, found that doping the B cation site with Mn²⁺ can significantly improve photoluminescence quantum yields of perovskite quantum dots. In addition to the Mn²⁺, many other B cations have been suggested as potential dopants, however, only a few other cations have been studied in perovskites thus far. In this work, we have explored a variety of cations with different atomic sizes and various oxidation states from +1 to +3 as dopants in perovskites. We have grown bulk perovskite crystals using these dopants and studied the changes in crystal structure, and optical properties. In a poster, I will discuss the impact of the dopants, both the type of the dopant and its concentration on the optical properties of perovskites. Our finding will eventually lay-down a platform for high performance, Pb-less perovskite light emitting diodes.

References

ET05.09.10

Environmental Gating and Galvanic Effects in Single Crystals of Methylammonium Lead Bromide Perovskite

Mahshid Ahmadl, Eric Mackley², Iliu Ivanov³, Eric Lukosi¹, Jeremy Tisdale¹, Ivan Kravchenko², Sergei V. Kalinin³, Bin Hu¹ and Liam Collins¹; ¹Joint Institute for Advanced Materials, University of Tennessee, Knoxville, Tennessee, United States; ²Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

Understanding the impact of environmental gaseous on the surface chemistry of organic-inorganic perovskite couples to the electronic and ionic transport is critically important. Here, we explore the transport behavior and origins of the gas sensitivity in MAPbBr₃, single crystals (SCs) devices using electrochemical impedance spectroscopy and current relaxation measurements. We show that the SC response to the environment is highly anisotropic and depends on crystal planes with respect to electrodes. Strong capacitive and resistive response occurs when crystals are exposed to N₂ and O₂. We discuss the possible interaction between N₂ and O₂ gases with the surface of MAPbBr₃ perovskite SC. The observed behaviors suggest that the redox state of the surface plays significant role in the transport phenomena but does not offer readily controlled redox environment. In addition, analysis of available data indicate that gas response of MAPbBr₃ SC is complex and likely related to volatilization phenomena which can change the defect mechanisms and it is highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment. We notice that the potential drop across SC device is significantly higher in air as compare to N₂ and O₂ gases. The potential drop causes by space charges highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment.

Understanding the impact of environmental gaseous on the surface chemistry of organic-inorganic perovskite couples to the electronic and ionic transport is critically important. Here, we explore the transport behavior and origins of the gas sensitivity in MAPbBr₃, single crystals (SCs) devices using electrochemical impedance spectroscopy and current relaxation measurements. We show that the SC response to the environment is highly anisotropic and depends on crystal planes with respect to electrodes. Strong capacitive and resistive response occurs when crystals are exposed to N₂ and O₂. We discuss the possible interaction between N₂ and O₂ gases with the surface of MAPbBr₃ perovskite SC. The observed behaviors suggest that the redox state of the surface plays significant role in the transport phenomena but does not offer readily controlled redox environment. In addition, analysis of available data indicate that gas response of MAPbBr₃ SC is complex and likely related to volatilization phenomena which can change the defect mechanisms and it is highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment. We notice that the potential drop across SC device is significantly higher in air as compare to N₂ and O₂ gases. The potential drop causes by space charges highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment. We notice that the potential drop across SC device is significantly higher in air as compare to N₂ and O₂ gases. The potential drop causes by space charges highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment.
Organic-inorganic hybrid lead perovskites have emerged as remarkable photovoltaic (PV) absorber materials in recent years. To date, polycrystalline thin-film perovskite photovoltaic devices have reached power conversion efficiencies reaching 22.7%. However, the involvement of a toxic element of lead and long-term instability are still the main issues in the large-scale commercial application of perovskites.

With excellent long-term durability and moisture tolerance, the possibility of flexible tuning of electronic properties, and coupled to low cost synthesis routes, the two-dimensional (2D) hybrid halide perovskites have recently attracted much attention, and have been successfully used as light absorbers in efficient photovoltaic devices. 2D hybrid halide perovskites which feature long chain alkylammonium cations are generally suggested for light emitting diode applications, due to their strong photoluminescence (PL), but none have been applied thus far for photovoltaic applications. Additionally, the previous study has shown the luminescence quenching in the Pb-based analogues, (AEQT)PbX4 (X = Cl, Br, I), the energy transfer and charge separation between organic and inorganic components of the structures are not fully understood.

Herein, we investigate the geometrical, electronic and optical properties of the semiconducting 2D perovskites (AEQT)BX4 (B = Pb, Sn; X = Cl, Br, I), using relativistic hybrid density functional theory calculations. We demonstrate that unlike the traditional 2D perovskites, the choice of the organic ammonium cation has a considerable effect on the carrier transport properties, and the energy transfer between the organic and inorganic components is symmetry-disallowed. The electronic structures of the series are flexibly tailored by different halides and metal cations, with band gaps from 2.06 to 2.68 eV. Unique energy level alignments greatly hinder the electron-hole recombination in (AEQT)PbCl4, (AEQT)PbBr4, (AEQT)PbI4 and (AEQT)SnBr4, and thereby enhance the PL efficiencies. With a moderate fundamental band gap (2.06 eV) and strong direct valence band to conduction band transition, (AEQT)SnI4 is the only composition that shows intense and broad optical absorption, and as expect displays a high spectroscopic limited maximum efficiency (SLME) of 21.9%. Our results indicate the (AEQT)SnI4 is a promising class of stable and efficient light-absorbing materials for photovoltaics.


**ET05.09.11 Two-Dimensional Hybrid Perovskites for Tunable Energy Level Alignments and Photovoltaics**

Zhenyu Wang1,2,3, Alex M. Ganose2,3, Chunming Niu1 and David O. Scanlon2,3,4; 1School of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China; 2Department of Chemistry, University College London, London, United Kingdom; 3Thomas Young Centre, University College London, London, United Kingdom; 4Diamond Light Source Ltd., Diamond House, Oxfordshire, United Kingdom.

Organic-inorganic lead halide perovskites have emerged as remarkable photovoltaic (PV) absorber materials in recent years. To date, polycrystalline thin-film perovskite photovoltaic devices have reached power conversion efficiencies reaching 22.7%. However, the involvement of a toxic element of lead and long-term instability are still the main issues in the large-scale commercial application of perovskites.

With excellent long-term durability and moisture tolerance, the possibility of flexible tuning of electronic properties, and coupled to low cost synthesis routes, the two-dimensional (2D) hybrid halide perovskites have recently attracted much attention, and have been successfully used as light absorbers in efficient photovoltaic devices. 2D hybrid halide perovskites which feature long chain alkylammonium cations are generally suggested for light emitting diode applications, due to their strong photoluminescence (PL), but none have been applied thus far for photovoltaic applications. Additionally, the previous study has shown the luminescence quenching in the Pb-based analogues, (AEQT)PbX4 (X = Cl, Br, I), the energy transfer and charge separation between organic and inorganic components of the structures are not fully understood.

Herein, we investigate the geometrical, electronic and optical properties of the semiconducting 2D perovskites (AEQT)BX4 (B = Pb, Sn; X = Cl, Br, I), using relativistic hybrid density functional theory calculations. We demonstrate that unlike the traditional 2D perovskites, the choice of the organic ammonium cation has a considerable effect on the carrier transport properties, and the energy transfer between the organic and inorganic components is symmetry-disallowed. The electronic structures of the series are flexibly tailored by different halides and metal cations, with band gaps from 2.06 to 2.68 eV. Unique energy level alignments greatly hinder the electron-hole recombination in (AEQT)PbCl4, (AEQT)PbBr4, (AEQT)PbI4 and (AEQT)SnBr4, and thereby enhance the PL efficiencies. With a moderate fundamental band gap (2.06 eV) and strong direct valence band to conduction band transition, (AEQT)SnI4 is the only composition that shows intense and broad optical absorption, and as expect displays a high spectroscopic limited maximum efficiency (SLME) of 21.9%. Our results indicate the (AEQT)SnI4 is a promising class of stable and efficient light-absorbing materials for photovoltaics.


**ET05.09.12 New Electron Transporting Materials for Perovskite LED**

Seokwoo Kang, Yeonhee Sim, Beomjin Kim and Jongwook Park; Kyung Hee University, Yongin, Korea (the Republic of).

In conventional organic light emitting diode (OLED), aluminium quinolone (Alq3) has been widely used as an electron transporting layer (ETL) in the past. And in the perovskite light emitting diode (pLED) device, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) has been generally used as an ETL because it has better ETL property based on the higher electron mobility than Alq3 in the device. However, TPBi has disadvantage in terms of device life time compared to the Alq3, because of the inferior thermal property. Therefore, we designed and synthesized new organic electron transporting materials for perovskite light emitting diode (pLED) which includes thiazolo[5,4-b]pyridine and benzo[h]quinolone moieties, respectively. We report the pLED device performance having new two ETL compounds as well as TPBi. The device configuration is ITO/PEDOT:PSS-P3SS-Na/perovskite of phenylethylationium-formamidiniumPbBr3/trioctylphosphine oxide/ETL/LiF/Al. When new ETL materials were used, it showed high luminance efficiency of more than 10 Cd/A in green PLED device.

**ET05.09.13 Continuously Tunable Photoluminescence of Two-Dimensional Layered Perovskite Semiconductors Under High-Pressure**

Sheng Liu1, Shishuai Sun2, Chee Kwan Gan3, Jun Xing4, Thau Ha T. Do3, Andres T. Granados del Aguil1 and Qhua Xiong1; 1Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore; 2Tianjin University of Technology, Tianjin, China; 3Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore, Singapore.

Organic-inorganic hybrid semiconductors with a perovskite lattice have recently attracted great attention due to their strong photoluminescence (PL), but none have been applied thus far for photovoltaic applications. Additionally, the two-dimensional (2D) hybrid halide perovskites have recently attracted much attention, and have been successfully used as light absorbers in photovoltaic applications.

In this work, pressure induced changes in the optical emission of two-dimensional perovskite crystals ((PEA)2PbI4), has been systematically studied at room temperature by several optical techniques, including photoluminescence (PL), time-resolved PL and Raman spectroscopy, all as a function of pressure. The crystals are pressurized inside a diamond anvil cell (DAC). At the pressure range of 0 to 3.5 GPa, the photoluminescence, originally at spectral position of ~2.3 eV, continuously shift to lower energies (red shift), and exhibits an ultra-wide tunable energy range of up to 350 meV spanning nearly the whole visible spectrum. Moreover, this energy tunability is fully reversible. In the used pressure range, the intensity of the emitted light is almost constant, while the PL lifetime keeps decreasing when increasing pressure, which implies that the efficiency of radiative recombination of excitons might be enhanced by pressure. First-principles simulations and X-ray diffraction (XRD) by synchrotron radiation both indicate that strong anisotropic compression along in-plane and out-plane directions should account for the red-shift of the band gap. Such a large optical tunability and constant emission quality within a relatively applied low pressure, has the potential to expands the applications of two-dimensional lead halide perovskite crystals in photonic and optoelectronic devices.

Sub-100nm Patterning of Perovskite Films by Self-Assembly of Block Copolymer

Hyowon Han, Euihyuk Kim and Cheolmin Park; Department of Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of).

While tremendous efforts have been made for developing thin organic lead halide perovskite films suitable for a variety of potential photovoltaic applications such as solar cells, field-effect transistors, and photodetectors, only a few works have focused on the micro or nanopatterning of perovskite films which is one of the most critical issues for large area and uniform micro or nanorarrays of perovskite-based devices. At present, patterning is only feasible at microscale, and at sub-100nm scale lithography of thin perovskite films has not yet been reported. Here, we demonstrate perovskite patterning at sub-100 nm scale without losing structural integrity and optical properties of the perovskite by an easy and simple method using self-assembly of the block copolymers. In order to make perovskite selectively segregated into one block, we utilized diblock copolymer, polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) consisting of non-interacting PS block and interacting Lewis base polymer P2VP block. By controlling the volume fraction (f_{PS}) and the amount of perovskite, the effective volume fraction (f_{PVE}) can be determined and various self-assembled nanostructures such as spheres, cylinders, lamellae could be successfully formed. The domain size of a perovskite crystal in the pattern could also be controlled by simply changing the molecular weight of the block copolymers. Our simple but highly controllable, nanoscale patterning of perovskites by self-assembly of block copolymers is promising and will enable applications of perovskite to highly integrated optoelectronic nanoscale devices.

ET05.09.15

Nanostructure and Optical Characterization of CH3NH3PbBr3 Perovskite via Ostwald Ripening

Kazuyuki Umemoto1, Yuki Tezuka1, Tornoko Inose2, Hiroshi Uji2, Satoshi Asakura2 and Akito Masuhara1; 1Yamagata University, Yonezawa, Yamagata, Japan; 2Hokkaido University, Sapporo, Japan; 3ISE Chemicals Corporation, Tokyo, Japan.

Methylammonium lead halide perovskites have been applied to versatile applications owing to their attractive optoelectronic properties such as long carrier diffusion length, ambipolar conductivity, broad color-tunablility exchanging by halide ions. These potentials for applications with high performance are based on perovskite electro-optical features and they are expected to be used as a next generation and solution processable semiconductor materials [1].

Recently, bright luminescence from methylammonium lead tri-bromide (MAPbBr3) perovskite nanocrystals (PeNCs) has been reported owing to the development of methods for preparing these PeNCs. Especially, MAPbBr3 PeNCs were prepared by ligand-assisted reprecipitation (LARP) inspired by the reprecipitation method for preparing organic and nano/micro crystals. LARP can provide uniform MAPbBr3 PeNCs with narrow emission, which applies for successful implementation of PeNCs into LED.

Herein, we propose Ostwald ripening as a size-tunable technique for MAPbBr3 for PeNCs using LARP. In a typical Ostwald ripening process, large crystals absorb from small ones in dispersion, as a result, large crystals grow bigger, and small crystals shrink. MAPbBr3 PeNCs could be size-controlled from several tens of nanometer size to 4 nm through shrinking of MAPbBr3 PeNCs and their PL peaks were consequently blue shifted from 514 nm to 457 nm. This suggests that Ostwald ripening can be expected to be an effective method for preparing PeNCs in the low nanometer size range.

References
2) F. Zhang, et al., ACS Nano, 2015, 9, 4533-4542.

ET05.09.16

Efficient Upconversion Photoluminescence in All-Inorganic Perovskite Colloidal Semiconductor Nanocrystals

Thu Ha T. Do, Andres T. Granados del Aguila, Jun Xing, Wen Jie Jee, Lulu Zhang and Qihua Xiong; Nanyang Technological University, Singapore, Singapore.

Semiconductor colloidal nanocrystals (NCs) are efficient fluorescence emitters, whose emission wavelengths can be tuned by varying their sizes and chemical compositions. Recently, lead halide NCs with perovskite lattices have opened access to the deep-blue and green regions of the electromagnetic spectrum [1], where traditional II-VI nanocrystals such as the prototypical CdSe, undergo rapid degradation.

In this work, we investigate the optical properties of all-inorganic CsPbX3 (X = Cl, Br, I, ClBr2, and BrI3) perovskite nanocrystals. Specifically, we focus on their ability to convert low-energy into high-energy photons in a so-called upconversion photoluminescence (UCPL) process. Overall, all the investigated nanocrystals exhibit robust and efficient UCPL, characterized as a function of temperature, excitation energy and laser power. The UCPL phenomenon takes place in two distinguishable ways: (i) multiple-phonon absorption and (ii) one-phonon with the subsequent lattice vibrational (phonon) absorption. The latter mechanism demands an energy of up to 200 meV from the thermal bath, equivalently to the total energy of about ten optical phonons of CsPbX3 compounds. However, after the first few consecutive absorption steps, the finite optical phonon population in the nanocrystals would become deficient, therefore decreasing the UCPL efficiency. We argue that the annihilation of multiple low-energy phonons creates a high-energy vibration, which repopulates the optical phonon bath and consequently increases the light upconversion probability [2]. This energy recycling mechanism is particularly strong in semiconductors having low thermal conductivity, such as lead halide perovskites [3]. Our work explains for the outstanding laser cooling effect in these materials [4] and reveals the potential of high-quality CsPbX3 nanocrystals for several applications such as biomaging, photovoltaic light-energy harvesting and optical refrigerators.

References

ET05.09.17

Anisotropic Excitons in Two-Dimensional Layered Lead Halide Perovskite Semiconductors

Thu Ha T. Do, Andres T. Granados del Aguila, Jun Xing, Sheng Liu, Chongyuan Jiang, Weibo Gao and Qihua Xiong; Nanyang Technological University, Singapore, Singapore.

Research on lead halide semiconductors with perovskite lattices is a rapidly growing field in nanoscience and semiconductor physics. They have great potential for low-cost yet efficient solar cells and light-emitting devices [1,2]. Their optical properties can be tuned by tailoring the chemical composition and/or the nanostructure spatial dimension with very high precision and high quality. For example, the perovskite semiconductors can grow in stable layered structures, which comprise alternatively stacked layers of lead-halide octahedra and long-chain organic molecules. The inorganic framework, sandwiched between two organic layers, forms an atomically thin quantum well with macroscopic continuity.

Herein, we study the optical properties of high-quality two-dimensional (PDA)PbI4 crystals. Four intrinsic optical transitions are resolved in the
luminescence spectrum, originating from the radiative recombination of coupled electron-hole pairs (excitons) [3]. Intriguingly, the light emission is dominated by two excitons, each of which is split into two linearly polarized and orthogonal states. Their energy splitting is in the range of ~1.2 meV, which is much larger than that of perovskite nanocrystals [4]. The highly anisotropic excitons may be resulted from the spin-orbit coupling and the exceptionally strong electron-hole exchange interaction. Moreover, at the low-energy side of the two doublets, we observe a feature arising from the recombination of a bright exciton. This line shows a circular dichroism, which can be induced either by circularly polarized excitation or by external magnetic field. This work is in line with the previous literature, where multiple excitonic features were resolved in bulk-like lead halide perovskites [5]. The observed energy landscape cannot be fully explained by available theoretical schemes for this material family. Our findings provide essential parameters for establishing a complete physical picture that governs the outstanding optical properties of two-dimensional layered perovskite semiconductors.

References

ET05.09.18
Volatility and Chain Length Interplay of In Situ Formed Primary Amines—Mechanistic Detail on Signal Transduction Properties of Hybrid Perovskites in Ammonia
Sayantan Sasmal1,2, Sri Sivakumar1, Raj Pala1 and Suresh Valiyaveetil2; 1IIT Kanpur, Kanpur, India; 2Chemistry, National University of Singapore, Singapore, Singapore.

Organic–inorganic halide perovskites, mainly known in photovoltaics possess promising signal transduction properties, which can be gainfully utilised in variety of sensing applications. Interestingly, highly polar nature of these class of materials, while being a bane in terms of stability, can be a boon for sensitivity while exposing with toxic gas like ammonia in a controlled atmosphere. This unusual signal transduction during sensing induces irreversible restructuring of perovskite crystal structure, which is one of the major lacuna preventing its utility in practical applications. To this end, we first elucidate the reasons behind the irreversibility of methylammonium lead iodide (MAPbI3) associated with structural transformations and then developed a generic mechanistic route on interaction of ammonia (NH3) with hybrid halide perovskite. The current investigation highlights that the vapor pressure of insitu formed alkylamine (due to facile proton exchange between alkylammonium cation present inside the hybrid perovskite crystal and approaching NH3) determines the reversibility and stability of the original perovskite lattice. In addition, packing of alkyl ammonium chain inside the hybrid halide perovskite crystal provides accessible voids, which allows diffusion induced proton exchange reaction ultimately influence the rapidity of interaction with NH3 gas. The mechanistic study addresses three important factors such as quick response, reversibility, and stability of perovskite materials in the presence of NH3 gas, which could lead to the design of stable and sensitive two-dimensional hybrid perovskite materials for developing sensors.

ET05.09.19
Combinatorial Synthesis and PV Activity of Mixed A or X ABX3 Halide Perovskites by Spray pyrolysis for Rapid and Systematic Parameter Space Mapping

Using ABX3, Halide Perovskites, compositions with several monovalent cations occupying the A site and 2 types of halides the X site, in PV cells has yielded cell performances better than with one type of species on the A and X sites. Performance differences are not limited to conversion efficiency, but also to material and cell stabilities, under a variety of conditions. To date, reports on compositional changes have been limited to multiple single experiments that cannot cover all parameter space, which, strongly hinders mapping trends in compositions. This is where combinatorial materials science, CMS, and accompanying high-throughput analysis methods are important. In CMS compositional ranges can be prepared on a single substrate, making possible to do many experiments faster and in a comparatively more controlled manner. We report on CMS to form MAPbI(1-x)Brx, with systematically varying x and Br compositions to form a library of materials, using a home-built, controlled-environment tri-needle spray pyrolysis system. High-throughput optical characterization shows absorbance onset shifts of up to ~150 nm depending on the composition (for MAPbI3 in the range of x=0.2-0.8), as measured by EDS), allowing for fine-tuning of the bandgap along the library. X-ray diffraction showed peaks, corresponding for the perovskite structure, which, for the (220) one, range between 2θ = 29.63° - 30.02°, i.e., from the neat MAPbI3 (220) towards 2θ =30.020, which we ascribe to Br replacing some of the I. Also libraries where Cs (replacing the A cation), Rb (maybe interstitial) or both, were added, to yield MAxRby(PbI3) , MAxCs1-xPbI3, and MAxCs1-xRbyPbzI3 were synthesized. We will report on characteristics of both the films alone, and of PV cells with architecture FTO/TiO2 meso-TiO2|Halide Perovskite|Spiro-MeOTAD |Ag, and discuss trends observed for the different composition ranges, as trend identification is one of the most powerful ways to use CMS.

Reference:

ET05.09.20
Ambipolar Hybrid Perovskite Based Phototransistors Grown by Chemical Vapor Deposition
Hyung-Do Kim and Hyun-suk Kim; Materials Science and Engineering, Chungnam National University, Daejeon, Korea (the Republic of).

Low-cost hybrid organic-inorganic perovskites such as methylammonium lead iodide(MAPbI3) have been developed intensively due to those high absorption coefficient and easily tunable band gap, and easily fabricated by various deposition method such as solution-based process. However, solution-processed device using hybrid organic-inorganic perovskite is unstable and sensitive to water and ambient moisture. Therefore, the device stability is one of most important properties to achieve high performance hybrid organic-inorganic perovskite based devices. In this paper, the electrical characteristics and stability of phototransistors using MAPbI3, active layer were investigated. MAPbI3, thin-film fabricated by chemical vapor deposition (CVD) with MAI and PbI2 sources, and its physical, chemical, optical properties were compared with the solution-processed MAPbI3 thin-film. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) revealed that solution-processed MAPbI3 thin-film was easily transformed (from MAPbI3 to PbI2) after 7 days later when exposed to air. However, CVD-grown MAPbI3 thin-film showed great air stability maintaining its chemical composition and crystalinity above 1 month. Furthermore, atomic force microscope (AFM) and scanning electron microscope (SEM) indicated that CVD-grown MAPbI3 thin-film has large grain size and small surface roughness as compared to solution-processed MAPbI3, MAPbI3 phototransistor exhibits insulating behavior in transfer characteristics, but ambipolar properties were observed when the visible light was irradiated. Finally, electrical stability such as negative bias stress (NBS), positive bias stress (PBS) of MAPbI3, phototransistors were examined for the optoelectronic application.

ET05.09.21
Anion Exchange Perovskite Quantum-Dots for Highly Efficient Light-Emitting-Devices

A unique aspect of hybrid halide perovskite materials is the presence of an organic cation that occupies the cages formed by lead (Pb) and iodide (I). In the basic perovskite CH3NH3PbI3, the methylammonium (MA) cation can rotate relatively freely, while slightly large cations can be restricted in their motion. Interestingly, the MA cation is dipolar and the organization of the dipoles in the material depends on the mutual interaction of the dipoles. It has been suggested that the formation of ordered domains can lead to electronic localized states that are different for electrons and holes, and therefore the dipolar disorder should influence the dynamics of charges formed on photo-excitation.

In this work we have performed a combined computational and experimental study to unravel the relation between dipolar disorder and charge dynamics. Using a combination of Monte Carlo simulations and classical molecular dynamics we have studied the dynamics of the MA dipole at different temperature and large scale ordered domains are formed at low temperature, while above a certain temperature the domains are very small and the dipole are rotation relatively freely. The temperature at which this transition occurs suggests that the phase transitions in the perovskite are induced by dipole alignment.

Subsequently, we have studied the effect of dipole orientation on the delocalization of electronic states in the material. It is shown that for organic cations with a relatively high dipole moment, such as MA, localized states are formed that are different for electrons and holes. For a low-dipole moment cation, formamidinium (FA) such localized states are not observed.

Finally, in order to gain insight in the effect of dipole motion on charge dynamics, we have performed time-resolved microwave conductivity measurements combined with generation of charges by irradiation with a short, high-energy electron pulse. We observe substantial changes in mobility and lifetime of charge carriers in CH3NH3PbI3 after the low temperature tetragonal (β) to orthorhombic (γ) phase transition. We observed that the mobility and lifetime of charge carriers increase as the temperature decreases and a sudden increment is seen after the β/γ phase transition. For CH3NH3PbI3 the mobility and the half-lifetime increase by a factor of three to six compared with the values before the β/γ phase transition. We attribute the considerable change in the dynamics at low temperature to the decrease of the inherent dynamic disorder of the organic cation (CH3NH3+) inside the perovskite crystal structure. When replacing the MA cation by FA such sudden changes in the charge dynamics are not observed. This indicates that the dipolar motion of the organic cation does influence the dynamics of charges, particularly at lower temperature.

**ET05.09.22**

Towards Stable Deep-Blue Luminescent Colloidal Lead Halide Perovskite Nanoplatelets—Systematic Photostability Investigation

Seung Kyun Ha, Catherine M. Mauck and William Tisdale; Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recently, colloidal lead halide perovskite nanoplatelets have emerged as promising semiconductor materials due to their exciting properties such as tunability, facile processability, and bright emission with high color purity. In particular, their quantum-and-dielectric-confined nature makes colloidal lead bromide perovskite nanoplatelets a favorable candidate for the next-generation deep-blue-emitting (437 nm) material platform. However, for light-emitting applications, poor photostability is one of the critical challenges that those nanoplatelets face. When exposed to UV excitation, they either suffer from photobleaching or transform into thicker–more bulk-like–structures with red-shifted emission.

In this study, we systematically investigate the factors that affect the photostability of the deep-blue-emitting perovskite nanoplatelets by monitoring the photoluminescence and absorption spectra over time. We find that freshness of the prepared precursor solutions for ligand-assisted recrystallisation is critical to obtain better stability with high photoluminescence quantum yield of perovskite nanoplatelets. Also, photobleaching is found to be the sign of intrinsic instability in nanoplatelets while transformation represents an extrinsic instability. Importantly, moisture is identified as the key extrinsic factor responsible for the transformation of nanoplatelets into more bulk-like structures. Furthermore, we observe that the substitution of the organic cation from formamidinium to methylammonium and addition of excess ligands significantly enhances the intrinsic stability of perovskite nanoplatelets. Lastly, we demonstrate that the dropcasted film of methylammonium-based nanoplatelets with excess ligands is impressively stable under ambient conditions and does not transform even under intense UV in the presence of moisture, as a result of improved intrinsic stability. This study expands our understanding of factors that affect perovskite nanoplatelet photostability and opens up new possibilities for fabrication of stable perovskite-nanoplatelet-based optoelectronic devices with enhanced stability.

**ET05.09.23**

Anion Exchange Perovskite Quantum-Dots for Highly Efficient Light-Emitting-Devices

Takayuki Chiba, Yukihiro Hayashi, Hinako Ebe, Satoru Ohisa and Junji Kido; Yamagata Univ, Yonazawa, Japan.

All-inorganic cesium lead halide perovskites quantum dots (QDs), CsPbX3 (X = Cl, Br, I), have recently attracted much attention for use in light emitting devices (LEDs), given their high colour purity and narrow full width at half maximum (FWHM) over the entire visible wavelength range as well as their low cost solution processing (1, 2). Here, we demonstrate anion-exchange red perovskite QDs CsPbBr3 from pristine CsPbBr3 using ammonium iodide salts, long alkyl based oleylammonium iodide (OAMI) and aryl based aniline hydoroiodide (AnHI), for use in highly efficient LEDs. The ester solvent ethyl acetate, which has a low dielectric constant, is used as poor solvent in recrystallization process to remove impurities and prevent surface defects in the perovskite QDs. The anion exchange CsPbBr3 films exhibit a strong red shift in their of photoluminescence (PL) spectrum from the green emission at 508 nm in the case of the pristine QDs to one in the deep-red region at 649 nm owing to the replacement of Br anions by I anions in the perovskite QDs. The anion exchange CsPbBr3 film based on OAMI shows a high surface coverage ratio and is free of pinholes, whereas that of AnHI based CsPbBr3 exhibits a slightly rough surface owing to a reduction in the surface ligand, which results in the aggregation of the QDs. LEDs formed using the anion-exchange CsPbBr3 based on OAMI show an remarkable high EQE of more than 20% as well as high color purity, with the Commission Internationale de l’Eclairage (CIE) at (0.72, 0.28), which completely cover BT 2020 color gamut. Similarly, the LEDs formed using the QDs based on AnHI show a peak EQE of 14.1% and CIE coordinates of (0.71, 0.28). Further, they exhibit longer operational stability as compared to that of LEDs formed using the OAMI based CsPbBr3.

Reference:

**ET05.09.24**

What Limits the VOC of Br-Based Perovskite Solar Devices?

David Cahen1, Arava Zohar1, Michael Kulbak1, Igal Levine1, Gary Hodes1 and Antoine Kahn2, 3; 1Weizmann Institute of Science, Rehovot, Israel; 2Princeton University, New Jersey, Idaho, United States.
Thanks to the efforts of many research groups worldwide in halide perovskite (HP) research, >22 % efficient small photovoltaic (PV) devices have been reported [1]. Such devices, based on HPs with mostly iodide as halide, can show a remarkably low voltage loss (E_{SC}-V_{OC}) of ~0.4 V. Unfortunately, up to now, for the higher bandgap HPs, where the halide is only Br, the highest reported V_{OC} still leaves (E_{SC}-V_{OC}) ~ 0.75 V [2]. This large loss severely detracts from the potential of HPs that have enough Br substitution for I, for optimal use in the higher E_{g}-based cell for tandem configurations or spectral splitting systems. The origin of this increased loss remains an open question.

There are 3 main issues to be checked to understand what limits the V_{OC} from getting closer to the theoretical maximum value for pure APbBr_{3}-based PV cells (~2.0 V).

-1- what is the absorber’s in-gap density of states and what range of energies have these states in the material’s band gap;

-2- as -1-, for interfacial in-gap states @ the HaP-hole/-electron transport layer interface;

-3- what is the mismatch in energy level alignment of the cell’s layers, to see if this can explain the significant energetic losses?

Here we used (FMAS_{x}MAS_{y}Cs_{1-x}PbBr) (from hereon mixed-cation) as the photo-absorber. Previously we showed that this mixed-cation HaP has relatively long carrier diffusion lengths and low carrier density compared to single cation Br-based HaPs, more resembling the I-based HaPs, with which the small (E_{SC}-V_{OC}) cells can be made [1].

By using optoelectronic measurements such as Contact Potential Difference, Surface Photovoltage, Electroluminescence and Capacitance Voltage on mixed cation Br-based HaP stand-alone films, as well in different device configurations, we can now provide insights into the origins of the large (E_{SC}-V_{OC}) for the BR-based HaP-based PV cells and suggest how these losses may be minimized.

Several discussions with Dr. Davide Ceratti (WIS) and Prof. Antoine Kahn (Princeton U) are gratefully acknowledged.

Reference

ET05.09.25
Optical Properties of One-Dimensional Single Crystals Based on Lead -Bromide Hybrid Perovskites Mai Huong T. Duong1, Shunpei Nobusue1, Eiichi Matsubara1,2, Hirokazu Tada1 and Masaaki Ashida1; 1Department of Materials Engineering Science, Osaka University, Osaka, Japan; 2Department of Physics, Osaka Dental University, Osaka, Japan.

Organic-inorganic lead halide hybrid perovskites have been receiving considerable attention for applications to optoelectronic devices such as photovoltaic cells and light emitting diodes because of their excellent electronic properties including strong absorption coefficient and long carrier lifetime [1]. The structure of hybrid perovskites can be tuned in various manners and classified by dimensionalities into three-, two- and one-dimensional (3D, 2D, and 1D) perovskites. Compared with 3D and 2D-layered crystals, the limited number of studies have been done for 1D crystals, while they are expected to show high and fast optical nonlinear effects owing to the enhancement of electron density of states and electron-electron interaction. Among the lead halides 1D perovskites, we have found that bromide compounds show some advantages for applications: stability in air and broadband emission of light. Here we report the structure of 1D lead bromide perovskites and structural dependence on their optical properties. We prepared three different structures (double-chain, face, and side shared) by inserting various aromatic organic compounds. We observed the yellow, green, and white light luminescence depending on the structures of lead bromide perovskites. Among them, double-chain lead bromide perovskite crystal showed extremely broadband white light photoluminescence similar to that of core-shell quantum wires structure [2]. The Stokes shift of the double-chain lead bromide crystals examined in the present experimental was much larger than that reported previously for core-shell 1D wires. The results open possibility of new application of 1D bromide perovskites to optoelectronic devices on the basis of chemical modification.


ET05.09.26
Structure-Controlled Optical Thermoresponse in Two-Dimensional Perovskites Daniele Cortecchia1, Stefanie Neutzi1, Jun Yin2, Teddy Salim3, Ajay Srimath Kandada1, Annalisa Bruno2, Yeng Ming Lam1, Javier Marti-Rujas1, Annamaria Petrozzal and Cesare Soci2; 1Centre for Nano Science and Technology, Istituto Italiano di Tecnologia, Milan, Italy; 2Solar Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia; 3School of Material Science and Engineering, Nanyang Technological University, Singapore, Singapore; 4Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore; 5Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Two-dimensional perovskites are emerging for their light emitting properties and applications in lasing, metamaterials and nanophotonic devices.2,3 The correlation between structure and optical properties is essential to improve the device performance and functionality and might lead to surpass films with adjustable optical properties dynamically tunable by external stimuli. Phase transitions in Ruddlesden-Popper perovskites such as (BA)_{x}(MA)_{y-x}I_{2x+1} (BA = butylammonium; MA = methylammonium),3,4 in combination with the high flexibility of the lead halide lattice, can allow to modulate the optoelectronic properties in a controlled and reversible way, through a thermal-induced structural changes and the optical properties is not yet established.

Here, we expose BA_{2}PbI_{3} (n=1) and BA_{3}MAPbI_{3} (n=2) to a wide temperature range (300-77K) and characterize two new low temperature phases of BA_{2}MAPbI_{3}. We combine spectroscopic and structural characterization with ab initio calculations to study their characteristic phase transitions and rationalize the structural changes affecting the optical properties and leading to a sharp thermo-optical response of their luminescence. Volume contraction at low temperature causes the increase of out-of-plane tilt of PbI_{6} octahedra resulting in a sharp bandgap blue-shift. On top of this, the dimensionality further impacts on the thermal evolution of the volume expansion and tilt system of the perovskite, reversing in BA_{2}PbI_{3} the trend of the continuous thermal shift of the band-gap typically observed in MAPbi.

Our results stress the importance of the structure-function relationship and show that heat-mode inter-conversion of the crystal packing can be exploited to design stimulus-responsive materials. Since the β→α phase transitions of these alkylammonium-based perovskites occur close to room temperature, they can be easily exploited to switch the structure-optical properties of the material.


ET05.09.27
Choice of Monovalent Cations Has Major Impact on Charge Carrier Recombination in Metal Halide Perovskites Katelyn Dagnall2, Benjamin
Metal halide perovskites (MHP) are promising next-generation materials for use in lightweight, flexible and inexpensive solar cells with power conversion efficiencies rivaling that of commercial silicon solar cells. The two main classes of MHP, hybrid organic-inorganic and fully inorganic, are hotly debated in the field as to which will become the commercially viable composition of MHP. Hybrid organic-inorganic perovskites have demonstrated high solar cell efficiency but relatively poor stability whereas fully inorganic MHPs are more stable with significantly lower solar cell efficiency. Therefore, it is important to understand whether or not organic cations play any roles in high solar cell efficiency so that the field can rationally decide which compositions to focus on for future development. Here we report our studies on the effect of cation composition on charge carrier recombination dynamics. Through a combination of novel ion exchange procedure, intensity dependent time-resolved photoluminescence (ID-TRPL) and transient absorbance (TA), the recombination rate constants were determined from systematically tuned compositions of various MHP thin films. Our results show that the choice of organic cations has a major influence in determining charge recombination dynamics. Implication of these results on selecting optimum compositions for higher solar cell efficiency and stability will be discussed.

**ET05.09.28**
Photoluminescence Intermittency in Micron-Size Hybrid Lead Halide Perovskites

Shaibal Sarkar; IIT Bombay, Mumbai, India.

Organic-metal-Halide perovskite materials recently attracted immense attention due to its unique optoelectronic properties, easy and versatile synthesis routes and its applicability in photovoltaic and light emitting devices. The existing literature demonstrates that the device performances depend heavily on the film morphology, shape and size of the crystal and of course the stoichiometry of the synthesized material. In this presentation, I will be discussing some interesting and unique optoelectronic properties of some “bad” perovskite materials when it is either synthesized under non-ideal conditions or as non-stoichiometric which is not ideal for high-performance devices. Here I will aim to justify a distinct correlation between the surrounding ambient and the PL intermittency of isolated and conjugated formamidinium lead bromide (FAPbBr3) microcrystals having dimension higher than the excited carrier diffusion length. A custom-built spectrally resolved epi-fluorescence microscopy is used to capture the wide-field optical emission properties of the material. With adequate experiments, we are able to describe the role of photoelectrochemically generated trap states that plays a deterministic role in PL intermittency. We further aim to establish a direct correspondence between the material degradation and the blinking.

Figure 1: Shows the photoluminescence intermittency in the FAPbBr3 microparticle.

**ET05.09.29**
The Formation of CsPbI3 and Its Effect for Device Characteristics in CsPbI3 Based Perovskite Solar Cells

Kohei Yamamoto1, Tetsuhiko Miyadera1, Tomoyuki Koganezawa1, Tetsuya Taizumi1 and Masayuki Chikamatsu1; 1AIST (National Institute of Advanced Industrial Science and Technology), Tsukuba, Japan; 2Kanazawa University, Kanazawa, Japan; 3JASRI, Sayo-gun, Japan.

Organometallic halide perovskite (PSCs) has recently emerged as promising cost-effective and highly efficient nanostructured solar cells. The organometallic halide perovskite such as CH3NH3PbI3 has poor thermal and air stability. To avoid this problem, there are many researchers who used the three-dimensional-type perovskite crystal structure with mixed cation such as cesium (Cs) and methyl amine (MA). The mixed cation perovskite has reported high thermal stability with improvement of the power conversion efficiency (PCE). The inorganic cesium lead iodide perovskite (CsPbI3) has been reported to have highly efficient thermal and electrical properties. It should also be noted that the reported CsPbI3 perovskite solar cells with highly efficiency has CsPbI3 in X-ray diffraction (XRD) measurement. In this study, we replaced MA with Cs and used vacuum deposition method to yield efficient inorganic planar heterojunction CsPbI3 solar cells. The CsPbI3 perovskite layer was formed by vacuum deposition of lead iodide (PbI2) and cesium iodide (CsI). The perovskite stoichiometry depends on the ratio of CsI and PbI2. The ratio of the codeposition rates of PbI2 and CsI was adjusted to PbI2/CsI molar ratio. The CsPbI3 film of PbI2/CsI molar ratio of 1 was deposited for obtaining ideal stoichiometry of CsPbI3. In this case, a power conversion efficiency of 5.71% was obtained with a short-circuit current density ($J_0$) of 13.50 mA/cm², an open-circuit voltage ($V_0$) of 0.55 V, and a fill factor (FF) of 0.51. This ideal film has not only CsPbI3 but also Cs4PbI6 was observed by XRD measurement. The Cs4PbI6 was considered to constitute 3CsI and PbI2/CsI molar ratio of 1 to 3. The pure CsPbI3 perovskite film had $J_0$ of 13.50 mA/cm², $V_0$ of 0.55 V, and FF of 0.51, leading to PCE of 3.77%. These results indicated the effect of CsPbI3 to improve the solar cell performance of $J_0$, $V_0$, and FF in CsPbI3 based perovskite solar cells.

**ET05.09.30**
Revealing the Relationship Between Structure and Opto-Electronic Properties of the Double Perovskite PV Candidate CsAgBiBr6

Laura Schade, Adam D. Wright, Roger Johnson, Markus Dollmann, Pabitra Nayak, Dharmalingam Prabhakaran, Laura Herz, Robin Nicholas, Henry Snaith and Paolo Radaelli; University of Oxford, Oxford, United Kingdom.

The discovery of hybrid halide perovskites materials heralded a new era in optoelectronic technologies, with an unprecedented rise to above 20% in the efficiency of photovoltaic devices in just a few years. However, several crucial issues, such as stability and toxicity, still need to be tackled before an industrial-scale use. Although the presence of Pb is a potential risk for use in PV electricity generation, Pb may prevent use in certain applications such as bioelectronics and consumer electronics products. Therefore, several efforts have been put in the research of a lead-free, stable all inorganic compound with improved thermal stability.

Recently, a new class of candidate photovoltaic materials – the double halide perovskites with chemical formula $A_B\text{Bi}_X_6$ ($A, B=$monovalent cations, $X=$halogen) – has been identified as a possible alternative to the better-known $A_Pb_X_6$ perovskites. In these materials, the $B^+$ cations (average valence 2+) substitute for lead and are fully ordered in a double perovskite superlattice. Of particular interest is CsAgBiBr6, which does not contain toxic elements, and is highly stable both structurally and chemically. Several studies exploring its implementation in devices have started to appear in the literature, yet very little is known about the relationship between the crystal structure and the opto-electronic properties of this double perovskite compound. Hence, there is an urgent need for a detailed understanding of these materials at a more fundamental level.

We have investigated the temperature-dependent structural behaviour of CsAgBiBr6 using heat capacity measurements, X-ray powder and single-crystal diffraction and neutron powder diffraction and discovered that this compound undergoes a low-temperature structural phase transition ($T_c$=122 K) from cubic to tetragonal. The crystal structures of both high- and low-temperature phases were refined based on our diffraction data. The temperature dependence of the exciton energy in proximity to the direct band gap was determined using reflectivity measurements. We found a direct, linear relationship between the tetragonal strain and the exciton energy, demonstrating that the latter is controlled by the Bi8 Br32 octahedral rotation. Meanwhile time-resolved photoluminescence measurements indicated a qualitative change in the charge-carrier recombination mechanisms at a temperature that correlates well with the phase transition. Further absorption and photoluminescence spectral measurements probing the temperature dependence of the...
Here, we present a case study of a PSC based on a new compound material (MA0.6FA0.4PbI2.8Br0.2) that does not show a phase transition for relevant important for further development of solar cells. In this work, we have fabricated the Bi-based perovskite materials (Cs3Bi2I9, CsBi3I10) by solution process structural-chemical interplay in MAPbI3, providing a new line of interpreting and understanding the ferroic, chemical, and optoelectronic behaviors of (DFT) calculations provide a picture describing the interaction of elastic strain, chemical segregation, and ferroelasticity. This work unveils a new impedance response is not fully understood. Basically, two main processes are identified but there is no general agreement on their physical origin.

Photoelectrochemical Impedance Measurements on Perovskite Solar Cells with Improved Thermal Stability

Recently, electrochemical impedance spectroscopy (EIS) on perovskite solar cells (PSC) has gained a lot of interest in the literature. The time constants are on a favorable timescale to enable high quality EIS measurements and the cells have become stable enough to allow for reliable and reproducible measurement results, making EIS a most promising tool for characterization and diagnosis of PSC. However, there are still elusive phenomena and the impedance response is not fully understood. Basically, two main processes are identified but there is no general agreement on their physical origin. Negative loops that appear in the medium and low frequency ranges further complicate a straightforward interpretation of the impedance response of PSC.

Here, we present a case study of a PSC based on a new compound material (MAxxFAyPb2x+3y−2) that does not show a phase transition for relevant ambient conditions and has proven to exhibit better thermal stability than standard MAPbI3. Measurements were conducted on samples based on either of these materials. Fresh samples as well as samples that have been subjected to a temperature treatment beyond the MAPbI3 phase transition temperature of 328 K were used. All cells were characterized by EIS and intensity modulated photocurrent/voltage spectroscopy (IMPS/IMVS). IMPS is usually only measured under short circuit conditions (SCC) and IMVS only under open circuit conditions (OCC). In contrast to this practice, we have measured EIS, IMPS and IMVS at various potentials including OCC and at different light intensities. We show that the three measurement techniques form a triplet where one of them can be calculated with good accuracy if the other two are available.

As a result of this study, we will show how impedance measurement under open circuit conditions (OCC) can help to distinguish between different mechanisms but are less sensitive to device degradation. Measurements at a voltage range between 0 Volts and OCC can help to quantify degradation, which is represented by a decrease in the impedance at voltages below the maximum power point (MPP) and by an increase beyond the MPP.

The similarity of EIS and IMVS results has been discussed in the literature. We will argue and demonstrate how a comparison of EIS and IMVS can help to distinguish between interface effects and the behavior of the bulk photoactive layers. This contribution will be complemented by a few practical guidelines for reliable photoelectrochemical impedance measurements, as this comprehensive study was performed on some of the most stable PSC for which a degradation of less than 20% after 500 hours has been demonstrated, even at an elevated temperature of 85°C.

Chemical Nature of Ferroelastic Twin Domains in CH3NH3PbI3

Recently, observations of twin domain in methylammonium lead triiodide (MAPbI3) have drawn significant attention. However, whether this twin domain is ferroelectric and/or ferroelastic remains unclear. In addition, previous investigations were limited to the ferroic properties of this twin domain, whereas, the chemical behavior which can correlate with either ferroelectricity or ferroelasticity, has rarely been studied. In this work, we unveil the correlation of ferroelastic domains and chemical variation in the MAPbI3 twin domains using multiple functional imaging techniques. We unambiguously show the mechanical origin of piezoelectric-like contrast by using multiple advanced piezoresponse force microscopy techniques, suggesting the non-ferroelectricity of this twin domain. The combination of helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) and nanoscale infrared spectroscopy (Nano-IR) indicates the ion segregation correlating with the twin domain. Emission excited by polarized light reveals large-scale ordering of crystallographic orientation/chemical make-up correlating with both twin domain and its alternative interaction with light. Moreover, density functional theory (DFT) calculations provide a picture describing the interaction of elastic strain, chemical segregation, and ferroelasticity. This work unveils a new structural-chemical interplay in MAPbI3, providing a new line of interpreting and understanding the ferroic, chemical, and optoelectronic behaviors of related HOIPs.

Suppression of Trion-Generation in Lead Halide Perovskite Nanocrystals by Surface Modification

All-inorganic cesium lead halide perovskites CsPbX3 (X = Cl, Br, I) have attracted much attention for their excellent optoelectronic properties. Since the nanocrystals (NCs) possess superior luminescent properties such as high photoemission quantum yields (PLQYs) at room temperature, these materials have been intensively studied for application in optoelectronic devices such as light emitting diodes and lasers [1]. Our previous studies have clarified that
Furthermore, we found that two independent trion generation pathways exist by analyzing the excitation power dependence of trion components. We analyzed the excitation power dependence of the differential TA signals for each sample, and compared the extracted components of excitons, trions, and biexcitons between the surface-treated and untreated samples. We clarified that the generation of trions are clearly suppressed by the surface treatment as observed in the difference in excitation power dependence, while exciton and biexciton components exhibit the same.

Furthermore, we found that two independent trion generation pathways exist by analyzing the excitation power dependence of trion components. We discuss the trion generation dynamics in CsPbBr3 NCs from the viewpoints of extrinsic surface traps and intrinsic Auger recombination.

Part of this work was supported by JST-CREST (JPMJCR16N3).

Low-dimensional organic-inorganic halide perovskites (OIHPs) have attracted intense interests recently for photovoltaic applications, owing to their markedly high chemical stability compared to the widely studied three-dimensional (3D) counterparts. However, low-dimensional OIHPs usually give much lower device performance than the 3D OIHPs. In particular, for the zero-dimensional (0-D) OIHPs, it is believed that the strong intrinsic quantum-confinement effects can lead to extremely low carrier motility which severely limit the photovoltaic performance. Herein, we predict a new family of 0-D perovskite variants that, surprisingly, exhibit outstanding optoelectronic properties. We find that some compounds based on V exhibit typical features of 0-D perovskites, such as low carrier mobilities and strong quantum confinement, thereby limiting their applications in optoelectronic devices. Sb and Bi based 0-D perovskites possess features of molecular crystal, such as comparable absorption spectrum of sun light, and carrier mobilities for PV application. The unique properties are due to the CBM shows strong hybrid state between Sb 5s orbital and Br 4p orbital in ASBnS, and the hybrid states have strong overlap among neighboring octahedrons. Moreover, the bandgap can be tuned over a wide range via tuning the composition in the mixing element strategy. The newly obtained insight into unique optoelectronic property of the 0-D perovskite devices offers a rational design strategy for low-dimensional perovskites to address some known challenging issues inherent in the lead halide perovskite solar cells.

References:

8:15 AM ET05.10.02
Optical and X-Ray Spectroscopy of the Ruddlesden-Popper Perovskite Sulfides Shanyuan Niu1, Debarghya Sarkar2, Kristopher Williams3, Kevin Ye4, Yuwei Li5, Elisabeth Bianco6, Wei Li2, Michael McConney7, Ralf Haiges8, Anderson Janotti9, David Singh10, William Tisdale11, Rafael Jaramillo12, Rehan Kapadia13 and Jayakanth Ravichandran14; 1Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Physics and Astronomy, University of Missouri, Columbia, Missouri, United States; 5Department of Chemistry, Rice University, Houston, Texas, United States; 6Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States; 7Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States; 8Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California, United States.

Transition metal perovskite chalcogenides are promising materials for photovoltaic applications with excellent optoelectronic properties, stability, and rich tunability. Recent experimental studies have revealed their promising potential, including band gap tunability all the way from 2.1 eV to 1.3 eV. We report in depth optical and X-ray spectroscopic study of Ruddlesden-Popper series of the perovskite sulfide, Ba_{n+1}ZrS_{3n+1}(n≥1). The polycrystalline samples were synthesized with an iodine catalyzed solid state reaction, and single crystals were grown with salt flux methods. Structural, chemical, and thermogravimetric studies establish that these materials have good optoelectronic properties and stability. High external luminescence efficiency, up to 0.15%, is obtained via quantitative photoluminescence measurements. An effective, bulk minority carrier lifetime longer than 60 ns and very low surface recombination are determined from time-resolved photoluminescence measurements. X-ray absorption spectroscopy illustrates the role of Zr-S covalent bonding in determining the electronic structure.

References:

8:30 AM ET05.10.03
From 3D to Lower Dimensional Perovskite Structures—The Change in Mobility and Solar Cell Performance Noor Titan Purti Hartono1, Shijing Sun1, Matthew Erodici2, Maria C. Gélvez-Rueda3, Fengxia Wei4, Ferdinand C. Grozema3, Meng-Ju Sher2, María C. Gélvez-Rueda3, Fengxia Wei4, Ferdinand C. Grozema3, Meng-Ju Sher2, Juan-Pablo Correa-Baena1 and Tonio Buonassisi1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Institute of Materials Research and Engineering, Agency for Science Technology and Research, Singapore, Singapore.

Although lead-halide perovskite (LHP) solar cells have reached 22.7% efficiency to date, they still face stability issues. Recent studies have suggested that shifting to lower dimensional (LD) perovskites may extend the cell’s environmental stability. However, these LD perovskite structures tend to have low photocurrents and solar cell performance. It has been suggested that their culprit is not only lifetime, but also their charge-carrier mobility. To understand this, we conduct a detailed study using PbI2-based LD perovskites, which are synthesized by intentionally introducing a pre-defined amount of large A-site cations to force the structure to split into a layered compound. We measure the LD perovskite device performance, and characterize the absorber using THz spectroscopy and time-resolved microwave photoconductivity to understand the mobility. Finally, we relate the mobility results with the structures and device performances.

8:45 AM ET05.10.04
Role of Anion Vacancies in Light-Induced Halide Phase Segregation in MAPb(1-x)Brx Anthony Ruth1, Michael C. Brennan1, Sergiu Draguta1, Yuriu Morozov1, Maksym Zhukovsky1, Boldizsar Janko1, Peter Zapol1 and Masaru Kuno1; 1University of Notre Dame, South Bend, Indiana, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.
Solution-processed mixed halide perovskites (e.g. MAPb(I$_x$Br$_{1-x}$)$_3$) are excellent materials for multi-junction solar cells due to their ideal characteristics, which include large optical absorption coefficients, long carrier diffusion lengths, long-lived carrier lifetimes, and tunable bandgaps. Unfortunately, light-induced halide phase segregation has prevented their effective integration into working devices. We present kinetic Monte Carlo simulations and complementary optical experiments which show that during illumination, halide migration is directed by the energetics of charge carriers. The nucleation of a low-bandgap, I-rich domain emerges as a mechanism to trap charge carriers and reduce their energy. Furthermore, migration rates in stoichiometric and halide-deficient MAPb(I$_x$Br$_{1-x}$)$_3$ thin films are dictated by halide vacancy hopping barriers and are modulated by the number of available vacancies. An established phase segregation mechanism involving thresholds in the number of vacancies and instead depend critically on parameters such as carrier diffusion length, lifetime and bandgap tunability. Superb agreement with experimental nucleation kinetics and optics validates the model and prompts its application to fundamental, experimentally-inevitable aspects of phase segregation. By simulating nucleation with varying ionic mobilities, we determine how domain formation is influenced by species dependent I$^-$ vs. Br$^-$ diffusion rates and asymmetric hopping in tetragonal vs. cubic symmetry. The simulations further suggest that near ubiquitous emission energies, which converge on that for MAPb(I$_x$Br$_{1-x}$)$_3$ (i.e. ~0.2) following phase segregation, arise from the existence of kinetically trapped Br$^-$ within nucleated I-rich domains surrounded by a pure I$^-$ barrier. These simulations ultimately prompt the idea that the ideal characteristics of mixed halide hybrid perovskites, specifically their large carrier diffusion lengths, are responsible for inducing phase segregation. The study thus sheds new light on important parameters that define photoinduced halide phase segregation in mixed halide hybrid perovskites and presents opportunities for ultimately controlling as well as managing the phenomenon.

9:00 AM ET05.10.05

Suppression of Halide Ion Exchange in Cesium Lead Halide Perovskites with PbSO$_4$-Oleate Capping
Prashant Kamat, Vikashkumar Ravi and Rebecca A. Schedit; University of Notre Dame, Notre Dame, Indiana, United States.

Metal halide perovskites are ionic in nature and its properties can be tuned through the exchange between halide ions. For example, by tailoring the ratio of Cl:Br and Br:Cl it is possible to modulate the absorption and emission properties of metal halide perovskites across the entire visible region. However, the ease of halide ion exchange property poses a problem to create a tandem structure with layers of metal halide perovskites of different compositions. In order to keep the lead halide perovskite nanocrystals intact without undergoing exchange of halide ions and retain the original band structure one needs to suppress the halide ion migration across the nanocrystals. We have now successfully achieved this task by capping CsPbBr$_3$ and CsPbI$_3$ nanocrystals with PbSO$_4$-Oleate. The linear assembly of the nanocrystals that resemble that of a peapod structure inhibits the exchange of anions. Absorption measurements show that the nanocrystal assemblies maintain their identity as either CsPbBr$_3$ or CsPbI$_3$, for several days. Furthermore, we have electrochemically deposited these assemblies as hierarchical structures on electrode surfaces and employ them in light emitting devices. The effectiveness of PbSO$_4$-Oleate capping of lead halide perovskite nanocrystals offers new opportunities to overcome the challenges of halide ion exchange and aid towards the novel design of perovskite light harvesting assemblies.

9:30 AM ET05.10.06

Titanium-Based Halide Perovskite Thin Films for Photovoltaic Applications
Min Chen¹, Minggang Ju², Xiaoli Cheng Zeng², Yuyuan Zhu¹ and Nitin Padture²;¹ Brown University, Providence, Rhode Island, United States;² Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Lead-based halide perovskites have demonstrated superior optoelectronic properties since the emergence of perovskite solar cells (PSCs). However, the toxicity and phase stability of lead halide perovskite brings inevitable concerns with the practical application for the solar panel. Based on the environmentally friendly element of Titanium (Ti), we have predicted a series of Ti vacancy-ordered double perovskite compounds, Cs$_2$TiI$_6$, Rb$_2$TiI$_6$, K$_2$TiI$_6$, and In$_2$TiI$_6$, which possess optimal bandgap and suitable absorption. Here, we successfully synthesis the Titanium-based materials which indicates indicated the possible photovoltaic applications because of the proper band-gap range. Furthermore, we prepared the pinhole-free titanium-based thin film by the evaporation method. The electrons/holes diffusion length of such thin films with proper crystallographic textures illustrates the good performance as champion material as well as for paving the way for second-generation materials. We expect this work provides new direction in the design and development of high performance Ti-based thin-film PSCs of the future.

9:45 AM BREAK

10:15 AM ET05.10.07

Accessing Small Bandgaps in Halide Double Perovskites
Adam H. Slavney¹, Linn Leppäri², Abraham Saldivar Valdes³, Davide Bartesaghi³, Tom Savojivi³, Jeffrey B. Neaton⁴ and Hemamala Karunadasa¹;¹ Stanford University, Stanford, California, United States;² University of Bayreuth, Bayreuth, Germany;³ Delft University of Technology, Delft, Netherlands;⁴ University of California, Berkeley, Berkeley, California, United States.

The outstanding photophysical properties of APbX$_2$ perovskites (A = organic/inorganic monocation, X = halide) for optoelectronic applications has prompted a vigorous search for analogs. Indeed, finding structural and functional analogs is a time-tested approach for both better understanding the current champion material as well as for paving the way for second-generation materials. In this regard, there has been intense recent interest in the photophysical properties of halide double perovskites, where Pb$_2$+ sites are replaced by two different metals that yield an average charge of 2+. However, despite this feature both high-bandgap insulators and metals, such diversity has not yet been seen in their halide analogs. I will present work from our labs aimed at expanding the electronic portfolio of halide perovskites for fundamental studies and applications in technology.

10:45 AM ET05.10.08

SnPb and Pb-Free SnGe Perovskite Solar Cells
Shuzi Hayase; Kyushu Institute of Technology, Kitakyushu, Japan.

Lead-free perovskite solar cell is one of the research issues on perovskite solar cells. We have focused on Sn perovskite material. One of these Sn-related solar cells is SnPb mixed metal perovskite solar cell. We discuss how to enhance the efficiency from the view point of less trap densities in hetero-interfaces and the bulk layer. SnF$_2$(DMSO)$_2$ doping to the perovskite layer and the introduction of spike band structure in the cell gave SnPb perovskite solar cells with 19% efficiency and stability. The SnGe is a promising alternative to Pb perovskite solar cells. Pb of SnGe perovskite layer was replaced by Ge. A theoretical study showed that it is possible to prepare a SnGe mixed metal perovskite material which absorbs the sunlight. In this study, a new type of SnGe mixed metal perovskite solar cells are reported with enhanced efficiency and stability. XRD spectra showed that the structure is perovskite. The structure of GeSn perovskite was discussed from the view point of the band structure, XPS analysis, and the Urbach energy. Most of the Ge atoms are at the hetero-interface of the perovskite/PEDOT-PSS as well as at the interface of the perovskite/C60. They passivate the surface of the Sn perovskite (so-called graded structure). For SnGe(0)-PVK device, where SnGeX$_2$ stands for SnGe perovskite with X% Ge content, the PCE was 3.31 %. Upon doping with 5 wt% of Ge, the overall efficiency was enhanced to 4.83 %. With the Ge content more than 10wt%, all the photovoltaic parameters decreased.
significantly which resulted in an efficiency as low as 0.80 % for SnGe(0.2)-PVK device. After optimization, 7.89% of SnGe(5)-PVK device is reported. In addition, the stability of the device in air without encapsulation has been improved significantly with the Ge doping. 80 % of efficiency was kept after doping with Ge (5%) from its original performance. However, only 10 % of the efficiency was retained for non-doped sample SnGe(0). This work provides a platform for further research on lead-free Sn-Ge based perovskite solar cells.

11:15 AM ET05.10.09
Optoelectronics Studies Based on Two-Dimensional Hybrid Perovskite Mauricio Solis de la Fuente, Sumanjeet Kaur, Dalía Martinez Escobar, Selene M. Coria and Ravi Prasher; Lawrence Berkeley, Berkeley, California, United States.

Hybrid Perovskite solar cells have been the subject of intense interest due to significant optoelectronic properties (high absorbance, long diffusion length, etc.). An accelerated competition is taking place to obtain highest performance in single junction and tandem solar cells with efficiencies up to 20 %. Nevertheless, huge scientific problem remains be solved that directly impact performance and future commercialization, namely the stability under external agents as light, oxygen, humidity and heat.

The organic ions play an important role in the perovskite stability, which make them sensitive to moisture; Some studies showed the perovskite 2D are more resistant to humidity conditions in contrast to 3D. However, a decrement in density of carriers photogenerated is obtained where the vertical orientation is wishing to get good performance in solar cells. We explore other strategies to extract carriers mainly doping 2D perovskite BAXMA3PbI6 with single walled carbon nanotubes and graphene. Experimental measurements to explain how structural changes (domain distributions, band gap positions) can modify optoelectronics properties as photoluminescence, conductivity, Seebeck coefficient, I-V curves and absorbance will be discuss.

References

11:30 AM ET05.10.10
Edge Management in Reduced-Dimensional Perovskites Enables Efficient and Stable Light-Emission Lina Qian1, 2 and Edward H. Sargent1; 1University of Toronto, Toronto, Ontario, Canada; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Halide perovskites, especially layered quasi-2D perovskites, offer a number of advantages to creating bright and efficient light-emitting applications. Their combination of excellent charge carrier mobility and low density of recombination centers have enabled their rapid ascent in electroluminescent devices. To bring perovskite LEDs to commercialization, a remaining issue of stability needs to be addressed. In this presentation, we pinpointed the chief cause of the dramatic degradation of halide perovskites in light-emitting diodes (LEDs). We studied photogenerated charges accumulating at exposed perovskite facets activate the physosorbed oxygen, converting it into reactive superoxide that triggers perovskite degradation. We thus aimed at developing a strategy to protect the perovskite facets. At an applied level, we achieve perovskite films that exhibit a near-perfect passivation, attested to by their photoluminescence quantum yields (PLQY’s) that closely approach 100%. These films are stable under continuous illumination in ambient conditions over hundred hours. In addition, we report orders of magnitude improvement in device operating stability relative to the best-performing prior perovskite reports.

11:45 AM ET05.10.11
Perovskites with a Twist—Discovery of the Mixed Valent Double Perovskites CsInX3 (X = Br, CI) Kyle M. McCall, Constantinos Stoumpos, Grant C. Alexander, Giancarlo Trimarchi, Bruce Wessels and Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

The success of halide perovskites as optoelectronic materials has spurred immense interest in these remarkable compounds. The perovskite structure has formula AMX3 and consists of corner-connected MX6 (M2+ a metal cation, X– a halide) octahedra with large A+ cations (Cs+, CH3NH3+, CH(NH2)2+ = FA+) in the voids. This framework is quite flexible, enabling substitution on all three sites to form a variety of compositions. Halide substitution tunes the band gap positions) can modify optoelectronics properties as photoluminescence, conductivity, Seebeck coefficient, I-V curves and absorbance will be discuss.

The success of halide perovskites as optoelectronic materials has spurred immense interest in these remarkable compounds. The perovskite structure has formula AMX3 and consists of corner-connected MX6 (M2+ a metal cation, X– a halide) octahedra with large A+ cations (Cs+, CH3NH3+, CH(NH2)2+ = FA+) in the voids. This framework is quite flexible, enabling substitution on all three sites to form a variety of compositions. Halide substitution tunes the band gap positions) can modify optoelectronics properties as photoluminescence, conductivity, Seebeck coefficient, I-V curves and absorbance will be discuss.

References
Strain-Related Defects in Metal Halide Perovskites Samuel D. Stranks; University of Cambridge, Cambridge, United Kingdom.

Metal halide perovskites are generating enormous interest for their use in optoelectronic devices including photovoltaics and light-emitting diodes. One of their most remarkable properties is their apparent defect tolerance – films can be produced using relatively crude processing methods yet they still exhibit very good device performance. Calculations have suggested that this is at least partly because many defects cause only shallow trap states which may not be catastrophic for device performance (unlike deeper trap states). Nevertheless, there is still substantial non-radiative losses suggesting defects are not entirely benign and they still must be understood and addressed before devices can approach their performance limits.

Here, I will cover our ongoing work focusing on defects and their impact on non-radiative losses, as well as their mitigation through passivation treatments. I will present recent results in which we use multimodal approaches to determine relationships between local chemistry, structural and luminescence properties in perovskite thin films using synchrotron nano X-Ray Diffraction (n-XRD) and nano X-Ray fluorescence (n-XRF) measurements, as well as confocal and wide-field luminescence imaging. We reveal an intimate connection between strain and non-radiative decay, revealing these strain-related defects as a primary origin of non-radiative losses. I will also outline the action of passivation treatments, such as chemical and light-induced treatments, on relieving these strain patterns.

The work provides a platform for designing new and more effective passivation post-treatments or film fabrication methods, which will push devices ever closer to their efficiency limits.

Metal halide perovskites are generating enormous interest for their use in optoelectronic devices including photovoltaics and light-emitting diodes. One of their most remarkable properties is their apparent defect tolerance – films can be produced using relatively crude processing methods yet they still exhibit very good device performance. Calculations have suggested that this is at least partly because many defects cause only shallow trap states which may not be catastrophic for device performance (unlike deeper trap states). Nevertheless, there is still substantial non-radiative losses suggesting defects are not entirely benign and they still must be understood and addressed before devices can approach their performance limits.

Here, I will cover our ongoing work focusing on defects and their impact on non-radiative losses, as well as their mitigation through passivation treatments. I will present recent results in which we use multimodal approaches to determine relationships between local chemistry, structural and luminescence properties in perovskite thin films using synchrotron nano X-Ray Diffraction (n-XRD) and nano X-Ray fluorescence (n-XRF) measurements, as well as confocal and wide-field luminescence imaging. We reveal an intimate connection between strain and non-radiative decay, revealing these strain-related defects as a primary origin of non-radiative losses. I will also outline the action of passivation treatments, such as chemical and light-induced treatments, on relieving these strain patterns.

The work provides a platform for designing new and more effective passivation post-treatments or film fabrication methods, which will push devices ever closer to their efficiency limits.

Perovskite Dynamics from the Nano- to the Macroscale Marina S. Leite; University of Maryland, College Park, Maryland, United States.

To date, the main limitation toward hybrid perovskites’ implementation into commercial light-absorbing and light-emitting devices is this material lack of stability upon exposure to: humidity, oxygen, temperature, light, and bias [1, 2]. Thus, understanding and controlling the driving forces for perovskites’ degradation and the possible pathways for recovery are imperative for the development of reliable devices. We resolve the influence of each abovementioned parameter onto the perovskites’ electrical and optical responses from the nano- to the macroscale. We demonstrate, in real-time, the dynamic open-circuit voltage of perovskite solar cells by novel scanning probe microscopy methods [3, 4], resulting from light-induced ion migration [5]. We determine the effect of chemical composition of the photoluminescence hysteresis of Cs-triple cation perovskites, as a function of humidity cycles [6]. Additionally, we identify a fully reversible voltage response within grains for Cs-triple cations perovskites upon exposure to 1-sun illumination. These measurements show the importance of correlating the local, nanoscale behavior with macroscopic electrical and optical responses. Finally, we will present a machine learning approach to track device performance [1], including a route to prevent material degradation, and to material recovery.


Ionic Properties of Twin Domain in Methylammonium Lead Triiodide Yongtao Liu1, Lian Collins2, Anton V. Iveliev2, Alex Beliaev2, Stephen Jesse3, Scott Retterer2, Kai Xiao4, Mahshid Ahmad1, Sergei V. Kalinin4, Bin Hu5 and Olga Ovchinnikova6; Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 6Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The twin domain in methylammonium lead triiodide (MAPbI3) has drawn extensive research efforts, starting the discussion on its ferroic nature. Given the earlier investigations revealed the ion segregation correlating to the ferroelastic domain contrast. To follow up, we systematically investigate the chemical evolution of the ion migration in the MAPbI3 twin domains in this work. Using Band Excitation Contact Kelvin Probe Force Microscopy (BE-cKPFM), we reveal the absence of ferroelectric origin of the previously observed butterfly and hysteresis loops in Switching Spectroscopy piezoelectric force microscopy (SS-PFM). In addition, Band Excitation Scanning Kelvin Probe Force Microscopy (BE-scKPFM) measurement, which was utilized to study the electrochemical activities in the twin domain, indicates that the difference in ion migration and/or surface charging effect in the adjacent domains. This result implies a different ionic conductivity and a variation of electronic properties in adjacent domains. Combining Band Excitation PFM (BE-PFM), nanoscale infrared spectroscopy (Nano IR), and scanning probe microscope (SEM), we clarify the correlation between ionic diffusion, electronic properties, and chemical segregation. We reveal that the methylammonium segregation leads to a decrease of electronic conductivity and an increase of ionic conductivity. Overall, this work provides new insights into understanding the role of the twin domain in photovoltaic action.

Phase Intergrowth and Structural Defects in Organic Metal Halide Ruddlesden-Popper Thin Films Navleen Venkatesan1, Rhiannon Kennard1, Ryan A. DeCrescent2, Erin Perry3, Clayton J. Dahlman1, David Hamill2, Jon A. Schuller1, Alberto Salles2 and Michael L. Chabinyc2; University of California, Santa Barbara, Santa Barbara, California, United States; 2Stanford University, Stanford, California, United States.

Hybrid organic metal halide Ruddlesden-Popper (R-P) phases have recently been the subject of intense research efforts due to their good power conversion efficiencies in photovoltaics and controllable emission for light emitting diodes, while possessing better environmental stability compared to their three-dimensional counterparts. The thin film structures of these layered perovskites are still poorly understood relative to the bulk. In this study, we use optical spectroscopy, X-ray scattering, and transmission electron microscopy to characterize the structures of these thin films of (C6H13NH3)2(C6H13NH3)2PbI3 and
(C$_2$H$_5$NH$_3$)$_2$(CH$_3$NH$_3$)$_3$Pb$_4$I$_{13}$ on the meso- and nanoscales. Previous studies suggest a preferential orientation of the Pb-I sheets in spin coated films, perpendicular to the substrate, so that the layer stacking direction is in the plane of the film. By measuring in-plane and off-specular X-ray diffraction with grazing-incidence wide-angle X-ray scattering (GIWAXS), we observe that some expected peaks along the stacking direction of the Pb-I sheets are missing, indicating disorder in perovskite layer stacking. Because the diffraction patterns represent a bulk, average structure, we used transmission electron microscopy (TEM) to explore film structure on a local scale and find that these films consist of small crystalline grains in an amorphous matrix, contradictory to previous reports suggesting single-crystalline quality thin films. When using known crystal structures to index these SAED patterns, we see that the thin films comprise not only the targeted R-P phase, but also regions with lower and higher Pb-I sheet thickness (i.e. phase impurities). This phase intergrowth creates structural defects that interrupt layer stacking and is the cause broadening of in-plane diffraction peaks, causing them to be absent from previous GIWAXS measurements. Finally, because these films produce efficient photovoltaics despite this high degree of structure disorder, we measured the absorption coefficient using photothermal deflection spectroscopy (PDS) and find Urbach energies of 32 meV for the R-P phases compared to 19 meV for methylammonium lead iodide. Despite the structural defects, the R-P films appear to maintain a low degree of electronic disorder suggesting that the Pb-I regions are electronically isolated from each other.

3:00 PM BREAK

3:30 PM ET05.11.05
Hybrid Inorganic-Organic Perovskites—From Film Optical Response to Device Functionality
Nikolay Podraza, Brius Subedi, Kiran Ghimire, Prakash Upadhyay, Maxwell Junda, Cong Chen, Chongwen Li, Dewei Zhao, Zhaoning Song and Yanfa Yan; University of Toledo, Toledo, Ohio, United States.

Solar cells with hybrid inorganic-organic lead halide based perovskite absorber layers have achieved remarkably high photovoltaic device performances in a relatively short amount of time when compared to comparable efficiency devices based upon other semiconductor absorbers. This perovskite family offers a wide range of tunable opto-electronic properties obtained via alloying of either/both the organic and inorganic components, and, even in their polycrystalline form, these perovskites are generally quite electronically forgiving semiconductors. However, as the material composition is manipulated, film stability and any increase in defect concentration remain issues. Here we will provide an overview of the optical properties, in the form of the complex index of refraction or complex dielectric function spectra, as well as the physical origin for the features present in those optical properties for perovskite layers with considerations toward composition, sample handling / environmental exposure, and incorporation in devices. Proper measurement and analysis yielding accurate values of the complex optical properties over the ultraviolet to millimeter wavelength range and complementary techniques sensitive to different levels of optical absorption enables tracking of the bandgap and higher energy critical point transitions, electrical transport properties manifested as free carrier absorption, sub-bandgap absorption due to defects, and film degradation or decomposition upon atmospheric exposure as deduced from in-situ / ex-situ spectroscopic ellipsometry, optical Hall effect, and photothermal deflection spectroscopy. Once acquired, these optical properties serve as input for external quantum efficiency simulations of photovoltaic device performance. Features observed optically will be correlated with full functioning device performance, illustrating how accurate optical property measurements over different wavelength ranges and levels of absorption provide insight into device functionality.

4:00 PM ET05.11.06
In Situ TEM Observation of Perovskite Solar Cells
Satoshi Uchida1, Tae Woong Kim1, Ludmila Cojocaru2, Takashi Kondo1 and Hiroshi Segawa1; 1The University of Tokyo, Tokyo, Japan; 2University of Freiburg, Freiburg, Germany.

Recently, organometal halide perovskite solar cells (PSCs) have received great attention. The power conversion efficiency (PCE) of PSCs have shown a dramatic increase and certified PCEs adopting mixed organic cations and halide anions have reached over 22%. The PCE is considerably affected by photovoltaic property of each component of a PSC. In spite of the significance in the crystallographic information, however, microstructural observation for crystal structure analysis of the perovskite layer has not been actively conducted. Until now it is widely believed that each phase of the organometal halide perovskite solely exists with orthorhombic phase < 165K < tetragonal phase < 327K < cubic phase. Nevertheless we newly observed that the tetragonal and cubic phases coexist at room temperature in the conventional MAPbI$_3$ thin film device.

Furthermore, surprisingly, superlattices composed of mixture of tetragonal and cubic planes without any compositional change was also found. Formation of the superlattice is achieved by only intrinsic structural transition without artificial modifications and, therefore, most phenomena concerned with the structural superlattice are expected to spontaneously and automatically occur in context with situation. The organometal halide perovskite self-adjusts their microstructural configuration and self-organizes buffer layers inside crystal or at hetero-interface by introducing the self-assembled superlattices. We believe, this report will be a vital cornerstone to bring the PCEs of the organometal halide perovskite solar cells one step closer to theoretical maximum point and redefine possibility of the organometal halide perovskite as promising materials for not only solar cell but also various application.

4:15 PM ET05.11.07
Strain Effect on Stability and Band Gap in CsPbBr$_3$ Crystal via NanoXRD
Xueying Li, Yanqi Luo1, Moses Koduri1, Rishi Kumar1, Martin V. Holz2, Zhonghao Cai2 and David P. Fenning1; 1University of California, San Diego, La Jolla, California, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

Despite the comparable power conversion efficiency between polycrystalline Si and perovskite solar cells (PSC), the commercialization of PSCs is inhibited by their low stability. A recent study demonstrated that the commonly used spin-casting and annealing for perovskite thin film create strain in the material and lead to decreased stability. Other publications have observed an association between lattice constant and band gap in halide perovskites ABX$_3$ (A= methylammonium, formamidinium, cesium; B=lead; X=Bromide, Iodide, chloride), suggesting their band gap can be tuned through the manipulation of strain in the material. However, the knowledge of strain distribution and its local effect is lacking for making highly stable PSCs or stress-sensitive optoelectronics. To study the local effect of strain, we map CsPbBr$_3$ crystals with nanoscale X-ray Diffraction Microscopy (nanoXRD) with approximately 100-nm spatial resolution and 0.1% sensitivity in strain detection. By exploiting the thermal expansion coefficient mismatches, a strain gradient is created in a CsPbBr$_3$ crystal at the edge of a platinum pad on quartz substrate and characterized by nanoXRD. We find that the observed compressive strain reduces the stability of the material, which proves that strain should be avoided for highly stable halide perovskites. We also characterize the same crystal with ex-situ photoluminescence (PL) mapping and observe PL peak shifts red at compressively strained locations in the crystal. This demonstrates the band gap narrowing by substrate-induced strain locally, which should be brought into attention for the fabrication process of halide perovskite on substrates. On the other hand, the strain effect on band gap shows potential of stress-sensitive optoelectronic applications with halide perovskites.

4:30 PM ET05.11.08
Probing the Microstructure of Methylammonium Lead Iodide Perovskite Solar Cells
Tobias Leonhard, Holger Röhm, Alexander Schulz, Fabian J. Altermann, Susanne Wagner, Wolfgang Rheinheimer, Michael J. Hoffmann and Alexander Colsmann; Karlsruhe Institute of Technology, Karlsruhe, Germany.
Germany.

The microstructure of absorber layers is pivotal for all thin-film solar technologies. Despite its unprecedented performance development in recent years, little is known about the microstructure of metal-halide perovskites and its effect on the macroscopic device performance. Yet, recent publications have frequently called attention to the urgent need of spatially resolved microstructure characterization techniques in order to correlate the microscopic structure with macroscopic device properties.

In this work, we report on the spatial investigation of methylammonium lead iodide (MAPbI3) grain properties by electron backscattered diffraction (EBSD) with high resolution. We resolve diffraction pattern ambiguities that are related to the close-to-cubic perovskite unit cell, and develop a comprehensive three-dimensional picture of the crystal orientation. We identify predominant orientation directions and observe orientation cross-talk between neighboring grains. The local crystal information correlates with ferroelectric and electronic properties that we probe with piezo-response force microscopy (PFM) and kelvin probe force microscopy (KPFM) measurements. If the ferroelectric polarization influences the charge carrier recombination and transport, as was predicted by simulations, then the orientation and shape of polarized domains within grains would directly influence the device performance. In turn, this renders engineering of the grain orientation and size a pivotal parameter for the optimization of perovskite solar cells which is not yet commonly investigated in most perovskite solar cell studies. These tools are indispensable for the future relation of the microscopic structure to the optoelectronic properties of perovskite devices as they allow to monitor device optimization and to understand fundamental processes of perovskite solar cells. Therefore, we expect EBSD and PFM to become the most often employed characterization techniques in the future for the correlation of microscopic structure and macroscopic device performance. Their strong correlation allows to draw conclusions about the microstructure from ferroelectric features and, likewise, to derive the ferroelectric polarization from crystallographic observations. Understanding the microstructure would not least be the key to future ab-initio engineering of new (non-toxic) and highly efficient perovskite solar cells.

References


4:45 PM ET05.11.09

Direct Optical Identification of Grain Boundaries and Carrier Diffusion in Perovskite Film Wenhao Li, Srinivas K. Yadavalli, Yuanyuan Zhou, Nituin P. Padture and Rashid Zia; Brown University, Providence, Rhode Island, United States.

Perovskite solar cells (PSCs) have attracted considerable attention in recent years due to their rapidly increasing power conversion efficiency (PCE), which currently exceeds 22%. Given that most high efficiency PSCs are made of polycrystalline films, an important feature is their grain size distribution, because grain boundaries can limit carrier diffusion and serve as nonradiative recombination sites, thereby reducing the PCE. Due to the formation of grain boundary grooves during perovskite film growth, many techniques for estimating grain size rely on surface morphology characterization using scanning electron microscopy (SEM) or atomic force microscopy (AFM). However, not all grain boundaries exhibit clear topographical features.

Here, we report the direct identification through photoluminescence (PL) microscopy of grain boundaries in formamidinium lead iodide (FAPbI3) thin film samples that cannot be observed by either SEM or AFM. We demonstrate that these “invisible” boundaries impede carrier diffusion and limit radiative recombination events. Optical characterization is further supported by electron backscatter diffraction (EBSD) measurements that are used to confirm crystal orientation differences across these otherwise imperceptible boundaries. Then, we present PL lifetime measurements that show how these “invisible” boundaries serve as nonradiative recombination sites, thereby decreasing carrier lifetimes, and likely reducing PCEs.

In order to quantify the carrier diffusion resistance in different types of grain boundaries, we developed a carrier density probing method. Using a high-speed intensified emCCD camera, we are able to measure the 2D PL intensity distribution with nanosecond resolution. Comparing the PL distribution with excitation near and far away from the grain boundary, we can see the effect of grain boundaries in blocking carriers. A carrier diffusion and recombination model is used to fit the observed PL evolution to extract the diffusion and recombination coefficients. Together with a mapping of steady state PL intensity distribution and the carrier density probing method, we are able to estimate the resistivity of carrier diffusion across grain boundaries. Finally, we will discuss the impact of these boundaries as well as this new characterization method for the synthesis and analysis of thin-film perovskite solar cells.

SESSION ET05.12: Poster Session IV: Fundamentals of Halide Perovskite Optoelectronics

Session Chair: Ivan Mora-Sero
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET05.12.01

Impact of Applied Bias, and Material Degradation on Ion Transport in Hybrid Perovskite Solar Cells Under Illumination Emily C. Smith1, Christie Ellis1, Hamza Javadi1, Lawrence A. Renna1, Yao Liu1, Thomas P. Russell1,2, Monojit Bag1 and Dhandapani Venkataramanan1; 1University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

We mapped ion transport in hybrid organic–inorganic perovskite solar cells under illumination using impedance spectroscopy (IS) as a function of applied bias and device degradation. We observe evidence of mass (ion) diffusion and extrapolate conductivities (∼10−7 S cm−1) and diffusion coefficients (∼10−7 cm2 s−1) for the mobile ionic species at varying applied bias. We show that ions respond to low applied forward bias in a predictable manner, as was predicted by simulations, then the orientation and shape of polarized domains within grains would directly influence the device performance. In turn, this renders engineering of the grain orientation and size a pivotal parameter for the optimization of perovskite solar cells which is not yet commonly investigated in most perovskite solar cell studies. These tools are indispensable for the future relation of the microscopic structure to the optoelectronic properties of perovskite devices as they allow to monitor device optimization and to understand fundamental processes of perovskite solar cells.

Therefore, we expect EBSD and PFM to become the most often employed characterization techniques in the future for the correlation of microscopic structure and macroscopic device performance. Their strong correlation allows to draw conclusions about the microstructure from ferroelectric features and, likewise, to derive the ferroelectric polarization from crystallographic observations. Understanding the microstructure would not least be the key to future ab-initio engineering of new (non-toxic) and highly efficient perovskite solar cells.

References


8:00 PM - 10:00 PM
Hynes, Level 1, Hall B
Organic inorganic hybrid perovskites (OHP) is the most promising material to achieved photovoltaic devices with high power conversion efficiency and low cost. The perovskites with the composition CsxFA_{1-x}PbBr_{3-y}I_{y} achieve high PCE, present better stability, photo-stability, and their band gap can be tuned by changing the composition, becoming interesting for tandem solar cells. The most used method to prepare this sort of composition is the solvent engineering method [1]. During the spin coating process, an antisolvent (chlorobenzene, dichlorobenzene, toluene) is dropped onto the substrate to remove the excess of the original solvents as DMF and DMSO. Thus, formation of perovskite or an intermediate can be attained. Despite of being the most popular method, the impact of many deposition parameters such as the temperature of spin coating the anti-solvent, the molar proportion between the precursors and DMSO during the spin coating, are not well understood. Here we used in situ-time-resolved grazing incidence wide-angle X-ray scattering (GIWAXS) in the Brazilian Synchrotron Light Laboratory (LNSLS) during film preparation to monitor and get insights about the perovskite formation. CsxFA_{1-x}Pb(Br_{1-y}I_{y}) was the composition of choice. Without antisolvent, the scattering signal is attributed to a disordered colloidal gel formed between perovskite and solvent. [2] This signal fades with time, and the lifetime changes with DMSO perovskite proportion and ambient moisture. Immediately after anti-solvent injection, new CsxFA_{1-x}PbI_{3} peaks emerged attributed to phase of the perovskite and intermediate. The intermediate’s peaks fade with time while the peak related to the perovskite becomes more intense. The results reveal that perovskite formation takes place without thermal annealing and the transformation occurs through the intermediates. With shorter times of anti-solvent injection, the morphology of the film is smooth, but with longer times, the morphology becomes more heterogeneous. This was attributed to intermediates formed before the injection of the anti-solvent, that remain stable in the film. In conclusion, in situ-time-resolved GIWAXS during the spin coating step provided important information about the best parameters to guarantee only perovskite formation or intermediates with shorter “lifetime”. Having these parameters in hands, films with better morphology, transport and optoelectronic properties can be obtained.

ET05.12.03
Exceptional Grain Growth in Formamidinium Lead Iodide Perovskite Thin Films Induced by Phase Transformation
Srinivas K. Yadavalli, Yi Zhang, Wenhao Li, Yunyuan Zhou, Rashid Zia and Nitin P. Padture; Brown University, Providence, Rhode Island, United States.

Formamidinium lead iodide (FAPI) based perovskites have attracted a great deal of interest as light absorbers in solar cells due to their superior thermal stability and more sustainable band gap compared to perovskites based on methylammonium (MA). However, preferential formation of a photo-inactive α-FAPI phase at room temperature has been a major impediment. The need for prolonged heat-treatments at temperatures >150 °C to obtain the desirable α-FAPbI3 perovskite phase often leads to film degradation. Heat treatment also produces fine-grained films with high grain-boundary density, which is detrimental to PSCs performance and stability. In this context, we have discovered a new phenomenon, where fine-grained (∼175 nm) α-FAPbI3 thin films transform rapidly to phase-pure α-FAPbI3 perovskite thin films with ultra-large grain size exceeding ~5 μm. The large-grained nature of the films is confirmed using appropriate materials characterisation techniques. The improved kinetics of thin film formation is explained by studying the phase and morphological evolutions during film-sonnet interaction. The nature of phase nucleation and growth is studied through in-situ microscopy techniques. In-situ X-ray diffraction and solvent polarity effects on the transformation rate are also studied to corroborate the proposed mechanism. Devices with high efficiency are fabricated with these ultra-large grained films and are characterized. The use of this novel approach to achieve 5-μm grains by a brief low-temperature treatment enables a promising path toward achieving ‘single-crystal’ films with superior optoelectronic properties and chemical stability.

ET05.12.04
Surface Doping of Metal Halide Perovskites
Nakita K. Noel1, Alba Pellaroque2, Federico Pulvirenti1, Henry Snaith2, Seth B. Marder3 and Barry P. Rand1; 1Princeton University, Princeton, New Jersey, United States; 2Physics, University of Oxford, Oxford, United Kingdom; 3Chemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.

Within the past few years, metal halide perovskites have been attracting significant interest due to their successful application to optoelectronic devices. These materials have been used in lasers, photodetectors, and most commonly, in photovoltaic devices and light emitting diodes. Despite the cheap and simple fabrication methods by which these materials are deposited, high quality perovskite films can be readily fabricated, and the power conversion efficiencies of lead halide perovskite solar cells are now approaching certified values of 23%. However, perovskite-based devices are yet to achieve their full potential. One of the major hindrances to achieving this potential is an incomplete understanding of perovskite surfaces and interfaces. Deficiencies at these interfaces may be responsible for the largest losses in perovskite based optoelectronic devices; hindering charge extraction, increasing non-radiative recombination rates and hysteresis, and significantly increasing the voltage loss in perovskite photovoltaics. We propose surface doping the perovskite material as a means to combat these interface deficiencies. Herein, we will discuss doping of the perovskite material at various interfaces using well-established charge-transfer dopants. We show the doping of the perovskite material through both solid-state NMR and surface characterisation techniques, and further characterise the material through photoluminescence measurements, showing a reduction in the non-radiative recombination of the material. Using this surface doped material, we show photovoltaic devices with reduced hysteresis, low voltage losses, and steady-state power conversion efficiencies in excess of 20%.

ET05.12.05
Advances in Bright Single Layer Perovskite Light Emitting Devices
Ross E. Haroldson1, Artur Ishteev2, Patricia Martinez1, Masoud Alahakoon1 and Anvar A. Zakhidov1; 1The University of Texas at Dallas, Richardson, Texas, United States; 2MISIS, Moscow, Russian Federation.

Exciting reports about single layer cesium lead halide perovskite LEDs have shown that conventional electron and hole injection layers are not necessarily needed. A sandwiched device structure consisting of a perovskite-polymer composite film between two electrodes can emit bright light at low operating and threshold voltages (~2.0 volts). We studied the role of grain size, polymers inclusion, morphology, emission changes, and electrode material in CsPbBr3 based LED. These simple single layer devices are easier and cheaper to fabricate as compared to their multilayered counterparts and removes the possible reaction routes between perovskite and the charge injection layers. We also investigate underlying mechanisms of how ion migration within the perovskite layer forms a p-n-n junction which allows efficient charge injection directly from the electrodes, independently of their work function, while still having efficient radiative recombination.

ET05.12.06
Photo-Inject Bismuth Doped MAPbI3 Thin Films for Optoelectronics Devices
Carlos D Redondo-Obispo1, Teresa S Ripollés1, Esteban Ciment-Iglesias2, Patricia Sanchis1, Alba Pellaroque2, Federico Pulvirenti1, Esteban Ciment-Iglesias1, Teresa S Ripollès1, Fernando de la Vanda3, Pablo del Rio4 and Carmen Coya1; 1ETSIT, Universidad Rey Juan Carlos, Madrid, Spain; 2ETSIIT, Universidad Politécnica de Madrid (UPM), Madrid, Spain; 3Facultad de CC Físicas, Universidad Complutense de Madrid (UCM), Madrid, Spain; 4Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain.

Hybrid organic-inorganic perovskite research continues gaining efforts to achieve high overall power conversion efficiencies due to their unique optoelectronic properties. [1] An intense activity is dedicated to overcome their high sensitivity to ambient atmosphere (especially water and oxygen) and to visible irradiation that strongly handicap their stability and performance. In particular, semiconductors doping strategy with heterovalent ions has been
tested to stabilize the perovskite material, to control phase transition, morphology improvements, or enhance the electrical and optical properties. Obtaining more stable compounds as well as understanding the complex behavior of the emission evolution upon illumination and time are main concerns to be addressed. The photoluminescence behavior is strongly sensitive to different parameters, mainly to the presence of defects and traps whose evolution with time is related to ion migration and perovskite transformations. [2, 3]

In the present work, the incorporation of Bi3+ in the MAPbI3 (MA=CH3-NH2) perovskite precursor solution leads up to around 7 at.% incorporation at the Pb2+ site in thin film lattice, which corresponds to 33% nominal. This doping effect is demonstrated by x-ray diffraction and their effect on phase purity, symmetry, lattice parameters, average crystalline domain and microstrain are carefully evaluated. A spurious MA3Bi2I9 phase is detected for nominal Bi > ca. 15% while the usual spurious PbI2 phase in undoped films is not observed for any Bi doping. Influence on optical and electrical properties are also studied. Novel effects as extraneous photostability and photosensitivity enhancement, compared to that of undoped MAPbI3 thin films are observed.

Bi3+ incorporation lead to a slight increment of the optical gap due to the reduction of lattice parameters. However, for the photoluminescences properties, the phenomenology for the Bi doped samples is drastically different at high power irradiation. We propose a mechanism to explain the observed trends using a model based on the migration of Bi3+ upon irradiation and its effect on the MAPbI3 cell volume and bandgap energy. These results provide a new path for obtaining highly stable materials which would allow an additional boost of hybrid perovskite based optoelectronics.


ET05.12.07
Nanoimprinted Plasmon Enhanced Perovskite Solar Cells Tianyi Shen, Stylianos Siontas and Domenico Pacifici; School Engineering, Brown University, Providence, Rhode Island, United States.

Perovskite solar cells have drawn great attention in the past years. Besides the high absorption and long carrier diffusion length of the material, perovskite solar cells have demonstrated potential for a promising alternative to conventional silicon solar cells due to their lower fabrication costs and reported power conversion efficiencies reaching 22.1%.

Plasmonic absorption enhancement has been extensively utilized to improve the performance of various solar cell technologies. Here, we report on a simulation study to further boost the efficiency of perovskite solar cells by embedding plasmonic nanostructures in the back metal contacts. Specifically, three-dimensional (3D) finite-difference time-domain (FDTD) simulations are performed on perovskite solar cells, consisting of perovskite films with varying thickness on top of flat or corrugated gold electrodes with varying light trapping geometries (nanodisk or nanohole arrays). The calculated electric fields in the simulation volume enable the decoupling of the absorption within the perovskite and gold films, respectively, which allows for the calculation of the cell power conversion efficiency (PCE) as a function of relevant design parameters. By systematically leveraging the geometry dimensions, the optimal nanostructure designs are obtained. The results show that 100nm-thick perovskite films on top of corrugated gold electrodes can exhibit up to 52% PCE increase compared to their flat counterparts (from 19.2% for a flat cell to 29.2% for an optimized nano-corrugated cell). Moreover, we show that a 150nm-thick perovskite film cell with opportunity corrugated back metal contacts can exhibit a PCE value (31.3%) comparable to that of a 400nm-thick bulk-like cell (31.6%).

These findings may pave the way for plasmon-enhanced high-performance thin-film perovskite solar cells fabricated via scalable methods such as nanoimprint lithography.

ET05.12.08
Long Electron–Hole Diffusion Length in High-Quality Lead-Free Double Perovskite Films Weihua Ning, Feng Wang and Feng Gao; Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden.

Developing environmentally friendly perovskites has become important in solving the toxicity issue of lead-based perovskite solar cells. Here, the first double perovskite (Cs2AgBiBr6) solar cells using the planar structure are demonstrated. The prepared Cs2AgBiBr6 films are composed of high-crystalquality grains with diameters equal to the film thickness, thus minimizing the grain boundary length and the carrier recombination. These high-quality double perovskite films show long electron–hole diffusion lengths greater than 100 nm, enabling the fabrication of planar structure double perovskite solar cells. The resulting solar cells based on planar TiO2 exhibit an average power conversion efficiency over 1%. This work represents an important step forward toward the utilization of environmentally friendly solar cells and also has important implications for the applications of double perovskites in other optoelectronic devices.

ET05.12.09
Combinatorial Investigation of Coevaporated CsPbI3 Thin Films with Large Quasi–Fermi Level Splitting Pascal Becker1–4, Jose Marquez Prieto1, Amran Al-Ashouri5, Charles Hages1, Hannes Hempel1, Justus Just1, Steve Albrecht4 and Thomas Unold1; 1Dept. Structure and Dynamics of Energy Materials, HZB, Berlin, Germany; 2Bergische Universität Wuppertal, Wuppertal, Germany; 3Lund University, Lund, Sweden; 4Young Investigator Group Perovskite Tandem Solar Cells, HZB, Berlin, Germany.

The new generation of photovoltaic materials is driven by the unprecedented rapid performance improvement of hybrid organic-inorganic perovskites solar cells (PSCs). Fully inorganic CsPbI3 perovskites have also demonstrated their great potential for photovoltaics in world record quantum dot solar cells and as an ideal material candidate for tandem devices with a band gap close to 1.8 eV. In this study we explore the composition-dependent phase stability of CsPbI3 films by combinatorial studies. We show that coevaporated CsPbI3 can be synthesised in a stable perovskite phase under Cs rich conditions without the need of a post deposition annealing treatment. We investigate the compositional dependence of the electronic properties by THz spectroscopy and quantitative hyperspectral photoluminescence imaging. Compositional regions with considerably large carrier mobilities and a high photoluminescence quantum yield are identified. From these measurements a maximum quasi-Fermi level splitting of 1.27 eV and charge carrier diffusion lengths of around 3 microns are estimated, indicating this material’s potential for high efficiency solar cells. We find that the charge carrier mobility decreases with increasing Cs content corresponding to a lowering of the electronic dimensionality as the Cs content is increased in the films. First planar pin-type solar cells have been fabricated showing stabilised efficiencies exceeding 11%. Based on the comparison of the optoelectronic characteristics performed in the CsPbI3 films and the solar cells properties of the corresponding devices we conclude that the devices are strongly limited by interface recombination. Optimisation of the device architecture with better matched extraction layers exhibiting less interface recombination could be expected to lead to 18%
efficient inorganic perovskites solar cells.

ET05.12.10  
Photodetectors and Solar Cells Using Indium (I) Iodide as Active Material  
So Min Park, Masud Abdullah A, Christopher I Richards and Kenneth R. Graham; University of Kentucky, Lexington, Kentucky, United States.

Organometal halide perovskites are emerging as promising photovoltaic (PV) materials due to their strong absorbance throughout the visible region, relatively high charge-carrier mobilities, and power conversion efficiencies (PCE) that are on par with polycrystalline silicon. As these materials progress towards commercial applications, understanding the factors limiting the PCE and stability is becoming essential. Interfaces and grain boundaries are some of the most influential aspects for both device performance and stability, as these are prime areas for defect formation and charge recombination. One

Design of novel advanced semiconductor materials usually defines the progress in the development of new photovoltaic (PV) technologies. In particular, recently discovered lead halide based perovskites demonstrated outstanding electronic characteristics and showed high efficiencies of >22% in single junction photovoltaic cells fabricated using low-cost solution process. Perovskite solar cells can potentially accomplish a revolution on the PV market due to their high efficiency and low cost. However, the practical application of perovskite photovoltaics is still limited severely by low stability of complex lead halides and their high toxicity. Therefore, many research groups worldwide explore different families of binary and complex metal halides with high electron/hole mobilities and long carrier lifetimes in order to find some feasible environment-friendly alternatives to the conventional lead perovskites.  
Bounassifi et al. have presented recently theoretical and spectroscopic study suggesting that InI might be considered as a valuable material for photovoltaics (Chem. Mater. 2017, 29, 4667-74).

Here we present the first to the best of our knowledge experimental study of InI as semiconductor material for photovoltaic devices. Planar junction PV cells with InI as active material demonstrated encouraging external quantum efficiency of 17% at short wavelength, while the overall power conversion efficiency (<1%) was limited mainly by low open circuit voltages and fill factors even after substantial optimization of interfacial layers, active layer thickness and morphology.

Strong phot conductivity effect revealed for thin films of InI allowed us to apply this material for fabrication of efficient photodetectors with lateral and vertical geometries. Both types of devices showed excellent light sensitivity and short response times pointing towards high potential of further development of this research direction.

ET05.12.11  
Energetics and Structural Effects of Degradation in Halide Perovskites  
Colin Freeman, Christopher M. Handley, Derek Sinclair, Ian M. Reaney, Vikas Kumar and Cornelia Rodenburg; University of Sheffield, Sheffield, United Kingdom.

With the massive interest in halide perovskites there has been a wide range of research into combinations of these materials. MAPbI$_3$, however, still demonstrates very desirable properties. The long term stability of MAPbI$_3$ remains a significant challenge to any true commercial uptake. The degradation can be significantly affected by many factors but remains unclear [16]. Particular attention has focussed on the effect of non-stoichiometry of the material [19] which may have a significant role in the stability.

Simulations can provide a very valuable tool for studying the defect behaviour, stability and degradation of these perovskite materials due their ability to design and explore exact conditions and examine the local atomic behaviour. Although very powerful, ab initio simulations are limited to modelling relatively small cells due to their computational demands. Classical mechanics provides a powerful method to reach larger sizes and far more configurations.

We use our recently published forcefield [3] to study defects in the MAPbI$_3$ system. We observe that defects are encouraged by non-stoichiometry in the system. We examine the local and long range structural effects of the defects with a particular focus on dynamic behaviour in the ions (rotation/vibrations) and tilt of the octahedra. From this we are able to comment on the influence in general on degradation. We couple these results to experimental probing of degradation in non-stoichiometric samples.

[3] C.M. Handley, C.L. Freeman, PCCP 2017, 19, 2322

ET05.12.12  
Understanding and Tuning the Energetic Landscape in Mixed Dimensionality Perovskites  
Haralds Abolins and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

Ruddlesden-Popper perovskites have recently been shown possess greatly enhanced environmental and thermodynamic stability relative to their bulk counterparts, which has proven the key challenge for the commercialization of perovskite-based photovoltaics. Nonetheless, when these low-dimensionality materials are deposited in thin films through a fast crystallization process, a mixed phase material will result with bulk-like perovskite domains intermixed with grains of Ruddlesden-Popper perovskite of varying configurations in the number of atomic layers between each set of spacer cations. The precise composition will depend on processing conditions and will inevitably have an effect on the charge transport characteristics of the resulting material. While it has been shown that high-efficiency solar cells and LEDs can be fabricated from mixed dimensionality perovskites, the charge transport characteristics between the different phases in these materials have not been well understood. To elucidate the carrier dynamics in Ruddlesden-Popper perovskites a deposition procedure for obtaining thin films with micron-sized single-phase grains is developed. The spatial configuration of the various dimensionality phases is subsequently revealed through photoluminescence mapping and is shown to be tunable in both distribution and relative abundance by varying the deposition conditions. Lastly, it is demonstrated through spectrally resolved photoluminescence lifetime studies that charges are funnelled to the lowest band-gap phases of the materials through an energy transfer process that considerably increases local carrier concentration, leading to enhanced photoluminescence quantum efficiencies. Crucially, the geometry, rate and efficiency of this funneling are shown to be tunable through only slight adjustments in processing conditions, allowing the energetic landscape to be tailored for individual applications.

ET05.12.13  
Surface Ligands on Methylammonium Lead Iodide Perovskites—Binding Group Effects on Photoluminescence and Photovoltaic Device Performance  
So Min Park, Masud Abdullah A, Christopher I Richards and Kenneth R. Graham; University of Kentucky, Lexington, Kentucky, United States.

Organometal halide perovskites are emerging as promising photovoltaic (PV) materials due to their strong absorbance throughout the visible region, relatively high charge-carrier mobilities, and power conversion efficiencies (PCE) that are on par with polycrystalline silicon. As these materials progress towards commercial applications, understanding the factors limiting the PCE and stability is becoming essential. Interfaces and grain boundaries are some of the most influential aspects for both device performance and stability, as these are prime areas for defect formation and charge recombination. One
means of improving both device performance and stability is to passivate these surfaces and grain boundaries by applying surface ligands. Although multiple surface treatments and additives have been applied to perovskite PVs, there is a lack of understanding of how these molecules are interacting with the perovskites. In this study, we show how the binding group influences photoluminescence (PL) and photovoltaic (PV) properties and stability for a series of surface ligands consisting of varying binding groups. These include ligands with both one and two potential binding groups, including zwitterionic molecules. We expected that zwitterionic ligands would display higher binding affinities and potentially improved trap state passivation, as the negatively charged part of the zwitterionic ligands can bind with positively charged undercoordinated Pb\textsuperscript{2+} ions of the perovskite film, while the positively charged group can fill in A-site vacancies. We find that zwitterions indeed lead to higher photoluminescence quantum yields (PLQYs) than monofunctional ligands.

**ET05.12.14**

**Electronic and Atomic Structure at the PCBM/CH3NH3/PbI\textsubscript{2} Interface in Perovskite Solar Cells from Ab Initio Molecular Dynamics**

Rahi Khanal\textsuperscript{1}, Nicholas Ayers\textsuperscript{1}, Sheila Briggs\textsuperscript{2}, Soumik Banerjee\textsuperscript{3} and Sanrat Choudhury\textsuperscript{1}; \textsuperscript{1}University of Idaho, Moscow, Idaho, United States; \textsuperscript{2}School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, United States.

In the perovskite solar cells, interfaces are crucial for efficient photovoltaic performance as they are responsible for both the injection and the transport of the charge carriers. Using *ab-initio* molecular dynamics simulations and density functional theory calculations, we have systematically determined the structural, electronic, and transport properties at a model CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) interface. The CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} is the photoactive layer while PCBM is the electron transport layer. We have observed that PCBM prefers to attach to the perovskite surface via ester moiety of PCBM molecule. Further, from the analysis of interatomic distances on several interface models, we found that the bonding at the interface and the stability of interface is sensitive to the chemical composition at the surface i.e. CH\textsubscript{3}NH\textsubscript{3}I vs. PbI\textsubscript{2} surface terminations of the perovskite. Different preferences in bonding at the interface leads to the change in electronic and transport properties across two chemical terminations. Finally, we have shown that the stability of the interface can be increased by the introduction of certain types of defects at the perovskite surface, which may result in the better coverage of PCBM on the perovskite surface. However, such kind of defects could deteriorate the photovoltaic performance due to an increase in the potential barrier for the transport of charge across the interface.

**ET05.12.15**

**Impact of Anti-Solvents on the Structure and Optoelectronic Properties of Lead-Tin Mixed Perovskite Photovoltaics**

Tranchupa Bandara R M\textsuperscript{1}, Imalka Jayawarden\textsuperscript{1}, Andrew Parnell\textsuperscript{2}, Benjamin G. Freeston\textsuperscript{3}, Stephanie Adeyemo\textsuperscript{2}, Hannah Joyce\textsuperscript{1}, Radu Sporea\textsuperscript{1} and Ravi Silva\textsuperscript{3}; \textsuperscript{1}Department of Electrical and Electronics Engineering, University of Surrey, Guildford, United Kingdom; \textsuperscript{2}Department of Physics and Astronomy, The University of Sheffield, Sheffield, United Kingdom; \textsuperscript{3}Department of Engineering, University of Cambridge, Cambridge, United Kingdom.

Lead-tin (Pb-Sn) mixed perovskites have gained increasing attention due to the possibility of forming all solution processed tandem perovskite PVs (PPVs). One of the major obstacles towards enhancing the performance of the Pb-Sn PPVs has been the formation of high performing, pin hole free absorber layer. This is generally achieved using the anti-solvent treatment during the deposition of the perovskite layer, followed by thermal annealing (Saliba et al., *Environ. Sci. 9*, 1989). Another complication for mixed Pb-Sn PPVs is the fast oxidation of Sn\textsuperscript{2+} to Sn\textsuperscript{4+} which results low efficiencies due to p-type self-doping (Herz et al. *Acc. Chem. Res.* 49, 146). Various pathways have been investigated in decreasing this oxidation process with the most widely used being the incorporation of SnF\textsubscript{2}. This process however, while inhibiting the perovskite oxidation, generates Sn\textsuperscript{4+} ions in the system by the oxidation of Sn\textsuperscript{2+} in SnF\textsubscript{2} which are hardly removed from the system. Interestingly, extraction of Sn\textsuperscript{4+} from ion mixtures, is reported to be most effective when using toluene as the extraction medium (Sargar et al. *JCCS*, 50, 841). Incidentally, toluene is one of the widely used aforementioned anti-solvents that enable high performing perovskite PVs (Jeon et al., *Nan. Mater.* 13, 897). However, there are no known studies reported on the effective removal of Sn\textsuperscript{4+} based on the anti-solvent route.

To investigate this, we discuss the impact of toluene and two other commonly used anti-solvents; anisole and chlorobenzene, on the triple cation Pb-Sn mixed perovskite system (Cs\textsubscript{0.02}(FA\textsubscript{0.83}MA\textsubscript{0.17})\textsubscript{0.1}Pb\textsubscript{0.85}Sn\textsubscript{0.15})\textsubscript{0.15}). We observe ~80% improvement in power conversion efficiency (with minimal optimization of the processing conditions) for the toluene treated Pb-Sn mixed perovskite with a champion efficiency of ~6% compared to chlorobenzene or anisole treated devices. This is reflected by enhancements in all the device parameters (open circuit voltage, short circuit current and fill factor). Terahertz mobility measurements carried out on the different anti-solvent treated perovskite films clearly indicate improvements in charge carrier lifetimes with toluene, where a slower decay time is observed. The impact on the use of the anti-solvent on the chemistry of the Pb-Sn mixed perovskite is further evident through grazing incidence wide angle X-ray spectroscopy where no noticeable differences in the diffraction spectra are evident for different anti-solvents. Based on the above we introduce a mechanism by which Sn\textsuperscript{4+} is extracted through toluene enabling a more purified Pb-Sn perovskite absorber layer growth.

The extraction of the Sn\textsuperscript{4+} by toluene is further strengthened by the studies on the, Cs\textsubscript{0.02}(FA\textsubscript{0.83}MA\textsubscript{0.17})\textsubscript{0.1}Pb\textsubscript{0.85}Sn\textsubscript{0.15})\textsubscript{0.15}Sn\textsubscript{4+} system where the impact of the anti-solvent used is not as pronounced. Finally routes towards improving the Pb-Sn mixed perovskite performance which enables efficiencies approaching 15% is discussed.

**ET05.12.16**

**Perovskite Nanocrystals—Shape-Controlled Synthesis to Self-Assembled Supercrystals with Tunable Optical Properties**

Jalakshminarayana Polyavarap\textsuperscript{1,2}; Ludwig-Maximilians-Universität München, Munich, Germany; \textsuperscript{2}Center for NanoScience (CeNS), Munich, Germany.

Perovskite nanocrystals (NCs) are gaining increasing attention in many fields ranging from chemistry to physics and engineering owing to their extremely interesting properties such as high photoluminescence quantum yields, tunable optical bandgap, enhanced stability, large diffusion lengths and shape controllability. [1–4] In spite of the rapid progress in the synthesis of perovskite NCs, very few attempts have been made toward the self-assembly of perovskite NCs and understanding their coupled optical properties. Shape-controlled synthesis and their self-assembly into ordered superlattices has emerged as a powerful tool for tailoring the nanoscale optical properties. Such coupled optical and electronic properties can be utilized for the development of novel optoelectronic devices.

In this talk, I will present a one-pot shape-controlled synthesis of highly crystalline and monodisperse Cs\textsubscript{2}Pb\textsubscript{X} (X=Cl, Br and I) perovskite NCs of various morphologies such as nanocubes, nanoplates (NPls), nanowires (NWs) and nanorods (NRs) starting from their precursor powders. [2–5] The morphology of perovskite NCs can be controlled by means of simple chemistry such as Cs/Pb precursor ratios, reaction time and ligand concentration. We discovered that the perovskite NCs spontaneously self-assemble into nanowires through oriented-attachment or supercrystals (SCs) depending on the reaction conditions. The optical bandgap of the perovskite NCs as well as SCs can be controlled over the entire visible range by varying the halide (Cl, Br, and I) composition. Our work not only provides a facile method for the shape-control of monodisperse perovskite NCs and their self-assembly, but also expands our current understanding of the morphology-dependent optical properties, and open new avenues for the fabrication of highly ordered architectures using perovskite NC building blocks for future optical and optoelectronic devices.

References
Investigation and Application of Carboxylic Acid Functionalized Perovskite Surfaces 

Kenneth Zielinski; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Methylammonium lead iodide perovskites can be functionalized by ammonium benzoic acids, yielding carboxylic acid groups capable of undergoing subsequent surface reactions. The ammonium salts of 4-aminobenzoic acid, 5-aminoisophthalic acid, and 3,3'-diaminobenzoic anhydride were synthesized and substituted onto the surface using previously explored techniques. The mechanism of substitution was elucidated via XPS. The molecular orientation was determined via infrared reflection absorption spectroscopy. The anhydride experiments were used specifically to examine the orientation due to the rigidity of the anhydride on the surface relative to the carboxylic acids in the other molecules. The carboxylic acids were also found to be useful chemical hooks in this system for atomic layer deposition and has been explored using organometallic reagents. This technique is a powerful tool, enabling an atom-
Organic–inorganic halide perovskite solar cells (PSCs) have drawn a great deal of attention in the photovoltaic research community due to their high efficiency over 22% and simple manufacturing process. A high quality perovskite film is critical to obtain PSCs with both superior performance and high reproducibility, especially when constructing large area polycrystalline films in ambient condition. Motivated by the common wisdom that thicker films are easier to process and therefore offer better controllability in large area production of optoelectronics device when compared with thinner ones. Here, we employ a simple perovskite functionalization process to fabricate perovskite films with thickness over 1 μm in ambient condition. By careful control of the perovskite component and formation process, the resultant perovskite films exhibit full coverage and excellent crystallinity with low surface roughness and low thickness variation. The high quality of the films is further evidenced by significantly enhanced photoluminescence lifetime, slower charge recombination constant, much lower intrinsic trap density, higher conductivity and much longer carrier diffusion length to achieve the balance of device efficiency and film thickness. These results suggest that we obtain high quality thick perovskite thin films with this simple method. Our resultant mesoscopic PSCs with active area of 0.1 cm² achieve an average power conversion efficiency (PCE) of 19.1% (with small PCE standard deviation) and a stabilized efficiency approaching 19%. Moreover, our 5 cm × 5 cm PSC module device with active size of 12 cm² also deliver a PCE of 15.3%, strongly suggesting that our method is compatible with further upscaling. In addition, the resultant un-encapsulated small size PSCs exhibit an excellent T80 lifetime exceeding 1600 h under continuous light illumination with maximum power point tracking in dry N₂ environment.

References
Highly Emitting Blue Inorganic Halide Perovskite Quantum Dots and Nanocrystals

Jianjun Tian; University of Science and Technology Beijing, Beijing, China.

All-inorganic perovskite cesium lead halide quantum dots (QDs) have been widely investigated as promising materials for optoelectronic application, because of its outstanding photoluminescence (PL) properties and benefits from quantum effects. Although QDs with full-spectra visible emission have been synthesized for years, the PL quantum yield (PLQY) of pure blue emitting QDs still stays at low level in contrast to their green or red emitting counterparts. Herein, we obtained core-shell structured cubic CsPbBr3@amorphous CsPbBr3 (A-CsPbBr3) perovskite QDs via a facile hot injection method and centrifugation process. The core/shell structure QDs showed a record pure blue emission PLQY of 84%, which is much higher than that of blue emitting cubic CsPbBr3 QDs and CsPbBrxCl3−x QDs. Furthermore, a blue emitting QDs-assisted-LED with bright pure blue emission was prepared and illustrated the core-shell QDs’ promising prospect in optoelectrical application. Recently, another work shows the transformation of the crystal structure and remarkably high crystallinity of the γ-crystals, leading to the record blue PLQY of 91% at 480 nm.

Spontaneous Iodide Loss from 2D Perovskite Single Crystals N-Dopes 2D Perovskites

Lianfeng Zhu1, He Tian2, Scott Silver1, Antoine Kahn1, Tian-Ling Ren1 and Barry P. Rand2; 1Princeton University, Princeton, New Jersey, United States; 2Tsinghua University, Beijing, China.

Despite the demonstrated high efficiency of perovskite solar cells and light emitting devices, the understanding of the intrinsic stability of perovskites is far from complete. In this work, using an ultra-sensitive, exfoliated 2D perovskite single-crystal sheet/graphene heterostructure device, we reveal spontaneous iodide loss as an important degradation pathway of 2D perovskite single crystals, which acts as a donor and n-dopes the 2D perovskite semiconductor, generating positively charged iodide vacancies.

Origin of Green-Light Emission of the Zero-Dimensional Bromide Perovskite CsPbBr3

Young-Kwang Jung1, Ji-Sang Park2 and Aron Walsh1, 5; 1Yonsei University, Seoul, Korea (the Republic of); 5Imperial College London, London, United Kingdom.

Halide perovskite families have been widely studied for photovoltaics [1-2] due to their unique opto-electronic properties, but recently, they are being studied for light-emitting applications [3]. Beyond regular perovskites based on a corner-sharing octahedral network, CsPbBr3, which is called as zero-dimensional perovskite, is getting attention because of its highly-efficient green light luminescence [4]. The reported band gap of CsPbBr3 of 3.9 eV is in the ultraviolet (UV) region, thus green light emission in this material cannot be due to its intrinsic band gap. The origin of the green light emission has not clarified and two hypotheses have been suggested to explain this phenomenon: (i) CsPbBr3 phase impurities within the material and (ii) luminescent defect states within the band gap of CsPbBr3. We investigate the chemical and physical properties of the CsPbBr3 based on first-principles simulations, including a thorough analysis within the modern theory of defect formation [5], from which we predict the origin of the green light emission.

Resonantly Generating Multiple Excitons with Multiple Below-Band-Gap Photons in Metal Halide Perovskite Nanocrystals

Aurora Manzi, Yu Tong, Julius Feucht, En-Ping Yao, Lakshminarayana Polavarapu, Alexander S. Urban and Jochen Feldmann; LMU Munich, Munich, Germany.

Multiple exciton generation (MEG) is a process that addresses the conversion of highly energetic photons by using their excess energy to promote additional electrons to the conduction band. However, this process requires that the energy of the exciting photon is at least twice the band-gap of the semiconductor, which is hardly achievable with visible light. In our studies we have shown that it is possible to use multiple low-energy photons to efficiently generate multiple excitons in metal halide perovskite nanocrystals. Additionally, high-order absorption processes, deviating from the expected two-photon absorption, can be observed at very specific energetic positions. We could associate these specific energies to multiples of the semiconductor band-gap energy. In such a way, we have developed a method by means of which we were able to describe this effect as a resonance behaviour between multi-photon absorption (MPA) and MEG, which has never been seen before.

Interestingly, the resonance effect between MPA and MEG could only be observed once the perovskites were assembled in an orderly fashion, forming supercrystals. This phenomenon can be attributed to the electronic coupling given by the close-packed arrangement of the individual nanocrystals that reduces the incidence of Auger recombination, which represents the main opponent of the survival of multiple excitons. When the supercrystal geometry is kept, the chemical composition of the perovskites can be varied to tune the energetic position of the MPA-MEG resonances. We have in fact demonstrated that the same effect can be obtained for different halides (X) in CsPbX3 perovskites.
Currently lead based all-inorganic cesium lead halide perovskite nanocrystals (NCs), have been shown great potential for high-performance light-emitting diodes (LEDs) and solar cells owing to their excellent optical properties and inexpensive synthesis process. Here, we successfully doped heterovalent Bi\(^{3+}\) ion into the lattices of CsPbBr\(_3\) perovskite NCs through a hot-injection method. The Bi\(^{3+}\) cation has been chosen as the dopant by reason of its similar ionic radius to preserve the integrity of perovskite structure. We achieved maximum 6.93% Bi doping which is considerably higher as compared to those achieved in previous reports via hot injection method.

It was found that by increasing the Bi\(^{3+}\) ion concentration, the morphology of CsPbBr\(_3\) NCs changed from cubic to hexagonal and precisely tune the band structure and photoluminescence (PL) of host CsPbBr\(_3\) NCs by inducing the trap states within the band gap. Time-resolved photoluminescence (TRPL) spectroscopy revealed that Bi\(^{3+}\) ion doping significantly enhance the lifetime of charge carriers. This work indicates that Bi doped CsPbBr\(_3\) NCs occurs better optical properties than pure CsPbBr\(_3\) NCs and can be a promising material for high-performance perovskite LEDs.

9:15 AM ET05.13.06
Understanding the Roles and Developing Strategies to Overcome Shallow Defect Levels in Cesium Lead Halide Colloidal Nanocrystals Brent A. Koscher\(^{1,2}\), Joseph Swabek\(^{1,2}\) and A. P. Alivisatos\(^{1,2}\); \(^{1}\)University of California, Berkeley, Berkeley, California, United States; \(^{2}\)Materials Science, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

An intellectual explosion in the ever-expanding world of nanoscience has led to the development of facile synthetic protocols for a high level of material control at the nanoscale. The culmination of several decades of research has led to the ability to routinely synthesize specific types of cadmium chalcogenide quantum dots with quantum efficiency exceeding 95%. However, enabled by a facile synthesis and driven forward by excellent optoelectronic properties, the all-inorganic perovskite quantum dots (CsPbX\(_3\); X = Cl, Br, I) have attracted considerable attention among academic researchers for a relatively nascent field. This is a material that performs with up to 90% photoluminescent quantum yield following the synthesis, quite encouraging, but accessing materials with the highest possible quality is crucial to fully realize the potential of the material. This leads to the interesting question: What prevents the quantum efficiency from truly being unity? The same property that enables easy access of the material, namely a low temperature synthesis, also opens the door for a number of very real problems. While it is generally accepted that the lead halide perovskites are positioned with an unusually high defect tolerance, they are not defect impervious, and are particularly susceptible to the pernicious shallow electronic states that result from the lead-rich synthetic conditions and labile surface halides. We have been working to carefully understand the role that the lead-rich surface conditions of CsPbX\(_3\) quantum dots have on the optoelectronic properties of the material, conditions that result in multi-exponential excited state lifetimes and sub-optimal quantum efficiencies. Through careful manipulation of the surface structure we are able to alleviate the deleterious lead-rich surface, changing the hard to describe multi-exponential excited state lifetimes to single-exponential lifetimes typical of two-level systems, an unusual property for a nanocrystal ensemble. For example, through our studies we have found that no more than 50 extra surface leads are responsible for reducing the photoluminescence quantum yield of a CsPbBr\(_3\) nanoparticle to 85%, these lead atoms represent a small but detrimental population of surface lead atoms. A careful manipulation and removal of harmful atoms while maintaining the integrity of the nanoparticle as a whole is crucial in being able to access the highest quality nanomaterials. To this end, tailoring approaches to manage atoms in specific locations or with specific energies is necessary to continue to improve material performance and understand how to best utilize the materials moving forward.

9:30 AM ET05.13.07
Highly Luminescent Phase-Stable CsPbI\(_3\) Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield Feng Liu\(^{1}\), Yaohong Zhang\(^{1}\), Chao Ding\(^{1}\), Taro Toyoda\(^{1}\), Shuzi Hayase\(^{2}\) and Qing Shen\(^{1}\); \(^{1}\)The University of Electro-Communications, Tokyo, Japan; \(^{2}\)Kyushu Institute of Technology, Tokyo, Japan.

Perovskite quantum dots (QDs) as a new type of colloidal nanocrystals have gained significant attention for both fundamental research and commercial applications owing to their appealing optoelectronic properties and excellent chemical processability. For their wide range of potential applications, synthesizing colloidal QDs with high crystal quality is of crucial importance. However, like most common QD systems, those reported perovskite QDs still suffer from a certain density of trapping defects, giving rise to detrimental non-radiative recombination centers and thus quenching luminescence. In this work, we developed a trioctylphosphine (TOP)-based route which yields phase-stable monodisperse CsPbI\(_3\) QDs with the best-so-far quantum efficiency up to 100%, signifying the achievement of almost complete elimination of the trapping defects. Ultrafast kinetic analysis with time-resolved transient absorption spectroscopy evidences the negligible electron or hole trapping pathways in our QDs, which explains such a high quantum efficiency. Solar cells based on these high-quality perovskite QDs exhibit power conversion efficiency of 9%, showing great promise for practical application.

9:45 AM BREAK

10:15 AM ET05.13.08
Phosphine-Oxide Assisted Synthesis of Perovskite Nanoparticles—A Bridge Between Nano and Macro Syntheses Olivia J. Ashton\(^{1}\), Guilherme Almeida\(^{2}\), Luca Goldoni\(^{2}\), Quinten Akkerman\(^{2}\), Liberato Manna\(^{2}\) and Henry Snaith\(^{2}\); \(^{1}\)University of Oxford, Oxford, United Kingdom; \(^{2}\)Istituto Italiano di Tecnologia, Genoa, Italy.

The fabrication and growth of both thin films and single crystals of metal halide perovskites, are typically done using highly polar solvents such as dimethyl sulfoxide, dimethylformamide and gamma-butyrolactone. Notably, these solvents all contain the functional group R=O. Conversely, the synthesis of perovskite nanocrystals employs a combination of non-polar solvents, and weaker aliphatic amines and carboxylic acids, which act as the ligands. It is well known that the ammonium capped nanoparticles are inherently unstable due to the lability of the ligands, resulting in the formation of defects on the nanoparticle surface. To date, there have been few attempts to impart the know-how which has been developed in macro scale syntheses to nanoparticle syntheses.

Here, we explore the application of a phosphate oxide (R=P=O) to synthesise cesium lead bromide perovskite nanocrystals, replacing the labile amine ligand and mirroring the R=O group required in the macroscale synthesis. The synthetic route we present provides us with exceptionally high yields of very monodisperse particles, which are not highly emissive, but can also be synthesised in air, obviating the need for laborious solvent degassing, and complicated oxygen and moisture free techniques.

Through a comparison of both synthetic routes, we observe improved stability of the R=P=O nanocrystals to washing. Additionally, we are able to expand this synthetic protocol to a variety of other amions and cations, as well as being able to replace the carboxylic acid with either phosphonic or phosphinic acids, demonstrating the robustness and versatility of this technique. By using nuclear magnetic resonance and x-ray photoelectron spectroscopy we are able to investigate the surface of our nanoparticles and determine the cause of increased stability and show the importance of phosphate oxide in the synthesis of perovskite nanocrystals.

10:30 AM ET05.13.09
Exciton Dynamics in Quantum Confined CsPbBr3 Nanoplatelets Moritz Gramlich1, 2, Bernhard J. Bohn1, 2, Yu Tong1, 2, Lakshminarayana Polavarapu1, 2, Alexander S. Urban1, 2 and Jochen Feldmann1, 2; 1Chair for Photonics and Optoelectronics, Department of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, Munich, Germany; 2Nanosystems Initiative Munich (NIM), Munich, Germany.

In contrast to bulk perovskite films, recent reports have shown that in perovskite nanocrystals the excitonic absorption onset and photoluminescence (PL) peak exhibit a blue shift due to quantum confinement when their size in at least one dimension approaches the exciton Bohr radius of the respective perovskite composition [1]. For decreasing thickness of organic-inorganic perovskite nanoplatelets – separated by centrationization – increasing exciton binding energies and decreasing PL decay times have been observed [2]. Recently, we have developed a new method which enables the direct synthesis of quantum-confined inorganic CsPbBr3 nanoplatelets of uniform thickness with an atomic layer precision. These nanoplatelets are characterized by a highly efficient light-emission in the blue spectral range. Here, transient absorption spectroscopy is applied to CsPbBr3 nanoplatelets of different thickness varying from two to six monolayers to gain additional insight into PL decay times on the dominant exciton dynamics in these systems. A special focus is put on the fast exciton-exciton annihilation process, which plays an increasingly important role for higher excitation powers.


Lead halide perovskites APbX3 [A = methylammonium (MA), formamidinium (FA), and Cs, X=I, Br, and Cl] has excellent properties suitable for optical devices. The halide perovskites have been extensively studied on single crystals and thin films. Moreover, the synthesis of high-quality nanocrystals has been developed in recent years [1]. Since excitons are strongly confined within nanocrystals, optical responses depends on the size of the nanocrystals. One advantage of nanocrystals is that a spatially confined exciton enhances the radiative recombination rate, and then nanocrystals exhibit high photoluminescence quantum yields (PLQYs) even at room temperature. On the contrary, such spatial confinement works negatively for multiple excitons leading to a decrease in PLQYs as the non-radiative Auger recombination rate of multiple excitons is enhanced [2, 3]. Therefore, it is necessary to elucidate the impact of spatial confinement on the radiative processes for nanocrystal device applications. In particular, size-dependent PL dynamics of nanocrystals should be elucidated.

In this study, we report on the size-dependent PL dynamics of perovskite nanocrystals revealed by single dot spectroscopy. The samples used in this study were two types of perovskite nanocrystals with different A site cations (FA/PbBr3 and Cs/PbBr3), which were prepared by hot injection method. Time-resolved and spectrally resolved PL measurements were performed for individual single nanocrystals. Single-dot spectroscopy enables us to analyze optical properties for each individual nanocrystal that cannot be obtained in ensemble nanocrystal measurements. From the obtained results, we clarified that those nanocrystals with larger absorption cross sections exhibit longer exciton lifetimes. Since this tendency was observed with both FA/PbBr3 and Cs/PbBr3 nanocrystals, it was suggested that spatial confinement is the dominant factor determining the exciton lifetime. Furthermore, since the trion (charged exciton) generation is a major factor lowering PLQYs, the size dependence of trion generation probability is analyzed from the proportion of on-state and off-state in PL blinking behavior. These nanocrystal size dependences of PL dynamics for excitons, trions and multiple excitons provide important insights for improving the performance of nanocrystal-based devices.

Part of this work was supported by JST-CREST (JPMJCR16N3).


11:00 AM ET05.13.11 Contactless Measurements of Lattice and Photogenerated Charged Carrier Dynamics in Organic-Inorganic Hybrid Perovskite Single Crystals Jian Wang1, 2, Eideh Metahardin,2, Lakshmi N. Murthy1, Marissa N. Higgins1, Diego Barrera1, Trey Daunis1, Yangzi Zheng1, Anton Malko1, Fernando Ely4, Manuel Quevedo-Lopez1, Mark Lee1 and Julia W. Hsu1; 1Chair for Photonics and Optoelectronics, Department of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, Munich, Germany; 2Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States; 3Chemistry, University of Washington, Seattle, Washington, United States; 4Physics, The University of Texas at Dallas, Richardson, Texas, United States; 5Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

Hybrid organic-inorganic lead halide perovskites have revolutionized optoelectronic applications, including solar cells, light-emitting diodes, and photo/radiation detectors. Despite the rapid advances in applications, fundamental understanding of these remarkable materials has just begun. While most applications use thin films that contain multiple grains, high-quality single crystals that contain minimal defects are pertinent to understanding the fundamental properties, hence the limit of attainable optoelectronic performance. However, depositing electrical contacts on fragile single crystals can often alter them, e.g. by inducing doping. Here we present two contactless techniques, far-infrared (FIR) reflectance and surface photovoltage (SPV) measurements, to probe lattice dynamics and photogenerated carrier dynamics, respectively, on high-quality methylammonium lead bromide (MAPbBr3) single crystals. FIR reflectance shows three coherent infrared-active phonon modes between 40 to 200 cm−1 that result in reststrahlen bands with much higher peak reflectance than has been previously reported for single crystal MAPbBr3. The phonon mode strength and damping are comparable to what is commonly observed in classical oxide perovskite single crystals, suggesting phonon coherency across macroscopic scale and that the crystal likely contains few grain boundaries or stacking faults. However, these crystals can still contain point defects, which contribute to SPV signals. By performing SPV measurements, to probe lattice dynamics and photogenerated carrier dynamics, respectively, on high-quality methylammonium lead bromide (MAPbBr3) single crystals.

11:15 AM ET05.13.12 Tetragonal to Cubic Phase Transition in FAx-CsPb(1-x)Br3—Temperature Dependence and Impact on Band Gap Julien Barrier1, Aryeh Gold-Park1, 2, Elin Wolf1, Rachel E. Beal1, 2, Michael D. McGeehe and Michael F. Toney1; 1SSRL. Materials Science Division, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 2Department of Chemistry, Stanford University, Stanford, California, United States; 3Department of Applied Physics, Stanford University, Stanford, California, United States; 4Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 5Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.
In the pursuit of efficient tandem solar cells, high band-gap photovoltaic absorbers are required for top cells. Hybrid perovskites are promising candidates, as their band gaps can be widely tuned via compositional adjustments. Specifically, perovskites of the form FA$_{1-x}$Cs$_x$Pb(I$_{1-y}$Br$_y$)$_3$ have shown high device efficiencies as well as high band gaps suitable for tandem applications [1]. In this family of perovskites, we have observed a tetragonal-cubic phase transition that is coincident with a change in the temperature coefficient of the band gap and also occurs within solar cell operating temperatures. It has been suggested [2] that the phase transition may impact light induced phase segregation, which has been identified as a major concern that lowers operating voltages in mixed cation perovskite solar cells [1]. Thus, it is key to understand the phase behavior of this family of perovskites, as well as the impact of structural changes on electronic properties.

We explore here a wide compositional space of FA$_{1-x}$Cs$_x$Pb(I$_{1-y}$Br$_y$)$_3$ thin films with temperature-dependent synchrotron X-ray diffraction. At room temperature, many of these compositions exhibit tetragonal peaks that we have indexed to the P4/mmb space group, corresponding to concerted octahedral tilting about the c axis of the perovskite crystal structure. This is distinct from tetragonal MAPbI$_3$, which has alternating tilt directions about the c axis corresponding to the I4/mcm space group. We compute the structure factors of a number of Bragg peaks that allow us to model the average octahedral tilt angle as a function of the temperature. Within the FA$_{1-x}$Cs$_x$Pb(I$_{1-y}$Br$_y$)$_3$ family, we show how varying the composition affects the phase transition temperature and we present a room temperature phase diagram. Additionally, we show that the temperature coefficient of the band gap presents a discontinuity at the phase transition temperature. This effect is related to band gap tuning observed in mixed Pb/Sn perovskites, which share the same tetragonal space group [3]. This work establishes a phase diagram that may help interpret photostability and will enable better prediction of band gaps in this family of hybrid perovskites.

References


11:30 AM ET05.13.13
Phase Transition and Anion Exchange in Lead Halide Perovskites
Minliang Lai$^1$ and Peidong Yang$^{1,2}$; $^1$Department of Chemistry, University of California, Berkeley, Berkeley, California, United States; $^2$Division of Materials Sciences, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Lead-halide perovskites are a family of semiconductor materials with excellent optoelectronic properties ideally suited for next-generation photovoltaic and light-emitting applications. Particularly, inorganic perovskites CsPbX$_3$ are drawing increasing research interests because of their better stability. There are rich structural phase transitions in the inorganic perovskites owing to their soft and dynamical ionic lattice. However, the fundamental understandings of intrinsic phase transition mechanism are still elusive. In this talk, I will focus on the systematical study of the phase transition between a non-perovskite and a perovskite phase using single-crystal CsPbX$_3$ nanowires platform. The non-perovskite phase with a large bandgap and poor photoactivity can be thermal-driven transformed to a meta-stable perovskite phase with a decreasing bandgap and excellent optoelectronic properties. Moisture introduces vacancy in the crystal lattice and lowers the kinetic barrier from perovskite phase to non-perovskite phase. We further realize robust thermochromic solar cells for smart photovoltaic window applications via stable, controllable and reversible phase transition. Another feature of the soft ionic lattice is facile ion migration. Anion exchange chemistry was demonstrated in CsPbX$_3$ nanostructures with high PLOY throughout the exchange reaction. Via developing a novel localized anion exchange, we demonstrate spatially resolved multi-color CsPbX$_3$ nanowire heterojunctions. These perovskite heterojunctions show tunable photoluminescence over the entire visible spectrum with high resolution down to 500 nm, which represent key building blocks for high-resolution displays. Moreover, the intrinsic solid-solid anion exchange dynamics can be resolved in these perovskite hetero-junction nanowires through non-destructive optical methods. These fundamental understanding can offer guidelines for engineering the perovskite materials with novel functional devices.

11:45 AM ET05.13.14
Understanding and Improving the Surface Ligand Capping of Cesium Lead Bromide Nanocrystals
Maryna Bodnarchuk$^{1,2}$, Simon C. Boehme$^3$, Stephanie ten Brinck$^4$, Caterina Bernasconi$^5$, Yevhen Shynkarenko$^{1,2}$, Maksym V. Kovalenko$^{2,1}$ and Ivan Infante$^6$; $^1$Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; $^2$ETH Zürich, Zürich, Switzerland; $^3$Vrije Universiteit Amsterdam, Amsterdam, Netherlands.

Colloidal lead halide perovskite nanocrystals (NCs) have recently emerged as versatile photonic sources. Their processing and luminescent properties are largely governed by the lability of their surface structure, that is the surface regions of the NC core and ligand shell. In this study and using CsPbBr$_3$ NCs as a model system,[1] we model the nanocrystal surface structure and its effect on the emergence of the trap states using density functional theory. We then rationalize the typically observed effects of the surface treatment and aging on the luminescent characteristics. We illustrate and discuss the utility of common elemental analysis methods, namely inductively-coupled plasma – optical emission spectrometry and X-ray photoelectron spectroscopy, for rationalize the typically observed effects of the surface treatment and aging on the luminescent characteristics. We illustrate and discuss the utility of common elemental analysis methods, namely inductively-coupled plasma – optical emission spectrometry and X-ray photoelectron spectroscopy, for elucidating the chemical changes induced by surface treatments. We propose a strategy for healing the surface trapping states and for improving the colloidal stability by the combined treatment with didodecyldimethyl ammonium bromide and lead bromide and validate this approach experimentally. This simple procedure results in robust colloids, which are highly efficient and exhibit high photoluminescence quantum yields of up to 95-100%.

[1] manuscript submitted
Bedzyk, Antonio Facchetti, Tobin J. Marks, Mercouri G. Kanatzidis and Richard D. Schaller; 1Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois, United States; 2Department of Chemistry, Northwestern Illinois University and Illinois IHMC Materials Research Center, Northwestern University, Evanston, Illinois, United States; 3Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois, United States; 4Applied Physics Program, Northwestern University, Evanston, Illinois, United States; 5Department of Physics and Astronomy, Northwestern University, Evanston, Illinois, United States; 6Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 7Flexterra Corporation, Skokie, Illinois, United States.

The recently re-emerged two-dimensional organic-inorganic hybrid perovskites (2DHFs) are solution processable semiconductors exhibiting strong quantum and dielectric confinement effects, as well as excellent luminescence properties. However, even some of the most fundamental optical properties, especially the complex refractive index (RI), currently are unknown for 2DHF single crystals. As for any optoelectronic materials, refractive index is crucially important since: 1) The real part (n) encodes the phase velocity of light, which, e.g., underpins the resonant condition of a laser cavity, and 2) the imaginary part (k) dictates absorption, which is key for optimizing the thickness of a solar cell. Herein, using a newly-developed dielectric-coating based technique, we determine the complex, anisotropic RI for 2DHF single crystals with various perovskite-layer thicknesses and different types of organic spacers. We found 2DHFs that are only one or two perovskite layers in thickness exhibit negative permittivity due to strong in-plane exciton resonances, but positive permittivity owing to substantially weaker out-of-plane exciton resonances. The extreme excitonic anisotropy in the periodic 2DHFs leads to a natural hyperbolic dispersion in the visible range, which has been previously achieved only with artificial metamaterials. Our observation opens new possibilities in enhanced emission & absorption properties, non-linear optics, and enhanced light-matter interactions.

1:45 PM ET05.14.02

 Templating Hybrid Perovskite Growth for Highly Efficient Light-Emitting and Photovoltaic Devices

 Silvia Colella, Antonella Giuri, Carola Corcione, Aurora Rizzo, Feng Gao, Michele Saba, Giovanni Bongiovanni, Jianpu Wang and Andrea Listorti; 1CNR-NANOTEC, Lecce, Italy; 2Università del Salento, Lecce, Italy; 3Linköping University, Linköping, Sweden; 4Università di Cagliari, Cagliari, Italy; 5Nanjing Tech University, Nanjing, China.

 Hybrid halide perovskites, extensively used in the field of optoelectronics, are a class of materials extremely promising for their excellent properties combined with the mild synthetic protocols. Mainly used in solar cells and light emitting diodes, perovskites are formed from solution by self-assembly of precursors. The resulting soft material is often unable to express its ideal potential, due to unsuitable morphology or elevated density of electronic defects as a consequence of the low-temperature processing. Based on our previous findings on the interaction between perovskite precursors and additives, here we explore the use of a tailored biopolymer, starch, as templating agent for the growth of formamidinium (FA)- and methylammonium (MA)-based tri-iodide perovskite films. The presence of the macromolecule brings the enormous technological advantage of allowing the deposition of the perovskite layer with a one-step method, avoiding solvent dripping or two-steps method. Furthermore, it allows a fine tuning of the solution viscosity (making the solution suitable for different area deposition techniques), of the perovskite grain size and of the layer thickness, by simply adjusting the polymer:perovskite relative concentration. Our approach was validated by outstanding performances in both light emitting (LED) and photovoltaic (PV) devices with outstanding results. We obtained an inverter, planar, mild temperature processed solar cell with a 17% efficiency and a LED characterized by an EQE of ~5% and, most important, among the highest reported radiances for NIR PLEDs. (i.e. 206.7 W/sr*m² obtained at very high currents; about 1000 mA/cm²). The micro and nano-structural changes and their influence on optoelectronic properties were studied as a function of starch concentration, confirming that the device performances are strongly related to the perovskite film structure. The overall picture that emerged is that the presence of starch influences i) the interface properties within the device stack, ii) the crystallographic scenario of the active material, iii) the dielectric landscape surrounding the perovskite crystals, allowing, for the LED device, a minimization of Auger losses at high current regimes and for an overall enhancement of the perovskite light emission and the device capability in sustaining high carriers densities.

1:45 PM ET05.14.03

 2D Homologous Organic-Inorganic Hybrid Ruddlesden Popper Perovskite Single Crystals Lasers with Low Thresholds

 Tzu-Pei Chen, Shao-Sain Li, Chinnamonba Murugesan Raghavan, Chia-Chun Chen, Yu-Ming Chang and Chun-Wei Chen; 1Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; 2Nanotechnology Program, Taiwan International Graduate Program, Academia Sinica and National Taiwan University, Taipei, Taiwan; 3Department of Physics, National Taiwan University, Taipei, Taiwan; 4Graduate Institute of Biomedical Optomechantronics, Taipei Medical University, Taipei, Taiwan; 5Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; 6Center of Atomic Initiative for New Materials (AI-MAT), National Taiwan University, Taipei, Taiwan; 7Taiwan Consortium of Emergent Crystalline Materials (TCECM), Ministry of Science and Technology, Kaohsiung, Taiwan; 8Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan.

 Two dimensional Ruddlesden-Popper perovskite (2D RPP) plays a key role in the current widespread investigations into the potential uses in optoelectronics because of the quantum well superlatice-like structure. This unique structure makes 2D RPP have higher moisture stability, and stronger exciton binding energy than 3D perovskite. However, the complexity in the wet-chemical processes make the synthesis of high purity homologous 2D perovskites still a big issue. In addition, the fundamental mechanism of the molecular origin of the phase transition and unusual blueshift of the emission in 2D RPP with different layered perovskite compounds is still lacking. In this direction, we grew a high purity millimeter-sized single crystal 2D RPP (BA$_2$MA$_2$Pb$_{5}$Br$_{19}$, and BA$_2$MA$_3$Pb$_{10}$Br$_{27}$, n=1, 2, 3) which cover whole visible light range by using slow evaporation at a constant-temperature (SECT) solution growth. Via the XRD, spectral mapping, and fluorescence lifetime mapping measurements, the large sized 2D RPP crystals show well crystallinity and highly phase purity. Furthermore, due to the pyramid step-like structure, we obtain cavity-free lasing behavior with around 3.7 uJ/cm² low threshold from these homologous large sized crystals. Also, with high phase pure crystals, we can identify the carrier dynamics before and after phase transition directly without defect state induced effect. Our result demonstrates that solution growth homologous organic-inorganic hybrid 2D perovskite single crystals open up a new window as a promising candidate for optoelectronic devices. (This work has been published in Nano Lett. 2018, 18, 3221–3228)

2:15 PM ET05.14.04

 Hybrid Perovskite Heterostructures for Efficient LEDs—Luminescence Performance, Carrier Kinetics and Optical Modeling

 Dawei Di, Baodan Zhao, Neil C. Greenham and Richard H. Friend; University of Cambridge, Cambridge, United Kingdom.
Perovskite-based optoelectronic devices have gained significant attention due to their remarkable performance and low processing cost, particularly for solar cells. However, for perovskite light-emitting diodes (LEDs), non-radiative charge carrier recombination has limited electroluminescence (EL) efficiency. Here we demonstrate perovskite-polymer bulk heterostructure LEDs exhibiting record-high external quantum efficiencies (EQEs) exceeding 20%, comparable with the best solution-processed OLEDs and quantum-dot LEDs. This performance is achieved with an emissive layer comprising quasi-2D and 3D perovskites and an insulating polymer.

Transient optical spectroscopy reveals that photogenerated excitations at the quasi-2D perovskite component migrate to lower-energy sites within 1 ps. The dominant component of the photoluminescence (PL) is primarily bimolecular and is characteristic of the 3D regions. From the near-unity PL quantum efficiencies and transient kinetics of the emissive layer with/without charge-transport contacts, we find non-radiative recombination pathways to be effectively eliminated. Light outcoupling from planar LEDs, as used in OLED displays, generally limits EQE to 20-30%, and we model our reported EL efficiency of over 20% in the forward direction to indicate the internal quantum efficiency (IQE) to be close to 100%. Together with the low drive voltages needed to achieve useful photon fluxes (2-3 V for 0.1-1 mA/cm²), these results establish that perovskite-based LEDs have significant potential for light-emission applications. In general, the ideal luminescence performance we observed is of critical importance for realizing perovskite optoelectronics operating near the radiative limits.

We also present some related results from our group and collaborating groups, on luminescent perovskites for LEDs and photovoltaics.

2:30 PM ET05.14.05
The Application of 2D Materials in Perovskite Solar Cells
Peng You and Peng Yan; Hong Kong Polytechnic University, Hong Kong, China.

We report a cost-effect approach for improving the performance of perovskite solar cells by using novel high-mobility 2-dimensional materials. The efficiency of perovskite solar cells can be substantially increased when 2-dimensional material flakes are coated on the perovskite grain boundaries. The flakes can conduct hole currents efficiently from grain boundaries to hole transport layers in the devices and lead to efficiency enhancements that increase with increasing hole mobilities of the flakes. The results indicate that perovskite grain boundaries are electrically benign and even favorable for photovoltaic performance if accumulated charges around them are conducted out by high mobility hole transport materials.

2:45 PM ET05.14.06
Photo-Induced Lattice Symmetry Improvement in Organic Lead Halide Perovskite and Its Beneficial Effect on Charge-Transfer Dynamics
Hui-Soon Kim and Anders Hagfeldt; Ecole Polytechnique Federale Lausanne, Lausanne, Switzerland.

The hybrid organic lead halide perovskites based on mixed-cations and -anions have been considered as an outstanding composition to achieve high efficiency with long-term stability of perovskite solar cells (PSCs). In this study, the effect of light on the crystal structure of perovskites employing triple cations and double halides was investigated and correlated to the charge-transfer properties. Under the continuous photon excitation, a gradual increase in photoluminescence was observed from the perovskite film, coupled with a minute red-shift. Furthermore, the continuous light soaking induced a gradual peak shift toward lower angle in the X-ray diffraction pattern of the perovskite, strongly suggesting a photo-induced structural response. Notably, a lattice expansion occurred in a certain preferred orientation, which exerted an influence on the crystal symmetry. The trap density of a complete PSC near maximum power point (mpp) was measured under continuous light, showing a gradual decrease. An increase in the photocurrent at mpp was readily observed due to this as a consequence of the reduced trap density. The beneficial charge-transfer properties of PSC under illumination were addressed by relating to the photo-induced structural response of the perovskite.

3:00 PM BREAK

3:30 PM ET05.14.07
Porous Fractals of MAPbI3 Perovskite—Characterization of Crystal Grain Formation by Irreversible Diffusion-Limited Aggregation
Malin B. Johansson1, Ling Xie1, Jakob Thyrl2, Tomas Edvinsson1, Mats Göthelid2, Gunnar Niklasson1 and Gerrit Boschloo2; 1Uppsala Universitet, Uppsala, Sweden; 2KTH, Stockholm, Sweden.

Isopropanol solution based methylammonium lead triiodide (MAPbI3) is studied during the crystallization process. The crystal growth starts in an unstable suspension far from equilibrium by forming different dendritic patterns and terminates with aggregation of stable cubic crystalline grains into fractal clusters. Using transmission electron microscopy (TEM), the time evolution of a newly mixed suspension was studied over a period of two weeks at room temperature and a sequence of the morphological changes was observed. The crystallization process started with single dendritic growth exhibiting branches at 90 degrees angles to one another. After 4 hours, a multi-dendritic growth pattern and a transformation into small crystalline quantum dots were observed. After a week, clusters of crystal grains were formed into a fractal pattern and these patterns appear to be stable also during the second week. Electron and x-ray diffraction revealed the crystallinity of the quantum dots and the clusters of micrometer-sized crystals. Scanning transmission electron microscope (STEM) together with energy dispersive X-ray spectroscopy (EDS) showed that newly formed large grains, from a one hour old solution, displayed a core-shell structure with higher percentage of Pb atoms as compared to iodine at the surface. In, the inner core of the grains the percentage of iodine was slightly higher. The electron diffraction (ED) scan over the newly formed grains revealed a polycrystalline surface whereas the inner part had a single crystal pattern. The same solution, now one-week-old, contained grains with only single crystal patterns in the ED scan and showed no core-shell character or polycrystalline surface. The measured percentage of iodine atoms compared to lead was 2:1 throughout the cross section, which is a quantitative value within the measurement. It can be concluded from these measurements that the suspension approaches higher crystallinity of the perovskite grains in an irreversible process, where the perovskite grains are insoluble in isopropanol. The perovskite material has also been characterized with scanning electron microscopy (SEM) and photoluminescence (PL) mapping where both techniques showed a very porous crystalline material. The PL mapping revealed two peaks at 730 and 760 nm for a thin film spin coated from a newly mixed solution, while a film deposited from a one week old solution showed three peaks, the last one at 830 nm. Because of the high crystallinity, it is suggested that all three peaks are due to band-to-band transitions and not due to localized states. These data will be analyzed further; however, the results contain information of the content of quantum dots versus larger crystals, as well as displaying emission intensity variations at different positions of the grains. The purpose with this project is to understand these phenomena of crystalline growth. A new mesoporous perovskite material has been designed for optoelectronic purposes.

3:45 PM ET05.14.08
Energy Level Alignment at Halide Perovskite Interfaces
Philip Schulz; IPVF, Centre National de la Recherche Scientifique, Palaiseau, France.

The ongoing development of halide perovskite (HP) based optoelectronics has revealed that the numerous interfaces in the device play a crucial role for device functionality, efficiency and stability.1 Importantly, many critical material and interfacial properties are still poorly understood and difficult to assess, a deficiency that often limits efforts to improve the performance.1 We present our most recent results exploring the mechanisms by which organic
semiconductor films, transition metal oxides, and carbon nanotube (CNT) interlayers enable or suppress charge transfer to an adjacent HaP semiconductor film. We use photoemission, X-ray absorption, and transient optical spectroscopy to probe the energy level alignment and exchange of charge carriers between a set of various lead halide based perovskite films and different charge transport layers. Therein, we show that ground state charge transfer between perovskite and a CNT layer can lead to band bending in the transport layer beneficial for charge extraction. Hence, in one example an integrated thin CNT interlayer facilitates rapid charge carrier collection and improves the performance of respective solar cells. In contrast to this observation, band bending induced in the perovskite film by the charge transport material such as high work function oxides or interface defects induced by the oxide formation process can be detrimental for charge carrier collection and thus impede the functionality of respective devices. After examining the recent key developments in chemical and electronic structure characterization of HaPs, I will iterate the next steps towards interlayer tailoring and analysis.


4:00 PM ET05.14.09
Surface Molecular Doping of Metal Oxide Nanocrystals for Interface Engineering of Perovskite Solar Cells Zhaohui Hu1,2, Wei Chen1,2, Bao Tu1,2 and Yinghui Wu1,2; 1Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China; 2Shenzhen Key Laboratory of Full Spectral Solar Electricity Generation (FSSEG), Shenzhen, China.

As a stable and promising hole transport layer (HTL) of planar perovskite solar cells (PSCs), the conductivity of the intrinsic NiO synthesized by solution doping is nevertheless low and its hole mobility is also decreased by the nickel vacancies at deep gap states. In contrast to successful cesium or copper ionic doping in NiO nanocrystals, we applied a novel molecular doping concept into tuning the electronic structure of NiO HTLs by TCNO molecule series. The electron transfer from NiO nanocrystals to the F5TCNNQ molecules absorbed at their surface was observed and verified for the first time by electrostatic force microscopy and the first principle calculations, respectively. The band level offset at the interface of perovskite/NiO shrank from 0.18 to 0.04 eV, which boosted the conversion efficiency of the CsFAMA mixed cations PSCs approaching 21%. Surface molecular doping can not only applied successfully to NiO, but also SnO2, which is also a promising component to planar PSCs. That will be also discussed in this presentation. This methodology definitely paves a novel way to modulate the doping in hybrid electronics more than perovskite and organic solar cells.

4:15 PM ET05.14.10

Hybrid organic-inorganic perovskite thin films or crystals are usually prepared from the perovskite precursor solution. The crystallization of perovskite is affected by the supersaturation of the perovskite precursors in solution and the interfacial energy between the perovskite and solvent. Here, I will present some of our methods to prepare high-quality perovskite thin films and crystals by varying the interfacial energy between perovskite and solvent. The high-quality perovskite thin films lead to highly efficient perovskite solar cells.

4:30 PM ET05.14.11
Quantification of Self-Illumination in >90% Internal Photoluminescence Quantum Efficiency Hybrid Perovskites Roberto Brenes1, Madeleine R. Laiz1,2, Dané W. deQuellet1, Joel Jean1, Zahra Andaji-Garmaroud1, Samuel D. Stranks1 and Vladimir Bulovic1; 1RLE, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Photon recycling is critical for achieving record-high open-circuit voltages (VOC) and power conversion efficiencies (PCE) in single-junction GaAs solar cells. This phenomenon can be observed only in materials with extraordinarily high photoluminescence quantum efficiency (PLQE) and small escape cones. Photon recycling has been observed in hybrid perovskite material qualities, photon recycling could produce practical gains in VOC and PCE. However, the achievable gains in today’s materials remain uncertain. Here we investigate photon recycling in the most emissive (>90% internal PLQE) perovskite films reported to date—humidity-passivated CH3NH3PbI3 and KI-passivated triple-cation perovskites (Cs0.8Na0.2FA0.75MA0.25PbI3) and CsFAMA. Using experimentally measured rate constants and material parameters, we develop a rigorous framework for quantifying (the extent of) photon recycling in thin-film samples and predicting the associated VOC and PCE gains. This analysis clarifies the opportunity for photon recycling to push the real-world performance of perovskite solar cells toward theoretical limits.

4:45 PM ET05.14.12
What Can Be Learned From Self-Healing in Halide Perovskites? Davide R. Cerati1, Yevgeny Rakita1, Llorenç Cremonesi2, Ron Tenne1, Vyacheslav Kalchenko1, Michael Elbaum1, Dan Oron1, Marco A. Potenza1, Gary Hodes1 and David Cahen1; 1Weizmann Institute of Science, Rehovot, Israel; 2Fisica, Universita’ di Milano, Milano, Italy.

Among the aspects of Halide Perovskites, HaPs, which make them such fascinating materials the different time-scales of the dynamics of interconnected processes stand out. Short-time behavior (< sec) is determined by electronic charge carrier dynamics, while longer time effects are typically due to atom/ ion dynamics, characteristic of halide perovskites, such as ion/defect movement, self-healing and others [1-3]. These slower processes are likely interdependent and hitherto not (well) elucidated, both as phenomena and in terms of effects on the performance of HaP-based devices. Our recent work [2] provides clear evidence for self-healing, i.e., under certain conditions damage in optical properties can be reversed and, in particular, the status quo ante [3] can be re-established completely or mostly, in several types of Br-based HaP single crystals, as measured by 2-photon confocal microscopy. We demonstrated qualitatively but unequivocally that the effect is an intrinsic property of the materials, as it was measured in the bulk of single crystals, with typical times of minutes to hours. Here we report on the products of decomposition and possible chemical pathways that can lead to self-healing, paying particular attention to the kinetics of the phenomena. We include new quantitative results of our experiments following the degradation/healing process kinetics in situ and of the energy-
dependent damage threshold. We also show results for the more intensely studied Methylammonium, MA-, and Formamidinium, FA-PbI$_3$. Furthermore, we measure, analyze and explain the crucial differences between the light-induced damaging and recovery mechanisms in the bulk and at the surface under different atmospheres (i.e. air, N$_2$, Br$_2$, I$_2$). Finally, we measure and analyze the temperature dependence of the healing process, as it provides information about the energy of formation of the material from their binary halide constituents. This follows and compares to the reported positive enthalpy of formation of the Br and I MAPb perovskites [4-5], viz. their entropic stabilization.

We will put our results in the broader perspective of other HaP physico-chemical properties and performances of HaP-based device characteristics.

References

SYMPOSIUM ET06

TUTORIAL: The History of Li- and Li-Ion Batteries
November 25 - November 25, 2018

2018 marks the 200th anniversary of the report on discovery of Li element by August Arfwedsen (1818). This incident set off a chain of events that eventually led to the invention of Li-ion battery, which deeply penetrated our daily life: powering our portable electronics, vehicles and gradually becoming part of the smart grid. As a device that integrates many materials and chemistries that were synchronized to work precisely with each other like a timepiece, Li-ion batteries did not happen all at once. It took decades of research and development, assisted by knowledge gradually accumulated in surface chemistry, electrochemistry, materials science and engineering.

Looking back at the history of Li-ion batteries, we will benefit not only from the monumental technical achievement by those great minds in the field, but more importantly, examining the missteps occurred then from a modern perspective will teach us to understand and rethink what could have been done better to accelerate the development of the related technologies in the future.

The tutorial program is designed to consist of 2 segments.

1:30 PM
Lithium Based Anodes: A Look Back into the History
Martin Winter; Helmholtz-Institute Muenster, University of Muenster

The most severe challenge during the development of LIB came from the anode side. In this section Prof. Winter will examine the historical events that gradually shifts people away from Li-metal anode to a carbonaceous and intermetallic host, and how the tide turned again in 2010s, bringing us back to think about the Li metal anode.

3:00 PM BREAK

3:30 PM
Electrolytes and Interphases in LIB
Kang Xu; US Army Research Laboratory

This tutorial intends to give a comprehensive retrospect of how the electrolytes play the central role in bringing together these individual key components of LIB, and how interphases among them synchronize them to work together in a single electrochemical device.
SYMPOSIUM ET06

Advanced Materials and Chemistries for High-Energy and Safe Rechargeable Batteries
November 26 - November 30, 2018

Symposium Organizers
Prashant Kumta, University of Pittsburgh
Xiaolin Li, Pacific Northwest National Laboratory
Xinping Qiu, Tsinghua University
Donghui Wang, The Pennsylvania State University

Symposium Support
ACS Energy Letters | ACS Publications
Angstrom Thin Film Technologies LLC
Bio-Logic USA, LLC
MilliporeSigma
Pacific Northwest National Laboratory

* Invited Paper

SESSION ET06.01: General Introduction, Reliability and Safety
Session Chairs: Daiwon Choi and Joshua Lamb
Monday Morning, November 26, 2018
Hynes, Level 3, Room Ballroom A

8:30 AM *ET06.01.01
Materials for High Energy Li and Li-Ion Batteries M. Stanley Whittingham; State University of New York at Binghamton, Binghamton, New York, United States.

Over the last decade the energy density of lithium-based batteries has gradually increased, but commercially available cells have now topped out at around 200-250 Wh/kg at the cell level. I will describe several materials-centered approaches that will allow in excess of 300-350 Wh/kg and 700 Wh/l. First the carbon-based anode must be replaced by a higher capacity material, preferably lithium metal itself; we have found that tin-based anodes can achieve 50-100% greater capacity than carbons with coulombic efficiencies over 99.5%. Second on the cathode side, I will describe two options: two-electron systems using lithium, and high nickel NMCAs, both of which have theoretical energy densities of around 1 kWh/kg and have the capability of attaining 1 kWh/liter. The safety aspects will also be covered. This work is supported by US DOE, BES-EFRC and EERE-VTO-BMR.

9:00 AM *ET06.01.02
Reliability of Li-Ion Batteries for Grid Application Daiwon Choi, Alasdair J. Crawford, Vilayanur V. Viswanathan, David M. Reed and Vincent L. Sprinkle; Pacific Northwest National Laboratory, Richland, Washington, United States.

Li-ion batteries are expected to play a vital role in stabilizing the electrical grid as solar and wind generation capacity becomes increasingly integrated into the electric infrastructure. In this work, different commercial Li-ion batteries based on LiNi0.8Co0.15Al0.05O2 (NCA), LiNi0.5Mn0.5CoO2 (NMC) and LiFePO4 (LFP) cathode chemistries have been tested under the grid duty cycle protocols recently developed for frequency regulation (FR) and peak shaving (PS) with and without being subjected to electric vehicle (EV) drive cycles. The lifecycle comparison derived from capacity, round trip efficiency (RTE), resistance, charge/discharge energy and total utilized energy of the battery chemistries will be presented. Furthermore, degradation mechanisms of different battery chemistries will be discussed. The results can be used as a guideline for selection, deployment, operation and cost analyses of Li-ion batteries used for different applications.

9:30 AM BREAK

10:00 AM *ET06.01.03
Mechanisms and Ramification of Overcharge on Battery Materials Joshua Lamb, Loraine Torres-Castro, Mohan Karulkar and Jane Stanley; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Overcharge testing has long been used as a standard abuse test evaluation for lithium ion batteries, which have notably poor tolerance for overcharge and overvoltage conditions. While this has historically been strictly an abuse test, large potential gradients created by high rate charge and discharge operations in electric vehicle and stationary storage applications may lead to areas of localized overcharge or overpotential on the electrodes. This work looks at high capacity (10 AH) prismatic pouch cells, applying overcharge from 105 – 200% total State of Charge (SOC), up to and including energetic thermal runaway of cells. The mechanisms of overcharge failure are investigated using electrochemical techniques including EIS and differential capacity measurements to evaluate the degradation and failure mechanisms that occur during the overcharge condition. This is supported with materials evaluations to further evaluate the impact of overcharge on the constituent materials.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.
Multifunctional Lithium-Ion Exchanged Zeolite Coated Separator for Lithium-Ion Batteries

Jiagang Xu, Xingcheng Xiao, Sherman Zeng, Mei Cai and Mark Verbrugge; General Motors, Warren, Michigan, United States.

The skyrocketing price of cobalt pushes battery manufacturers to look back into low cost manganese containing positive electrodes. However, manganese dissolution has been considered as a critical problem for the majority of manganese containing positive electrodes. Although many efforts have been devoted to stabilizing the crystal structure and exploring new electrolyte additives, less progress has been reported so far. In this work, we have developed a novel multifunctional separator, targeting the root cause of manganese dissolution. A lithium-ion exchanged zeolite has been coated on polymer separator as the ceramic coating, which provides multi-functions to mitigate the issues arose from sequential scenario associated with manganese dissolution, including: 1. Trapping trace water: the high surface area in zeolite traps the trace water in the electrolyte, mitigating the hydrolysis of lithium salt and HF generation. 2. HF scavenger: in case of the HF already existing in the electrolyte, Al2O3 in the zeolite can preferentially react with HF as the scavenger due to the high surface area, therefore protecting the oxides in positive electrodes 3. Trapping Mn ions: in the worst scenario of Mn dissolved into electrolyte, the Li ion in zeolite will have the ion exchange with Mn ions in the electrolyte and trap Mn ions in the separator to avoid its damage to the SEI layer on anode side. In addition, lithium-ion exchanged zeolite separator can improve the wettability and thermal stability of the plain separator on which zeolite is coated. Based on this technology, we have demonstrated that Lithium-ion exchanged zeolite separator leads to the enhanced cycle performance (high capacity and Coulombic efficiency) of graphite/ (LiNi0.5Mn1.5O4+Li2MnO3) full cells at both room temperature and elevated temperature, comparing with the plain separator and commercial alumina coated separator. The coin cell with Li-zeolite coated separator exhibits an average Coulombic efficiency of 99.89% and achieves a capacity retention rate of 78.3% after 500 cycles at 25°C. We find out that a lower amount of manganese is present on the cycled graphite electrode when Li-zeolite coated separator is used, suggesting less side reactions resulted from Mn.

Novel Battery Separators Enabled by Ultrathin, Robust Solid Electrolytes

Shaofei Wang1, Andrew S. Westover2, Sergiy Kalnaus2, Andrew Kercher2, Nancy J. Dudney3, William C. West3 and Wyatt Tenhaeff4; 1University of Rochester, Rochester, New York, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3NASA Jet Propulsion Laboratory, Pasadena, California, United States.

Solid electrolytes with low area specific resistance must be developed to enable high energy density lithium metal batteries. In addition to high ionic conductivities and large electrochemical stability windows, solid electrolytes also require robust mechanical properties to allow for large-scale production and successful integration into conventional lithium battery cell designs. To achieve these features, a novel solid electrolyte separator design was developed, in which a 50 - 100 nm fully dense solid electrolyte layer was coated onto microporous Celgard separators. The supporting Celgard made the solid electrolyte more robust and flexible, which enabled integration into coin cells. Due to its thinness, the resistance of the solid electrolyte layer was 5 - 10 Ω-cm². The solid electrolyte also showed low interfacial resistance with liquid electrolyte. The total resistance of solid electrolyte-Celgard membrane was determined to be 40 Ω-cm² in alkyl carbonate electrolytes, which is much lower than Garnet and Ohara solid electrolytes. The solid electrolyte membrane also was also shown to inhibit the crossover between anode and cathode in Li-S cells. The solid electrolyte membranes showed high coulombic efficiency and stable cycling performance. The advent of the new solid electrolyte paves the way for the commercialization of high energy density lithium metal batteries.

This work was supported by the ARPA-E IONICS program, U.S. Department of Energy, award DE-AR0000775.

Long-Term Calendar Degradation in Li-Ion Batteries

Aziz Abdellahi, Berislav Blizanac and Brian Sisk; A123 Systems LLC, Waltham, Massachusetts, United States.

With the increased penetration of electrified vehicles in the automotive market, requirements pertaining to battery durability are becoming increasingly stringent. To meet the requirements of the automotive industry, lithium-ion batteries must exhibit extensive life before reaching a terminal state of capacity loss and impedance growth. For battery designers and manufacturers, it is therefore of paramount importance to understand and predict long-term battery cell degradation based on a necessarily limited set of accelerated degradation tests.

Long-term calendar aging, defined as the temperature-induced cell degradation in the absence of current, is especially difficult to predict at relevant battery operating temperatures (25°C – 45°C). Unlike cycling tests, which can be rapidly conducted to the end-of-life by removing rest periods between cycles, calendar tests cannot be directly accelerated. To this end, a variety of empirical and physics-based models have been developed to predict the long-term storage behavior of battery packs based on a set of accelerated storage tests conducted at high temperatures. However, the validity of these calendar predictions has not, to the best of our knowledge, been extensively studied against actual long-term storage data surpassing the 4 year mark.

In this presentation, we present a set of long-term storage experiments performed over the course of 4- to 6- years on LiFePO4/graphite cells, at various states of charge and temperatures. Analysis of the storage data sheds light on the long-term degradation mechanism in the cell, and demonstrates a transition between a reaction-controlled to a diffusion-controlled growth of the anodic solid electrolyte interphase (SEI). The dependence of state of charge and temperature on the degradation rate is clarified, and the predictive performance of empirical calendar life models is assessed. This work provides a mechanistic analysis of the nature of long-term degradation mechanisms in Li-ion batteries and paves the way towards an improvement of the predictive ability of empirical calendar life models. The conclusions of this study can also serve to understand long-term calendar degradation in higher-voltage NMC/graphite batteries, in which both the anode and the cathode may experience calendar degradation at high states-of-charge.

Adaptive Current-Collectors for Safe High-Energy Rechargeable Batteries


High energy density rechargeable batteries are critical for the widespread adoption of EVs, however their high energy density leads to an inherent safety risk if an internal short circuit (ISC) forms and releases all the energy in the battery in seconds. When an ISC occurs – from dendrite formation, cell deformation/damage, or a manufacturing defect – the entire battery capacity rapidly discharges. This release of energy leads to extremely high temperatures near the short that can induce thermal runaway, cell rupture or venting, and fire. While the use of shutdown separators can help mitigate ISCs in smaller cells, they are often ineffective in the larger, high-energy batteries used in EVs and grid storage applications. Rather than relying on thermally-induced shutdown that may fail to shut down regions of the battery far from the ISC, it is preferable to directly detect and stop the internal current that flows during an ISC. In this presentation, I will introduce our work on adaptive current-collectors, which allow for direct control over the local current that flows between the current-collector and the active material by simple printed electronic circuits. I will show how the electrical properties of printed electronics

ET06.01.04

10:30 AM ET06.01.05

10:45 AM ET06.01.06

11:00 AM ET06.01.07

11:15 AM ET06.01.07
can be tuned to meet the demanding requirements of adaptive current-collectors, including low resistance during normal operating currents and high resistance under DC. Our simulations indicate that adaptive current-collectors can reduce the current flowing through ISCs by more than 90%, converting this catastrophic failure mode into a graceful one. In addition to enabling safe high-energy rechargeable batteries, the development of adaptive current-collectors will give battery users finer control over current flow at the sub-cell level, which is expected to improve battery reliability and rate capability.

SESSION ET06.02: All Solid-State Battery
Session Chairs: Xiaolin Li and Donghai Wang
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room Ballroom A

1:30 PM ET06.02.01
All-Solid-State Lithium Metal Batteries Utilizing Polyrotaxanes as New Family of Solid Polymer Electrolytes
Laura Ihnhol1, Gunther Brunklaus1, Isidora Cekic-Laskovic1 and Martin Winter1, 2; 1Helmholtz Institute Münster HI MS, Forschungszentrum Juelich GmbH, Muenster, Germany; 2MEET Battery Research Center, University of Münster, Münster, Germany.

Lithium metal constitutes an attractive anode material mainly due to its high theoretical specific capacity of 3860 mAh g⁻¹, ten times higher than graphite (372 mAh g⁻¹). The use of lithium metal in rechargeable batteries with typical liquid organic solvent based electrolytes suffers so far from severe safety problems associated with the formation of high surface area metallic lithium (HSAL) upon repeated charge/discharge.[1] Solid polymer electrolytes (SPEs) designed to be compatible with lithium metal are able to mechanically suppress HSAL formation and are considered as viable alternative. Solvent-free SPEs exhibit advantages in terms of mechanical stability, operational safety and simplicity of cell design.[2] However, application of polymer electrolytes to all-solid-state lithium ion batteries (ASS-LIBs) and all-solid-state lithium ion batteries (ASS-LMBs), requires improvements in respect to lithium ion conductivity, especially at ambient temperature. Although high ionic conductivities can be achieved by high chain mobility linked to low molecular weight polymers, they are mostly too soft and therefore cause deterioration in mechanical stability of the SPE. In order to use low molecular weight polymers for fast lithium ion transport with sufficient mechanical strength at the same time, one strategy is related to utilization of a hyperbranched co-polymer where one segment represents a stable, hard backbone while the second segment is derived from a soft polymer with high ionic conductivities.[3] With this in line, a new generation of Li⁺-conducting SPEs obtained from supramolecular self-assembly of PEO, cyclodextrin (CD) and lithium salt was designed and thoroughly investigated for application in lithium metal batteries (LMBs) and LIBs. When mixing an aqueous solution of PEO together with an aqueous solution of CD, a precipitate forms where the CD is threaded onto a PEO chain.[4] The channel-type structure formed by self-assembly of PEO and CD can be used as the backbone structure whereas the hydroxyl groups of CD rings can be modified. Here, we use the ability of CD being the initiator for ring-opening polymerization of cyclic carbonates. This strategy enables synthesis of grafted polycarbonate side chains with low molecular weight. The obtained inclusion complexes show impressive ionic conductivity up to 1 mS cm⁻¹ at 60 °C, together with high oxidative stability and allow for application in LFP/Li cells at 40 °C for more than 200 charge/discharge cycles. Post mortem XPS and SEM studies confirm that the polymer/LiTFSI penetrates the cathode upon cycling, facilitating improved contacts. This new system provides a platform for further modifications of the polymer side-chains.

2:00 PM ET06.02.02
First-Principles Modeling of Polymer Electrolyte/Lithium-Metal Interfaces for High Energy Batteries
Maha Ebadi2, Cleber Marchiori1, Daniel Brandell2 and Movses Arujo1; 1Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden; 2Department of Chemistry, Uppsala University, Uppsala, Sweden.

Lithium metal combines the lowest reduction potential in the electrochemical reactivity series with a high theoretical specific capacity, and using metallic Li as anode would therefore significantly improve the energy density of the Li-battery. There exist, however, some challenges in the application of the Li metal electrode, such as safety risks and low coulombic efficiency [1]. In recent years, there has been a growing interest to find more stable electrolytes when in contact with the reactive Li electrode in Li-metal batteries. It has in this context been found that solid polymer electrolytes (SPEs), formed by doping a polymer with a lithium salt, are promising candidates, which can provide both high mechanical stability and better battery safety [2,3]. The major disadvantage of SPEs – their low inherent ion conductivity – can be resolved by a somewhat higher operational temperature. We have, in a number of studies [4-6], modelled the Li metal/electrolyte interface using different simulation techniques. In this current study, we apply computational materials modelling to investigate the interface between the ion-conductive polymeric systems and Li metal surfaces by first principle calculations. To this end, Density Functional Theory (DFT) have been used to study several potential SPE host polymers such as poly(trimethylene carbonate) (PTMC), poly(vinyl alcohol) (PVA) and polycaprolactone (PCL), in order to get insights into their electronic structures and their stability when in contact with the Li metal surface. Using this knowledge, conclusions are drawn on which ion-conductive polymers are stable at the Li-metal surface, and which can adhere well to it.

References:

2:15 PM ET06.02.03
Stabilizing Polymer Electrolytes in High-Voltage Lithium Batteries
Snehashis Choudhury and Lynden Archer; Cornell University, Ithaca, New York, United States.

More than forty years after the first report of a rechargeable lithium battery, electrochemical cells that utilize metallic lithium anodes are again under active study for their potential to provide more energy dense storage in batteries. Electrolytes based on small-molecule ethers and their polymeric counterparts are known to form stable interfaces with alkali metal electrodes and for this reason are among the most promising choices for rechargeable lithium batteries.
Uncontrolled anionic polymerization of the electrolyte at the low anode potentials and oxidative degradation at the working potentials of the most interesting cathode chemistries have led to a quite recession in the field that solid-state or flexible batteries based on polymeric electrolytes can only be achieved in cells based on low- or moderate-voltage cathodes. In this work, we show that cationic chain transfer agents in an ether electrolyte provide a fundamental strategy for limiting polymer growth at the anode, enabling long term (at least 2000) cycles of high-efficiency operation of asymmetric lithium cells. Building on these ideas, we also report that cathode electrolyte interphases composed of anionic polymers and the superstructures they form spontaneously at high electrode potentials provide as fundamental a strategy for extending the high voltage stability of ether-based electrolytes to potentials well beyond conventionally accepted limits. Through computational chemistry, we discuss the mechanistic processes responsible for the extended high voltage stability and on this basis report Li||NCM cells based on a simple diglyme electrolyte that offer unprecedented stability in extended galvanostatic cycling studies.

2:30 PM COFFEE BREAK

3:00 PM *ET06.02.04

Design Principles for Solid Electrolyte–Electrode Interfaces in All-Solid-State Li-Ion Batteries Yifei Mo; University of Maryland-College Park, College Park, Maryland, United States.

All-solid-state Li-ion battery is a promising next-generation energy storage technology, providing intrinsic safety and higher energy density. Currently, high interfacial resistance and interfacial degradation at the solid electrolyte-electrode interfaces are the critical issues limiting the cycling and rate performance of all-solid-state battery. Fundamental understanding about the interfaces is yet lacking due to the difficulties of direct experimental characterizations. In this presentation, I will show how we use first principles computation to bring new understanding about these buried interfaces. Using our developed computation approach based on large materials database, we calculated the true electrochemical stability window of solid electrolytes and predicted interphase decomposition products, which are verified by in-situ experiments at solid electrolyte-electrode interfaces. I will discuss the critical role of decomposition interphase layers at electrolyte-electrode interface and their effects on the battery performance. From these insights, we are able to classify different interface types for different solid-electrolyte and cathode pairs and to estimate their impacts on battery performance. Moreover, specific interfacial engineering strategies are proposed to address potential issues at these interfaces in all-solid-state Li-ion batteries. I will present the predicted novel chemistry and strategies to stabilize lithium metal anode, which is greatly impeded by the lack of knowledge about lithium-stable materials chemistry. With first-principles calculations based on large materials database, we found that most oxides, sulfides, and halides, which were commonly studied as protection materials, are reduced by lithium metal due to the reduction of metal cations. New materials chemistry that are stable against Li metal are predicted, as promising candidates for lithium metal anode protection to achieve long-term stability. This series of computational studies provides novel insights and general design principles for interface engineering in all-solid-state Li-ion batteries.

3:30 PM *ET06.02.05

Recent Advances in Electrode Materials and Solid Electrolytes for Li-Metal Batteries Yu-Guo Guo; Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

The attempt to build high-energy density solid-state Li-metal batteries (SBLMBs) has attracted more and more attention. Here, we report our recent progress in SBLMBs. Regarding to the key issues of Li metal anodes, 3D current collectors (e.g., 3D Cu), nanostructured carbon materials (e.g., carbon spheres, solid or hollow carbon fibers, nitrogen-doped graphitic carbon foams), artificial SEI layers (e.g., Li2PO3, LiPAA), functional electrolyte additives (e.g., Al-based colloidal particles, ionic liquids), as well as multilayered solid electrolytes have been demonstrated feasible as functional materials for stable plating of Li to address the above issues. The rapid capacity decay caused by the poor contact and large polarization at the interface between the cathode and solid electrolytes is still a big challenge to overcome for high-power-density solid batteries. Recently, we have reported three strategies to address this issue. (i) A superior Li conductive transition layer LATP is introduced to coat NCM622, as a model cathode, to mitigate polarization and enhance dynamic characteristics. The critical attribute for such superior dynamics is investigated by the atomic force microscopy with boundary potential analysis, revealing that the formed interfacial transition layer provides a gradual potential slope and sustain-released polarization, and endows the battery with improved cycling stability and excellent rate capability at room temperature, which enlightens the comprehension of interface engineering in the future solid batteries systems. (ii) The interfacial interface of can also be ameliorated by coating the cathode of MCN622 with a LiBO2 glass layer. The continuous coating acts not only as a physical barrier hindering the decomposition of polymer electrolyte but also as a buffer layer promoting lithium diffusion across the space charge layer. (iii) This issue can be effectively addressed by constructing a poly (acrylonitrile-co-butadiene) coating layer onto the surface of NCM622 cathode materials. The polymer layer plays a vital role in working as a protective shell to retard side reaction and ameliorating the contact of the solid-solid interface during the cycling process. The key bottleneck troubling the application of solid electrolyte is the contradictory requirements from Li metal and cathode, which need high modulus to block Li-dendrite penetration and flexibility to enable low interface resistance, respectively. Our recent study describes a thin asperometric galvanostatic discharge of solid electrolyte to address these shortcomings. We propose a rational strategy to construct a thin and asymmetric solid electrolyte with a rigid ceramic LLZO layer modified with 7.5 nm polymer and a soft polymer layer for SBLMBs to fulfill the requirements of Li-metal and cathode, obtaining a dendrite-free Li-anode and low interface resistance. This ingenious arrangement endows solid Li-metal batteries with extremely high Coulombic efficiency and cyclability.

4:00 PM ET06.02.06

Effects of Polymer Coatings on Electrodeposited Lithium Metal Jeffrey F. Lopez1, Allen Pei2, Yi Cui2 and Zhenan Bao3; 1Chemical Engineering, Stanford University, Stanford, California, United States; 2Materials Science and Engineering, Stanford University, Stanford, California, United States.

The electrodeposition of lithium metal is a core process in next-generation, high energy density energy storage devices. However, the high reactivity of the lithium metal causes short cycling lifetimes, and there are safety issues due to the growth of dendrites. Recently, a number of approaches have been pursued to stabilize the lithium metal interface, including soft polymeric coatings that have shown the ability to enable high-rate and high-capacity lithium metal cycling, but a clear understanding of how to design and modify these coatings has not yet been established. In this work, we studied the effects of several polymers with systematically varied chemical and mechanical properties as coatings on the lithium metal anode. By examining the early stages of lithium deposition we determine that while global morphology depends on the coating quality and mechanics, the local morphology of the lithium particles is strongly influenced by the chemistry of the polymer coating. We have identified polymer dielectric constant and surface energy as two key descriptors of the lithium deposit size. Low surface energy polymers were found to promote larger deposits with smaller surface areas. This is consistent with a reduction of the coatings interactions with the lithium surface and thus an increase in the interfacial energy. On the other hand, high dielectric constant polymers were found to increase the exchange current and gave larger lithium deposits, suggesting improved Li+ ion solvation in the coating and decreased nucleation rate. We also note that the thickness of the polymer coating should be optimized for each individual polymer, and that polymer reactivity is an important parameter to be considered as it was found to strongly influence the Coulombic efficiency. Overall, this work offers new fundamental insights into lithium electrodeposition processes and provides direction for the design of new polymer coatings to better stabilize the lithium metal anode.
Design and Architecture of a Stable Solid-Electrolyte Interphase for the Lithium Metal Battery Anode Using a Reactive Polymeric Composite Yue Gao, Tianhao Chen, Qingquan Huang, Thomas Mallouk and Donghai Wang; The Pennsylvania State University, University Park, Pennsylvania, United States.

Rechargeable battery technology based on the lithium (Li) metal anode is plagued by the unstable solid-electrolyte interphase (SEI), which grows upon cycling and is associated with dendritic/mossy Li deposition. A key challenge in improving SEI stability lies in regulating its chemical composition and nanostructure. Here we report a new approach that enables the design of SEI layers with tunable structure and stable properties. This involves the use of a reactive polymeric composite, which can generate a stable SEI layer in situ by reacting with Li to occupy surface sites and then electrochemically decomposing to form nanoscale SEI components. Cryo-TEM shows that the resulting SEI layer is composed of organic polymeric Li salts, nanoparticles of inorganic Li salts, and two-dimensional nanosheet components. This conformal nanocomposite SEI layer exhibits excellent passivation, homogeneity, ionic conductivity, and mechanical strength and stabilizes the interface for dendrite-free Li deposition in a conventional carbonate electrolyte. 950-cycle life was achieved in a full cell paired with a LiNi0.5Co0.2Mn0.3O2 cathode. Moreover, under lean electrolyte conditions, the full cells also show significantly extended cycle lives, owing to the excellent stability of the polymeric nanocomposite SEI.

Design and Characterization of a Solid Hybrid Electrolyte for Lithium-Ion Batteries Florent Leclercq, Cédric Lorthioir, Laura Coustan and Christel Laberty-Robert; Sorbonne Université, Faculté de Science et D’ingénierie, Laboratoire de Chimie de la Matière Condensée de Paris, Paris, France.

Despite the development of new technologies, such as lithium-sulfur or sodium-ion cells, lithium-ion devices remain the most used batteries: they are found in a majority of electronic devices and the demand for electric vehicles keeps growing. Their performance and characteristics vary according to the chosen electrode but their main advantages are their high energy density and their low self-discharge. However, lithium-ion batteries suffer safety risks which are mainly due to the use of liquid electrolytes. These electrolytes are based on a lithium salt dissolved in a mix of organic solvents and therefore are highly flammable. A safer alternative is to replace this liquid electrolyte by a solid one. Ceramic electrolytes are a first possibility but they are often complex to synthesize and too rigid. Thus, solid polymer electrolytes are good candidates regarding their flexibility but they have a rather low conductivity and poor mechanical properties.

This work focuses on the conception of a solid hybrid electrolyte. The organic part is composed of a mix of polyethylene oxide (PEO), known for its lithium conductivity, and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP), known for its mechanical properties. The inorganic part is a silica network formed in situ via a sol gel reaction. This network is functionalized with an immobilized ionic liquid in order to increase the conductivity of the electrolyte. These components are dissolved in N,N-dimethylformamide altogether with a lithium salt, LiTFSI, and a first set of solid electrolyte is accomplished by solvent casting. Conductivity and lithium transference number are measured in temperature while the structure and the transport at different scales are analyzed by NMR, SAXS-WAXS, and Differential Scanning Calorimetry (DSC). Electrochemical performances at different rates are assessed in full cell using LiFePO4 as the cathode and metallic lithium as the anode. Then, the importance of microstructure is investigated by achieving a second set of solid electrolyte. A skeleton of PVDF-co-HFP and functionalized silica is electrosyn, producing a mat of fibers of 100nm in diameter. The space between fibers is then filled by concentrated LiTFSI or PEO/LiTFSI salts. The structure as well as their performances will be discussed using the same techniques.

Effects of Ionic Correlation on Transport in Solid Polymer and Concentrated Ionic Liquid-Based Electrolytes from Molecular Dynamics Simulations Nicola Molinari1, 2, Jonathan Mailoa2 and Boris Kozinsky1, 2; 1SEAS, Harvard University, Cambridge, Massachusetts, United States; 2Robert Bosch LLC, Cambridge, Massachusetts, United States.

Electrolytes have become key players in the design of modern high-energy solutions as they can be leveraged to enhance various important aspects of the device such as recharge time and efficiency, anode/cathode stability, and safety. However, conductivity and general transport properties of the cation/anion pair(s) dissolved in the electrolyte often pose a technological limit to the viability of the battery, and progress in fundamental insights into the origin of transport limitations are challenging yet extremely valuable. In our group, molecular modelling techniques are adopted in order to shine light on transport properties and correlation effects in electrolyte system.

Poly(ethylene) oxide (PEO) -based solid polymer electrolytes have a long history of research due to the easy processability and good transport properties, yet new observations that challenge our conventional understanding are still reported, especially at high salt concentrations relevant for technological applications. Our molecular dynamics simulation study of such regimes for one of the most prominent materials, PEO-LiTFSI, reveals the central role of NaFSI concentrations. Several recent studies focus on assessing the performance of different mixtures. Given the highly-correlated nature of these systems, understanding the role of species correlation is non-trivial yet crucial for a rational design of future solutions. As a case study we investigated the promising NaFSI-C3C1PyrrFSI system at different Na concentrations and focus on highlighting the correlations in this system as well as how they effect the transference number for high NaFSI concentrations.
Understanding the surface reactivity between electrode and electrolyte is critical for cycle life of Li-ion batteries. The composition, properties and mechanisms behind electrolyte/electrolyte interface (EEI) on positive electrode are still unidentified for most lithium ion battery positive electrode materials [1,2]. Especially at high potentials, EEI layer on positive electrode becomes more critical since it approaches electrolyte instability limit for oxidation. The EEI layers on carbon-free, binder-free and thin film LiCoO2 electrodes were investigated by using X-ray photoelectron spectroscopy (XPS). The growth of oxygenated and carbonated species was observed together with salt decomposition starting at 4.1 V\textsubscript{Li} [3]. By DFT calculations, we correlated the EEI composition to the thermodynamic tendency of the EC solvent for dissociative adsorption on the LiCoO2 surface, which can have a role in the salt decomposition on oxide surfaces [4]. The salt decomposition products had been also observed by solution 19F-NMR measurements. Finally, we demonstrated that the addition of diphenyl carbonate to the electrolyte has a strong impact on EEI layer and salt decomposition on LiCoO2 surface. With this study, we also highlight the strength of using the carbon-free, binder-free electrodes to get fundamental insights in the reactivity of the positive electrode with the electrolyte.


ET06.03.02
Examining the Conductivity of Swollen Crosslinked Ionic Liquid Gels
Prevyo Kuray, Jiho Seo, Clara Capperelli, Carlos Fernandez and Michael Hickner; The Pennsylvania State University, University Park, Pennsylvania, United States.

Gel polymer electrolytes (GPEs) are a branch of solid polymer electrolytes obtained by swelling liquid solvent, plasticizer, or ionic liquid into a polymer-salt matrix. Due to their solid-like nature and conductive properties, GPEs are attractive as electrolytes in battery applications and other areas where liquid electrolytes are undesirable. Here, 1-methylimidazolium2-acrylamido-2-methylpropanesulfonate ([AMPs][Mim]) and poly(ethylene glycol) (PEG) were cross-linked and solvated to create a novel set of non-volatile conductive gels. We employed dielectric relaxation spectroscopy to measure the conductivity as a function of temperature for different solvents in our base material. By cross-linking [AMPs][Mim] and incorporating various solvents, we obtain a conductive polymeric gel material that is mechanically robust, circumvents issues of leakage and flammability found in traditional ionic liquid electrolytes. This study opens the door to safer polymer electrolytes for electrochemical applications.

ET06.03.03
Porous Single-Crystal NaTi(PO4)2 via Liquid Transformation of TiO2 Nanosheets for Flexible Aqueous Na-Ion Battery
Yanhao Dong and Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recently, aqueous energy storage systems (AESSs), such as Na-ion battery & capacitor, have demonstrated their uniqueness compared with their non-aqueous counterparts due to the excellent safety performance in nature. Furthermore, the advantage of their low cost derived from the high abundance of sodium and the simplified process in ambient endows AESSs the possibility of application in large-scale power grid. However, restricted by the narrow electrochemical window (~1.23 V) of water, the common used electrode materials in non-aqueous batteries/capacitors such as transition metal oxides/sulfides/selenides are directly excluded from the scope due to the high voltage platform, other than limited kinds of materials like NASICON-type NaTi(PO4)2 with appropriate voltage platform. Nevertheless, conventional NaTi(PO4)2 materials with irregular morphology and large size prepared by solid-state reaction still hinder the application of AESSs. Herein, a newly structured porous single-crystal NaTi(PO4)2 with uniform sizes was fabricated via a well-designed novel liquid transformation of ultrathin TiO2 nanosheets, followed by coating a conductive carbon sheath. To best of our knowledge, this is the first report of the porous single-crystal structure of NaTi(PO4)2 materials. Examined in a three-electrode cell, this NaTi(PO4)2 electrode demonstrates an outstanding rate capability of 80-102 mAh g\textsuperscript{-1} at varied current densities of 0.5-3 A g\textsuperscript{-1} due to the synergistic effect between porous nanostucture and outstanding stability originated from single-crystal structure. The high-quality NaTi(PO4)2 was also assembled with N-doped carbon to fabricate an aqueous Na-ion battery with robust flexibility. This work paves the way for designing advanced NASICON based materials for aqueous energy storage systems.

ET06.03.04
Solid State Synthesis Revisited—Ni-Rich Cathode
Yanhao Dong and Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Ni-rich cathode materials for lithium-ion batteries, commonly in the forms of LiNi\textsubscript{x}Co\textsubscript{1-x}Mn\textsubscript{2}O\textsubscript{4} (NMC) and LiNi\textsubscript{x}Co\textsubscript{1-x}Al\textsubscript{2}O\textsubscript{4} (NCA), are of great interests in commercial applications due to their high reversible capacity and relative low cost compared to LiCoO2. Due to the well-known Ni/Li cation mixing problem, such a multicomponent (high-entropy) compound cannot be synthesized at elevated temperatures, the more so the higher Ni concentration. This temperature doctrine suppresses the inter-diffusion kinetics between transitional metal ions (Ni, Co, Mn, Al etc.) during material synthesis, hindering a homogeneous distribution and electrochemical properties, and limits the achievable particle size, impeding electrode packing and volumetric energy density. This is part of the reason why solid state synthesis of NCM/NCA materials was not successful. The comundum is tentatively solved by introducing a specialized co-precipitation technique and self-agglomerated secondary particles (~10 micron) for NCM/NCA systems. Yet the secondary particles would still crack along grain boundaries during electrode pressing and electrochemical cycling. Therefore, micron-size single-crystalline NCM/NCA with good electrochemical properties is a great treasure. In our recent work, we revisited the solid state synthesis of such single-crystalline Ni-rich cathodes and obtained compelling capacities with the state-of-the-art co-precipitation technique, thus re-opening the doors to process Ni-rich cathodes in the same synthesizing route as classical LiCoO2 and genius control of doping and coating at the primary-particle level.

ET06.03.05
Superoxide Dismutase-Mimetic Fullereene Derivative as a Mobile Catalyst for Lithium-Oxygen Batteries
Chihyun Hwang1, JongTae Lee2, Gwan Yeong Jung3, Seun Joo1, Jonghak Kim1, Aming Cha1, Soek-Ju Kang1, Sang-Kyu Kwak1, Sang-Young Lee1 and Hyun-Kon Song1; 1UNIST, Ulsan, Korea (the Republic of); 2KISTEP, Seoul, Korea (the Republic of).

Reactive superoxide triggers side reactions during discharge of lithium-oxygen batteries (LOBs) and therefore affects seriously harmful effects on LOB performances. In living organisms exposed to oxygen, superoxide dismutase (SOD) manages superoxide in a way of converting the reactive species to less
reactive oxygen and peroxide. Herein we adopted a functionalized fullerene molecule (MA-C$_{60}$ where MA = maleic acid) that mimicked dismutation or decomposition function of SOD. Superoxide-triggered side reactions during discharge were significantly reduced by MA-C$_{60}$ so that desired oxygen evolution reaction was dominantly encouraged during charge with less CO$_2$ evolution. Toroidal lithium peroxide particles were generated, which indicated that solution mechanism for peroxide formation was favored. Resultantly, MA-C$_{60}$-containing LOB cells exhibited tremendously improved capacities especially at high rates.

ET06.03.06
New 4V-Class and Zero-Strain Cathode Material for Na-Ion Batteries Jongsoo Kim; Sejong University, Seoul, Korea (the Republic of).

We developed NaN$_3$V(PO$_3$)$_3$N as a novel 4V-class and zero-strain cathode material for Na-ion batteries. Through the combined studies using neutron and X-ray diffraction, it was identified that the NaN$_3$V(PO$_3$)$_3$N contains 3-dimensional channels, which enables the facile Na diffusion in the structure. The Na (de)intercalation of NaN$_3$V(PO$_3$)$_3$N was occur at ~4 V (vs Na/Na$^+$) via the V$^{3+}$/V$^{4+}$ redox reaction and its capacity retention over 3000 cycles was ~67% of the initial capacity. The remarkable cycle stability was due to the near-zero volume change (~0.24%) and the unique centrosymmetric distortion that occurs during a cycle despite the large ionic size of Na ions for (de)intercalation, as demonstrated by ex-situ XRD analyses and first-principles calculations. We also demonstrated that the NaN$_3$V(PO$_3$)$_3$N could show the outstanding power capability with ~84% retention of the theoretical capacity at 10C, which is attributed to its intrinsic 3-dimensional open-crystal framework. The combination of this high power capability and extraordinary cycle stability enables the application of NaN$_3$V(PO$_3$)$_3$N to a promising cathode material for Na-ion batteries.

ET06.03.07
Vanadium Oxide Nanosheets for Flexible Dendrite-Free Hybrid Al-Li-Ion Batteries Xuefei Gong and Pooi See Lee; MSE, NTU, Singapore, Singapore.

Although lithium (Li) ion batteries have been the focus of research in energy storage devices for the last decades and significant progresses have been made towards high energy densities and improved safety, the dendrites formation with lithium metal as anodes is still difficult to address effectively and fundamentally. In contrast, aluminum (Al) ion batteries with Al anodes inherently possess the advantages of resisting dendrite growth and lower in cost, which make Al-ion batteries attractive as an alternative to Li-ion batteries. In addition, based on three electron transfer redox reactions, Al delivers high volumetric and gravimetric capacities, which provides promising applications in cost-effective and large-scale energy storage systems. However, the developments of Al-ion batteries are restricted by the sluggish kinetics of Al$^{3+}$ ions diffusion and insertion/extraction, due to large ionic size of Al$^{3+}$ ions and strong electrostatic force between host materials and trivalent Al$^{3+}$ ions. It can lead to decreased intercalation sites in host materials.

In this work, a concept of hybrid Al-Li-ion battery has been proposed, which utilizes the Li$^+$ ions intercalation/deintercalation into/from the cathode materials because of smaller size, less charge and faster ion transport of Li$^+$ compared to Al$^{3+}$ and Al stripping/deposition on the surface of aluminum foil anode due to higher redox potential of Al/Al$^{3+}$ (~1.67 V vs. SHE) compared to Li/Li$^+$ (~3.04 V vs. SHE), thus circumventing the sluggish kinetics and maintaining the dendrite-free formation of Al-ion batteries. Subsequently, a hybrid Al-Li-ion battery, composed of vanadium oxides on carbon fibers as cathode, Al foil as anode and [EMIM][Cl]/AlCl$_3$/LiCl as electrolytes, has been successfully fabricated. This hybrid battery delivered a high volumetric capacity of 325 mAh/cm$^3$ at a current density of 10 mA/cm$^2$ (based on the total volume of cathode including carbon fibers as current collectors) and maintains 215 mAh/cm$^3$ even at 100 mA/cm$^2$. More impressively, the capacity could be retained 70.1% after 3000 cycles, much better than other Al-ion batteries reported. The excellent electrochemical performance could be attributed to the improved kinetics with the introduction of Li$^+$ ions into the electrolyte as well as the 3-D porous structures of cathode materials. Moreover, structural integrity under different bending conditions could be achieved because of good flexibility of cathode and anode. Therefore, this work unveils a safe, cost-effective and flexible hybrid Al-Li-ion battery that presents highly competitive advantages among various energy storage devices.

ET06.03.09
Encapsulating Segment-Like Antimony Nanorod in Hollow Carbon Nanotube as a High-Performance Anode for Rechargeable K-Ion Battery Wen Luo1, Feng Li2, Kang Han1, Jewel J. Gaum4 and Liqiang Mai1; 1Department of Physics, Wuhan University of Technology, Wuhan, China; 2Hefei National Laboratory for Physical Sciences at the Nanoscale, University of Science and Technology of China, Hefei, China; 3State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China; 4LCP-A2MC, Université de Lorraine, Metz, France.

K-ion battery (KIB) is a new type energy storage device that possesses potential advantages of low-cost and abundant resource of potassium. To develop advanced electrode materials and electrolytes for accommodating the relatively large size and high activity of potassium is of great interests. In order to address the fast capacity decay caused by severe volume expansion of Sb anode, a novel segment-like antimony nanorod encapsulated in hollow carbon nanotube electrode material (so called Sb@N-C) was prepared by hydrothermal synthesis, polymerization coating and followed by an in-situ pyrolysis and reduction process. The potassium storage performance and mechanism of Sb@N-C in rechargeable KIB were also investigated.

Beneficial from the virtue of abundant nitrogen doping in hollow carbon nanotube, one-dimensional nanotube structure and hollow structure advantages, Sb@N-C exhibited excellent potassium storage properties: based on potassium hexafluorophosphatite (KPF$_6$) electrolyte, the reversible capacity could be maintained 318.6 mAh g$^{-1}$ at a current density of 0.5 A g$^{-1}$, whereas the cycle stability and rate performance were unsatisfactory. Electrolyte optimization strategy was further advanced to boost its potassium storage performance, and the optimization mechanism was also disclosed. In the absence of the solution bis(fluorosulfonyl)imide (KFSI) electrolyte, Sb@N-C displayed a reversible capacity of up to 453.4 mA h g$^{-1}$ at a current density of 0.5 A g$^{-1}$. Additionally, Sb@N-C demonstrated excellent long-cycle stability at ultra-high current of 5 A g$^{-1}$ over 600 cycles, its reversible capacity could be retained at 234.7 mA h g$^{-1}$. The results confirm that Sb@N-C nanocomposite is an advanced and superior promising electrode material for KIB. Besides, electrolyte chemistry optimization is an effective strategy for greatly improving electrochemical performance.

Reference:

ET06.03.10
Mesoporous Reduced Graphene Oxide as a High Capacity Cathode for Aluminum Batteries Jasmin Smajic1, Amira Alazmi1, Nitin M. Batra1, Tamilarasan Palanimasiv1, Dalaver Anjum2 and Pedro M. Da Costa1; 1Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Imaging and Characterization Core Lab, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Mesoporous battery chemistries are seen as a promising alternative to energy storage systems based on lithium-ions. Among those, aluminum-based
Mechanically Reinforced Silicon Anodes for Lithium-Ion Batteries

ET06.03.13
applied to observe the changes during charge/discharge process. Microporous carbon nanofibers, which was encapsulated with SeS2. The resultant cathode materials possesses a free standing structure, which could avoid V2O5 nanostructured active materials, and the binder-free processing are found to mainly contribute the promising electrochemical performance. This stable rate capability is also confirmed. The synergistic effects among the hierarchical structure, microchanneled Ni current collectors, two-dimensional superhierarchical Ni/Porous–Ni/V2O5 nanocomposite exhibits superior electrochemical performance as a binder-free cathode for lithium storage. The material. This system boasts a gravimetric capacity of 171 mAh g−1 at 100 mA g−1 and remarkable stability over a wide range of current densities. These structural quality and low defect density of graphitic carbons are crucial to obtain superior performance and cycling stability in these batteries.3, 4 Still, and despite all effort, the capacities reported for these systems remain stubbornly low, particularly when compared to the ~300 mAh g−1 attained by commercial lithium-ion batteries.

We wish to communicate an Al-chloride battery where reduced graphene oxide powder, dried under supercritical conditions, is used as the active cathode material. This system boasts a gravimetric capacity of 171 mAh g−1 at 100 mA g−1 and remarkable stability over a wide range of current densities. These properties are thought to be the consequence of the cathode’s tailored porosity.4 On one hand, its microporosity assists in breaking down the Coulombic ordering of the electrolyte; on the other, the mesoporosity (originated from the drying conditions) facilitates the movement of the large chloroaluminate ions within the active material.

REFERENCES

ET06.03.11
Superhierarchical V2O5-Ni Cathodes for Lithium Storage Yuan Yue1 and Hong Liang1, 2, 1Materials Science and Engineering, Texas A&M University, College Station, Texas, United States; 2Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Mechanical Engineering, Texas A&M University, College Station, Texas, United States.

New materials are critically needed for advanced energy storage devices. In this research, an alternative approach to fabricate novel nanostructured cathodes with three-dimensional configuration that shows superior performance. We designed and synthesized Ni/porous–Ni/V2O5 nanocomposites using a simple electrodeposition process followed by a hydrothermal treatment. Hierarchical structured V2O5 ultrathin two-dimensional nanosheets (thickness ~ 50 nm) and three-dimensional peony-like microflowers (diameter ~ 4 μm) were deposited directly on a Ni microchannelled current collector. The superhierarchical Ni/porous–Ni/V2O5 nanocomposite exhibits superior electrochemical performance as a binder-free cathode for lithium storage. The maximum reversible discharge capacity of 165.6 mAh g−1 and retention of 90.9% after 100 cycles at 0.2 C are highlights of the capacity performance. The stable rate capability is also confirmed. The synergistic effects among the hierarchical structure, microchannelled Ni current collectors, two-dimensional V2O5 nanostructured active materials, and the binder-free processing are found to mainly contribute the promising electrochemical performance. This research opens a new avenue for the novel design of electrodes in future of rechargeable batteries.

ET06.03.12
Confined Selenium Sulfide in ZIF-8 Derived N-Doped Microporous Carbon Nanofibers as a Binder-Free Cathode for Lithium-Sulfur/Selenium Battery Zibin Yi, Ying Liu and Zhouguang Lu; Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China.

Lithium-sulfur batteries have been extensively considered as a promising alternative for lithium-ion batteries (LIBs) owing to their high theoretical energy density (2500 Wh kg−1) based on the reaction of lithium with sulfur to form Li2S. In addition, S is inexpensive, abundant and nontoxic. However, the practical application of lithium–sulfur batteries is hindered by the low conductivity and huge volume expansion of S during the charge-discharge process. Recently, selenium, a congener of sulfur, has also been used as a cathode material with a theoretical capacity of about 675 mA hg−1. Compared with sulfur, selenium has a better conductivity and it is found that the polyselenides are insoluble in carbonate based electrolytes, indicating that the shuttle effect could be suppressed effectively. Combining the merits of sulfur and selenium, selenium–sulfur solid solution (like SeS2) incorporated with carbon materials display an excellent performance when using as the cathode materials lithium–sulfur/selenium batteries. Herein, we designed a MOF derived N-doped microporous carbon nanofibers, which was encapsulated with SeS2. The resultant cathode materials possesses a free standing structure, which could avoid the utilization of non-active additives, thus ensuring a higher energy density. As a result, the Li-S batteries with C–SeS2 composites deliver a high specific capacity (950 mA hg−1 @ 0.5C) and outstanding rate performance. The nanofibers could buffer the volume expansion of the S/Se species as well as increase the contact area between the cathode and electrolyte to decrease the ion transmission distance. Furthermore, the in-situ Raman technology was applied to observe the changes during charge/discharge process.

ET06.03.13
Mechanically Reinforced Silicon Anodes for Lithium-Ion Batteries Jasmine M. Wallas1, Brian Welch2, Simon Hafner2, Taeho Yoon3, Steven M. George4 and Chunmei Ban1; 1University of Colorado, Boulder, Colorado, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Silicon (Si) is a high energy, low cost anode material for lithium-ion batteries. With a theoretical specific capacity that is almost tenfold higher than graphite, Si has been the focus of extensive research recently for its potential use in electric vehicles and other devices. Unfortunately, Si anode technology has been held back by its lack of cyclability, largely attributed to the structural disintegration of Si electrodes associated with large volume changes during electrochemical cycling. This work aims to address this problem by stabilizing the electrode structure with a robust polymeric coating, allowing for reversible electrochemical reactions. Moreover, spatial molecular layer deposition (MLD) has been developed and applied here to realize the distinct all-organic polymer film chemistry deposited. The aromatic polyamide film chosen for this work has the desired mechanical properties of strength and elasticity that help stabilize Si anodes upon cycling. A very thin film polyamide coating on a Si anode enabled a stable and reversible capacity of 2186 mAh g−2 over 100 electrochemical cycles. Using a spatial MLD configuration usually fasts growth rates on the order of minutes, thereby permitting ease of future scale-up. This spatially deposited, all-organic thin film coating is a promising material that may enable high energy, low cost lithium-ion batteries.

ET06.03.14
Pil Sung Choi1, Won Seok Choi2, Young Joon Kwon2 and Sung Hun Ryu1; 1Kyung Hee University, Yongin, Korea (the Republic of); 2Cholwon Plasma

atomic layer two-dimensional MoS2 as a passivation layer for Li metal anode. With the Li-intercalated atomic layer of MoS2 formed, stable Li
electrochemical performance demonstrating specific energy density of over 652 Wh kg⁻¹ and capacity retention (~84%) for up to 1200 cycles with a
inhibited due to the parasitic growth of Li dendrites and high reactivity of Li with electrolyte and other active species of polysulfides. Here, we introduce an
atom layer two-dimensional MoS2 as a passivation layer for Li metal anode. With the Li-intercalated atomic layer of MoS2 formed, stable Li

electrodeposition is realized with the nucleation sites for dendrite growth inhibited. The deposition/dissolution process of a symmetric cell for the
MoS2-coated Li metal operates at a current density of 10 mA cm⁻² with low voltage hysteresis, it shows three-fold improvement in cycle-life than that of the
bare Li metal. Using Li-S full cell configuration, the MoS2 coated Li anodes assembled with 3D carbon nanotube-sulfur cathodes provide superior
electrochemical performance demonstrating specific energy density of over 652 Wh kg⁻¹ and capacity retention (~84%) for up to 1200 cycles with a
nominal Coulombic efficiency of ~98%. These exceptional results open a new pathway towards the realization of high energy density and safe Li-metal
based batteries.<span style="font-family:times new roman,serif; font-size:12pt; line-height:115%; margin:0px;">ET06.03.15

Effect of Polymeric Binder on the Performance of Graphene/SnO2 Pillared Carbon Anode Material in Li-Ion Battery

Hyung Jin Mun1, Jae Ik Kim1, Pil Sung Choi2, Won Seok Choi2, Young Joon Kwon2 and Sung Hun Ryu1; 1Kyung Hee University, Yongin, Korea (the Republic of); 2Cholwon Plasma Institute, Cholwon, Korea (the Republic of).

Demand with higher energy density LIB is increasing in many areas such as automobile and group IV elements, such as Si, Ge and Sn, have been received much interest for this purpose. However, the use of these elements is limited due to the large volumetric change during long term charge-discharge cycle which results in undesirable rapid capacity fading, low initial coulombic efficiency and poor rate performance.

Among various approaches to avoid this limitation, chemically modified graphene and SnO2 has been hybridized to accommodate volume change and improve the capacity and cycling stability of the electrode material. Hybridization of SnO2 with carbonaceous materials has been used to circumvent this limitation [1-3]. Reddy et al studied hybridization of SnO2 with long chain alkylamine rafted graphene oxide and specific capacities decreased more with increasing alkylamine chain length [4]. Compared with traditional polymer binders, the self-healing chemistry is designed to enable spontaneous repair of the mechanical damage in the electrode and enhance the lifetime of the anode materials.

In the present study it is attempted to synthesize SnO2 nanopillared carbon structures using dodecylamine grafted graphene oxide as templates. Self-healing polyurethane is synthesized with disulphide and it is compared with commercial PVDF as a binder.

Structural and morphological characterizations of self-healing polyurethane and electrode were done using FT-IR, XRD, SEM and TEM. Electrochemical studies, such as charge-discharge, cyclic volatametry abd impedance, were carried by fabricated 2032 type coin cells using RGO-SnO2 as electrode. Self-healing characteristics of prepared polyurethane is confirmed from restored tensile property and SEM photographs of cutted samples. Electrochemical measurements revealed that the SnO2 pillared carbon based anode materials with self-healing polyurethane binder showed improved cycling performances with excellent reversible capacity relative to the electrode prepared by poly(vinylidene difluoride).

References

ET06.03.16

Electrochemical Mechanism and Effect of Carbon Addition During Hydrothermal Synthesis to Improve the Electrochemical Performance of Fe1.19(PO4)(OH)0.57(H2O)0.43 Cathode Material for Li-Ion Batteries

Abdelfattah Mahmoud1, Claude Karegeya2, Moulay Tahar Sougrati2, Jérôme Bodart1, Bénédicte Vertruyen1, Rudi Cloots1, Pierre-Emmanuel Lippens2 and Frederic Boschini1; 1University of Liege, Liege, Belgium; 2Institut Charles Gerhardt, Université de Montpellier, Montpellier, France.

Since the introduction of lithium-ion batteries (LIBs) to market in 1991, their performance has improved significantly, which has been achievable through development in materials technologies. However, further breakthroughs are still needed to ameliorate cycle-life, safety and energy density of LIBs. This requires new electrode materials and a detailed understanding of the electrochemical mechanisms during cycling. Transition metal phosphates are interesting candidates as cathode materials for LIBs [1]. In this work, we report the electrochemical performance of FPHP/C and FPHP/CNT composites where FPHP represents Fe1.19(PO4)(OH)0.57(H2O)0.43 while carbon black and carbon nanotubes (CNT) were used as precursors in the one-pot hydrothermal synthesis, respectively. We show that the addition of conducting carbon black into the solution has a strong influence on reducing the particle size and tailoring their morphology, but does not interfere with the formation of the FPHP phase. Thanks to its favorable microstructural characteristics, the FPHPH-10 wt% C and FPHPH-20 wt% C materials exhibited good performance [2]. The CNT also improve the performance of FPHPH such as capacity retention (500 cycles at 1 C).

The mechanisms of lithiation-delithiation were investigated by combining operando X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy. FPHPH undergoes a monophasic reaction based on Fe⁶⁺/Fe²⁺ redox process. However, the variations of the lattice parameters and ⁵⁷Fe quadrupole splitting indicate a more complex mechanism than a random occupation of the vacant sites within FPHPH. This can be related to the peculiar structure of FPHPH formed by chains of face sharing (Fe₅O₆.9O₈) octahedra connected by PO₄ tetrahedra and by channels for Li diffusion along {100} and {101} directions. The existence of Fe vacancies provide interconnections between the one-dimensional channels, improving lithium diffusion within FPHPH. This mechanism, combined with the addition carbon black or nanotubes in the solution prior to hydrothermal treatment as a simple and effective way to reduce particle size and improve electronic conductivity, provides good cycle life and rate capability for FPHPH.

Acknowledgements
A. Mahmoud is grateful to University of Liege and FRS-FNRS for the grants and thanks to the Walloon region for a Beware Fellowship Academia 2015-1, RESIBAT n° 1510399. Part of this work was supported by the Walloon Region under the “PE PlanMarshall2.vert” program (BATWAL – 1318146).

References
Graphite as a material for Li-ion batteries has been ubiquitous in modern electronics and electric vehicles. However, the supply chain of lithium is a concern for grid-scale applications, while Li-ion batteries have been ubiquitous in modern electronics and electric vehicles. An efficient large-scale energy storage solution has become the bottleneck of the employment of sustainable but volatile energy sources like solar and wind. Therefore, Na-ion batteries (NIBs), for the abundant resources and low cost of sodium, become promising for large-scale energy storage applications. Therefore, Na-ion batteries (NIBs), for the abundant resources and low cost of sodium, become promising for large-scale energy storage applications.

Li-ion batteries (LIBs) took over the lead in rechargeable battery technologies since their introduction in the early 1990s. However, the price and abundance of lithium are still issues, and alternative cell chemistries based on abundant elements might become important especially when stationary energy storage reaches its market breakthrough. Therefore, alternatives to “lithium-ion technology” are being examined. Sodium-ion batteries (SIBs) are recently revisited as an alternative. The hope to realize more cost-effective batteries arises due to the large abundance of sodium. Although LIBs often have lower energy densities and cell voltages compared to their lithium analogues, the lower polarization of the sodium-ion might enable cells with peculiar advantages over conventional lithium-ion technology[1].


due to its low cost, safety, and good cycling performance, graphite is currently the preferred choice as an anode material for LIBs. Graphite is also favored in SIBs but storage of sodium-ions is only possible by formation of ternary intercalation compounds [2]. Instead of the naked ion, the solvated ion is intercalated in between graphene layers. The co-intercalation of the ether-based solvent molecule causes an enormous volume change in graphite lattice and so in the electrode. In order to observe this change, in situ electrochemical dilatometry (ECD) can be used to measure changes in the electrode thickness during charging and discharging. Phase transitions during de-insertion of ions, irreversible reactions such as solid electrolyte interphase (SEI) formation or structural changes such as delamination of graphite can be followed on-line. Overall, the studied electrode reaction behaves very different from conventional intercalation reactions of graphite. Finally, and maybe most intriguingly, the reaction is possibly the first case of an SEI-free graphite anode material [3]. Moreover, formation of gasses is examined during cycling by online electrochemical mass spectrometry (OEMS).

Moreover, was also present a systematic study on temperature effects related to the intercalation of solvated sodium ions into graphite. For this, a series of gymes (mono- to pentaglyme) and several crown ethers are used.

References:

ET06.03.18
Aramid Nanofiber Composite Separators for Metal-Sulfur Thin-Film Batteries
Ahmet Emre1, 2 and Nicholas A. Kotov1, 2, 3
Biomedical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Biointerfaces Institute, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 3Chemical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

High theoretical specific energy density (2600 Wh/kg) and high specific capacity (1675 mA/g) have been attracting significant attention for development of an alternative battery system to replace traditional lithium ion batteries which suffer from safety and capacity/energy density limitations. However, challenges such as polysulfide dissolution and shutting prevent mass commercialization of sulfur cathode batteries. Here we show a practical yet comprehensive approach for development of high performance metal sulfur batteries. Aramid nanofiber (ANF) based composite asymmetric separator [1] not only prevent dendrite formation [2] but also confine polysulfides on the cathode side. ANF composite battery separators provide diverse and opposing properties including high mechanical properties, high ionic conductivity and high thermal/chemical stability. These separators therefore provide a safe and long cycle life as well as high performance metal sulfur batteries. Fabrication of such safe, affordable, flexible and high energy density battery is quite crucial in powering next generation electronics including but not limited to portable, wearable and implantable biomedical devices.

References:

ET06.03.20
Synthesis and Electrochemical Characterization of Cr-Doped Lithium-Rich Li1.2Ni0.16Mn0.56Co0.08-xCrxO2 (NMC) Cathodes for Lithium-Ion Batteries
Umair Nisar1, Ruhul Amin2, R.A. Shakoor1, Rachid Esselli1, Siham Al-Qaradawi1, Ramazan Kahraman2, and Ilia Belharouak1; 1Center for Advanced Materials (CAM), Qatar University, Doha, Qatar; 2Quantum Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar; 3Department of Chemistry & Earth Sciences, College of Arts and Science, Qatar University, Doha, Qatar; 4Department of Chemical Engineering, Qatar University, Doha, Qatar; 5Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Lithium-rich layer oxide Li1.2Ni0.16Mn0.56Co0.08-xCrxO2 (NMC) is a potential cathode candidate for high-energy density batteries. Issues such as cycling stability, rate performance, and cost are yet to be overcome before successful commercialization of the material. Here, we report on the synthesis of Cr-doped lithium-rich phases Li1.2Ni0.16Mn0.56Co0.08-xCrxO2 (where x=0.0, 0.01 & 0.02) (NMC-Cr) by the sol-gel technique. Cr is homogeneously distributed in the crystal structure evidence by XRD, XPS and elemental mapping measurements. The Cr-doped materials exhibit much better cycling stability with 100% capacity retention versus 44% for the undoped sample after 50 cycles. The Cr-doped samples show excellent electrochemical performance at higher C-rate in comparison with the undoped NMC. The latter shows rapid capacity fading from 220 to 50 mAhg-1 at the 0.1 to 1C rates, respectively. Moreover, the Cr-containing materials do not show significant signs of voltage fading during cycling owing to the stabilization of the crystal lattice by chromium. The electrochemical impedance spectroscopy measurements also indicate the stable cell resistance on cycling for the Cr-doped phases compared to the undoped phase.

ET06.03.21
Air-Stable P2-Type Na2Mg2Sn2O7 for High Capacity Sodium-Ion Batteries
Jing Mao1, Xin Liu1 and Kehua Dai2; 1Zhengzhou University, Zhengzhou, China; 2Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

An efficient large-scale energy storage solution has become the bottleneck of the employment of sustainable but volatile energy sources like solar wind. While Li-ion batteries have been ubiquitous in modern electronics and electric vehicles, the supply chain of lithium becomes a concern for grid-scale applications. Therefore, Na-ion batteries (NIBs), for the abundant resources and low cost of sodium, become promising for large-scale energy storage applications. Therefore, extensive efforts have been put into the understanding and developments of materials for NIBs with improved capacity and stability.

For NIB full cells, because the capacity of a cathode material (<200 mAh/g) is much lower than that of anode (300–600 mAh/g), enhancing the energy...
density of cathode materials is determinative for high energy-density NIBs. In order to improve the capacity of SIB cathode materials, Manganese-based sodium transition-metal (TM) oxides with low-valence dopants, Na$_x$M$_{1-x}$Mn$_2$O$_4$ ($0 \leq x \leq 1$, $M = $Ni, Mg, Li, etc.), have recently been studied for higher energy density than other NIB cathode materials. Na$_x$M$_{1-x}$Mn$_2$O$_4$ has two common structures: P2 and O3 type. In comparison, P2-type materials show higher discharge capacity (up to ~200 mAh/g) and better rate capability. Nevertheless, it is easy to be neglected is that both initial charge (desodiation) and discharge (sodiation) capacity of cathode materials are important because all the sodium ions are provided by cathode in most common full cell system. Thus, the lower initial charge capacity (~140 mAh/g) due to Na deficiency limits the potential capacity in full cells. Herein, we report a P2-type Na$_2/3$Mg$_1/3$Mn$_2/3$O$_2$ with high capacity for both charge and discharge. The initial charge capacity is 162 mAh/g at 0.1 C. This is one of the highest values among previous reported P2-type sodium transition metal oxides. The discharge capacity is 167 mAh/g and 205 mAh/g at 2.0 V and 1.5 V cut-off voltage, respectively. The capacity retention at 1C is 80% after 100 cycles.

ET06.03.22 Preparation and Electrochemical Properties of Li$_2$RuO$_3$ for High-Capacity Lithium-Ion Batteries Jing Mao¹, Xin Liu¹ and Kehua Dai²; ¹Zhengzhou University, Zhengzhou, China; ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Lithium ion batteries (LIBs) have been successfully used in portable electric devise since the first commercial usage of LiCoO$_2$ in 1990s. However, it is limited by the capacity of the cathode materials to reach the requirement of the high energy density to power the electric vehicles. Li$_2$RuO$_3$ and other substrates were proposed as possible cathode materials with high capacity. Herein, we report a simple synthesis process to prepare Li$_2$RuO$_3$ with high capacity, good rate capability and cycling stability. The first discharge capacity is 283 mAh g$^{-1}$ at current rate of 1 C between 2.0 and 4.6 V (vs. Li/Li$^+$). The discharge capacity is as high as 250 mAh g$^{-1}$ at 5 C rate. After 100 cycles, the capacity still remains 180 mAh g$^{-1}$. The Li$^+$ ion diffusion coefficients at different stage were determined by potentiostatic intermittent titration technique (PITT) method. The as-prepared Li$_2$RuO$_3$ shows improved Li$^+$ ion diffusion coefficients.

ET06.03.23 Synthesis and Performance of Li,Mn-Rich Cathode Materials for Li-Ion Batteries Panawan Vanaphuti and Yan Wang; Materials Science and Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

As Li-ion batteries are long advanced for its electrochemical properties in application to both electric vehicles and devices, many ongoing researches are focusing on the improvement of energy density, capacity, cycling stability and rate performance. These can divide into three main parts in Li-ion batteries; cathode, anode, and electrolyte. One of the solutions for this enhancement is to find novel cathode materials. This work focuses on the synthesis and characterization of Li,Mn-rich cathode, LiCo$_{0.16}$Mn$_{0.84}$O$_2$, for Li-ion batteries. The layered Mn-rich transition metal (Mn, Co, Ni) hydroxide precursor was synthesized via facile co-precipitation method in a continuous stirred tank reactor (CSTR). Under proper control of pH, temperature, time, concentration of the reactants, and feeding rates in the reactor, uniform spherical particles were obtained. The hydroxide precursor was then undergone two-step heat treatment process to achieve Li,Mn-rich cathode powder. Morphology and structure were examined using SEM and XRD, respectively, showing plate-like primary particles which intercalated into spherical secondary particle shape (average size ~ 17 μm). Chemical stoichiometry was confirmed by ICP-OES technique and electrochemical performance was studied to examine the reliability of this cathode for large scale production and its future commercial use in Li-ion batteries. Drawback of Li,Mn-rich, such as capacity fading and voltage decay, were discussed with an effort to minimize these issues.

ET06.03.24 Investigating Transport Properties of VO$_2$(M) and VO$_2$(R) via Temperature Dependent Electrochemistry and Diffraction Lisa Housel¹, Calvin Quilty¹, Alyson Abraham², Christopher Tang², Alison McCarthy³, Genesis Renderson¹, Diana Lutz¹, Ping Liu¹, Amy C. Marshchiklo², Esther Takeuchi¹,² and Kenneth Takeuchi¹; ¹Stony Brook University, Stony Brook, New York, United States; ²Brookhaven National Laboratory, Upton, New York, United States.

The VO$_2$(M/R) system undergoes a structural change from monoclinic [VO$_2$(M)] to rutile [VO$_2$(R)] phase at a temperature that is easily accessible and corresponds to an electrical conductivity increase two orders of magnitude. The ability to exploit electrical conductivity makes the system attractive for study as a lithium ion battery electrode considering uniform electron access can be a limiting factor in producing electrodes that deliver high capacities. In the work presented, several forms of characterization were employed to gain insight on the relationship of structure and electrochemical function. Synchrotron based x-ray powder diffraction (XPD) data was used to monitor the structural changes as a function of temperature. Electrochemical impedance spectroscopy was utilized to track impedance as a function of temperature. Further, the VO$_2$ system was then tested in two electrode cells to determine the impact of the structural transition on functional electrochemistry. The results from the compliment of experiments provides a foundation for investigating charge transport properties in polymorphic materials and sets a precedent for understanding the impact of phase changes on electrochemistry in a complex energy storage system.

ET06.03.25 The Benefit of a Multiscale Perspective for Investigating the Complex Chemistry of Functional Energy Storage Systems Alyson Abraham¹, Lisa Housel³, Amy C. Marshchiklo¹,², Kenneth Takeuchi¹ and Esther Takeuchi¹,²; ¹Stony Brook University, Stony Brook, New York, United States; ²Brookhaven National Laboratory, Upton, New York, United States.

A critical challenge for electrical energy storage is to achieve more useful work (w) and minimize the generation of waste heat (q). Batteries have often been approached at the macro level, where bulk parameters are identified and manipulated, with optimization as an ultimate goal. However, such a strategy may not provide insight toward the complexities of electric energy storage, especially when addressing multiple length scales in application and demands on devices. Beginning from a fundamental approach of identifying and reducing sources of localized resistance facilitates the understanding of the inherent heterogeneity of ion and electron flux both at multiple interfaces and length scales. At a fundamental level, it is necessary to identify and reduce sources of localized resistance and to understand the inherent heterogeneity of ion and electron flux at numerous interfaces found at several scale lengths within a battery. Benefits from experimentation and characterization over multiple length scales will be highlighted in this presentation.
8:00 AM ET06.04.01
Design of Lithium-Metal Anode for Enhanced Dendrite-Proof Capability Xin Li; Harvard University, Cambridge, Massachusetts, United States.

The suppression of lithium dendrite is critical to the application of lithium metal batteries. Many approaches have been applied previously to demonstrate the improved cycling performance with lithium metal anode, which include the 3D conductive framework, lithium metal surface protection and the formation of special SEI protection layer, etc. In this talk a combined simulation and experiment approach is used to understand the new principles behind these approaches. Innovative synthesis procedures, electrochemical battery tests and morphology and spectroscopy characterizations are used to demonstrate the advanced dendrite proof capabilities. Specifically, new approaches to construct the general 3D conductive framework from nonconductive materials and to apply the surface protection layers are demonstrated. Moreover, combined thermodynamic modeling, DFT simulation and new modeling approach is used to understand the dendrite growth thermodynamics and kinetics down to the atomic scale. We further propose some new design principles behind these technological approaches based on our experiment and theory.

8:30 AM ET06.04.02
Quantitative Measurement of "Inactive" Lithium in Li-Metal Batteries Chencheng Fang, Jungwoo Lee, Yihui Zhang, Yangyuchen Yang, Xuefeng Wang and Y. Shirley Meng; University of California, San Diego, La Jolla, California, United States.

Enabling stable and safe reversible Li metal anode is essential to achieve a specific energy density of 500 Wh/kg from a cell level in next-generation Li batteries. The low Coulombic efficiency and dendrite growth issues significantly hinder the commercialization of Li metal anode. It is well accepted that after electrochemical cycling, formation of "inactive" Li, consisting of Li ions that form SEI (Li+) and SEI wrapped Li metal (Li0), is a direct reason for capacity loss. Differentiating and quantifying Li+ and Li0 after cycling is one of the most critical yet challenging problems that impedes the thorough understanding of the failure mechanism of Li metal anode. A new chemical analytic method has been introduced in this work and provides a solution enabling the quantitative measurement of Li+ content in cycled Li metal cells at microgram (µg) level for the first time. Combining with Cryo-FIB-3D reconstruction, Cryo-TEM and XPS, a correlation among mass content, microstructure, SEI nanostructure and chemical composition has been established to investigate the properties of "inactive" Li generated in different electrolytes.

8:45 AM ET06.04.03
From Macro to Nano—Measurements of the Mechanical Properties of Lithium Metal Coleman Fincher1, Daniela B. Ojeda1, 2 and Matt Pharr1; 1Department of Mechanical Engineering, Texas A&M University, College Station, Texas, United States; 2Mechanical and Aerospace Engineering, University of Central Florida, Orlando, Florida, United States.

Lithium metal is known as the “Holy Grail” of anode materials, as it has the highest theoretical capacity, lowest density, and most negative electrochemical potential of known anode materials for rechargeable batteries. Unfortunately, dendrites of lithium form during repeated cycling, posing a safety hazard and deteriorating commercialization of lithium metal batteries. Previous studies, each with different methods of sample preparation and testing methods, show that Lithium’s yield strength may vary by more than 2 orders of magnitude (from ~1 MPa to 100-300 MPa). However, comprehensive knowledge of the mechanical behavior of Li remains a key obstacle to understanding how to engineer anode-separator interfaces that can mitigate or suppress dendrites. Through a combination of in-glovebox tensile testing and nanoindentation in as-received lithium ribbon, we probe the mechanical properties of Li metal at different length scales.

9:00 AM ET06.04.04
Investigating the Origins of Dendrite Nucleation on Li Metal Surfaces Perla B. Balbuena1, Luis E. Camacho-Forero1, Ethan P. Kamphaus2, Maria S. Angarita-Gomez2 and Xueping Qin1, 2; 1Texas A&M University, College Station, Texas, United States; 2Chemical and Biological Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong.

Formation and growth of dendrites on Li metal surfaces is a well-known problem and is one of the main reasons that prevent the successful operation of Li-metal batteries. Numerous mitigation strategies are continuously being developed such as electrode coatings, artificial solid electrolyte interphase (SEI) films, electrolyte design for specific SEI compositions, and use of solid electrolytes among others. In some of these processes, mitigation is induced by chemical or mechanical (or both) modifications of the environment surrounding the sites where Li ions are plated. Here we use first principles calculations first to investigate why dendritic nucleation occurs and what properties should be tuned to mitigate such phenomena. We then analyze the microscopic mechanisms behind some of the proposed strategies and determine which ones have the best probabilities of a long-term solution to this problem.

9:30 AM ET06.04.05
Dendrite-Free Li Metal Anode in Safe Rechargeable Batteries Xin-Bing Cheng, Xiang Chen, Rui Zhang, Chen-Zi Zhao, Xue-Qiang Zhang, Chong Yan and Zhan-Guang; Tsinghua University, Beijing, China.

Li metal is considered as the “Holy Grail” of energy storage systems. The bright prospects give rise to worldwide interests in the metallic Li for the next generation energy storage systems, including highly considered rechargeable metallic Li batteries such as Li-O2 and Li-sulfur (Li–S) batteries. However, the formation of Li dendrites induced by inhomogeneous distribution of current density on the Li metal anode and the concentration gradient of Li ions at the electrolyte/electrode interface is a crucial issue that hinders the practical demonstration of high-energy-density metallic Li batteries. In this talk, we review the lithium metal anode protection in a polysulfide-rich environment. Firstly, the importance and dilemma of Li metal anode issues in lithium–sulfur batteries are underscored, aiming to arouse the attentions to Li metal anode protection. Specific attentions are paid to the surface chemistry of Li metal anode in a polysulfide-rich lithium–sulfur battery. Next, the proposed strategies to stabilize solid electrolyte interface and protect Li metal anode are included. Finally, a general conclusion and a perspective on the current limitations, as well as recommended future research directions of Li metal anode in rechargeable batteries are presented.

References
Li metal has been considered as the ultimate anodic material for high-density electrochemical energy storage technology, not only because of its extremely high specific capacity (3860 mAh/g) and the lowest redox potential, but also because it enables battery chemistries with lithium free cathode materials, such as Li-S and Li-O2 batteries. However, the practical application of Li metal anodes is still prohibited.

This talk presents a facile and scalable preparation of a lithium-carbon composite for high performance Li anodes. It will be demonstrated that molten Li metal can be easily impregnated into the porous particles composed of carbon nanotubes (CNTs) to form a Li-CNT composite. When used as anodic materials, the Li-CNT composite not only shows high specific capacity (2000 mAh/g) and low lithium dissolution/deposition potential, but also shows significantly suppressed dendrite formation, high CE and stable cycle life. When paired the Li-CNT with a commercial LiFePO4 (LFP) cathode, a CE of around 90.1% can be achieved, which is much higher than the value (75.4%) obtained from a lithium foil anode.

Upon further optimization, a dual-carbon host matrix composed of CNT and acetylene black (AB), Li-CNT-AB, is found to absorb more Li and show even lower potential than Li-CNT. The lithiophilic AB particles not only helps to utilize the pore space of the sphere thus increasing the lithium content of the composite, but also acts as a lithium deposition promoter during battery cycling because AB has lower lithium nucleation barrier. As a result, the Li-CNT-AB composite exhibits a specific capacity as high as 2800 mAh/g and a life span of ~700 cycles can be achieved when it was cycled with a commercial LFP cathode at 1C (0.7 mA cm^-2) in an ether-based electrolyte with cathode capacity to anode capacity at 1:8, corresponding to a high Coulombic efficiency (CE) of ~98.7%. Furthermore, it was observed that there is no lithium dendrite formation and negligible volume change on the Li-CNT during electrochemical cycling.

Acknowledgements: This work was supported by a NSF Career Award (DMR-1055526) and a DOE award (DE-SC0010074) to D.Cao.

References:

organic surface chemistries using polymeric thin films. We have developed two approaches to apply polymer thin films on battery electrodes. The first approach is surface-initiated radical polymerization. Polylefinic radical initiators are tethered to the surface of a model thin film Li anode and then used to synthesize poly(methyl methacrylate) (PMMA) brushes of tunable thicknesses from approximately 20nm to several hundred nanometers. It was shown that the presence of 75nm brushes reduces the first cycle irreversibility on thin film Si anodes to 23.7%. The irreversibility in untreated Si is 37.6%. Post-mortem FTIR-ATR confirmed that less ethylene carbonate is reduced on the PMMA-coated Si in the first cycle, and electrochemical impedance spectroscopy showed that the PMMA brushes inhibit the growth of a resistive surface layer during extended cycling. In the second approach, initiated chemical vapor deposition (iCVD) is used to apply ultrathin conformal polymer layers on conventional lithium ion battery electrodes prepared by slurry casting. The conformity and coverage of the polymer coatings was confirmed by scanning electron microscopy and x-ray photoelectron spectroscopy. For coatings on lithium ion battery anodes, polymer compositions with high crosslinking densities were developed to exclude liquid electrolyte from the electrochemical interface. For these applications, we have developed two distinct polymer chemistries that have been applied by iCVD: crosslinked poly(lithium methacrylate) (PLiMA), poly(ethylene glycol diacrylate) (PEGDA), and poly(1,3,5-trimethylcyclotrisiloxane) (PV3D3). With these crosslinked films, there is a trade-off between the reduction in irreversible side reactions and an increased area specific resistance. We have also demonstrated that capacity retention of full cells (NMC vs. graphite in 1M LiPF6 in EC:DMC:DEC) at 55°C is improved by coating both cathode and anode with these ultrathin films. Our efforts to understand how polymer film chemistry and morphology influences the electrochemical reactions in lithium ion cells will be discussed.

11:45 AM ET06.04.10
Directing the Complex Behavior of Metallic Anodes Using Two Dimensional Materials Tara Foroozan, Soroosh Sharifi-Asl and Reza Shahbazian-Yassar; University of Illinois at Chicago, Chicago, Illinois, United States.

The demand for large-scale renewable energy generation and electric mobility is rising the need for high capacity and safe energy storage systems. Utilizing metal anodes are gaining momentum, owing to their very high energy densities compared to conventional intercalation-based electrodes. Nevertheless, considering the hostess nature of the metal anodes and their interfacial instability, the practical utilization of such systems has been restricted. Inhomogeneous metal electrodeposition (dendrites) and unwanted byproduct formation during cyclic life and safety of the metal anode-based batteries. Therefore, research community has focused on designing innovative approaches to regulate the deposition behavior of metal anodes. In this context, one of the most reliable methods is the use of ultra-thin and ultra-stable materials on the metal anode to prevent the side reactions at the interface and also suppress the formation of dendritic deposits. Among the proposed solutions, 2D materials are promising candidates, owing to their ultrahigh mechanical strength, superflexibility and chemical stability. However, it is not truly clarified that how these approaches affect the nucleation and growth modes of the metal during the electrodeposition. In this work, we have studied the nucleation and growth mechanism of lithium (Li) and zinc (Zn), as examples of metal anodes, in the presence of high-quality graphene (Gr) layer. Interestingly, addition of an ultra-thin layer of carbon is able to significantly regulate the morphology and electrochemical performance of these metal anodes. Utilizing electrochemical potential tests and scanning electron microscopy (SEM) the nucleation mechanism was explored. Accordingly, Li forms homogeneous spherical nucleation electrodeposits all over the Gr-coated electrode surface, being different from randomly whisker like deposition in case of bare electrode. Utilizing transmission and scanning electron microscopy we detected that upon further electrodeposition, in contrast to the expected highly dendritic Li deposition, Li spheres can develop into a uniform and compact structure composed of vertically aligned Li nanorods. Moreover, despite the randomly oriented inhomogeneous deposition of multi-crystalline Zn on the bare substrate, a planar Zn deposition, composed of single crystalline flat flakes, was observed in case of Gr-coated sample. Therefore, we can conclude that high quality graphene not only provides a homogeneous metal-ions nucleation, but also regulates the morphological and growth orientation of the final deposition products, significantly.

Further experimental and computational efforts are being carried out to provide comprehensive explanations for our observations in this research. Overall, we believe that such systematic studies can pave the way in the evolution of such surface engineering approaches into the industrial scale applications of rechargeable metal batteries.

SESSION ET06.05: Li-Metal II
Session Chairs: Xiaolin Li and Qiang Zhang
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room Ballroom A

1:30 PM *ET06.05.01
Stabilization of Metal Anodes by Localized High Concentration Electrolytes Ji-Guang Zhang, Shuru Chen, Xiaodi Ren, Jianming Zheng, Lu Yu, Wu Xu and Xia Cao; Pacific Northwest National Laboratory, Richland, Washington, United States.

A stable and high efficiency metal anode (such as Li, Na, Zn, Mg) is critical for all rechargeable metal batteries, including the batteries with various cathodes such as ion intercalation compounds, conversion materials, sulfur, and oxygen. An ideal metal anode not only needs to have a very high Coulombic efficiency, but also need to have a low concentration, high conductivity and low cost. Recently, we have developed a series of “localized high-concentration electrolytes (LHCE)” by diluting high-concentration electrolytes with electrochemically “inert” solvents or poorly solvating diluents. Unlike the high concentration electrolytes reported before, the electrolyte reported in this work exhibits low concentration, low cost, low viscosity, improved conductivity, and good wettability to separator and electrodes. With selected Li salt, solvent, and the diluent, we demonstrated a fire-retardant LHCE that enables stable, dendrite-free cycling of LMAs with high Coulombic efficiency of up to 99.2%. Moreover, this electrolyte exhibits excellent anodic stability even up to 5.0 V and greatly enhances the cycling performance of LMBS. A Li||LiNi0.2Mn0.7O2||C60 battery using this electrolyte can retain > 97% capacity after 600 cycles at 1C rate (ca. 1.6 mAh cm⁻²), corresponding to a negligible capacity decay of < 0.005% per cycle. Similar concept of “localized high-concentration electrolytes (LHCE)” have also been used to stabilize Na metal anode for more than 40,000 cycles. In addition, this concept was also used to expand the electrochemical windows of water based electrolytes in a salt concentration much less than those reported before. Therefore, this new approach opened a window for further development of novel electrolyte for practical high-energy metal batteries.

2:00 PM ET06.05.02
Dual-Salt Ether Electrolytes for Stable High-Voltage Lithium Metal Batteries Xiaodi Ren1, Shuhong Jiao1,2, Zhiqiang Gao1,2, Mark H. Engelhard1, Yuzi Liu1, Dehong Hu1, Donghai Mei2, Jun Liu1, Ji-Guang Zhang1 and Wu Xu1; Pacific Northwest National Laboratory, Richland, Washington, United States; 2Department of Materials Science and Engineering, University of Science and Technology of China, Hefi, China; 3Argonne National Laboratory, Lemont, Illinois, United States.

With the fast-growing demands for high energy storage, lithium (Li)-ion batteries (LIBs) can no longer satisfy the application needs due to their relatively
low energy densities. Li metal batteries (LMBs) are regarded as one of the most promising next-generation energy storage systems. The key to enable long-term cycling stability of high-voltage LMBs is the development of functional electrolytes that are stable against both Li anodes and high-voltage (>4 V vs. Li/Li⁺) cathodes. Due to their limited oxidative stability (< 4 V), ethers have so far been excluded from being used in high-voltage batteries, in spite of their superior reducible stability against Li metal compared to the conventional organic carbonate electrolytes. Here we design a concentrated dual-salt/ether electrolyte that can form stable interfacial layers on both the high-voltage LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{2} cathode and the Li metal anode, thus realizing an unprecedented capacity retention >90% over 300 cycles and ~80% over 500 cycles with a charge cut-off voltage of 4.3 V. Various characterization techniques were used to reveal the detailed mechanisms for the enhanced electrode stabilities. All these fundamental findings extend the conventional knowledge on ether-electrolyte systems, and provide an effective approach to achieve high energy density LMBs.

2:15 PM ET06.05.03
Redox Active Glyme-Li Salt Solvate Ionic Liquids Based on Tetrahalogeno-ferrate(III) Complex as a Catholyte for Lithium Secondary Batteries Yuta Kemmizaki¹, Yu Katayama¹, Hiro Mori Yotsuami¹ and Kazuhide Ueno²; ¹Department of Applied Chemistry, Graduate School of Sciences and Technology for Innovation, Yamaguchi University, Ube, Japan; ²Department of Chemistry and Biotechnology, Yokohama National University, Yokohama, Japan.

Solvate ionic liquids (SILs) are classified as one of the subclasses of ionic liquids, composed of long-lived complex ions.¹ Equimolar molten complexes consist of an appropriate combination of oligoethers (glymes) and Li salts ([LiX]+ [Li[n]glyme][Y]⁻), have shown to yield a highly Li-ion conductive and non-flammable SILs, which can be employed as an electrolyte for lithium secondary batteries.² Furthermore, recent studies have shown that SILs consist of the complex anions with reversible redox behavior can be used as liquid cathode materials (catholyte) for various energy conversion devices including redox flow batteries.³,⁴, sodium-ion batteries,⁵ and lithium secondary batteries.⁶ In this work, we obtained series of novel redox active SILs consist of an symmetric ([Li(G3)])⁺ and asymmetric ([Li(G3Bu)])⁺ triglyme-Li complex, and redox active tetrahalogeno-ferrate ([FeX]⁻ (X = Br, Cl, Br, Cl)). The physicochemical properties of [Li(G3/G3Bu)][FeX] were investigated by differential scanning calorimetry (DSC), Raman spectroscopy, electrochemical impedance spectroscopy, and thermogravimetry (TG). Cyclic voltammetry confirms the reversible redox property of the [FeX][FeX]²⁺ couple for all SILs. Among the SILs tested, [Li(G3Bu)][FeCl]⁺, consist of the complex cation with asymmetric structure and small complex anion, showed the lowest melting point (T_m) of <30 °C. The lithium secondary batteries utilizing [Li(G3/G3Bu)][FeX] as a catholyte exhibits a high coulombic efficiency of over 90 % after 50 cycles as well as stable discharge capacities of approximately 80 % of the theoretically predicted value, suggesting a new and promising path to enhance the performance of lithium secondary batteries.


2:30 PM BREAK

3:00 PM ET06.05.04
Surface and Interface in Lithium Rechargeable Batteries—Challenges and Opportunities Xingcheng Xiao¹, Jiagang Xu¹, Binsong Li¹, Qinglin Zhang¹, Yikai Wang², Yang-Tse Cheng², Kai Guo³, Huajian Gao³, Brian W. Sheldon⁴ and Yue Qi⁵; ¹University of Kentucky, Lexington, Kentucky, United States; ²University of Providence, Providence, Rhode Island, United States; ³Michigan State University, East Lansing, Michigan, United States.

Low cycle efficiency and dendrite growth are two critical barriers for rechargeable batteries using Li metal as negative electrodes, mainly due to the coupled mechanical/chemical degradation of the SEI layer formed on Li metal surface. We have developed a comprehensive set of in situ diagnostic techniques combined with atomic/continuum modeling schemes to investigate and understand the coupled mechanical/chemical degradation of the SEI layer/Li system including fundamentally understanding the surface and interface phenomena. We have found that the mechanical incompatibility between SEI and soft Li leads to the complicated mechanical behaviors of the lithium metal electrode during the plating and stripping process. We systematically investigated the relationship between surface morphology and current density distribution which results in an inhomogeneous Li plating/stripping process. Based on this understanding, we have developed a new coating design strategy to achieve high cycle efficiency/dendrite free and extend the cycle life of lithium rechargeable batteries.

3:30 PM ET06.05.05
Solubility-Mediated Sustained Release Enabling Nitrate Additive in Carbonate Electrolytes for Stable Lithium Metal Anode Yayuan Liu and Yi Cui; Stanford University, Stanford, California, United States.

The physiochemical properties of the solid-electrolyte interphase (SEI), primarily governed by electrolyte composition, have a profound impact on the electrochemical cycling of metallic lithium (Li). Herein, we discovered that the effect of nitrate anions on regulating Li deposition previously known in ether-based electrolytes can be extended to carbonate-based electrolytes, which can dramatically alter the morphology of Li nuclei from dendritic to spherical, albeit extremely limited solubility. The effect can be attributed to the preferential reduction decomposition of nitrate anions during SEI formation that modifies the interfacial environment. And the mechanistic origins behind the phenomenon were investigated based on the structure, ion-transport property and charge transfer kinetics of the modified SEI utilizing advanced characterization techniques such as cryo transmission electron microscopy and ultramicroelectrode. Furthermore, to overcome the solubility barrier, a solubility-mediated sustained release methodology was introduced, in which nitrate anions were encapsulated in porous polymer gel and can be steadily dissolved during battery operation to maintain a high concentration at the electroplating front. As such, effective Li dendrite suppression and remarkably enhanced cycling stability can be achieved in both half- and full-cell configurations in corrosive carbonate electrolytes, significantly outperforming conventional electrolyte additives. The proposed approach is generally applicable in various carbonate-based electrolyte systems and can improve the reversibility of Li metal anode without sacrificing the stability, ionic conductivity, or the cost of electrolytes.

3:45 PM ET06.05.06
Artificial SEI on Lithium-Metal Anodes to Acetonitrile-Based Electrolytes in Lithium-Metal Batteries David Lepage¹, Ngoc Duc Trinh¹, David Aymé-Perron², Antonella Badia¹, Mickael Dollé¹ and Dominic Rochefort¹; ¹Chemistry, Université de Montreal, Montreal, Quebec, Canada; ²Prospective Lab, Total S.A., Materials for Energy, Paris, France.

One way to achieve high energy density batteries is to use Li metal as the anode material due to its very high theoretical specific capacity of 3860 mAh g⁻¹.
This approach however bring many challenges. Since over 40 years scientists spent important efforts to find the right strategies to overcome the high reactivity of Li metal and the formation of lithium dendrites during cycling. So far, only technologies based on solid polymer electrolytes (e.g. poly(ethylene oxide)) have been commercialized. One recent approach to employ Li metal anodes relies on the use of superconcentrated electrolytes in which the amount of solvent molecules reaches that of ions. It has been proposed that, under such conditions, the absence of free (i.e. non coordinating to the ions) solvent molecules prevent thermodynamically favourable decomposition at Li. With such system, acetonitrile (ACN) have been used with lithium metal. Because of its high oxidative stability and is high dielectric constant, ACN represent an interesting option as a solvent for the electrolyte.

Here we propose a different approach consisting in the formation of an artificial solid electrolyte interface (SEI) on the lithium to hinder the reaction between ACN and the metallic anode. To do so, we studied the spontaneous decomposition of neat fluoroethylene carbonate (FEC) on lithium metal (Li-FEC)\(^1\) to form a protective layer. This film have been characterized by AFM, XPS and by SEM to determine its composition and its morphology and a dense film made of a mixture of LiF with a polymeric phase have been found. This artificial SEI is porous to the lithium ions but impermeable to ACN, allowing the use of this solvent with conventional Li salt concentrations which maximise electrolyte conductivity. We demonstrate the protective properties of such artificial SEI using a 1 M LiPF\(_6\) in acetonitrile (ACN) electrolyte into a symmetric cell (both electrodes Li-FEC). This cell was cycled with a current density of 0.1 mA/cm\(^2\) during 30 min per half-cycle and for a total of 1500 hours. The electrochemical performance of a full cell made of c-LiFePO\(_4\) as cathode and Li-FEC as anode with the 1 M LiPF\(_6\) in ACN electrolyte have been analysed and shown a capacity of 162 mAh/g at 0.2C (theoretical capacity is close to 170 mAh/g). This approach opens new possibilities for the use of metallic anodes to improve energy storage in batteries.


4:00 PM ET06.05.07
Water-Tolerant Interphase Formation and Transplantation for Lithium-Metal Anodes Nikhilendra Singh, Timothy S. Arthur and Kensuke Takechi; Toyota, Ann Arbor, Michigan, United States.

The ability to directly utilize Lithium (Li) metal anodes in rechargeable batteries presents itself as an ideal, albeit challenging, situation. Li metal anodes could provide a maximum possible theoretical specific capacity (3860 mAh/g) in comparison to commercially used anodes (e.g. graphite – 380 mAh/g). However, Li metal anodes remain absent in commercial applications due to inherent safety concerns associated with the formation of Li dendrites during high rate cycling, as well as Li metals’ susceptibility to exhibit high reactivity towards commercially used organic electrolytes. Due to the possibility of thermal runaway, such concerns have adversely affected the potential use of Li metal in commercially available batteries. Additionally, Li metal reacts vigorously with water or passivates in the presence of small quantities of moisture rendering it unusable. This presents a significant hurdle for systems where water-tolerant Li cycling is of practical necessity (e.g. Li-air). Hence, significant efforts in recent literature have targeted the development of robust systems, capable of use with Li metal.

To date, various strategies have been employed to overcome such hurdles; the use of solid electrolytes as a mechanical barrier, or the use of specific organic solvent-based electrolytes which control the properties of the solid-electrolyte interphase (SEI), being noted observations. Amongst the available classes of Li batter electrolytes, ionic liquids (ILs) have been shown to facilitate enhanced Li cycling efficiencies and favorable Li plating morphologies while being inherently non-volatile/non-flammable alternatives to commercially available organic electrolytes. Through the capability to combine various cations, anions and salts; the use of such ILs could produce robust SEIs, resulting in the improved cycling behaviors reported in literature.

Recently, we reported that certain ILs allowed for successful Li metal cycling in the presence of water mixed into the IL electrolyte. To our knowledge, no reports have shown the capability to sustain morphologically friendly Li deposition upon application of high rates while sustaining stable cycling in a water containing electrolyte. In recognition of this unique capability, we now introduce a new method to artificially form these SEIs on Li metal via the screening of various IL electrolyte (cation, anion and salt) combinations. The electrochemical results, along with fundamental analytical analyses of the ILs capable of water-tolerant interphase formation and transplantation on Li metal, while sustaining commercially feasible Li morphologies at practical cycling rates in the presence of water containing electrolytes will be presented and discussed.

4:15 PM ET06.05.08
Facile Stabilization of Sodium Metal Anode with Additives—Unexpected Key Role of Sodium Polysulfide and Adverse Effect of Sodium Nitrate Huan Wang, Chuanlong Wang and Weiyang Li; Dartmouth College, Hanover, New Hampshire, United States.

Sodium (Na) metal is an attractive anode for next-generation energy storage systems due to its high specific capacity, low cost and high abundance. Nevertheless, uncontrolled Na dendrite growth caused by the formation of unstable solid electrolyte interphase (SEI) leads to poor cycling performance and severe safety concern. Herein, we first reveal that sodium polysulfide (Na\(_2\)S\(_n\)) alone can serve as a positive additive or pre-passivation agent in ether electrolyte to improve the long-term stability and reversibility of Na anode, while Na\(_2\)S\(_n\)Na\(_2\)O as co-additives has an adverse effect on Na anode, which is contrary to the prior findings in lithium (Li) metal anode system. A superior cycling behavior of Na anode is first demonstrated at a high current density up to 10 mA cm\(^{-2}\) and a capacity up to 5 mAh cm\(^{-2}\) over 100 cycles. As a proof of concept, we present a high-capacity Na-S battery via pre-passivating Na anode with Na\(_2\)S\(_n\). Our study gives new insights into understanding the differences between Li and Na systems.

4:30 PM ET06.05.09
Deposition-Stripping Mechanism of Lithium Metal in Batteries Feifei Shi and Yi Cui; Material Science and Engineering, Stanford University, Stanford, California, United States.

Rapid growth of electric vehicles has stimulated the development of high-energy storage systems, especially the lithium–sulfur and lithium–air batteries that employ lithium metal anodes. However, the wide deployment of Li-metal batteries has been hindered by its poor cycling efficiency and safety concerns, both of which stem from the uncontrollable Li deposition-stripping process. While various theories have been raised in the past, the underlying mechanisms of lithium redox couple are still controversial.

Here, we report the texturing behavior of lithium metal in batteries and reveal the mechanism of lithium electro-deposition from crystallographic perspective. Additives in electrolytes and the cross-over molecules from the cathode play crucial roles on the crystallographic texture because they inhibit the cathodic process and adsorb/react on different crystal planes selectively. Exchange current density has been identified as an indicator for the additive adsorption, which can only be accurately measured with microelectrode. Nano-void formation at interface of Li and SEI is found during the lithium stripping, which is attributed to the accumulation of lithium metal vacancies. High rate dissolution of lithium drives vigorous growth, subsequent aggregation of voids, and eventually collapse of the SEI layer, i.e. pitting. The polarization behavior and pitting potential of lithium are systematically measured by 3-electrode cell. Metallurgical factors, such as grain boundaries and slip lines, are found greatly accelerate the local dissolution of lithium. The understanding of the electro-crystallization and stripping beneath interface process of lithium will shed light on future lithium anode and electrolyte design.

Acknowledgement: The work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of
Vanadium diselenide (VSe₂) is a transition metal dichalcogenide with metallic conductivity, which makes it a potentially promising electrode material for electrochemical applications. However, the developments of VSe₂ electrodes for such applications has been severely hampered by the difficulty of preparing nanosized products. In this work, a new facile solvothermal synthesis process is developed to synthesize ultrathin VSe₂ nanosheet assemblies. To obtain the ultrathin nanosheets, N-methyl pyrrolidone, which has the similar surface energy to many transition metal dichalcogenides, was used as the solvent to limit the crystal growth along the c-axis direction. The resulted ultrathin VSe₂ nanosheets exhibit good performance toward the alkaline ions (Li⁺ and Na⁺) storage, yet the performance can be further significantly enhanced by carbon coating. Specifically, the carbon-coated VSe₂ nanosheets can deliver high capacities of 768 mA h g⁻¹ (Li⁺ storage) and 571 mA h g⁻¹ (Na⁺ storage) along with outstanding stability. This work presents general strategies for Li⁺ and Na⁺ storage, yet the performance can be further significantly enhanced by carbon coating. Specifically, the carbon-coated VSe₂ nanosheets can achieve four or five times the theoretical specific energy of a commercial C-LiCoO₂ system. Despite the theoretical capacity of the sulfur, the practical capacity of 10 times that of the existing intercalate cathode. Sulfur is an interesting cathode material due to its high theoretical capacity of 1,673 mAh / g, yet the practical capacity of 10 times that of the existing intercalate cathode. Sulfur is an interesting cathode material due to its high theoretical capacity of 1,673 mAh / g, yet the practical capacity of sulfur is much lower due to its poor rate capability. In this study, we use a polymer with a channel to enclose sulfur particles to prevent volume expansion and dissolution and try to approach to impart mass transfer capability through hybridization with conductive graphene. The polymer with a channel is synthesized through a low-temperature heat treatment based on the difference of the vaporization temperature according to the degree of polymerization of the polymer. Through the channel, the lithium ion and the electron to be delivered to the sulfur contained in the polymer. All of the synthesis processes attempted in this study are scalable and very easy to mass-produce.

The polymer used in this study is an aliphatic rubbery synthetic polymer and has a vaporization temperature of 60 °C or less when it is in a monomer state. However, the vaporization temperature raises sharply according to the degree of polymerization, and when it is completely cured, it has a vaporization and decomposition temperature of 300 degrees or more. But in this work, the polymer in the hybrids mostly had a very low degree of polymerization in the MALDI-TOF analysis of the synthesized whole hybrids. This is because of the polymerization reaction, which originated from sulfur, terminated very quickly and the reaction was complete when the polymer met the sulfur and graphene particles. Due to the very low degree of polymerization of the polymer, the polymer can be vaporized at temperatures below 90 degrees, which results in many pores and channels on the surface and inside of the polymer from low-temperature heat treatment. Such a pore-forming polymer has superior mass transfer characteristics and high lifetime performance while offsetting the disadvantages of sulfur.
transfer kinetics particularly at higher cycling rate. Particle morphology thus needs to be engineered in order to obtain higher surface area and shorter diffusion length for practical use. On the other hand, the electrochemical performance of lithium-ion battery at different temperatures due to the change of composition of SEI (solid electrolyte interface) layer. Based on that, three different types of electrolyte compositions were formulated and the charge-discharge behavior is tested at 25 °C and 45 °C temperature. It reveals that the cell with EC-PC combination exhibits lower capacity than DMC-EC-PC and DEC-EC compositions at room temperature. The DMC-EC-PC electrolyte combination shows best electrochemical performances. This material shows the capacity close to 119, 130 and 125 mAh g⁻¹ at 0.1C with EC-PC, DMC-EC-PC and DEC-EC, respectively and at 1C rate performance is not much promising. Whereas at 45°C with the same electrolyte compositions exhibit above 100 mAh g⁻¹ at 1C rate. This observation also suggests that electrochemical rate performance of the material is limited by the interfacial charge transfer kinetics and the ionic diffusivity of the material.

ET06.06.04
Exploring Anionic Redox Reactions of Non-Overlithiated Layered Oxides—LiNi₀.₃Co₀.₃Mn₀.₄O₂—Gi-hyeok Lee¹, Dhuo Kim², Jinsong Wu¹, Kyeyongj Cho³, Maenghyo Cho⁴, Wanli Yang² and Yong-Mook Kang¹;¹Department of Energy and Materials Engineering, Dongguk University, Seoul, Korea (the Republic of);²Seoul National University, Seoul, Korea (the Republic of);³Lawrence Berkeley National Laboratory, Berkeley, California, United States;⁴The University of Texas at Dallas, Dallas, Texas, United States.

In recent years, an interesting charge compensation mechanism by anions, also called anionic redox, has attracted a lot of attention in lithium ion battery society because it has considered as promising strategy to overcome the capacity limitations of classical cathode materials. Another important implication of this research trend is that it triggered the interest on anionic contribution in charge compensation of cathode materials. However, recent studies dealing with anionic redox are all concentrated on overlithiated materials. Here, we tried to unveil the anionic redox behavior in LiNi₀.₃Co₀.₃Mn₀.₄O₂ (NCM111), one of the representative layered oxide cathode materials, by reexamining the charge compensation mechanism of NCM111. Even though charge compensation mechanism of NCM111 in the practical voltage range (~4.5 V) have revealed in detailed by a variety of studies, the charge compensation mechanism in the high voltage region still remains unclear. Finally, through the detailed analysis, it is reconfirmed that the oxygen in the metal-oxygen bond contributes to the charge compensation in the low-voltage range, and the lone-pair oxygen participates in charge compensation in the high-voltage range. This finding is expected to not only provide a new perspective for anion redox researchers but also help establish a high voltage stabilization strategy for layered oxide materials.

ET06.06.05
Biomass-Derived Carbon as Bifunctional Oxygen Catalysts for Zinc-Air Batteries Mi-Ju Kim³, J. Eric Park⁴, Sung-Jun Kim⁵, Yong-Hun Cho¹ and Yung-Eun Sung¹;¹Seoul National University, Seoul, Korea (the Republic of);²Institute for Basic Science, Daejeon, Korea (the Republic of);³Kangwon National University, Samcheok, Korea (the Republic of).

Electrochemical oxygen reduction and oxygen evolution reactions are critical reactions in many energy conversion and storage system including metal-air batteries and fuel cells. Efficient and sustainable oxygen catalysts have been required to replace noble metal based catalysts. In this regards, application of biomass for catalysts have attracted increasing attention due to abundance and low cost. In this study, N, S-co-doped porous carbon were prepared from pyrolysis of bamboo stems following doping process. As zinc-air battery cathodes, the N, S-co-doped carbon exhibit extremely high maximum power density, based on the superior catalytic activity when compared to the previously reported biomass-based catalysts. These excellent performances can be attributed to adequate micro/mesoporosity and the presence of sufficient active sites. This work will provide sustainable and efficient strategies to design high-performance cathode materials for zinc-air batteries.

ET06.06.06
Graphitic Carbon Nitride-Based Materials as Synergistic Catalysts for Oxygen Electrocatalysis and Their Applications in Rechargeable Metal-Air Batteries Ji Eun Park¹, ², Mi-Ju Kim³, Yang-Hun Cho¹ and Yung-Eun Sung¹;³Institute for Basic Science, Seoul, Korea (the Republic of);³Seoul National University, Seoul, Korea (the Republic of);⁴Kangwon National University, Samcheok, Korea (the Republic of).

The development of a low-cost, highly active, and durable catalyst for oxygen electrocatalysis is crucial for water electrolyzer and rechargeable Zn-air batteries. Here we report the carbonaceous material, graphitic carbon nitride-carbon nanofiber material (g-CN-CNF), as bifunctional catalyst of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in alkaline media. g-CN-CNF catalyst exhibits enhanced catalytic performances for oxygen reactions, with high electron transfer number, low Tafel slopes, and low overpotentials. We applied the synthesized g-CN-CNF catalyst on primary and rechargeable Zn-air battery. The g-CN-CNF showed the comparable performance of primary cell with Pt despite the same catalyst loading. Furthermore, rechargeable Zn-air battery revealed that g-CN-CNF had a good retention of capacity for 156th cycling, resulting in the catalytic activity and stability of bifunctional catalyst. Therefore, g-CN-CNF is a good candidate for carbonaceous bifunctional catalyst which can be applied on practical electrochemical devices.

ET06.06.07
SnS₂, Sb₂S₃ and Ge-Containing Anode Materials for Potassium-Ion Batteries Lakshmi Vazhapully¹, Jimmy Wu¹, Ying I. Chen¹, Mokhlesur Rahman¹, Alexey Glushenkov¹, Alexey Mikhyailov⁴, Alexey Medvedev⁴, Neeraj Sharma⁴, Ovadia Lev⁵ and Petr Prikhodchenko⁵;¹Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia;²Kurnakov Institute for General Science and Organic Chemistry, Moscow, Russian Federation;³The University of Melbourne, Melbourne, Victoria, Australia;⁴Kurnakov Institute for General Science and Organic Chemistry, Moscow, Russian Federation;⁵The Casali Center of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.

The development of potassium-ion batteries as new energy storage systems using potassium ions as ionic shuttles has recently attracted significant attention [1]. It has been discovered that graphite has an ability to intercalate K⁺ ions reversibly, which results in a series of intercalation compounds and a theoretical capacity of 278 mAh g⁻¹. This has greatly stimulated the field to develop further. Apart from graphite and carbonaceous materials, families of inorganic compounds have been extensively studied as high capacity anodes in lithium-ion and sodium-ion batteries [2]. However, these inorganic phases have not been significantly explored as potassium-ion battery anodes yet.

Some of the candidate inorganic phases of metalloids and sulphides are studied by this team as prospective anode materials [3]. This includes germanium as well as sulphides of tin and antimony. These inorganic phases have been showed to deliver capacities of 350 - 1024 mAh g⁻¹ in lithium-ion and sodium-ion batteries [4, 5]. Here, we present an overview of potassium electrochemistry of these compounds. In order to prepare model materials, the phases of interest (Ge, SnS₂, and Sb₂S₃) are dispersed on sheets of reduced graphene oxide. The electrochemical activity and gravimetric capacities of anode materials are evaluated. Phases formed during the discharge and charge are probed via ex-situ X-ray diffraction measurements. It is demonstrated that capacities in excess of that of graphite are possible in the inorganic phases studied here. Conclusions on possible reaction mechanisms in these materials are made and are presented in this contribution as well.
Improved Electrochemical Performances of P- and O-Type Mixed NaMnO2 for Sodium-Ion Battery—A Study on the Natural Formation of Sodium Carbonate and Its Activation Method

Sodium manganese oxide (NaMnO2) is a representative cathode material for sodium ion batteries. Because of the preferred coordination of sodium ions in the MnO2 layer, sodium manganese oxide can be constructed into either P2 or O3 structure. Among them, sodium manganese oxide with the P2 structure exhibits better electrochemical performances compared to not only the O3 structure, but also other sodium ion cathode materials. However, the low sodium content of its initial state is one of its biggest limitations as a cathode material. Furthermore, many reports showed that the initial charge capacity of the P2 phase is lower than its theoretical capacity. Despite this, in-depth studies into the low initial charge capacity of the P2 phase have been so far absent.

At the same time, the formation of sodium carbonates on the surface of layered Na ion cathodes looks typical and more severe compared to that on layered lithium ion cathodes. This carbonate formation may be due to the reaction between atmospheric CO2 and sodium ions on the surface of the cathode materials. The formation of surface sodium carbonate is detrimental because it is electrochemically inactive and generally consumes significant amount of sodium ions during its formation. Our study indicated that the formation of sodium carbonate is one of the major causes for the deterioration of their electrochemical performance, including initial charge capacity, coulombic efficiency etc. We hypothesise that the formation of sodium carbonate alters the oxidation state of manganese on the surface, leading to lower electrochemical activity during its first charge. Therefore, we attempted to study the natural formation of sodium carbonate on the surface of sodium manganese oxide and suggest novel ways to enable the activation of the electrochemically inactive sodium carbonate, so as to achieve higher initial charge capacity.

Vertically Oriented Layered Sulfides MoS2 with Controlled Spatial Arrangement for Enhanced Sodium-Ion Battery

Layered transition metal sulfides are promising sodium intercalation hosts due to the opening van der Waals gap. However, deformation of its layered structure during repeated intercalation of sodium always result in undesirable cycle performance. Here we report vertically oriented MoS2 with controlled spatial arrangement on nitrogenous reduced graphene oxide sheets as a strategy to achieve unimpeded and stable sodium diffusion way. Controlled spatial arrangement were realized via a facile gel-precursor-based solvothermal method. Sheet density and height of MoS2 were gradually modulated and further tested as anode materials for sodium ion batteries. The optimized MoS2 with short sheet height and high sheet density can deliver remarkably reversible capacities of 255 mAh/g under a current density of 0.2 mAh/g and outstanding cycle performance with a total capacity fluctuation of 5.35% over 1300 cycles. The improvement electrochemical performance were verified due to the close-packed but short-length structure which can suppresses additional SEI layer formation and reduces the sodium diffusion resistance together with alleviates the structural deformation.

Impact of Calcination Temperature on Size Controlled Microstructure of NCA Cathode Material for Lithium-Ion Batteries

Due to its excellent cycling ability and high energy density, lithium-ion batteries (LIBs) are playing a crucial role in today’s technology. Unlike the technological advancement on LIBs anode electrodes, where they have high capacities and low manufacturing cost; cathode materials are facing weighty drawbacks like lower capacity, volume changes and distortions affecting the mechanical integrity of cathode and as a consequence of these limitations quite high manufacturing cost. LiNi0.50Co0.20Al0.30O2 (NCA) is one of the promising cathode materials that has been comprehensively utilized with various synthesis methods. The objective of the study is to synthesize NCA via solid-state reaction method and investigate the influence of sintering temperature of 750, 800 and 850 °C on the morphology of the powders by SEM. In this work, we started the NCA synthesis with a sol-gel method. The powder obtained from the dried sol was calcined as the initial thermal treatment. After that, the calcined samples were sintered with a stoichiometric amount of lithium carbonate at different temperatures. XRD analysis was performed in order to observe the phase analysis of the samples sintered at several temperatures. Electrochemical tests including cycle performance and cyclic voltammetry were also performed. Results indicated that the synthesized NCA cathode that was sintered at 750 °C had a favorable electrochemical performance and the capacity retention of NCA sintered at 750 °C is better than the ones sintered at 800 and 850 °C without capacity loss at various high C rates. The correlation between the cathode performance and the final microstructure was developed and this was directly related to the specific surface area and porosity of the materials.

Direct Hierarchical Fabrication of Sheet Like SnS2 Nanostructure on CNT as an Anode Material for High-Performance Lithium-Ion Battery Application

In recent years, two-dimensional (2D) layer structure metal dichalcogenides and their composites with 1D and 2D carbonaceous materials are considered as promising anode materials for lithium-ion battery due to their higher theoretical capacitance and conversion reaction with Li. Among several 2D metal chalcogenide SnS2 has appeared as an anode material for Li-ion battery applications due to optimistic high efficiency at lower redox potential. However, in practice the SnS2 as an anode material in Li-ion battery is suffering from its low intrinsic electric conductivity, structural instability and large volume expansion during charging reaction.

References

In this study, we have fabricated hierarchical SnS$_2$-CNTs composite on carbon cloth (CC) as an anode by binder free direct growth method for Li-ion application. We adopted two-step fabrication methods: CNTs were prepared by a microwave plasma-enhanced chemical vapor deposition (MPECVD) and followed by solvothermal process to synthesize uniform tin disulfide (SnS$_2$) nanosheet on CNTs (SnS$_2$-CNTs). X-ray diffraction, Raman's spectroscopy, FE-SEM and HR-TEM studies showed that the as synthesized SnS$_2$-CNTs possessed a hierarchical composite nanostructure anode. The optimized hybrid SnS$_2$-CNT anode showed superior electrochemical performance in Li-ion battery, indicating highest performance of 1250 mAh/g at 645 mA g$^{-1}$ after 120 cycles with high rate capability. The direct growth SnS$_2$-CNT hybrid hierarchical architectures showed the synergistic effect for superior electrochemical performance due to improved surface reactivity, electrical conductivity and strong mechanical strength of insulating SnS$_2$ in composite anode material. We believe our hierarchical SnS$_2$ nanosheet grown on CNT makes this a promising anode material for Li-ion battery application.

Reference

ET06.06.12
Visualizing Live-Formation of Interphase at Atomic Scale

ET06.06.13
Computational Study of LiO$_2$: Clustering in Solvent in Li-Air Batteries

ET06.06.14
Highly-Doped 3D Graphene Na-Ion Battery Anode by Laser Scribing Polyimide Films in Nitrogen Ambient

ET06.06.15
Electrode Design from Atomic to Mesoscale Dimensions

ET06.06.16
LiSICON Structured Ortho-Germanates as Cathode Material for Li-Batteries
including Li2MnGeO4 and Li2MnPO4F (M = Fe, Mn or Co). In the case of Li2FeSiO4, its operating voltage vs. Li/Li+ (2.8 V) and specific capacity of 166 mAh g⁻¹ lead to energy densities in the range of 500 Wh kg⁻¹, which is only slightly less than that of LiFePO4. Recently, another lithium iron silicate, Li2Fe2O4·SiO2 has been investigated. Li2Fe2O4·SiO2 has a similar structure to lithium super ionic conductor (LiSICON) Li2Zn3GeO4 and exhibits better kinetics than Li2FeSiO4 at higher discharge rates. However, iron silicate-based materials have an operating potential of 2.8 V vs. Li/Li⁺ and compounds possessing the features of Li2Fe2O4·SiO2 with higher operating voltages are of considerable interest.

The similarity in structure between the LiSICON Li2Zn3GeO4 and Li2Fe2O4·SiO2 has motivated us to investigate the electrochemical properties of compounds with the chemical composition of Li2MnGeO4 (M = Mn, Co). While Li2MnGeO4 has already been studied, to the best of our knowledge, this is the first report of the synthesis and properties of the Mn isomorph, Li2MnGeO4. In contrast to the Co compound that can be synthesized at 900°C in air, the Mn compound has been synthesized under argon at 700°C to obtain the proper Mn valence. The Co and Mn materials show very different electrochemical properties. Whereas the Li2MnGeO4 exhibits very little redox activity, the Li2MnGeO4 can be charged and discharged between 1.5 and 4.8 V vs. Li/Li⁺ with lithium capacities in excess of 100 mAh g⁻¹, which is close to the capacity of 97 mAh g⁻¹ for one electron redox reaction. Interestingly, the (de)charge curves vary monotonically with lithium content, suggesting a single phase (de)chemical mechanism. Additional details regarding the kinetics of Li2MnGeO4 and comparisons to Li2Fe2O4·SiO2 will be presented.

**ET06.06.17**

Conventional Carbon Coated CZTS Anode Material for High Capacity and High Rate Capability in Lithium-Ion Battery Applications

Bhav Venu Gopal,1,2,.Zero Syunn Hidaru,1 Satyanarayana Moru,2 Indrajit Shown,1 Anir Sabbah,1 Heng-Liang Wu3, Chih Wei Chu1, Chih-Han Lee1, Li-Chyong Chen1 and Kuei-Hsien Chen1,4; 1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan; 3Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei, Taiwan; 4Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; 5Research Centre for Applied Sciences, Academia Sinica, Taipei, Taiwan.

Investigation of novel electrode materials with high areal capacity, faster electron transport kinetics, and high Li ion diffusion are currently one of the most active frontiers for improving energy density of lithium ion batteries (LIBs). In order to fulfill these demands of LIB’s, herein, we developed 3D structure of CZTS flowers by hydrothermal method and followed by simple and facile carbon coating in ex-situ step. A systematic electrochemical performance behavior has been carried out at different amount of carbon coating. The developed nanoscale carbon coating enhanced conductivity of CZTS and buffer the mechanical stress/strain induced over extended cycling. As a results, carbon-coated 3D structured CZTS showed high areal capacity about 1-2 mAh/cm² as well as high gravimetric capacity (1210 mAh/g) combined with excellent stability (100 cycles) and high rate capability (1500 mAh/g, 920 mAh/g and 425 mAh/g at 500 mA/g, 2000 mA/g and 5000 mA/g) is superior to other metal chalcogenide materials. This study highlights the potential importance of conformal carbon coating over electrode material as an effective strategy for enhancing the columbic efficiency and charge storage kinetics of active material.

**ET06.06.18**

Exploring Novel LiCe(WO4)2 Polymorphs as Anode Materials—Synthesis, Crystal Structure and Electrochemical Studies

Archanaka K. M1, Debasmita Dwibedi2, Prabeer Barpanda3, James Hester3, Diptikanta Swain4 and Nalini G. Sundaram1; 1Poornaprajna Institute of Scientific Research, Sadashivanagar, India; 2Materials Research Centre, Indian Institute of Science, Bengaluru, India; 3Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales, Australia; 3Solid State and Structural Chemistry Unit, Indian Institution of Science, Bengaluru, India.

Rechargeable batteries have attracted much attention in recent years with the growing demand for energy to empower modern consumer electronics and stationary power grids. Electrode stability is found to play critical role in determining electrochemical activity of polyanionic compounds, among many (MoO₃)ₓ (and (WO₄)ₓ) that have gained recent attention due to their greater polyanionic stable framework. In this context, AT(MOₓ)₂ₙ where A=alkali metal ion, T=Transition metals such as (Fe, Co, Y and Rare earths), M=MnxMoₙ based oxide materials are multifunctional disordered materials recently studied for lithium ion batteries. Although the existence of polymorphism is well established in many of the alkali rare earth double tungstates, to date, detailed phase transformation, precise crystal structure analysis of LiCe(WO4)₂ polymorphs and electrochemical properties is not yet discussed. Therefore, an attempt has been made to correlate the electrochemical activity of α-phase and β-phase with the crystal structure insights obtained via high temperature neutron diffraction and further supported by Raman studies.

Polymorphs of LiCe(WO4)₂ [α-LiCe(WO4)₂ and β-LiCe(WO4)₂] were successfully synthesized by citric acid assisted sol-gel method for the first time. Phase purity and crystallinity was confirmed by powder X-ray diffraction studies; and further characterized by FESEM, Raman spectroscopy and TG-DTA techniques. Investigation of the effect of calcination temperature and time suggested the existence of an irreversible structural phase transition from low temperature (LT) β-phase to high temperature (HT) α-phase, which was systematically followed by high temperature neutron diffraction (HT-NPD) studies. Rietveld refinements using room temperature NPD data revealed that the α-LiCe(WO4)₂ crystallizes in tetragonal crystal system (I4/m) in a Scheelite type structure, while β-LiCe(WO4)₂ material crystallizes in triclinic system (P-1) in a LiPb(WO₄)₂ type structure. Further, β-LiCe(WO4)₂ undergoes a reconstructive phase transition where the WO₆ octahedra rearranges to WO₄ tetrahedra at high temperatures in α-phase and this is further supported by Raman analysis. Electrochemical analyses of the anodic redox activities of these polymorphs were carried out via galvanostatic and cyclic voltammetry measurements. Interestingly the β-phase showed promising charge-discharge cycling compared to the α-phase, which could be attributed to the easy diffusion of Li-ions in between the parallel layers of WO₆ octahedra. To the best of our knowledge this is the first study elucidating the synthesis, detailed crystal structure analysis, phase transitions and the electrochemical properties of LiCe(WO4)₂ polymorphs.

**ET06.06.19**

Conversion Reaction of Nanoporous ZnO for Stable Electrochemical Cycling of Binderless Si Microparticle Composite Anode

Donghyuk Kim1,2, Min Kyu Park1, Sang-Min Kim1,2, Seungmin Hyun2 and Seung Min J. Han1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Novel binderless, additive-less Si electrode design was developed where a nanoporous ZnO matrix is coated on a Si microparticle electrode to accommodate extreme Si volume expansion for stable electrochemical cycling. Conversion reaction of nanoporous ZnO forms an ionically and electrically conductive matrix of metallic Zn embedded in LiO that surrounds the Si microparticles. Upon lithiation, the porous Li+Zn matrix expands with Si preventing extensive pulverization and Zn serves as active material to form LiZn to further enhance capacity. Electrodes with high Si mass loading of 1.5 mg cm⁻² were fabricated and a high initial capacity of ~3,900 mAh/g was achieved with excellent reversible capacity of ~1,500 mAh/g (areal capacity ~1.7 mAh/cm²) even after 210 cycles. A high first cycle coulombic efficiency of 117% was obtained owing to the conversion reaction of nanoporous ZnO, which is a unique feature in comparison to conventional Si anodes. Ex-situ imaging confirmed that the nanoporous ZnO coating maintained the coalescence of SiMPs throughout extended cycling. Therefore, the Li/ZnO matrix derived from conversion reacted nanoporous ZnO acts as an effective
buffer to lithium induced stresses from voltage expansion and served as a binder-like matrix that contributes to overall electrode capacity and stability.

ET06.06.20
Pore-Filling of Waste Biomass Carbon by 3D Nanoflowers and Many-Fold Enhancement in Capacitive Charge Storage
Mashtahat Mohd Yusoff, Bincy Lathakumary Vijayan, Bhupender Pal, Izzan Izwan Misnon and Jose Rajan; University of Malaysia Pahang, Kuantan, Malaysia.

Storage of electrical energy in media and protocols with high energy and power densities have received a revived interest due to high power mobile electrical devices, electric vehicles, and other disconnected from grid but electrically powered technologies such as drones and robots. As a result, many new battery concepts such as sodium batteries, lithium-air, and lithium-sulphur are currently under intensive research as a replacement for traditional lithium ion batteries. One of the promising replacement for batteries is supercapacitors owing to their potentially higher power density (~5 kW kg⁻¹) and longer life cycle (>100,000) compared to that of batteries; however, they have an unimpressive energy density, which is at least an order of magnitude lower than that of batteries. Allotropes and polymorphs of carbon from diverse sources are a universal choice to fabricate supercapacitor electrodes; owing to their renewability carbons from waste biomass is now an active area of research. Most of these biomass-derived carbons process a large volume of passive pores which do not contribute to the final functionality of the devices. In this paper we show that the passive pores could be effectively filled using 3D hierarchical ceramic nanostructures such as flowers and the resulting composite offer charge storage capabilities several fold higher than its constituents or when they are filled using conventional nanoparticles. Finely powdered kernels of oil palm seeds are used as the source of carbon; nanoparticles and 3D flower-shaped ceramic nanostructures are integrated into the pores of carbon via a simple wet impregnation method. The pure carbon showed a specific surface area of ~500 m² g⁻¹; and when used as an electrode for supercapacitive charge storage gave a specific capacitance (Cₑ) of 150 F g⁻¹ with cyclic stability (97% after 5000 cycles) in 1 M Na₂SO₄ electrolyte (achievable potential ~1 V). When the flowers are impregnated, the Cₑ increased five-folds whereas the carbons impregnated with nanoparticles did not even doubled. In addition to the enhanced charge storage, flowers-filled carbons showed improved potential window also; carbon with MnCoO₃ flowers showed the highest (530 F g⁻¹) with a potential window of ~1.2 V. The reason for many fold enhancement in Cₑ is systematically studied and shown that this increment resulted from efficient ion transport through pore channels. Newly prepared carbon composites could retain ~97 % of their initial capacitance even after 5000 cycles. The adopted methodology is simple, scalable as well as applicable for a broad range of pseudocapacitive materials.

ET06.06.21
Electrocatalysis of Polysulfide Conversion by MnO₂: Nanoflakes in High-Performance Lithium-Sulfur Batteries
Zhihao Yu, Ying Yang, Tiaoji Gao and TrungHieu Le; Department of Electrical Engineering, Tsinghua University, Beijing, China.

The MnO₂/CNF composite was synthesized from CNF and KMnO₄ by a one-step facile method. This composite was utilized as the cathode interlayer to suppress the shuttle effect of polysulfides in lithium-sulfur (Li-S) batteries. In addition, from the X-ray photoelectron spectroscopy data, the change of chemical valence of manganese was observed during charge-discharge cycling, which indicated the electrocatalysis progress in batteries. Thus, the Li-S batteries with MnO₂/CNF interlayer appeared a high-performance in high current rate due to the improved kinetic rate with the introduction of catalyst. The cells with MnO₂/CNF achieved an initial capacity 893 mAh/g, and remained at a reversible capacity of 640 mAh/g after 150 cycles in 1C, nearly three time higher than the retention of capacity cells without interlayer.

ET06.06.22
Intercalation Materials (Pyrophosphate and Metaphosphate) as Next-Generation Electrocatalysts for Rechargeable Sodium-Air Battery
Sou Yasuhara1, Yumi Yoshikawa2, Takashi Teranishi3, Shintaro Yasui3, Tomoyasu Taniyama1,3 and Mitsuru Itoh1;1 Tokyo Institute of Technology, Yokohama, Japan; 2Okayama University, Okayama, Japan; 3Nagoya University, Nagoya, Japan.

Due to rapid increase in energy demand present world needs to harvest energy in the form of electricity to fulfill the everyday growing demand. Electrical energy can be efficiently stored in electrochemical energy storage devices such as supercapacitors, batteries, and fuel cells. Among them, rechargeable (metal-ion/metal-air) batteries form the most promising and commercially viable solution. Owing to the light weight and high energy density, Li-ion battery (LIB) has been considered a major success in electric vehicles. However, phosphorus-based polyanionic materials (e.g. LiFePO4) have been proposed as robust and safe cathode materials for the next generation LIB. In addition to efficient intercalation chemistry, various phosphate-based compounds have been exploited to efficient bifunctional catalysis for water splitting showing good oxygen evolution reaction (OER) with appreciable oxygen reduction reaction (ORR) activity. Also low theoretical capacity associated to the high molecular weight of such phosphate-based system has withdrawn attention towards electrocatalysis and found to shown activity close to conventional and commercial electrolysis catalysts such as Pt/C and RuO₂ for air-battery application. Off-late, sodium-ion batteries (SIB) are being extensively explored as economic alternatives to LIB. Here, the electrochemical and electrocatalytic performance of pyrophosphates [Na₂MP₂O₇] and metaphosphates [NaM(PO₃)₃], have been explored to develop Na-ion and Na-air batteries. They can be easily synthesized by solution combustion as well as conventional solid-state method involving moderate annealing at 600 °C for 6 h.

Pyrophosphates: We have investigated the binary Naₓ(Feₓ₋₀.₅Znx)P₂O₇ (0 ≤ x ≤ 1) pyrophosphate family, where NaₓFeₓP₂O₇ (P = 1, 2) and NaₓZnP₂O₇ (P = 1, 2) end members are anisochronous. We will report the structural and electrochemical characterization of novel Naₓ(Feₓ₋₀.₅Znx)P₂O₇ (0 ≤ x ≤ 1) binary pyrophosphates. Further, we will describe the Na-insertion mechanism in Naₓ(Feₓ₋₀.₅Znx)P₂O₇ (x = 0, 0.25) obtained by a small-amplitude (incremental) techniques such as galvanostatic intermittent titration (GITT) and potentiostatic intermittent titration (PITT). Pursuing pyrophosphate chemistry, the superior bifunctional electrocatalytic activity of NaₓCoP₂O₇ will be demonstrated.

Metaphosphates: We will showcase (i) a 2.8 V Fe⁷⁺/Fe⁴⁺ redox activity in orthorhombic Na₅Fe₅P₄O₁₄ developed by combustion synthesis and (ii) a 3.2 V Co⁷⁺/Co⁴⁺ redox activity in cubic polymorph of Na₅Co₅P₄O₁₄. However, their high molecular weight leads to limited reversible capacity. Nonetheless, the presence of metal redox centres can be exploited to enhance electrocatalytic performance. We will demonstrate the electrocatalytic properties (e.g. OER) of the Fe, Mn, and Co analogues of metaphosphate. Synergising experiments with computational modelling, we will showcase the electrochemical and electrocatalytic activity of Na₅Fe₅P₄O₁₄ and Na₅Co₅P₄O₁₄ for the first time.

ET06.06.23
Enhancement of High-Rate Performance by High Permittivity Supported Materials in Thin-Film Lithium-Ion Battery
Seo Yasuhara1, Yumi Yoshikawa2, Takashi Teranishi3, Shintaro Yasui3, Tomoyasu Taniyama1,3 and Mitsuru Itoh1; 1 Tokyo Institute of Technology, Yokohama, Japan; 2Okayama University, Okayama, Japan; 3Nagoya University, Nagoya, Japan.

Li ion battery (LIB) is a most famous secondary battery because of its superior characteristics such as high working voltage, large specific capacity, lightweight and so on. However, capacity of LIB fades under applying large current, therefore the charge speed(current) is still restricted at least below 2C. For example, we needs approximately 2-3 hour to fully charge the smartphone. Realization of high-speed rechargeable LIB will make us possible to eliminate the charging time. We have reported that BaTiO₃ dot supported LiCoO₂ cathode exhibit better chargeability under high-rate charge/discharge.

Sou Yasuhara1, Yumi Yoshikawa2, Takashi Teranishi3, Shintaro Yasui3, Tomoyasu Taniyama1,3 and Mitsuru Itoh1; 1 Tokyo Institute of Technology, Yokohama, Japan; 2Okayama University, Okayama, Japan; 3Nagoya University, Nagoya, Japan.

Li ion battery (LIB) is a most famous secondary battery because of its superior characteristics such as high working voltage, large specific capacity, lightweight and so on. However, capacity of LIB fades under applying large current, therefore the charge speed(current) is still restricted at least below 2C. For example, we needs approximately 2-3 hour to fully charge the smartphone. Realization of high-speed rechargeable LIB will make us possible to eliminate the charging time. We have reported that BaTiO₃ dot supported LiCoO₂ cathode exhibit better chargeability under high-rate charge/discharge.
Gas-Phase Synthesis of Si/SiNx Nanoparticles as Anodes for High-Performance Lithium-Ion Batteries—Study of the Effect of the Carbon Source on Electrochemical Performance Nicolas Eshraghi1, Abdelfattah Mahmoud2, Jérôme Bodart1, Bénédicte Vertruyen1, Rudi Cloots1 and Frederic Boschuhn2; 1GREENMat Laboratory, University of Liège, Liège, Belgium; 2LCIS Laboratory, University of Liège, Liège, Belgium.

Lithium-ion batteries have enjoyed great success and have outperformed other rechargeable battery system since 1980. However, Li-ion batteries face many challenges and limitations: safety, the low abundance of lithium in the Earth’s crust. Recently, Sodium-ion batteries attracted a lot of interest as a potential alternative to lithium-ion batteries for large-scale energy storage applications, due to the large natural abundance and lower cost of sodium. In recent years, fluorophosphates with the NASICON (Na Super-Ionic Conductor) type structure are considered among the most interesting series of cathode materials for Li/Na-ion batteries, because they exhibit rich chemistry, attractive lithium/sodium insertion properties and thus offer promising electrochemical properties [1]. Na2V3(PO4)3F0.5 (NVPF) attracted high attention thanks to its promising electrochemical properties. The inductive effects of both PO43- and F- allow for a high working potential combined with a high theoretical specific capacity due to the multiple oxidation states of vanadium[1-2]. One of the key drawbacks of Na2V3(PO4)3F electrodes is their low intrinsic electronic conductivity.

NVPF and NVPF/carbon composite materials were prepared by spray-drying method using the same conditions used in our previous work [2]. Spray drying is an effective and easily up-scalable route to prepare homogeneous multi-component powders, thus making it a suitable method to incorporate carbon in the composite powder. We used different carbon sources like conductive carbons (MWCNTs, Carbon Black, etc) and organic sources (PVA, Citric Acid, Ascorbic acid, etc) to prepare NVPF/carbon composite powders.

the structural, electrochemical, and morphological properties of the synthesized Na2V3(PO4)3F0.5 samples were systematically investigated in order to understand the influence of carbon source on structural and morphological properties and most importantly electrochemical performance of NVPF and NVPF/carbon composite cathode materials for Na-ion batteries. The chemical diffusion of Na ions was studied using results obtained by varying scan rates in cyclic voltammetry measurements. Raman spectroscopy is used to evaluate the quality in disordered carbon materials and its electronic conductivity [3] and compared the results with the results from EIS and cycling performance of different samples.

Gas-Phase Synthesis of Si/SiN nanoparticles as Anodes for High-Performance Lithium-Ion Batteries Stefan Kilian1, Lisong Xiao1, Hartmut Wiggers1, 2 and Christof Schulz1, 2; 1Institute for Combustion and Gas Dynamics – Reactive Fluids, Universität Duisburg-Essen, Duisburg, Germany; 2Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, Duisburg, Germany.

Silicon has emerged as the most promising component in anode materials for next-generation lithium-ion batteries (LiIBs) owing to its natural abundance, relatively low working potential, and its high theoretical storage capacity of 3579 mAh/g. However, the practical application of Si-based anodes is severely hindered by its low intrinsic electrical conductivity and its large volume change (~300%) during charging and discharging. The resulting mechanical stress causes rapid pulverization of the silicon, and insulation and disconnection of the active material from the current collector. These failure events can cause rapid degeneration of the Si electrode and is especially prominent for silicon particles exceeding the size of a few hundred nanometers. Thus, recent research mainly focuses on nanostructures and nanocomposites that tolerate the volume change.

A very promising way to stabilize silicon in LIB anodes is the incorporation of nitrogen, which has been shown to significantly improve the cycle performance. We therefore developed a scalable gas-phase synthesis method based on the pyrolysis of monosilane in ammonia-rich atmosphere. Therefore, we are able to synthesize Si3N4 core/shell nanoparticles for high-performance anodes. Their electrochemical performance can be increased by adjusting the synthesis parameters, thus affecting stoichiometry, Si3N4 ratio, morphology, particle size, and crystallinity. FTIR measurements confirm the synthesis of high-purity silicon nitride coatings avoiding SiH, Si-O, or Si-OH functional groups that might increase parasitic surface reactions. First results show significantly enhanced cycling performance of LIB-electrodes comprised of Si3N4 nanoparticles. Electrodes made of materials with low nitrogen content (approx. 5 at.%) show an initial specific discharge capacity as high as 720 mAh/g and a highly stable cycle performance with a capacity retention of 92% after 100 cycles. LIB electrodes comprised of Si3N4 nanoparticles with high nitrogen content (approx. 56.5 at.%) show much lower initial specific discharge capacities of 350 mAh/g. However, repeated electrochemical cycling seems to increasingly activate the material leading to a highly stable cycle performance and a retention of 125% after 100 cycles. These results imply that Si3N4 based LIB electrodes are promising candidates for high-performance lithium-ion batteries with very high durability.


Demands for rechargeable batteries with higher energy density have continued to rise as the amount of the energy required for next-generation portable electronic devices and electric vehicles increases. Rechargeable lithium sulfur (Li/S) batteries have been intensively studied over the past several years to fully utilize their high theoretical energy density (2600 Wh kg-1). However, the fundamental challenge to the commercialization of Li/S batteries is the practical design of sulfur cathodes that enable competitive electrochemical performance while maintaining the sulfur content and the loading high enough for the electrolyte/sulfur ratio and the cost of inactive components low. This paper presents a novel solvent drying method that is designed to help the wet-dry surface of the slurry endure the local tension stress from the shrinkage rate difference. Using our scaffold-supported drying approach, we have fabricated a crack-free sulfur electrode of ultrahigh loading (16 mg cm-2) with a high sulfur content of 65%. The compact structure without excessive carbon interlayers or 3D arc-architectured scaffolds allows the electrolyte/sulfur ratio to be as low as 7 and exhibits a good capacity retention of 11 mAh cm-2 over 80 cycles. Our results show that the crack-free and compact structure enhances the electrical network, the uniform reaction throughout the whole active mass, and thus the reversibility of the active mass. We also confirmed the applicability of the scaffold-supported drying approach to other types of scaffolds.
When coupled with a thoroughly-designed scaffold, the facile scaffold-supported drying approach provides limitless directions for high energy density batteries, closing the gap between research and commercialization of Li/S.

**ET06.06.29**

**Synthesis, Characterization and Comparison of Phosphonium and Piperidinium Based Ionic Liquid Electrolytes**

Jennifer Chapman Varela, Alexander Hino, Karthika Sankar, David Coker and Mark Grinstaff; Boston University, Boston, Massachusetts, United States.

The operation of lithium ion batteries (LIB) at elevated temperatures is a unique chemical challenge as the electrolyte materials must be thermally, electrochemically, and chemically stable at temperatures from 60 to 150 °C. Currently, carbonate based electrolytes do not satisfy these requirements and new materials are needed to fabricate high temperature operational LIBs. To that end, we have synthesized three phosphonium and three piperidinium based ionic liquids (ILs), and prepared 1.0 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) salt electrolytes and characterized the thermal stability, viscosity, conductivity, and electrochemical stability window of each compound. An alkyl ether chain was introduced into the structure of both the phosphonium and piperidinium cationic cations and analogues containing one or two ether atoms were prepared. With these structural changes, we hypothesize: (1) that the distinct structural differences between the phosphonium and piperidinium cationic center will have substantial impacts on the conductivity and viscosity; and (2) the incorporation of the alkyl ether will have a concurrent reduction in viscosity and increase in conductivity. The phosphonium and piperidinium based ILs displayed large differences in all measureable outcomes; the phosphonium ILs were more conductive, less viscous and have larger electrochemical stability windows. For example, phosphonium ILs with one alkyl ether incorporated were electrochemically stable from -1 to 5 V at 25 °C while the analogues piperidinium ILs were only stable from -1 to 2 V at 25 °C. Furthermore, inclusion of the alkyl ether affected the viscosity and conductivity of the ILs; at 25 °C the piperidinium based ILs displayed varied conductivities with values of 1.40, 2.29, and 1.99 mS/cm with zero, 1 and 2 alkyl ether substitutions, respectively. These findings support further exploration of the phosphonium based ILs for high temperature operations of LIB.

**ET06.06.30**

**A First Principles Study of Spinel ZnFe₂O₄ for Electrode Materials in Lithium-Ion Batteries**

Haoyue Gao, Amy C. Marschilok, Kenneth Takeuchi, Esther Takeuchi, and Ping Liu; Department of Chemistry, Stony Brook University, Stony Brook, New York, United States; Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States; Energy Sciences Directorate, Brookhaven National Laboratory, Upton, New York, United States; Chemistry Department, Brookhaven National Laboratory, Upton, New York, United States.

Spinel zinc ferrite (ZnFe₂O₄) is a candidate anode material for Lithium-ion batteries (LIBs), owing to its large theoretical capacity of 1000 mAh g⁻¹. Although the structure of ZnFe₂O₄ has been well studied, the origin of the high performance in LIBs materials is not well understood, in particular the fundamental understanding of the discharge mechanism is lacking. Here, we report a density functional theory (DFT) study of the discharge process at early stage from ZnFe₂O₄ up to Li₃ZnFe₂O₄ (x = 2), where both bulk and various relevant surfaces are into consideration. The estimated open-circuit voltages based on the stable intermediate bulk and surface structures identified by the DFT calculations are in good agreement with the experimental values, which enables the in-depth understanding of the discharge mechanism at the atomic level. Our study not only highlights the importance of the interplay among Li, O²⁻, Fe³⁺ and Zn²⁺ in enabling the high performance as LIBs materials, but also provides a design strategy for more stable particle morphologies with enhanced discharge performance.

**ET06.06.31**

**Mechanisms of (De)lithiation of Silver Containing α-MnO₂—Impact of Transition Metal Dissolution and Structural Evolution**

Lisa Housel, Jianping Huang, Paul Smith, Alexander B. Brady, Alyson Abraham, Mikaela Dunkin, Esther Takeuchi, Amy C. Marschilok, and Kenneth Takeuchi; Stony Brook University, Stony Brook, New York, United States; Brookhaven National Laboratory, Upton, New York, United States.

Crystallite size reduction of an electroactive material is a tool to increase deliverable capacity of a lithium ion battery by decreasing the path length for lithium ion diffusion. However, the reduction of crystallite size may also negatively impact the cycle life of the battery by promoting unfavorable reactions. The impact of crystallite size on the capacity retention, reversibility and rate capability of silver containing α-MnO₂ will be presented in light of two contributing mechanisms. First, delivered capacity may be hindered by the irreversible loss of the electroactive material to electrolyte. The transition metal may deposit on the anode, forming a layer that prevents ion migration and increases internal resistance of the cell. Quantitative dissolution studies conducted as a part of this work will be discussed. Second, capacity losses in α-MnO₂ materials may result from structural distortion of the 2x2 MnO₂ tunnels that make up the crystal structure. Observations regarding structural evolution as a function of (de)lithiation as determined by several complementary characterization modalities, including synchrotron based x-ray absorption spectroscopy, will also be discussed. In summary, this work quantitatively deciphers the effect of structural distortion and transition metal dissolution on capacity retention of electrodes with different crystallite sizes, facilitating rational future development of long life, high capacity energy storage systems based on tunnelled crystallographic motifs.
Metallic zinc has been regarded as an ideal anode material for the aqueous batteries systems for its high theoretical capacity (820 mAh/g), low negative potential (0.762 V vs. SHE), abundance, low toxicity and the intrinsic safety advantages that arise from nonflammable aqueous electrolytes. Recently, rechargeable batteries using zinc metal anode have been investigated extensively. However, an important barrier of the Zn based batteries is the poor cycle life. The cyclability of the traditional alkaline Zn based batteries is mainly restricted by dendrite growth, high solubility of discharge product (i.e. zincate) in the electrolytes, water loss from the liquid electrolyte, electrolyte depletion caused by the narrow electrochemical window. In most previous studies, the zinc-based aqueous batteries suffered from low columbic efficiency (CE) even using the high rate to minimize the side reaction. Significant excessive zinc has to be used to keep the cycle stability, results in the suboptimal utilization of the zinc theoretical capacity, as in the case of the lithium metal anode. The goal of achieving high CE in aqueous zinc metal batteries remained elusive.

The poor reversibility and low CE of the Zn metal anode are closely related with the Zn (II) cation solvate structure in the aqueous electrolyte. The hydration effects of the Zn (II) cation in water is so significant that the zinc hydroxide is easily formed. The slight but nonignorable water decomposition caused by the narrow stability window produces more hydroxyl ion and certainly aggravates the formation of zinc hydroxide. Zinc hydroxide converts into insoluble zinc oxide (ZnO) when the solubility limit of the hydroxide species is reached. Formation of solid ZnO can be a difficult process to reverse during recharge.

We report the development of a highly concentrated neutral electrolyte that alters Zn(II) solvation structure resulting in the dendrite-free plating of Zn metal with high CE. The suppression of the zinc hydration was achieved through the formation of [ZnTFSI] solvation structure instead of the [Zn(H2O)6]2+ solvation structure. The solvation structure change is ascribed to the introduction of the TFSI anion, which has the strong coordination to the Zn (II) cation in concentrated electrolytes. The solvation structure change was investigated via a combination of IR spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, density functional theory (DFT) calculations and molecular dynamics (MD) simulations using polarizable force fields. We demonstrate an exceptional performance of zinc metal cells containing Zn-based aqueous electrolyte that delivered an unprecedented high practical energy density of 300 Wh/kg (based on both the cathode and anode electrolytes). This study opens an avenue for the highly efficient utilization of zinc metal electrodes for advanced energy storage applications while the fundamental knowledge gained can also be applied to other metal anodes.

The greatest remaining challenges facing the development of electrochemical energy storage – such as durability, safety and fast charging – lie in the development of appropriate materials. We present a concept where redox-active conjugated polymers are specially designed to operate in safe electrolytes (e.g. salty water). After identifying suitable organic conjugated polymer backbones which can be reversibly charged and discharged in aqueous solutions, we studied the role of the side chain on the electrochemical redox reactions. Polar side chains were attached to the backbone to increase ion conduction to allow for a reversible and fast charging and discharging of the materials in pH neutral sodium chloride water based electrolytes. In particular, ethylene glycol based side chains were attached for the polymer which becomes oxidized (p-type polymer) and zwiterion side chains for the polymer which becomes reduced (n-type polymer). This strategy enables the reversible charging and discharging of non-porous, single phase films (additive free) with non-toxic aqueous electrolytes on timescales of seconds. Finally, we demonstrate the use of the developed concept in a battery device combining the p- and n-type conjugated polymers as the cathode and the anode of a water based electrochemical storage cell that can be operated under a nearly unpolar
Lithium-ion batteries have reshaped our life with their omnipresence in portable electronics. However, increasing the specific energy of these batteries is reaching its limit and high-profile fire accidents (e.g., cell phones spontaneously combusting) cast doubt on their applications in electric vehicles and large-scale energy storage. Intrinsically safe batteries such as aqueous batteries and all-solid-state batteries are being actively studied in the battery community. Aqueous batteries use water-based electrolytes and offer robustness and environmental friendliness over lithium-ion batteries that feature flammable organic electrolytes. However, their adoption is plagued by the poor cycle life due to the structural and chemical instability of the anode materials. In the first part of talk, I will report several redox-active quinones (oxidized derivatives of aromatic compounds) as anodes for aqueous batteries by exploiting their structurally stable ion-coordination charge storage mechanism and chemical inertness towards aqueous electrolytes. We demonstrate three systems that coupled with industrially established cathodes and electrolytes exhibit long cycle life (up to 3,000 cycles/3,500 h), fast kinetics (320°C), high anode specific capacity (up to 200-395 mA h g⁻¹), and state-of-the-art specific energy/energy density for several operational pH values (-1 to 15), charge carrier species (H⁺, Li⁺, Na⁺, K⁺, Mg²⁺), and atmosphere (with/without O₂). Reversible proton-coupled electron transfer process is also first demonstrated in organic crystals. In the second part, I will discuss the application of quinones in all-solid-state batteries. One main challenge is the mismatch between low anodic decomposition potential of solid-state sulfide electrolytes and high operating potentials of cathodes which lead to a volatile cathode–electrolyte interface. I will show how molecular engineering of quinone molecules leads to high-capacity cathode materials in all-solid-state batteries that is chemically and electrochemically compatible with sulfide electrolyte.

10:30 AM ET06.07.07
Concentrated Mixed Cation ‘Water-in-Salt’ Solutions as Green and Low Cost High Voltage Electrolytes for Aqueous Batteries
Maria Lukatskaya1, Jeremy Feldblum2, David Mackanic1 and Zhenan Bao1; 1Chemical Engineering, Stanford University, Stanford, California, United States; 2Chemistry, University at Albany, State University of New York, Albany, New York, United States.

Electrolytes are an essential component of energy storage devices. Electrolyte composition has a significant impact on the safety, price and performance of the battery. Intrinsically nonflammable aqueous electrolytes can offer safer battery operation and decreased associated toxicity, but suffer from a smaller electrochemical stability window (and hence energy density) compared to traditional organic electrolytes. To circumvent the small electrochemical stability window, highly concentrated “water-in-salt” lithium organic ionic liquids which demonstrate significantly wider stability windows were recently proposed. However, the toxicity often associated with organic imides and very high price make the practical implementation of current water-in-salt electrolyte chemistries into commercial energy storage devices challenging. Herein, we address the challenge of developing new formulations of water-in-salt electrolytes caused by the lack of lithium salts having water solubility high enough to satisfy the water-in-salt condition. The proposed mixed cation strategy is whereby cheaper (by at least an order of magnitude) and more soluble salts featuring alkali cations beyond lithium, such as potassium, are used to create the water-in-salt condition. Co-dissolved lithium salts enable compatibility with traditional intercalation battery electrodes. We show that such highly concentrated electrolytes can provide the same benefits of the extended voltage window as imide-based electrolytes and, once combined with lithium salt, demonstrate compatibility with traditional Li-ion battery electrode materials while being low-cost and environmentally benign.

10:45 AM ET06.07.08
Stable Li-O₂ Battery Operations Using Water-in-Salt Electrolyte Qi Dong1, Xiahui Yao1, Yanyan Zhao1, Miao Qi1, Xi Zhang1, Hongyu Sun2, Yumin He1, Jingru Luo1 and Dunwei Wang1; 1Boston College, Brighton, Massachusetts, United States; 2Technical University of Denmark, Kongens Lyngby, Denmark.

Developing Li-O₂ batteries into a practical electrochemical energy storage technology hinges on the availability of a stable electrolyte. Because of the high reactivity of oxygen species in the Li-O₂ battery system, no known organic electrolytes satisfy the requirements for stable cell operations. The search for a compatible electrolyte system remains a significant challenge in Li-O₂ battery research. Here, we show that the water-in-salt electrolyte system, which is essentially super-concentrated aqueous LiTFSO₄ solution, is stable against parasitic chemical reactions with reactive oxygen species for Li-O₂ battery operations. This electrolyte provides the necessary functionalities to support aprotic Li-O₂ chemistries via reversible Li₂O₂ formation and decomposition. The lack of organic solvent molecules is a key advantage shown here. It eliminates the known decomposition pathways that would result in by-product formation from organic solvent degradations. Qualitative as well as quantitative product analysis show no measurable by-products formation in the WiS system. When the conventional carbon cathode is used, greatly improved cyclability of over 70 cycles can be achieved with the WiS electrolyte compared with the organic ones. When the carbon cathode is replaced with a stable carbon-free material, Ru catalyst decorated TiO₂ nanomets, up to 300 cycles of stable Li-O₂ battery operations are measured. The result sets the new benchmark in Li-O₂ battery research with quantitative product detection. It presents the stage for future studies to achieve the full potentials held by Li-O₂ battery as a stable, high-capacity electrochemical energy storage technology.

11:00 AM ET06.07.09
Fluorinating Interphases in Non-Aqueous, Aqueous and Hybrid Electrolytes Kang Xu; Electrochemistry Branch, U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Solid electrolyte interphases (SEI) enable the Li-ion intercalation chemistries to operate reversibly beyond the thermodynamic stability limits of non-aqueous electrolytes. The chemical building blocks of SEI mainly come from solvents decomposition products. Exceptions arise, when salt anion are reduction-labile, or when salt concentration exceeds certain thresholds, where anion starts to participate in the interphases chemistry. In those latter cases, usually high F-content were often found in the interphases, and unexpected benefits from such interphases chemistry arose. However, high F-content in interphases were not always welcomed, thus, the morphology and structure of interphases should play an equally important role as their chemical compositions.

In this work, we explore the different manners that interphases could be fluorinated via the electrolyte sources, and the various battery chemistries that could benefit from such fluorination.
11:30 AM *ET06.07.10
New Electrolytes for Safer High Energy Li-Ion and Li-Metal Batteries Jun Liu; Pacific Northwest National Laboratory, Richland, Washington, United States.

There is a great need to significantly increase the energy and power density of Li-ion batteries while ensuring battery safety. Nonflammable electrolytes have been studied for a long time, but their compatibility with common electrode materials, particularly anode materials, remains an obstacle. Recently, electrolytes with high Li salt concentrations have demonstrated great promise for improved electrolyte stability. In this talk, we will discuss the key role of the salt to solvent ratio in nonflammable phosphate electrolytes. At a high Li salt-to-solvent molar ratio (~1:2), the phosphate solvent molecules are mostly coordinated with the Li⁺ cations and the reactivity of the solvent molecules toward the graphite anode can be effectively suppressed. High cycling coulombic efficiency (99.7%), good cycle life, and safe operation of commercial 18650 Li-ion cells with these electrolytes are demonstrated. In addition, these nonflammable electrolytes show significantly reduced reactivity toward Li-metal electrodes. Non-dendritic Li-metal plating/stripping in the Li/Cu half-cells is demonstrated with high coulombic efficiency (>99%) and good stability. Electrolytes developed using this approach significantly improved the cycling stability in high energy Li metal pouch cells.

SESSION ET06.08: Si Anode
Session Chairs: Xiaolin Li and Donghai Wang
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room Ballroom A

1:30 PM *ET06.08.01
Si Anodes for Li-Ion Batteries Based on Dual Particle/Polymer Nanofiber Electrospinning Peter Pintauro¹, Ryszard Wycisk¹, Abhishek Mondal¹, Ethan C. Sel⁴, Rose Ruther² and Jagjit Nanda¹; ¹Vanderbilt University, Nashville, Tennessee, United States; ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Particle/polymer electrospinning is a cost-effective and robust technique for the fabrication of high performance nanofiber electrodes for batteries and fuel cells. For Li-ion battery application, the advantages of fiber mats over conventional slurry cast electrode designs include: (i) a large electrode/electrolyte interfacial area for enhanced electrochemical reaction kinetics, (ii) a controllable interfiber void volume to ensure good electrolyte infiltration into the electrode, and (iii) micron/sub-micron diameter fibers with high nanoparticle content and short Li⁺ transport pathways in the radial fiber direction. Pintauro and coworkers have created and evaluated a number of electrospun electrodes for Li-ion batteries; C particles, mixtures of TiO₂+C particles, or mixtures of Si+C particles for the anode and a LiCoO₂+C mixture for the cathode, where the polymer binder was either poly(acrylic acid) (PAA) or poly(vinylidene fluoride). More recently, a new dual fiber design has been developed/investigated to prepare Si-based nanofiber anodes, where separate fibers of Si particles with PAA binder and carbon powder with polyacrylonitrile (PAN) binder are electrospun simultaneously onto a common collector surface at controlled solution flow rates. Such an anode worked well in half-cell tests, due to the presence of numerous intersection cross-points between electrochemically active but non-conducting Si/PAA fibers and electrically conductive C/PAN fibers. In this presentation, methods for preparing these internally nano-wired fiber composite anodes will be discussed, along with their performance and capacity during charge/discharge cycling. The effects of fiber composition (particle/binder weight ratio) and mat configuration (the relative amounts of Si and C fibers) on gravimetric, volumetric, and areal capacities at different C-rates will be presented.

2:00 PM DISCUSSION TIME

2:15 PM ET06.08.03
Room-Temperature Synthesized SiOₓ, Negative Electrode Materials with Tunable Oxygen Content for Li-Ion Batteries Yidan Cao¹, ², J. Craig Bennett¹, R.A. Dunlap¹ and M.N. Obrovac³, ⁴; ¹Physics and Atmospheric Sci, Dalhousie University, Halifax, Nova Scotia, Canada; ²Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada; ³Physics, Acadia University, Wolfville, Nova Scotia, Canada.

SiOₓ is a promising Li-ion battery negative electrode material because of its high capacity and unique microstructure that leads to good cycle life[1,2]. However, SiOₓ is typically made by high temperature methods that are expensive and difficult to realize, especially at lab scale. Here, SiOₓ negative electrode materials were synthesized using a simple and scalable method by controlling the air exposure time during ball milling at room temperature[3]. This method allows efficient control of oxygen content, and results in a similar microstructure as a commercially purchased SiOₓ. XRD and TEM results show that the SiOₓ negative electrode materials prepared by ball milling in air are composed of nanocrystalline Si embedded in an amorphous silicon oxide matrix. The very low initial coulombic efficiency (ICE) of conventionally made SiOₓ (measured here to be ~55% for Aldrich SiOₓ) is one of its major drawbacks. The ball milled SiOₓ samples synthesized here have much higher reversible capacities (>1500 mAh/g) and higher ICE values (>70%). The advantages of the synthesized SiOₓ are many: an inexpensive and simple synthesis process, high capacity, high ICE, and a special microstructure that protects Si from reaction with electrolyte, resulting in excellent cycling performance.

Here, a detailed study will be presented describing SiOₓ synthesis and how SiOₓ electrochemical performance in Li-ion cells is related to its composition and microstructure.

References

2:30 PM BREAK

3:30 PM ET06.08.04
Pre lithiated Si and How It Affects the Early Stage Solid Electrolyte Interphase Formation Yun Xu¹, Kevin N. Wood¹, Jaclyn Coyle², Glenn Teeter¹ and Andriy Zakutayev¹; ¹National Renewable Energy Lab, Lakewood, Colorado, United States; ²University of Colorado Boulder, Boulder, Colorado, United States.

The solid electrolyte interphase (SEI) has been well acknowledged as a key component of the stability of Si anodes. During cycling, the fresh surface of lithium silicide is exposed because of the volume expansion and contraction of silicon. The exposed lithium silicide surface chemically reduces electrolyte...
and forms SEI. However, due to the lithium silicide being buried under SEI during formation, it has been difficult to characterize the SEI formed by chemical reduction of lithium silicide. In this work, lithium silicide (prelithiated silicon) thin films were prepared and chemically reacted with electrolyte. XPS was used to characterize the SEI formed on surface. This is the first time SEI formed by chemical reduction has been characterized directly. It was found that the SEI is composed of LiF, Li2O, Li2CO3 and organic species which are commonly found in SEI layers. The ratio between organic species and inorganic species is dependent on the additives. When Fluoroethylene carbonate (FEC) was added into electrolyte, more organic species formed, and less LiF formed. Early stage SEI formation was investigated by looking at the voltage profile and the irreversible capacity. It was found that at the first cycle, the Si anode only forms SEI by electrochemical reaction while the lithium silicide anode only forms SEI by chemical reaction. Cycling performance shows the SEI formed by chemical reduction is possibly better SEI than the SEI formed by electrochemical reduction. Prelithiated Si not only increases the columbic efficiency by reducing the electrochemical reduction, but also forms beneficial SEI by chemical reduction.

Prelithiation of anode materials is an important strategy to compensate for lithium loss as a result of the formation of a solid electrolyte interphase (SEI) at the surface of anodes in lithium-ion batteries. Conventional prelithiation reagents often present serious safety concerns due to the high flammability and unstable chemical nature. Here, we successfully developed a general one-pot metallurgical process to prelithiate group IV elements and their corresponding oxides, yielding prelithiation capacity approaching the theoretical specific capacity. As-synthesized Li2Zn, Li2Zr, Li2TiO3 and Li2ZnO composites (Z = Si, Ge, Sn etc) can serve as prelithiation reagents to increase the first cycle Coulombic efficiency of both graphite and alloy-type anode materials. Among all lithiated group IV alloys, Li4Ge exhibits the best stability under ambient-air conditions, consistent with the simulation results showing the large binding energy between Li and Ge atoms in Li2Ge2 crystal. Metallurgical lithiation of ZO2 results in composites with homogeneously dispersed active LiZ nucleus, the Si anode only forms SEI by electrochemical reaction while the lithium silicide anode only forms SEI by chemical reaction. Cycling performance shows the SEI formed by chemical reduction is possibly better SEI than the SEI formed by electrochemical reduction. Prelithiated Si not only increases the columbic efficiency by reducing the electrochemical reduction, but also forms beneficial SEI by chemical reduction.

3:45 PM ET06.08.05
A General Prelithiation Approach for Group IV Elements and Corresponding Oxides Jie Zhao; Stanford University, Stanford, California, United States.

Prelithiation of anode materials is an important strategy to compensate for lithium loss as a result of the formation of a solid electrolyte interphase (SEI) at the surface of anodes in lithium-ion batteries. Conventional prelithiation reagents often present serious safety concerns due to the high flammability and unstable chemical nature. Here, we successfully developed a general one-pot metallurgical process to prelithiate group IV elements and their corresponding oxides, yielding prelithiation capacity approaching the theoretical specific capacity. As-synthesized Li2Zn, Li2Zr, Li2TiO3 and Li2ZnO composites (Z = Si, Ge, Sn etc) can serve as prelithiation reagents to increase the first cycle Coulombic efficiency of both graphite and alloy-type anode materials. Among all lithiated group IV alloys, Li4Ge exhibits the best stability under ambient-air conditions, consistent with the simulation results showing the large binding energy between Li and Ge atoms in Li2Ge2 crystal. Metallurgical lithiation of ZO2 results in composites with homogeneously dispersed active LiZ nucleus, the Si anode only forms SEI by electrochemical reaction while the lithium silicide anode only forms SEI by chemical reaction. Cycling performance shows the SEI formed by chemical reduction is possibly better SEI than the SEI formed by electrochemical reduction. Prelithiated Si not only increases the columbic efficiency by reducing the electrochemical reduction, but also forms beneficial SEI by chemical reduction.

4:00 PM ET06.08.06
Bifunctional Star-Shaped Poly(amic acid) for Stable Silicon Anode in Lithium-Ion Batteries Jiangxuan Song; State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, China.

Development of efficient polymer binders is a promising means to stabilize intermetallic anodes with large volume change in lithium-ion batteries. Here, we develop a star-shaped poly(amic-acidic) binder for high capacity silicon (Si) anode, which can assist to form reliable and robust electrodes thanks to the high flammability and unstable chemical nature. Here, we successfully developed a general one-pot metallurgical process to prelithiate group IV elements and their corresponding oxides, yielding prelithiation capacity approaching the theoretical specific capacity. As-synthesized Li2Zn, Li2Zr, Li2TiO3 and Li2ZnO composites (Z = Si, Ge, Sn etc) can serve as prelithiation reagents to increase the first cycle Coulombic efficiency of both graphite and alloy-type anode materials. Among all lithiated group IV alloys, Li4Ge exhibits the best stability under ambient-air conditions, consistent with the simulation results showing the large binding energy between Li and Ge atoms in Li2Ge2 crystal. Metallurgical lithiation of ZO2 results in composites with homogeneously dispersed active LiZ nucleus, the Si anode only forms SEI by electrochemical reaction while the lithium silicide anode only forms SEI by chemical reaction. Cycling performance shows the SEI formed by chemical reduction is possibly better SEI than the SEI formed by electrochemical reduction. Prelithiated Si not only increases the columbic efficiency by reducing the electrochemical reduction, but also forms beneficial SEI by chemical reduction.

References
1. Ye, Hu; Bing, Li; Xingxing, Jiao; Chaofan, Zhang; Xiaohan, Dai; Jiangxuan, Song, Advanced Functional Materials 2018, 28 (23), 1801010.
2. Cheng, Xin-Bing; Zhang, Rui; Zhao, Chen-Zi; Zhang, Qiang, Chemical Reviews 2017, 117 (15), 10403-10473.
3. Jiangxuan, Song; Mingqiong, Zhou; Ran, Yi; Terrence, Xu, L.; Gordin Mikhail; Duihai, Tang; Zhaoxin, Yu; Michael, Regula; Donghai, Wang, 2014, 24 (37), 5904-5910.

4:15 PM ET06.08.07
Role of Polymeric Binders in the Degradation of Silicon Composite Electrodes Yikai Wang1, Dingying Dang1, Jiazhi Hu1, Xingcheng Xiao2 and Yang-Tse Cheng1; 1University of Kentucky, Lexington, Kentucky, United States; 2Chemical and Materials Systems, General Motors Global Research and Development Center, Warren, Michigan, United States.

Because of its high capacity (3579 mAh g−1 based on Li2Si) and proper delithiation voltage (~0.4 V vs. Li/Li+), silicon (Si) is considered one of the most promising negative electrode materials for future lithium ion batteries (LIBs). However, rapid capacity fading due to the huge volume change (~300 %) of Si during lithiation/delithiation hinders practical applications of Si electrodes. To address the problem of the volume change and to improve the performance of Si composite electrodes, polymeric binders are required to buffer the volume change of Si particles, maintain electrical conductivity, and improve mechanical integrity of Si composite electrodes. Desirable binders should be electrochemically stable, mechanically robust, and have high adhesion strength with Si particles. Nevertheless, limited attention has been paid to the role of binders in the degradation of Si composite electrodes from the viewpoint of mechanics, which is crucial for the design of polymeric binders for Si composite electrodes. In this study, we investigated the mechanical degradation of Si composite electrodes made with different polymeric binders, including polyvinylidene fluoride (PVDF), sodium-carboxymethyl cellulose (Na-CMC), and sodium-alginate (SA). The porosity, at both lithiated and delithiated states, and irreversible thickness change of all electrodes increased with increasing cycle number. Si/PVDF electrodes have larger volume change than Si/Na-CMC and Si/SA electrodes. Environmental nanoindentation measurements (in liquid electrolytes) showed that stiffness and hardness of Si composite electrodes decrease as the cycle number increases [Adv. Energy Mater. (doi.org/10.1002/aenm.201702578)]. Compared with Si/Na-CMC and Si/SA electrodes, Si/PVDF electrodes have poor mechanical integrity after 100 cycles. The mechanical degradation of composite electrodes correlated well with mechanical properties of binders and mechanical interactions between polymeric binders and Si particles. Our results provide insights into designing effective polymeric binders to improve mechanical integrity, microstructure stability, and electrochemical performance of Si composite electrodes.

4:30 PM ET06.08.08
Early-Stage Solid-Electrolyte Interphase Formation and Evolution for Silicon Anodes Yanli Yin1, Lei Cao1, Taeho Yoon1, Kevin N. Wood1, Elisabetta Arca1, Caleb Stetson2, Chunxiao Xiao1, Manuel Schnabel1, Glenn Teeter1, Chunsheng Jiang1 and Chunjie Ban2; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Colorado School of Mines, Golden, Colorado, United States.

Lithium ion batteries containing silicon as anodes have gained much attention due to their potential high energy density. The electrolyte reduction and interaction with the surface of silicon anodes result in the formation of solid electrolyte interphase (SEI) at the interface, which determines the cycling performance and the battery reversibility. The electrolyte reduction and its interaction involve in the early stage of SEI formation for silicon anodes. The chemical properties of the early-stage SEI is absolutely vital in stabilizing the surface of silicon anodes, and determines the following electrochemical cycling performance. In this research, two questions will be addressed: Can the early-stage SEI layer prevent further reduction of electrolyte? Is the early-stage SEI stable in electrolyte? In order to better understand the early-stage SEI chemistry, a new methodology has been developed here to decouple the
Lithium ion batteries (LIBs) are widely used in several electric devices as the prominent energy storage system. The performance of LIBs with organic liquid electrolyte is closely related to the formation of the solid electrolyte interphase (SEI) film on the electrode surfaces, which is essentially composed from the decomposition products of both electrolyte and electrolyte additives [1]. In particular, it is widely accepted that electrolyte additives have strong influence on the capacity retention of LIBs as a result of improving and altering the resulting SEI structure. Organosilicon compounds have attracted recent attentions as a new candidate for electrolyte additives [2]. Intriguingly, it has been reported that the added organosilicon compounds improve the thermal and electrochemical stability of the electrolyte. However, since it is still difficult to experimentally observe the transient process of the SEI growth on the electrode surface, it has not shown how the organosilicon additive affects the SEI formation process. In order to gain physical insights into this mechanism, we theoretically investigated the SEI growth on the graphite anode surface by means of the atomistic reaction technique, called the hybrid Monte Carlo (MC)/molecular dynamics (MD) reaction method. As denoted by Takenaka et al., this reaction simulation allows us to numerically study the submicroscopic structure produced by a number of complex chemical reaction processes, such as the electrolyte reduction reaction on the electrode surface [3].

Employing the MC/MD method, we firstly investigated changes in the SEI film structures in the ethylene carbonate (EC)-based electrolyte systems with and without the organosilicon additive. Remarkably, the obtained results revealed that the excessive growth of the SEI film was suppressed by adding the organosilicon additive, which was consistent with the experimental observations. It was further elucidated that the products derived from the organosilicon molecules was stably aggregated in the vicinity of the anode surface, and protected the electrolyte solvents and lithium salts from the reduction decomposition reaction. These findings indicate that the organosilicon additive possibly improve the cycle performance of LIBs owing to the formation of the effective SEI film.


ET06.09.01
Phenyl Selenosulfides as Cathode Materials for Rechargeable Lithium Batteries Yi Cui1, 2, Joseph D. Ackerson1, Ying Ma1, Amruth Bhargav1, Jonathan Karty1, Wei Guo1, Likun Zhu1 and Yongzhue Fu1; 1Mechanical Engineering, Indiana University-Purdue University Indianapolis, Indianapolis, Indiana, United States; 2Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; 3Materials Science and Engineering, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, United States; 4Department of Chemistry, Indiana University, Bloomington, Indiana, United States; 5College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, China.

In Lithium-ion (Li-ion) batteries, transition metal oxides have reached their capacity limits. The growing demand for high energy batteries has inspired great interest in exploring high-capacity cathode materials. In this regard, Li-S and Li-Se batteries are promising because elemental sulfur and selenium have high theoretical specific capacities of 1672 mAh g⁻¹ and 679 mAh g⁻¹, respectively. Although sulfur has an insulating nature (5.4×10⁻²⁸ S m⁻³), selenium below sulfur in the periodic table has a much higher electronic conductivity (1×10⁻³ S m⁻¹) and it also has a high volumetric capacity density of 3253 mAh cm⁻³ because of its high mass density (4.8 g cm⁻³). Recently, our group has demonstrated that organopolysulfides (RS⁻₃⁻) are a class of high-capacity cathode materials for rechargeable lithium batteries. The unique character of linear organopolysulfides is that short sulfur chains are chemically capped by R groups, therefore high-order polysulfides are significantly reduced initially and upon cycling. The obvious benefit is their low dependence on liquid electrolyte, in another word, it can enable high energy densities of batteries.

In this contribution, we select phenyl diselenide (PDSe, PhSeSePh) as a model compound which has a low specific capacity and poor cycling performance. The Se-Se bond can break in a 2e⁻ reduction reaction, but it has limited capacity as a cathode material. To increase its capacity, redox active species (e.g., sulfur) could be added in the middle of the selenium atoms. Herein, we mix PDSe with sulfur to form two hybrid compounds with 1:1 and 1:2 molar ratios, which almost double and triple the capacity of PDSe, respectively. Differential scanning calorimetry (DSC), Mass spectrometry (MS), scanning electron microscopy (SEM) and X-ray diffraction (XRD) are applied as characterizations. The experimental study is combined with the first-principles calculations based on the density functional theory (DFT) to reveal the electrochemical phenomenon.

Theoretical calculations suggest that phenyl selenol sulfide (PDSeS, PhSeS-SePh) and phenyl selenol disulfide (PDSeS₂, PhSeS₂-SePh) could form via addition reactions, which is supported by mass spectrometry analysis. These hybrid compounds show interesting electrochemical behavior in lithium batteries with three reversible discharge voltage plateaus involving frequent Se-S and S-S bond break and formation. PDSeS and PDSeS₂ show initial capacities of 252 mAh g⁻¹ and 330 mAh g⁻¹, respectively, followed by stable cycling performance with a capacity retention of >73% after 200 cycles at C/5 rate. In addition, they show steady rate capabilities. This study reports a novel strategy to increase the electrochemical performance of organo-diselenide by addition of sulfur. This strategy adds new members to the family of high-capacity cathode materials and provides a new way to explore Se/S containing hybrid compounds, which are valuable for rechargeable lithium batteries and beyond.

ET06.09.02
Wet-Chemical Synthesis of 1-5 nm Silicon Nanoparticles—Potential Applications in Various Technological Fields Mohamed Teyb Ould Ely;
Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

Wet-chemical synthesis of nanosilicon with diameters in the range of 1-5 nm has been challenging due to the lack of appropriate precursors that decompose in mild conditions. Conventional synthetic procedures use extreme temperatures. For example; carbothermal synthesis occurs at 1700 °C, molten salts synthesis takes place between 200-850 °C and aluminomagnesiothermal synthesis typically takes place above 600 °C. On the other hand, bottom up wet-chemical synthesis employs unsafe reagents such as sodium naphthalide, lithium hydrides, sulfuric acid, while top-down synthesis uses dangerous reagent such as HF-etching (of silicon wafers) followed by an elaborate post-annealing treatment to temperature exceeding 900 °C to mitigate surface oxidation problems.

We will discuss our recent synthesis of metallic nanosilicon by thermal decomposition (< 500 °C) of organometallic precursors in the absence of any reducing agent, molten salts or HF-etching process. This mild temperature synthesis prevents excessive growth leading to nanoparticles in the sub-5 nm ranges. The particles size can be increased by gradual sintering.

These nanoparticles are smaller than silicon Bohr Exciton radius (4.5 nm), luminescent and potentially useful for a variety of applications spanning from energy storage, displays, medical imaging to tunable LED lighting.

ET06.09.03
Combinatorial Screening of Ternary Li-Alloy Anodes for High Performance Lithium-Ion Batteries Yaoyu Ren1, Kedar Manandhar1, Drew Stasak1, Huilong Hou1, Jing Xu1, Joonho Koh1, John Lennon2 and Ichiro Takeuchi1; 1Department of Materials Sciences and Engineering, University of Maryland, College Park, Maryland, United States; 2NICE America Research Inc., Mountain View, California, United States.

Li-alloy anodes have long been recognized as a promising substitute for commercial graphite anode in lithium-ion batteries in terms of high specific capacity and safety. Alloying the active anode material (element A) with a buffer matrix material (element B) to alleviate the large volume change of the former during lithiation/delithiation cycle is a promising strategy to solve the major issue impeding the commercialization of Li-alloy anodes. However, while several Li-A-B alloys have been investigated previously, many more other combinations are waiting to be explored. Moreover, even in those reported combinations, the investigated compositions are limited. Thorough investigation on these materials using the traditional material synthesis strategy is more of a labor-intensive and time-consuming task than a scientific investigation. This then offers a great opportunity to the combinatorial material screening technique characteristic of high throughput exploration, which could be employed as a high efficient screen tool to narrow down the interesting material combinations and compositions for further investigation in a real battery condition.

Here, based on two model ternary alloy combinations, i.e., Li-Si-Al and Li-Co-Sn, we successfully demonstrated the efficacy and accuracy of the combinatorial material screening technique on exploring potential Li-alloy anode materials for lithium-ion batteries. Specifically, the lithium-free binary alloy thin film composition spreads were firstly deposited on silicon wafer using combinatorial co-sputtering. The crystallinity was tuned by varying the sputtering temperature. The as-deposited thin film was then lithiated in pouch cell to form Li-alloy ternary thin film for further characterization. XRD and Synchrotron XRD were used to identify the structural variation after and before lithiation. XPS was used to precisely determine the lithium concentration within the films.

ET06.09.05
Carbon Coated Si Nanosheets as Anode Materials for Li-Ion Batteries Sangwon Park1, Heonjin Choi1, Jung Hoon Ha2 and Byung-Won Cho2; 1Yonsei University, Seoul, Korea (the Republic of); 2Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Silicon (Si) has been extensively studied as an anode material in lithium ion batteries (LIBs) due to the high theoretical capacity of 4,200 mAh/g. However, Si is structurally unstable during lithium (Li) insertion into Si due to a 400% volume expansion and it acts as main cause of capacity fading. Herein, we report carbon coated silicon nanosheets (SiNSs) as anodes for LIBs. First, SiNSs are synthesized on grafoil current collectors with thickness and diameter of < 15 nm and > 10 μm, respectively. Our previous work demonstrated that SiNSs have great mechanical flexibility to accommodate the structural instability of Si during Li insertion. It is also ideal materials for fast Li storage by the high specific surface area and short diffusion length in SiNSs. Parylene is then coated on SiNSs as carbon source and thermally decomposed to carbon. The process provides excellent homogeneous coating of carbons on the SiNSs that have highly anisotropic morphology on a nanometer scale. The carbon coated on SiNSs (C-SiNSs) showed high capacity and stable cycle performance by the carbon layer that works as buffer for the Li insertion into Si and volume expansion. The C layer also provide high electrical conductivity that stabilize the electrochemical performance during cycles. These findings can contribute to fabricating high performance Si based anodes for LIBs.

ET06.09.06
Microstructure Evolution During Lithiation of Crystalline Silicon Wafer Jun Liu, Taeho Yoon, Chunmei Ban and Mowafak Al-Jassim; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

Silicon is a promising anode material for lithium-ion batteries due to its large theoretical capacities [1]. The large volume expansion upon lithiation results in cracks, accompanied with a phase transformation from crystalline to amorphous silicon [2]. In this study, we investigate the surface morphology and microstructure of initial lithiated crystalline Si wafer by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Cracks propagate along (100) and (110) directions. Interestingly, we find a crack-direction dependence of the amorphous Si layer. The distribution of Li is presented by STEM-EELS. We further use a coated Si wafer by MLD with ~ 5nm thickness coating layer, and this Si wafer is free of cracks after lithiation. The thickness of amorphous Si layer is significantly reduced to ~ 15nm, which is one magnitude thinner than that of lithiated Si wafer without coating.

ET06.09.07
Effects of Solvent-Salt Charge-Transfer Complexes on Oxidative Stability of Li-Ion Battery Electrolytes Eric R. Fadel1, Francesco Faglioni2, Georgy Samsonidze2, Nicola Molinari1, Boris Merinov4, William Goddard4, Jeffrey C. Grossman1, Jonathan Mailoa1 and Boris Koziński3, 2; 1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Robert Bosch LLC, Cambridge, Massachusetts, United States; 3John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 4Materials Science and Applied Physics, California Institute of Technology, Pasadena, California, United States; 5Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio, Modena, Italy.

Electrochemical stability windows of multi-component electrolytes, both solid polymer and organic liquid, largely determine the limitations of operating
regimes of Li-ion batteries. In order to increase energy densities and lifetimes of batteries, new electrolyte materials need to be discovered and optimized. Achieving higher operating voltages requires better understanding of electrolyte degradation and oxidation. Electrolyte degradation is difficult to probe experimentally, but computational tools allow one to study the relevant phenomena at the atomistic level, and thus obtain insights into oxidation mechanisms and possible design rules, as well as the ability to screen for better materials. However, reliable computational studies of the complex oxidation mechanisms remain challenging, considering the difficulty in obtaining material properties with greater accuracy than density functional theory (DFT) for large systems.

We present new insights into the oxidation mechanism that governs stability of multi-component polymer and liquid electrolytes and introduce an efficient computational method and a simple general model predicting the overall electrolyte stability. We find that explicitly including solvent molecules in the computation of the anion stability has a strong impact, and we show that this effect stems from electrostatic interactions between the molecules. Particularly, we find that across all chemistries studied, only one molecule in the system is oxidized. Building on this, we construct a model where two oxidation scenarios lead to different stability behaviors for the anion-solvent pairs, depending on their relative strength and geometry. Thus, we are able to provide a simple model that accurately predicts the stability of the pair depending on the ionization potential of the isolated anion and solvent. This model is not only useful for predicting the ionization potential (and thus the breakdown voltage) of the electrolyte species, but also gives insight into the atomistic details of bulk oxidation. This understanding of the microscopic details of oxidation allows one to formulate design rules as well as it provides better grounds to study subsequent degradation mechanisms and reactions. This simple model also allows for very fast screening of solvents and salts to find stable electrolytes.

ET06.09.08
High Performance Rechargeable Na/Ni Battery with Hierarchical NiCoAl-Layered Double Hydroxide/Carbon Electrodes
Seungyoung Park, Youngsik Kim and Hyunhyub Ko; UNIST, Ulsan, Korea (the Republic of).

With the increasing demand for renewable energy resources, sodium based-batteries have attracted enormous interest to realize the cost-effective and grid scale electrochemical energy storage (EES) devices because of high abundance and low cost of sodium in contrast to lithium worldwide. In the available sodium based-batteries, aqueous sodium batteries have fundamental advantages over non-aqueous due to safe and cost-effective aqueous electrolyte system. However, low operating voltage of aqueous Na-ion battery is a great challenge to realize high energy storage system. Here, we firstly report a high performance rechargeable battery that utilizes a metallic Na anode and a redox couple cathode of hierarchically nanostructured NiCoAl-layered double hydroxide (NiCoAl-LDH) cathode with enhanced performance by adopting trivalent atomic doping (Co³⁺, Al³⁺) into the Ni(OH)₂ layer. In this design, the wide potential range of the Na metal anode and the high capacity of NiCoAl-LDH enable an aqueous rechargeable Na/Ni battery with excellent energy storage performances. We employed hybrid electrolyte system using both non-aqueous and aqueous electrolytes, which are separated by the alkali-ion solid electrolyte (NASICON, Na₂Zr₂Si₂PO₈). Furthermore, the binder-free strategy was implemented to create the efficient cathode material of NiCoAl-LDH/carbon microfiber which eventually improve the electrochemical performance. The Na/Ni battery exhibits a stable operating voltage of ~3.1 V during discharge which outperforms the low cell voltage (~1.23 V) of aqueous rechargeable battery, a high capacity of ~350 mA h g⁻¹, and a resulting energy density of ~1085 W h kg⁻¹.

ET06.09.09
Synthesis of V₂O₅ Microstructures as Advanced Cathode Material for High Performance Lithium-Ion Batteries
Hemlata Dhoundiyal, Pintu Das and Mukesh Chander Bhatnagar; Physics, Indian Institute of Technology Delhi, New Delhi, India.

In the present time transition metal oxide vanadium pentoxide (V₂O₅) is consider as an excellent candidate for energy storage device material for Li-ion batteries (LIBs) with reference to its high charge storing capacity, low cost, superior layered structure and abundant material. With respect to its rich layered structure, which can reversibly accept the intercalation and deintercalation of Li-ions in the process of charging and discharging of LIBs. In this study, we report a simple hydrothermal procedure to synthesize the porous microstructure of V₂O₅ as a cathode electrode for LIBs with subsequent annealing temperature. The structural analysis stands for the orthorhombic phase of V₂O₅ and other sub oxides phase of vanadium are absent. The morphological study of V₂O₅ shows the flower like three dimensional micro flowers (having diameter ~5µm) self-assembled by Nano rods. In electrochemical cyclic voltammetry measurement three anodic peaks were observed corresponds to 3.27V, 3.05V and 2.08V as Li⁺Li²⁺ refers to three crystal phase α-V₂O₅ to β-Li₃V₂O₇, β-Li₃V₂O₇ to 6LiV₂O₇ and δ-Li₂V₂O₇ to γ-Li₃V₂O₇ respectively. And also three anodic peaks corresponds to Li-ion deintercalation. Which indicate the good reversibility of the electrode. In this report V₂O₅ microflowers deliver very high specific discharge capacity of 290mAhg⁻¹ and after 50cycles the capacity reduced to 196mAhg⁻¹, cycled between the voltage range 2.0-4.0V at the current rate 0.1C.

ET06.09.10
Bifunctional Conducting Polymer Coated CoP Core–Shell Nanowires on Carbon Paper as a Free-Standing Anode for Sodium-Ion Batteries
Jing Zhang and Yong-Mook Kang; Dongguk University, Seoul, Korea (the Republic of).

Recently, Na-ion batteries (SIBs) are attracting the scientific community as an alternative to the already well established Li-ion batteries, due to the more abundant reserves and lower price of Na resources. However, the larger radius of the Na⁺ than that of Li⁺ results in huge volume variation of electrode materials during Na⁺ insertion/extraction, leading to poor cyclability, which inhibits the NIBs widely application in the energy storage. Metal phosphides as potential anodes for SIBs have been recently been demonstrated owing to their higher specific capacities compared with those of carbonaceous materials. Unfortunately, most reported metal phosphides showed irregular particle sizes ranged from several hundred nanometers to tens of micrometers, leading to limited cyclic stability. Herein, polypyrrole (PPy), which is one of the representative conducting polymers, encapsulated cobalt phosphide (CoP) nanowires (NWs) grown on carbon paper (CP), finally realizes 1D core–shell CoP@PPy NWs/CP. The CoP core is connected to the PPy shell via strong chemical bonding, which can maintain a Co–PPy framework during charge/discharge. It also possesses bifunctional features that enhances the charge transfer and buffers the volume expansion. Consequently, 1D core–shell CoP@PPy NWs/CP demonstrates superb electrochemical performance, delivering a high areal capacity of 0.521 mA h cm⁻² at 0.15 mA cm⁻² after 100 cycles, and 0.443 mA h cm⁻² at 1.5 mA cm⁻² even after 1000 cycles. Even at a high current density of 3 mA cm⁻², a significant areal discharge capacity reaching 0.285 mA h cm⁻² is still maintained. The outstanding performance of the CoP@PPy NWs/CP free-standing anode provides not only a novel insight into the modulated volume expansion of anode materials but also one of the most effective strategies for binder-free and free-standing electrodes with decent mechanical endurance for future secondary batteries.

ET06.09.11
Strategic Architectures of Silicon Nanolayer-Embedded Graphite Hybrid for High Energy Lithium-Ion Battery Anodes
Minsung Kang, Pilgun Oh, Kwonhoon Kim and Chang Woo Kim; Metallurgical Engineering, Pukyong National University, Busan, Korea (the Republic of); Graphic Arts Information Engineering, Pukyong National University, Busan, Korea (the Republic of).
As the widespread emergence of modern technologies combined with human life, lithium ion battery (LIBs) has become one of the most important power supplier for mobile electronic devices, electric vehicles and stationary applications. However, the current LIBs provide a low energy density with approaching to the capacity limits, which emphasize the urgent need for high energy density battery systems. Herein, we have prepared the amorphous silicon nanolayer-embedded graphite/carbon (SGC) hybrids by chemical vapor deposition (CVD) method with developing the cost-effective and scalable pyrolysis system. With developing an industrial-relevant modified CVD process, sophisticated structure of optimum SGC hybrids achieved high reversible capacity (523 mAh g⁻¹) and unprecedented columbic efficiency (92%) at a 1° cycle in the industrial standard electrode density (> 1.6 g cm⁻³) and areal capacity loading of > 3.3 mAh cm⁻². Moreover, fabricated SGC electrode confirmed rapid increase of cycling efficiency upward of 99.5% over only 6° cycles and exactly allowed favorable cyclability of 96% capacity retention after 100 cycles and high rate capability comparable to the industrial graphite anode. In addition, the electrode composed of SGC hybrids entirely overcame the detrimental effects of the volume variation problems, exhibiting 23° of additional expansion excepting for graphite counterpart. This, in turn, completely preserved the electrical interconnectivity and mechanical integrity without any cracks and contact losses. Finally, a prototype full cell device is demonstrated with high voltage lithium cobalt oxide (LCO) cathode through the coin cell configuration, which achieved 92° of capacity retention after 100 cycles with considerable potential toward next generation target as practical devices. Consequently, this successful SGC hybrid anodes could be proposed for commercial extension to the next generation high-energy battery systems as a major breakthrough for electric vehicle or grid energy storage applications.

ET06.09.12

B₄C-Decorated Cotton-Derived Hollow Carbon Fibers as Free-Standing Electrode for Lithium-Sulfur Batteries with Excellent Cycling Stability Ruifan Zhang, Haoran Jiang, Maochun Wu, Ke Liu and Tianzhuo Zhao, Department of Mechanical and Aerospace Engineering, HKUST Energy Institute, Hong Kong, Hong Kong.

Lithium-sulfur (Li-S) battery has been regarded as one of the most promising candidates for traditional lithium-ion batteries (LIBs) in the practical application of electric vehicles, portable electronic devices, and other energy-storage areas because of its high gravimetric and volumetric energy densities (~2600 Wh kg⁻¹ and ~2900 Wh L⁻¹). However, there are still three main challenges before the Li-S battery is applied commercially feasible, including the insulating nature of sulphur and Li₂S, the polysulfide “shuttle effect”, and the large volume fluctuation of sulfur during lithiation and delithiation processes. Boron carbide (B₄C), a lightweight and low-cost refractory material, exhibits a remarkably intrinsic chemical stability and good electrical conductivity, which has been studied as potential electrode for batteries and fuel cells. However, to the best of our knowledge, the reports of this material applied in the Li-S battery system are almost none. In this regard, we here developed a B₄C-decorated cotton-derived hollow carbon fibers (B₄C-COHCF) as free-standing electrode for Li-S batteries, which was fabricated by a sintering method using the commercially cotton textile as both matrix and carbon source, amorphous boron powders as B source with Ni²⁺ as catalyst. Contrary to the conventional hollow carbon fiber electrode, the B₄C-COHCF was covered with numerous B₄C nanoparticles, and after sintering process, the hollow structure became porous: there were plenty of micro pores formed on the surface of the hollow fiber, which was beneficial for the specific surface area of the electrode. With the B₄C-COHCF electrode, the Li-S battery exhibited an initial specific capacity as high as 1200 mAh g⁻¹ at 0.1C, and when the current density increased to 4C, it still displayed a specific capacity of 600 mAh g⁻¹, indicating that the B₄C-COHCF electrode can truly improve the rate capability of the Li-S battery system. Besides, the battery showed an excellent cyclability, which has been stably operated for 2000 cycles with a Coulombic efficiency of 90% at the current density of 0.5C. More importantly, the capacity decay rate of the battery is as small as 0.022% per cycle over 2000 cycles. The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. T23-601/17-R).

ET06.09.13

Flow Lithium Batteries—From Materials to Cell Design Francesca Soavi1,2, Francesca De Giorgio1,2, Federico Poli1,2, Alessandro Brillon1,2, Irene Ruggeri1, Catia Arbizzani1, Antonio Terella1 and Luca Morici1, 1University of Bologna, Bologna, Italy; 2BETTERY s.r.l, Massa, Italy.

Flow lithium batteries (FLB) represent an emerging technology that bring in a unique solution the advantages of the high specific energy of lithium batteries and the design flexibility of redox flow batteries that in turn permits to decouple energy and power. Different kinds of FLBs have been proposed, including batteries featuring semi-solid anolyte and/or catholyte with Li-ion intercalation powders, like LiFePO₄ or Li₄Ti₅O₁₂, dispersed in organic electrolyte, and Li/S and Li/O₂ flow batteries. In order to increase energy and power of FLB advancements in materials, design and concepts are required. Semi-solid slurries need to be properly formulated to provide high electronic and ionic conductivity for fast electrochemical processes and suitable rheological features for an efficient flow. Current collectors and electrolyte have to be properly selected to control solid electrolyte interface formation and enable electron transfer between the fluid electrode and the current collector. Furthermore, FLBs inherently need a smart cell design capable to maximise the power output and minimize the power loss related to the flow. This is particularly important in the case of viscous fluidic electrodes. A study on FLB semi-solid slurries that highlights the mutual effect of the half cell components on electrochemical performance is here reported. The nature of active material, conductive additive and electrolyte impacts on the electronic percolating network, and then on the cyclability of the flowable electrodes. Supercapacitated electrolytes based on tetraethylenglycol dimethyl ether-bis(trifluoromethane) sulfonimide electrolyte and slurries with different carbon content and type are investigated for use in flow Li-ion and Li/O₂ batteries. The electrochemical results are presented and discussed and related to the morphology, rheology and electrical conductivity of the slurries.

A semi-empirical study on the evaluation of the cell flow frame provide indications on design strategies that maximize power output of FLBs.

References:

ET06.09.14

Controlled Formation of Artificial Solid Electrolyte Interfaces on Lithium-Metal via Fluorinated Gases Minfa He, Rui Guo and Betar M. Gallant; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Replacing graphite anodes with lithium metal in Li-ion batteries can significantly boost achievable anode capacities by more than 10-fold (3860 mAh g⁻¹ vs. 372 mAh g⁻¹ for commercial) and also pave the way for other “beyond Li-ion” batteries such as Li-O₂ and Li-S batteries. However, the use of Li metal as the anode faces several challenges including the virtually infinite volume expansion, parasitic reaction with electrolyte, and dendrite growth during the Li plating-stripping cycling process. One promising strategy to overcome the latter two issues is to design an artificial solid electrolyte interface (SEI) which
can circumvent the compositional inhomogeneity and mechanical instability of the native SEI. Among multiple studies, lithium fluoride (LiF) has been suggested to play an essential role in the formation of SEI on Li metal; however, a safe and facile approach to grow a LiF-only SEI layer on Li still remains lacking. In this study, we report the formation of an artificial Li-only SEI layer on Li metal via the reaction between Li and perfluorinated gases under controlled conditions. After systematically employing different reaction conditions including gas pressure, reaction temperature, and reaction time, we are able to control the formation of the LiF layer with different crystallinity and spatial homogeneity, as confirmed by combined X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy analyses. We also investigate the effect of this LiF layer on the chemical stability of Li in common Li-ion electrolytes via electrochemical impedance spectroscopy, and probe the behavior of this LiF layer and identify its eventual failure mode under repeated Li plating-stripping cycling. This study sheds light on the controlled growth of an artificial inorganic SEI layer on Li, and its intimate link with the Li chemical stability and cycling behavior. Moreover, it presents a strategy to finely tailor the properties of artificial SEIs using safe and scalable SEI-forming reactants, which can potentially impart clean, well-characterized films that can address some of the major safety risks of previous approaches.

References

Impact of Aluminum Doping Methodologies on NCM622 Properties Michael Murphy1, Jessica Durham1, Wang Lixin2, Fu Zhou2, Derek C. Johnson3 and Albert Lipson4 1Argonne National Lab, Argonne, Illinois, United States; 2A123 Systems, Waltham, Massachusetts, United States.

Nickel-rich cathodes such as LiNi0.5Co0.2Mn0.3O2 (NCM) and Li[Ni0.5Co0.2Mn0.3]F0.05O2 (NCMF) cathode active materials with various amounts of Fe via hydroxide coprecipitation and calcination processes, which simulate the resynthesis of NCM in leach liquor containing Fe from spent lithium ion batteries (LIBs). The crystal structure and electrochemical performances of the synthesized NCM (i.e., NCM (0.05%), NCM (0.25%) and NCM (1.0%)), are investigated and compared with NCM. Structural analysis demonstrates that the incorporated Fe does not affect their layered structure with space group of the lattice parameters of NCMF increase as the Fe content increases. On the other hand, the structural perfection of NCMF gradually deteriorates with increasing the amount of Fe because of undesirable cation mixing between Ni2+/Fe3+ and Li+ sites. Moreover, the additional post-mortem analysis of energy dispersive spectroscopy on graphite surface after full cell cycling tests further confirms the positive effect of Fe on the improved capacity retention performance of NCMF. Therefore, even if Fe is regarded as an impurity component in the LIB recycling process, a small amount of Fe in the resynthesized NCM cathode material could favor high power and high cycling stability.

Impact of Aluminum Doping Methodologies on NCM622 Properties Michael Murphy1, Jessica Durham1, Wang Lixin2, Fu Zhou2, Derek C. Johnson3 and Albert Lipson4 1Argonne National Lab, Argonne, Illinois, United States; 2A123 Systems, Waltham, Massachusetts, United States.

Nickel-rich cathodes such as LiNi0.5Co0.2Mn0.3O2 (NCM622) have received considerable attention as a result of their high capacity and relatively low cost. However, owing to high nickel content NCM622 cathodes suffer from reduced cycle life and thermal stability. (1) Traditional approaches for modifying cathode materials have been employed in the past to improve the performance of Ni-rich cathodes, this includes incorporating a surface coating (Al2O3, AlF3, SiO2) or dopant (Al3+, Mg2+, F-) species which acts as a passivating layer between the cathode surface and reactive electrolyte or stabilizes the material, respectively. (2-9) The work reported in this poster illustrates NCM622 doped with Al during two distinct stages of the materials synthesis, either during co-precipitation of the MOH (M = 6:2:2 ratio of Ni, Mn, and Co) using a CSTR (continuous stirred tank reactor) or during the calcination process. The resulting product from both synthetic processes demonstrates the distribution of Al3+ throughout the entirety of the NCM622 particles. The presence of Al3+ in NCM622 was established via EDX/SEM mapping of a cross-sectional particle and slight expansions of the crystal lattice observed in XRD which is consistent with the inclusion of Al3+ atoms in the transition metal sites. Significant differences are observed in the capacity, rate performance, and thermal stability of the NCM622 cathode depending on whether doping occurred during co-precipitation or calcination. In particular, Al3+ doping during the co-precipitation process results in substantial improvements in all measured categories relative to both the pristine NCM622 control and materials doped via calcination. Since there are only trivial changes in particle size, morphology, and composition, this difference in performance appears to be the result of the synthesis methodology.

References

Piperidinium and Phosphonium Ionic Liquids as Electrolytes in Supercapacitors and Batteries at Elevated Temperatures Karthika Sankar, Jennifer Chapman Varela and Mark Grinstaff; Boston University, Boston, Massachusetts, United States.

The current organic electrolytes used for energy storage applications suffer from volatility, flammability, and limited cyclability at elevated temperatures. Ionic liquids being non-flammable and non-volatile are an ideal replacement for the unsafe organic solvents used today. The performance of supercapacitors containing piperidinium and phosphonium based ionic liquids (ILs) with an alkyl ether chain introduced into its structure are compared to
the traditional propylene carbonate (PC) electrolyte at 25 ℃ and 100 ℃. The phosphonium ILs are relatively stable with an electrochemical window of -1 to 5 V at room temperature while the piperidinium ILs are stable only up to 2 V. An activated carbon electrode based supercapacitor with the piperidinium IL electrolyte with 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) at 100 ℃ cycles for more than 10000 cycles. There is a decrease of 30% capacitance after 10000 cycles at 100 ℃ for the piperidinium based electrolyte whereas a supercapacitor with PC having 1 M LiTFSI fails at 3200 cycles. A 3.5 X improvement in energy density for piperidinium based supercapacitor is observed upon going from room temperature to 100 ℃. The wider electrochemical stability window makes the phosphonium IL a better candidate as an electrolyte in lithium ion batteries. Studies on phosphonium ILs as electrolytes in supercapacitors and lithium ion batteries at 25 ℃ and 100 ℃ are ongoing. These successful findings support the basis for the replacement of organic electrolytes with IL based electrolytes in energy storage devices at high temperatures.

ET06.09.18
Investigation of Li2O2 Nucleation on Flat Graphene Cathodes Dahyun Oh1, Erik Lara2, Noel Arellano2, Yong Cheol Shin2, Phillip Medina2, Jangwoo Kim3, Toan T4, Esin Akca4, Cagla Orgit-Akgun4, Gokhan Demirel5, Ho-cheol Kim6, Shu-jen Han6, Harleen Maune6 and Mahesh Samantar6; 1Chemical and Materials Engineering Department, San Jose State University, San Jose, California, United States; 2IBM Almaden Research Center, San Jose, California, United States; 3Korea Institute of Science and Technology Evaluation and Planning, Seoul, Korea (the Republic of); 4ASELSAN Inc., Ankara, Turkey; 5IBM T.J. Watson Research Center, Yorktown Heights, New York, United States.

Observing Li2O2 nucleation and oxidation on various cathode surfaces in Li-oxygen batteries was challenging with three-dimensional porous electrodes. In particular, examining the effect of a catalyst on preventing cathode clogging in porous cathode was hard to investigate visually. Here we study the use of CVD grown graphene in two-dimensional configurations as Li-oxygen battery cathodes to easily examine the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on various cathode surface structures. The composite structure made of metal oxides and carbon surface is created by electron-beam lithography or simple wet transfer method to investigate the Li2O2 distribution during Li-oxygen battery discharging and charging on composite cathodes. Furthermore, since CVD graphene can be transferred to different substrates, the Li-oxygen battery cathode can be built by coating the graphene layer on top of structural components. We investigate few possible materials as a substrate for Li-oxygen battery graphene electrodes to demonstrate the easy incorporation of CVD graphene cathode to an existing device architecture. After investigating polymer, ceramic, or metal substrates, we learned that this structural material needs to be electrochemically inactive, and does not attenuate the ORR activity of graphene. In particular, we maximized the Li-oxygen battery discharge capacity of this planar graphene electrode by using the electrolyte formulations that promote the solvation of intermediate discharge products. Thus, not only serves as a model cathode, but 2D graphene also presented an improved storage capacity as a potential micro-battery cathode compared to one of the most common lithium-ion insertion based cathodes (e.g., LiCoO2). We obtained 20 % higher areal cathode energy density and 2.7 times higher cathode specific energy than that can be derived from the same volume or mass of LiCoO2. In summary, we investigate the Li2O2 distribution during ORR and OER and demonstrate the fabrication of micron scale devices where CVD grown graphene structures are used as 2D Li-oxygen battery cathodes. We believe that two dimensional CVD graphene cathode can facilitate the microscale device fabrication by simply transferring or coating the target device structure with flexible graphene layers to integrate the energy storage component without complications.

ET06.09.19
Stable Metal Anode Enabled by Porous Lithium Foam with Superior Ion Accessibility Ahmed M. Hafez and Daxian Cao; Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States.

Lithium metal anodes attract much interest recently for high energy battery applications. However, low coulombic efficiency, infinite volume change, and severe dendrite formation limit its reliable implementation in a wide range. In this study, we reveal outstanding stability in Li metal anode by designing a highly porous Li foam in a hollow structure with graphene as backbone. This unique porous structure is capable of tackling many lithium metal problems simultaneously: First, it assures uniform electrolyte distribution over the inner and outer surface of the lithium foam electrodes due to it is porous and hollow tube structure, and enhances the charge mobility by increasing the electrolyte contact area between the electrolyte and lithium electrode; Second, the foamy structure uniformly distributes the current throughout the 3D structure, and effectively suppresses dendrite formation; Third, the 3D porous structure can accommodate volume expansion and dissipate heat efficiently. This structure shows superior stability compared to its fully lithium covered foam, and bulky lithium foil electrode counterparts. The lithium foam exhibits small overpotential (~25 mV at 4 mA cm-2) and high cycling stability for 160 cycles at 4 mA cm-2. Furthermore, when assembled the porous lithium metal as anode in full cell with LiFePO4 as a cathode, the battery revealed high rate performance of 138 mAh g-1 at 0.2 C. The beneficial structure of lithium hollow foam is further studied through density functional theory (DFT) simulations, which confirms better mobility and uniform deposition of lithium during charging/discharging in porous structure, that can effectively suppress lithium dendrite formation.

ET06.09.20
Sulfur/Selenium Sulfide Composites as Promising Cathode Materials for High-Energy Lithium Batteries Gaind P. Pandey, Kobi Jones and Lamartine Meda; Xavier University of Louisiana, New Orleans, Louisiana, United States.

Lithium-sulfur (Li-S) batteries have attracted considerable attention as one of the most promising next-generation energy storage system owing to the high theoretical specific capacity (1675 mAh g-1), low cost, abundance and environmentally benign nature of sulfur. However, the poor electrical conductivity of elemental sulfur results in low utilization of sulfur specific capacity, and hence, insufficient specific energy of Li-S batteries. Selenium disulfide (SeS2), with a theoretical specific capacity of 1342 mAh g-1, is a promising cathode material as it has attractive merits over elemental sulfur. Because of the better conductivity of SeS2 than S, the electrochemical reaction kinetics of S/SeS2 are expected to be remarkably improved. Herein, to combine the high conductivity and higher density of SeS2 and high specific capacity of elemental sulfur, we investigated hierarchical architectures of carbon as effective hosts for S and SeS2. By a facile one-step melt infiltration method, we synthesized S/SeS2@carbon nanofibers (CNFs) composites in which S and SeS2 were uniformly distributed over the CNFs. The hierarchical S/SeS2@CNFs (S:SeS2, 1:2 w/w) electrodes shows good initial discharge capacity of 940 mAh g-1 at 0.1C rate with high mass loading of material (~6-8 mg/cm2 of composites) and >90% initial coulombic efficiency. The composite electrode shows more than 830 mAh g-1 specific capacity after 100 charge-discharge cycles at 0.1C rate.

ET06.09.21
Leveraging Titanium to Enhance the Performance of Silicon Anodes in Lithium-Ion Batteries Pui Kit Lee and Denis Y. Yu; City University of Hong Kong, Hong Kong, Hong Kong.

Silicon (Si) is one of the most promising materials for next-generation Li-ion battery anode since Si has a high gravimetric capacity (3570 mAh g-1) and a relative low lithiation and de-lithiation voltage (0.4 V vs Li/Li+). However, the major challenge when applying Si as anode material in Li-ion battery is its poor cycle performance. It can be attributed to drastic volume expansion of lithiated silicon (300% theoretical expansion). Approaches such as yolk-shell silicon-carbon or silicon-titanium dioxide composites have been proposed to improve the cycle stability of Si-based electrode. Basically, void space was created by forming a carbon or titanium dioxide layer with larger volume, which accommodates the expansion of Si during lithiation and improves cycle performance. However, these approaches do not fundamentally reduce the intrinsic lattice expansion of the Si. The larger volume in fact reduces the overall
In this work we focus on designing a successful direct bottom-up pathway to synthesize both the 2D monoclinic $\text{MFeF}_4$ and 3D orthorhombic $\text{M}_2\text{Fe}_2\text{F}_7$ (M = alkali metal) from 1D−fluoride precursor at low temperatures, utilizing a blend of topochemical approaches. Notably, the linear 1D chains originating from the precursor have significantly transformed throughout the topochemical conversion of 1D $\rightarrow$ 2D $\rightarrow$ 3D frameworks. In fact, the as−synthesized orthorhombic weberite $\text{M}_2\text{Fe}_2\text{F}_7$ has shown exquisite cycling stability and also the reversible capacity of $\sim 55$ mAh/g with low polarization. Hence, we have designed a new topochemical strategy by which multidimensional fluoride structures can be developed. This study is expected to open a new avenue on the topochemical synthesis which allows the transformation of the precursor attaining topological resemblance with the final product.

In this work we focus on designing a successful direct bottom-up pathway to synthesize both the 2D monoclinic $\text{MFeF}_4$, and 3D orthorhombic $\text{M}_2\text{Fe}_2\text{F}_7$ frameworks. The resultant Si−Ti thin film is dense and is firmly deposited onto the foil. Therefore, the intrinsic electrode thickness variation can be monitored by in-situ dilatometer. 100 at% Si film electrode shows a 1st discharge capacity of 3415 mAh g$^{-1}$ which is close to the theoretical capacity of Si (3570 mAh g$^{-1}$). However, its cycle life is poor and the capacity fades linearly for the first 10 cycles. At the 15th cycle, no capacity can be obtained. Addition of Ti into the thin film reduces available capacity but improves cycle performance. A film with 20 at% Ti gives a capacity of 1500 mAh g$^{-1}$, and the capacity retention is about 95% after 50 cycles with a high average coulombic efficiency of 99.58% (from 3rd to 50th cycle).

To understand the role of the Ti inside the Si matrix, the thickness change of the thin film during lithiation and de-lithiation is monitored by in-situ dilatometry. While 100 at% Si film electrode exhibits a thickness increase of 345% after full lithiation, the thickness change is reduced significantly to 130% when 20 at% Ti is added. Furthermore, Ti addition allows full mechanical reversibility after Li removal. Moreover, Raman spectroscopy shows that the interaction between Si and Ti is still observed after cycling, suggesting that Ti is playing an active role to maintain the integrity of the Si electrode.

More results on Si−Ti thin films will be presented at the meeting.

**ET06.09.22**

**An Aqueous Ca-ion Full Cell Comprising BaHCF Cathode and MCMB Anode**

Prasit Dutta and Sagar Mitra; Indian Institute of Technology Bombay, India, Mumbai, India.

There is a pressing need of new and effective cost and energy storage systems in concomitance with the fast development of solar, wind and other types of renewable sources of energy. The capability of high-rate cycling and environmental benignity at less expensive defines the ingress of upcoming energy storage systems. Multivalent ion batteries are emerging as a promising alternative of Li ion technology due to their natural abundance, safety, low cost proposition and higher volumetric capacity. But these batteries are still challenged by sluggish cation diffusion in the electrode material and high polarisation of the respective cations ($\text{M}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}$). Calcium ion on the contrary have low polarisation compare to Li-ion, thus enjoying the benefits of overcoming the kinetics issues in large. Here, we introduce a reversible electrochemical Ca-ion cell in conjunction with inexpensive aqueous electrolyte, 1 M aqueous $\text{Ca}(<\text{O})_2$; Prussian Blue analogue barium hexacyanoferrate (BaHCF) cathode half-cell provides a capacity of 70 mAh/g with around 93% reversibility and 97% discharge capacity retention after 200 cycle was observed. In full cell, carbon cloth, BaHCF and meso-carbon microbeads (MCMB) have been explored as the current collector, cathode and anode material, respectively. The full cell provides 40 mAh/g (based on the mass of cathode active material) capacity at 5 C rate till 100 cycles. We believe, the investigation of this simple full cell at the early stage of Ca-ion battery will pave a fast transition in the forthcoming energy storage systems.

**ET06.09.23**

**A Novel Topochemical Paradigm to Design Multidimensional Fluoride Cathodes for Sodium-Ion Batteries**

Nabadyuti Barman, Utsav K. Dey and Premkumar Senguttuvan; New Chemistry Unit (NCU), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

Electrochemical energy storage is highly sought-after for mankind owing to increasing concerns regarding renewable energy resources. Albeit, invincible in the domain of battery research, Li−ion based materials possess some major drawbacks regarding the limited abundance, thermal runaway, expressiveness and environmental issues which refrain their inordinate usage. To unravel these intricacies, researchers have successfully employed sodium as a potential alternative which has significantly revitalized the field of battery research. Still, the discovery of Na−ion electrodes is basically centralized on the imported “know−how” knowledge from Li-ion chemistry. Primarily the layered oxides and polyanionic compounds have shown a long-standing impact on Na-ion battery (SIB) cathodes. Among all those myriad of compounds, the transition metal fluorides scintillate the structural, as well as electrochemical aspects due to the rich crystal chemistry, lies within, especially when it comes to the case of Iron-based fluorides which are inexpensive and consisted of earth−abundant precursors. For instance, ReO$_3$−type FeF$_3$ and NaFeF$_3$−based electrodes were reported to have good reversible capacity in SIBs. But this rich crystal chemistry can only be probed if suitable synthetic strategies are performed, by careful modulation of the spatial arrangement inside the crystals. The extreme challenge is to manipulate the homogenous connectivity between the anions without destroying the main crystalline matrix itself. This can be achieved by the unique methodology known as ‘Topochemical synthesis’ which allows the transformation of the precursor attaining topological resemblance with the final product.

**ET06.09.24**

**The Effect of Physical Properties of Manganese Dioxides in Aqueous Rechargeable Zinc Manganese Batteries**

Yang Wu1, Biswanath Dutta2, Jared Fee3 and Steven L. Suib1; 1Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States; 2Chemistry, University of Connecticut, Storrs, Connecticut, United States; 3Chem. Mater.

Rechargeable aqueous zinc ion batteries have been considered as reasonable substitutes for current primary batteries, since zinc manganese dioxide batteries were proved to be reversible in mild-acidic electrolyte. Recently, manganese dioxide polymorphs have attracted extensive attention as cathode materials due to zinc intercalation in their host tunnel or layer structures. Although phase-transfers from tunnel to layer or spinel have been reported, the complex intercalation chemistry remains ambiguous, especially effect of relative physical properties, such as electronic conductivity, tunnel size, morphology and porosity. The focus of this study will be a variety of porous nanostructured manganese dioxide with tunnels ranging from 1 X 1 (pyrolusite), 1 X 2 (ramsdellite), 2 X 2 (cryptomelane), 2 X 3 (romanechite), 2 X 4 (RUB-7). Our study shows zinc ion selectively yield an appropriate tunnel structure (1 x 2 or 2 X 2) based on current density. Urechinline morphology and mesopore are the key to enhance the battery performance as well.

**References**


**ET06.09.26**

**Foretops Metal Oxides/Carbon Composite Nanofibers as High Performance Anode Materials for Lithium-Ion and Sodium-Ion Batteries**

Mataz

foretops metal oxides are promising materials for high-performance anodes in lithium-ion and sodium-ion batteries due to their high theoretical capacity, low cost, and high energy density. However, these materials also exhibit several challenges, such as fast capacity fading, poor rate capability, and low Coulombic efficiency. In this work, we focus on synthesizing foretops metal oxides/Carbon Composite Nanofibers (FCNFs) as high-performance anode materials for lithium-ion and sodium-ion batteries. FCNFs are synthesized by a simple and scalable electrospinning process, followed by carbonization in an argon atmosphere. The resulting FCNFs exhibit a high surface area, well-defined pore structure, and high electrical conductivity. This study provides new insights into the properties and performance of foretops metal oxides/Carbon Composite Nanofibers as anode materials for lithium-ion and sodium-ion batteries.
We present results on the force spinning (FS) of Fe₂O₃/SnO₂/PAN and MoO₂/MoS₂/PAN precursors for the mass production of Fe₂O₃/SnO₂-carbon and MoO₂/MoS₂/C as anode materials for Lithium-ion and Sodium-ion batteries. The composite nanofiber anodes of Fe₂O₃/SnO₂/C and MoO₂/MoS₂/C are produced using centrifugal spinning and subsequent thermal treatment (calcination). The composite nanofiber anodes were porous and flexible. The nanofiber preparation process involved the centrifugal spinning of Fe₂O₃/SnO₂/PAN and MoO₂/MoS₂/PAN precursors into nanofibers and subsequent stabilization in air at 250°C and calcination at 700°C under an inert atmosphere. The flexible composite nanofibers were directly used as working electrode in lithium-ion and sodium-ion batteries without a current collector, conducting additives, or binder. The Fe₂O₃/SnO₂/C and MoO₂/MoS₂/C electrodes delivered high specific capacity of 550 mAh/g and 600 mAh/g respectively during the first sodiation cycle. The composite fiber electrodes showed high irreversible capacity and low coulombic efficiency at the first caused by the high surface area of the fibers and the SEI formation at the first cycle. The pre-lithiation of the composite fiber anodes resulted in improved capacity, lower irreversible capacity and high columbic efficiency of 99%. The simple processing method of Fe₂O₃/SnO₂/C and MoO₂/MoS₂/C composite fibers and corresponding electrochemical performance make them promising candidates for next generation and cost effective flexible binder-free anodes for Lithium-ion and Sodium-ion batteries.

Alcoutlabi, Jonathan Ayala, Jorge Lopez and Antonio Elizondo; Mechanical Engineering, University of Texas Rio Grande Valley, Edinburg, Texas, United States.

Effects of Heat-Treatment Atmosphere on the High-Voltage Electrochemical Performance of Li₂ZrO₃-Coated LiNi₀.6Co₀.2Mn₀.2O₂ Electrodes

Xiaowen Zhan, Shuang Gao and Yang-Tse Cheng; University of Kentucky, Lexington, Kentucky, United States.

Layered Ni-rich oxide cathode materials have attracted much attention for the next-generation lithium-ion batteries due to their low cost and high energy density. However, they still suffer from poor cycling performance and rate capability especially at high voltage. Li₂ZrO₃ has been widely used as a coating material for high-voltage Ni-rich layered cathode materials due to its relatively high Li⁺ conductivity and good thermal, chemical, and electrochemical stabilities. In previous studies, the coating was heat-treated in either air or oxygen. However, the effect of the atmosphere on the composition and structure of the Li₂ZrO₃, as well as the electrochemical performance of the coated cathode materials is still unclear. Herein, we surface-modified LiNi₀.6Co₀.2Mn₀.2O₂ cathode material with a Li₂ZrO₃ coating prepared under dry air and oxygen flow, and systematically investigated the effect of coating atmosphere on their electrochemical behaviors. The Li₂ZrO₃ coating prepared in oxygen is largely amorphous. It not only provided surface protection against the electrolyte corrosion but also enabled faster lithium-ion transport. Additionally, oxygen atmosphere facilitated Zr diffusion from the surface coating to the bulk of LiNi₀.6Co₀.2Mn₀.2O₂, which stabilized the crystal structure and enhanced lithium ion diffusion. Consequently, LiNi₀.6Co₀.2Mn₀.2O₂ cathodes coated with Li₂ZrO₃ in oxygen achieved a significant improvement in high-voltage cycling stability and high-rate performance.

Alcoutlabi, Jonathan Ayala, Jorge Lopez and Antonio Elizondo; Mechanical Engineering, University of Texas Rio Grande Valley, Edinburg, Texas, United States.
Oxygen redox has garnered intense interest as a means to increase the energy density of transition metal (TM) oxide positive electrodes in lithium-ion batteries, as it enables additional lithium (de)intercalation capacity at high voltages beyond the usual TM redox capacity. However, most oxygen-redox-active materials discovered to date suffer from large charge-discharge voltage hysteresis and irreversible voltage fade over extended cycling, limiting their practical use. Several hypotheses have been proposed to explain the nature of the oxidized oxygen species in order to guide improvements to the electrochemical properties of oxygen redox. The general consensus is that in more ionic oxides (e.g., those with certain 3d TMs), reactive and unstable O\textsuperscript{2−} species are created when oxygen is oxidized, whereas in more covalent systems (e.g., those with 4d and 5d TMs) the increased hybridization allows for the formation of stabilizing, long (~2.3 Å) O\textsuperscript{2−} dimers. Accordingly, recent work has attempted to tune the covalency of the TM–O interactions to improve the reversibility of oxygen redox in 3d materials, but has found limited success. In this presentation, I propose that consideration of only electronic structure properties is insufficient to explain the electrochemical behaviors associated with oxygen redox, and that the intrinsic coupling of oxygen redox to defect formation and disordering is in fact more significant in determining its reversibility. I first show that in the commercially promising lithium-rich Ni/Mn/Co oxides, oxygen oxidation occurs simultaneously with migration of TMs into Li sites, forming TM\textsubscript{i} defects in the material bulk. By drastically altering the local oxygen coordination environment, these defects lower the oxygen redox voltage, which we observe experimentally to fall by ~1 V after the first charge. This redox voltage shift is a major driver of the charge-discharge voltage hysteresis in oxygen-redox-active materials and cannot be explained without considering the link between oxygen redox and structural evolution. By then investigating two model systems, I reveal the origin of the correlation between oxygen redox and TM\textsubscript{i} formation, wherein the oxidation of oxygen is not sufficiently stabilized by either long (~2.3 Å) O\textsuperscript{2−} dimers or O\textsuperscript{2−} species, and instead promotes the formation of short (~1.4 Å) O\textsuperscript{2−} dimers and short TM–O bonds. These species require the decoordination of oxygen to single-TM-coordinate, which is realized in the layered structure through the formation of TM\textsubscript{i} defects. I show spectroscopically that these defect-localized oxidized oxygen species exist in 3d, 4d, and 5d systems, suggesting that the electrochemical properties of oxygen redox in TM oxides may depend more on the structural mechanism of oxygen decoordination than the identity of the TMs. Finally, I use this understanding to propose a new pathway to achieving reversible oxygen redox by employing new structures outside the layered framework.

Significant research efforts have focused on improving the specific energy of lithium-ion batteries for emerging applications, such as electric vehicles and renewable energy resources. A rocksalt-type nanostructured Li\textsubscript{4}Mn\textsubscript{2}O\textsubscript{5} cathode material has been recently discovered that exhibiting a large discharge capacity of >350 mAh g\textsuperscript{−1}, involving cationic (Mn\textsuperscript{3+}/Mn\textsuperscript{4+}/Mn\textsuperscript{5+}) and anionic (O\textsuperscript{2−}/O\textsuperscript{−}) redox processes. However, the detailed structure of Li\textsubscript{4}Mn\textsubscript{2}O\textsubscript{5} and its corresponding phase transformation, as well as the origins of higher capacities are poorly understood. In this work, we use first-principles density functional theory (DFT) calculations to investigate both the disordered rocksalt-type Li\textsubscript{4}Mn\textsubscript{2}O\textsubscript{5} structure [using the special quasi-random structure method (SQS)] and also the ordered ground state structure. The ionic ordering in the ground state structure is determined via a DFT-based enumeration method, by exploring symmetrically-distinct Li–Mn and O–vacancy ionic configurations on the cation and the anion sites in the rocksalt structure, respectively. We use both the ordered and disordered structures to interrogate the delithiation process, and find that it occurs via a three-step reaction pathway involving the complex interplay of cation and anion redox reactions: i) an initial metal oxidation, Mn\textsuperscript{3+} → Mn\textsuperscript{4+} (Li\textsubscript{4}Mn\textsubscript{2}O\textsubscript{5}, 4 > x > 2), ii) followed by anion oxidation, O\textsuperscript{2−} → O\textsuperscript{−} (2 > x > 1), and iii) finally, further metal oxidation, Mn\textsuperscript{4+} → Mn\textsuperscript{5+} (1 > x > 0). This final step is concomitant with Mn migration from the original octahedral site to the adjacent tetrahedral site, introducing a kinetic barrier to reversible charge/discharge cycles. Armed with this knowledge of the charging process, we utilize high-throughput DFT calculations to study metal mixing in this compound, screening potential new materials for stability and kinetic reversibility. We predict that mixing with M = V and Cr in Li\textsubscript{4}(Mn,M)\textsubscript{2}O\textsubscript{5} will produce new stable compounds with substantially improved electrochemical properties. Our discoveries should generate considerable interest in the experimental battery community and give guidance to experimental studies of simultaneous cation/anion redox in high-energy-density electrodes.

1. Yao, Z., Kim, S., He, J., Hegde, V. I. & Wolverton, C. Interplay of Cation and Anion Redox in Li\textsubscript{4}Mn\textsubscript{2}O\textsubscript{5} Cathode Material and Prediction of Improved Li(Mn,M)\textsubscript{2}O\textsubscript{5} Electrodes for Li-Ion Batteries. Science. Adv. 4, eaaao6754 (2018).

8:30 AM *ET06.10.03

Next Generation Battery Materials—Ni-Rich NMCs and LLZO

Marco M. Dossif; Lawrence Berkeley National Lab, Berkeley, California, United States.

Ni-rich NMCs (Li\textsubscript{Ni-x}Mn\textsubscript{x}M\textsubscript{y}O\textsubscript{2}; x > 2) are emerging as the next generation cathodes of choice for lithium-ion batteries intended for electric vehicle battery applications. While these materials have the potential of raising energy density due to higher practical capacities than NMCs with lower Ni content, they also suffer from abbreviated cycle life and thermal stability issues, particularly at high states-of-charge. To better understand what determines the thermal characteristics, we have prepared Ni-rich NMC materials with varying amounts of lithium content using the chemical oxidant NO\textsubscript{2}BF\textsubscript{4} and heated them at 950 °C for 10 hours. XRD studies show that there is a general trend to lower thermal stability with respect to phase conversion as lithium content decreases with nickel content increases, as well as a tendency to form products containing progressively more reduced transition metal ions and lower oxygen contents. While hard XAS Ni, Co and Mn K-edge experiments confirm this trend, showing that reduction occurs upon heating, soft XAS, which probes surfaces, portrays a more complicated picture. In some cases, metals on surfaces oxidize although they are reduced in the bulk. Transmission X-ray microscopy (TXM) experiments also show evidence of Ni migration upon heating for some of the materials. While modifications such as partial substitution or coatings may improve the thermal stability of Ni-rich NMCs in conventional cells, a longer term strategy may be to design completely solid state cells containing non-flammable ceramic electrolytes such as variants of LLZO (Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}), to
amplify safety hazards associated with thermal stability issues. In this talk, we will briefly discuss the properties of LLZO solid electrolytes and our strategies for the design of high-energy all solid-state lithium cells using LLZO and Ni-rich NMC cathode materials.

9:00 AM *ET06.10.04
Towards Low Cobalt and Cobalt Free Cathodes for High Energy Density Lithium-Ion Batteries Jagjit Nanda, Ethan C. Self, Chengyu Mao and Ilia Belharouak; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Commercialization of lithium-ion batteries began in 1991 by Sony with development of LiCoO2 cathode coupled with graphite anode. Since then cobalt constitutes an important role in stabilizing current commercial cathodes for lithium-ion whether it is LiNi0.5Mn0.3Co0.2O2 (NMC) or LiNi0.85Co0.15Al0.05O2 (NCA). Apart from battery application, cobalt is widely used in electronics and magnetic recording industry with limited reserves and supplies worldwide. With growing market demand for advanced lithium-ion for both automotive and stationary storage, there is an increasing research activity in developing cathodes with minimal or no cobalt content. The talk will highlight some recent progress in stabilizing Ni and Mn based lithium excess composition using early transition metal such as Mo and Cr. Early stage electrochemical results and oxygen stability at high voltage (>4.4 V with respect to Li+/Li) of these composition will be presented. Recent progress related to compositional and interfacial modifications such as creating cation disorder, doping/substitution, surface coating to attain high oxygen stability and reversible anion redox will be discussed. 

Acknowledgment This research performed at Oak Ridge National Laboratory, is managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, is funded by Asst. Secretary, Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO).

9:30 AM BREAK

10:00 AM *ET06.10.05
High-Nickel Layered Oxide Cathodes for High-Energy-Density Lithium-Ion Batteries Arumugam Manthiram; The University of Texas at Austin, Austin, Texas, United States.

Among the various cathode materials pursued over the years for lithium-ion batteries, layered LiMO2 (M = Mn, Co, Ni, and their solid solutions) oxides offer the highest energy density with an operating voltage of around 4 V. Each of the three transition-metal ions (Mn, Co, and Ni) in LiMO2 has its advantages and disadvantages with respect to structural stability, chemical stability, electronic conductivity, and environmental impact. The position of the metal 3d redox energies with respect to the top of the oxygen 2p band determines the chemical stability with respect to oxygen release from the lattice. On the other hand, the relative stability of the transition-metal ions in the octahedral vs. tetrahedral sites in the cubic close-packed oxygen array controls the structural stability. Since Ni2+ can be oxidized fully to Ni4+ without releasing oxygen from the lattice unlike Co3+, which can be oxidized only to ~3.5+ to avoid oxygen release from the lattice, and Ni3+ ion exhibits high stability in octahedral sites, there has been tremendous interest to develop layered LiMO2 cathodes with high nickel contents. However, cathodes with high Ni contents suffer from poor cycle life, thermal stability, and air stability.

This presentation will focus first on developing a fundamental understanding of the complexities that control the capacity fade, thermal stability, and air-reactivity of high-nickel layered oxide cathodes, employing samples with secondary particle sizes of ~10 microns and advanced bulk and surface characterization methodologies. In-depth understanding obtained with high-nickel layered oxide cathodes with Ni contents of as high as 94% and graphite anodes retrieved from full cells before and after thousands of cycles based on a combination of characterization techniques, viz., X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectroscopy, and high-resolution transmission electron microscopy, will be presented. Based on the profound understanding gained, the presentation will then concentrate on the design and development of layered oxide compositions with controlled bulk and surface structures as well as novel electrolyte solutions that are compatible with both the high-nickel layered oxide cathodes and graphite anodes to realize a robust electrode-electrolyte interphase. Based on the findings, viability to realize lithium-ion cells with cathode capacities of >220 mAh g^-1, high energy density, high power capability, and long cycle life will be discussed. Finally, approaches towards designing low-cobalt or cobalt-free cathode compositions will be pointed out.

10:30 AM ET06.10.06
Heterogeneous Cathode Materials Towards High Energy Density and Stable Alkali-Ion Batteries Linqin Mu, Muhammad Momirunnah Rahman and Feng Lin; Virginia Tech, Blacksburg, Virginia, United States.

The ever-increasing demand for renewable energy storage and electrifying transportation vehicles calls for developing high energy density electrode materials for rechargeable alkali-ion batteries. As one of the most important components of energy storage devices, cathode materials, such as alkali-ion containing layered oxide compounds play a crucial role in determining the energy density of batteries. Major efforts have been invested to push the cathode capacity approaching its theoretical limit while reducing the cost of raw materials. However, novel design strategies must be considered to reach the envisioned goal. Three-dimensionally homogeneous or gradient distribution of transition metals has been acclaimed the design principle for obtaining good performing layered oxide cathode materials. Counterintuitively, we discovered that highly heterogeneous cathode materials at multiple length scales can give rise to unexpected good battery performance. Such phenomenon is equally pertinent for multiple types of layered alkali-ion cathode materials (Li-ion, Na-ion, and K-ion). The heterogeneous nature of the cathode materials was characterized through variously advanced spectroscopy and imaging techniques (STEM, TXM, SEM, EDX, and XAS). Batteries assembled using such cathode materials in half/full cells with high-mass loading delivered unexpectedly excellent and stable electrochemical performance. The results show the promise of heterogenizing the elemental distribution of multicomponent alkali layered oxide materials and open up a new pathway to further develop the layered oxide cathode for high energy and stable alkali-ion batteries.

Reference:

10:45 AM ET06.10.07
Unexpected Superior Cycleability of LiCoO2 at Upper Voltage of >4.6 V (vs. Li/Li+) for High-Energy Density Lithium-Ion Batteries Won Mo Seong, Kyungho Yoon, Myeong Hwan Lee, Sung-kyun Jung and Kisuk Kang; Seoul National Univ, Seoul, Korea (the Republic of).

The instability of LiCoO2 layered structure at >0.5 Li extraction has been considered as an obstacle for the reversible utilization of its near theoretical capacity at higher voltage cut-offs in lithium-ion batteries (LIBs). To date, much of previous researches have been focused on the surface engineering of LiCoO2 to extend its usable state-of-charge (SOC) range, which has proven to be effective in suppressing the phase transformation. Herein, in contrast to conventional belief, we verify the superior reversibility of bulk LiCoO2 with extended lithium extraction by ruling out the effect of damaged surface. A high-voltage cycling of uncoated LiCoO2 at 4.8 V (vs. Li/Li+) cut-off offers unexpectedly better cycle stability and lower polarizations than those at 4.6 V (vs. Li/Li+). In detail, it is revealed that the rigid cycle degradation at high-voltage cycling is mostly caused by the formation of a surface reactive layer...
composed of spinel phase, however these damaged surfaces are leached out at 4.8 V enabling its superior cycleability to 4.6 V-cycling. In the absence of the resistive surface, the capacity retention of LiCoO2 electrode with 4.8 V cut-off cycling could be remarkably high. This work découps the effect of the intrinsic instability of highly delithiated LiCoO2 and the surface degradation on the capacity fades toward practical high-voltage cycling and proposes that a rational strategy against the formation of the resistive phases would be a critical step for the full utilization of LiCoO2 with higher cut-off voltage cycling.

11:00 AM **ET06.10.08**

Concentrated Electrolytes for Safe and High-Voltage Batteries  
Yuki Yamada, Jianhui Wang and Atsuo Yamada; The University of Tokyo, Tokyo, Japan.

Severe safety concerns are impeding the large-scale employment of lithium/sodium batteries. Conventional organic electrolytes are highly flammable and volatile, which may cause catastrophic fires or explosions. Efforts to introduce flame-retardant solvents into the electrolytes have generally resulted in poor charge-discharge cycleability, because those solvents do not suitably passivate carbon-based negative electrodes. Here we report salt-concentrated electrolytes3-5 to resolve this dilemma. Our previous works demonstrate that concentrated electrolytes can form a salt-anion-derived passivation film via the downward shift of anion’s LUMO level resulting from the extensive anion coordination to Li+. Applying this strategy to a popular flame-retardant solvent (trimethyl phosphate), we demonstrate that fire-extinguishing concentrated electrolytes, without any additive or soft binder, allow stable charge-discharge cycling of hard-carbon and graphite negative electrodes for more than 1,000 cycles (over one year) with negligible degradation; this performance is comparable or superior to that of conventional flammable carbonate-based electrolytes. The unusual interphasial character of the concentrated electrolytes couple with their fire-extinguishing property contributes to developing safe and long-lasting batteries, unlocking the limit toward development of much higher energy-density batteries.


11:30 AM **ET06.10.09**

Enabling the High Capacity of Lithium-Rich Anti-Fluorite Lithium-Iron Oxide by Simultaneous Anionic and Cationic Redox  
Jun Lu; Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States.

Anionic redox reactions in the cathodes of lithium-ion batteries are enabling opportunities to double or even triple the energy density. However, it is still challenging to develop a cathode exploring the anionic redox for real-world applications using earth-abundant materials, due to the limited strategy to intercept the oxygenates from further irreversible oxidation to O2 gas. Here we report simultaneous iron and oxygen redox activity in a Li-rich anti-fluorite Li5FeO4 electrode. During the removal of the first two Li ions, the oxidation potential of O2 is lowered to approximately 3.5 V vs. Li+/Li0, at which potential the cationic oxidation occurs concurrently. These anionic and cationic redox reactions show high reversibility without any obvious O2 gas release. Moreover, this study provides an insightful guideline to design high-capacity cathode with reversible oxygen redox by simply introducing oxygen ions coordinated exclusively by Li+.


1:30 PM **ET06.11.01**

Using Multi-Modal and Multi-Scale TEM and TXM Imaging Techniques to Study the Structural Stability of High Ni-Content Cathode Materials  
Ruojian Lin1, Zulipia Shadike1, Seongmin Bak1, Hoolin L. Xin2, Xiao-Qing D. Yang3, YoungHo Shin4, Xiaojing Huang5 and Yong Chu5; 1Chemistry, Brookhaven National Laboratory, Upton, New York, United States; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 3Energy Systems Division, Argonne National Laboratory, Argonne, Illinois, United States; 4National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States; 5Chemical Sciences and Engineering Division, Argonne National Laboratory, Upton, New York, United States.

The promising application of high Ni-content layered oxide materials in Li-ion batteries has attracted increasing attention from the research community. Compared to traditional layered oxide materials such as LiCoO2 (LCO) or LiNi0.5Mn0.3Co0.2O2 (NMC333), high Ni-content materials can provide higher specific capacity and energy density. However, capacity fading and thermal runaway remain the main issues for high Ni-content layered oxides. In order to overcome these challenges, the in-depth understanding of the relationship between the structural changes and perform deterioration of high-Ni-content materials during charge-discharge cycling are critically needed. Using multi-modal and multi-scale TEM and TXM imaging techniques, the structure stabilization mechanism has been thoroughly studied to provide valuable guidance for future material design. The results obtained from our newly developed multi-scale characterization techniques will be reported, including the state-of-the-art aberration-corrected scanning transmission microscopy (STEM) imaging, STEM- electron energy loss spectroscopy (EELS), transmission X-ray imaging(TXM), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). These results show that such multi-modal and multi-scale characterization tools can help us to study the structural changes of high Ni-content materials during cycling. The structure degradation is highly correlated to the irreversible cation migration and intermixing at atomic level during extensive cycling. Also, we found that the surface plays a vital role in these materials.

Acknowledgement: Dr. Z. Shadike, Dr. S. Bak, and Dr. X.-Q. Yang were supported Vehicle Technologies Office, Office of Energy Efficiency and Renewable Energy, the U.S. Department of Energy, through the Advanced Battery Materials Research (BMR) Program, including Battery500 Consortium, under contract number DE-SC0012704. The TEM studies were supported by the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704. This research used the Hard X-ray Nano-probe Beamline of the National Synchrotron Light Source II, a U.S. Department of Energy Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. Dr. Y. Shin was supported by the Vehicle Technologies Office, Office of Energy Efficiency and Renewable Energy, the U.S. Department of Energy, under Contract No. DE-AC02-06CH11357.

2:00 PM **ET06.11.02**
Multi-modal correlative microscopy has been used extensively through the last decade in various research fields in order to overcome optimization challenges of complex materials systems. The multiscale aspects of these new functional or structural materials, such as nanostructured energy storage systems, and the complexity of their physical interactions, require new multi-modal and multiscale characterization tools in order to shed light on pertinent parameters controlling the process at a given scale, and the link between various scales.

3D Correlative microscopy allows simultaneous quantification of structural, morphological and compositional spatial distributions throughout scales, from which constitutive governing laws and effective properties can be derived. Main obstacles to its wide range usage are the simultaneous tracking of the sample within various instruments and the correlation between data sets obtained on dispersed zoomed-in ROIs (region of interest) within the sample. As a result, 3D correlative microscopy remains a time consuming, cumbersome, non-reproducible and limited-precision methodology.

In this abstract, an innovative procedure for multi-scale µCT (X-ray microtomography) and multiple volume-based ROIs with FIB/SEM is proposed. The procedure is applied to cutting edge NMC type (LiNi0.5Mn1.5O4) Li-ion batteries in order to study the effects of both defects and morphology on the batteries transport properties such as grain connectivity, porous media percolation and effective diffusivity.

This will allow nearly automatized data correlation and fusion between structural information provided by µCT with the morphological and compositional information obtained by FIB/SEM imaging at both micro and nano scales.

Two battery samples have been considered for this correlative study. First sample consists of a micro-layer of NMC type cathode material on an aluminum substrate. Micro-nano delamination features and cathode phase grain connectivity morphologies have been studied. Localized electric conductivity and effective diffusivity have also been calculated. Second sample considered is a LG MJ1 cell with the NMC type cathode and a Graphite/Si hybrid anode. Both structural and compositional anode/electrolyte and cathode/electrolyte interfacial distributions have been studied in micro and nano scales.

2:15 PM ET06.11.03
Chemical Origin of Oxygen Redox in LiFeO4 Revealed by Experimental and Theoretical XANES
Liang Li, Eungje Lee, John w. Freeland, Tim Fister, Michael M. Thackeray and Maria K. Chan; Argonne National Laboratory, Lemont, Illinois, United States.

It is commonly recognized that utilization of oxygen redox is an intriguing route for obtaining higher capacity of Li-ion batteries (LIBs). Despite numerous experimental and theoretical attempts to unravel the mechanism of oxygen redox behavior, the electronic origin of oxygen activities in energy storage of Li-rich LIB materials remains under intense debate. In this work, the onset of oxygen activity was examined using a Li-rich antifluoride material that has been reported to exhibit oxygen redox, namely Li1Fe0.5O2. Ab-initio Molecular Dynamics (AIMD) simulations were performed to investigate the structural response of oxygen matrix to delithiation. The oxygen K-edge X-ray absorption near-edge spectra (XANES) were modeled using Bethe-Salpeth equation (BSE) approach and compared with experiments, from which the oxygen redox mechanism was uncovered.

2:30 PM BREAK

3:00 PM ET06.11.04
O2 Li-Rich Cathode Material for High-Energy-Density Li-Ion Batteries
Dingguo Xia; Peking University, Beijing, China.

The exploration of new high-energy-density cathode materials is one of the most challenging issues facing the development of next-generation lithium-ion batteries. The extraordinarily high capacity delivered by lithium-rich oxide cathodes have been nested to the contributions from both cationic and anionic redox processes. However, the oxygen anionic redox caused by the activation of the Li2MnO3 domain promotes the transition metal ion migration, leading to the transition of layer to spinel phases, demonstrating a severe voltage decay during cycling, which is the major obstacle preventing industrial application. Therefore, the exploration of new cathode materials that could enhance the energy density of Li-ion batteries is still one of most challenging issues that must be solved. Herein, we succeeded in preparing a new O2-type layered Mn-based Li-rich oxide with an atomic-size superstructure, which demonstrates a reversible capacity of ~400 mAh g−1 with a stable discharge voltage and a high charge/discharge efficiency during cycling.

3:30 PM ET06.11.05
Anomalous Segregation in Lithium-Rich Layered Oxide Uncovers New Theoretical Design Rule for Stable Cathode in Lithium-Ion Battery
Huolin L. Xin, Ruoqian Lin, Xia-Qing Ding, Yang Yang, Xiqian Yu, Enyuan Hu, Kristin A. Persson, Mingjie Liu, Qin Wu and Jincheng Zheng; 1 Brookhaven National Laboratory, Upton, New York, United States; 2 University of California, Irvine, Irvine, California, United States; 3 Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4 IOP, Chinese Academy of Sciences, Beijing, China; 5 Xiamen University, Xiamen, China.

There is increasing interest in utilizing lithium-excess cathode materials as new generation energy storage material instead of traditional layered materials such as LiCoO2 and LiNi0.5Mn1.5O4 because of their ultra-high charge capacity. However, lithium-rich materials still suffer problems such as low coulombic efficiency for the first cycle, voltage and capacity fading with extended cycling. Here we report the investigation of a promising high-capacity lithium-rich 3d-4d transition-metal layered compound. The incorporation of 4d transition metals here offers an uncharted phase space for mechanistic exploration as compared to the well documented 3d transition metal (TM) oxides. Utilizing state-of-the-art tools, we found that that a three-dimensional porous structure is formed in the interlayer and the 3d and 4d transition metals can segregate at the sub-micron scale after extended cycling. More surprisingly, at the nanoscale, we found that the 4d metal is expelled from the surface. In conjunction with ab initio thermodynamics calculations, this study for the first time reveals the intricate connection between the instability of the surface and the degradation of the layered cathode materials. More importantly, the revealed mechanism allows us to provide predictive guidance for future design of lithium-rich as well as stoichiometric layered cathode materials.

This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

3:45 PM ET06.11.06
First-Principles Investigation of the Stability of the Oxygen Framework of Li-Rich Battery Cathodes
Marnik Berx, Bart Partoens and Dirk Grzegorz Pyka and Bartlomiej Winarski; 1 Application Software Group, ThermoFisher Scientific, Merniguac Cedex, France; 2 CT Core, Thermo Fisher Scientific, Brno, Czechia; 3 GS BU Materials-Science, Thermo Fisher Scientific, Brno, Czechia.

3D Correlative microscopy applied to NMC Type Li-Ion Battery Transport Properties Study
The growth of the electrical vehicle market has led to a significant interest in developing safe high-capacity batteries with good cycling properties. Lithium-rich layered oxides such as Li$_2$MnO$_3$ have shown great potential as cathodes in Li-ion batteries, mainly because of their large capacities which have been demonstrated to be caused by a cumulative cationic and anionic redox activity. However, these materials still suffer from structural degradation as the battery is cycled, reducing the average voltage and capacity of the cell. This voltage fade is believed to be related to the migration of transition metals into the lithium layer, which results in a transformation of the structure to a spinel-type phase. Recent theoretical works have linked the migration of transition metals to the formation of O-O dimers with a short bond length, driven by the presence of oxygen holes due to the participation of oxygen in the redox process. However, so far such studies have been limited to fully charged structures, which are inherently very unstable and difficult to achieve in practice. Moreover, very few results in the literature have studied the O1 stacking of the layered structure, to which Li$_2$MnO$_3$ is expected to transform when the cathode is delithiated by 75%. We investigate the formation of O-O dimers for partially charged O1-Li$_{0.5}$MnO$_3$ using a first-principles density functional theory approach by calculating the thermodynamic driving force for dimer formation, as well as the kinetic barriers. Next, we perform similar calculations for partially charged Li$_2$IrO$_3$, a Li-rich material for which the voltage fade was not observed during cycling. When we compare the stability of the oxygen framework, we conclude that the formation of O-O dimers is both thermodynamically and kinetically viable for O1-Li$_{0.5}$MnO$_3$. For O1-Li$_{0.5}$IrO$_3$, on the other hand, we observe that the oxygen lattice is much more stable, either returning to its original state when perturbed, or resulting in a structure with an O-O dimer that is much higher in energy. This can be explained by the lower participation of oxygen in the redox process for Li$_2$IrO$_3$, which is also clear from the calculated magnetic moments on oxygen. The lack of O-O dimer formation in O1-Li$_{0.5}$IrO$_3$, as well as its connection to the migration of transition metals, provides valuable insight as to why Li$_2$IrO$_3$ does not demonstrate a voltage fade as the battery is cycled, which can be used to design Li-rich battery cathodes with an improved cycling performance.

4:00 PM ET06.11.07
Antimony Oxychloride/Graphene Aerogel as Cathode Material for Chloride-Ion Batteries

Lauren Marbella$^1$ and Clare Grey$^1$
$^1$Chemistry, University of Cambridge, Cambridge, United Kingdom; $^2$Argonne National Laboratory, Argonne, Illinois, United States; $^3$Diamond Light Source, Didcot, United Kingdom.

Lithium-ion batteries have emerged as dominant power sources for portable electronics and vehicular applications. However, the ever-growing market has put higher demands in terms of energy and power needs, and hence alternative rechargeable battery systems, for example sodium-ion batteries, are being explored. Recently, there has been growing interest in rechargeable batteries based on an anion shuttle, for example, chloride or fluoride battery that operates at room temperature. With a high theoretical energy density (~ 2500 Wh L$^{-1}$), chloride ion battery show a noticeable potential as future power source and several proof-of-principle have been already reported. The electrode dissolution of metal chlorides in the electrolyte causes stability issues and thus limits its performance as an efficient cathode material for chloride ion battery. Several metal chlorides have been studied as cathode material for chloride ion batteries, developing an efficient cathode material that is stable in electrolyte and with lower volume expansion than metal chlorides, still remains a challenge. Metal oxychlorides such as FeOCl, BiOCl, VOCl$_3$ have been explored as cathode material and show better electrochemical performance and stability compared to metal chloride based cathodes. Here, we demonstrate antimony oxychloride as a new cathode material for chloride ion battery. ShbOCl$_2$ microstructures synthesized through hydrothermal route undergoes reversible redox reactions when cycled as cathode for chloride ion battery. With an aim to address the poor conductivity and huge volume expansion of metalalloychloride based cathodes upon on cycling, we prepared ShbOCl$_2$-graphene aerogel composite (ShbOCl$_2$-GAG) which exhibited improved electrochemical performance, with a stable capacity of ~80 mAh g$^{-1}$ after 100 cycles. The electrochemical reaction mechanism of antimony oxychloride electrode as cathode material in chloride ion battery has been studied through ex-situ XRD and XPS characterization techniques. The obtained results are promising and demonstrate 3D networked antimony oxychloride/graphene aerogel composite as a potential cathode material for Chloride Ion batteries.

4:15 PM ET06.11.08
Surface Orientation Dependence of Oxygen Vacancy and Ni/Li Cation Mixing Defects Formation in Li(Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$)O$_2$ Cathode Materials

Ganes Shakij$^1$, Randy Jalemi$^{2,3,4}$ and Yoshitaka Tateyama$^{1,5}$
$^1$Kyoto University, Kyoto, Japan; $^2$National Institute for Materials Science, Tsukuba, Japan; $^3$Japan Science and Technology Agency, Kawaguchi, Japan.

Layered Ni-rich Li(Ni$_{x}$Mn$_{y}$Co$_{z}$)O$_2$ (x+y+z=1) or NCM has been considered as one of the most promising candidates for the next-generation Li-ion battery cathodes because of its high energy density. However, its commercial usage is still hindered partly due to the following two critical issues: (1) safety issue that closely relates to significant NCM lattice oxygen release during operation, (2) capacity fading due to the irreversible layered to spinel/rock-salt phase transformation triggered by Ni/Li mixing defect formation [1].

Herein, by means of density functional theory (DFT)-based calculations we study the aforementioned oxygen release phenomena by examining the oxygen vacancy (Ovac) formation energy, taking Li(Ni$_{0.6}$Mn$_{0.4}$)O$_2$ or NCM811 as the representative of Ni-rich NCM. We also investigate the Ni/Li mixing defect formation at surface and near-surface regions of NCM811.

Based on the energetics analysis, we found that the bulk and the low-index surfaces considered in this work viz. (104), (110) and (012) are stable against spontaneous oxygen evolution in the fully lithiated state. Further, our results also suggest that the Ovac formation in the bulk has a high energy while there is a large variation of Ovac formation energy at the surfaces. These results can be mainly attributed to the difference of transition metal (TM) oxidation states distribution at each surface facets and bulk. While the pristine bulk of NCM811 is exclusively composed by Ni$^{2+}$ and Ni$^{3+}$, we observed presence of less stable Ni$^{4+}$ ions at the surface and sub-surface regions. Our results suggest that one way to stabilize this unstable Ni$^{4+}$ is releasing Oxygen nearby (i.e. the Ovac formation) that subsequently lower the oxidation state to Ni$^{3+}$. In the case of Ni/Li mixing defect, we found that the polar (012) surface has more resistance against the Ni/Li mixing as compared to the non-polar (104) and (110) surfaces in which Ni/Li mixing is predicted to spontaneously occur. This can be attributed to the existence of surface Ni$^{3+}$ that can interchange with Li$^+$ without further reduction at (104) & (110) surfaces, while on the contrary pristine polar (012) has only Ni$^{3+}$ at its outermost TM layer. Our results indicate that the choice of surface orientation and termination may play an important role in determining the formation of both Ovac and Ni/Li mixing defects.

References

4:30 PM ET06.11.09
Anomalously High-Rate Energy Storage at Large Length-Scales in Complex Oxides

Kent J. Griffith$^1$, Kamila Wiaderek$^2$, Gianantonio Cibin$^1$, Lauren Marbella$^1$ and Clare Grey$^1$; $^1$Chemistry, University of Cambridge, Cambridge, United Kingdom; $^2$Argonne National Laboratory, Argonne, Illinois, United States; $^3$Diamond Light Source, Didcot, United Kingdom.

The maximum power output and minimum charging time of a lithium-ion battery – key parameters for its use in, for example, transportation applications –
depend on mixed ionic–electronic diffusion. While the discharge/charge rate and capacity can be tuned by varying the composite electrode structure, ionic transport within the active particles represents a fundamental limitation. Thus, to achieve high rates, particles are frequently reduced to nanoscale dimensions despite this being disadvantageous in terms of volumetric packing density as well as cost, stability, and sustainability considerations. As an alternative to nanoscaling, we show that complex niobium tungsten oxides with topologically frustrated polyhedral arrangements and dense μm-scale particle morphologies can rapidly and reversibly intercalate large quantities of lithium. Multielectron redox, buffered volume expansion, and extremely fast lithium transport approaching that of a liquid lead to extremely high volumetric capacities and rate performance as very recently reported in both crystallographic shear structure and bronze-like niobium tungsten oxides[1]. The active materials Nb_{x}W_{y}O_{z} and Nb_{y}W_{x}O_{y} show new strategies toward designing electrodes with advantages in energy density, scalability, electrode architecture/complexity and cost as alternatives to the state-of-the-art high-rate anode material Li_{3}Ti_{5}O_{12}. The direct measurement of solid-state lithium diffusion coefficients (D_{Li}) with pulsed field gradient NMR demonstrates room temperature D_{Li} values of 10^{-12}-10^{-13} m^{2}s^{-1} in the niobium tungsten oxides, which is several orders-of-magnitude faster than typical electrode materials and corresponds to a characteristic diffusion length of ~10 μm for a 1 minute discharge. Structural and chemical analysis of high-rate and multielectron energy storage will be discussed with insights from operando X-ray diffraction and multi-edge X-ray absorption spectroscopy. Materials and mechanisms that enable lithiation of μm particles in minutes have implications for high power applications, fast charging devices, all-solid-state batteries, and general approaches to electrode design and material discovery.


ET06.12.02
Optimization of an Alkoxide-Based Electrolyte for Magnesium-Ion Batteries Anushka Dasgupta, Princeton University, Princeton, New Jersey, United States.

Rechargeable Mg-ion batteries boast a high theoretical volumetric capacity and an absence of dendrite formation, making them a promising candidate for energy storage applications in the electric grid and in transportation. However, many electrolytes which have been developed for the Mg-ion battery chemistry thus far passivate the Mg anode surface or suffer from a low anodic stability or ion conductivity. We report on a Mg-ion electrolyte, based on the weakly coordinating anion [Al(HFIP)]- in DME, which can reversibly and efficiently deposit magnesium metal and is stable at voltages greater than 3V vs. Mg/Mg2+ on various current collectors. The electrolyte is characterized via a variety of electrochemical methods, including cyclic voltammetry and impedance spectroscopy. The kinetics of Mg-ion transport in the electrolyte vary with its concentration, with optimal ion conductivity achieved between 0.45M and 0.50M. In this range, the electrolyte displays its lowest deposition overpotentials. These overpotentials decrease with cycling, signaling the ability of the electrolyte to break down passivating layers and activate the anode surface. The properties of this electrolyte, which has a simple, scalable, Grignard-free synthesis, suggest interesting directions for future research.

ET06.12.03
Examination of SEI Variation in Patterned Li Anodes Using Scanning Probe Microscopy, with Insight into the Suppression Mechanisms of Dendrite Formation Colin T. Campbell1,2, Yong Min Lee3, Kuk Young Cho4, Young-Gi Lee4, Byeongdu Lee6, Charudatta Phatak4 and Seungbum Hong6, 1Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 2Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea (the Republic of); 3Materials Science and Chemical Engineering, Hanyang University, Ansan, Korea (the Republic of); 4ICT Materials and Components Research Laboratory, Electronics and Telecommunications Research Institute

Examination of SEI Variation in Patterned Li Anodes Using Scanning Probe Microscopy, with Insight into the Suppression Mechanisms of Dendrite Formation Colin T. Campbell1,2, Yong Min Lee3, Kuk Young Cho4, Young-Gi Lee4, Byeongdu Lee6, Charudatta Phatak4 and Seungbum Hong6, 1Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 2Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea (the Republic of); 3Materials Science and Chemical Engineering, Hanyang University, Ansan, Korea (the Republic of); 4ICT Materials and Components Research Laboratory, Electronics and Telecommunications Research Institute
Li metal batteries have been projected to outperform the current graphite anode batteries in both storage capacity and potential (3860mAh/g Li vs. 372mAh/g graphite). However, significant research needs to be performed in order to alleviate potential materials problems of dendrite formation and associated capacity loss and cell shorting before they can be commercially available. Integral to the development of not only Li metal anodes, but all metallic electrodes, is an understanding of the mechanisms of dendrite formation. In this work, the effect of patterned electrodes on the nucleation and growth of dendrites will be examined by atomic force microscopy (AFM), with specific focus on surface potential variations due to patterned geometry. These surface potential variations can then give insight into nonuniform solid electrolyte interphase (SEI) formation.

There are two factors that contribute to the SEI formation that are unique to patterned electrodes: (i) local curvature of the electrode, and (ii) nonuniform electrolyte depletion. Curved conductive surfaces produce higher electric field magnitudes than flatter surfaces for a given applied voltage, and so produce higher local current densities, leading to inhomogeneous Li deposition. This can be inhibited by the formation of a thicker SEI as a result of this higher current, leading to a suppression of nonuniform current. The second factor, nonuniform electrolyte depletion, also directly affects SEI formation. In a flat, parallel electrode system the concentration of Li ion at every point in the system can be calculated with relative ease for sufficiently low current using Fick’s law. The inhomogeneities associated with a patterned electrode break this simple derivation, often requiring numerical simulation of the diffusion-supplied flux of Li delivered to the electrode surface. In regions where diffusion is insufficient to supply the electrode with Li, a large overpotential (and consequently, electric field) develops; this accelerates electrolyte decomposition, even in “low current” limits, promoting SEI formation and consequently limiting nonuniform deposition. A combination of these effects can lead to suppression of dendritic growth of Li.

We will present results using Kelvin probe microscopy, and Electrostatic force microscopy to visualize variations in the conductivity and/or thickness of the SEI as a function of patterning. Both of these measurements will be conducted on a series of scratches with varying aspect ratio in Li metal anodes. The nucleation and growth of the Li dendrites will be monitored using an in-situ electrochemical cell for the AFM. Together, this information about inhomogeneous or nonuniform SEI formation can be used to inform future efforts in nanopatterned electrodes for Li batteries.

**ET06.12.04**

**Hybrid Silicate Coatings for Stable Lithium Metal Anodes** Fang Liu and Yunfeng Lu; University of California, Los Angeles, Los Angeles, California, United States.

Lithium metal anode is one of the most promising candidate for next–generation rechargeable batteries. However, their implication has been hampered by the unstable electrochemical behaviors, such as the formation of dendritic structures and continuous chemical reactions with liquid electrolyte. Herein, we report the fabrication of hermetic coatings of hybrid silicate on lithium metal surface under ambient conditions. Such coatings consist of a “hard” inorganic moiety that helps to suppress lithium dendrites and a “soft” organic moiety that enhances the toughness. Furthermore, functional groups, which can immobilize anions, can also be attached to the coating layers to facilitate the transportation of lithium cations. Lithium–metal batteries made with such coated anodes show significantly improved lifetime and cycling stability. This work provides a simple and effective approach to stabilize lithium metal anodes for high performance lithium metal batteries.

**ET06.12.05**

**Effect of Polymer Binder on the Nature, Formation and Location of Solid Electrolyte Interphase Layer in Silicon Based Lithium-Ion Batteries** Richard Johnson1, Gordon Waller2 and Siva P. Nadimpalli2; 1New Jersey Institute of Technology, Montvale, New Jersey, United States; 2NSWC Carderock Division, Bethesda, Maryland, United States.

Polymeric binders are a critical component of all composite electrodes used in today's lithium ion batteries (LIB). Binders also play an important role in ensuring the cycling stability of Li alloy forming anode materials such as Si which are known to degrade due to expansion and contraction during cycling. Meanwhile, the formation of solid electrolyte interphase (SEI) can also exacerbate capacity loss in novel anode materials, however the contribution of the binder to SEI formation and stability of alloying anodes has not been emphasized. It has been suggested that elastomeric binders such as polyvinylidene fluoride (PVDF) could be utilized in order to mitigate the high stress that occurs between particles during cycling. However, experimental studies have shown that the use of carboxymethyl cellulose (CMC) improved both coulombic efficiency as well as cyclic life when compared to elastomeric binders. This result was counterintuitive because CMC is a stiffer material than PVDF and from these results it has been speculated that CMC may alter the Si particle surfaces in order to form an SEI that improves the cyclic life[1]. This phenomenon has not been fully investigated. The objective of this study is to understand the effect different polymer binders on the nature, formation, and location of the SEI layer of silicon based anodes. In this study Si wafers coated with thin films of CMC and PVDF binders were utilized as the active material. Half cells containing either bare crystal Si or a crystal wafer with a thin film of CMC or PVDF were cycled in a standard lithium-ion electrolyte (1 molar LiPF6 in 1:1:1 vol. ratio of EC:DC:DMC) to form a stable SEI. After cycling, the cells were opened in an inert atmosphere and x-ray photoelectron spectroscopy (XPS) was carried out to analyze and compare the surface chemistries. In addition, the morphology of the substrates and binder films were characterized by SEM. Preliminary results indicate that binder layers on the order of hundreds of nm thick do not impede the lithiation and delithiation of Si, but do play a role in the observed coulombic efficiency and SEI composition. These results can help inform the optimization of Si containing anodes in commercial LIB, which are expected to enter the market in the near future.


**ET06.12.06**

**Stabilizing Lithium on the Surface of Laser Written F-Doped Carbon Nano-Union Film Towards Stable Li Metal Batteries—A Case of Dendrite Suppression by Li Loading Inside Nanopores** Dhanya Pathmasuriy, Malik A. Wahid, Aniruddha Basu, Rohit Babar, Mukul Kabir and Satishchandra Ogale; Indian Institute of Science Education and Research, Pune, India.

The low energy densities associated with Li-ion batteries compared to Li-metal batteries has necessitated a revisit to the latter. Li metal barriers have remained the attraction since their discovery and early commercialization attempts, mainly because of highest gravimetric capacity (3860 mAh g−1) of metallic Li, which translates to higher energy density. While as the state of art Li-ion battery delivers the energy density in the range of 200-250 Wh kg−1, the Li-metal cell (with transition metal oxides as cathodes) can deliver an energy density of 400-450 Wh kg−1. Moreover, the Li metal anodes form the heart of promising high energy systems like Li-air and Li-S which can go up to 650 Wh kg−1 to 950 Wh kg−1 on energy density scale. However, working with metal anodes is a difficult ploy owing to rampant underlying chemistries. The processes like Li dendrite growth, uneven deposition, non-facile Li/electrolyte charge transfer and huge volume changes upon metal reduction (charging), has hampered the progress of this technology towards targeted commercialization.
Herein we demonstrate direct laser writing of interconnected porous network of fluorine-doped carbon nano-onion film (F-CNOF) on copper current collector to stabilize Li metal anode by preventing dendrite formation. The unique morphology of interconnected carbon nano-onions leads to high lithium intake and long-term cyclic stability due to the availability of uniform lithiophilic sites that control the lithium nucleation. The F-CNOF electrode shows a high Li plating capacity of 10 mAh cm$^{-2}$ at low overpotential -25 mV. An impressive Coulombic efficiency -100% was achieved for long 1500 hours corresponding to more than 300 cycles capacity. The first principles DFT calculations show that the high curvature of the nano-dimensional carbon onions (~ 20 nm) achieved herein can significantly enhance the binding energy of Li to the carbon surface, which helps to improve lithiophilicity and long-term stability. A full cell fabricated using Li$_{1.6}$Si$_{1.74}$P$_{1.44}$S$_{11.7}$Cl$_{0.3}$ as the positive electrode showed cyclic stability of 700 cycles. This impressive performance exhibited by F-CNOF electrodes indicate laser scribing as an efficient tool for direct writing of porous network of carbon nanostructures that can be used as an efficient and stable scaffold to stabilize Li metal anode.

ET06.12.07
Unconventional Mechanisms in Niobium Tungsten Oxides for High-Rate Lithium-Ion Charge Storage
Kent J. Griffith$^{1,2}$, Kamila Wiaderek$^4$, Giannantonio Cibin$^2$, Laurent Marrella$^2$ and Clare Grey$^1$; 1University of Cambridge, Cambridge, United Kingdom; 2Northwestern University, Evanston, Illinois, United States; 3Diamond Light Source, Didcot, United Kingdom; 4Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States.

The maximum power output and minimum charging time of a lithium-ion battery – key parameters for its use in, for example, transportation applications – depend on mixed ionic-electronic diffusion. While the discharge/charge rate and capacity can be tuned by varying the composite electrode structure, ionic transport within the active particles represents a fundamental limitation. Thus, to achieve high rates, particles are frequently reduced to nanosize dimensions despite this being disadvantageous in terms of volumetric packing density as well as cost, stability, and sustainability considerations. As an alternative to nanoscaling, we show that complex niobium tungsten oxides with topologically frustrated polyhedral arrangements and dense µm-scale particle morphologies can rapidly and reversibly intercalate large quantities of lithium. Multielectron redox, buffered volume expansion, and extremely fast lithium transport approaching that of light elements lead to extremely high volumetric capacities and rate performance for both crystallographic shear structure and bronze-like niobium tungsten oxides. The active materials Nb$_6$W$_{16}$O$_{48}$ and Nb$_6$W$_{19}$O$_{51}$ offer new strategies toward designing electrodes with advantages in energy density, scalability, electrode architecture/complexity and cost as alternatives to the state-of-the-art high-rate anode material Li$_4$Ti$_5$O$_12$. The direct measurement of solid-state lithium diffusion coefficients ($D_L$) with pulsed field gradient NMR demonstrates room temperature $D_L$ values of $10^{-10}$ to $10^{-13}$ m$^2$s$^{-1}$ in the niobium tungsten oxides, which is several orders-of-magnitude faster than typical electrode materials and corresponds to a characteristic diffusion length of ~10 µm for a 1 minute discharge. Materials and mechanisms that enable lithiation of µm particles in minutes have implications for high power applications, fast charging devices, all-solid-state batteries, and general approaches to electrode design and material discovery.

ET06.12.08
Enhanced Transport Properties of CuO-Doped Li$_{1.8}$Si$_{1.7}$P$_{1.6}$S$_{1.5}$Cl$_{0.5}$ Solid Electrolyte
Alexis G. Lavin; Universidad de Puerto Rico, San Juan, Puerto Rico, United States.

Better solid electrolytes need to be developed in order to achieve the long envisioned all-solid-state lithium batteries. This new generation of batteries is expected to improve the safety of Li-ion batteries while achieving both high power and high energy density. Among solid electrolytes, Li$_{1.8}$Si$_{1.7}$P$_{1.6}$S$_{1.5}$Cl$_{0.5}$ is particularly promising. In order to enhance its transport properties, we have doped the solid electrolyte with CuO nanoparticles. XRD crystallography studies provided evidence of the structural changes undergone by the material. The doped and undoped solid electrolytes were tested in coin cell batteries with Li and Graphite electrodes. Cyclic voltammograms and charge-discharge data were obtained. The results indicate that CuO doping caused an improvement in the transport properties of the solid electrolyte. More cycling is underway in order to study the stability of the solid electrolyte and the structural changes undergone during cycling.

ET06.12.09
Li$_2$RuO$_4$—Understanding the Role of Li/M Ordering in Triggering the Oxygen Redox
Haifeng Li$^1$, Liang Li$^1$, John w. Freeland$^2$, Andrey Yakovenko$^2$, Maria K. Chan$^2$ and Jordi Cabana$^2$; 1UIUC, Chicago, Illinois, United States; 2‘Argonne National Laboratory, Chicago, Illinois, United States.

Besides transition-metal redox, anionic solid-state redox has become a crucial constituent in boosting capacities of Li-rich layered cathodes more than 300 mAh/g. Compared with a thorough study of the intercalation mechanism involving oxygen redox in canonical oxides Li$_2$MO$_3$ (M = 3d/4d/5d transition metal), Li$_2$MoO$_4$ series offer a possibility exploring the detailed intercalation chemistry of a compound with high O/M ratio and the role of Li/Ru ordering in triggering oxygen redox. Here two distinctive phases, disordered and ordered, of Li$_2$RuO$_4$ (O/M = 4) with various polymorphs in terms of temperature was synthesized to probe the intercalation chemistry and structural changes. A comprehensive study by spectroscopic methods coupled with computations of the electronic structure revealed that the 2.5-3.9 V voltage window evidences an exclusive oxygen redox for delithiation process with irreversible structural evolution followed by Ru$^{4+}$ redox while solo reversible Ru$^{3+}$-Ru$^{4+}$ redox accounts for the Li uptake-removal mechanism of 1.5-2.5 V. Furthermore, the ordered polymorph exhibits better electrochemical properties due to the regular ordering of Li/Ru within the transition-metal layer. The investigation demonstrates that the high O/M ratio and inerratic ordering of Li$_2$RuO$_4$ could promote the occurrence of the anionic redox, further guiding the design of high capacities Li-rich cathode materials.

ET06.12.10
Na Wetting Layer of Layered Reduced Graphene Oxide on a β”-alumina for Low Temperature Na-BASE Batteries
Dana Jin$^1$, Sori Son$^2$, Younki Lee$^2$, Yoon-Cheol Park$^3$, Keeyoung Jung$^3$, Wooyoung Shim$^1$ and Youngjun Cho$^1$; 1Yonsei University, Seoul, Korea (the Republic of); 2Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, United States.

As the importance of renewable energy grows, Sodium/β”-alumina(BASE) cell has been recognized as one of the most effective energy storage device because of its high specific energy, high efficiency of charge/discharge and long cycle life. For better operation of Sodium-BASE cell, poor wettability of electrolyte on liquid sodium anode should be enhanced. Oxygen is a highly reactive element and can react rapidly with Alkali metals. Using high affinity between sodium and oxygen, we fabricated ‘sodiophilic’ r-GO sheet for use as a Na-wetting layer in the anode of Na-BASE cell. Thermal reduction and expansion of interlayer gaps of GO sheets triggered by contact with liquid sodium carefully controls the density of oxygen-functional group and produce nano and microscale gaps that host liquid sodium. Liquid sodium can diffuse into the interlayer spacing of the r-GO sheets and rapidly cover the entire surface area of the sheet due to the high affinity between Na and residual oxygen-functional group of r-GO and capillary force produced by the nano and microgaps. These characteristics give rise to stable cycling with low overpotential of Na-BASE battery.

ET06.12.11
Enabling Reliable Lithium-Metal Batteries by a Bifunctional Anionic Electrolyte Additive

Li-S batteries, one of the most promising candidates of electrochemical energy storage systems due to their advantages of high energy density, low cost and good capacity and so on, have attracted high attention and intense research in last two decades. Despite tremendous efforts, the commercial use of Li-S batteries is still blocked by their poor stability caused by polysulfide shuttle effects and large volume expansion during the insertion of lithium ions. Herein, we report a facile strategy to prepare submicron sulfur particles which are coated by phytic acid shell directly via ball-milling method and further, produced by carboxylic and hydroxyl groups, respectively. Meanwhile, the P hybrid carbon can be further used to improve the reaction kinetics and enhance ionic conductivity, which can achieve a good long life span, high reversible energy density and good rate performance with a very low cost and straightforward approach for Li-S batteries.

Acknowledgements

This work was financially supported by Special Funds for the Cultivation of Guangdong College Students' Scientific and Technological Innovation (pdjhb0450).

Reference


ET06.12.13

In Situ Chemically/Electrochemically Building Superior Hybrid Solid Electrolyte Interface Layer for Li-Metal Anode

Yuming Zhao, Guoxing Li and Donghui Wang; The Pennsylvania State University, State College, Pennsylvania, United States.

The practical application of next generation high energy density storage systems has long been delayed by the unstable lithium (Li) metal anode with problems like uncontrollable Li dendrites growth, low Coulombic efficiency (CE) or short cycle life. Here, we demonstrate a multifunctional and chemically cross-linked composite film that can provide excellent protection for Li metal anode. By a chemical and electrochemical process, this film can help Li metal anode in-situ form a stable organic/inorganic hybrid SEI layer at the interface between the film and deposited Li, which is mainly composed of polymer based organosulfides, inorganic sulfides (LiPSn,n, LiS, LiS2) and Li salts (LiCl, LiF, etc.). Furthermore, this film as a robust and solid layer can provide extra mechanical protection or acting as a material inventory for this in-situ formed robust SEI layer, so that guarantee its long-term cycling stability. Half cells with this composite film show dendrites free Li deposition, high CE and excellent cycling performances at different cycling conditions (e.g. 98.5% CE for over 460 cycles at 2 mA cm-2 and 2mAh cm-2). Full cells with either sulfur (S) or LiFePO4 as cathode and composite film protected Li as anode show clearly enhanced capacity retention and superior cycle life. This study will inspire new pathway to design functional SEI layer for Li metal anode and promote the practical application of rechargeable Li metal batteries.

ET06.12.14

Theoretical Overpotentials and Nucleation Rates for Electrodeposition on Metal Negative Electrodes

Kyle Nagy, Saeed Kazemianbavi, Katsuyo Thornton and Donald Siegel; Univ of Michigan, Canton, Michigan, United States.

Rechargeable batteries employing metal negative electrodes (i.e., anodes) are attractive next-generation energy storage devices due to their potential to achieve higher theoretical energy densities compared to standard, intercalation-based anodes. An important consideration for a metal’s viability as an anode is the efficiency with which it undergoes electro-deposition and –dissolution during cycling. This study assesses the thermodynamic deposition/dissolution efficiencies and associated nucleation rates for seven metals (Al, Ca, K, Li, Mg, Na, and Zn) of relevance for battery applications. First-principles calculations were used to evaluate thermodynamic overpotentials at several deposition/stripping sites – terraces, steps, and kinks – on low-energy surfaces of these metals. Kink sites are observed to be the most energetically favorable sites for metal deposition, and thus exhibit the lowest overpotentials. These sites are expected to play a prominent role at low current densities, where moderate rates of adsorption/desorption allow access to the most thermodynamically-favored sites. In contrast, the largest overpotentials occur for plating/stripping at terrace sites. These sites are expected to dominate at high current densities, where kinetic limitations can hinder exchange at kink sites. The difference in the coordination number for a surface atom from that in the bulk was found to correlate with the plating efficiency. Consequently, due to their low bulk coordination, the body-centered alkali metals (Li, Na, and K) are predicted to be among the most thermodynamically efficient for plating/stripping. In contrast, metals with higher bulk coordination such as Al, Zn, and the alkaline earths (Ca and Mg), generally have higher thermodynamic overpotentials. The calculated formation energies for electro-deposition were used as input to a classical nucleation model to estimate the rate of steady-state nucleation. Nucleation rates on alkali metal surfaces are predicted to be several orders of magnitude higher than on the surfaces of other metals in this study for both terrace and step deposition sites. Our approach demonstrates a technique for linking atomistic data with an analytic nucleation model and highlights the sensitivity of nucleation behavior on the chemistry and structure of the metallic substrate.
Recent research has focused on developing layered oxide cathode materials such as lithium-rich 3d-transition-metal oxides for high-energy-density lithium-ion batteries. However, practical applications of these materials are challenging due to a continuous voltage decay on cycling, which is associated with internal and interfacial material degradation. Here we show that the formation of a stable surface structure on layered lithium transition-metal oxide particles can prevent the further structural and chemical evolution of the lithium-ion diffusion-surface layers. This is demonstrated by creating a few atomic layers with a cation-disordered structure on the specific facet of the layered oxide nanoparticles during the synthesis. Through the advanced atomic-scale analysis by high-resolution electron microscopy, we investigate the atomic arrangement and valence states of transition metals from the bulk to the surface region. In addition, combined analysis with in-situ X-ray characterization reveals the understanding of the origin of the bulk and surface chemistries and cationic redox mechanism upon electrochemical reaction. Our findings will provide new insights for designing and preparing future layered oxide cathode materials.

This work is supported by the National Research Foundation of Korea (NRF-2011-C1AAA001-0030538).
Polypyrrole (PPy) is a p-doped conducting polymer composed of repetitive bonds of five-membered heterocyclic rings including amine (N-H) groups, thus allowing the formation of hydrogen bonding forces between PPy chains. When PPy is made of nanomaterials, it has following advantages over bulk materials: (1) higher surface area; (2) better reactivity; (3) enhanced electrical conductivity. Among the various nanomaterials, the core-shell is very suitable as a stable electrode material because the Si core can protect the CP shell from swelling and shrinkage problems. In addition, high surface area of the Si cores enable rapid adsorption/desorption of electrolyte ions within the electrodes. On the other hand, the CP shell plays roles in reinforcing the poor electrical properties of Si cores. Thus, the synergistic effect from the PPy shell and the Si core would be advantageous for making a supercapacitor electrode that provides robustness and high electroactivity. In conventional synthesis, the SiOx templates limit the growth of polymer chains, resulting in undesirable α,α’-linkages in between the PPy chains. In addition, the low electrical properties of SiOx-PPy composites are highly related to the low efficiency of core-shell formation in the in-situ syntheses. Therefore, there is a need for optimization and development for producing SiO2-PPy core-shells with high efficiency of core-shell formation, which may result in the improved electrical and electrochemical performances.

In this presentation, we report the preparation and optimization studies of PPy-encapsulated silica nanoparticles (SiO2 NPs) using ex-situ method. The SiO2-PPy core-shell NPs prepared by the ex-situ method are well dispersed in water and facilitate the mass production of thin-film electrodes with improved electrical and electrochemical performances using a simple solution process. By using the ex-situ method, the PPy shell can be produced without the influence of SiO2 NPs, and the resultant PPy will have higher doping level and better electrical performance than the conventional ones. As-prepared SiO2-PPy core-shell NPs with different particle sizes were applied to electrode materials for two-electrode supercapacitors based on coin cell batteries. It was confirmed that the areal capacitance (73.1 mF/cm2), volumetric capacitance (243.5 F/cm3), and cycling stability (88.9 % after 5000 cycles) of the coin cell employing the ex-situ core-shell was superior to that of the conventional core-shell (4.2 mF/cm2, 18.2 mF/cm3, and 82.2%). Considering these facts, the ex-situ method enables a facile way to produce highly-conductive thin-film electrodes with enhanced electrical and electrochemical properties for the coin cell supercapacitor application.

**ET06.12.19**

**Using Compact SEI Formation to Enhance Electrochemical Properties of the SiOx Anode for Li-Ion Batteries**

Nayoung Kang and Sun-Jae Kim; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).  

The growing demand for high-performance portable electronic devices and large-scale electrical energy storage systems has promoted lots of efforts to develop up-to-date lithium-ion batteries (LIBs) with greater capacity and cycle stability. Along this requirements, silicon (Si) is the material of choice for anode materials because of its high theoretical capacity (~4200 mAh/g), which is almost 10 times higher than that of conventional graphite anodes (372 mAh/g). However, the practical application of Si has been frustrated by rapid capacity fading, due to the unavoidable large volume change during charge-discharge processes, which results in particle fracture and loss of electrical contact between active materials, consequently causes an unstable solid electrolyte interphase (SEI) growth on the Si interface. Therefore, a SiOx has aroused interests as the most promising alternatives for practical application for the lithium-ion batteries (LIBs) as a modification for Si. Compared to Si, the formation of inactive components, Li2O and/or lithium silicmates, coming with generation of Si anodes during the initial lithiation process at SiOx matrix can buffer the volume variation and maintain the structural stability. Nonetheless, some disadvantages of SiOx such as low initial coulombic efficiency (ICE) and unstable SEI layer result in unsatisfactory electrochemical performance. To overcome these problems, there were many efforts to develop coating methods to protect the anode surface as an artificial SEI layer. However, it is still limited to improve ICE and long lifetime of SiOx, because these treatments were only for electrode surface.

In this study, the formation of electrode has modified with the stable SEI by applied potentiostatic which is inspired by electrodeposition. In electrodeposition, the film made by AC has less porosity than by DC and formed uniformly. The electrochemical impedanse spectroscopy (EIS) measurements were performed to understand electrical and ionical conductivities. The surface microstructure and components of the electrode were characterized by using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and transmission electron microscope (TEM). As a result, the as-prepared electrode delivered an initial charge and discharge capacity of 2603 mAh/g and 1140 mAh/g, respectively with an initial coulombic efficiency (ICE) of 42.3 % at 0.1 A/g. In contrast, the electrode charged by potentiostatic method showed initial charge and discharge capacities of 1180 mAh/g and 1105 mAh/g, respectively with an ICE of 93.6 %. Also, the electrode charged by potentiostatic method at 1 A/g was a capacity retention of 85.1% maintained over 1000 cycles, whereas the as-prepared electrode was a capacity retention of 70.1% under the same conditions. These results have been noted that it is important to make the compact electrode structure to improve electrochemical properties such as ICE, cycling, and capacities.

**SESSION ET06.13: Li-S and Na Battery**

Session Chairs: Hailong Chen and Xiaolin Li  
Friday Morning, November 30, 2018  
Hynes, Level 3, Room Ballroom A

**8:15 AM ET06.13.01**

**Electrochemically Controlled Solid Electrolyte Interphase Layers for Superior Li-S Batteries**

Yaxing Wang, Chuan-Fu Lin, Jiancun Rao, Karen Gaskell, Gary Rubloff and Song Bok Lee; University of Maryland, College Park, Maryland, United States.

Lithium-sulfur (Li-S) batteries suffer from shuttle reactions during electrochemical cycling, which cause the loss of active material sulfur from sulfur-carbon cathode, and simultaneously incur the corrosion and degradation of the lithium metal anode by forming passivation layers on its surface. These unwanted reactions therefore lead to the fast failure of batteries. The preservation of the highly reactive lithium metal anode in sulfur containing electrolyte has been one of the main challenges for Li-S batteries. In this study, we systematically controlled and optimized the formation of smooth and uniform solid electrolyte interphase (SEI) layer through electrochemical pretreatment of the Li metal anode under controlled current densities and cycle number. A distinct improvement of battery performance in terms of specific capacity and power capability was achieved in charge-discharge cycling for Li-S cells with pretreated Li anodes compared to pristine, untreated ones. Importantly at higher power density (1 C rate, 3mA/cm²), the Li-S cells with pretreated Li anodes protected by controlled elastomer (LPE) show the suppression of the Li dendrite growth and exhibit 3-4 times higher specific capacity than the untreated ones after 100 electrochemical cycles. The formation of such controlled uniform SEI was confirmed and its surface chemistry, morphology and electrochemical properties were characterized by X-ray photoelectron spectroscopy (XPS), focused-ion beam (FIB) cross-sectioning, and scanning electron microscopy (SEM). Adequate pretreatment current density and time are critical in order to form the continuous and uniform SEI, along with good Li ion transport property.

**8:30 AM ET06.13.02**

**Effect of Nitrogen/Oxygen Dual-Doped Carbon Nanofiber on High Sulfur-Loading High Stability Lithium-Sulfur Batteries**

Ying Yang1, Tianji Guo1, Zhishao Yu1, TongHeu Le1, Hao Tian1 and Feiyu Kang2; 1Department of Electrical Engineering, Tsinghua University, Beijing, China; 2Department of Electrical Engineering, Tsinghua University, Beijing, China.
A self-standing N/O dual-doped carbon nanofiber was prepared based on polymer chain design with one-step carbonization. The interlayer can not only substantially improve the charge-discharge performance of Li-S battery, but also suppress the shuttle effect during charge-discharge process because of the strong adsorption effect between interlayer and lithium polysulfides. The first discharge specific capacity of the cell was 946.7 mAh g⁻¹ and it also contained more than 908 mAh g⁻¹ and 800 mAh g⁻¹ after 100 and 200 cycles at 0.1 C with such an interlayer. It was found that the capacity contribution from S₈ to Li₂S₈ was improved 35% with an interlayer, which is the main reason for the improvement of the cell higher capacity. We believe that the cell configuration presented here coupled with further improvements in the sulfur electrode itself could help to alleviate some of the persistent problems of Li-S cells.

8:45 AM ET06.13.03 Poly sulfides Immobilization by Metal Carbide Filled Nitrogen Doped Carbon Nanotubes for High-Performance Lithium-Sulfur Batteries Garapati M. Seshadri and Ramaprabhu Sundara; Indian Institute of Technology Madras, Chennai, India.

Lithium-sulfur (Li-S) batteries gain more attention as a secondary battery because of low cost, abundant and non-toxic sulfur as an active cathode material. As the sulfur possess high specific capacity (1672 mAh g⁻¹) and energy density (2600 Wh kg⁻¹) which enables to reach the high scale energy demands like hybrid electric vehicles and power grid applications. The lower cyclic stability, the poor electrical conductivity of sulfur, and dissolution of intermediate lithium polysulfide into the electrolyte and its migration towards the anode (shuttle effect) are the major challenge for the commercialization of Li-S batteries. To address these challenges, many porous carbon materials and polar metal oxides and sulfides have been studied as a lithium polysulfide trapping materials. In this work, we focus on the polar and conductive metal carbides for polysulfide confinement. For this, we have synthesized Fe₃C filled nitrogen doped carbon nanotube (Fe₃C@NCNT) and NCNT by an easy single step process. Sulfur infiltrated NCNT (NCNT/S) have been synthesized by melt diffusion technique. The high surface area and large pore volume of NCNT can enhance the diffusion of Li⁺ ions and electrolyte during the charge-discharge process. Fe₃C@NCNT has used an interlayer where polar Fe₃C can adsorb lithium polysulfides through polar-polar interactions and therefore immobilized lithium polysulfides by minimizing the shuttle effect. NCNT/S-Fe₃C@NCNT cathode shows the enhanced specific capacity at different C-rates (1C 1672 mAh g⁻¹) and long cyclic stability than the cathode without Fe₃C@NCNT. This signifies the Fe₃C@NCNT can minimize the active material loss in the cathode and enhance the sulfur redox kinetics.

9:00 AM BREAK

9:30 AM ET06.13.04 Superior Performance of Lithium-Sulfur Battery Enabled by a Dimethyl TrisulfideContaining Electrolyte Daiwei Wang; The Pennsylvania State University, State College, Pennsylvania, United States.

The lithium-sulfur (Li-S) battery offers a high theoretical energy density of ~2600 Wh/kg and low cost, positioning it as a promising candidate for next-generation battery technology. However, problems including disastrous Li polysulfides dissolution and irreversible Li₂S deposition have severely retarded the development of Li-S batteries. To solve these issues, we have reported a functional dimethyl disulfide (DMDS)-containing electrolyte that promoted an alternate electrochemical reaction pathway for sulfur cathodes by a formation of dimethyl polysulfides and Li organosulfides as intermediates and reduction products, leading to significantly boosted Li-S cell capacity with improved cycling reversibility and stability. Recently, we further investigated using dimethyl trisulfide (DMTS), a primary discharge-charge intermediate in the DMDS-containing electrolyte, which is also a commercially available reagent, as a co-solvent in functional electrolytes for Li-S batteries. We found that, DMTS, with higher theoretical capacity (851 mAh g⁻¹) than DMDS (570 mAh g⁻¹), functions similarly to DMDS to promote an alternate electrochemical reaction pathway for sulfur cathodes and to enable good cycling performance for cathodes with high sulfur content by way of an automatic discharge shutoff mechanism. In addition, owing to the better reactivity of DMTS with Li₂S to form lithium polysulfides, the irreversible capacity loss caused by insoluble Li₂S deposition and separation of active material from conductive networks could be efficiently mitigated. Thanks to all these advantages, a 25 vol% DMTS-containing electrolyte enables Li-S batteries with even higher cell capacity and improved cycling performance than using previous optimal 50 vol% DMDS-containing electrolyte. And capacity fading rate as low as 0.11% per cycle was achieved for cathodes with high sulfur content of 70 wt% in carbon/sulfur composite using an optimal 25 vol% DMTS-containing electrolyte.

9:45 AM ET06.13.05 Dense Monolithic Hybrid of MOF and Carbon Nanotube Sponge for High-Volumetric-Energy-Density Lithium-Sulfur Batteries Hai Zhang; Peking University, Beijing, China.

Compact energy storage is of great significance especially in portable electronics and electric vehicles. Lithium-sulfur battery represents an advanced energy storage system because of its environmental benignity, high theoretical energy density (2600 Wh kg⁻¹) and natural abundance of sulfur. However, the cathodes of lithium-sulfur battery usually contain low-density porous carbon hosts for sulfur to alleviate polysulfides dissolution and improve the conductivity, which will lead to the low volumetric energy density (~500 Wh L⁻¹). Although enormous efforts have been devoted to improve the specific capacity and cycling stability of lithium-sulfur batteries, little attention has been payed to the aspect of high volumetric capacity simultaneously, which plays a key role in practical use.

Here, we for the first time fabricated the monolithic hybrid of metal-organic framework (MOF) and carbon nanotube (CNT) sponge, which was embedded within the MOF monolith to achieve the high-volumetric-energy-density lithium-sulfur batteries. Specifically, we first synthesized the ZIF-8 methanol suspension (~50 mg mL⁻¹), and dropped the suspension into the CNT sponge afterwards. The CNT sponge filled with ZIF-8 suspension was finally dried at the room temperature. Previously, MOFs or hybrids of MOFs and CNTs were always dried at the condition of vacuum and high temperature, which results in the rapid evaporation of the solvent, leaving a loose structure with a lot of void space among MOF particles. Room temperature drying in our study can make the solvent evaporate slowly and provide enough time for MOF particles aggregating into a dense monolith. Although the hybrid is highly dense, the large amount of micropores from ZIF-8 can still guarantee the high and safe sulfur loading. Besides, the embedded CNT networks act as conductive agent and supportive scaffold to improve the sulfur utilization and mechanical properties, respectively. Furthermore, superior rate performance can be achieved through optimizing the density of the monolith, which was controlled by the time period of room temperature drying. As a result, our novel free-standing electrodes exhibit a much superior volumetric energy density (~1553 Wh L⁻¹) than previously reported MOF-based electrodes in recent literature without compromising the specific capacity, rate performance and cycling stability.

10:00 AM ET06.13.06 Full Dissolution of Li₂S₈ to Li₂S in Safe Eutectic Solvent for Rechargeable Lithium-Sulfur Batteries Qian Cheng, Weiheang Xu and Yuan Yang; Columbia University, New York, New York, United States.
In this talk, we report a new safe eutectic solvent composing of amides as an electrolyte for lithium-sulfur batteries. Such eutectic solvents are safe, highly stable, and low-cost. It shows strong resistance against fire, which even cannot be ignited. In contrast, conventional ether-based electrolyte catches fire immediately after ignition. Moreover, it can dissolve the whole sulfide family, including Li$_{2}$S/Li$_{2}$S which are not dissolved in the conventional ether-based electrolyte. This unique property help address the dead sulfur issue caused by insoluble Li$_{2}$S/Li$_{2}$S in Li-S batteries, which is a major reason for low cycling lifetime of Li-S batteries. By using the eutectic solvent which can dissolve all sulfides species, a high specific capacity of 1360 mAhg$^{-1}$ and a capacitance retention of 88% over 40 cycles were achieved at 0.1 C without any electrode modification. With the further addition of TiO$_{2}$ nanoparticles on carbon electrode, stable capacity retention of 81% over 100 cycles is achieved, which prove the effectiveness of the strategy. More importantly, its cost is only ~$2-3/kg, even lower than traditional ether-based electrolyte, not to mention those expensive ionic liquids or solid electrolytes. Thus it will have great practical application in lithium-sulfur batteries. The development of eutectic solvent as electrolyte will improve lithium-sulfur batteries from aspects of safety, performance, and costs.

10:15 AM ET06.13.07
X-Ray Scattering Studies of Polysulfide Interactions in Li-S Battery Electrolytes
Elizabeth C. Miller, Noel Hayes, and Michael F. Toney; SLAC National Accelerator Laboratory, Menlo Park, California, United States; Department of Information Technology and Electrical Engineering, ETH Zürich, Zurich, Switzerland.

Lithium-sulfur (Li-S) batteries are a next generation Li battery technology that provides large theoretical capacity (1672 mAh g$^{-1}$) while also being earth-abundant and low cost$^{1}$. Li-S delivers its high capacity via a chemical transformation mechanism rather than Li intercalation as in Li-ion. Elemental sulfur (S$_{8}$) is reduced to a final solid discharge product lithium sulfide (Li$_{2}$S) through a series of soluble lithium polysulfides (Li$_{2}$S$_{2}$, 2 ≤ x ≤ 8); upon charging, this reaction is reversed. Many of these reactions occur in the electrolyte solution phase, but the interactions of the polysulfides, lithium salts, and solvent molecules are not well-established, making effective electrolyte development challenging.

In this study, we investigated the behavior of lithium polysulfides (Li$_{2}$S, Li$_{2}$S$_{x}$, x = 4, 6, 8) and lithium salt (LiTFSI). Li bis(trifluoromethane)sulfonimide in solutions using small angle X-ray scattering (SAXS). SAXS probes the nanoscale structure of the electrolyte and determines the size and shape of scatterers in solution due to their differences in electron density. Isolated LiPS have a chain-like configuration but may form dimers, aggregates, or other structures in solution$^{2}$. A concentration range (200-1000 mM) of polysulfides in two solvents, 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME; 1:1 by volume), which freely solvates LiPS, and acetonitrile (ACN), which sparingly solvates LiPS$^{3}$ were examined.

Some aggregation of LiPS was observed at high concentrations (1000 mM based on the mass of sulfur) in both solvents, although shorter chain polysulfides exhibited larger populations of smaller scatterers. Polysulfide solutions of lower sulfur concentration showed multiple aggregate populations below about 10 nm in size. A greater population of larger scatterers on the order of 10 nm were observed in higher concentrations in DOL/DME. Most of the features in the SAXS pattern for ACN-based polysulfide solutions were below 10 nm, indicating isolated LiPS structures, and these features remained at roughly the same location, even at higher concentrations. Agglomeration of polysulfides was both solvent and chain length dependent; however, at higher concentrations, the chain length differences present in the SAXS disappear. Addition of 1 M LiTFSI to DOL/DME, which is the conventional electrolyte used in Li-S batteries, resulted in an additional weak peak at 0.7 Å$^{-1}$, representing a change in the small scatterers on the order of 1 nm, indicating that salt ions interfere with LiPS clustering. These results add molecular level insight into Li-S electrolytes, aiding in understanding electrolyte-salt interactions.

References

10:30 AM ET06.13.08
Understanding the High Performances of Li-Doped P2 Layered Oxide Cathode Materials for Sodium-Ion Batteries
Lufeng Yang, Xiang Li, Xuetian Ma, Shan Xiong, Yan-Yan Hu, and Haolong Chen; Chemistry, Florida State University, Tallahassee, Florida, United States; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Layered oxide cathode materials with P2 structure and general formula A$_{M}$MO$_{2}$ (0.4 < x < 0.8, M = transition metals) demonstrated high reversible capacities in sodium ion batteries$^{1,2}$. However, commonly the capacity retention of the P2 compounds are not ideal when deeply cycled, majorly due to the mechanical damage caused by the irreversible phase transitions during the sodium intercalation/deintercalation processes. Previously we developed a novel strategy to dope lithium into the transition metal sites in the P2 structure with precisely controlled synthesis. The lithium in the transition metal layer helps to stabilize the P2 structure and eliminate the P2-O2 transition in the model compound Na$_{x}$Li$_{1-y}$Mn$_{1}$O$_{2}$. Currently we designed another compound P2-Na$_{x}$Li$_{1-y}$Fe$_{x}$O$_{2}$ in order to improve the capacity retention and the high voltage stability. This compound was successfully synthesized and electrochemically tested. The reversible capacity was as high as 190 mAh/g and the capacity retention after 80 cycles was 87%. In-depth structure characterizations with using in situ and ex situ synchrotron X-ray diffraction, neutron diffraction and solid state NMR were performed. The results showed that the P2-O2 transitional was also eliminated in this compound. Meanwhile, more Li was kept in the transition metal layer after long term cycling, compared with that of Na$_{x}$Li$_{1-y}$Mn$_{1}$O$_{2}$ implying the doping of Fe at the transition metal layer effectively helps to lock lithium in the lattice. This result provides new insights of the cycling mechanism of P2 structured cathodes, as well as new opportunities in designing next generation cathode materials for sodium ion batteries with ultrahigh reversible capacity and excellent capacity retention.


11:00 AM ET06.13.09
Lithium-Pretreated Hard Carbon as High-Performance Sodium-Ion Battery Anodes
Biwei Xiao, Mark H. Engelhard, David M. Reed, Vincent L. Sprengle and Xiaolin Li; Pacific Northwest National Laboratory, Richland, Washington, United States.

Hard carbon (HC) is the state-of-the-art anode material for sodium-ion batteries (SIBs). However, its performance has been plagued by the limited initial Coulombic efficiency (ICE) and mediocre rate performance. Here, we combined experimental and theoretical studies to demonstrate the application of lithium-pretreated HC (LPHC) as high-performance anode materials for SIBs by manipulating the solid electrolyte interphase (SEI) in tetraglyme...
(TEGDME)-based electrolyte. The LPHC in TEGDME can 1) deliver >92% ICE and ~220 mAh g⁻¹ specific capacity, twice of the capacity (~100 mAh g⁻¹) in carbonate electrolyte; 2) achieve >85% capacity retention over 1000 cycles at 1000 mA g⁻¹ current density (4C rate, 1C=250 mA g⁻¹) with a specific capacity of ~150 mAh g⁻¹, ~1.5 times of the capacity (10 mAh g⁻¹) in carbonate. The full cell of Na₃V₂(PO₄)₃-LPHC in TEGDME demonstrated close to theoretical specific capacity of ~98 mAh g⁻¹ based on Na₃V₂(PO₄)₃ cathode, ~2.5 times of the value (~40 mAh g⁻¹) with non-treated HC. This work provides new perception on the anode development for SIBs.

11:15 AM ET06.13.10
Design of Nanostructured Materials for Na and Li-Ion Energy Storage Applications Junhua Song¹, Xiaolin Li², Min-Kyu Song¹ and Yuehe Lin¹; ¹Washington State Univ, Pullman, Washington, United States; ²Pacific Northwest National Laboratory, Richland, Washington, United States.

Nanostructured materials are important for boosting the performance of energy storage devices. Here, we report our recent efforts on designing nanocomposites for rechargeable Na- and Li-ion batteries and Li-S batteries. For Na-ion battery anodes, we constructed ultra-fine SnO₂ nanocrystals anchored on a unique reduced graphene oxide (rGO) porous matrix and showed excellent rate capability and long cycle life. The improved capacity and superior rate capabilities were rooted in the enhanced transport kinetics of both electrons and ions within the electrode structure because of the well-interconnected, macro-porous rGO matrix. Besides 2D graphene supported materials, we also explored yolk-shell antimony nanoparticles as high-performance Na-ion battery anodes. The unique low-dimensional nanostructure rendered stable cycling and high rate capability, despite ~300% volume change at full sodiation/desodiation. For Li-ion battery anodes, we designed a sandwich-structured N-doped graphene anchored with nearly monodisperse Fe₃O₄ nanoparticles. The unique sandwich structure enabled good electron conductivity, Li⁺ accessibility and accommodated a large volume change upon cycling. Hence, it delivered good cycling reversibility and rate performance. Carbon nanotube aerogels (CNA) with controlled nitrogen and phosphorus dopants also are introduced as a promising cathode host for rechargeable Li-S batteries. The combined theoretical study and electrochemical evaluation revealed the role of heteroatom dopants in enhancing chemical interaction of CNA towards various polysulfide intermedia species.

1:45 PM ET06.14.01
Redox-Active Heterocyclic Azine Compounds for High Voltage and High Energy Organic Cathode Materials Eun Kwon, Kyu Nam Lee and Soo Young Park; Seoul National University, Seoul, Korea (the Republic of).

Recently, the rapidly increasing demands for electric vehicles (EVs) and smart-grid systems further require high-performance batteries with sustainability and high safety. In this regard, organic electrode materials which consists of only earth abundant elements have been considered to be a very promising alternatives to the conventional inorganic ones because of their great potential in high energy and power density, low cost, and environmental friendliness. Although a lot of organic cathode materials showing high cyclability and rate capabilities have already been developed, most of them have redox potentials below 3.0 V vs Li/Li⁺, which is considerably inferior to the commercial metal oxide cathodes. This is due to that their redox mechanisms are mostly relied on the reduction reactions; however, stabilizing the LUMO energy level of the organic molecules, which is responsible to the reduction, below 5.0 eV is difficult to achieve.

Here, we report a series of novel p-type organic electrode materials bearing redox-active heterocyclic azine compounds such as phenoxazine and phenothiazine, which exhibit high discharge voltage above 3.5 V vs. Li/Li⁺. They delivered large specific capacity more than 120 mAh kg⁻¹ with high specific energy as high as 450 Wh/kg at even high rate in Li-ion coin cell. We found out that 3-dimensional molecular design but maintaining π-conjugation could facilitate the redox reactions and capacity utilization with increased redox potential.

2:00 PM ET06.14.02
Tailoring Molten Sodium-Halide Battery Chemistry for Safe, Low Temperature, Rechargeable Batteries Erik D. Snoeke, Leo J. Small, Stephen J. Percival, Joshua Lamb, Amanda Peretti and Babu Chalamala; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Identifying safe, low-cost, effective solutions to evolving electrical energy storage challenges remains a national priority, essential to meeting rapidly growing global energy demands. Here, we describe a promising approach to using low-intermediate temperature molten sodium batteries as a candidate technology offering high performance with long cycle life and inherent, engineered improvements in battery safety. Here, we describe molten salt-based batteries that integrate molten sodium anodes, solid state ceramic electrolytes, and sodium iodide-based molten salt catholytes to create high performance battery constructs that operate below 150°C. The inherent nature of the material chemistries in these all-inorganic systems further eliminates common hazards associated with runaway exothermic reactions, polymer separators, and organic electrolytes that plague other battery systems. Here, we specifically highlight recent advances in materials chemistry of developing NaI batteries. By refining the composition and chemistry of the molten salt catholyte, we influence catholyte performance while optimizing electrochemical interactions at both the separator and current collector interfaces. These refinements to catholyte chemistry stand to improve battery performance, reduce effective operating temperatures, and makes the batteries fundamentally safer as well. Accelerated rate calorimetry reveals neither runaway exothermic reactions, nor hazardous pressurized gas generation that make other battery systems inherently more hazardous in nature. Continued improvement in battery performance through optimization of the materials chemistry in these molten-salt sodium batteries promises exciting new solutions to impact a growing national need for safe, robust rechargeable electrical energy storage.


2:15 PM ET06.14.04
Cellulose Hydrogel as a Flexible Gel Electrolyte Layer for Al-Based Batteries Aswani Poosapati¹, Eunhwa Jang¹, Nathaniel Jang², Liangbing Hu² and Deepa Madan¹; ¹University of Maryland Baltimore County, Baltimore, Maryland, United States; ²University of Maryland College Park, College Park, Maryland, United States.

For electrochemical device applications such as high energy density rechargeable batteries, fuel cells, supercapacitors, electrochromic displays, etc., polymer based electrolytes are favorable materials. Previous research on most electrolytes, were made compatible for diffusion of Li ions only, due to its
wide usage. Though Li-ion batteries are most abundantly used today, they have drawbacks such as being inherently toxic to the atmosphere, limited availability compared to other metals and its high costs. Here, we focus on preparing an electrolyte compatible to diffuse Al ions. Al is chosen due to its abundant availability, potentially dendrite free deposition and high capacity. In addition to gel electrolyte preparation, we also try to improve the room temperature ionic conductivity ($\sigma$) of the synthesized electrolyte layer.

We use a nanofiber cellulose (NFC) hydrogel as the base constituent for preparing the electrolyte. NFC hydrogel is favored due to its inherent ability to be strong, excellent flexibility, and lightweight. Initially, $\sigma$ of pristine hydrogel was measured to be $10^{-6} - 10^{-7}$ S/cm. In an effort to improve $\sigma$ of the pristine hydrogel, varying amounts of KOH were added to hydrogel as an additive and casted to form films, but during preparation we had difficulties with coagulation of fibers. Also, the resulting films were flaky, brittle and not stable enough to be characterized. In order to make hydrogel more flexible and stable various additives such as Gelatin, Polyvinyl alcohol (PVA), Polyacrylic acid (PAA) were added in different ratios individually and tested. Various weight ratios of Gelatin (1, 0.75, 0.5, 0.25): Hydrogel (1): PAA (0.25): KOH (0.1, 0.2, 0.3, 0.4) were added respectively individually into vials and sonicated for 90 minutes to obtain a homogeneous mixture. The mixture was then drop casted into silicon molds and dried in a vacuum oven for about 30 hours. The obtained gel electrolytes turned out to be much more stable and flexible as compared to hydrogel with KOH. These samples were then tested against Stainless steel (SS) and Aluminum (Al) block electrodes. The best average $\sigma$ recorded was 1.086 mS/cm for 1:1:0.25 sample against Al electrodes, which are at least 3 magnitudes higher than the pristine hydrogel. The results obtained were also compared against $\sigma$ values of samples made with PVA as an additive. PVA (1, 0.75, 0.5, 0.25): Hydrogel (1): KOH (0.1, 0.2, 0.3, 0.4) ratio gel samples were made similar to gelatin samples and characterized. An average highest ionic conductivity of 0.564 mS/cm was obtained for 1:1:0.4 sample against SS electrodes and 0.115 mS/cm for 1:1:0.3 sample against Al electrodes respectively. When comparing the results, Gelatin along with PAA and KOH turned out to be better with hydrogel rather than PVA and KOH. These results are comparable to that of Li ion batteries and are twice for gel polymer electrolytes for Al-based batteries.

2:30 PM BREAK

3:00 PM ET06.14.05
A New Method for Determining the Concentration of Electrolyte Components in Lithium-Ion Cells Using Fourier Transform Infrared Spectroscopy and Machine Learning
Leah Ellis, Samuel Buteau, Samuel Hames, Lauren Thompson, David Hall and Jeff Dahn; Dalhousie University, Halifax, Nova Scotia, Canada.

A new method is introduced for determining unknown concentrations of major components in typical lithium-ion battery electrolytes. The method is quick, cheap, and accurate. Machine learning techniques are used to match features of the Fourier transform infrared (FTIR) spectrum of an unknown electrolyte to the same features of a database of FTIR spectra with known compositions. With this method, LiPF6 concentrations can be determined with similar accuracy and precision as an inductively coupled plasma optical emission spectrometry (ICP-OES) method. The ratios of organic carbonate solvent species can be determined with more rapidity than gas chromatography (GC). This FTIR method is faster and less expensive than GC and ICP-OES, and has the added benefit of being able to determine LiPF6 concentration and solvent fractions simultaneously. It will be shown how the application of this tool facilitates electrolyte analysis of aged lithium-ion cells, and helps elucidate mechanisms for cell degradation.

3:15 PM DISCUSSION TIME

3:30 PM ET06.14.07
Crumpled MXene Nanosheets Obtained via Acid or Base Induced Deflocculation as High Capacity Anodes in Na-Ion Batteries
Varun Natu1, Di Zhao1, Mallory Clites1, Guobing Ying1, Sankalp Kota1, Ekaterina Pomerantseva1, Michel Barsoum1 and Minhua Cao2; 1Drexel University, Philadelphia, Pennsylvania, United States; 2School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, China.

MXene are a recently discovered family of two-dimensional, 2D, transition metal carbides, nitrides and carbonitrides that have shown a lot of promise in the field of energy storage with applications ranging from high capacity anodes for lithium, sodium, potassium, and aluminum ion batteries, supercapacitors and catalyst for hydrogen evolution among several others. Typically, to form MXene films, neutral, aqueous colloidal suspensions are vacuum filtered. Even though this method produces free-standing films, the process is slow and the MXene films obtained are densely packed which hampers ionic mobility resulting in low capacities when tested as anodes in Na-ion batteries.

Herein, we show that by simply decreasing or increasing the pH of a Ti3C2Tx (where T are the terminations on the MXene sheet) colloidal suspension, the 2D nanosheets crash out into crumpled flakes, resulting in randomly oriented mesoporous powders. Electrodes made with the crumpled powders deflocculated using an acid or alkali hydroxides have Na ion capacities of $\approx 180$ mAh g$^{-1}$ and $\approx 230$ mAh g$^{-1}$ at 100 mA g$^{-1}$ respectively. As importantly, we also found that when deflocculated with alkali hydroxides, the intercalation of the alkali cations that occurs resulted in smaller first cycle capacity losses and suggest a method to potentially solve this pesky problem.

3:45 PM ET06.14.08
High-performance NaV3(PO4)3/C Composites as a Safe and Stable Anode Material for Sodium-Ion Battery
Pingyuan Feng, Wei Wang, Jie Hou, Kangli Wang, Shijie Cheng and Kai Jiang; Huazhong University of Science and Technology, Wuhan, China.

A lot of phosphate-type polyanion-type compounds, such as NaV2(PO4)3, NaTi2(PO4)3 et al. have been widely researched as electrode materials for Na-ion batteries (SIBs), and they are usually endowed with enhanced structural stability through modification. However, anode materials with low operation potential lower than 2.0 V and high cyclic stability based on polyanion-type phosphate materials are hardly reported. Owning to the chemical versatility of vanadium element, vanadium-based phosphates generally have multiple redox couples at a wide potential range. Therefore, it is possible to explore a kind of vanadium-based phosphate compound with multiple electron transfer as high stable anode for SIBs. Herein, a type of NaV3(PO4)3/C as high-performance anode material is reported. The obtained NaV3(PO4)3/C composite shows high capacity (152 mAh g$^{-1}$ at 75 mAh g$^{-1}$ and 113 mAh g$^{-1}$ at 750 mAh g$^{-1}$), excellent cyclability (145 mAh g$^{-1}$ after 200 cycles at 150 mAh g$^{-1}$ and 124 mAh g$^{-1}$ after 1200 cycles at 750 mAh g$^{-1}$) and outstanding rate performance (88 mAh g$^{-1}$ at 4.5 A g$^{-1}$). According to the achieved results, it can be seen that the as-prepared NaV3(PO4)3/C is a promising anode of SIB for large-scale energy storage applications.

Acknowledgements: The authors greatly acknowledge the financial support from National Natural Science Foundation of China (No. 21405053), and the National Thousand Talents Program of China.
Lithium (Li)-ion batteries are widely used for many applications today, but there is an increasing demand to increase their specific energy (Wh kg⁻¹) and energy density (Wh L⁻¹). Among the many options, Li metal is considered one of the most promising electrode materials for future batteries. When coupled with a high capacity cathode material, such as high-nickel-content lithium nickel manganese cobalt oxide (high-Ni NMC) or sulfur (S), rechargeable Li metal batteries have the potential to achieve a specific energy much higher than 350 Wh kg⁻¹. However, achieving such goals requires fundamental breakthroughs and new knowledge to optimize and integrate all active inactive components on relevant scales with appropriate cell architectures. This talk will discuss the materials science and materials chemistry challenges, along with potential solutions, of using Li metal anodes based on the system level requirements of a high-energy cell. The important relationships between the Li anode and other cell components, such as high cathode loading and restricted amounts of electrolyte and Li, are reviewed in order to inspire new ideas to effectively address the grand challenges in rechargeable Li metal batteries.

I will start by giving an overview of active research activities in my research group located at University of Maryland Energy Research Center, including wood materials toward sustainability, 3000K high temperature materials and processing, and beyond-Li ion batteries (solid state, Na-ion). Then I will focus on our recent development on:

- Garnet-based solid-state Li-metal batteries including interface engineering to improve the wetting between Li metal anode and Garnet solid-state electrolyte (Nature Materials 2016; JACS 2016; Advanced Materials 2017; Science Advances 2017; Garnet based 3D Li ion conductive framework toward high energy density Li-S batteries (EES 2017); Garnet nanofiber based flexible, hybrid electrolyte with a high Li ion conductivity (PNAS 2016).
- Assembly and functionalization strategies of wood nanocellulose aimed at specific properties, with an eye toward high impact applications including energy, electronics, building materials and water treatment, including nanomanufacturing and light management in transparent nanopaper for optoelectronics (as a replacement of plastics); mechanical properties of densely packed nanocellulose for lightweight structural materials (replacement of steel, Nature 2018); artificial tree for high-performance water desalination and solar steam generations; mesoporous, three-dimensional carbon derived from wood for advanced batteries (replacement of metal current collectors for beyond Li-ion batteries).

The growing interest in using manganese dioxide (MnO₂) for supercapacitor (SC) electrodes is attributed to its high theoretical specific capacitance (1400F g⁻¹), relatively large voltage window, natural abundance and environmental friendliness. However, the low electronic conductivity of MnO₂ impedes its further development in commercial applications. Normally, the conductive additives such as multiwalled carbon nanotubes (MWCNT) are introduced to enhance the electronic conductivity of MnO₂ for the fabrication of SC electrodes. However, it is critical to achieve a high electrochemical performance of SC with high active mass loading at high charge-discharge scan rates. The important task is to avoid agglomeration of MnO₂ nanoparticles and MWCNT. New strategies are developed to address this problem. In this work, liquid-liquid extraction method (LLEM) is developed to prepare non-agglomerated small sized MnO₂ nanoparticles with porous surface and improved mixing of MnO₂ and MWCNT. Head-tail (HT) surfactants, containing amine, phosphonate or carboxylic groups, are used as extractors for extraction of MnO₂ nanoparticles. Moreover, it was found that conceptually new
multifunctional head-to-head (HTH) surfactants containing one phosphate end and one carboxylic end can be used as efficient extractors for LLEM. Furthermore, HTH surfactants can be used as dispersing and charging agents to prepare stable MnO2 suspension for electrophoretic deposition (EPD) of thin film. The influence of molecular structure of different extractor molecules such as hexadecylammonium (HDA), hexadecylphosphonic acid (HDPA), palmitic acid (PA) and 16-phosphonoheptadecanoic acid (16PHA) on the electrochemical performance of SC electrodes have been investigated systematically. Various interactions between nanoparticles and extractors molecules such as covalent, ion-pair or electrostatic interactions play role in preparing the non-agglomerated MnO2 nanoparticles. Compared to other HT surfactants such as HDA, HDPA and PA, the HTH surfactant 16PHA used as an extractor for preparation of SC electrodes with active mass loading of 37mg cm⁻² showed highest capacitance of 5.7 F cm⁻² (157 F g⁻¹) and 2.5 F cm⁻² (67 F g⁻¹) at a scan rate of 2 mV/s and 100mV/s, respectively. Additionally, MnO2 particles extracted by 16PHA, are negatively charged and deposited on the anode surface by EPD forming a relatively smooth, dense and agglomerate-free thin film. The conceptually new strategy using multifunctional HTH surfactants as extractor for preparation of non-agglomerated nanoparticles by LLEM paves the way for the fabrication of different functional nanomaterials for advanced applications.

9:45 AM ET07.01.04

Electrochemical Supercapacitor Based on CoO2-x-MnO2-Graphene Oxide Nanocomposite Dipali S. Patil, Sachin A. Pawar and Jae Cheol Shin; Yeungnam University, Gyeongsan-si, Korea (the Republic of).

Various metal oxide nanostructures of RuO2, MnO2, NiO, Co3O4, SnO2, MnO4, and V2O5 have been used widely as promising electrode materials for supercapacitor applications. Among these Cobalt oxide (Co3O4) is believed to be one of the best materials among transition metal oxides owing to its high theoretical capacitance (3560 F g⁻¹), environmental friendliness, and better electrochemical performance. On the other hand, MnO2 is one of the most favorable pseudo-capacitor electrode materials because of its low cost, environmentally friendly characteristics, and excellent capacitance performance. The intrinsically low conductivity of MnO2, however, limits its practical applications as a pseudo-capacitive material. Several strategies have been employed to improve the electrical conductivity of MnO2-based electrode. One simple strategy is to combine MnO2 with other metal oxides to form hybrid nanostructures with sufficient electrical conductivity. Another approach is to integrate it with electrically conducting materials like carbon materials or graphene to enhance the electrochemical stability and electric conductivity of the electrode. In the present study, we developed new CoO2-x-MnO2-graphene oxide based electrode by simple hydrothermal technique. The synthesized electrode materials are characterized by, XRD, XPS, FE-SEM, TEM, HRTEM etc. The supercapacitor performance of all the prepared electrodes was assessed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements. The important parameters of electrochemical supercapacitor like specific capacitance, energy density and electrochemical stability are measured in this work.

10:00 AM ET07.01.05

Design and Development of Sodium-Ion Batteries Based on Layered Transition Metal Oxide Cathode Material Zifeng Ma; Shanghai Electrochemical Energy Devices Research Center, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China.

Rechargeable Li-ion batteries have been considered as a promising power source for the electric vehicles and the grid energy storage systems. However, lithium resources are limited and will restrict the huge applications of Li-ion batteries. It is of great significance to develop eco-friendly sodium ion batteries which employ abundant sodium resources. Recently, we developed the large-scale synthesis route of NaNi1/3Fe1/3Mn1/3O2 (NFM) by using hydroxide co-precipitation combined with solid-state reaction, and the optimization reaction condition was studied by using in situ XRD. The metastable structure change of NaNi1/3Fe1/3Mn1/3O2 during electrochemical sodium ion intercalation which cycled at 0.1C rate between 2.0 to 4.0V, and 2.0 to 4.3V, were studied by using in operando TXM-XANES and XRD, and the thermal decomposition behavior and structure evolution of charged NaNi1/3Fe1/3Mn1/3O2 cathode material during heating process was measured by using in situ high-energy X-ray diffraction (HEXRD) technique. The effect of Ca-substitution in Na sites on the structural and electrochemical properties of NaNi1/3Ca1/3Mn1/3O2 (NFM) (x=0, 0.05, 0.1). X-ray diffraction patterns of the prepared NaNi1/3Ca1/3Mn1/3O2 samples show single α−NaFeO2 type phase with slightly increased alkali-layer distance as Ca content increased. The cycling stabilities of Ca-substituted samples are remarkably improved. The NaNi1/3Ca1/3Mn1/3O2 cathode delivers capacity of 116.3 mAh g⁻¹ with capacity retention of 92% after 200 cycles at the 1C rate. In operando XRD indicates a reversible structural evolution through an O3-P3-O3-3P-O3 sequence of the NaNi1/3Ca1/3Mn1/3O2 cathode during cycling. Compared to NaNi1/3Fe1/3Mn1/3O2, the NaNi1/3Ca1/3Mn1/3O2 cathode shows wider voltage range in pure P3 phase state during charge/discharge process and exhibits better structural recoverability after cycling. The superior cycling stability of NaNi1/3Ca1/3Mn1/3O2 makes it a promising material for practical applications in sodium ion batteries. A new portable energy storage device based on SIB has been designed and assembled. Layered oxide NaNi1/3Fe1/3Mn1/3O2 and hard carbon were used as cathode and anode, respectively. The SIB pouch cell has been designed and the electrochemistry and safety performance were tested.


11:00 AM ET07.01.06

Evaluation of Li-Ion Batteries Built with Recycled NCM 111 Cathode Jun Wang1, Paul Gionet1, Dennis Bullen1, Ronnie Wilkins1, Ian O'Connor1, Leslie Pinnell1, Derek C. Johnson1, Zhangfeng Zheng2, Mengyuan Chen2 and Yan Wang2; 1A123 Systems LLC, Waltham, Massachusetts, United States; 2Mechanical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Recycling of Li-ion batteries that have reached end-of-life (EOL) becomes increasingly critical to long term sustainability of electrochemical energy storage ecosystem, as the number of Li-ion battery powered portable devices and vehicles continues to increase rapidly. Many components incorporated in commercial Li-ion batteries face limited raw materials supply, such as Lithium, Nickel and Cobalt. Recovering those elements from spent batteries serves a dual purpose of reducing the environmental impact of hazardous materials disposal as well as providing a stable stream of the necessary metals to meet ever-growing manufacturing demand. This research focused on evaluating nickel cobalt manganese oxide (NCM 111) cathode powder regenerated from a closed loop recycling process which...
targets end-of-life electric vehicle Li-ion batteries. This process starts with spent batteries regardless of cathode chemistry, produces stoichiometric LiNi0.8Co0.18Mn0.02O2 (NMC 111) cathode material with electrochemical properties rivaling commercial control NCM 111. Prismatic pouch cells consist of recycled NCM 111 were fabricated at small and large capacity, 1.0 Ah and 11.0 Ah, respectively. Subsequent performance benchmarking against control cells was conducted through an array of metrics including rate capability, HPAC, cold crank, cycle life and calendar life. Cells built with recycled NCM 111 demonstrated similar cyclability to control at ÷2500 cycles to 80% retention under +1C, -2C cycling conditions, and no obvious difference was observed for cold crank, HPAC and calendar life between commercial control and recycled cells. The rate capability, however, seems to slightly favor recycled cell at rates above 2C. Those results undoubtedly validate the recycled NCM 111 cathode as a legitimate contender for commercial electric vehicle Li-ion battery applications.

References:

11:30 AM ET07.01.07
High-Performance Energy Storage from Biomass Materials Yunya Zhang and Xiaodong Li; Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia, United States.

Considering the irreversible environmental damages and the huge cost induced by fossil fuel consumption and Co/graphite mining, it is environmentally and socially significant to produce energy storage devices from low cost and renewable materials. In order to achieve lightweight, mechanical robustness, and various functionalities, nature often constructs hierarchically porous structures or thin films. These delicate structures, if well utilized, can largely improve the performances of energy storage devices. Thusly, a rational design strategy is to derive high-performance electrodes from biomass materials. Banana peels, as the inedible part of the most popular fruit, have a typical porous structure. After treated by NiNO3, the micron sized pores on activated banana peel (ABP) effectively enhanced the accessibility of electrolyte, nanoparticles immobilized and encapsulated polysulfides, and graphene coated Ni nanoparticles improved conductivity, leading to a high specific capacity of the assembled Li-S batteries. To increase the utilization efficiency of graphene, graphene oxide sheets were incorporated with activated paper carbon (APC) via capillary method. Thin graphene layer were coated around cellulose fibers with nano sized bulges and wrinkles, which not only increased sulfur loading, but also encapsulated polysulfides and buffer volume fluctuations, rendering an ultra-long lifespan of 1000 cycles with over 60 % capacity retention rate of Li-S batteries. In addition to optimize the performance of biomass derived electrodes, we also seek holistic utilization of biomass materials. An all-solid, flexible supercapacitor was fabricated from a whole egg. Eggshell was used as templates and egg white/yolk was employed as carbon source for 2D graphene like carbon films. Solid electrolyte was produced by egg white/yolk and KOH. Egg shell membrane was then used as separator. The assembled supercapacitors exhibited superior performances.

References:

11:45 AM ET07.01.08
Controlling Charge Transport in Spinel Oxides through Manipulation of Cation Site Occupation Anuj Bhargava and Richard Robinson; Cornell University, Ithaca, New York, United States.

Ternary spinel oxides are actively used and researched for applications ranging from electronics, sensors, catalysis, data storage, to energy storage due to their useful magnetic, catalytic, and electronic properties. One intriguing nanomaterial is the non-stoichiometric p-type spinel CoxMn3-xO4, in which cation site occupation is an important determinant of materials properties. Therefore, by manipulation of cation configurational disorder, properties such as the charge carrier density and the associated electrical conductivity can be easily controlled. The manipulation of cation configuration disorder is carried out by changing the Co to Mn ratio (or the ‘x’ value in CoMn3-xO4), which leads to the variation of (1) atomic distribution of Co and Mn atoms present at tetrahedral (Td) and octahedral (Oh) sites in the spinel system, and (2) oxidation states of the cations. In this work, we utilize a new technique to characterize the configurational disorder in spinels. We demonstrate that x-ray emission spectroscopy (XES) is a more reliable method than traditionally used K-edge x-ray absorption spectroscopy (XAS) to extract cation site occupation. Comparison between the XAS and XES techniques reveal that XES provides not only the site occupation information that XAS reports, but also additional information on the valence states of the cations at each site. We show that the XES error is lower than the EXAFS error in all cases, by up to ~20%. Additionally, the error for EXAFS is as high as 35% whereas for XES, the error determined is consistently smaller than 10%. Furthermore, we correlate the extracted site occupation data to the electrical conductivity and the supercapacitor performance and observe a strong correlation between structural properties and electronic properties of spinels. We show that the number of hole acceptor/donor pairs of Mn2+/Mn3+ at Oh sites is proportional to both the electrical properties and the energy density of the supercapacitors. Finally, via the optimization of configurational order in the CoMn3-xO4 nanoparticles system, we were able to increase the energy density and specific capacitance of the supercapacitors by 2x as compared to previously reported values.

SESSION ET07.02: Materials Processing
Session Chairs: Sergiy Kalnauas and Jianlin Li
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 312

1:30 PM ET07.02.01

The widespread adoption of electric vehicles using advanced battery technologies and the development of their manufacturing base in the United States are critically important goals for the US economy and therefore a major focus of research and development sponsored by DOE’s Office of Energy Efficiency and Renewable Energy. Materials development is often touted as the most important enabling activity, however in a rank of major cost items, manufacturing costs ranks just below the cathode components. In addition to the need to reduce costs, US R&D should also focus on new, yet-to-be-scaled processing technologies that, when developed and implemented in the US provide both a strong component of US energy security and US-based employment in a field expected to grow to over $100B in the next twenty years. Processing science and engineering has traditionally been underrepresented in federally funded electrochemical energy storage R&D. Over the last eight years, the Vehicle Technologies Office (VTO) has been building an advanced processing R&D portfolio. This includes competitively funded research at universities, small businesses, and large corporations as well as programs supported across the array of the national laboratory complex. This presentation will provide an overview of the sub-program’s history and some examples of early successes. Future research directions and scenarios for possible funding opportunities will also be discussed.
Despite the societal and economic importance of advanced batteries, the complicated relationships between electrode processing, structure, and performance are still poorly understood. In this work, we combine fundamental rheological and electrochemical studies to investigate the relationships between slurry microstructure, electrode morphology, and battery rate capability at industrially-relevant compositions of inactive material. In one example of our approach, dry-mixing LiNi0.5Mn0.3Co0.2O2 (NMC) with carbon black decreases the free carbon concentration and consequently the ability of the slurry to form a gel network, as revealed by small-angle oscillatory shear measurements. Less free carbon weakens the strength of the slurry’s viscous and elastic moduli and is also reflected in a decrease in electronic conductivity of the dried electrode. Despite a clear dependence of slurry moduli and electronic conductivity on free carbon concentration, there is no useful relationship between in-plane electronic conductivity and battery rate capability, demonstrating that short-range electronic contacts are more important than either ion transport or long-range electronic conductivity to cathode rate capability [1]. We further explain this finding by measuring the critical gelation concentration of carbon black and showing that it is independent of the NMC volume fraction, indicating that active material resides in the interstitials of the percolating carbon network [2].

Our identification of short-range electronic contacts as the key parameter for electrode performance motivates the development of new methods to observe and quantify these contacts. We use SEM-EDS to quantify the carbon black heterogeneity and show its sensitivity to a variety of manufacturing parameters, including the impact of polymer chain scission during mixing. In order to adapt this approach for carbonaceous active materials such as graphite, we substitute carbon black with commercial carbon-coated Fe nanoparticles as a contrast-enhancing agent that permits spectroscopic distinction between active material, conductive additive, and binder [3]. The Fe nanoparticles further enable nanoscale computed tomography (XCT) to obtain three-dimensional images of the active material and carbon-binder-domains with 126 nm voxel resolution. Future work will discuss the relationships between the observed microstructure and the battery performance in more detail, as well as our efforts towards alternative electrode designs with optimal carbon connectivity.


2:15 PM ET07.02.03
A Systematic Approach for Characterizing the Surface Free Energy of Composite Electrodes for Li-Ion Batteries
Ali Davoodabadi1, Jianlin Li2, David Wood3 and Congrui Jin1; 1Mechanical Engineering Department, Binghamton University, The State University of New York, Binghamton, New York, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

One of the crucial steps in battery manufacturing is the electrolyte wetting step which typically requires a relatively long time to be completed. It is known that the relationship between polar and dispersive components of the electrolyte surface tension and the electrode surface free energy (SFE) plays a vital role in the extent of wetting and, thus, tuning the SFE can accelerate the wetting step in battery manufacturing. This work developed and validated a systematic approach to characterize surface free energy of composite electrodes for lithium-ion batteries, which has never been reported in literature. We introduced two main surface parameters, \( r \) and \( f \), that represent the surface roughness ratio and surface solid fraction, respectively. These parameters are crucial in determining the so called actual SFE of the electrodes. The effect of slurry formulation and electrode porosity on the SFE of electrodes were investigated. It is demonstrated that the SFE of LiNi0.5Mn0.3Co0.2O2 cathode was higher than the graphite anode. Replacing the conventional Polyvinylidene fluoride (PVDF) with water soluble binder significantly increased the polar component of the electrodes surface free energy. The increased polar component is expected to enhance the wetting of the electrodes toward different common electrolytes. The results from this work provide insights in slurry formulation for optimal slurry wetting on current collector and electrolyte wetting on dry electrodes.

2:30 PM ET07.02.04
Enhancement of Cost Effective Pt-Based Catalyst Activity and Durability for Proton Exchange Membrane Fuel Cell Application
Ali Abdelhafiz2; Jianhuang Zeng1, Bote Zhao2 and Meilin Liu1; 1South China University of Technology, Guangzhou, China; 2Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Proton exchange membrane fuel cells (PEMFCs) have tremendous potential to be the preferred power sources for many emerging technologies, from electric vehicles to portable/mobile devices and smart grids, because of their numerous inherent advantages such as high efficiency, high energy density, low emissions, and fast start-up and shut-down capability. While PEMFCs are expected to use platinum group metal (PGM)-based catalysts in the near-term, the cost of the Pt-based catalyst alone constitutes over 40% of the fuel cell stack cost. Enormous efforts have been devoted to reducing the high cost of catalyst. To date, the catalysts can be classified into three groups according to the active component used: PGM-based catalyst (supported on carbon or other supports); PGM-based catalysts that are modified or alloyed with other metals such as Cu, Co, and Ru; and PGM-free catalysts such as non-noble metals and organometallic complexes. PGM-free catalysts are attractive for cost reduction of PEMFC technology, however, in reality it is still a long way to go to before they can be used to run actual fuel cell application. Here in, we are proposing a facile, one-step, synthesis of Pt-based alloy nanoparticles for cost effective low temperature oxygen reduction reaction electrocatalysis at industrial scale.

Direct Pt nanoparticles synthesis is performed under room temperature to form a branched triple and quadruple-pods particles with an average size of ~3.5 nm, as confirmed by X-ray diffraction (XRD) and Scanning transmission electron microscope (STEM) analysis. Rotating disc electrode (RDE) setup is used to probe ORR. Results showed that synthesized Pt-nanoparticles superior catalytic activity for oxygen reduction reaction compared to state of the art Pt-XC/72R commercial catalyst. Pt-nanoparticles periphery are conformed of high index family crystallographic planes, as observed by STEM analysis. High index planes contain lower density of kinks, which optimize the adsorption/desorption energies to be neither too weak nor too strong. Pt-nanoparticles under accelerated durability testing (ADT) outperform their state of the art commercial catalyst counterparts, surviving 81% of electrochemical active surface area (ECSA) after 10,000 testing cycles.

Using a catalyst coated membrane (CCM) technique membrane electro assembly (MEA) was prepared to test Pt nanoparticles under actual PEMFC operation conditions (i.e. temperature and humidity). MEA prepared using the synthesized Pt-nanoparticles outperformed their counterparts prepared by Pt-XC/72R state of the art commercial catalyst with 27% enhancement factor. The reported Pt-based nanoparticles propose a competitive and more efficient synthesis route to prepare large scale commercial catalyst without the need of sophisticated apparatus or special heating conditions.
Li-ion batteries are complex systems whose electrochemical performance depends on properties and design of many components that are combined to make a cell. Manufacturing of these components involves complicated processing, from slurry preparation, to casting and drying, to electrode calendaring. Each step depends on several variables, for example drying rate or calendaring pressure. Relationships between these variables and the resulting performance of the electrochemical cell has not been completely established. This talk reports on efforts towards establishing such relationships through characterization and mathematical modeling. Methods for computing elastic and inelastic properties of battery electrodes from their microstructure will be presented and the results will be correlated with degree of electrode compression during calendaring. Predictive capabilities of the models in terms of electrochemical performance will be discussed.

This research at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Program for the Office of Energy Efficiency and Renewable Energy.

Light-Directed BiVO4–C Fuel Cell with Simultaneous Production of H2O2 Xinjian Shi and Xiaolin Zheng; Stanford University, Stanford, California, United States.

Photoelectrochemical (PEC) systems have been researched for decades for their great promise to convert sunlight to fuels. Majority of the research on PEC has been focusing on using light to split water to hydrogen and oxygen, and its performance is limited due to the need of additional bias. Another research direction on PEC focuses on using light to decompose organic materials while producing electricity. In this work, we report a new type of unassisted PEC system that uses light, water and oxygen to simultaneously produce electricity and valuable hydrogen peroxide (H2O2) on both electrodes, with each consisting of BiVO4 photoanode where water is oxidized to H2O2 and carbon cathode where O2 is reduced to H2O2. In addition to producing H2O2, this PEC system also generates electricity, achieving a maximum power density of 0.194mW/cm2, an open circuit voltage of 0.61V, and a short circuit current density of 1.09mA/cm2. The electricity output can be further used as a sign for cell function when accompanied by a detector such as a LED light or a multimeter. This is the first work that shows H2O2 two-side generation with strict key factors study on such system, with clear demonstration on electricity output ability for it using low-cost earth abundant materials on both sides, which represents an exciting new direction for PEC systems.

Light-Driven BiVO4–C Fuel Cell with Simultaneous Production of H2O2 Xinjian Shi and Xiaolin Zheng; Stanford University, Stanford, California, United States.

Frequency stable, high permittivity nanocomposite capacitors produced under mild processing conditions offer an attractive replacement to MLCCs derived from conventional ceramic firing. Here, 0–3 nanocomposites were prepared using gel-collection derived barium titanate (BTO) nanocrystals, suspended in a poly(furfuryl alcohol) matrix, resulting in a stable, high effective permittivity, low loss dielectric. The nanocrystals are produced at 60 °C, emerging as fully crystalized cubic BTO, 8 nm, with a highly functional surface that enables both suspension and chemical reaction in organic solvents. The nanocrystals were suspended in furfuryl alcohol where volume fraction of nanocrystal filler (νf) could be varied. Polymerization of the matrix in situ at 70–90 °C resulted in a nanocomposite with a higher than anticipated effective permittivity (up to 50, with νf only 0.41, from 0.5–2000 kHz), exceptional stability as a function of frequency, and very favorable dissipation factors (tan δ < 0.01, νf < 0.41; tan δ < 0.05, νf < 0.5). The increased permittivity is attributed to the covalent attachment of the poly(furfuryl alcohol) matrix to the surface of the nanocrystals, homogenizing the particle−matrix interface, limiting undercoordinated surface sites and reducing void space. XPS and FTIR confirmed strong interfacial interaction between matrix and nanocrystal surface. Effective medium approximations were used to compare this with similar nanocomposite systems. It was found that the high effective permittivity could not be attributed to the combination of two components alone, rather the creation of a hybrid nanocomposite possessing its own dielectric behavior. A nondispersive medium was selected to focus on the frequency dependent permittivity of the 8 nm barium titanate nanocrystals. Experimental corroboration with known effective medium approximations is evident until a specific volume fraction (νf ≈ 0.3) where, due to a sharp increase in the effective permittivity, approximations fail to adequately describe the nanocomposite medium.

Simple Process for Preparing Core–Shell Type Hybridized Nanoparticles for Polymer Electrolyte Membrane Akiko Masubara1,3, Keiji Shito1, Yuki Takahashi1, Satoshi Sekine1, Kazuki Koseki1, Keisuke Tabata1, Tomohiro Nohara1 and Toshihiko Arita1; 1Yamagata University, Yonezawa, Japan; 2IMRAM, Tohoku University, Sendai, Japan; 3Roel, Yamagata University, Yonezawa, Japan.

We designed a novel polymer electrolyte membrane (PEM) for PEFC using inexpensive materials and fabricating precise nanostructures. Hence, we have focused on general inorganic filler filling method, which has advantage on improvement of heat resistance and gas barrier properties of the membrane. Novel model PEM consists of silica nanoparticles (NPs) with proton conductive polymer layer prepared by Reversible Addition-Fragmentation chain Transfer Polymerization with Particles (RAFT PwP) on its surface. RAFT PwP can prepare precisely adsorbed hydrophilic polymer layer on particles surface. Effective medium approximations were used to compare this with similar nanocomposite systems. It was found that the high effective permittivity could not be attributed to the combination of two components alone, rather the creation of a hybrid nanocomposite possessing its own dielectric behavior. A nondispersive medium was selected to focus on the frequency dependent permittivity of the 8 nm barium titanate nanocrystals. Experimental corroboration with known effective medium approximations is evident until a specific volume fraction (νf ≈ 0.3) where, due to a sharp increase in the effective permittivity, approximations fail to adequately describe the nanocomposite medium.
Radio frequency (RF) dielectric barrier discharge plasma was used to exfoliate graphite oxide (GO) into graphene. The GO was synthesized from a modified Hummers method. The exfoliation occurred swiftly once the RF power and gas pressure reached a level that enabled sufficient energy transfer from the plasma to the GO. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed that graphene or carbon nanosheets were successfully prepared. The plasma exfoliation mechanism was revealed based on the microstructure characterization and optical emission spectroscopy, which indicated that oxygen was released at the moment of exfoliation. Inspired by the success of GO exfoliation, N-doping was realized by treating pyrrole-modified GO with plasmas. The N concentration in the resulted graphene depended strongly on the plasma gas. Of the gases studied, CH4 treated pyrrole-modified GO (GO-PPY-CH4) contained considerable concentration of N that was beneficial to electrical double layer capacitors (EDLCs).

Supercapacitors made of the N-doped graphene exhibited promising capacitive characteristics. Electrochemical measurements showed that the GO-PPY-CH4 presented an initial specific capacitance of ~312 F g⁻¹ under 0.1 A g⁻¹ charge/discharge current and ~100% retention after 1000 consecutive cycles under currents ranging from 0.1 to 10.0 A g⁻¹ in 6 mol L⁻¹ KOH electrolyte. This study demonstrated that the plasma exfoliation was an efficient approach to fabricating graphene and N-doped graphene that had promising potential to be high-performance electrode materials for EDLCs.

Furthermore, flexible solid-state supercapacitors featuring lightweight and large capacitance have many attractive applications in portable and wearable electronics. The study demonstrates a magnetically enhanced dielectric barrier discharge that has the potential to efficiently exfoliate polyaniline-modified graphene at low input power. The plasma exfoliated N-doped graphene is subsequently used to fabricate flexible solid-state supercapacitors, which exhibit large specific capacitance of 45 mF cm⁻² at 0.2 A cm⁻² charging rate, ~100% capacitance retention after 1000 charge/discharge cycles at different current densities, and outstanding mechanical flexibility. The magnetically enhanced plasma exfoliation of graphite oxide offers a potentially cost-effective approach to producing high-quality carbon nanomaterials for energy storage.
component. We characterized our films using Scanning Electron Microscopy, X-ray Diffraction, and Raman Spectroscopy. Electrochemical characterization, i.e., cyclic voltammetry and charge-discharge cycling, were carried out in three-electrode cell configuration (where Hg/HgO, Pt, and our sample are the reference, counter and working electrodes respectively) with 1 M KOH as the electrolyte. The presence of redox peaks in cyclic voltammetry curves confirms the pseudocapacitive behavior of the sample while identical CV curves even at higher scan rates further suggest excellent rate capability and ideal supercapacitor behavior. The galvanostatic charge-discharge measurements (GCD) performed at 0.25 mA current resulted in specific capacitance as high as 12 mF/cm² for the electrode prepared with 2-pulses of irradiation. After performing GCD measurements for 5000 cycles, we found that the electrode retains as high as 80% capacitance, which shows that as prepared electrode possesses excellent stability and long cycle-life. Next steps will be the work on other mixed oxides electrodes, such as Ni-Mn oxides, Mn-Fe oxide and thicknesses and different fluence values during irradiation.

ET07.03.03

CNT Flexible Membranes for Energy Conversion and Fuel Cells


We have successfully employed charge transfer mechanism to nanosegregate the surface of CNT powder and converted into CNT flexible membranes. The processing protocol has limited or no impact on the intrinsic properties of the CNTs. The CNT membranes have bulk mass density greater than that of water (1.0 g/cc). We have demonstrated the use of the CNT membranes as electrode in a pristine and oxidized single/stacked solid-state capacitor as well as pristine interdigitated microcapacitor that show time constant of ~32 ms with no degradation in performance even after 10,000 cycles. The capacitors maintained very excellent performance even at temperature up to 90°C. We will present these results including the specific capacitance, leakage current, energy and power densities, as well the effects of flexing on these properties.

ET07.03.04

Stretchable Wire-Shaped Supercapacitor Based on Biodegradable Metal and Polymer

Hanchan Lee, Geumbee Lee and Jeong Sook Ha. Korea University, Seoul, Korea (the Republic of).

Recently, there has been extensive interest in transient devices which experience the complete biodegradation after use for certain desired time since they can contribute to the realization of environmentally friendly electronic devices, wearable/implantable devices, or various transient systems for internet of things. In this study, we report on a facile fabrication of stretchable wire-shaped supercapacitor (WSC), in which all components are completely resorbable in water or biofluid; water-soluble molybdenum (Mo) wire as a current collector, molybdenum oxide as a pseudocapacitive electrode, polyvinyl alcohol containing sodium chloride as an electrolyte, and poly (1,8-octanediol-co-citrate) (POC) film as an encapsulant as well as a deformable substrate. Mo oxide film is grown on the Mo wire surface via electrochemical oxidation by application of constant voltage of 0.8 V to Mo wire in electrolyte. Along with the duration time for applied bias voltage, the thickness of the oxide layer increases. Such fabricated WSC exhibits areal capacitance of 4.15 mF/cm² at a current density of 0.05 mA/cm² and a total cell capacitance increases in proportion to a cell length. Compared to the bare Mo, the capacitance increases dramatically by 47 times with electrochemically grown Mo oxide owing to the pseudocapacitance. A free-standing WSC maintains stable electrochemical properties under various deformation of bending, knotting, and a wavy WSC embedded in the stretchable POC films also maintains initial capacitance after repetitive stretching cycles. Finally, electrochemical performances of the WCS decreases with time in phosphate-buffered saline (0.01 M, pH 7.4) at body temperature, confirming the biodegradable WSC. This work suggests a facile way to fabricate a high performance transient WSC with a stretchability.

ET07.03.05

Vertically Aligned Insulating Nanotubes as a Structural Separator for Multifunctional Energy Storing Composites

Luiz Acauan, Yue Zhou and Brian L. Wardle. Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The use of carbon fiber reinforced polymers (CFRP) as multifunctional structural supercapacitors has been limited by the low ionic conductivity and/or mechanical properties of the insulator separator. Here we propose a novel type of “structural separator” based on aligned insulating nanowires “nanostitched” between carbon microfibre laminates. Proof-of-concept composites were fabricated using aligned alumina nanotubes (ANTs) as well as standard commercial separators between carbon CF prepregs. ANTs nanostitched-composite laminates showed similar mechanical properties as the structural composite with no separator, while the commercial separator exhibited reduced strength due to interface failure. ANTs embedded in polymer electrolyte revealed 2X higher ionic conductivity than the pure electroactive polymer due to the nanowires disrupting the polymer semi-crystallinity. This new structural separator architecture allows standard CFRP structural composites to act as a multifunctional energy storage device, with the potential to enhance energy storage capabilities due to the process-structure coupling in ionically-conductive polymer.

ET07.03.06

Microstructure Engineering to Improve Wettability of Thick, Porous Electrodes for Energy Storage

Katherine Stoll, Thomas Carney and Fikile Brushett, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Rechargeable batteries are well suited for energy storage due to their high energy density and efficiency. However, these devices are limited to the use of electrodes less than 300 µm thick to avoid diffusion limitations. Thin electrodes significantly increase the number of inactive components needed for the battery to function, leading to high costs as well as low energy and power densities. Transitioning to thicker electrodes requires novel electrode and cell architecture design to simultaneously enable sufficient ion transport through the flooded pores of the electrode and electron transport through the solid-phase material. Here, we investigate the permeability and wettability of different engineered electrodes as well as the compatibility of various electrode-electrolyte combinations with an overarching goal of enabling low-resistance thick electrodes. Specifically, we examine the electrolyte surface tension and viscosity as well as the electrode microstructure (e.g., porosity, pore size, pore geometry, and topology) in accordance with the Lucas-Washburn equation, to determine the effect on battery performance.

We employ two methods, varying the particle size and altering the binder material, to fabricate electrodes with tailored microstructure. Theoretical models indicate that electrodes with graded porosity decrease resistance and improve capacity retention. Inks of varying particle size will be systematically utilized to optimize the pore size distribution and total porosity, while contact angle goniometry will be used to quantify the electrolyte-electrode interactions as a function of pore geometry, surface chemistry, and applied voltage. The electrode permeabilities will be characterized using pressure drop testing in accordance with Darcy’s law. The methods developed in this work are portable and can be applied to a wide range of materials and energy storage systems.
storage devices.

References

ET07.03.07
Effect of Rheological Properties on Microstructure and Electrochemical Performance of Si Composite Electrodes [Hanzhi Hu] and Yang-Tse Cheng; University of Kentucky, Lexington, Kentucky, United States.

Silicon has been intensively studied as one of the high capacity negative electrode materials for lithium-ion batteries (LIBs). Typically, a silicon electrode is prepared by a wet coating process during which a slurry is made by mixing the components in a solvent and then casted onto a current collector, followed by a drying process. Thus, the rheological properties and stability against sedimentation may affect the microstructure and the electrochemical performance of the electrode. In this work, slurries consisting of Si nano-particles, carbon black (CB), and Na-carboxymethyl cellulose (Na-CMC) with various solid loading were prepared in an aqueous medium, and their rheological properties were compared. The effects of rheological properties on the microstructure and electrochemical performance of electrodes were investigated as well. The results show that, due to the formation of an internal network of solid particles bridged by polymer chains, slurries with higher than 6% solid loading are solid-like. With decreasing solid loading, the slurries become more liquid-like. The Si/CB/Na-CMC electrodes prepared using slurries with high solid loading are more uniform in microstructure than that prepared using low viscosity slurries. The propensity to aggregation, porosity, and the adhesion of the electrode laminate are also influenced by the rheological properties of the slurries. This work demonstrates the importance of slurry property on the microstructure and electrochemical performance of silicon electrodes.

ET07.03.08
Aluminum–Air batteries with Ultrahigh Energy Density [Sangjin Choi] and Wooyoung Shim; Yonsei University, Seoul, Korea (the Republic of).

There is growing interest in high-performance energy storage systems to meet the strong needs for high-energy-density and high-power devices. Metal-air battery systems could offer a low cost, environmental friendliness, and outstanding energy-storage capability. In particular, aluminum-air batteries are attractive systems due to their safe and energy-density property. However, actual performances of them are far below the theoretical performances. Here, we show aluminum-air batteries adopting a sparkled graphene oxide/silver nanoparticle cathode. The spark reaction makes the graphene oxide very porous structure that can provide a wide oxygen diffusion path. Moreover, silver nitrate is reduced by the reaction and becomes a silver nanoparticle which acts as a catalyst for the oxygen reduction reaction. The resultant aluminum-air cell shows very remarkable electrochemical performance close to the theoretical value, and showed enough power to turn on a smart watch when connected in series. This work represents an advancement in aluminum-air batteries using a facile one-step spark reaction concept, showing a practical applicability of aluminum-air batteries.

ET07.03.09
Fabrication of All-Solid-State Lithium-Ion Batteries [Simon E. Hafner]1, 3, Lei Cao1, Hyukkeun Oh1, Harvey Guthrey2, Sehee Lee1 and Chunmei Bao2; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Mechanical Engineering, University of Colorado, Boulder, Colorado, United States.

The complexity and expense of manufacturing all-solid-state batteries has long hindered the development of large-scale solid-state batteries for transportation and grid storage applications. Electrolyte-electrode interfacial resistance, air stability, and mass production capabilities pose particular challenges. In our work, we demonstrate a new battery manufacturing method that overcomes the challenges of scaling and interfacial resistance by depositing very dense cathode, solid-state electrolyte, and anode layers directly on top of one another. This method enables using a variety of battery and solid-state electrolyte materials and manufacturing all-solid-state batteries in an ambient environment. Furthermore, the approach could ensure a straightforward transition to a roll-to-roll process and incorporate a wide range of materials for future large-scale manufacturing. This presentation will discuss the manufacturing process and electrochemical cycling performance of the as-fabricated all-solid-state batteries.

ET07.03.10
Photofuel Cells Consisting of a Particulate TiO2 Photoanode with Using Cellulose as a Direct Fuel [Takumi Yoshimura, Youseke Kageshima and Hiromasa Nishikiori; Department of Engineering, Graduate School of Science and Technology, Shinshu University, Nagano, Japan.

Recent population growth and the resultant increase of energy consumption have caused the serious energy and environmental issues, that is, global warming and depletion of fossil resources. Renewable energy sources, such as solar energy and biomass, have been regarded as one of the promising alternatives to supply reliable electricity. Fuel cells have been intensively studied as clean energy systems with less environmental load. However, since H2 utilized as the fuel is typically produced by steam reforming of the fossil fuels, the conventional fuel cells are not truly environmentally friendly. The alternative direct fuel cells with using biomass-derived fuels, such as methanol1, glucose2 and cellulose3 have also been developed. Above all, cellulose can be expected as one of the most attractive biomass-derived fuels, since a tremendous amount of cellulose is disposed without effective reuse or recycle and is free from worry about competition against biological resources for edible use. It should be noted that the reports of the direct fuel cells with using cellulose as a fuel are still limited due to rigid crystalline structure of cellulose and its resulting insolvency in solvents. Most of the cellulose-based fuel cells are designated to use a large amount of expensive enzyme.3 Y. Sugano et al. reported a novel method for direct electrochemical oxidation of cellulose dissolved in strong alkaline aqueous electrolyte on the inorganic metal electrode.4 In the present study, we demonstrated a photofuel cell consisting of a particulate TiO2 photoanode, where cellulose is oxidized on the photoanode to generate electricity in an external circuit. The TiO2 particles (P25, Nippon Aerosil) were coated on an FTO/glass substrate and evaluated as a photoanode. Cellulose was fed to the photofuel cells as a direct fuel by several methods: 1) with covering the photoanode surface by cellulose thin film or 2) by dissolving cellulose in a strong alkaline electrolyte. In the presentation, (photo)electrochemical investigations for cellulose oxidation, influence of methods for cellulose supply, effects of photoelectrode preparation conditions, and performances of the photofuel cells will be discussed in detail.

References
ET07.03.11 Mussel-Inspired Polydopamine Treated Reinforced Membranes with Self-Supported CeO₂ Radical Scavengers for Highly Stable PEMFC Ki Ro Youn¹, Kyung-Ah Lee¹, Sun-Hee Choi¹, Seung-Ho Yook³, Il Doo Kim¹ and Jim Young Kim¹; ¹Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Seoul, Korea (the Republic of); ²Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of).

The physical and chemical degradations of proton exchange membranes (PEMs) in fuel cells induced by the harsh operation environments such as high humidity, high pressure, and repeatable wet/dry conditions and the free-radical attacks are critical factors limiting long-term operation of the PEMFCs. Mussel-inspired polydopamine (PD) with defective ceria nanoparticles (CeO₂ NPs) is introduced into porous polytetrafluoroethylene (PTFE) substrates for highly durable and chemically stable composite membranes in proton exchange membrane fuel cells (PEMFCs). The hydrophilic functionalities of PD coated PTFE (PD@PTFE) films enable uniform coating of Nafion ionomer dispersion during blade casting and allow strong mechanical adhesion between PTFE and Nafion layers in PD@PTFE membrane (m-PD@PTFE). Furthermore, the redox properties of catechol at PD surface render the cerium salts to be self-supported CeO₂ NPs as sustainable radical scavengers. Improved properties of prepared CeO₂ and PD coated PTFE membrane (m-CePD@PTFE) were characterized via water uptake, dimensional stability, proton conductivity, elongation test, Fenton’s test, and ex-situ observation. Finally, it was found that m-CePD@PTFE shows superior mechanical stability and long-term cell performance during repeated wet/dry cycling tests (6,000 cycles) via suppressed physical fracture and radical attacks on PFSA ionomer.

ET07.03.12 “Nanoscale Nucleation” In Situ Polymerization Method for Preparing Dielectric Nanocomposites with High Energy Density Tao Zhang, Yang Shen and Ce-Wen Nan; Tsinghua University, Beijing, China.

Polymer nanocomposite dielectrics, composed of polymer matrix with high breakdown strength and nanofillers with high dielectric constant, can achieve outstanding energy density. However, the large electrical mismatch between polymer and nanofillers will lead to poor compatibility and thus damage dielectric properties of the composites. Introducing a transition layer to the filler surface can significantly reduce the degree of mismatch. In this work, a “nanoscale nucleation” in-situ polymerization method was developed to successfully synthesize a series of BaTiO₃-based nanofillers with core-shell structure. Due to the “nucleation” role of the nano-BT particles, the polymerized monomers tend to form a stable coating layer on their surfaces. Nano-BT particles coated with three different monomers (TFEMA, HFPMA, DFHMA) were fabricated, respectively. The results demonstrate that the core-shell structures are all successfully achieved and the thickness of shell can be controlled between 2 to 7 nm. With great interfacial compatibility and thus alleviating electrical mismatch, BT@PDFHMA-P(VDF-HFP) nanocomposite with 1 wt.% BT@PDFHMA fillers showed higher energy density of ~18 J cm⁻³ compared with the conventional solution blended BT nanocomposites BT-P(VDF-HFP) (~12 J cm⁻³). We consider that this novel and versatile method can be widely used in the preparation of core-shell structures in dielectric nanocomposites.

ET07.03.13 MXene/Carbon Nanotube Yarn Supercapacitor Jong Woo Park and Seon Jeong Kim; Hanyang University, Seoul, Korea (the Republic of).

Development of wearable electronics and flexible energy harvesters such as piezoelectric or triboelectric energy harvesters largely demand flexible and wearable energy storage devices especially, supercapacitors. Yarn type supercapacitors which are flexible, knittable, and stretchable are receiving large interests. However, the energy density of the yarn supercapacitors should be increased when their limited footprints are considered. The asymmetric configuration of yarn electrodes is one of the strategies to increase the energy storing performance, the low capacitance of conventional carbon materials such as activated carbon, graphene, and carbon nanotube (CNT) hinders the overall performance of the asymmetric supercapacitor. To accomplish high capacitance of the negative electrode, there have been reported some other materials such as PPy, VN, MoS₂, recently. MXene, especially Ti₃C₂Tx, denotes surface functional groups is an emerging material for its high volumetric capacitance in aqueous electrolyte and high electrical conductivity. The high volumetric capacitance makes this material great candidate for the active material of yarn structured supercapacitors. Also, MXene could be utilized for the negative electrode in asymmetric supercapacitors owing to its potential range. In this work, MXene was biscalculated with CNT sheets to form a high-performance yarn electrode. The biscalculated MXene/CNT yarn exhibited high areal and volumetric capacitance in 1 M sulfuric acid electrolyte. Using the MXene/CNT yarn as the negative electrode, MnO₂/CNT yarn as the positive electrode, and PVA/LiCl gel as a solid electrolyte, resulted yarn-type asymmetric supercapacitor could operate up to 2 V and store high energy density. The all-solid-state yarn supercapacitor could be woven into commercial cotton textile and perform without degradation under mechanical deformations.

ET07.03.14 Direct Urea Fuel Cells Based on CuNi Plated Polymer Cloth as Anode Catalyst Keiichi Kaneto¹, Mao Nishikawa¹, Sadahito Uto¹ and Toshiyuki Osawa²; ¹Department of Biomedical Engineering, Osaka Institute of Technology, Osaka, Japan; ²Department of Environmental Engineering, Osaka Institute of Technology, Osaka, Japan.

Direct and passive type urea fuel cells were studied based on CuNi plated polymer cloth for the anode catalyst and current collector. Pt-black and cation exchange membrane were used as the cathode catalyst and polymer electrolyte, respectively. The output power was significantly enhanced by coating the CuNi cloth with a conducting polymer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). The cell exhibited the open circuit voltage (Eₒ), 0.68V and the maximum output power (Pmax), 1.88 mWcm⁻² for 0.5 M urea solution. Similar results of Eₒ = 0.65V and Pmax = 1.74 mWcm⁻² were obtained for 0.5 M ammonia solution. The cell performances and mechanisms of anode reactions were discussed taking the results of various biofuel cells using the other conducting polymers and polymer electrolytes into consideration.

ET07.03.15 Direct Observation of Dehydrogenation of Mg₂FeH₆ by Using In Situ Transmission Electron Microscopy Hyunmin Kimp¹, Joseph Song¹, Julien Fadonougbo¹, Jee-Hwan Bae¹, Jaeyoung Hong², Soongju Oh², Younghwan Choi², Jaeyoung Ahn², Wooyoung Shim³, Dongwon Chun³ and Jinyoo Suh¹; ¹High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Korea University, Seoul, Korea (the Republic of); ³Yonsei University, Seoul, Korea (the Republic of); ⁴Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ⁵Electronic Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Magnesium-based ternary hydrides have been considered as a promising candidates in fuel cell and hydrogen transport in light of their high hydrogen capacity and cycling ability. Understanding hydrogenation /dehydrogenation mechanism is, however, hampered by difficulties in the in-situ observation.
of nanostructured ternary hydrides. For example, rapid dehydrogenation process at high temperature hinders proving the decomposition mechanism of ternary hydrides through electron microscopy. Currently, developed equipment such as in-situ electron microscopy (EM) holder, high resolution/fast image acquisition (One-view charge-coupled device (CCD) camera, Gatan) and fast energy-dispersive X-ray spectroscopy (Super-EDS) have enabled studies of fast reaction phenomena through electron microscopy.

Here, we investigated the dehydrogenation process of Mg2FeH6. The nanostructured Mg2FeH6 sample was loaded on the in-situ TEM holder (Fusion, Protochips) and heated the sample with temperature of 250 degrees - 400 degrees for 1 hour to trigger the decomposition of Mg2FeH6 by hydrogen desorption. We imaged dynamics and diffraction patterns of Mg2FeH6 on dehydrogenation by one-view camera, attached on the Titan (G2, FEI) 25 pictures were acquired every second. In addition, high-speed EDS analysis was performed by super-EDS embedded TEM (Talos F200X, FEI) before and after the dehydrogenation. We utilized profile analysis of the SAD pattern (PASAD) program for the quantitative analysis of diffraction patterns. Upon heating, intensities of Mg2FeH6 diffraction spots were decreased and eventually disappeared within a couple of minutes. Sequentially, diffraction spots of Fe and Mg were appeared and its intensity increased through the dehydrogenation process. This is because the phase segregation in immiscible elements of Fe and Mg by the hydrogen desorption from Mg2FeH6. It is noteworthy that MgO diffraction spots were observed simultaneously after the extinction of Mg2FeH6 diffraction spots, which might be possibly due to the oxidation of segregated Mg in TEM column. Super-EDS results reveal that nanosized Mg and Fe were produced after the dehydrogenation of Mg2FeH6 which was not observed in the sample before dehydrogenation at a temperature below 300 degrees. On the contrary, at a temperature above 300 degrees, size of segregated Mg and Fe increased much. Also, chemical composition of Mg was decreased appreciably. This suggests induced Mg was evaporated even below its melting points, indicating high energy electron beam promotes Mg evaporation.


SESSION ET07.04: Electrode Manufacturing
Session Chairs: Wilhelm Pfleging and Pu Zhang
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 312

8:30 AM *ET07.04.01
Towards High Energy Density Electrodes—Ultrathick Cathodes and Prelithiation Lukas Ibinger1, Florian Holstiege2, Tobias Gallasch2, Tobias Placke2, Falko Schappacher2 and Martin Winter2; 1 Helmholtz Institute Münster HI MS, Forschungszentrum Jueltich GmbH, Münster, Germany; 2MEET Battery Research Center, University of Münster, Münster, Germany.

The production of cost effective, high energy and environmentally friendly electrodes is key for the success of lithium ion batteries (LIBs) to be used in electro-mobility or grid storage. To overcome the remaining drawbacks new ways towards cost effective processing of LIB electrodes and higher energy density battery cells are main topics of nowadays research. One way to combine both requirements is the preparation of ultra-thick electrodes using aqueous processing: Thick dry film thicknesses (large active mass loadings) allow an increase in energy density, while the relative reduction of copper and aluminum current collectors reduces the costs. However, compared to conventional processing, aqueous electrode formulation also goes along with disadvantages like surface crack formation and basic pH values accelerating active material degradation, especially in case of cathode materials like NMC (LiNi0.5Mn0.25Co0.2O2 with x ≥0.33 and y,z ≤ 0.33). Our approach to successfully overcome mechanical electrode instability is to develop a suitable “binder package” combining the water soluble components polyacrylic acid (PAA), polyethylene oxide (PEO) and sodium-carboxymethylcellulose (CMC). This mixture combines high flexibility (PEO) with low viscosity (PAA) and sufficient adhesion (CMC) resulting in a superior water compatible binder system to manufacture ultra-thick cathode sheets. Using this binder composition it was possible to achieve NMC based cathodes free from cracks with high amounts of active material and active mass loadings up to 50 mg cm-2 delivering discharge capacities of 120 mAh g-1 at 0.2 C.

A further issue, which decreases the gravimetric energy and volumetric energy density of LIBs is active lithium loss, caused by solid electrolyte interphase formation on the surface of the anode, occurring mainly in the first cycle of operation. In order to compensate the loss of active lithium, various pre-lithiation methods have been developed that result in an increased reversible capacity and, consequently, in a higher gravimetric energy and volumetric energy density. Thereby, the term “prelithiation”, describes the addition of lithium to the active lithium content (= reversibly transferable lithium ions between positive and negative electrode) of a LIB prior to battery cell operation. Therefore, with help of prelithiation it is possible to use novel active materials inside LIB full cells which otherwise could not be utilized due to high active lithium losses.

9:00 AM *ET07.04.02
New Approaches to Cathode Manufacturing to Meet Emerging Environmental Restrictions Stuart D. Hellring; PPG, Allison Park, Pennsylvania, United States.

NMP remains the most commonly used solvent in the lithium ion battery cathode manufacturing process. However, NMP faces mounting global regulatory pressure, and recently issued EU directives could effectively eliminate NMP usage by 2021. These new restrictions will place enormous challenges on the industry’s ability to locally manufacture lithium ion batteries for electric vehicles. Novel solutions will be needed to manufacture cathodes without NMP. PPG is actively engaged in developing innovative solutions to the challenges presented by this historic transition. These solutions address eco-friendly battery manufacturing as well as providing other performance improvements in energy storage. Applying these unique approaches for NMP-free cathode production enables the manufacturing of lithium ion batteries within this new regulatory environment to support the predicted growth in EV production.

9:30 AM ET07.04.03
An Advanced Dry-Powder Manufacturing of Lithium-Ion Batteries Applicable to Various Electrode Designs Yangtao Liu1, Jin Liu1, Brandon Ludwig2, Heng Pan* and Yan Wang1; 1 Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2 Mechanical Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

The slurry casting method currently dominates the manufacturing of electrodes for lithium-ion batteries. There exists a recognized shortcoming of this conventional method that the liquid solvent, mostly as the organic (N-methyl-2-pyrrolidone), is indispensable to fluidize the electrode material during casting, which is toxic and high cost during the entire processing. To overcome this restriction, an advanced power-based technology was developed by us to fabricate electrodes of the lithium-ion batteries through additive manufacturing. Gas-driven spraying guns are chosen to address a direct dry-powder printing of electrode structures onto the current collectors without involving solvents. Therefore, the removal of solvents shortened the production time. 
from days to seconds, analyzed to reduce 20% of production cost, and enabled a more precise control of electrode microstructure during manufacturing. We have demonstrated this technology with a wide range of compatibility on different electrodes design, including cathodes (LCO, LMO, NCM), anodes (Graphite), advanced architecture designs (Ultra-low binder recipe (<1%), High-energy thick electrodes (~280um), Layered structured). Based on our current study, the dry printed electrodes outperformed the reference slurry cast electrodes at a few performance parameters (80% capacity retained in 500 cycles), high bonding strength, high structural integrity, high materials homogeneity Integrality. Along with better electrochemical and physical properties, this dry-powder manufacturing method could be attractive and competitive for nowadays production of electrodes and has the potential for further design.

9:45 AM ET07.04.04
Dry Process for Fabricating Low Cost and High Performance Electrodes for Energy Storage Devices Qiang Wu1, Jim Zheng1, M. Hendrickson2 and E.J. Plichta3; 1Florida State University, Tallahassee, Florida, United States; 2U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

We report a roll-to-roll dry processing for making low cost and high performance electrodes for lithium-ion batteries (LIBs) and lithium-ion capacitors (LICs). Currently, the electrodes for LIBs and LICs are made with a coating or slurry casting procedure (wet method). The dry electrode fabrication is a three-step process including: step 1 of uniformly mixing electrode materials powders comprising an active material, a carbonaceous conductor and the soft polymer binder; step 2 of forming a free-standing, continuous electrode film by pressing the uniformly mixed powders together through the gap between two rolls of a roll-null; and step 3 of roll-to-roll laminating the electrode film onto a substrate such as a current collector. A prototype hybrid lithium ion capacitor cell with lithium iron phosphate (LFP)/activated carbon (AC) composite cathode and Li doped hard carbon (HC) anode has been made by our dry method, which has a breakthrough energy density of ~30 Wh kg\(^{-1}\), high power density of 2,000 W kg\(^{-1}\), as well as long cycle life over 30,000 cycles (90% retention). LIBs of LiNi\(_{0.6}\)Mn\(_{0.2}\)Co\(_{0.2}\)O\(_2\) (NMC622)/graphite and LiNi\(_{0.6}\)Mn\(_{0.2}\)Co\(_{0.2}\)O\(_2\) (NMC622)/graphite-silicon also has 250 Wh kg\(^{-1}\) and 300 Wh kg\(^{-1}\) energy density, respectively.

Compared with the conventional wet slurry electrode manufacturing method, the dry manufacturing procedure and infrastructure are simpler, the production cost is lower, and the process eliminates volatile organic compound emission and is more environmentally friendly, and the ability of making thick (~120um) electrodes with high tap density results high energy density of final energy storage device.

10:00 AM BREAK

10:30 AM *ET07.04.05
Reduce Electrode Manufacturing Cost—Transition from Batch to Continuous Production David Ventola; B&W MEGTEC LLC, De Pere, Wisconsin, United States.

The basics of Li-ion battery electrode manufacturing have not changed much in the last twenty years. Ten years ago, B&W MEGTEC developed a method to utilize their extensive knowledge and experience in flotation drying to enable simultaneous 2-side coating of Li-ion electrodes. This development included a unique slot die coating arrangement along with proprietary technology to stabilize the thin foil current collector substrate. These advancements enabled world class battery manufacturers to reduce costs of manufacturing and increase productivity. Simultaneous 2-side coating allows for a simplified factory layout which reduces total floorspace required and reduces material moves. Additionally, when compared to a more typical sequential coating process the 2-side coating and flotation dryer only requires roughly half of the utilities which greatly reduces the operating expenses.

The focus of this talk will be to leverage the benefits of 2-side coating and flotation drying; linking other unit operations to streamline the electrode manufacturing process. Specifically, the following technologies are usually separate and distinct unit operations each with varying levels of materials in que, WIP and material transfers between operations.

- Slurry Mixing
- Electrode Coating & Drying
- Calendering / Roll Pressing
- Secondary Drying

These unit operations can be linked to create a streamlined continuous processing plant with a focus on increasing productivity, improving quality and reducing manufacturing costs.

Continuous mixing leads directly into simultaneous 2-side coating and flotation drying. Traditionally after drying the coated electrode rolls are removed, stored and put in queue to move on to the calendaring/pressing operation. This movement and storage is wasted effort and floorspace. Linking calendaring/pressing directly after drying in the processing line eliminates this waste. The new process methodology allows for the dried electrode to move directly to the inline calendner/press, bypassing the intermediate rewind and unwind steps.

In many electrode manufacturing processes, a secondary drying step is required to achieve the final level of drying or residual solvent retained on a percent or parts per million scale. Typically, this is done by loading full rolls of coated electrodes into a drying chamber and essentially “baking” the electrode for an extended period. The period could be as short as 8 hours or as long as 24 hours. The mechanics of extracting solvent and/or water out of a coated electrode wound into several hundred if not a thousand layers are very difficult. A new approach exists to employ continuous secondary drying inline with the other unit operations presented. Inline secondary drying provides more consistent drying of the entire electrode surface area, which leads to a more consistent and higher quality electrode.

11:00 AM *ET07.04.06
Present and Future Methods of Li-Ion Battery Electrode Slurry Preparation Bernhard Stalder; Buhler AG, Uzwil, Switzerland.

An overview over present and near future preparation methods of electrode slurries will be presented:

1. The traditional methods with batch mixers (usually planetary type mixers) which have been used from the very first of the Li-ion battery history. The method is well known and has advantages in R&D use but shows low hanging limitations as soon as mass production is considered: The scalability via the mixer size has reached its upper end. The only way for a further scale up has to be performed via the number of mixers which is very expensive. Further, the reproducibility of the slurry quality shows some challenges due to the batch operation method.

2. An advanced semi-continuous thin film method in combination with simple batch mixers or existing planetary mixers for increased throughput rates and improved reproducibility of the slurry quality. Mainly the reproducibility of the viscosity as a key property of a slurry is on a high level and allows an easy electrode coating process. The method can be used in R&D scale (some 10 milliliters) but can be scaled up to manufacturing size with throughput rates of more than 1000 liters per hour.
Coating technologies for functional materials by solution based (“wet”) processing methods are a highly promising approach for production upscaling towards industrial scales. The use of flexible polymer substrates not only allows the preparation of ultrathin bendable devices, but also enables roll-to-roll (R2R) manufacturing, with all its associated benefits such as high volume, large area and high throughput production. Whereas for certain sectors like the packaging and paper industries, R2R printing and wet coating have been the established standard already for decades, its use in more demanding application areas like printed electronics has only recently started to emerge. Within this branch of industry, energy conversion and storage devices are a core application area with intense research activity going on to introduce R2R production technologies. This contribution presents technical approaches for solution based R2R manufacturing methods which can be applied in the large scale fabrication of flexible printed electronics devices for energy conversion and harvesting. The development of a R2R line with two slot-die coating stations is presented which can deposit two functional layers consecutively in a single run (“tandem coating”) at web speeds up to 30 m/min. Whereas slot die coating typically is a technology for the uniform deposition of continuous functional thin films, additional adjustments to the equipment also allow patterning both in the web transport direction (stripe coating) and perpendicular to it (intertmittent coating). These patterning options are a crucial prerequisite for the manufacturing of properly encapsulated devices with high stabilities and long lifetimes. Particularly for functional inks with low viscosities, well controlled intermittent slot die coating with proper edge definition of the resulting patches is far from trivial. It requires specially designed ink supply systems able to actively remove (suck back) fluid from the die opening in a precisely timed manner to achieve a uniform and sudden start and stop of the coating process. It will be demonstrated how, employing this approach in combination with stripe coating, patterns can be produced at high R2R speeds with definitions in the millimetre range using inks relevant for the manufacturing of energy conversion and harvesting devices.

Advantages and challenges of each method will be discussed and compared. Remarks concerning the interaction of slurry preparation and the subsequent coating process will be shared.
Recent progress in developing three-dimensional graphene macro-structure has resulted in a diverse array of bulk graphene aerogels for a plethora of applications. However, these aerogels generally exhibit compromised electrochemical performance compared to their two-dimensional counterparts, particularly when engineering into supercapacitor electrodes. This drawback is due mainly to their highly tortuous and stochastic pore networks that retard ion diffusion throughout the entire electrode. These structural limitations can be well addressed by developing graphene-based architectures with ordered macro pores to provide ions with straightforward diffusion "expressways". Our recently pioneering work developed a direct ink writing, one of the 3D printing techniques that manufactured the first group of 3D graphene aerogels with periodic macropores as supercapacitor electrodes. These aerogels, though possess thickness 10-100 times thicker than most other reported carbon-based supercapacitor electrodes, display exceptional capacitance retention of ~90% from 0.5 to 10 A/g, a performance that is comparable or even outperforms those of conventional thin film supercapacitor electrodes. This talk will first present the key factors in developing an extrudable graphene oxide-based ink for electrode printing. Another emphasis will be given to the electrochemical analyses elucidating the links between the 3D printed structure and the excellent rate capability performance. This presentation is expected to highlight the power of direct ink writing (or generally, 3D printing) as an advanced manufacturing technique to revolutionize the production of electrochemical energy storage devices.

Co-Extrusion (CoEx) is a high speed, scalable deposition process for creating finely patterned, interdigitated thick films. Our CoEx printhead is designed to be a drop-in replacement for slot-die heads on web coaters, enabling novel geometric structuring of electrodes with minor changes to existing battery electrode processing lines. Here, we present the use of CoEx to prepare thick (~120 µm) NMC cathode electrodes consisting of alternating regions of high lithium-ion transport and high lithium-ion storage capacity. By structuring the cathode electrode, we enable full lithium utilization at C/2, despite near doubling of the electrode thickness compared to conventional baseline electrodes. CoEx cathode electrodes are paired with thick, graded graphite anode electrodes and assembled into 1 Ah pouch cells for electrochemical testing. CoEx pouch cells demonstrate 10 – 20% improved energy density with respect to conventional electrodes and >30% improved power density with respect to thick conventional (unstructured) electrodes at high discharge rates.

Battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. However, the electrochemical and mechanical properties of slurry cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). We have now made considerable advances in the direct electrodeposition at modest temperatures of high performance tin-based Na and Li-ion anodes and LiCoO2, NaCoO2, LiMn2O4, and Al-doped LiCoO2-based Na and Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 ~ 1000 °C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

A new concept for making battery electrodes to simultaneously control macro-/micro-structures of electrodes is developed to address present energy storage technology gaps and meet future energy storage requirements. This new fabrication process fully utilizes the benefits of additive manufacturing, which provides a pathway for inexpensive and flexible production of specialized products. Furthermore, the process allows a simultaneous control of the microstructure and macrostructure of electrodes which cannot be achieved via conventional manufacturing techniques. Modern batteries are fabricated in a form of laminated structures that are composed of randomly mixed constituent materials. Due to this randomness, there is an ample room in the conventional method to enhance performance by developing viable processing techniques to construct well-organized structures. The synergistic control of micro-/macro-structures is a novel concept in energy material processing that has considerable potential for providing unprecedented control of electrode structures and enhancing performance. Electrochemical tests show that the new electrodes exhibit superior performance in their specific capacity, areal capacity, and cycle life. It is concluded that the macro-micro-controlled structure showed 21%, 16%, and 7% more areal capacity than a structure with no control, a macro-controlled structure, and a micro-controlled structure, respectively. The proposed control of 3D structures, with a well-organized distribution of energy materials, demonstrated more superior properties and advantages than structures with randomly distributed materials.

Silicon as high-energy anode material for next generation lithium-ion batteries has recently become of great interest. Graphite active material mixed with silicon nanoparticles is under development in order to increase significantly the practical capacity of commercial anodes and to overcome the drawbacks of silicon due to large volume changes during electrochemical cycling. However, it is well known that pure silicon will form a native oxide layer during exposure in ambient air. During battery operation, this native oxide layer will restrain the lithiation process and a drop in silicon capacity will be achieved. Therefore, carbon-coated silicon nanoparticles were applied in order to maintain a high specific capacity of 3579 mAh/g. In order to reduce the intrinsic...
mechanical stress of silicon/graphite electrodes and to improve the lithium-ion transport kinetic, free-standing electrode structures were generated by applying ultrashort laser ablation. For comparison, a thin alumina layer (thickness ~5 nm), which acts as an artificial solid electrolyte interphase, was coated on structured silicon/graphite electrodes by applying atomic layer deposition. Cyclic voltammetry measurements were performed to investigate the fundamental properties of carbon- and alumina-coated silicon/graphite electrodes. Galvanostatic measurements reveal that the cells with structured electrodes exhibit excellent electrochemical properties and improved lithium-ion diffusion kinetics compared to cells with unstructured electrodes.

4:15 PM ET07.05.08
3D Architectured Pyrolytic Carbon as Efficient Battery Electrode Kai Narita, Michael Citrin, Heng Yang and Julia R. Greer; California Institute of Technology, Pasadena, California, United States.

Engineering optimal electrode architecture in rechargeable batteries can improve volumetric power and energy density by controlling factors such as diffusion path of ions in electrode and electrolyte, mass loading of active materials, thickness of electrodes and migration path of electrons. Electrode engineering has been incorporated into batteries, for example, by utilizing 3D current collectors, by aligning active materials by an external field and by employing sacrificial template methods. These efforts are still being developed because powder electrodes require having a binder and methods that involve sacrificial templates offer limited flexibility in local geometry. Aiming at greater flexibility in electrode structure without such limitations, we developed a facile and scalable fabrication method of 3D architectured carbon anodes using direct light processing (DLP) 3D printing with UV-curable resin and a subsequent pyrolysis process in an inert atmosphere. The architectured pyrolytic carbon electrode is free-standing and binder-free enabled by the monolithic structure and electrical conductivity of carbon. The specific architecture of these electrodes is fully controllable over every length scale: from local geometry (micrometer-scale) to control tortuosity and mass loading, as well as global geometry (centimeter-scale), to intergrade into any device geometries. We fabricated 1mm-thick 3D periodically architectured carbon electrodes with simple cubic-like geometry and 12% relative density composed of ~30 micron-diameter beams. We characterized its electrochemical performance by constructing a half-cell against a lithium metal counter electrode. X-ray diffraction (XRD), energy dispersed spectroscopy (EDS), Raman spectroscopy and transmitted electron microscope (TEM) showed that the pyrolytic 3D lattice was mainly amorphous, with a few interdispersed sp²-hybridized regions. Battery cycling of these electrodes using a coin cell showed reversible capacity of ~230 mAh/g, which corresponds to 7 mAh/cm² at a current density of 16 mA/g or 0.6 mA/cm². Varying cycling rate from 0.6 to 10.1 mA/cm² revealed that the 3D carbon electrodes are capable of good performance enabled by low tortuosity of the periodic structure, for instance, ~3.5 mAh/cm² at 3.4 mA/cm². These electrodes showed stable capacity over 50 cycles at 16 mA/g.

This methodology offers a facile and scalable fabrication method of 3D architectured carbon that can serve as an efficient approach to create high energy density battery electrodes that can potentially be integrated into 3D interdigitated batteries.

4:30 PM ET07.05.09
Additive Manufacturing of Three-Dimensional (3D) Micro-Supercapacitors Based on MXenes Jafar Orangi and Majid Beidaghi; Materials Engineering, Auburn University, Auburn, Alabama, United States.

Energy storage devices are crucial for the future development of portable/wearable electronic devices, wireless sensors, and self-power microsystems. The first requirement for fabrication of energy storage devices with high energy and power densities is using electrode materials and electrolyte with superior electrochemical properties. Another critical requirement is to develop manufacturing methods that enable the assembly of the electrode material and electrolytes in structures that promote high electrical and ionic conductivities. Recently, a family of two-dimensional (2D) materials, referred to as MXenes, has been introduced as high performance electrode materials for electrochemical capacitors (ECs, also called supercapacitors). It is demonstrated that a MXene with the composition of Ti3C2Tx can deliver specific volumetric capacitances as high as ~1500 F/cm³, which has set a new record for the electrochemical performance of EC electrodes. In this talk, we present our recent research on using 2D MXenes as building blocks for the fabrication of three-dimensional (3D) supercapacitors using an additive manufacturing process. In this process, a water-based ink of MXene with viscoelastic properties was developed and directly used for extrusion-based 3D printing of supercapacitors. The fabrication process follows a layer-by-layer deposition of the MXene ink using a programmable printing machine. This process allows rapid fabrication of supercapacitors on a variety of substrates, while the thickness of the electrodes can be controlled by the number of deposited layers. The evaluation of the electrochemical performance of the printed devices shows their excellent electrochemical properties. For example, a flexible device fabricated using Ti3C2Tx electrodes and a gel polymer electrolyte delivered an extremely high areal capacitance of ~1100 mF/cm². Our study suggests that due to its high electrical conductivity and electrochemical properties, MXene is an excellent choice as the building block for the fabrication of 3D energy storage devices.

4:45 PM ET07.05.10

Flow batteries are a promising technology for large scale energy storage and load balancing from intermittent power sources, but their viability hinges on our ability to attain high-power outputs while minimizing costs and meeting performance constraints. Effective engineering of these systems is further complicated both by limitations on the control of the electrochemical cell component morphologies across scales and accurate modeling of the multiple, simultaneous physical processes. At Lawrence Livermore National Lab, we have pioneered a potential solution to this problem using additive manufacturing techniques which enable hierarchical structures controlled from the sub-micron through the centimeter length scales. Yet, even with this expanded design space, the complexity and tight coupling of the underlying physical processes remains as an obstacle to effective design. Apparently obvious choices can nevertheless lead to an unexpected adverse performance impact. To address this challenge, we present an automatic design methodology to optimize flow-through electrode topologies over precisely defined performance criteria. We combine forward physics solvers for the full, multidisciplinary electrochemical problem, including fluid flow, electrochemistry and mass transfer, with adjoint solvers to determine topological sensitivities. Our algorithms compute optimal electrochemical cell architectures which are then physically created using additive manufacturing techniques and post-processed to create carbon electrodes. We compare the predicted performance of computationally optimized designs against standard, bulk electrodes and focus on the tradeoff between high surface areas and pressure drop. Our work provides a systematic path toward rational design of cost-effective, high-power flow batteries and other porous electrode systems.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
Recently, many inorganic metal chalcogenides based on earth abundant elements such as copper zinc tin selenide (CZTS), lead sulfide (PbS), copper(I) sulfide (Cu2S), tin sulfide (SnS) and antimony sulfide (Sb2S3) have been investigated as an absorber material for solar cell. Among them, Sb2S3 has received intense attention as a light absorbing material due to its suitable band gap (~ 1.7 eV), high absorption coefficient (~106 cm⁻¹), low cost, less toxicity, and high air stability.\(^1,3\)

In this study, Sb2S3 was deposited through a simple spin-coating process previously reported by Wang et al. using an antimony-complex precursor solution prepared by dissolving antimony oxide (Sb2O3), carbon disulfide (CS2), and n-butylamine in an ethanol solvent.\(^4\) In order to enhance the performance of Sb2S3 solar cells, we applied surface treatment on TiO2 layer by Cs2CO3 solution to adjust the work function of TiO2 to the conduction band of Sb2S3 light absorption layer. Figure 1(a) shows a scheme of the device architecture. The bottom layer is composed of compact TiO2 layers acting as electron transporting. Light is absorbed by the Sb2S3 while holes are transported by the P3HT, and collected at the Au counter electrode.

As can be seen in figure 1(b), the power conversion efficiency (PCE) of 3.51% was obtained under AM1.5G illumination in a planar type device consisting of FTO/Cs2CO3 treated TiO2/Sb2S3/P3HT/Au, which is significantly higher than that of the control device without Cs2CO3 treatment (2.48%). The higher PCE of planar type Sb2S3 solar cell based on Cs2CO3 treated TiO2 is attributed to uniform surface formation, suitable energy level alignment, and efficient electron transport properties. We believe that this solution processable surface treatment can provide simple and effective way of device performance improvement in planar type inorganic metal chalcogenide solar cells.

\(^{1}\) N. Maiti, S. H. Im, C.-S. Lim, S. I. Seok, Dalton Trans., 41, 11569 (2012)

(Acknowledgements; This work was supported by the DGIST R&D Program of the Ministry of Science and ICT of Korea (18-ET-01).)
The Washington Clean Energy Testbeds opened at the University of Washington in February of 2016. The Testbeds are a group of facilities that allow researchers from academia and industry to collaborate on clean energy solutions at low cost, representing an open-access model reducing risk and capital outlays for developing commercial-scale, clean energy systems that get to market faster. Specifically, the Testbeds provide best-in-class fabrication and characterization for photovoltaic and energy storage material processing, device prototyping, pilot commercial scale manufacturing, performance verification, and systems integration. Fabrication of current state-of-the-art and next-generation photovoltaics and battery architectures is enabled through variety of advanced and additive manufacturing techniques, such as roll-to-roll printing, sheet coating, and 3D printing with options for processing in controlled environments. A full suite of material analysis instrumentation allows for rapid iteration of novel material formulations and manufacturing processes. Finished devices can be tested on industry-best solar simulators with NREL traceability, battery test channels, and/or integrated into simulated grid environments. The Testbeds serve as an innovation hub, providing access to key resources, including capital funding to startups, a relevant talent base, and new innovation programs for established companies. The presence of private companies and investors in the Testbeds represents a higher level of public-private coordination necessary to harvest the fruits of research and bring them to market faster than we see today. The Testbeds’ first year of operation provided early successes with UW spin-out companies, Battery Informatics and Membrion, achieving proof of concept, gaining early customers, and raising funds. Now in the second year of operation, the Testbeds management has evaluated a number of successful elements that will be key to helping researchers developing energy products. Facilities like the Testbeds are essential to ensuring that new materials and processing techniques make significant impact on the energy market.

**ET07.06.05**

**Industry Scale Additive Manufacturing of Photovoltaic Devices Using Advanced Roll-to-Roll Processing**  

The Washington Clean Energy Testbeds provide researchers with a cost-effective solution for accelerating product development by offering pay-per-use open access to state-of-the-art R&D instrumentation. Our staff scientists have pioneered large-scale printing of both organic and perovskite photovoltaic materials using state-of-the-art additive manufacturing techniques. This expertise is essential to driving the development of scalable next-generation photovoltaic devices and systems. This know-how is passed on to Testbeds users from around the world through related proprietary work with industry partners and hands-on workshops designed to train researchers on ink preparation and analysis, slot-die coating, screen printing, and film characterization. Using cutting-edge process-scalable solar materials such as PCE-11 polymer and methylammonium lead halide perovskites, users learn the latest techniques to scale up solar cell manufacturing. Workshops are fully customizable to accommodate specific interests and applications. Our unique industrial-scale roll-to-roll printer is specially designed to fabricate printed, flexible solar modules and is used to develop advanced methods for manufacturing the next generation of low-cost solar materials. By fine-tuning crystal growth kinetics through innovative ink formulations and film drying methods, we demonstrate fast and effective conversion of methylammonium lead halide perovskite inks, yielding flexible perovskite films on meter length scales in just minutes. Furthermore, implementation of in-line characterization methods (e.g. light-scattering, photoluminescence and Raman spectroscopy) is underway for assessing film quality during printing. In addition to active solar material coatings, we demonstrate greater than 20 meter per minute flexographic printing of thin and smooth patterned silver electrodes on 12-inch-wide plastic substrates. High precision web guiding and registration offers the ability to print and coat full solar cell device stacks. Fabrication activities at the Testbeds are supplemented with industry-leading characterization equipment. A large suite of rapid-scan materials analysis equipment provides immediate, comprehensive feedback on formulations and fabrication processes. Completed devices can be thoroughly tested on world-class equipment against NREL traceable reference devices.

**ET07.06.06**

**Optical Manipulation Using Microlens Arrays of Various Sizes in Organic Photovoltaics**  
Dongwook Ko, Hyojin Song, Seobum Chu and Jongbok Kim; Kumoh National Institute of Technology, Gumi, Korea (the Republic of).

Organic photovoltaics (OPV) are attracting much attention because they can be made light and flexible. However, due to low power conversion efficiency (PCE) compared to silicon-based solar cells, much research is underway to improve the PCE. In order to improve the PCE, many researchers have tried to synthesize noble materials with high light absorptivity or to control a complex interface. However low charge carrier mobility of organic materials have not allowed increasing the PCE. As an alternative, researches have been conducted to introduce various physical structures such as microlens, wrinkle into OPV to control the optical path. Here, we fabricated the microlens of various diameter (0.5μm – 20μm) and confirmed that the optical path and PCE can be dramatically increased with microlens array of optimum diameter. To study the optical manipulation with microlens array, we first prepared the microlens of various diameter (0.5μm – 20μm) by rubbing and water transfer printing method and then replicated them with Polydimethylsiloxane (PDMS). The replicated PDMS lens were analyzed by scanning electron microscope (SEM) and AFM to examine their surface morphology and by UV-VIS-NIR spectrometer to examine optical properties. The total transmittance was almost the same regardless of the diameter of microlenses, but the specular transmittance was decreased by increasing diameter of microlens. It indicated that the dispersed light increased with increasing microlens diameter. Specifically, we found that dispersive transmission was similar above 7μm of microlens diameter. The increase of dispersive light resulted in the enhancement of the light extinction in photactive layer. Similar to dispersed light, the light extinction was similar from 7μm or more. Then, we measured J-V characteristic under the condition of AM 1.5G, 100mW / cm2 to confirm the increase of dispersive light improve PCE in OPV. We observed that short circuit-current density (Jsc) increased with increasing microlens size, and it was similar from 7μm diameter or more. We also confirmed that the PCE increased by 12% compared with the OPV without microlens. As a result, we fabricated various diameter of lens (0.5μm – 20μm) through rubbing and water transfer printing method. Then, we confirmed that dispersive light and light extinction was increased with larger diameter of microlens. Similar to these optical properties, we confirmed that Jsc increases with microlens array and the PCE increases by up to 12%.

**ET07.06.07**

**The Effect of Substrate Roughness on the Properties of Sputtered AZO Thin Film**  
Kairi Hamada1, Hideyuki Okumura1, Takaya Ogawa1, 2 and Keiichi N. Ishihara1; 1Socio-Environmental Energy Science, Kyoto University, Kyoto, Japan; 2The Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan.

Transparent conductive oxide (TCO) for thin film solar cells requires special features such as not only transparency and conductivity but also light scattering in order to increase optical path length and promote more photon absorption for its efficiency. Representative TCO material is indium tin oxide (ITO), while it contains scarce metal, indium (In), and is expensive. Workhorse AZO (AZO) thin film, which has many advantages such as low cost, low sheet resistance, and high transmittance, is one of the most promising alternative candidates to replace ITO as transparent electrodes. However, AZO has the problem of low durability, and it is difficult to combine or satisfy dual properties i.e. the stability and light scattering of the film. In order to obtain simultaneously excellent light scattering characteristics and good stability of AZO film, here, we focus on roughness of the substrate as well as roughness of AZO film surface.

We prepared textured substrates and nontextured substrates, and compared them in terms of structural, optical, electrical properties and environmental stability. In addition, we employed different substrates including of quartz plate and various types of glass slides. The roughness of the substrate surface
was formed by abrasive papers on a rotary polishing machine for 2 minutes, and on the roughened substrate AZO film was made with radio frequency magnetron sputtering.

We expected a high haze value of the textured sample, which is one of the widely known parameters to represent the light scattering capability of rough surfaces. The visible haze value of the textured glass slide sample increases from 1.4% which nontextured glass slide sample showed to 39.2% with a sheet resistance of 8.0 Ω/sq and a visible transmission of 81.1%.

The notable result of this study is to change the absorption edges. For the AZO film on the glass slides, the absorption edge showed a red shift and the optical band gap changed from 3.66eV to 3.48eV by roughening. On the other hand, for the AZO on the quartz plate, the absorption edge showed a blue shift and the optical band gap changed from 3.56eV to 3.68eV by roughening. These results suggest a simple method to control a band gap of a material just by grinding surface of substrates.

The possible origin of these shifts can be the difference of thermal expansion coefficients among AZO, glass slides and quartz plate. The difference could cause the thermal stress, which leads to the occurrence of defects inside the film. These defects could change the Al content in the film, which may lead to the shift in the absorption edges due to the Burstein-Moss effect.

We will continue to study an origin of the altered absorption behavior through investigating more details to confirm above hypothesis and will discuss at the conference.

ET07.06.08
Solution-Processed, Shape-Controlled Sb2Se3 Light Absorber for Efficient Photoelectrochemical Water Splitting Wooseok Yang1, Jaemin Park1, Jeiwan Tan1, Hyungsoo Lee1, Yunjung Oh1, Joosun Kim2 and Josho Moon1; 1Yonsei University, Seoul, Korea (the Republic of), 2Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Sb2Se3 is recently spurred great interest as a promising low-cost light-absorbing material for solar energy conversion applications, such as thin film solar cells and photoelectrochemical (PEC) water splitting. The properties of Sb2Se3 strongly depend on its crystallographic orientation and surface morphology due to the anisotropic crystal structure. In this study, we synthesized Sb2Se3 light absorbers with various morphological variation from thin films to 1-D nanostuctures via a simple solution processing with two different Sb-Se molecular solutions. The first molecular solution is synthesized by using the solvent mixture of thioglycolic acid (TGA) and ethanolamine (EA) and the aspect ratio of 1-D Sb2Se3 nanostuctures can be controlled by adjusting the relative mixing ratio of TGA and EA. In the other Sb-Se molecular solution using the mixture of 2-mercaptoethanol and ethylenediamine, adjusting the relative amount of the Se precursor with respect to the Sb precursor results in the significant morphological change. The growth mechanism of the various structures of Sb2Se3 was elucidated by liquid Raman spectroscopy. In addition, electrical and photoelectrochemical properties of the shape-controlled Sb2Se3 were investigated depending on the structures. After deposition of TiO2 and Pt, an appropriately oriented Sb2Se3-based photocathode exhibits a significantly enhanced PEC performance; the photocurrent reached 12.5 mA cm-2 at 0 V versus reversible hydrogen electrode under AM 1.5 G illumination.

ET07.06.09
Assessing Adhesive Degradation in Photovoltaic Backsheets Using the Single Cantilever Beam Test Scott Julien1, Jae Hyun Kim2, Xiaohong Gu2 and Kai-Tai Wan1; 1Northeastern University, Boston, Massachusetts, United States; 2Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The photovoltaic (PV) backsheet, a multilayered polymer sheet that is laminated to the back side of a PV module, is used for protecting the internal components from corrosion and insulating outside users from the internal electrical components. The backsheet is typically comprised of several layers of polymer, adhered or coextruded together. Over prolonged exposure to the elements (extreme temperatures and humidities, and UV radiation), these layers can undergo adhesive degradation, resulting in weakening of the interfaces or delamination, that cause reduced heat dissipation and provide sites for moisture collection. Testing methods are needed in the industry to assess the adhesive durability of new candidate backsheets, and predict their longevity.

In the present work, we assess the interlayer adhesive strength of a polyethylene terephthalate (PET)-based backsheet, using the single cantilever beam (SCB) test. Backsheet samples of PET/PET/ethylene co-vinyl acetate (EVA) were obtained, and exposed to artificial UV radiation in the integrating sphere-based weathering device, located at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, USA. Samples were exposed to between 290-400 nm of light for varying lengths of time, to simulate field-induced UV degradation. SCB tests were then conducted by adhering a titanium beam to the outer layer of the backsheet and pulling the beam at one end, generating delamination at the weakest interface. The applied force, beam end displacement, and location of the “delamination front” were measured, and used to compute the critical adhesion energy of the delaminating interface.

Preliminary results have been obtained for two types of unaged PPE backsheets, of identical model but acquired during different years. The results show a marked difference in adhesion between the two (250-300 J/m2 vs. 1000-3000 J/m2), which illuminates the significant differences in adhesion that can occur with slight changes in manufacture or formulation. These results will be compared to those obtained from the UV-exposed samples, and the results will be used to correlate UV exposure with long-term adhesive durability. Ultimately, this knowledge is of critical need in the community, for developing predictive models of the longevity of PV backsheet samples deployed in the field.

ET07.06.10
Adhesive Durability of Photovoltaic Backsheets as a Function of Indoor Accelerated Weathering Exposure Scott Julien1, Jianfeng Sun1, Yu Wang2, Andrew Fairbrother1, Xiaohong Gu2, Sophie Napoli1, Liang Ji3, Kenneth P. Boyce1, Mike Kempe6, Gregory S. O’Brien1, Adam W. Hauser4 and Kai-Tai Wan1; 1Northeastern University, Boston, Massachusetts, United States; 2Materials Science & Engineering, Case Western Reserve University, Cleveland, Ohio, United States; 3Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 4Arkema, Inc., King of Prussia, Pennsylvania, United States; 5Renewable Energy, Underwriter’s Laboratories Inc., Northbrook, Illinois, United States; 6Photovoltaics Research, National Renewable Energy Laboratory, Golden, Colorado, United States.

Photovoltaic (PV) backsheets are polymer sheets used to protect the backside of a PV module from moisture and mechanical damage. They typically consist of multiple layers of polymers, adhered or coextruded together. Over prolonged exposure to harsh outdoor elements—extreme temperatures and humidity, and ultraviolet (UV) radiation—delamination between the layers of the backsheet can occur. The resulting interlayer voids diminish heat dissipation, reduce the effective thickness of the backsheet as a physical barrier, and serve as collection sites for moisture. There is a need within the PV community for methods to quantify the adhesive integrity of the backsheet.

In the present work, we apply a wedge test to measure the interlayer adhesion energy of backsheet samples exposed to indoor accelerated weathering. Test
coupons are prepared by laminating a backsheet sample to a glass substrate, then exposing it to an indoor accelerated weathering protocol. Wedge tests were performed by adhering a titanium beam to the outer layer of the backsheet, then pulling the beam at one end, generating delamination at the weakest interface. A wedge subsequently inserted into interface was used to drive delamination in a displacement-controlled manner. The location of the “delamination front” was measured at intermittent points, and used—in conjunction with the known elastic properties of the beam and wedge thickness—to compute the adhesion energy of the interface.

Tests were performed on backsheets of several different polymer types, and exposed to several different accelerated weathering conditions. Backsheet polymer types included polyamide (PA)-, polyvinyl fluoride (PVF)-, polyethylene terephthalate (PET)-, and polyvinylidene fluoride (PVDF)-based backsheets. Exposure conditions included several UV protocols (e.g. 65°C at 20% relative humidity (RH) with an irradiance of 0.8 W/m².nm at 340 nm) as well as “dark” protocols (e.g. 85°C at 85% RH). The results show a clear difference in adhesive strength among the different types of backsheet, as well as an observable decrease in adhesive strength with exposure time, for several backsheet types. Furthermore, they show a change in location of the delamination interface with prolonged exposure duration. The results are useful in developing correlations with adhesive degradation measured in field-deployed modules, and are currently being used as part of a large-scale study to develop predictive models for the long-term reliability of PV modules.

Optical and Electrical Properties of Bulk Heterojunction CISe Films Aida Torabi; Texas A&M-Central Texas, Killeen, Texas, United States.

Bulk heterojunction CISe films are being developed as a new candidate for PV applications. The structures of these films are complex with the fabrication process dictating film properties. Herein we present our study on the optical and electrical properties of these materials deposited via electrodeposition. Cathodoluminescence (CL), Electron beam-induced current (EBIC), and energy dispersive X-ray spectroscopy (EDS) were measured from different films. Photoluminescence (PL) measurements were also taken to study large areas of the film. We observed peaks in the luminescence which may correspond to both the n and p semiconductors as well as trap states. These responses were mapped across the film to determine possible fabrication improvements.

The Voltagemmtric Hysteresis Behavior and Potential Scan Rate Dependence of a Dye Sensitized Solar Cells T. M. W. J. Bandara1, Ajith DeSilva2, K. Vignaroonbanh1 and L. N. Senaviratna1; 1Physics, University of Peradeniya, Peradeniya, Sri Lanka; 2Physics, University of West Georgia, Carrollton, Georgia, United States; 3Physics, University of Jaffna, Jaffna, Sri Lanka.

During last three decades the field of dye sensitized solar cells (DSSCs) gained significant advancement; however, there are some unresolved issues related to characterization of DSSCs. For example, the volumetric photovoltaic hysteresis such as current density versus cell potential (J-V) curves, is a serious concern because it is known that the performance of DSSCs depends on the direction and the rate of cell potential scan. The present work is focused on studying the dependence of solar cell performance on the direction and the rate of cell potential scan in a DSSC prepared with a novel gel polymer electrolyte. For this purpose, the photo electrode was prepared by sensitizing TiO2 double layers with NiTiO dye. The new gel polymer electrolyte used in this work is based on polyacrylonitrile (PAN) (Mw. 150,000) tetrahydroammonium iodide, KI, 4-tertbutylpyridine (4TPB), Butyl-3-methylimidazolium iodide (BMI) and plasticizers, propylene carbonate (PC) and ethylene carbonate. J-V characteristics of the cells were obtained by varying the scan rate (from 0.01 to 0.1 V s⁻¹) and the direction (from forward bias to reverse bias and reverse bias to forward bias). The quasi solid state DSSC prepared in this work exhibited short circuit current density, open circuit voltage and efficiency 13.63 mA cm⁻², 0.76 V and 6.4% respectively under 1000 W m⁻² irradiation. The energy conversion efficiency of the DSSC increased from 5.9 to 6.4% with the increase of the scan rate (from 0.01 to 0.1 V s⁻¹), when the scanning is conducted from forward bias to reverse bias direction. However, when the scanning direction is reversed a drop of the efficiency was observed with increasing rate of potential scan. Therefore, different trends of efficiency variation were exhibited with the change of the direction of potential scan. The properties of the electrolyte and the DSSC were characterized further by analyzing complex spectroscopic data. Present work emphasizes the importance of reporting the rate and direction of potential scan with solar cell performance parameter.
adjusting the mass loading of active materials, the capacitance parameters of various electrodes and devices were investigated. Excessive contents of Mn were discovered to be detrimental to ionic transport and Faradaic charge transfer, and inferior capacitance performance has thereby resulted. Mass overloads of active materials were demonstrated to reduce conductivity, leading to worse capacitor characteristics. After calculation by the CV results, the asymmetric solid-state supercapacitor 3-NGM1/G1 exhibited the highest specific capacitance of 579 Fg\(^{-1}\). Its corresponding energy and power densities were 73.6 Whkg\(^{-1}\) and 4400.0 Wkg\(^{-1}\), respectively, implying the good charge-discharge capacity. After 2000 bending cycles of GCD under the current density of 1 Ag\(^{-1}\), the retention rate of specific capacitance was approximately 86.7 %. The high flexibility, cycling stability, and good capacitance properties could be attributed to the synergistic effect of mixed-phase \(\text{MnO}_2\), and nitrogen-containing graphene. By combining the electric double-layer material with a pseudocapacitive material, two charge storage mechanisms were in conjunction to improve charge transfer, conductivity, and thus capacitor performance.

9:00 AM ET07.07.03
**Demonstration of a Self-forming Solid State Rechargeable Li\(_2\)I\(_2\) Battery** Alyson Abraham1, Jianping Huang1, Paul Smith1, Amy C. Marschiliok1,2, Kenneth Takeuchi1 and Esther Takeuchi1,2; Stony Brook University, Stony Brook, New York, United States; Brookhaven National Laboratory, Upton, New York, United States.

Lithium-based battery systems are attractive due to their higher energy densities, however, safety issues resulting from use of organic electrolytes and formation of Li dendrites remain major concerns. Solid-state electrolytes provide an alternative to organic electrolyte, but present their own challenges, including limits in ionic conductivity and the lithium-solid-state electrolyte interface. Self-forming batteries, where the anode and cathode are formed upon charge from a single solid electrolyte, can be a promising avenue to address and reduce interfacial resistance. The Li\(_2\)I\(_2\) couple is an attractive target due to its high energy density (1536 Wh/L, 560 Wh/kg) and opportunity to self-heal. Notably, the primary Li\(_2\)I\(_2\) battery has been a successful technology as the power source for pacemakers.

Herein, we describe a fully self-forming solid-state rechargeable battery based on the Li\(_2\)I\(_2\) couple using LiI rich lithium iodide-(3-hydroxyproprionitrile) electrolyte. To our knowledge, this is the first demonstration of a rechargeable fully self-forming solid-state lithium battery with the inclusion of LiI(HPN)\(_2\). Characterization to verify the formation of the self-forming active battery will be discussed. The impact of variables such as LiI and LiI(HPN)\(_2\) ratio and charging condition on the resulting impedance of the battery system will also be described. These results show promise for the future development of high energy density solid state self-forming self-healing batteries.

9:15 AM ET07.07.04
**3D Interconnected Binder-Free Electrospun MnO@C Nanofibers for Supercapacitor Devices** Najeh K. Allam, American University in Cairo, New Cairo, Egypt.

Rational design of binder-free materials and high cyclic stability are a great need for high-performance supercapacitors. We demonstrate a facile one-step synthesis method of binder-free MnO@C nanofibers as electrodes for supercapacitor applications. The topology of the fabricated nanofibers was investigated using FESEM and HRTEM. The X-ray photoelectron spectroscopy (XPS) and the X-ray diffraction (XRD) analyses confirm the formation of the MnO structure. The electrospun MnO@C electrodes achieve high specific capacitance of 578 Fg\(^{-1}\) at 1 Ag\(^{-1}\) with an outstanding cycling performance. The electrodes also show 127% capacity increasing after 3000 cycles. An asymmetric supercapacitor composed of activated carbon as the negative electrode and MnO@C as the positive electrode shows an ultrahigh energy density of 35.5 Wh/kg with a power density of 10.7 kW/kg. The device shows a superior columbic efficiency, cycle life, and capacity retention.

9:30 AM ET07.07.05
**Electrochemical Supercapacitor Based on a Heterostructure of 1D MoTe\(_2\) Nanowires and Few Layer 2D 1T’-MoTe\(_2\) Sachin A. Pawar1, Dipali Patil1, Donghwan Kim1,2, Tae-Wan Kim1 and Jae Cheol Shin1,2; 1Yeungnam University, Gyeongsan-si, Korea (the Republic of); 2Korea Research Institute of Standards and Science, Daejeon, Korea (the Republic of).

Transition metal dichalcogenides (TMDs) with the layered structures are an analogue of a graphite which consists stacked graphene monolayers. TMDs are having many technologically essential and scientifically amazing properties due to their anisotropy. The layered TMDs demonstrate the most favorable electrochemical properties owing to their better electrical conductivities due to intrinsically layered structure and large surface areas. Among all TMDs viz., S, Se and Te, Te-based TMDs display higher electrical conductivities which are advantageous to enhance the superior performance of electrochemical supercapacitors. The semiconducting nature in S, Se based TMDs and 2H phase largely hinders their electrochemical performance owing to poor electronic conductivity. Moreover, Te-based TMDs as supercapacitors are gaining a lot of attention nowadays with a few reports. Integration of one dimensional (1D) 1T’-MoTe\(_2\) nanowires into few layered two dimensional (2D) 2H MoTe\(_2\) as a multilayer heterostructure can enhance the performance of supercapacitor. Here, we demonstrate the growth of 1D 1T’-MoTe\(_2\) NW/2D 2H MoTe\(_2\) thin film heterostructure through metal organic chemical vapor deposition (MOCVD) on Si/SiO\(_2\) and thereby successful transfer of these heterostructure on flexible nickel (Ni) foam current collector by simple chemical etching protocol for high performance supercapacitor. A layer by layer study of MoTe\(_2\)/MoTe\(_2\) heterostructure is carried out by varying the number of transfer layers on Ni foam. The resultant supercapacitors demonstrate a threefold enhancement in areal capacitance (1412 mFcm\(^{-1}\)) than a single layer transferred electrode with excellent electrochemical stability (96%) and high energy density (140.36 mWcm\(^{-2}\)). These supercapacitors outperform the TMD based (Te-based) supercapacitors presented in the past portraying the abundant potential for energy conversion devices.

9:45 AM ET07.07.06
**Golden, Grey and White Titanias—Controlled Surface Oxidation Towards Visible Light Assisted Water-Splitting** Larissa S. Chaperman, Fayna Mammeri and Souad Ammar; ITO Dys, Université Paris Diderot, Paris, France.

The search for energy alternatives to reduce our dependency on fossil fuels has been a very pressing topic for the last few decades. Despite significant advances, oil remains the most used fuel worldwide, while also being the fuel that emits the most CO\(_2\) apart from coal. [1] In contrast, hydrogen rises as a carbon-free fuel with the highest known energy content, while producing only water as a byproduct. [2] When comparing different routes for hydrogen production, unfortunately the ones that rely on fossil fuels are still the most economically viable, since the low efficiencies of routes that use renewable raw materials or energy sources result in a high cost. [2] The key to balance this equation is to improve the efficiency of cleaner routes such as photo electrolytic water-splitting to make the hydrogen production cheaper and more widespread as fuel alternative. In this work, we propose a controlled surface oxidation of metallic titanium plates as a mean to enable its use as photo anode in visible light assisted water-splitting systems. The different degrees of oxidation and predominant treatment mechanisms led to different characteristics and photoelectrochemical properties of the treated samples, allowing us to tune the oxidized layer and obtain very promising materials. By varying key parameters, we managed to increase the TiO\(_2\) visible light absorption band while keeping its semiconductor behavior, which is crucial to its application in photo electrolytic water-splitting systems.

We show, then, that the structural defects and composition variations generated during the productive process are an effective way to improve the photo
Electrospinning (ES) is a versatile and straightforward process to fabricate high porous membranes with high surface to volume ratio. It is a relatively simple and efficient technique to create continuous fibers at nanoscale. The electrospun fibers are collected in ranges of micro- and nano-meters. Although the ES has been widely studied and the electrospun membranes have been created for many biomaterial and energy applications, the electrospun separators have specific characteristics to meet with the requirements of lithium-ion battery (LIB) separators. The separators are electrochemically inactive but crucial for providing safety to the battery. The primary commercial separator materials for LIB are polyolefin, which is anisotropic. Because of the anisotropic characteristic, it is easily damaged by puncture force, tension force and dendrite growth in a certain direction (transverse). The damages allow internal short circuits leading to battery fire and explosion. Properties of the electrospun membranes in a form of non-woven mats are independent to the membrane characteristic, it is easily damaged by puncture force, tension force and dendrite growth in a certain direction (transverse). The damages allow internal short circuits leading to battery fire and explosion. The overall mission of the CAMP Facility is to enable the transition of new advanced battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 pouch, xx6395 pouch, and 18650 rigid cells). It is an integrated team designed to support production of prototype cells using semi-automated cell fabrication equipment, and includes activities in materials validation, modeling, and diagnostics - it is ideally suited to address this new field of R&D.

Initial focus here is on coating ceramic-based films onto the negative electrode. Later efforts may include developing methods of coating functional materials and/or polymer films onto negative or positive electrodes. Two ceramic materials (Al2O3 and MgO) were chosen to scope out the techniques needed for coating onto graphite electrodes. These ceramics are relatively benign in a typical lithium-ion battery system, and could thus serve the purpose of functioning as an added safety refractory layer to support a standard polymer separator during thermal abuse, or as a complete replacement of the polymer separator. Other ceramic materials were used later. In the work presented here, a PVDF-based slurry was used to adhere the ceramic particles to the graphite electrode.

Early coating attempts used a hand coating (doctor blade) method. Attempts were made with a roll-to-roll reverse-comma coater, but process issues arose. Other coating technologies are needed to enhance the coating process, which will be discussed in the presentation. Successful coatings were used in various electrochemical tests in prototype cells (coin & pouch), with and without separators, versus cathodes and lithium counter electrodes. The results from these cell tests are promising. In addition, Argonne's state-of-the-art facility in battery failure analysis (Post-Test Facility - PTF) inspected the interface between the anode and ceramic layer. These results will also be discussed in more detail.

Support from Peter Faguy, Steven Boyd, and David Howell of the Department of Energy’s Vehicle Technologies Office is gratefully acknowledged.

11:00 AM ET07.07.08
Electrospinning Process for Lithium-Ion Battery Electrodes Wisawat Keaswejjareansuk1, Jianyu Liang1 and Xiang Wang2; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2Department of Material Science and Engineering, Wuhan University of Technology, Wuhan, China.

Electrospinning is a versatile and straightforward process to fabricate high porous membranes with high surface to volume ratio. It is a relatively simple and efficient technique to create continuous fibers at nanoscale. The electrospun fibers are collected in ranges of micro- and nano-meters. Although the ES has been widely studied and the electrospun membranes have been created for many biomaterial and energy applications, the electrospun separators have specific characteristics to meet with the requirements of lithium-ion battery (LIB) separators. The separators are electrochemically inactive but crucial for providing safety to the battery. The primary commercial separator materials for LIB are polyolefin, which is anisotropic. Because of the anisotropic characteristic, it is easily damaged by puncture force, tension force and dendrite growth in a certain direction (transverse). The damages allow internal short circuits leading to battery fire and explosion. Properties of the electrospun membranes in a form of non-woven mats are independent to the membrane directions. The operation principle of the ES is simply a high electric potential is applied to a spinneret, which is connected to a polymer solution syringe. Polymer solution is fed by a syringe pump and spun in the electric field. The charged spun solution is elongated to a fiber-like jet, and then collected on a collector. The characteristics and properties of the electrospun membrane can be customized by simultaneously adjusting the materials parameters and regulating the process parameters. The material parameters are types of polymer, solvent systems and concentration of polymer solution. The process parameters include electric potential, spinneret-to-collector distance, solution feed rate and collector configuration. In this presentation, we will briefly explain the requirements of LIB separators and discuss in detail the effects of material and process parameters, the process control, and characterizations for customized electrospun separators’ characteristics and properties.

11:15 AM ET07.07.09
Ultra Lightweight, High Power Density Lithium-Ion Batteries Mihai Duduta, Sebastien de Rivaz, David Clarke and Robert Wood; Harvard University, Cambridge, Massachusetts, United States.

Existing fabrication technologies cannot be used to make lightweight, high power density lithium ion batteries (>300mg). The need is increasing for these small, powerful batteries, as advances in fabrication techniques push the limits of miniaturization in robotics, haptics, wearable and biomedical technologies, and mobile computing for the Internet of Things. Unfortunately, current fabrication methods for lithium ion cells force the end user to make a choice between high energy density and lightweight batteries. Supercapacitors can provide even higher power density (>10 kW/kg), but have very short discharge times (0.1 - 5s) which limits the range of potential applications. To push the limits of performance, we have developed a hybrid manufacturing approach which uses commercially available lithium ion materials and a laser micro machining method to build lightweight (10-200 mg) high power...
Conversion of dissipated heat into electricity is the basic principle of thermoelectricity. It has wide variety of applications in the areas such as automobile engineering, refrigerating coolants, satellite etc. These days there is a high demand of materials which are efficient in converting heat in to electricity [1]. In search of such materials thermoelectrics has given wide scope to complex materials like Tellurides, Clatharates, Zintl compounds, Half Heusler alloys, Silicides, Skutterudite etc. The defining factor for thermoelectric materials is ZT, thermoelectric figure of merit. This attributes to the power factor (electrical conductivity S-Seebbeck coefficient enhancement and thermal conductivity reduction). Band gap tailoring, carrier concentration are a few ways to improve power factor where as in parallel, grain size reduction, point defects, dislocations are key ways to thermal conductivity reduction. These can be achieved experimentally through microstructural engineering and processing [2]. The issues existing with available thermoelectric materials are associated with stability of performance for a long range of temperatures. Fine tuning of microstructure is the key factor in overcoming the thermal stability issues.

Currently we are exploring a program of microstructure-transport properties correlation of newly processed thermoelectric alloys by fine tuning the eutectic microstructure. In this current work, we have synthesized a set of thermoelectric alloys eutectic and off eutectic compositions in Sn-Te alloy system (Sn₄Te₉ (at%)) [3]. These as melted alloys show eutectic microstructure consisting of Sn₅₀Te₅₀ and Te phase with varied volume fraction. Variations of transport properties with respect to secondary phase fraction have also been studied. Eutectic microstructure with different phase boundary will always help in minimizing lattice thermal conductivity by disrupting phononic movement. Hypo and Hyper eutectic composition are (Sn₂₀Te₈₀ (at%)) and (Sn₄₅Te₅₅ (at%))

The elemental distribution mapping and the compositional analysis using electron probe microanalysis (WDS), demonstrates that the matrix is rich in tellurium and the continuous phase has the composition of Sn₅₀Te₅₀ (at%). Transport properties of the current alloy are attractive in terms of standard thermoelectric material(S−133µV/K and P−3µW/cm-K² at 420oK). We are presently calculating Figure of Merit and detailed structural characterization of this alloy. Further attempts are being made for achieving more improved properties by elemental additions and fine tuning the microstructure. The detailed microstructure-transport properties correlation will be presented.

Acknowledgement: The authors would like to acknowledge the facility of the AFMM.

References:

from the surface down to the current collector interface. Furthermore, LIBS provides a great potential for enabling advanced fundamental studies on 3D electrode micro-structures for discovering their impact on performance enhancements regarding battery life-time and capacity as a function of electrochemical cycling parameters. In general, the main objective is to develop an optimized 3D cell design with improved electrochemical properties, which can be correlated to a characteristic lithium distribution along the laser generated 3D architectures. For this purpose, 3D elemental imaging and depth profiling was performed for the entire electrode. The measurements were carried out in ambient air, applying a multivariate calibration technique “Partial Least Squares Regression”. It could be clearly shown that the generation of 3D architectures tremendously influences the electrochemical performance. Results achieved from post-mortem studies will be presented for cells with unstructured and laser-structured electrodes.

2:30 PM BREAK

3:30 PM *ET07.08.03
Critical Size Scale and Effects of Manufacturing Defects on Plating in Li-Ion Batteries Craig B. Arnold; Princeton University, Princeton, New Jersey, United States.

Lithium plating is an important degradation mechanism in Li-ion batteries that not only reduces battery capacity, but also can lead to catastrophic failures. The plated lithium can turn into dendrites and gradually grow through the separator, leading to a short circuit. In this study, we show that certain types of manufacturing defects can create conditions favorable to enhanced lithium plating in these cells under normal cycling conditions due to transport gradients within the systems. In particular, we explore effects of defect size and distribution within the cell and the corresponding effect on the plating behavior. Below a critical defect size, plating is unlikely to occur and we develop a simple phenomenological approach to guide manufacturing and quality control in assessing this situation for a given battery cell. Such studies help elucidate the fundamentals behind heterogeneous plating and can provide practical insights into battery safety and product control.

4:00 PM *ET07.08.04
Observing the Volume Change Process of Si/C Electrode by In Situ SEM at Elevated Temperature Yuefei Zhang1, Rui Wu1, Hui Feng Shi3 and Yijing Zheng2; 1Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing, China; 2Karlsruhe Institute of Technology, Karlsruhe, Germany.

Compared to the conventional graphite electrode, the silicon-carbon electrode has attracted much interest from researchers due to its high theoretical capacity. However, the Si/C composite electrode is still limited by the low rate capability and cyclability induced by the microstructural challenges such as mechanical failure, SEI crack, and low ionics kinetics, et al. Since the volume expansion rate of silicon is about 300% during charging and discharging, while graphite only expands by 10%, the different expansion rate could lead to poor contact of the electrodes and even pulverization. Among all the improved methods, 3D-structured electrode could potentially alleviate the structural damage caused by volume expansion through the empty space formed by the high-energy laser beam. Therefore, understanding the precise evolution mechanisms of 3D electrode under working conditions and its possible failure mode during the charge/discharge process helps researchers to improve the performance of batteries more purposefully.

The in-situ, real-time, dynamical studying of electrode can directly provide the evidence of structure evolution under charge-discharge cycles. Here, we use the self-developed joint SEM-electrochemical system with the temperature controller to observe the morphological evolution of 3D Si/C composites electrodes. According to the experiment results, we found the separation process of active materials from current collectors because of the electrode’s volume expansion, which leads by the insertion of lithium ion, and the separation direction is from edge to center. As temperature rise from 20°C to 60°C, the discharge voltage platform and discharge time also increase due to the more intense ion movement. Besides, the electrode with 3D structured has better cycle performance than the ordinary plane electrode.

4:30 PM ET07.08.05
Geometry and Size Dependence of Transport Non-Uniformities on Localized Plating Xinyi M. Liu, Alta Fang, Mikko Haataja and Craig B. Arnold; Princeton University, Princeton, New Jersey, United States.

Lithium plating, the formation of metallic lithium, is an important degradation mechanism that not only reduces battery capacity but also can lead to catastrophic failures. While most lithium plating can be prevented under normal cycling conditions, it is difficult to avoid localized plating. In previous work, we demonstrated that the heterogeneity of materials or defects in cells can create non-uniform ionic transport, leading to regions with high current densities and therefore induce plating [1]. In this work, we look further into the importance of the size scale and geometry of transport non-uniformity on localized plating, and directly relate the size scale to the capacity fade of a battery.

We create transport non-uniformities by mechanically compressing separators to close all the pores and cutting the compressed separators into different patterns and sizes. The compressed separator defects were then placed inside the coin cell along with a pristine layer of separator. After a number of cycles, cells were disassembled to record the amount of plating on the electrode surface.

In this work, we show that certain geometric features are more vulnerable to plating than others and localization strongly depends on size[2]. A single continuous feature in a separator induces more plating than a collection of smaller features with same total area. By defining a simple IE ratio, which is a characteristic of size and geometry, we relate the ratio to the propensity of plating. A region with a high IE ratio means more concentrated ionic flow and is more vulnerable to plating. A large defect feature induces more capacity fade of a battery than a small feature. We also demonstrate numerically and experimentally that there exists a critical size scale below which localized plating is unlikely to occur, and such critical size depends on the current density. Finally, we look into the interactions between multiple features that are spaced at various distances. This work not only elucidate the fundamentals behind localization, but also provide insights into battery safety and product control.


4:45 PM ET07.08.06
Laser-Engineering and -Analytics in Electrode Manufacturing for Lithium-Ion Batteries Wilhelm Pfleging1,2, Peter Smyrek1,2, Yijing Zheng1, Jan-Hendric Rakebrandt1, Yangping Sheng1, Marissa Wood1, David Wood1, Jianlin Li3 and Hans J. Seifert1; 1IAM-AWP, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Karlsruhe Nano Micro Facility, Eggenstein-Leopoldshafen, Germany; 3Energy & Transportation Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.
So far, high production costs, restricted process reliability, small energy and power density, and short operational lifetime are the main issues of lithium-ion batteries (LIBs). Manufacturing of thick film electrodes is one suitable approach for achieving high-energy densities in LIBs. However, thick film electrodes suffer from electrolyte transfer limitations. Therefore, electrodes with film thickness of about 40-50 μm are currently used for high-power operation while thick film electrodes (thickness ≥100 μm) are developed for high-energy applications. LIBs with high-energy and high-power density can be realized by introducing a three-dimensional (3D) battery concept, which offers an improved electrolyte transfer in thick film electrodes and an improved lithium-ion transport kinetic. For developing next generation batteries, the 3D battery concept, originally invented for micro-batteries, will be transferred to LIBs with large footprint areas. For this purpose, laser materials processing was recently introduced in research and industry enabling advanced design rules for new and state-of-the-art electrode materials. A significant increase of active surface area in lithium-ion cells is achieved by direct ultrafast laser-assisted structuring of composite electrodes. 3D micro-structures and capacillary features in thick film anodes and cathodes are formed in order to shorten the electrolyte diffusion distance and consequently for the improvement of rate performance. The electrochemical performance of lithium-ion cells (coin cells, pouch cells) with laser-structured electrodes were analyzed and compared to cells with unstructured electrodes. The 3D micro-structured electrodes demonstrate high rate capability and an improved liquid electrolyte wetting. Laser-induced breakdown spectroscopy was applied as an analytical tool for chemical characterization of entire electrodes. Elemental mappings were performed for the development of coating processes. Additionally, post-mortem studies were carried out for investigating degradation processes related to thick film electrodes.

SESSION ET07.09: Poster Session III: Energy Conversion and Applications
Session Chairs: Corie Cobb and Yijing Zheng
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET07.09.01 Diffusion Controlled Molecular Doping in Conjugated Polymers and Its Effect on Thermoelectric Power Jaehong Park1, Yeonggwon Kang1, Sang Eun Yoo1, So Yoon Noh2, Joongwoo Park3, Dae Woon Lee2, Taekyeong Kim4, Gun-Ho Kim5, Dong Wook Chang5, Jong H. Kim5 and Bong-Gi Kim5
1Department of Organic and Nano System Engineering, Konkuk University, Seoul, Korea (the Republic of); 2Department of Molecular Science and Technology, Ajou University, Suwon, Korea (the Republic of); 3School of Mechanical, Aerospace and Nuclear Engineering, UNIST, Ulsan, Korea (the Republic of); 4Department of Physics, Hankuk University of Foreign Studies, Yongin, Korea (the Republic of); 5Department of Industrial Chemistry, Pukyong National University, Busan, Korea (the Republic of).

The low dielectric constant of organic materials and inhomogeneous distribution of molecular dopants in a conductive matrix impose difficulties in populating free charge carriers in organic materials, leading to practical challenges in developing highly conductive organic materials. We designed two different CPs with long side chains and an electron-donating isodindoloindole derivative in a way that the CPs strongly interact with molecular dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethan (F4-TCNQ), and the doping efficiency was further enhanced through sequential doping to promote the diffusion degree of F4-TCNQ. With these strategies, electrical conductivities of the doped CPs films were significantly improved (over 140 S cm⁻¹), much larger than that obtained from the conventional blending approach (5 S cm⁻¹). Furthermore, the doping level is scalable with the exposure duration in the ET07.09.02 Mustard Seed Based Triboelectric Nanogenerator Sachin K. Singh1, Subas Muduli2, Ramamurthy Boomishankar2 and Satishchandra Ogale2
1Chemistry, Indian Institute of Science Education Research, Pune, India; 2Physics, Indian Institute of Science Education and Research, Pune, India.

Mechanical energy from a local domain is seldom recovered due to its fluctuating amplitude and low frequency and is therefore usually designated as “unsystematic” energy. With several new ideas and device schemes introduced by Z. L. Wang and coworkers as well as others, it has now become feasible to tap such energy systematically. Herein we introduce an idea of using mustard seeds as a vehicle for construction of a green Triboelectric Nano Generator (TENG). There have been only a few attempts to make such devices using natural materials.1,2 Mustard seeds shells charge highly by friction and hence are susceptible to charge separation, a property that we have utilized in our device.

The flexible TENG furnished an impressive output voltage of 50 V and a maximum current of 5.25 μA. The seed-TENG with good adaptability rendered the maximum output power of 45μWcm⁻², which is capable of driving advertising LEDs and commercial electronic temperature sensors.

ET07.09.03 SLIPS-Designed Electrodes in Monolithic PV-Electrolysis Water Splitting System for Membraneless Gas Separation, Transport and Collection Ki Duk Han, Sangkuk Kim, YongJae Jeung, Seunghyeon Bae, HyunSik Moon and Kijung Yong; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Recently, PV-electrolysis is attracting much attention as a potential method for hydrogen production by water splitting due to high solar to hydrogen conversion (STH) efficiency. Although there are remarkable advances in modular performance and multifunctional design of PV-electrolysis systems, this artificial leaf system still has critical issues associated with product gas separation. In current monolithic PV-electrolysis modules, the H₂ gas product is inevitably mixed with the O₂ gas. Therefore, in order to obtain pure H₂ gas fuel, additional energy is required for gas separation, such as application of high cost, complex membrane system. To overcome this problem, we invented a simple and very compact gas separation system for monolithic PV electrolysis, which is based on biomimetic surface design. The key idea is adopting slippery lubricant-impregnated porous surface (SLIPS) in designing hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) electrodes, which enables gas bubble manipulation, separation and collection. When H₂ and O₂ gases are generated at the respective SLIPS-edged, inclined HER and OER electrodes, buoyancy drives gas bubbles to move up along each slope of the electrode. In this process, SLIPS-tracks deposited on the lateral edges of cathode electrode catch and transport gas bubbles along the inclined electrodes.
surface to the collection port and prevent air bubbles from escaping and cross-over from the electrode surface. Due to this smart design of electrodes, most generated H2 and O2 gases could be successfully collected at each product port without crossing or loss. Our monolithic PV-electrolysis device could capture, transport and collect H2 and O2 gases very efficiently with a separation efficiency of over 90%. Furthermore, we have realized a monolithic PV-electrolysis system with membraneless gas separation by combining the interconnected CuInS2 (CIS) PV cell with inclined HER/OER electrodes consisting of an inverted triangle configuration. This unique membrane-free artificial leaf encapsulates free space inside and can float on the surface of the water, providing additional benefits such as total light utilization and reusability.

ET07.09.04
Near-Surface Water Currents Based Triboelectric Nanogenerators
Abdelsalam Ahmed1, Islam M. Hassan1, Ali Radhi1 and Jean Zu2; 1University of Toronto, Toronto, Ontario, Canada; 2Stevens Institute of Technology, Hoboken, New Jersey, United States.

This work presents an entirely parallel network of triboelectric nanogenerators (TENGs) for functional hydrokinetic energy harvesting from near-surface water currents. To the best of our knowledge, this is the first report on using the near-surface water current as a potential energy source. The TENG operates with a free-standing mode with low-cost fabrication and high throughput from incidental water currents. The device is designed for a single unit to contain four TENG components operated in parallel for use within the neritic zone of the ocean. The hybridized TENG parallel network within a single underwater TENG unit attained a voltage of 400 V, a current of 0.8 mA and generated power of 0.2 W, approximately. The observed hydrokinetic power harvesting performance is one of the highest achieved with TENG technology, suggesting significant potential for portable coastal and shallow water applications in sustainable and underwater self-powered sensors.

ET07.09.05
Synthesis and Photocatalytic Properties of Semiconducting Composite Powder
Kensuke Akiyama1,2, Sakiko Nojima1, Ryo Takahashi1, Hiroshi Funakubo2 and Hiroshi Irie1; 1Kanagawa Institute of Industrial Science and Technology, Ebina, Japan; 2Materials Science and Engineering School, Tokyo Institute of Technology, Yokohama, Japan; 3Clean Energy Research Center, University of Yamanashi, Kofu, Japan.

Photocatalytic water-splitting is an ideal method for solar energy harvesting. Some photocatalysts that can split water under UV light have been discovered. However, development of visible-light sensitive photocatalysts is indispensable due to the effective utilization of incoming solar energy. On the other hand, semiconducting iron disilicide (β-FeSi2) has a band gap of approximately 0.80 eV and a very large optical absorption coefficient over 105 cm−1 at 1 eV. Moreover, it has recently been reported that this semiconducting material acts as a hydrogen-evolution photocatalyst. As a hydrogen-evolution photocatalyst, β-FeSi2 is expected to enable the use of infrared light longer than 1300 nm, which is the longest wavelength of light to be utilized. This semiconducting material is composed of the elements which are naturally abundant and less toxic than the elements used in conventional compound semiconductors.

In this paper, we report on the novel fabrication method of β-FeSi2/SiC composite powder by using metal-organic chemical vapor deposition (MOCVD) method which is general in semiconductor process technology. Moreover, we report on the hydrogen evolution over this composite powder under irradiation of not only UV but also visible light and near-infrared light from methyl-alcohol aqueous solution. 10-nm-thick gold (Au) was deposited on the surface of SiC powder, average diameter of 60 nm, at room temperature by rf-sputtering. β-FeSi2 was deposited on the Au-coated SiC powder by using metal organic chemical vapor deposition (MOCVD) method. Iron pentacarbonyl [Fe(CO)5] and monosilane (SiH4) were used as sources, and the substrate temperature was 923K and the deposition rate was 1.6 nm/min, respectively. ARD 8-20 scan profile showed the formation of poly-crystalline β-FeSi2 phase for the powder after MOCVD deposition of 1 hour. From the SEM observation of this composite powder, the inhomogeneous grains with sizes of the order 10 nanometers were confirmed to be formed on the SiC surface. The hydrogen gas was evolved by irradiation of UV light (250-430 nm) from methyl-alcohol aqueous solution. Moreover, similar hydrogen evolution was confirmed under visible light (420-650 nm) and near-infrared light (1050-1600 nm) light irradiation.

ET07.09.06
Spectroscopic Study for Hydrophilic Surface of TiO2: Photocatalysts Modified with Au Nanoparticles
Hayato Kondo, Yosuke Kageshima and Hiromasa Nishikiori; Department of Engineering, Graduate School of Science and Technology, Shinshu University, Nagano, Japan.

Semiconductor photocatalytic materials have attracted a great attention as a promising approach to solve worldwide energy and environmental issues derived from mass consumption of fossil fuels. Above all, there are tremendous reports about TiO2 photocatalysts. It is well-known that TiO2 exhibits high photochemical activity and durability and is capable of driving decomposition of organic compounds and formation of hydrophilic surface under illumination of UV light. These unique characteristics enable us to utilize TiO2 for various applications of environmental cleanup (i.e., air purification, water purification, and antibacterial self-cleaning), as well as energy conversion (i.e., dye-sensitized solar cells and water splitting). Although hydrophilic surface of TiO2 under UV irradiation should play an important role for its photocatalytic properties, detailed mechanisms and processes for expression of hydrophilic TiO2 surface are still unclear. Therefore, in this report, expression mechanisms of hydrophilic surface of TiO2 photocatalysts modified with Au nanoparticles were studied via the spectroscopic measurements. Here, it should be noted that Au nanoparticles were modified in order to increase the sensitivity for spectroscopic measurements by surface plasmon resonance. TiO2 particles (P25, Nippon Aerosil) were coated by Au nanoparticles via the photodeposition method. The TiO2 particles were suspended in an aqueous solution containing Au salt, such as AuCl3, and irradiated by UV light for various duration, followed by filtration, drying, and annealing in air. The objective Au/TiO2 particles modified with Au were referred to as Au/TiO2 hereafter. IR spectra of the surface hydroxyl group on Au/TiO2 showed the formation of hydrophilic surface on Au/TiO2, expression mechanisms of hydrophilic surface will be discussed.

References

ET07.09.07
High-Efficiency Power Conditioning System for Autonomous Triboelectric Nanogenerator Devices
Aravind Ravichandran and Marc Ramaz; EMSE-CMP, Gardanne, France.

With the rapid development of wearable electronics and sensor networks, batteries cannot meet the sustainable energy requirements due to their limited lifetime, size and degradation. With miniaturization leading to high-power and robustness, triboelectric nanogeners (TENGs) have been conceived as a promising technology by harvesting mechanical energy for powering small electronic systems. However, low output power conversion efficiency has
restricted its practical application because of its own extremely high output impedance.

In this work, a state of the art high efficient power conditioning system is proposed which increases the conversion efficiency by 60% but also with lower impedance matching. Our work represents a nomenclature in the process and experimental methods to achieve effective energy harvesting and storage by TENGs.

In order to solve the limited life problem of typical battery power supply, an autonomous device is conceptualized that is based on the environmental energy harvesting has emerged as an amazing power supply approach. In order to match the high output impedance of TENGs and increase the output power, this work presents a highly efficient power conditioning system, which is composed of a diode rectifier bridge, a control circuit, impedance matching circuit and an energy storage device. Experimental results show that, in less than 3 secs, the storage capacitor reached a voltage of 5 V by the proposed conditioning technique. The charging efficiency increased by 60%.

By considering these merits of simple fabrication, outstanding performance, robust characteristic and low-cost technology, we believe that advanced power management of TENGs can open up great opportunities not only for powering small electronics but can contribute to large-scale energy harvesting through engineering design being complementary to existing energy sources allowing clean and uninterrupted energy production.

ET07.09.08 Fabrication of Nanoscale Multilayered Thin Film Based Integrated Triboelectric Devices Alandria Henderson, Joevonte Kimbrough, Kenneth Davis, Zackary Duncan, John Elie, Sam Chance, Brandon Whitaker, Michael Howard, Michael Glenn, TeAndrea Wimbley and Zhigang Xiao; Electrical Engineering and Computer Science, Alabama A&M University, Normal, Alabama, United States.

We report the growth of nanoscale multilayered triboelectric thin films and fabrication of integrated triboelectric devices for high-efficiency energy conversion. Nanoscale multilayered thin films such as $\text{Sb}/\text{Sb}_2\text{Te}_3$ and $\text{Te}/\text{Bi}_2\text{Te}_3$ thin films were grown using the e-beam evaporation. Integrated triboelectric devices were fabricated with the nanoscale multilayered thin films using the clean room-based microfabrication techniques such as UV lithography. X-ray diffraction and reflection and high-resolution tunneling electron micrograph (HR-TEM) were used to analyze the e-beam-grown nanoscale multilayered thin films. SEM was used to image and analyze the fabricated devices. The open-circuit voltage and output power produced from the fabricated devices will be measured and analyzed, and highly-efficient triboelectric thin-film materials and integrated devices will be demonstrated and reported.

ET07.09.09 Triboelectrically Self-Powered, Structural Carbon-Fiber-Reinforced Composites Seonghwan Lee¹, Changyoon Jeong¹, Maria Q. Feng² and Young-Bin Park²; ¹Mechanical Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); ²Columbia University, New York, New York, United States.

As fossil fuel depletion is accelerating and energy saving is becoming increasingly critical, intensive efforts are being made to develop environmentally friendly, ultra-lightweight materials for applications in weight-sensitive structures, such as automobiles, aircraft, ships and civil structures. Carbon-fiber-reinforced plastic (CFRP), which is an ultra-lightweight material with a density only a fraction of steel, is well suited for structural applications, where a high strength-to-weight ratio is demanded. Here, we present a proof-of-concept study and demonstration of multi-functional CFRPs that serve as the “structural electrodes” – owing to the high electrical conductivity of carbon fibers - in a triboelectric generator system. If a dielectric material is deposited on the CFRP electrodes and rubbed against one another, the surfaces of the two dielectrics become oppositely charged, and the change in the gap between the two dielectrics induces electrostatic induction. This leads to the accumulation of negative charges along the carbon fiber electrode, thus, generating the electrical energy. Harvesting energy from friction allows high efficiency at low frequency, affordability and low weight due to relatively simple mechanisms and implementation, and this adds a great value and functionality to lightweight, structural CFRPs. The self-powered CFRPs transform the abandoned mechanical energy into usable electrical energy, which will find numerous applications where repetitive loading-unloading is applied, including power-generating speed bumps, roads, railways, doormats, and vibrating structures.

Acknowledgments
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science and ICT, Korea (NRF-2017R1A5A1015311) and the 2018 Research Fund (1.180015) of UNIST (Ulsan National Institute of Science and Technology).

SESSION ET07.10: Novel Fabrication for Energy Devices
Session Chairs: Wilhelm Pfleging and Yijing Zheng
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 312

8:30 AM *ET07.10.01 Challenges and Opportunities in Primary Electrodeposition of Lithium Films for Secondary Batteries Daniel Steingart and Wesley Chang; Princeton University, Princeton, New Jersey, United States.

In theory, a clear pathway to improving the energy density of lithium based electrochemical energy storage is replacing the intercalation or alloy host negative electrode with lithium metal itself. The challenges of realizing a version of this electrode suitable for secondary batteries are manifold and most are well documented. A practical aspect that receives less attention, however, is how one creates a lithium foil in a practical manner thin enough to leverage the energy density advantages without “overbuilding” the negative electrode.

Electrodeposition is a well established industrial process for creating metal films and foils of thicknesses from nanometers to millimeters, but the reactivity of lithium has made it difficult to use electrodeposition to produce lithium from an electro refining setup or a primary electrowinning process. In this presentation we demonstrate an multi-electrolyte system which can electrodeposit function lithium films from 5 nm to 20 nm, and explore the morphologies and electrochemical behaviors of these films.

9:00 AM *ET07.10.02 From Laboratory to Industrial Manufacturing—Scale-Up Production of Advanced Lithium-Ion Batteries Marcus Jahn and Corina E. Täubert;
Austrian Institute of Technology GmbH, Vienna, Austria.

The rising need for advanced energy storage solutions due to the increased electrification of global car brands has not only highlighted the need for more materials research, but also increased innovation to bring such novel materials into production. The often-non-trivial scale-up process has become more important and is bridging the gap along the chain of technology readiness levels that is observed between fundamental research efforts and innovation actions taken by industry. In this work the critical manufacturing steps and scale-up parameters for Lithium-Ion battery manufacturing are analysed. Influencing parameters from materials to process are portrayed with particular focus on advanced, as well as post-lithium ion battery materials. Conventional manufacturing techniques are presented and critical parameters are identified, which are often ignored during the fundamental research stage of materials development. Advanced mixing and coating technologies are presented as well as electrode design work applied in order to increase energy or power density at a cell level. There is a rising need for moving away from conventional manufacturing methods to accommodate novel systems, such as all-solid-state batteries, but also to fulfill the demanding requirements for current storage systems, which push the limits of modern day cell chemistries. The need for increased energy density can not only be addressed on a materials level, but also on a manufacturing and processing level, which is part of the work conducted at the Research Pilot Line at AIT. This work shows how research pilot lines for Lithium-Ion battery manufacturing have become increasingly important, especially in Europe, and are considered a key enabler of the future of electric vehicles and to the success of the research needed to meet tomorrow’s demands in energy storage.

9:30 AM ET07.10.03
Thin Continuous Films Built Using Electro spray Atomization of Nanoparticle Aggregates Yaqun Zhu and Paul Chiarot; Mechanical Engineering, Binghamton University, Binghamton, New York, United States.

Using electrospray atomization, we have built thin continuous films with controllable nano- and micro-structure from nanoparticle aggregates. The aggregates were assembled in-flight (i.e. after electrospray emission) and delivered to a target substrate in a dry state. Our research provides insights into the nanoparticle aggregation and thin film deposition phenomena for varying aggregate sizes and morphologies. Titanium dioxide nanoparticles (p25, ~21 nm) were used as a model system given their importance in photovoltaic applications. We have discovered the relationship among all the essential operating parameters and the micro-/nano-structure of the aggregates and films. We reveal how properties such as nanoparticle concentration, solvent volatility, Taylor cone pulsation frequency, and substrate electrical properties (among others) govern the size and morphology of an individual aggregate. We then further report how the aggregate size and morphology governs the structure of the continuous film. Aggregates formed using electrospray possess an excess electric charge that can be maintained after deposition on to the target substrate. We found that this charge accumulation and its decay rate play a significant role in the film formation. For example, films on a conducting substrate are thick and exhibit periodic islands. In contrast, films on semiconducting and insulating substrates are thin and tend to be uniform. To further probe the influence of charge accumulation, we used “periodic printing” (i.e. periodically turning the electrospray on-and-off during deposition). The structure of the films was significantly different when printing periodically compared to continuous printing. This further highlights the strong influence of the excess charge on deposit structure.

9:45 AM ET07.10.04
Large-Scale Printing of Micro-Wire Electrodes for Roll-to-Roll Manufacturing of Transparent Electrodynamic Screen (EDS) Films for Self-Cleaning Solar Collectors Malay K. Mazumder, Caroline Ellinger, Kevin O’Connor, Sean Garner, Julius Yellowhair, Ryan Eriksen, Annie Rabi Bernard, Cristian Morales, Mark Horenstein and Ramakrishnan Lakshmanan; 1Boston University, Boston, Massachusetts, United States; 2Eastman Kodak Company, Rochester, New York, United States; 3Corning Research and Development Center, Corning, New York, United States; 4Sandia National Laboratories, Albuquerque, New Mexico, United States.

A Manufacturing process for producing Transparent Electrodynamic Screen (EDS) films by flexographic printing of micro-wire electrodes on optically clear dielectric films is discussed. The EDS film consists of a series of parallel transparent electrodes embedded between two transparent dielectric layers, which can then be retrofitted or integrated onto the optical surfaces of solar collectors, such as CSP mirrors and PV Modules. Activation of the electrodes by phased voltage pulses creates a non-uniform electric field distribution on the EDS film surface, which charges and levitates the dust particles and then removes the dust layer by a sweeping action of the traveling electric field created by the three-phase drive. Application of EDS film provides water-free cleaning as frequently as needed to maintain high optical efficiency of solar mirrors and solar panels minimizing energy-yield losses caused by dust deposition. Silver nanowire (AgNW) and passivated Cu micro-wire (micro-wire) electrodes were used as scalable and durable inks for solar field applications of EDS films. We screen-printed AgNW ink electrode directly on Willow Glass (Corning) film for producing lab-scale EDS films. For commercializing the technology, an existing roll-to-roll production facility at Eastman Kodak was used. EDS films were produced in medium scale (26 cm x 30 cm) with catalyst electrodes using flexographic printing on PET films. After printing, the substrate is conveyed through a touchless plating line where electroless copper is deposited on the printed catalyst pattern. The deposited copper is treated in-line with an environmental passivation and darkening agent, simultaneously protecting the micro-wires from corrosion and minimizing front-side reflection with a neutral color, all without contacting a roller to minimize the risk of conveyance related defect formation. For laminating the film on an optical surface of a solar collector, the following architecture of the EDS film is used: Willow Glass (sun facing)/Optically Clear Adhesive (OCA)/Kodak-printed EDS electrodes on PET substrate/ OCA laminated on a solar panel or a mirror. The electrodes of the EDS film are connected to a compact power supply unit. A single power supply unit may serve several holoists or PV modules. Cleaning operation can be activated automatically or manually from a control room without any interruption of the plant operation or human labor. Laboratory- and field- evaluations show that the EDS films can be operated in a wide range of ambient temperature (range of PV module application), relative humidity (varying from 20 to 70% RH and RH cycling) in an environmental chamber used for simulating conditions of solar fields. Limited field evaluations were carried out at the National Solar Thermal Test Facility located at the Sandia National Lab in New Mexico and at the Atacama Desert solar fields in Chile. Experimental data taken with EDS film laminated solar collectors would be presented showing (1) dust removal efficiency ≥ 90%; for solar mirrors: (2) specular reflection (SR) efficiency ≥ 90%; (3) specular reflection restoration (SRR) efficiency ≥ 90% and for solar panels: (4) the light transmission efficiency (TE) ≥ 90%; and (5) output power restoration (OPR) efficiency ≥ 95%. Each cleaning cycle requires less than two minutes and expends a negligible amount of energy (0.2 Wh/m2/cleaning cycle).

10:00 AM BREAK

10:30 AM *ET07.10.05
Investigation of Additive Distribution in Electrodes for Lithium-Ion Batteries Werner Bauer; Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

The performance of lithium-ion batteries is not only determined by the used active cathode and anode materials, as these components only set the maximum achievable values for capacity and rate capability. The energy and power densities actually achieved in the cells are influenced primarily by the inactive additives and by the processing conditions. In order to understand the impact of additives and processing on cell properties, it is necessary not only to know material specific properties but also to analyze the entire structure of the electrodes. From this, it is feasible to derive processing-structure-property relationships that can close the understanding gap between the applied processing conditions and the resulting electrodes properties.
Structural and chemical investigations of electrodes can be carried out on different length scales. The study of interface effects, such as contact resistance or binder adhesion, is performed on the nanoscale range. For many macroscopic effects, however, distribution of components on meso- and microscopic orders of magnitude is relevant. On the one hand, the mesoscale formation of clusters between the binder and carbon black and their localization in the proximity of the active particles is important for the fundamental mechanical and electronic properties of the electrode. On the other hand, the overall electrode properties are also determined by the distribution of binder and conductive additives on a microscale level, i.e., over the entire cross-section and surface of the electrode.

Investigations of the electrode structure are challenging not only by the different orders of magnitude of the structural units, but also by the large number of materials used. As a result, the standard method for structure elucidation of diverse electrodes does not exist. Instead of that, one must have a pool of methods available and make appropriate adjustments for various electrodes. Examples, which illustrate these limitations, as well as successful application of methods, will be shown for common cathode and anode systems. The focus is placed on determining the microscopic binder distribution of standard electrodes, as knowledge of this feature is an essential prerequisite for understanding and optimizing of drying conditions. Most investigations are performed by using SEM based methods, which are available in many laboratories. A rather new user-friendly approach applies laser-induced breakdown spectroscopy for achieving a 3D elemental mapping of the entire electrodes, which can be used either for a rapid screening of 3D binder distribution or for post-mortem analysis of electrochemical degradation processes.

11:00 AM ET07.10.06
WITHDRAWN 10/31/2018 ET07.10.06 Al-Air Rechargeable Batteries on Flexible Polyimide Substrates Anming Hu1,2; 1University of Tennessee Knoxville, Knoxville, Tennessee, United States; 2Beijing University of Technology, Beijing, China.

We reported a rechargeable Al-air battery fabricated on polyimide substrates. For air anode, Pt decorated carbon particles mixed with TiC nanoparticles worked an OER/ORR catalyst. This combination has a better performance than individual Pt catalyst or TiC. Ionic liquid (1-ethyl-3-methylimidazolium chloride) mixed with AlCl3 as electrolyte. For Al cathode, we have compared Al foils, later-nanostructured Al foils and 3D printed Al nanoparticles. A stable charge-discharge of capacity of 0.3 mAh/cm2 is achieved for more than 100 cycles.

11:30 AM ET07.10.07
Wire-Shaped Supercapacitor Fabricated via Layer-by-Layer Assembly with Enhanced Voltage Window Kayeon Keum1; Geumbbee Lee2 and Jeong Sook Ha1,2; 1Korea University, Seoul, Korea (the Republic of); 2KU-IST Graduate School of Converging Science and Technology, Seoul, Korea (the Republic of).

As wearable electronics receives vast interest nowadays, various shapes and forms of wearable devices have been studied. Among them, wire-shaped supercapacitor (WSS) shows a great potential as a wearable energy storage device because its 1-dimensional structure makes it highly flexible and be easily incorporated into conventional textile substrates. Here, we report a thin, reproducible WSS fabricated via layer-by-layer (LbL) assembly of multi-walled carbon nanotubes (MWCNTs) with organic electrolyte of propylene carbonate (PC) – acetonitrile (ACN) – lithium perchlorate (LiClO4) – poly-(methyl methacrylate) (PMMA), extending the voltage window to 1.6 V. LbL assembly gives uniformly deposited MWCNTs on a curved surface of Au wire, resulting in linearly increased areal capacitance of the fabricated WSS. Vanadium oxide is encapsulated onto LbL-assembled MWCNTs electrode to induce pseudo-capacitance, enhancing overall capacitance of the fabricated WSS. Cyclic stability of the WSS is enhanced via optimizing the mixing ratio of PC to ACN in the electrolyte. As a result, the fabricated WSS exhibits areal capacitance of 5.23 mF/cm2 at 0.2 mA/cm2, energy density of 1.86 μWh/cm2, and power density of 8.5 mW/cm2, in addition to 94% capacitance retention after 10,000 galvanostatic charge-discharge cycles. Furthermore, the WSSs are easily integrated into a textile to drive integrated μ-LEDs. This work demonstrates a high potential of the scalable WSS as an energy storage device in application to high performance textile electronics.

SESSION ET07.11: Novel Energy Devices and Materials
Session Chairs: Peter Smyrek and Yuefei Zhang
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 312

1:30 PM ET07.11.01
Fabrication and Performance Analysis of All-Solid-State Flexible Porous 3D Graphene/Waste Composite Micro-Supercapacitor Gourav Bhattacharya1, Sam Fishlock2, James McLaughlin2 and Susanta Sinha Roy1; 1Department of Physics, Shiv Nadar University, Gautam Buddha Nagar, India; 2NIBEC, University of Ulster, Newtownabbey, United Kingdom.

Rapid depletion of non-renewable energy resources and ever-increasing demands for power made researches to focus into advanced energy materials for power generation and green energy storage. Among several other energy storage devices, supercapacitor has garnered large attention as an alternative portable power source and storage device. Recently, to encounter the huge global requirement of portable and wearable electronics, high-performance, flexible, inexpensive, and sustainable micro-supercapacitor systems are being studied. Herein by employing electrochemical technique, the potential application of an all solid-state flexible solid-state hybrid micro supercapacitor was investigated. A 3-D hierarchically porous graphene nano-ribbon structure (LIG) with high surface area, was synthesized on a flexible polymer substrate (polyamide) using Laser scribing technique. An industrial waste material red mud which is an abundant source of iron oxide (Fe2O3) was further mechanically processed to produce metal oxide nanoparticles. These nanoparticles were decorated on the LIG film and acted as the pseudocapacitor component of the hybrid electrode. The composite electrode material was further characterized using transmission electron microscopy (TEM), field effect scanning electron microscopy (FESEM), Raman spectroscopy, cyclic voltammetry (CV) etc. An interdigitated planar hybrid micro-supercapacitor device was fabricated over the polymer substrate where polymer-based composite ionic liquid-gel electrolyte was casted over the hybrid electrodes. Inkjet printing was further employed to print silver and was acted as the current collector. The performance of the device was monitored using CV, charging/discharging (CD) and electrochemical impedance spectroscopy (EIS). The device exhibited a high sp. capacitance within an active working potential of ~3.8 V which further enhances the energy density of it. The micro-supercapacitor also exhibited good long-term cycling stability. The swift lateral ion movement in the planar device, more accessible electrochemically active surface area, better charge transfer kinetics, presence of composite electrolytes contributed to the high electrochemical performance of the device. The inexpensive, lightweight, easy to construct device is thus a great potential and can offer new opportunity for integration of energy storage units with flexible electronic devices.

1:45 PM ET07.11.02
Ultra-High-Rate Aqueous Zinc-Ion Batteries for Shape-Conformal Integration of Wearable Electronics Chanhoon Kim1, Bok Yeop Ahn1, Teng-
The push towards miniaturized electronics requires the development of smaller battery, which has typically been one of the biggest components in the small electronics. With the selective miniaturization, customized geometries of the batteries may allow unprecedentedly comfortable and form-fitting design in the miniaturized electronics as well as wearable electronics. Nevertheless, the conventional battery design is confined to the rigid shapes, limiting its versatility. Here, we introduce the customized battery geometries for miniaturized and wearable electronics by optimized combination of 3D printing, electrospinning, and laser micromachining techniques. Pursuing easy processing and high safety, we have devised aqueous zinc-ion battery (ZIB) system in the customized geometries which consist of a conductive polyaniline (PANI) coated carbon fiber cathode, a porous separator, and a zinc (Zn) anode. The highly conductive 3D structured CF mat facilitates fast electron transfer even for relatively thick cathodes (~320 um) and the highly porous PANI conformally coated on the CF also significantly contributes to fast ion diffusion in cathode layers. By the virtue of the rationally designed cathodes, the ZIBs were charged to about 50% and 20%, respectively. Moreover, we use laser micromachining for customizing cell components (electrodes, separator, and terminals) corresponding to the shapes of SLA-printed packaging geometries. Notably, this is the first demonstration of the SLA technique, which has been widely used in many fields for prototyping custom-shaped complex plastic structures in ~ 100 μm resolutions for designing small batteries. The ZIBs with various geometries, including rectangular, cylindrical, H-, and ring-shapes retained the excellent electrochemical performances. Furthermore, we fabricated a wearable photosensor by shape-conformally integrating a ring-shape battery pack with electronic components to demonstrate the merit of our approach. We believe that the ability to fabricate power sources in any shapes and sizes as needed may open new revenues to shape-conformal integration of miniaturized and wearable electronics.

2:00 PM ET07.11.03
Light-Assisted Polymer-Based Electrochemical Energy Storage
Abdelaziz M. Gouda1, Ri Xu1, Francesca Soavi2 and Clara Santato1; 1Engineering Physics, Ecole Polytechnique Montreal, Montreal, Quebec, Canada; 2Chemistry, University of Bologna, Bologna, Italy.

The development of efficient solar energy conversion/storage technologies is critical to limit the negative effects of anthropogenic climate change on Earth. Electrochemical technologies have been widely investigated to capture the power generated from intermittent sources, like the Sun. High performance storage solutions, such as batteries and supercapacitors, make use of toxic electrode materials and organic electrolytes with limited environmental sustainability. Nature could be the source of abundant and environmentally benign materials to be used in next generation batteries and supercapacitors, paving a way towards a sustainable use of resources. Among natural materials, eumelanin is a functional biomacromolecule found in flora and fauna with fascinating properties, such as strong broadband UV-visible absorption, redox activity, metal binding affinity, humidity-dependent electrical response as well as good thermal and photostability [1]. DH1 (5,6-dihydroxyindole) and DHICA (5,6-dihydroxyindole-2-carboxylic acid) are the two building blocks of melanin. The synergy between the reduction/oxidation (redox) activity of the building blocks and the capability of several of their functionalities to reversibly bind cations constitutes the foundation for the use of eumelanin in energy storage systems [2]. Photoconductivity of melanin in different form such as pellets and thin films has been reported in the literature [3] motivating current efforts for using this photoactive bio-pigment in solar assisted electrochemical energy storing systems. [2][4][5]. We were capable to overcome the limited processability of melanin by adopting a solid state polymerization strategy for its fabrication. In this way we could keep the environmental friendliness of the melanin controlling its (supra)molecular structure and processability.

In this work, we report about a two symmetric electrode-system based on chemically controlled melanin wrapped with PEDOT: PSS on carbon paper current collectors. PEDOT:PSS enhances electronic transport and intermolecular connectivity between the melanin chains [6]. The electrode materials are processed by simple, solution-based methods. The electrochemical storage properties are evaluated for different chemically controlled eumelans: polyDHI, polyDHICA and polyDHI:polyDHICA in dark and light condition, using cyclic voltammetry and galvanostatic charge/discharge cycles.


2:15 PM ET07.11.04
Electrodeposition of MoS2 on Three-Dimensional Graphene/Nickel Foam for Electrocatalytic Water Splitting
Narasimman Rajaram, Mannoohansingh Waldiya, Indrajit Mukhopadhyay and Abhijit Ray; Pandit Deendayal Petroleum University, Gandhinagar, India.

Rapidly depleting fossil fuel and CO2 emission from the utilization of fossil fuels lead to the development of sustainable, clean and renewable alternate energy sources. Hydrogen is considered as a suitable candidate because it is having high energy density and zero gas emission. Among the various methods of production of hydrogen, electrochemical water reaction (HER) in electrochemical water splitting is considered as the most promising and environmentally friendly approach. Noble metals like Pt, Pd, etc., are known to effectively catalyst the HER, however, scarcity and high-price is restricting the large-scale production of hydrogen. Transition metal dichalcogenides (TMDC) such as MoS2, WS2 are widely studied electrocatalysts for HER in acidic medium. Also, three-dimensional (3D) electrodes are advantageous because of the porous and interconnected structure which increases the surface area and effective mass transport. In this study, we have electrodeposited MoS2 on to the graphene coated nickel foam (graphene/nickel foam). Graphene/nickel foam was prepared by APCVD technique at 800°C. The graphene was coated uniformly on nickel foam and it consists of 5-8 layers. The graphene/nickel foam was used as the electrode for the electrochemical deposition of MoS2. The cathodic electrodeposition of MoS2 on graphene/nickel foam was carried out by applying the potential of -1.2 V vs. (Ag/AgCl) for 20 mins. The morphology was evaluated by scanning electron microscopy and formation of MoS2 was confirmed by Raman spectroscopy. Freshly prepared samples were evaluated for HER in 0.5 M H2SO4 by linear sweep voltammetry, Tafel slope and electrochemical impedance study.

2:30 PM ET07.11.05
Enhanced Photoelectrochemical Water Splitting of Heteroisopetaxial Grown Hematite Nanowires
Kirtiman D. Malviya and Avner Rothscheld; Technion–Israel Institute of Technology, Haifa, Israel.

Hematite (α-Fe2O3) is a promising photoanode candidate for photoelectrochemical (PEC) cells for solar water splitting due to a unique combination of visible light absorption, stability in alkaline aqueous solutions, low cost, and abundance. However, the performance of the hematite photoanode is reported to be low and therefore different nanostructuring, and novel design microstructure is adopted to improve PEC performance. A simple and optimal design to facilitate the charge transfer in bulk is paramount important to achieve enhanced solar to fuel efficiency. Herein we report a simple and highly reproducible method of fabrication of multilayer heteroepitaxial grown Nb-doped SnO2/ hematite film on c-plane Al2O3 single crystal substrate and a series of systematic experiments to elucidate the effect of the microstructural variation on the photoelectrochemical properties. The microstructure varies from dense film to...
nanowire to defected porous structure depending on the growth conditions. To the best of our knowledge first time, we are reporting the heteroepitaxial growth of thin film hematite consists of dense nanowires (~10-30 nm diameter and ~600 nm length) with a photocurrent of 1.3 and 1.1 mA/cm² at reversible (1.23 V_RHE) and thermonutral potentials (1.48 V_RHE) respectively with bare hematite. Also, the reported results are higher than the most of the recently reported state-of-art fabrication methods. In this work, we have investigated the effect of polycrystalline/heteroepitaxial film thickness, the deposition temperature, oxygen partial pressure and the dopant concentration and their effect on the bulk and surface charge separation and injections efficiency. The effect of the surface treatment and the deposition of co-catalyst can further enhance the PEC properties which will be discussed during the presentation.

2:45 PM BREAK

3:15 PM ET07.11.06

Exploration of V Doped SnO2 Nanocrystals for Thermochemical H2 Generation Vined Kumar1, Dinesh Gupta2 and Sachin Kumar Sharma3; 1Conversion & Catalysis Division, Indian Institute of Petroleum, Dehradun, India; 2Chemistry, KIITR Mal College, University of Delhi, Delhi, India; 3Chemical Engineering, Indian Institute of Technology Delhi, Delhi, India.

Production of energy is the global concern, which needs to be addressed soon; otherwise, we will be in great problem. Dihydrogen is one of the reliable green energy source having high caloric value. There are several techniques to generate hydrogen as a fuel such as electrolysis, photoelectrochemical, photocatalytic approach, thermochemical water splitting etc. However, practically mass production, economic value, storage and usage of hydrogen as a fuel is still a challenging task. The hydrogen generation by splitting of water using various metal oxides has been reported for many years but their use is not applicable off-sun hours, cloudy or rainy day that restrict them for their commercialization. However practically mass production and usage of hydrogen as a fuel is still a challenging task. An alternative approach needed to be explored for commercial mass production of hydrogen. It is an hour of need to explore better approach for commercial and economical production of dihydrogen. Among these techniques, thermochemical water splitting can be utilized for mass production of hydrogen as a fuel. Several materials have been used for thermochemical water splitting especial binary metal oxides CeO2, TiO2, SnO2, CuO2, MnO etc. CeO2 is having the good efficiency for 100 cycles but require high thermal energy. SnO2 may be the promising material; in reversible (1.23 V_RHE) and thermonutral potentials (1.48 V_RHE) respectively with bare hematite. Also, the reported results are higher than the most of the SnO2 at lower thermal energy and show good efficiency for 10 cycles.

References

3:30 PM ET07.11.07

Low Temperature Fabrication of Dense Y-Doped BaZrO3 Electrolyte by Utilizing the Co-Firing with the Anode Substrate Shrinking Well for Proton Conducting Solid Oxide Fuel Cell Yuki Yamaguchi, Hiroyuki Shimada, Toshiaki Yamaguchi, Hirofumi Sumi, Katsuhiro Nomura and Yoshinobu Fujishiro, AIST, Nagoya, Japan.

Y-doped BaZrO3(BZO) is widely known as a proton conducting material which shows the high ionic conductivity at intermediate temperature between 400 and 700°C. Thus, it is promising candidate of electrolyte material for the intermediate temperature solid oxide fuel cells (IT-SOFC). BaZrO3(BZO) base proton conducting material has a good durability for CO2-composed with BaCeO3 base materials. However, the sintering temperature of BZO is quite high. High temperature heat-treatment more than 1700°C is required to obtain the dense body of BZO. Particularly for the fabrication of anode supported type SOFC, an electrolyte layer was prepared by co-firing with anode substrate. When the cells are fired at higher temperature to obtain the dense electrolyte, the porosity in anode will be disappeared due to the densification of anode. Therefore, we developed the low temperature fabrication process of the proton conducting SOFC by utilizing the fine powder of BZO having a good sinterability, in this study.

BZO powders were prepared by the novel low temperature synthesis which can prepare the BZO by only mixing the zirconia hydrous gel and the barium hydroxide octahydrate at 100°C for 12 h. The 2 mol% doped BZO had ca. 30 nm of primary particles with quite high crystallinity. Y doping amount could be controlled up to 30 mol% by the addition amount of Y ions to the zirconia hydrous gels. For the strongly shrinking anode substrate, Sr and Ti co-doped BZO powders were also prepared by the same method. It has been reported that the addition of some metal elements, such as Zn and Ni, were effective to decrease the sintering temperature of BZO. However, the cell voltage of BZO was decreased by the hole conduction in the electrolyte layer, because the holes were generated in the BZO electrolyte by the substitution of lower valence metal elements to Zr⁴⁺ sites. In this study, Sr²⁺ and Ti⁴⁺ were substituted to Ba²⁺ and Zr⁴⁺ sites, respectively. The sintering temperature of Sr and Ti co-doped BZO (BSZTY) powder was 200°C lower than that of BZO. BSZTY could be sintered at 1400°C. Then, BZO electrolyte layers were fabricated on the anode substrates including BZY-NiO by firing at 1400°C. When the BZO electrolyte layer was fabricated on the anode including the BZY-NiO, the electrolyte layer could not densify due to the high sintering temperature. In the contrast, the dense BZO electrolyte on the anode substrate of BSZTY-NiO was successfully obtained by firing at 1400°C. Besides, the grain growth of BZO was also observed. It was considered that the large shrinkage of anode substrate including BSZTY enhanced the sintering the BZO electrolyte layer. Using the BSZTY for anode material, the proton conducting cell having BZO electrolyte could be obtained by co-firing at 1400°C. This cell showed a high open circuit voltage (OCV) more than 1.0 V at 600°C. It was considered that the excessive hole generation did not occur.

3:45 PM ET07.11.08

Titanium Oxynitride Thin-Films with Large Power Conversion Efficiency in Photovoltaic Solar Cells Nikhil R. Mucha1, Michael Froeschle2, Mark Anderson3, Panupong Jaipan1, Hemali Rathnayake2, Christian Binek3, Jeffrey Shield3 and Dhananjay Kumar1; 1North Carolina A&T State University, Greensboro, North Carolina, United States; 2Nanoscience, University of North Carolina at Greensboro, Greensboro, North Carolina, United States; 3Earth Science, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 4Physics, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

A novel TiO₃N₂(Ti-N-O) material system in thin film form has been synthesized using a pulsed laser deposition method. The photovoltaic solar cells constructed out of Ti-N-O in ITO-TiNO-Cu configuration have yielded a maximum power conversion efficiency (PCE) of 12.5% with short circuit current
density ($J_{sc}$) of 36.50 mA/cm², open circuit voltage ($V_{oc}$) of 0.21 V, and fill factor (FF) of 57.4%. This is the highest PCE reported to date for any derivative of thin film based-Ti-N-O system as an active layer material in bulk heterojunction (BHJ) solar cells. The extraordinarily high values of power conversion efficiency have been attributed to the existence of a multi-bandgap-mediated electron-hole transfer pathway. X-ray diffraction and x-ray photoelectron spectroscopy measurements lend evidence in support of multi-bandgap mediated transfer of charge carriers by confirming the presence of Ti-N-O, Ti-N, and Ti-O chemical bonding states. The titanium oxynitride (TiNₓOᵧ) system has the potential to absorb visible light in the full solar spectrum.

4:00 PM ET07.11.09
MnFe₂O₄ Nanoparticle-Pigmented High-Temperature, Thermodynamically-Stable, Long-Term Antioxidation Solar Selective Absorber Coatings Eldred Lee¹, Can Xu¹, Katerina Kekalo¹⁻², Jifeng Liu¹ and Xiaoxin Wang¹; ¹Dartmouth College, Hanover, New Hampshire, United States; ²U.S. Air Force, Hanover, New Hampshire, United States.

Photovoltaic (PV) technology for solar electricity is in high demand but the flexibility on long term energy storage. Therefore, concentrated solar power (CSP) systems need to complement the PV technology to increase energy output. The efficiency of CSP systems can improve with high absorption in the solar spectrum regime and low emittances in the infrared spectrum. However, CSP systems can be expensive. High-temperature, air-stable solar selective absorbers made with cermet composite materials that have optimal properties of both ceramic and metal can be the solution to this goal; however, this achievement has been difficult due to metal oxidation at high temperatures. Here, we demonstrate outstanding optical responses of thermodynamically-stable, high-temperature, low-cost long-term antioxidation cermet solar selective absorbers using MnFe₂O₄ nanoparticles (NPs) with silicone precursors as low-cost Si-rich matrices that undergo interdiffusion reaction with Stainless Steel 310 (SS310) and Inconel 625 substrates. Current state-of-the-art product such as the Pyromark® black paint has a significantly high solar absorbance (~95%) in the solar spectrum regime but also has a high emittance loss (~87%) in the infrared spectrum. To decrease the emittance while maintaining high absorbance, we have undergone antioxidation interfacial engineering in Ni/SiO₂ by creating low-cost solution-processed Ni nanochain-SiO₂ (X<2) selective solar thermal absorber coatings. When these coatings are deposited on metal substrates, the oxidation of the metal as well as the interdiffusion between the coatings and the substrates can exceed the optical responses of the coatings themselves. As there are low-cost NPs that exceed the optical responses of Ni in the desired spectrum, further investigation has been done with interdiffusion-induced selectivity testing using silicone precursors with varying molecular weight as low-cost Si-rich matrices for interdiffusion reaction with different low-cost NPs that have metal-like optical absorption properties and ceramic-like chemical stability and metal substrates. Thin layers of various NP-silicone matrix coatings were deposited on metal substrates using market-available low-cost perfume sprays. To test the stability, the samples were annealed in air at 750°C up to 1000 hours. Up to this date, solar selective absorber coatings with 28nm MnFe₂O₄ NPs and a high molecular weight silicone matrix on SS310 and Inconel 625 substrates result in the most ideal absorption up to 97% in the solar spectrum regime and the reduction of emittance down to 30-40% in the infrared regime, which are confirmed by UV/VIS/NIR spectrophotometer and an FTIR spectrometer. These coatings on SS310 and Inconel 625 substrates were found to be stable in air in 750°C and the optical responses in the desired spectrum have either maintained or improved. Such solution can lead to a newer and innovative approach to create better low-cost and improved solar selective absorber coatings.

4:15 PM ET07.11.10
A Solvent Toolkit for Electrochemical Characterization of Hybrid Perovskite Films Mehdedhi Hasan¹, Dmitry Lyashenko¹, Jason D. Slinker² and Alex Zakhidov¹; ¹Texas State University, San Marcos, Texas, United States; ²The University of Texas at Dallas, Dallas, Texas, United States.

Organohalide lead (hybrid) perovskites have emerged as competitive semiconducting materials for photovoltaic devices due to their high performance and low cost. To further the understanding and optimization of these materials, solution based methods for interrogating and modifying perovskite thin films are needed. In this work, we report hydrofluoroether (HFE) solvent based electrolyte for electrochemical processing and characterization of organic-inorganic trihalide lead perovskite thin films. Organic perovskite films are soluble in most of the polar organic solvents and thus allow electrochemical characterization of the electronic structure, investigation of charge transport properties and potential electrochemical doping of the films with in situ diagnostic capabilities.

4:30 PM ET07.11.12
Spray-on “CdO:Mn:Sn/PhS:Na:CdS” Thermoelectric Energy Harvester Francesco Javier Gonzalez²⁻¹, Isaiah Oladeji²⁻³ and Robert E. Peale²⁻⁴; ¹Universidad Autonoma de San Luis Potosí, San Luis Potosí, Mexico; ²Truentive LLC, Orlando, Florida, United States; ³SISOM Thin Film LLC, Orlando, Florida, United States; ⁴Physics, University of Central Florida, Orlando, Florida, United States.

Thermoelectric (TE) thin films have promise for harvesting electrical energy from waste heat, which could power wearable electronics and enable conformal application to complex surfaces for enhanced thermal coupling. We demonstrate an n-type CdO-Mn:Sn and p-type P6S:Na:CdS thin-film TE device that was deposited by aqueous spray deposition on glass and flexible Uplex S substrates using a shadow mask. With the junction at 100 deg C, the open circuit voltage between p- and n-type free ends at 25 deg C is +13.6 mV. The short circuit current is 15 nA, giving ~0.2 mW of power for the single junction and the given temperature difference. Several thermocouples connected electrically in series and thermally in parallel will multiply the output voltage. The Seebeck coefficient (thermoelectric power) for this first device is ~0.2 mV/C, which is comparable to known values for other semiconductor thermocouples and may be improved by optimization. Numerical simulations using COMSOL. Multiphysics are used to obtain figures of merit for comparison to experimental results.

SESSION ET07.12: Poster Session IV
Thursday Afternoon, November 29, 2018
8:00 PM – 10:00 PM
Hynes, Level 1, Hall B

ET07.12.01
Synergy of Optimized Topological Structure and Phase-Composition Boosts Ultrahigh Discharge Efficiency in High-Energy-Density Polymer Nanocomposites Jianyong Jiang, Yang Shen and Ce-Wen Nan; Tsinghua University, Beijing, China.

Poly(vinylidene fluoride) (PVDF)-based dielectric polymers are in great demand for the future electronic and electrical industry because of their high

Here we introduce a sustainable and general method for fabricating 2D heterostructures from solution. Assembly of 2D materials from solution may allow fabrication of 2D heterostructures. There has not been any systematic study and attempt at developing a method to systematically optimize these solutions for Layer-by-Layer self-assembly of multilayered pillared structures. These results can pave the way for large-scale production of 2D heterostructures.

The problem, however, is that stacking of 2D materials at large scale and with high precision is difficult. It has been suggested that Layer-by-layer assembly of 2D materials from solution may allow fabrication of 2D heterostructures. There has not been any systematic study and attempt at developing a method to systematically optimize these solutions for Layer-by-Layer self-assembly of multilayered pillared structures. These results can pave the way for large-scale production of 2D heterostructures.

This work was partly supported by JSPS KAKENHI Grant Number 16K05885, Japan. We also acknowledge supports from ARC DP fund (DP180103815) and ARC LIEF fund (LE170100235), Australia, and Office for Industry-University Co-Creation at Osaka University. States.

The climax of photocatalytic overall water splitting in powder suspension form is the simultaneous occurrence of electrocatalytic hydrogen evolution and oxygen evolution. In order for a semiconductor powder to achieve both reactions, the chemical potential at the surface should be shifted negatively and positively at the redox sites. It is however difficult to quantitatively describe such potentials of the powder suspension system. Knowledge transfer from electrocatalytic measurement to photocatalysis is effective to estimate the difficult-to-measure potentials of the photocatalytic system. This contribution discusses the effectiveness of electrocatalytic measurements to understand photocatalytic behavior, mainly focusing on hydrogen evolution catalysis and water-forming back reaction.

Successful photocatalytic overall water splitting is achievable when the water-forming back reaction from H2 and O2 to form H2O does not prevail. Although decoration of hydrogen evolution catalysts on the semiconductor powder is often essential to achieve high photocatalytic efficiency, the same catalyst surfaces often introduce the thermodynamically-favorable back reaction. We show that the suppression of the back reaction is achievable when the semiconductor powder is decorated with highly dispersed noble metal catalysts, such as Pt species, with tungsten carbide nanoparticles, or with hydrogen-evolving catalysts covered with membrane-function layers, such as CrOx, MoOx, and SiOx. To elucidate the catalytic rates for both forward (hydrogen evolution) and backward (water formation) reactions, electrocatalytic measurements are effectively utilized where the potential of the catalysts is determined.

In a similar way, the importance of electrolyte identity is evaluated mainly at near-neutral pH by effectively comparing electrocatalysis and photocatalysis. It is well accepted that buffering action is considered inevitable especially at high rates, but our elucidation pins down such effects quantitatively, dividing the functions into solution resistance, concentration overpotential, and kinetic contribution in a photocatalytic system. Such electrolyte engineering may lead to the discovery of new reaction environments for water electrolysis in more benign conditions and more towards membrane-less systems.

8:30 AM *ET08.01.01
Elucidation of Electrocatalysis to Understand Photocatalytic Overall Water Splitting Kazuhiro Takanabe1, 2; 1The University of Tokyo, Toride, Japan; 2King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The developing of renewable fuel sources requires highly efficient and robust pathways to convert earth abundant resources into high energy fuels, as well as efficient methods to convert the energy stored in chemical bonds into useable power. At each step of the fuel cycle, high performance catalysts are essential. Transition metal phosphides (TMP) have proven to be highly active and stable catalysts and are of great interest for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and carbon dioxide reduction to hydrocarbon fuels. However, a detailed understanding of the role of phosphorous is still emerging, and even for the case of HER the performance has previously lagged behind that of the Pt benchmark.

We presented a detailed theoretical and experimental study in which we synthesize nanocrystalline CoP, particles with highly uniform size, allowing a systematic comparison of performance. The phosphorous rich CoP and CoP2 TMPs, as oppose to Co2P, are highly effective and selective catalyst toward HER and ORR. In fact CoP2 exhibits Pt-like performance at small overpotential of 39mV to achieve -10 mA/cm2 and long term stability. The role of P in promoting catalysis must be understood by considering multiple effects: reducing the number of tightly bound multi-coH adsortion sites, increasing the surface disorder, and increasing the Co-H bond length. We will present both data from our recent publication (Adv. Mater. 2018, 30, 1705796) as well as our new results for high-performance CoP2 HER catalysts. The conclusions drawn from this study will be highly relevant to the broader energy catalysis community, and the study of TMP catalysts in particular.

9:00 AM ET08.01.02
Comprehensive Kinetic Analysis of Photocatalytic Water Oxidation and Reduction at TiO2 Surface Maning Liu1 and Yasuhiro Tachibana1, 2; 1RMIT University, Bundoora, Victoria, Australia; 2Osaka University, Osaka, Japan.

Solar water splitting is one of the most attractive energy generation reactions to utilize solar energy. Light generated hydrogen is clean energy source, since their consumption for energy generation produces only water. Moreover, it can be stored and used whenever required. Semiconductor TiO2 is known as a photocatalyst and was investigated for solar water splitting reactions over the last several decades. TiO2 has still been employed to assess the capability of photocatalysis reactions. The water splitting kinetic reaction mechanism at the TiO2 surface has been elucidated, particularly employing transient absorption spectroscopy, however detailed understanding of the mechanism remains to be clarified.

In this presentation, we will demonstrate quantitative assessment of photocatalytic water splitting mechanism at the TiO2 surface by employing a series of transient absorption spectroscopies covering from fs to 10 s over UV-VIS-NIR wavelength ranges. The reaction paths and their dynamics at the charge trap states will be discussed.

This work was partly supported by JSPS KAKENHI Grant Number 16K05885, Japan. We also acknowledge supports from ARC DP fund (DP180103815) and ARC LIEF fund (LE170100235), Australia, and Office for Industry-University Co-Creation at Osaka University.

9:15 AM ET08.01.03

The developing of renewable fuel sources requires highly efficient and robust pathways to convert earth abundant resources into high energy fuels, as well as efficient methods to convert the energy stored in chemical bonds into useable power. At each step of the fuel cycle, high performance catalysts are essential. Transition metal phosphides (TMP) have proven to be highly active and stable catalysts and are of great interest for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and carbon dioxide reduction to hydrocarbon fuels. However, a detailed understanding of the role of phosphorous is still emerging, and even for the case of HER the performance has previously lagged behind that of the Pt benchmark.

We presented a detailed theoretical and experimental study in which we synthesize nanocrystalline CoP, particles with highly uniform size, allowing a systematic comparison of performance. The phosphorous rich CoP and CoP2 TMPs, as oppose to Co2P, are highly effective and selective catalyst toward HER and ORR. In fact CoP2 exhibits Pt-like performance at small overpotential of 39mV to achieve -10 mA/cm2 and long term stability. The role of P in promoting catalysis must be understood by considering multiple effects: reducing the number of tightly bound multi-coH adsortion sites, increasing the surface disorder, and increasing the Co-H bond length. We will present both data from our recent publication (Adv. Mater. 2018, 30, 1705796) as well as our new results for high-performance CoP2 HER catalysts. The conclusions drawn from this study will be highly relevant to the broader energy catalysis community, and the study of TMP catalysts in particular.

9:30 AM ET08.01.04
Defect-Engineered Interface Assembly for Efficient Electrocatalyst Kishwar Khan and Zhengtang Luo; Hong Kong University of Science & Technology, Kowloon, Hong Kong.
The expansion of economical, effective, and durable electrocatalysts for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) have significant importance aimed at numerous electrochemical devices, such as fuel cells, water electrolyzer, and rechargeable metal-air batteries. Heterometal-doped catalyst has arisen as one of the best emergent candidate to replace the metal based marketable catalyst for electrochemical reactions. But, their delicate structure parameters to optimize the catalytic capability, and atomic-level mechanistic understanding are still a challenging issue. Herein, we advocate the assembly of separate single atoms of Ni and Fe (SSAs-NiFe) dual sites, anchored in defects engineered graphene (DG) substrate prepared by a facile nitrogen (N) elimination procedure from an N-doped precursor by an adsorption-calcination strategy. The concept of defect mechanism, exhibited the topological defect (e.g. multiple pentagon—octagon—pentagon or pentagon—heptagon—pentagon rings) correspondingly appeared in carbon atoms combination that avoid dislocations and disclinations. We believe that these specific combination of carbon atom rings in defective substrate with the decoration of Ni and Fe SSAs can provide more active sites, better electrical conductivity, and lowest energy barrier during catalytic reaction. We used the combination of high resolution transmission electron microscopy/high-angle annular dark field (HAADF) images established in scanning transmission electron microscopy (S/TEM) for studying the atomic structure of Ni and Fe isolated atoms on DG. At very low magnification (1nm) the individual atoms Ni and Fe in the field of view is detected through S/TEM, and resolved in graphene lattices. The electron energy loss spectroscopy (EELS) atomic spectra are used to identify the Ni/Fe SSAs in DG. The chemical insights structure of the material are examined by pre-edge peaks in X-rays absorption near edge structure (XANES) spectra. We demonstrated the electrocatalytic performance of SSAs-NiFe-DG hybrid material in acidic/alkaline mediums, and found it very active and stable trifunctional electrocatalyst for ORR, OER and HER. This work offers new prospects and underscores the importance of identifying the active species for multiple reactions catalysts and demonstrates how such knowledge can be applied to develop better multifunctional catalysts.

Carbon Nanodots as Efficient Photosensitizers for “Green” Solar Fuel Production Demetra S. Achilleos, Haticke Kasap and Erwin Reisner; Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK., University of Cambridge, Cambridge, United Kingdom.

The accelerated consumption of fossil fuels and the emerging ecological concerns, due to the alarming concomitant rise in greenhouse gas emissions, emphasize the need for the society to move towards renewable “green” resources. Photocatalysis is a promising approach for mitigating simultaneously both the energy and environmental concerns, since it allows the storage of the abundant solar energy in high energy density fuels, such as H2(120 MJ/kg,1) in benign aqueous media. However, the development of economically sustainable processes for this purpose, creates the pressing need for new photosensitizers and catalysts of low cost and toxicity, which however maintain substantial performances. Carbon dots (CDs) can efficiently serve as photocatalysts for this purpose since they fulfill all these requirements.2-4 In particular, CDs are hydrophilic nanoparticles of low toxicity, which can be synthesized at low cost, are chemically and photochemically robust and show optimum photocatalytic properties upon pre-designed synthesis.5-6 In this work, we focus on the synthesis of CDs from naturally abundant and inexpensive biopolymers of various compositions and nanoarchitectures, which bestow the derived photocatalysts with distinctive photocatalytic performances. These light harvesters when combined with noble-metal free molecular catalysts in aqueous-based photocatalytic systems, not only allow for substantial “green” fuel synthesis but also simultaneously facilitate waste oxidation. Such substrates which originate from numerous resources and are abundantly available at no cost, serve as electron donors to quench the photogenerated holes and maintain the photocatalytic stabilities of the systems. The use of waste materials for this purpose, eliminates the need for additional sacrificial reagents,4 traditionally used in great excess, which add to the overall cost of the processes, and often result in by-products which need to be disposed. We anticipate that this approach, could be a breakthrough in the development of scalable, economically and environmentally sustainable photocatalytic systems, which could efficiently serve the increased energy needs of our societies.

References
spectrum up to the visible region, as well as to achieve a high quantum efficiency in the photocatalytic process. Introducing two-step photoexcitation (i.e., Z-scheme) in water splitting has been recently proven as one of the most promising strategies for harvesting a wider range of visible light. In this system, the water-splitting reaction is broken up into two stages: one for H₂-evolution, and the other for O₂-evolution. These are combined using a shuttle redox couple in solution. In Z-scheme water splitting systems with an IO₃⁻/I⁻ redox couple, the reduction of IO₃⁻ on O₂-evolving photocatalysts via a six-electron process often represents the rate-determining step of the overall process, and therefore necessitates effective cocatalysts such as RuO₂ and Ru₂O₃. However, these cocatalysts cannot be loaded onto thermally unstable materials via conventional impregnation processes involving calcination. In the present study, we introduce a new Ru-based cocatalyst that can be loaded without calcination and effectively promotes the reduction of IO₃⁻ on various photocatalysts, including non-oxide materials. The results reveal for the first time that the Ru species adsorbed via simple stirring of photocatalyst particles such as WO₃ in an aqueous RuCl₃ solution effectively trigger O₂ generation in the presence of IO₃⁻ as electron acceptor; moreover, the O₂ evolution rate on the present Ru-

Solar to hydrogen (H₂) energy conversion represents the Holy Grail of energy science and technology. For decades, numerous materials have been developed and used as photocatalysts for this purpose. However, their inadequate visible light absorbance, poor stability and fast charge recombination have prevented their widespread industrial-scale deployment. Additionally, the use of noble metal-based co-catalysts and the toxicity of the majority of electron donors employed in these photocatalytic systems limit the profitability of this technology. This study aims to tackle these issues using a two-fold strategy. Firstly, we systematically studied the impact of different transition metal-based co-catalysts towards the photocatalytic water reduction, when they are physically mixed with the visible-light active MIL-125-NH₂. All co-catalyst/MIL-125-NH₂ photocatalytic systems were found to be highly stable after photocatalysis, with some systems exhibiting high hydrogen (H₂) evolution rates of >2000 μmol h⁻¹ g⁻¹. Secondly, we investigated how different electron donors affected the stability and H₂ generation rate of the best photocatalytic system and found that triethylamine fulfills both requirements. We then replaced the electron donor with dyes that are commonly used as simulant organic pollutants, with the aim of integrating the visible-light driven H₂ evolution with dye degradation in a single process. This is the first study where a metal-organic framework (MOF) system is used for this dual-photo catalytic activity under visible light illumination and our proof-of-concept approach envisions a sustainable waste-water remediation process driven by the abundant solar energy, while H₂ is produced, captured and further utilized. [1]

---

**SESSION ET08.02: Catalytic OER**

**Session Chairs:** Yu Han and Yugang Sun

**Monday Afternoon, November 26, 2018**

**Hynes, Level 3, Room 306**

**1:30 PM **

**ET08.02.01**

**Resolution of Electronic and Structural Factors Underlying Oxygen-Evolving Performance in Amorphous Cobalt Oxide Catalysts**

David M. Tiede¹, Gihan Kwon², Hoyoung Jang², Jun-Sik Lee², Anil Mane¹, Alex Martinson¹, Hacksung Kim³ and Jungho Kim³; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois, United States; ²Stanford Synchrotron Radiation Light Source, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States; ⁴X-ray Science Division, Argonne National Laboratory, Argonne, Illinois, United States.

Non-noble-metal, thin-film oxides are widely investigated as promising catalysts for oxygen evolution reactions (OER). A key challenge for gaining insight into mechanisms for thin-film photo- and electro-catalytic OER function lies in resolving the interplay between intrinsic catalytic activity of
catalytic sites and the electronic structure and charge transport properties of the thin-film OEC. Transition metal (oxy)hydroxides show linked electron-proton conductivity which confers a volume rather than a surface area dependent activity to the films. This is understood to arise from homogeneously distributed and accessible catalytic sites though out the film, and with the catalytic current densities determined by the product \( \kappa_{a} \kappa_{e} \) of the catalytic rate, \( \kappa_{a} \), and electron-proton conductivity, \( \kappa_{e} \). As a result, understanding OER function for transition metal (oxy)hydroxide requires the structural basis for both catalysis and electron-proton conductivity to be addressed.

We have investigated amorphous cobalt oxide films electrochemically formed in the presence of borate (CoBi) and phosphate (CoPi) as a means to resolve structural and electronic factors that underlie OER performance in cobalt (oxy)hydroxides. CoPi and CoBi share a common cobaltate domain building block, but differ significantly in OER performance that has been proposed to derive from different electron-proton charge transport properties. In this report, we provide a comparison of CoBi and CoPi OER performance and bulk electronic properties, and correlate these to the electronic and structural properties measured at the atomic scale using a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS), and resonant vibrational Raman scattering (RR) techniques. This combination of analytical approaches show CoBi and CoPi to have characteristic differences in electronic structure that provide a basis for understanding enhanced conductivities for CoBi compared to CoPi as thin film OEC. In particular, the results show that the cobaltate domains for these OEC differ in the content of tetrahedral Co(II) “defect” sites, the extent of oxygen-mediated metal-metal delocalization, and mesoscale ordering that can be understood to combine and support enhanced electron-proton conductivity in CoBi compared to CoPi. More generally, this work demonstrates opportunities to use the combination of soft XAS, RXES, RIXS for investigating the interplay between intrinsic catalytic activity of catalytic sites and the electronic structure and charge transport properties of thin-film catalysis.

2:00 PM ET08.02.02
Dinuclear Heterogeneous Catalyst on Metal Oxides for Solar Water Oxidation
Yanyan Zhao, Ke. R. Yang, Xingzu Yan, Zechao Wang, Sufeng Cao, Yifan Ye, Qi Dong, Xiux Zhang, James Thorne, Lei Jin, Kelly Materna, Antonios Triplasis, Sirine Fakra, Shashu Zhu, Xiaoyan Zhong, Peng Wang, Xiaoxing Pan, Jinghua Guo, Maria Flytzani-Stephanopoulos, Gary W. Brudvig, Victor Batista, Dunwei Wang
1Boston College, Chestnut Hill, Massachusetts, United States; 2Yale University, New Haven, Connecticut, United States; 3University of California–Irvine, Irvine, California, United States; 4Tsinghua University, Beijing, China; 5Tufts University, Medford, Massachusetts, United States; 6Lawrence Berkeley National Laboratory, Berkeley, California, United States; 7Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Jülich, Germany; 8Nanjing University, Nanjing, China.

Atomically dispersed catalysts refer to substrate-supported heterogeneous catalysts featuring one or a few active metal atoms that are separated from one another. They represent an important class of materials ranging from single atom catalysts (SACs) and nanoparticles (NPs). While SACs and NPs have been extensively reported, catalysts featuring two atoms with well-defined structures are poorly studied. The difficulty in synthesizing such structures has been a critical challenge. Here we present preparing dinuclear heterogeneous catalysts (DHCs) by a facile photochemical method that produces catalytic centers consisting of two iridium metal cations, bridged by O and bound to a support. Direct evidence unambiguously supporting the dinuclear nature of the catalysts anchored on metal oxides is obtained by aberration-corrected scanning transmission electron microscopy. In addition, different binding modes have been achieved on two metal oxides with distinguishable surface oxygen densities and interatomic distances of binding sites. Side-on bound DHCs was demonstrated on iron oxide where both Ir atoms are affixed to the surface with similar coordination environment. The three-fold hollow binding sites on the OH-terminated surface of Fe2O3 anchor the catalysts to provide outstanding stability against detachment or aggregation. The competing end-on binding mode, where only one Ir atom is attached to the substrate and the other one is dangling was observed on WO3. Evidence supporting the binding modes was obtained by in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy. The resulting catalysts exhibit high activities toward H2O photooxidation. Density functional theory calculations provide additional support for atomic structure, binding sites modes on metal oxides, as well as insights into how DHCs may be beneficial for solar water oxidation reactions. The results have important implications for future studies of highly effective heterogeneous catalysts for complex chemical reactions.

2:15 PM ET08.02.03
Bismuth Substituted Strontium Cobalt Perovskites for Catalyzing Oxygen Evolution
Jiayu Peng, Denis A. Kuznetsov, Livia Giordano, Yuriy Roman and Yang Shao-Horn
1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The distribution and on-demand use of electrical energy from sustainable resources requires storage technologies that are cost effective and involving earth-abundant elements [1-2], such as storing solar energy in form of chemical bonds by water splitting or CO2 reduction. The efficiency of these storage technologies is, however, severely limited by the catalysis of the oxygen evolution reaction (OER) [3], which is characterized by slow kinetics and the need for precious metal catalysts such as RuO2 and IrO2 [4]. The development of the efficient electrocatalysts for OER composed of earth-abundant materials is therefore crucial for the large-scale implementation of these technologies. Here we employ the recently reported inductive effect [5] associated with metal substitution to examine the redox potentials and OER activity of cobalt-based perovskites, where bismuth-substituted strontium cobalt perovskite, Bi4Sr3CoO9.6, showed a record intrinsic activity for OER in basic solution. OER kinetics of Bi4Sr3CoO9.6 were found to have a low Tafel slope (<30 mV/decade) and pH dependence on RHE scale implying the decoupling of proton and electron transfer during one of the OER steps. The enhanced OER kinetics of Bi4Sr3CoO9.6 relative to other active catalysts such as SrCoO2, δ can be attributed to the presence of electronegative strong Lewis acid Biδ+ ions which can influence the surface charge facilitating deprotonation kinetics, and also enhance oxide stability by having lowered O p band center of Bi4Sr3CoO9.6 relative to the Fermi level via partial Co reduction and inductive effect. This work demonstrates a novel design strategy for enhancement of the OER activity and stability of oxide catalysts by the inductive effect induced by metal substitution to enable efficient and sustainable energy storage.

References:

2:30 PM ET08.02.04
Ultraporous Amorphous Iron-nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production
Jean Marie Vianney Nsanzimana and Xin Wang
1Nanyang Technological University, Singapore, Singapore.

Electrochemical Hydrogen production has gained great interest over the past decades as a cleaner, higher purity and sustainable production technology for carbon-neutral alternative fuel sources. However, poor oxygen evolution reaction (OER) thermodynamic up-hill reaction limits the efficiency of H2 production from water electrolysis and photoelectrolysis routes to large-scale energy storage. Thus, it is crucial to develop efficient and low-cost.
material to boost the sluggish kinetics step of four-electron OER process. The state-of-the-art are the precious metal-based catalyst which suffers from higher cost and makes them lesser desirable for industrial applicable scale. Thus, developing low cost, durable, earth-abundant, and high-performance non-precious metal electrocatalyst for oxygen evolution reaction (OER) is a cornerstone for energy technologies. Despite a well-documented approach for synthesizing metal borides, it is recently that the application as promising OER electrocatalyst has emerged.\textsuperscript{2, 3} Furthermore, the synergetic effect had been reported for multimetal borides materials which were found to be the most OER among the reported metal borides materials.\textsuperscript{4} Additionally, an improvement in metal borides based catalyst had been reported when supported on a higher conductive substrate such as graphene.\textsuperscript{5}

A cost-effective and efficient electrocatalyst for oxygen evolution reaction during water electrolysis is highly desired. In an effort to develop an economical material for replacing precious metal-based catalysts, a novel and self-standing, amorphous ultrathin nanosheets of bimetallic iron-nickel boride (FeNiB NSs) on Ni foam is presented, which displays better oxygen-evolving activity compared to precious metal catalyst RuO\textsubscript{2}. In 1.0 M KOH electrolyte, it requires an overpotential of only 237 mV to reach a current density of 10 mA/cm\textsuperscript{2} with a small Tafel slope of 38 mV/dec\textsuperscript{1} and shows prominent longterm electrochemical stability. The synergistic effect between highly abundant catalytically active sites on 3D porous substrate, improved electron transport arising from the presence of highly negative boron, and high conductivity of the substrate results in an outstanding electrocatalytic activity. The advanced catalytic activity, facile electrode fabrication, and low cost makes it a potential oxygen evolving material which may be extended to other energy conversion and storage technologies.

References


2:45 PM ET08.02.05
\textbf{CoSb\textsubscript{2}O\textsubscript{6} as a Stable Oxygen Evolution Catalyst in Acidic Media} Taylor A. Evans and Kyoung-Shin Choi; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States.

The electrochemical generation of hydrogen fuel via water reduction requires a counter reaction, typically the oxidation of water. This four electron, kinetically complex reaction has been intensely studied in basic media using a variety of inexpensive metal oxide materials (NiO\textsubscript{x}, FeO\textsubscript{x}, CoO\textsubscript{x}, etc). However, in acidic media these catalysts have been shown to be unstable and degrade rapidly. While noble metal oxides, such as RuO\textsubscript{2} and IrO\textsubscript{2}, are able to perform water oxidation in a stable manner with relatively low overpotentials in acidic media, their scarcity and high cost leave significant room for the development of inexpensive novel catalysts. Antimony (V) oxides are expected to be stable under oxidizing conditions in acidic media on account of their high oxidation state and low solubility in acid. In this presentation, the investigation of CoSb\textsubscript{2}O\textsubscript{6} as a stable water oxidation catalyst is reported. Synthesized through a facile electrochemical method, CoSb\textsubscript{2}O\textsubscript{6} films are demonstrated to be stable in acidic media while applying the necessary potentials for water oxidation. CoSb\textsubscript{2}O\textsubscript{6} opens the door as a possible replacement for noble metal oxide catalysts and encourages the investigation of other transition metal antimony oxide materials for use as water oxidation catalysts in acidic media.

3:00 PM BREAK

3:30 PM *ET08.02.06
\textbf{Porous Transition Metal Oxides for Selective Oxidations} Steven L. Suib\textsuperscript{1, 2, 3}; \textsuperscript{1}Chemistry, University of Connecticut, Storrs, Connecticut, United States; \textsuperscript{2}Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; \textsuperscript{3}Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States.

This presentation will focus on synthesis, characterization, and applications of novel microporous and mesoporous materials. Such mesoporous metal oxide materials have crystalline walls, high thermal stability, and monomodal pore size distributions. These systems can be made for most elements throughout the periodic table. They have unique catalytic activity in a number of reactions including selective oxidations, total oxidations, coupling reactions, water splitting, one pot Wittig reactions, dehalogenations, and others. A key focus is on the mechanisms of these selective oxidation reactions. The role of reactive oxygen species in these reactions is of considerable interest. This presentation will focus on synthesis, characterization, and selective catalytic oxidations applications using both microporous and mesoporous materials. Reactive oxygen species can be detected with a variety of methods. \textit{In situ} methods to observe these species have been developed. How such reactive oxygen species are important in selective oxidation reactions will be discussed.

4:00 PM ET08.02.07
\textbf{Advanced Structural Characterization of Ni-NW Catalysts Showing Enhanced OER Electroactivity} Sagar Prabhudesai\textsuperscript{1}, Minghui Hao\textsuperscript{2}, Sebastien Garbarino\textsuperscript{2}, Daniel Guy\textsuperscript{2} and Gianluigi A. Bottoli\textsuperscript{1}; \textsuperscript{1}McMaster University, Hamilton, Ontario, Canada; \textsuperscript{2}INRS, Montreal, Quebec, Canada.

Hydrogen is arguably one of the most promising energy carriers which can mirror all the appealing attributes of electricity. To answer whether it can meet the global demand for energy while at the same time also be an effective clean and sustainable energy carrier, however, requires a low-cost and environmentally friendly means of production. Although Electrolytic methods of producing Hydrogen provide an attractive pathway to producing Hydrogen renewably (e.g., from water), they further entail employing electrolyzer systems such as the Anionic Polymer Electrolyte Membrane Water Electrolyzers that are yet to be optimized for their Oxygen Evolution Reaction (OER) kinetics.

In this work we discuss a new class of Ni-Nanowire Catalysts that were found to exhibit a significant decrease in the OER Overpotential (~200 mV) at 10 mA/cm\textsuperscript{2} current densities. With the use of advanced electron microscopy tools for structural and compositional characterization we provide insights into their entire synthetic pathway, where a template-assisted electrodeposition procedure first formed the Ni-filled Aluminium Anodic Oxide (AAO) membranes, from which the usable pristine 1D Ni nanowires were then recovered by electrochemical dissolution of the AAO in 1M KOH. A detailed analyses of their SEM and high-resolution TEM images reveals that the as-received AAO membrane bears a close resemblance to the hexagonal assembly of pore arrangement, which is still preserved even in the case of pristine Ni NWs that are recovered in the final synthetic step. More importantly, a detailed analyses of the NW micrographs post electrochemical testing using advanced image processing methods suggests that the hexagonal assembly can be further retained, thus highlighting the electrochemical stability observed in this 1D Ni-NW catalysts.

Similar to the above analyses performed with TEM-imaging, we performed a detailed investigation of the NW compositions using electron energy loss
Mechanistic Investigations of Alkaline Hydrogen Electrocatalysis via Kinetic Modeling and Single-Crystal Voltammetry

In order to deduce the thermodynamic phase of the oxide layer formed (i.e., NiO vs. Ni(OH)₂) in the two samples (NWs pre-/post- treatment in 1M KOH), we further estimated their Ni-L3/L2 white-line intensity ratios over the core- and surface- regions. Our results indicate that the L3/L2 ratio in the shell-region for the Pristine is comparable to the Ni(OH)₂ state, and there is no apparent changes in the chemical state of Ni following the extensive electrochemical characterization.

4:15 PM ET08.02.08
Origin of High Activity of Mn₃O₄ Nanoparticle in Oxygen Evolution Reaction—An Atomic-Resolution STEM/EELS Study

We have explored the atomic structure and electronic structure of Mn₃O₄ nanoparticles using aberration-corrected STEM and EELS to understand its high resolution local compositional variations between the NW core/shell regions. Our results indicate that the NW surfaces form an oxide layer over the metallic core, surrounded by the (011) and (001) facets, and both of the facets undergo the surface reconstructions. In addition, the EELS analysis reveals that the surface reconstructions are accompanied with the suppression of Mn³⁺ ions on the surface. Importantly, such Mn³⁺ ions are still exposed at the edge of the nanoparticle. Currently, it is recognized that Mn³⁺ ions are deeply correlated to active sites of OER in Mn-based electrocatalysts[1]-[4]. Our results suggests that the edges are the active sites of Mn₃O₄, therefore, Mn₃O₄ nanoparticles encloed by active edges compactly can show remarkably high activity in OER whereas its bulk counterpart which mostly has reconstructed surfaces do not have catalytic property.


4:30 PM ET08.02.09
Multiple Coordination of ZIFs with Transition Metal in Metal-Organic-Frameworks as Efficient Electrocatalysts for Energy Conversion

Clean energy technologies such as fuel cells, rechargeable metal-air batteries, and water splitting, are promising for future energy sources owing to their nature of no pollution and greenhouse gas emission. The key reactions in these technologies are the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that generate power. The state-of-the-art electrocatalyst in OER is RuO₂ and in ORR is Pt, but their high cost and poor durability hindered their application in clean energy technologies. Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), mainly composed of a transition metal (TM) center and organic ligands, exhibits the excellent ability as electrochemical catalysts in clean energy conversion and storage. However, their ligand or coordination of metal ions must be modified to enhance their catalytic activities. To rationally design the ZIF catalysts, we have calculated the OER and ORR activities of TM-ZIFs and found an intrinsic descriptor which can describe the catalytic activities of the TM-ZIFs by density-functional theory (DFT) method. Our DFT calculations show that the unsaturated metal sites show high catalytic activities comparable to that of RuO₂ / Pt electrocatalyst. This theoretical result was confirmed by the experiment.

4:45 PM ET08.02.10
Mechanistic Investigations of Alkaline Hydrogen Electrocatalysis via Kinetic Modeling and Single-Crystal Voltammetry

Mechanistic Investigations of Alkaline Hydrogen Electrocatalysis via Kinetic Modeling and Single-Crystal Voltammetry

It has long been recognized that the reaction rates of the hydrogen oxidation and hydrogen evolution reactions (HOR /HER) are up to 200 times slower in basic than acidic electrolytes, even though the surface intermediate of adsorbed hydrogen is independent of solution pH [1]. The mechanistic origins of this difference have been hotly debated in the literature. In this work, we investigate possible explanations for the effect of pH by combining single-crystal voltammetry with microkinetic modeling and electroanalytical methods. We specifically determine the viability of the proposed ‘bifunctional mechanism’, in which slow water dissociation is overcome by mediation of adsorbed hydroxide [2].

Our previous work [3] has shown that on Pt(110) either a direct (hydroxide-as-spectator) or indirect (hydroxide-mediated) Volmer step can describe the measured reaction thermodynamics, but that only the direct Volmer step is consistent with realistic adsorption energies. Furthermore, increasing hydroxide adsorption strength via the electrolyte cation decreases kinetics, as observed by the dependence of peak-potential splitting on scan rate. Comparison with theory shows that this observation is consistent only with the direct mechanism. These results strongly suggest that adsorbed hydroxide serves as a competitive spectator in the alkaline Volmer step, and that the bifunctional HOR/HER mechanism plays only a minor role at best.

The inability of the bifunctional mechanism to describe experimental data is further reinforced by investigating a two-site model recently proposed in the literature [2], in which oxophilic ruthenium or nickel sites are responsible for facilitating water dissociation. We find that such chemical dissociation steps result in anomalous trends with potential, and that oxophilicity has no effect on hydrogen coverage or HER/HOR rates. Comparison with experiment strongly indicates that the observed bifunctional mechanism is unrelated to hydroxide binding strength [4]. Overall, our work resolves a long-standing paradox in electrocatalysis and surface science by determining that oxophilicity is not an accurate descriptor for alkaline hydrogen electrocatalysts. Other parameters, such as water orientation and non-covalent interactions, must play a greater role in overall activity. Efforts to identify and measure these parameters are ongoing.

The electrochemical reduction of CO2 into fuels and chemicals is an attractive route to store renewable electricity. Efficient CO2 reduction catalysts need to yield high activity, high selectivity, and low overpotential, simultaneously. The design of catalysts that exhibit tailored properties such as favourable facets for a given reaction, number of active sites, and oxidation state, is challenging: catalyst can undergo an extensive reconstruction under high productivity operating conditions such as high current densities, reducing potentials, and variable pH. Earth-abundant transition metals such as tin, bismuth, and lead have been proven stable and product-specific, but exhibit limited partial current densities. We present a strategy that employs bismuth oxyhalides as a template from which 2D bismuth-based catalysts are derived. The BiOBr-templated catalyst exhibits a preferential exposure of highly active Bi (110) facets, which we track in operando using grazing-incidence wide-angle X-ray scattering (GIWAXS) and X-ray absorption spectroscopy (XAS). The templated catalyst exhibit an enhanced CO2 reduction reaction selectivity to over 90% Faradaic efficiency for formic acid that is sustained up to stable current densities of 200 mA cm^-2. This represents more than a twofold increase in the production of the energy-storage liquid formic acid compared to previous best Bi catalysts.

8:15 AM ET08.03.02

Electrochemical transformation of CO2 into energy-dense fuels may prove key towards the realization of economically viable, renewable fuels. However, the rational design of CO2 reduction catalysts guided by well-grounded chemical intuition or first-principles computational approaches, have so far been met with limited success. To address this important question of how to activate a molecule as stable and unreactive as CO2 and convert it into complex hydrocarbons, there may be no better place to look than biological systems capable of CO2 activation, for crucial guidance and inspiration.

Recent findings have demonstrated the utility of MoS2 and MoSe2 edge sites in catalyzing the transformation of CO2 to CO. Although this is a promising start, CO is not an easy product to work with industrially nor to transport due to its gaseous nature. Meanwhile, a close look of formate dehydrogenase (FDH), the key enzyme in formate metabolism which catalyzes the reversible two-electron oxidation of formate or reduction of CO2, reveals a catalytic center that is defined by Mo4+/6+ or W4+/6+ coordination with sulfide ligands (from molybdopterin prosthetic groups and cysteine residues) and a selenocysteine side chain. Translation of these chemical moieties, which are recognized as integral to the FDHs architecture and functions, into solid-state semiconductor devices, would suggest that the inclusion of Se ions in Mo/WS2 semiconductors as a dopant may promote the preferred generation of liquid formate, rather than gaseous CO, from CO2. In this project, we want to explore interstitial Se doping of W/MoS2 materials as potential CO2 reduction cathodes, with the ultimate goal of generating reduced liquid hydrocarbon products.

8:30 AM ET08.03.03
Coupling Solar Energy into Catalytic CO2 Conversion Yujie Xiong; Department of Chemistry, University of Science and Technology of China, Hefei, China.

Considering the excessive emission of atmospheric carbon dioxide (CO2) caused by the combustion of fossil fuels, the sunlight-driven CO2 reduction into higher energy chemicals, such as carbon monoxide, formic acid, methanol or methane, offers a more promising approach to alleviate both global warming and energy crisis. Designing new photocatalytic materials for improving the photoconversion efficiency is a promising route to achieve this goal. Despite the invention of a large number of catalytic materials with well-defined structures, their overall efficiency in photocatalysis is still quite limited as the three key steps - light harvesting, charge generation and separation, and charge transfer to surface for redox reactions - have not been substantially improved. To improve each step in the complex process, there is a major trend to develop materials based on inorganic hybrid structures, in which surface and interface engineering holds the promise for boosting the overall efficiency. In this talk, I will demonstrate several different approaches to designing inorganic hybrid structures with improved photocatalytic performance via surface and interface engineering. It is anticipated that this series of works open a new window to rationally designing inorganic hybrid materials for photo-induced applications.

9:00 AM ET08.03.04
Development of Semiconductor-MOF Ternary Photocatalyst Toward Intensified Charge Carrier Density and Molecule Activation in Heterogeneous Photocatalysis Xiang He and Wei-Ning Wang; Virginia Commonwealth University, Richmond, Virginia, United States.

Heterogeneous photocatalysis, such as carbon dioxide (CO2) photoreduction, is a promising engineering approach to reduce atmospheric CO2 levels and simultaneously convert CO2 into hydrocarbon fuels. Among the numerous catalysts for CO2 photoreduction, semiconductors have been studied intensively because of their low cost, easy availability, nontoxicity, and exceptional chemical stability. However, the semiconductor-based CO2 photoreduction still suffers from low efficiency and selectivity, mainly due to low charge carrier density and weak ability to activate the adsorbed CO2 molecules. Towards addressing the aforementioned long-standing issues in CO2 photoreduction (i.e., low charge carrier density and inefficient CO2 activation), we herein report a rational development of MOF-based ternary nanocomposites composed of TiO2/CuO/Cu(OH)2 heterojunction and Cu(CBTC)3, where the roles of semiconductor heterojunction and MOF in charge transfer and CO2 activation are systematically explored. Specifically, the nanocomposites were synthesized via facile and rapid self-assembly of TiO2/CuO nanoparticles within microdroplets, followed by in situ growth of Cu(OH)2 (BTC)3 on the TiO2/CuO surface, where part of CuO serves as the sacrificial metal source. The unique ternary TiO2/CuO/Cu(CBTC)3 composite possesses heterojunction and abundant coordinatively unsaturated copper sites, which results in not only increased charge carrier density but also efficient activation of CO2 molecules, therefore leading to high CO2 conversion efficiency and preferential formation of CH4. With systematic measurements (e.g., gas chromatography, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, and time-resolved in situ diffuse reflectance infrared Fourier transform spectroscopy), a plausible pathway of CO2 activation and subsequent reduction in this ternary system was proposed. The outcome of this work provides new insights in rational design of MOFs-based hybrid nanomaterials for efficient CO2 photoreduction.
Photocatalytic and Optoelectronic Studies of SnS2 Thin Film by Controlled Implantation of Carbon Ions

Tadesse Billo Reta, Indrajit Shown, Weiwen Woor, Rwei-San Chen, Chih-Hao Lee, Li-Chyong Chen and Kuei-Hsien Chen; Institute of Atomic and Molecular Sciences, Academia Sinica, Nangang, Taiwan; Department of Physics, National Central University, Taoyuan, Taiwan; Graduate Institute of Applied Science and Tech. National Taiwan University of Science of Technology (NTUST), Taipei, Taiwan; Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan; Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

A significant increase of CO2 in the atmosphere has a profound impact on global climate change, which has become a central challenge of the 21st century. Photocatalytic reduction of CO2 into chemical fuel is an appealing strategy to resolve greenhouse gas emissions and alleviate the energy crisis. The efficiency of CO2 conversion relies on the catalytic sites and microstructure of photocatalyst. In this work, we successfully synthesized SnS2/SnO2 heterogeneous multi-shelled hollow spheres by the sequential templating approach. Multi-shelled hollow structures not only have the characteristics of the large specific surface area and high loading capacity; more importantly, they have multiple adjustable shells and inter-shell spaces, enabling sequential light reflection and scattering, which greatly improve the light-harvest capability and light conversion efficiency. These unique features make them promising candidate for photocatalytic reduction of CO2. The SnS2/SnO2 multi-shelled hollow spheres exhibited an enhanced efficiency and good stability for photocatalytic reduction of CO2 to CO. Photocatalytic activity of SnS2/SnO2 multi-shelled hollow spheres is increased with the shell number significantly. As a result, the quadruple-shelled SnS2/SnO2 hollow spheres steadily photocatalyzed CO2 to CO at a rate of 50 μmol g\(^{-1}\) h\(^{-1}\) under AM 1.5 G simulated solar irradiation, and the rate can maintain 72 hours without decline. This work paves the way for enhancing photocatalytic performance by structural design of the emerging materials.

10:00 AM BREAK

Designing Nanostructured Materials for Electrochemically Recycling Carbon Dioxide

Michael B. Ross and Peidong Yang; University of California, Berkeley, Berkeley, California, United States.

Electrochemical carbon dioxide (CO2) recycling enables the synthesis of high-value fuels and chemicals using renewable energy. Doing so requires the development of catalysts that both efficiently and selectively reduce CO2 into desirable products. Nanomaterials are particularly powerful for doing so due to their high surface areas, tunable chemical and physical properties, and unique reactivities that can differ from the bulk. Thus the synthesis, characterization, and integration of nanostructured electrocatalysts for CO2 reduction is a promising strategy for realizing breakthrough performance. Synthesis gas (syngas), a mixture of H\(_2\) and CO, can be converted into a variety of fuels and chemicals using established industrial processes that require different syngas compositions. Here we will describe the synthesis, characterization, and catalytic properties of nanostructured electrocatalysts that are versatile and modular, and which also provide dynamic access to a wide variety of desirable syngas compositions. Strategies for generating multi-carbon products will also be discussed.

11:00 AM ET08.03.08

Controlled Selectivity of CO\(_2\) Reduction via Electrochemical Potential Modulation

Kevin Kimura, Jin Suntivich and Tobias Hanrath; Cornell University, Ithaca, New York, United States.

We present the product distribution of the CO\(_2\) reduction reaction (CO\(_2\)RR) when the driving force is a pulse of electrochemical potential. The use of renewable electricity to convert CO\(_2\) into energy-dense fuels and high-valued feedstocks is an enabler of many sustainable energy and chemical technologies. The CO\(_2\)RR offers a pathway to achieve this goal using electrochemistry. However, the CO\(_2\)RR suffers from poor selectivity, especially on Cu, despite its ability to produce hydrocarbons (such as methane, ethylene, etc.). In this presentation, we present a strategy for manipulating the CO\(_2\)RR selectivity by applying the CO\(_2\)RR driving force (‘overpotential’) as pulses. By applying pulses of overpotential with controlled duration and magnitude, we demonstrate that the CO\(_2\)RR selectivity can improve > 97% of faradaic efficiency (FE) with respect to the competing hydrogen evolution reaction, and the selectivity toward methane can be as high as 83% FE. We will discuss the possible mechanisms for why the temporal control of the overpotential pulse can lead to the CO\(_2\)RR selectivity control and the possible implications on the timescale of the competing pathways in the CO\(_2\)RR.

11:15 AM ET08.03.09

Transition Metal Single Atom Electrocatalysts for Selective CO\(_2\) Reduction in Water—From Identification to Scaling-up

Haotian Wang; 1Harvard University, Cambridge, Massachusetts, United States; 2Rice University, Houston, Texas, United States.

The development of highly selective and earth-abundant electrocatalysts for CO\(_2\) reduction is becoming increasingly important for renewable energy applications. The challenge here is the strong competition from water reduction, as well as the low selectivity towards a desired product. In this talk I will introduce the rational tuning of electronic properties of catalytic materials for their significantly improved CO\(_2\) reduction performance. By dispersing transition metals into isolated single atoms with electronic structures significantly different from their bulk counterparts, we can dramatically suppress the competing hydrogen evolution and deliver an ultra-high CO\(_2\) reduction selectivity of more than 95% under ambient conditions in water. I will also talk about the successful scaling-up of both the catalytic materials synthesis as well as the CO\(_2\) reduction current density while maintaining ultra-high CO\(_2\) reduction efficiency.
selectivity.

11:30 AM ET08.03.10
Rational Design of Terrace, Step and Corner Sites of The Metal or Bimetallic Catalysts for Hydrogenation and Hydrodeoxygenation of Biomass-Derived Platform Molecules
Shelaka Gupta, Tuhin Suverya Khan, Md. Imteyaz Alam and M. Ali Haider; Chemical Engineering Department, Indian Institute of Technology Delhi, New Delhi, India.

Deoxygenation and valorization of biomass-derived platform molecules was studied using ring-opening (RO), decarboxylation, hydrogenation and hydrodeoxygenation (HDO) reactions. The platform molecules studied here included cellulose-derived lactones, furans, 2-pyrones and lignin-derived phenolic compounds.

Study on the conversion of lactones was focused to understand the mechanism of RO and decarboxylation reaction. More specifically, oxocarbenium ions were proposed as an intermediate to play an important role in controlling the rate of RO step. The mechanism of RO and decarboxylation reaction in 2-pyrones formed an interesting case, wherein the reaction in partially saturated 2-pyrones followed a retro-Diels-Alder (rDA) route. Both solvents and substituents were expected to influence the rDA reaction of partially saturated 2-pyrones, which was studied using density functional theory (DFT) simulations.

6-arylt-α-pyrones (6PP) was suggested as a potential platform chemical, which may be obtained directly from the fermentation of waste lignocellulosic biomass. On RO and decarboxylation, 6PP was converted to C6 linear ketones which are proposed as precursors for jet and diesel range fuels. All of these catalytic transformations of 6PP can be integrated with the upstream fermentation of biomass to form a unique bio- and chemo-catalytic process for providing high value fuels and chemicals. However, biogenic impurities present in ppm levels (<100 ppm) along with the fermentation-derived molecules pose a detrimental effect to heterogeneous catalyst stability. Interaction of such impurities with the metal catalyst surface was studied using DFT simulations.

Bimetallic alloy of NiAu was proposed as a more stable surface for hydrogenation reactions. Catalytic hydrogenation reaction carried out on the Pd catalyst was an interesting case to further explore the influence of catalyst particle size and morphology on the selectivity of a desired product. Detailed mechanistic studies were carried out on Pd (111) and Pd (100) surfaces using DFT calculations to corroborate experimental finding. Since Pd (111) are the majority (~70%) sites, high selectivity observed towards the partially hydrogenated product (cyclohexanone) in the experiments is thought to be from the Pd (111) surface. Contrary to this prevalent thought, on using a combined theoretical and experimental approach, Pd (111) surface was demonstrated to selectively produce the cyclohexanol. Surprisingly, Pd (100), the minority (~25%) sites were selectively producing cyclohexanone. These results lead to the development of a comprehensive understanding on facet-dependent selectivity control in phenol hydrogenation on the Pd catalyst. Final reaction in this sequence was HDO of biomass-derived furan compounds, wherein the synergistic interaction of Zn with the Pd catalyst was studied using DFT simulations. Zn was shown to participate in C-O bond activation step while Pd surface participated in the hydrogenation step.

SESSION ET08.04: Novel Structures for Catalysis
Session Chairs: Hongyou Fan and Yugang Sun
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 306

1:45 PM *ET08.04.01
Self-Assembly and Formation of Nanostructured Porphyrin Photocatalysts
Hongyou Fan1, 2; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2The University of New Mexico, Albuquerque, New Mexico, United States.

Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanocatalysts for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, I will present our recent progress in the synthesis of such nanocatalysts through a surfactant-assisted interfacial self-assembly process using optically active porphyrins as a functional building block. The self-assembly process relies on specific interactions such as π–π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanocatalysts, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for redox synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

2:15 PM *ET08.04.02
Membrane Coated Electrocatalysts for Stable, Active and Selective Electrocatalysis
Daniel Esposito; Chemical Engineering, Columbia University, New York, New York, United States.

Conventional electrocatalysts used in fuel cells and electrolyzers are comprised of metallic nanoparticles that are attached to a conductive electrode support that allows for the transfer of electrons between an external circuit and the electrocatalyst/electrolyte interface. Typically, these nanoparticles are partially or fully exposed to a bulk liquid or gaseous phase to facilitate mass transfer of reactants and products. In contrast, this presentation describes recent studies on an emerging class of electrocatalysts for which the active metal electrocatalysts are completely encapsulated by ultrathin layers of permeable oxides that can exhibit membrane-like properties. These so-called membrane coated electrocatalysts (MCECs) offer many potential advantages over conventional electrocatalysts, including the ability to simultaneously mitigate degradation, alter reaction selectivity, and improve reaction kinetics at the buried interface between the overlay layer and active catalyst. This talk will describe three case studies of silicon oxide (SiOx)-encapsulated Pt electrocatalysts that separately demonstrate the ability of the SiOx overlayer to enhance catalyst stability, activity, and selectivity. Of particular interest to the last two studies are the task of developing a deeper understanding of the buried interfaces of MCECs, which represent confined environments where structure can, in principle, be tuned to alter reaction energetics and selectivity for a wide variety of electrochemical reactions.

References


2:45 PM ET08.04.03

**Colloidal Hexagonal Copper Phosphide (Cu₃P) Nanosheets for Selective and Low-Overpotential CO₂ Electroreduction to Ethylene**

Hui Li¹, Peng Wen², Dominique S. Iunza³, Zachary D. Hoed⁴, MiaoFang Chi⁵, Lin Jiang⁶, Yejun Qu⁷ and Scott M. Geyer¹; ¹Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States; ²Department of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen, China; ³Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, United States; ⁴Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou, China.

Electrochemical CO₂ reduction provides a fascinating pathway to produce valuable carbon-based fuels, but limited by low conversion efficiency, high overpotential for certain selectivity, and sluggish reaction rate. Herein, we report that colloidal hexagonal copper phosphide nanosheets (Cu₃P NSs) show a remarkable onset potential of -0.33 V vs. RHE and achieves a maximum Faradaic efficiency of 62% at -0.88 V vs. RHE for selective CO₂-to-C₂H₄ in a 1:1 volume ratio of EMIM-BF₄ ionic liquid and H₂O electrolyte. By contrast, Cu₃P and Cu nanoparticles (NPs) tend to selectively reduce CO₂ to CH₄ and CO/CH₄, respectively. DFT calculation reveals that the delocalized P atoms enhance the stabilization of CO* intermediate and the stepped facets of (111) on nanosheets favor C-C coupling step rather than the low-index (111) facets on nanoparticle. Moreover, only 8% decay for a high partial C₂H₄ current density of 20.6 mA cm⁻² at -1.0 V vs. RHE during 24 h stability test is observed on Cu₃P NSs.

3:00 PM ET08.04.04

**2-pyridinide as an Active Catalytic Intermediate for CO₂ Reduction on p-GaP Photoelectrodes—Lifetime and Selectivity**

Shenzhen Xu¹ and Emily Carter²; ¹Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; ²School of Engineering and Applied Science, Princeton University, Princeton, New Jersey, United States.

The active intermediate responsible for the highly selective reduction of CO₂ to methanol at p-GaP photoelectrodes is currently under debate. Adsorbed 2-pyridinide (2-PyH*), produced from a two-electron reduction and protonation of adsorbed pyridine (Py*), was recently proposed by Carter and coworkers to be a key intermediate that facilitates hydride transfer (HT) to CO₂ to produce formate. However, the lifetime of 2-PyH*, most likely controlled by the rate of 2-PyH* protonation to form adsorbed dihydropropyridine (DHP*), is still in question. In this work, we provide evidence for the transient existence of 2-PyH* on a p-GaP surface by comparing the activation energy for HT to CO₂ to those predicted for 2-PyH* being protonated to form either DHP* or PyH*+H₂ via a hydrogen evolution reaction (HER). We predict that 2-PyH* situated next to an adjacent surface hydroxide (OH*) will be the most effective intermediate leading to CO2 reduction on p-GaP. Predicted high barriers of HER (via either 2-PyH* or H*) also explain the high selectivity toward CO₂ reduction observed in experiments.

3:15 PM BREAK

3:45 PM ET08.04.05

**Facet-Controlled Palladium Nanocrystals for Selective Catalysis**

Younan Xia; Georgia Institute of Technology, Atlanta, Georgia, United States.

For a structure-sensitive reaction, the activity and selectivity of a heterogeneous catalyst can both be enhanced by controlling the type of facet and thus the arrangement of atoms on the surface of nanocrystals. This concept, however, could not be materialized until recently when it became possible to synthesize facet-controlled nanocrystals, including those with high-index facets. In addition, the size of a facet-controlled nanocrystal determines the surface-to-bulk atomic ratio and the proportions of different types of atoms (e.g., vertex, edge, vs. face). In this talk, I will use palladium (Pd) as an example to illustrate how facet-controlled synthesis has enabled the development of catalysts with enhanced activity and selectivity toward an array of reactions, including formic acid oxidation and selective hydrogenation.

4:15 PM ET08.04.06

**Morphological Effects of In Situ Reduction of Cuprous Oxide Interfaces for the Electrochemical CO₂ Reduction Reaction**

Hamed Mehrabi¹, James M. Lowe² and Robert H. Coridan³; ¹Microelectronics-Photonics, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States; ²Chemistry and Biochemistry, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States.

Copper-based electrodes have shown uncommon promise for catalyzing the electrochemical reduction of CO₂ to a variety of high-value products. Cuprous oxide (Cu₂O) is a particularly interesting starting material, as it can be reduced in situ to generate active Cu metal sites on the surface. In recent work, we have demonstrated that the electrochemical properties and nanoscale morphology of photoelectrodedeposited Cu₂O can be modified by the illumination conditions during growth. Photogenerated electrons have sufficient energy to induce the formation of Cu metal nano-inclusions in a predominantly Cu₂O matrix. The presence of Cu disrupts the micro-crystalline growth observed in Cu₂O electrodedeposited without illumination. Here, we will describe the experiments that study the effects of photodoping on electrodedeposited Cu₂O electrodes for the CO₂ reduction reaction. The transition from oriented microcrystals to disordered nanocrystalline films with increasing light intensity during growth has a significant effect on the reduction of the electrode surface. This alters the dynamics and electrochemical behavior of the electrode for CO₂ reduction. We will also explore how chemical modifications to the surface, such as the thermal oxidation of the Cu nano-inclusions or the addition of a co-catalyst, can affect the branching ratios and dynamics of electrocatalysis. The work outlined here helps to inform further use of electrodes prepared by the in situ reduction of Cu₂O for this application.

4:30 PM ET08.04.07

**Controlling Proton and Electron Transfer to Molecular Electro catalysts for Enhanced Selectivity**

Christopher Barile, Rajendra Gautam and Jason Mennel; University of Nevada, Reno, Reno, Nevada, United States.

The O₂ reduction reaction and the CO₂ reduction reaction are both central to important renewable energy devices. Since both reactions require the transfer of multiple electrons and protons, they can proceed by a variety of mechanisms depending upon the relative rates of these transfer events. We have developed electrode architectures that enable the modulation of proton and electron transfer kinetics to molecular catalysts such that the selectivity of catalysts can be improved. These electrodes are comprised of a metal-centered catalyst such as a Cu-triazole or an Fe-porphyrin attached via a self-assembled monolayer (SAM), which is then covered by a proton-permeable membrane. By altering the identity of the SAM, the kinetics of electron transfer to the bound catalyst can be tuned. Changing the proton permeability of the membrane enables control over the kinetics of proton transfer to the catalyst.

One of the major challenges in designing catalysts for both the O₂ and CO₂ reduction reactions is selectivity. Using a membrane-modified electrode, we
demonstrate that the selectivity of a Cu-based O2 reduction catalyst can be improved by controlling proton transfer rates such that the catalyst produces exclusively water. In contrast, the same Cu catalyst produces ~10% deleterious H2O2 side product when proton transfer is unregulated. We also explore how altering proton and electron transfer kinetics affects the selectivity of molecular CO2 reduction catalysts.

**ET08.04.08**

**Electrochemical CO2 Reduction to CO on Au—Isolating the Intrinsic Activity of the Most Common Crystal Facets**

Brian J. Seger1, Stefano Mezzavilla2, Ian E. Stephens2 and Ib Chorkendorff3; 1Technical University of Denmark, Kongens Lyngby, Denmark; 2Department of Materials, Imperial College London, London, United Kingdom.

Due to the drastic drop in renewable electricity prices, electrochemical CO2 reduction has received renewed interest. While CO2 reduction can lead to a wide variety of products, almost all go through a CO intermediate, thus understanding the electron transfer reaction of CO2 to CO is important not just for CO production, but also for products such as ethylene, ethanol, methane and others. Au has been shown to be the most active electrocatalyst for CO production, however major fundamental knowledge on this reaction has yet to be discovered. While most works focus on highly active nanostructured Au electrodes, there has yet to be a comprehensive study on the intrinsic electrochemical activity of individual Au facets.

This talk will discuss our work on the electrochemical conversion of CO2 to CO on single crystal Au <110>, <111>, <110>, and <211> facets as well as polycrystalline Au. Our results show a 25 fold difference between the least and most active crystal facets. All facets follow approximately the same Tafel slope between the tested potentials of -0.6 V to -0.8 V vs. RHE. Pb underpotential deposition (UPD) was used to deposit a monolayer of Pb on the Au gold surface to determine surface area. However, the potential at which Pb UPD deposits is facet dependent. By setting a correct potential we could selectively deposit lead on a given facet. While Pb UPD favored depositing on the most active sites, we still could gain fundamental catalysis knowledge. On polycrystalline Au, 20% of a monolayer of Pb yielded a 50% decrease in CO production, but only a 30% decrease in H2 production. 50% of a Pb monolayer on Au yielded a 95% decrease in CO production, but only a 50% decrease on H2 production. The decrease in CO production as a function of Pb coverage indicated that not only could we passivate the most active sites, but also that the facet dependent activity was quite different for CO production versus the competing H2 evolution side reaction.

To further utilize Pb UPD to isolate sites we reinvestigated one of our least active facets, Au <111>. Single crystals are never completely flat and thus there are always a small percentage of step sites. We used selective Pb UPD to deposit 4% of a monolayer in the attempt to passivate these sites. This led to a 50% decrease in CO activity, but the same H2 evolution activity. Covering the Au <111> with 15% of a monolayer led to a 90% drop in CO activity, but the same H2 evolution activity. These results suggest that the intrinsic activity of the least active facets is probably much lower than measured and the experimental results are actually dominated by a small number of highly active defect sites. While these results focus on Au, no single crystal is defect free. Thus these results may lead us to also question whether there are other situations where the non-optimal facets for a given reaction are actually much less active than originally thought.
Compared to traditional wash-coated powder-form catalysts, array ensembles of one-dimensional (1D) nanostructures possess stronger gas-solid phase interaction, larger surface area and enhanced materials utilization efficiency [1, 2]. Unlike a layer of ZSM-5 film (MF framework) grown on cordierite[3], array-structured ZSM-5 with c-orientation was synthesized by a secondary-growth hydrothermal method. Although the BET surface area and pore size distribution were similar with traditional film, the hydrocarbon trapping efficiency over as-synthesized ZSM-5 arrays was significantly improved. The higher extent of the exposed a- and b- planes to reactant molecules could facilitate the catalytic reactions and adsorptions by improving the mass transportation. The novel ZSM-5 array-structure could provide a promising class of structured devices for hydrocarbon trapping and separation.

Furthermore, first-principles Density Functional Theory (DFT) calculations are performed to investigate the Al substitution site preference on the ZSM structure, as well as the adsorption energetics of the reactant molecules.

References


ET08.05.04 Sulfur Segregation and Surface Site Vacancy Compensation During Methanol to Methoxy Reactions on MoS2 Prescott E. Evans1, Hae K. Jeong1, Zahra Hooshmand2, Duy Le2, Takat B. Rawal2, Sahar N. Alvillar4, Ludwig Bartels3, Tatat S. Rahman1 and Peter Dowben2, 1Daegu University, Gyeongsan, Korea (the Republic of); 2University of Central Florida, Orlando, Florida, United States; 3University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 4University of California, Riverside, Riverside, California, United States.

Coverage dependent, sulfur vacancy defect formation on the MoS2(0001) basal plane resulting from the adsorption of methanol on MoS2 and its subsequent conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission, photoluminescence, and modeled by density functional theory (DFT). The adsorption of methanol on MoS2 at 110 K followed by annealing near 350 K or the adsorption of methanol on MoS2 at 350 K results in the formation of numerous point defects at the MoS2 basal plane. Larger patch defects, nominally ~2 nm in size as well as line defects on the MoS2 sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of MoS2 to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and significant shifts in oxygen binding energies. Additionally, shifts in sulfur binding energy and temperature dependent sulfur to molybdenum integrated XPS intensities ratios near the critical 350 K formation temperature indicate sulfur segregation to the surface and compensation of surface vacancy sites. The experimental results indicate a small but persistent activation energy for the reaction consistent with DFT predicted energetics. The energy favorability of coinciding defect creation and methoxy formation is also suggested by DFT calculations. A strongly bound methanol surface kinetics is not favored on the defect free MoS2 surface.

ET08.05.05 Developing Descriptor of Keggin Heteropolyacid for Application in Biomass Conversion Catalysis Fiaz Ahmad, Tuhin Suvaraa Khan, Md. Inteyaz Alam, Kamal K. Pant and M. Ali Haider; Indian Institute of Technology Delhi, New Delhi, India.

Bio-renewable resources have great potential to supersede conventional fossil fuel to meet energy and chemicals demands. Nevertheless, most of the processes employed for biomass conversion essentially requires the presence of an acid catalyst for sustainable production of fuel and chemicals. In this context, catalysts belonging to the family of Heteropolyacids (HPA) are extensively used owing to their excellent activity in biomass conversion reactions[1]. Although a wide range of HPA’s have been classified based on their geometrical arrangements, Keggin HPA’s represented by general formulae, [XM12O40]n+ have prevalence in industrial applications owing to their super acidic nature, high thermal stability at elevated temperatures in liquid phase reactions and ease of synthesis as compared to other HPA’s. In general, the central atom X can be either P, Si, Ge, B, or Al whereas the heteroatom M can be either W6+ or Mo6+ or W6+ in which 12 linked octahedra containing addenda atoms (M2+O4) surrounds a central tetrathiod (XO4)4+. Interestingly, the higher activity of Keggin HPA’s is attributed to the combined effect arising from their stability, acidity, and structural accessibility, nevertheless no conclusive evidence has been suggested for the rational design of Keggin HPA’s. Moreover, the effect of changing central atom X on the activity of Keggin HPA’s is yet to be explored. Therefore, we have employed both theoretical and experimental approach to conclude deprotonation energy (DPE) as a suitable descriptor for rational design and selection of Keggin HPA’s. In this regard, Density functional theory (DFT) have been employed to calculate the DPE of known Keggin HPA’s with heteroatom W and Mo as well as propose the novel and futurist catalysts by changing the central atom with elements from group 13-17 of the periodic table. Parallally, esterification reactions have been performed with biomass-derived levulinic acid to produce additives for “green gasoline” in the presence of phosphotungstic acid and phosphomolybdic acid to validate the theoretical results. Interestingly, it was found that activity of Keggin HPA’s is a direct function of their DPE and difference in DPE remained constant when same elements from group 13-17 of the periodic table were put as central atom X in each of the Keggin HPA’s with W6+ and Mo6+ heteroatom. Nevertheless, change in the central atom of the Keggin HPA’s with W6+ and Mo6+ heteroatom caused a significant change in individual DPE’s, yet the overall difference in DPE remained constant when same central atoms were placed in both the catalysts. Interestingly, experimental results suggested similar trend and difference in activation barriers of both the catalysts with same central atom remained same even though esterification reactions were performed in different alcohols. Besides several tools and techniques such as XRD, BET, FT-IR, SEM, TEM, HPLC, GC-FID have been used for the characterization of catalysts and the product.

ET08.05.06 Deciphering Graphene Supported Metal-Nitrogen Active Center on CO Reduction Reaction—Structure, Magnetic and Catalytic Properties from First Principle Simulations Minjie Liu1, Guangjin Wang1 and Qin Wu1; Brookhaven National Laboratory, Upton, New York, United States; 1College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan, China.

The dispersing single atom catalysts have been developed recently and reveal highly catalytic activities. The materials of single transition metal embedded in nitrogen-doped graphene display great potential as the catalysts for many reactions. For example, single atomic Ru in nitrogen-doped graphene exhibits excellent activity for oxygen reduction reaction [1]: single Fe-Co-Ni in Mn3C4 moieties show tunable electrocatalytic activity in oxygen evolution reaction [2], and Fe dispersed on nitrogen-doped graphene has been demonstrated as an efficient electrocatalyst for CO2 reduction reaction [3]. In those systems, the single atom center contributes as the active site, while the interaction between the single atom and the substrate is crucial. In our study, we applied density functional theory (DFT) simulations to elaborate different nitrogen doping concentrations and configurations surrounding the metal center. The stability of graphene supported metal-nitrogen active center, magnetic and catalytic properties have been explored. Take CO2 reduced into CO on Fe-N-graphene system as an example, our results show that the chemical environment around the single atom is critical, and the metal center and nitrogen atoms nearby determine the catalytic performance synergistically. Regulating single atom coordination tunes catalytic activity which will be instrumental for designing catalysts with the desired properties.
In this work, we investigated the effect of the Pt-precursor, on the catalytic properties of the PtCeO2-NR catalysts for H2 production. The CeO2-1D support was synthesized by the hydrothermal method, using a (NaOH) solution 10 M as precipitating agent [1,2]. The active phase Pt 0.5% (w/w) was impregnated to the catalytic support CeO2-1D by impregnation method. The Pt/CeO2-(X) catalysts were characterized by N2 adsorption, XRD, TPR, TEM and EDS. Afterwards, the activity and selectivity in the SRM reaction was evaluated by using a commercial system RIG-100-ISRI in a temperature range of 200 - 450 °C at atmospheric 204 Pressure. The reaction products were analyzed by using a Gow-Mac 580 Gas chromatograph with a thermal conductivity detector equipped with a two column system. The characterization results showed a specific surface area of 89 and 95 m2/g respectively for the support and the best Pt/CeO2-(Nit) catalyst. The XRD results showed the typical diffraction pattern of the fluorite cubic structure for CeO2 and a peak associated with Pt is not detected, which confirms a small particle size and a high dispersion of the metal. TPR profiles of the Pt/CeO2-(X) catalysts, showed peaks of H2 consumption associated with the reduction of PtO, to Pt° at low temperature as well as a partial reduction of surface ceria from Ce4+ to Ce3+, associated to the presence of the noble metal on the surface of the support [3]. Catalytic activity in the steam reforming methanol reaction, the Pt/CeO2-(Nit) catalyst exhibited a higher catalytic activity reaching a conversion yield of 99% at 350 °C, as well as higher H2 production. In addition, it exhibited a higher yield, as well as the lower production of CO and CH4. None of the synthesized catalysts exhibited a significant deactivation over the evaluated time period.

Authors gratefully acknowledge financial support from the ININ projects CA-607, CO-081 and CONACYT-SENER 226151

References:

ET08.05.08
Tuning of Activity and Selectivity of Ni(Al)-SBA-15 Catalysts in Hydrogenation of Naphthalene
Tatiana Klimova, Haydee Vargas Villagran and Mark Eugenii Martinez-Klimov
Universidad Nacional Autónoma de Mexico, Ciudad de Mexico, Mexico.

In the present work, two series of nickel catalysts with 4 wt. % of Ni loading were evaluated in the hydrogenation of naphthalene in order to elucidate the effect of surface acidity (Broomsted or Lewis) and preparation method used on the catalyst's activity and selectivity. On the one hand, two supports, SBA-15 silica and Al-SBA-15 with Si/Al molar ratio ~ 30, were synthesized by hydrothermal method in order to obtain 2D nanostructured supports with and without Broomsted acidity. On the other hand, three Ni catalysts were prepared by the incipient wetness impregnation method using two different nickel precursors: nickel nitrate (N) and a Ni-EDTA complex (ED). We were also interested in the effect of the preparation method on the nickel dispersion and the acidity of the prepared catalysts.

Prepared catalysts were labeled as: Ni/SBA(NN), Ni/SBA(ED), Ni/AlSBA(NN) and Ni/AlSBA(ED). Characterization of the catalysts was performed by nitrogen physisorption, powder X-ray diffraction, temperature programmed reduction, temperature programmed desorption of ammonia, infrared spectroscopy of adsorbed pyridine and high resolution transmission electron microscopy. Characterization results showed that both SBA-15 and Al-SBA-15 supports had attractive textural properties. However, the characteristic hexagonal pore arrangement of SBA-15 was not preserved in the Al-SBA-15 support. The IR of adsorbed pyridine allowed us to confirm and quantify the Broughton (B) and Lewis (L) acid sites present in the SBA-15 and Al-SBA-15 catalysts prepared from both precursors used, being the Ni/AlSBA(ED) catalyst the most acidic one. Catalytic activity of the catalysts in hydrogenation of naphthalene increased in the following order: Ni/SBA(NN) < Ni/AlSBA(NN) < Ni/AlSBA(ED) < Ni/SBA(ED). Acidity of the catalysts and the dispersion of the reduced Ni nanoparticles also affected the selectivity of the catalysts to decalins (completely saturated products). Both catalysts prepared using a Ni-EDTA complex (Ni/SBA(ED) and Ni/AlSBA(ED)) showed high selectivity to decalins, whereas those prepared from a nickel nitrate solution (Ni/SBA(NN) and Ni/AlSBA(NN)) were selective for tetralin production. Therefore, the nickel precursor used and the support’s acidity affected the activity and selectivity of the tested Ni catalysts.

ET08.05.09
Enhanced CO2 Reduction in Lead-Free Perovskite CsxSb2Br6 Nanocrystals—Performance and Selectivity
Chang Lu, Xiao Ma, Dominique S. Itanze, Hui Li and Scott M. Geyer; Wake Forest University, Winston Salem, North Carolina, United States.

The last decade has witnessed the burgeoning development of halide perovskite materials with a significant focus on solar and light-emitting diodes applications. However, halide perovskites have received less attention as a catalyst for energy application, for example, water splitting and CO2 reduction reaction. Moreover, the development for Pb-free perovskite is highly desired for all applications. To this end, in our work, we developed a facile synthesis method for Sb-based halide perovskite nanocrystals (NCs). These exhibit structure uniformity and high thermal stability, with only a 2 % weight drop (attributed to the ligand loss) under 200 °C annealing. For solar driven CO2 reduction the Cs2Sb2Br6 produces 400 umol(CO)/g, a 40-fold more improvement in CO per gram compared to CsPbBr3. Interestingly, the use of Pb-based perovskite also generates CH4, which is not observed in Sb-based reaction batch, and we will present DFT calculation results to shed further light into the differences in reaction mechanism for the Pb-based and Sb-based system. This brings new insights into the emerging field of Pb-free perovskite alternatives and perovskite materials for catalytic applications.

ET08.05.10
Development of Catalytic La-Based Perovskite Redox Materials for Solar Thermochemical Conversion of CO2 into Syngas
Rahul R. Bhosale and Gorakshnath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

The energy consumption of the world today is around 15TW and it is expected that it will raise up to 30TW by the year 2050. In addition to this, due to the excessive utilization of fossil fuels (for the production of required energy), the concentration of CO2 in the environment increases rapidly. The production of syngas (which can be used as a precursor for the production of liquid transportation fuel) by using H2O, CO2, and solar energy provides a promising path.
to solve the issues associated with the utilization of fossil fuels and increase in the CO₂ concentration.

Direct photo-reduction of syngas via thermolysis of H₂O and CO₂ is possible; however, it needs a very high temperature and chances of forming a gaseous explosive mixture of H₂ and O₂ is also very high. Utilization of solar driven metal oxide based catalytic thermochemical H₂O and CO₂ splitting cycle reduces the requirement of higher temperatures and avoids the formation of explosive gas mixture. Various non-volatile redox materials have been investigated towards the thermochemical production of solar fuel via H₂O and CO₂ splitting reactions. In addition to the ferrite and ceria based materials, recently the researchers are focused towards perovskite based redox materials as an active catalyst for the solar splitting process. In particular, La-based perovskite materials are of particular interest as they are capable of producing higher amounts of O₂ and H₂/CO₂ at lower operating temperatures as compared to ceria and ferrites.

In this study, a variety of La-based perovskite materials were synthesized using combustion method and tested towards multiple H₂O/CO₂ splitting cycles using a high temperature thermogravimetric analyzer. It is very important to note that in most of the previous investigations the maximum number of cycles performed in case of La-based perovskites are 3 to 4. Hence, this study has a uniqueness that it tested the La-based perovskites in more than 50 thermochemical cycles.

**ET08.05.11**
Enhancement of CO₂ Reduction Activity Under Visible Light Irradiation Over Zn-Based Metal Sulfides by Combination with Ru-Complex Catalysts
Tomiko M. Suzuki¹, Tomoaki Takeyama¹, Shunsuke Sato¹, Akihide Iwase², Akihiko Kudo² and Takeshi Morikawa³; ¹Toyota Central R&D Labs Inc, Nagakute, Japan; ²Tokyo University of Science, Tokyo, Japan.

The reduction of CO₂ to obtain useful energy-rich chemicals utilizing photocatalysts has attracted attention as a potential means of artificial photosynthesis operating under sunlight irradiation. Although the use of powdered systems for CO₂ reduction is challenging owing to the inherent difficulty in achieving the highly selective reaction of CO₂ in solution, the system is attractive as a practical cost-effective system to utilize sunlight [1]. In this regard, we have demonstrated visible light-induced selective reduction of CO₂ to HCOOH using metal-complex/semiconductor hybrid photocatalyst consisting of a Ru-complex and a p-type metal oxide semiconductor particles (N-doped Ta₂O₅) in acetonitrile (MeCN)/triethanolamine (TEOA) solution with quantum efficiencies of 1.9% and more [2, 3]. Among various semiconductors, Zn-based sulfide are also attractive semiconductor for the hybrid photocatalyst, because ZnS possesses a relatively negative conduction band minimum (E_{CBM}) formed by the Zn 4s4p orbitals, which facilitates the electron transfer from the CBM of the semiconductor to the metal-complex.

In the present study, the powdered Zn-based sulfides which were reported to be active for sacrificial H₂ evolution, were investigated in combination with various Ru-complex catalysts with regard to the promotion of visible light driven CO₂ reduction. Hybrid photocatalysts consisting of a Ru-complex and a semiconductor anchored by organic groups were prepared by an adsorption method. Photocatalytic CO₂ reduction was performed in MeCN/TEOA solution under visible light (≥410 nm) irradiation. The photocatalytic activities were largely dependent on the basic characteristics of the Ru-complex and the metal sulfide. The results demonstrate that several of semiconductors improve the photocatalytic CO₂ reduction selectivity of the hybrid system, and that n-type (AgIn)₀.₂₂Zn₁.₅₆S₂ [4] and ZnS:Ni (Ni 0.2 mol%) [5] linked with a neutral Ru-complex containing phosphonate anchors ([Ru(dpbpy)(CO)₂Cl]², dpbpy: 4,4'-diphenyl-2,2'-bipyridine) exhibited highest turnover number with above 100 after 16 h irradiation. The carbon source for the HCOOH evolved in the reaction over the hybrid photocatalysts was confirmed to be CO₂ based on ¹³C analyses [6].

These results suggest that Zn-based metal sulfide are potential candidates for use in powdered semiconductor/metal-complex systems for active and selective CO₂ photoreduction. Our results also suggest that future success in powdered Z-scheme systems utilizing water as an electron donor and proton source.

**References**

**ET08.05.12**
High Yield Preparation of Two-Dimensional Cu Nanocatalysts for Carbon Dioxides Reduction Reaction
Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., Columbus, Ohio, United States.

Cu-based nanostructures have been explored for catalyzing CO₂ electroreduction due to their lower working function and cost, and higher earth-abundancy. However, the practical application of CO₂ electroreduction reaction requires Cu catalysts hold a high percentage of exposed surface atoms, which can improve the utilization efficiency of catalysts and products selectivity. Here we reported a high temperature reduction method to prepare Cu nanosheets in hydrophobic system. The feeding molar ratio of trioctyphosphine/Cu ion precursor plays a critical role for the formation of Cu nanosheets. The shape of Cu nanosheets were controlled by adjusting the reaction interval, the types of Cu ion precursor, and the purity of trioctylphosphine. The size and thickness of Cu nanosheets were variable from 50 nm to 13 μm and 15 nm to 500 nm, respectively. Moreover, pure Cu nanosheets are stable in solution for more than three months. As a result of high percentage {111} of surface area, these nanosheets as catalysts have demonstrated the enhanced catalytic activity and selectivity to convert CO₂ to fuels.

**ET08.05.13**
CO₂ Activation on Defective MoS₂ Surfaces for CO₂ Photo-Reduction Applications
Yi-Fan Huang¹, Hsiang-Ting Lien², He-Yun Du², Ying-Ren Lai², Ting-Li Lin¹, Yu-Chung Chang³, Michitoshi Hayashi³, Li-Chyung Chen² and Kuei-Hsien Chen²; ¹Academia Sinica, Taipei, Taiwan; ²National Taiwan University, Taipei, Taiwan.

CO₂ activation on catalyst surface is the very first and critical step in CO₂ photo conversion into valuable chemicals. However, CO₂ is a thermodynamically stable and chemically inert molecule. How to select and treat the photocatalyst surface to enhance the chemisorption of CO₂ and improve its reactivity remains a scientific challenge. Photocatalyst surfaces with functional modifications, such as creating atomic vacancies on surface by H₂ plasma treatment are promising candidates for this purpose.

This report reveals the essential first step of CO₂ adsorption/activation on a defective MoS₂ surface by using near ambient pressure X-ray photoelectron spectroscopy (APXPS), scanning tunneling microscope (STM) experiments and density functional theory (DFT) calculations. These studies not only suggest the atomic sulfur defects on the MoS₂ surface particularly play a critical role in activating CO₂ to form chemisorbed CO₂, but also provide further mechanistic information for the intermediates species, thus guiding the design of better photocatalyst in the future.

**ET08.05.14**
Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope
Caifeng Wang¹,², Wei-Cheng D. Yang¹,² and Renu Sharma³; ¹National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ²University of Maryland, College Park, Maryland, United States.
Minimizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, current efforts towards miniaturizing chemical processes have been limited by the achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor, utilizing localized surface plasmon (LSP) resonance as the energy source, in an aberration-corrected environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within the proximity of the nanoparticle while taking advantage of the high spatial resolution measurement capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system and analyzed using a residual gas analyzer. Electron energy-loss spectrum (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within the proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm, we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transitions between crystalline phases, are monitored using atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined within a nanometer scale volume, and modulated by electron flux. Important parameters of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale. [3]

[3] The authors acknowledge funding from the Cooperative Research agreement between the University of Maryland and the National Institute of Standards and Technology Center for Nanoscale Science and Technology, Award 70NANB14H209, through the University of Maryland.

ET08.05.15
Co-Based Bimetallic Nitride Flakes Grown on N-Doped Carbon Nanofibers as an Efficient Bifunctional Electrocatalysts for Oxygen Evolution and Reduction Reactions
Seokwun Song and Il Doo Kim; Korea Institute of Science and Technology, Daejeon, Korea (the Republic of)

In recent years, oxygen electrocatalysis has attracted great attention due to the desire for many energy storage or conversion devices such as metal-air batteries, fuel cells, and water electrolyzer. However, the sluggish kinetics of oxygen-based electrochemical reactions hinder the efficiency. Although, noble metal-based electrocatalysts are widely used to reduce the energy loss, their high cost is critical limitation for broad and practical applications. Thereby, many trials to replace noble electrocatalysts with highly efficient and inexpensive non-noble metal-based oxygen electrocatalysts by employing transition metals such as Co, Mn, and Ni. Especially, transition metal nitriles such as Co4N are considered as a promising candidate material due to their superior electrical conductivity and chemical stability. Furthermore, bimetallic compounds can further induce oxygen-based catalytic activity by effective tuning of d-band structure.

Here, we proposed facile synthetic method for Co-based bimetallic nitride flakes grown on n-doped carbon nanofibers (Co-M-N@NCNF, M = Ni, Mn, Fe) by using Co-based bimetallic leaf like zeolite imidazole framework (ZIF-L), which is composed of cobalt and other metal ions (Ni, Mn, Fe) with organic linkers. Firstly, electrospun Polyacrylonitrile (PAN) nanofibers were treated by NaOH for smooth growth of Co-based bimetallic leaf like zeolite imidazole framework (ZIF-L), which is composed of cobalt and other metal ions (Ni, Mn, Fe) with organic linkers. Secondly, electrospun Polyacrylonitrile (PAN) nanofibers were treated by NaOH for smooth growth of Co-based bimetallic leaf like zeolite imidazole framework (ZIF-L), which is composed of cobalt and other metal ions (Ni, Mn, Fe) with organic linkers. Finally, the Co-N based ZIF-L nanofiber was precipitated in a solution of ammonium hydroxide, resulting in amorphous Co-N nanofiber. Followed by subsequent stabilization and nitridation process under ammonia gas, it converted to Co-M-N@NCNF. The Co-M-N@NCNF nanofibers showed remarkable electrochemical properties for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). We demonstrated enhanced catalytic activity of Co-M-N@NCNF for both OER and ORR in terms of overpotential, Tafel slope, and charge transfer. These are mainly attributed to the synergistic effects from Co-based bimetallic compounds with nitrogen atoms. Also, unique structure of active two dimensional flakes grown on one dimensional carbon nanofiber fiber offered more exposed active sites and high surface area. The proposed strategy of ZIF-derived bifunctional nanomaterials provides prospects for developing highly active electrocatalysts in electrochemical energy devices.

SESSION ET08.06: Hot-Electron-Driven Catalysis
Session Chairs: Yuzi Liu and Yugang Sun
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 306

8:30 AM *ET08.06.01
Minimizing Energy Use for Surface Reactions by Using Both Light and Heat—Plasmonic Catalysts and Non-Plasmonic Catalysts Enabling Photocexcitation of Adsorbates
Chanyeol Kim and Hyunjo Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of)

Many heterogeneous catalytic reactions occur at high temperatures, which may cause a large energy cost, poor safety, and thermal degradation of catalysts. Here, we propose a “light-assisted surface reaction”, which catalyze the surface reaction using both light and heat as an energy source. Plasmonic metal nanoparticles absorb light energy and release the energy through radiative or non-radiative channels. Surface catalytic reaction would take advantage of the non-radiative energy relaxation of plasmon with enhanced activity. Particularly, binary nanoparticles are interesting because diverse integration would be possible consisting plasmonic part and catalytic part. Herein, we demonstrated ethanol dehydrogenation under light irradiation using Ag-Ni binary nanoparticles with different shapes, snowman and core-shell, as plasmonic catalysts. The surface plasmon formed in the Ag part enhanced the surface catalytic reaction that occurred at the Ni part, and the shape of the nanoparticles affected the extent of the enhancement. The surface plasmon compensated the thermal energy required to trigger the catalytic reaction. The absorbed light energy was transferred to the catalytic part by the surface plasmon through the non-radiative hot electrons. Non-plasmonic conventional metal catalysts such as Ru, Rh, Pt, Ni, and Cu were tested for CO2 hydrogenation, and Ru showed the most distinct change upon light irradiation. CO2 was strongly adsorbed onto Ru surface, forming hybrid orbitals. The energy gap between the HOMO and LUMO was reduced significantly upon hybridization. Hot electrons could be generated by jumping the shortened energy gap upon light irradiation, enhancing CO2 dissociation. The light-assisted CO2 hydrogenation used only 37% of the total energy with which the CO2 hydrogenation occurred using only thermal energy. The CO2 conversion could be turned on and off completely with a response time of only 3 min, whereas conventional thermal reaction required hours to terminate the CO2 conversion. These unique features can be potentially used for on-demand fuel production with minimal energy input.
Light interacting with catalysts via surface plasmon resonances has the potential to dramatically improve catalytic reactions by photothermal heating and hot-electron transfer. This project investigates plasmonic light enhancement of the CO oxidation reaction over supported Au catalysts. Optimization of this reaction empowers removal of poisonous CO at room temperature which has the potential to improve human health. This reaction also features a negative activation energy which leads to a minimum in the temperature dependent conversion curve near 80 °C. Results show that catalytic activity around room temperature doubled under light and catalyst lifetimes increased by a factor of 5. From these results, an analysis of the relative magnitude of the photothermal catalytic enhancement and non-thermal catalytic enhancement effects were performed by utilizing the temperature dependent change from positive to negative activation energy. This demonstrated that the effect of photothermal heating is more substantial and that both effects enhance the reaction rate and improve catalytic lifetimes. From further experiments coupling light induced desorption of CO₂ to the regeneration of catalytic activity, a mechanism for light enhancement on gold catalysis is proposed. Light reactivates the catalyst by removing surface carbonates which otherwise act as poison, allowing for dramatically increased catalytic activity and lifetime to demonstrate a new path for highly active CO oxidation.

Here, we exploit the LSP resonance of a triangular Au nanoprim excited by an electron beam to drive CO disproportionation (2CO → C + CO₂), known as the Boudouard reaction that typically takes place between 300 °C to 600 °C, at room temperature, in an environmental scanning transmission electron microscope (ESTEM). Using in situ electron energy loss spectroscopy (EELS) mapping, combined with density functional theory (DFT) and electromagnetic boundary element method (BEM) calculations, we show that amorphous carbon deposits, resulting from the CO disproportionation reaction, occur only at selective sub-particle locations where preferred CO adsorption sites and plasmon modes antinodes are coincident. Low-loss and core-loss EELS are used to locate the maximum LSP resonance intensity excited by the electron beam and the adsorbed CO molecules, respectively, on a Au nanoprim. Amorphous carbon deposited on the cantilevered corner of a nanoprim, measured after CO is evacuated from the sample chamber, confirms that (a) CO molecules disproportionate at room temperature and (b) the location corresponds to where the CO adsorption probability and the intensity of dipolar LSP mode overlap. The combination of high energy and spatial resolution, along with simulations, provide an unprecedented insight that (a) CO molecules disproportionate at room temperature and (b) the location corresponds to where the CO adsorption probability and the intensity of dipolar LSP mode overlap. The combination of high energy and spatial resolution, along with simulations, provide an unprecedented insight into the catalytically active sites, for LSP induced chemical reactions.

Reference:

Controlling Energy Flow in Plasmonic Photocatalysis Through the Design of Hybrid Plasmonic Nanostructures for Selective Catalysis Suljo Linic; University of Michigan, Ann Arbor, Michigan, United States.

It has been shown that photo-excitation of plasmonic metal nanoparticles (Au, Ag, and Cu) can induce direct photo-chemical reactions on the nanoparticles. However, the widespread application of this technology in catalysis has been limited by the relatively poor chemical reactivity of noble metal surfaces. In this presentation, we present our recent work in which we conceptualized and designed hybrid nanostructures in which a plasmonic metal harvests the energy of visible light photons and selectively channels that energy into catalytically active centers on the nanostructure. To accomplish this, we developed a synthetic protocol to deposit a few monolayers of Pt onto plasmonic Ag nanocubes. This model system allows us to conclusively separate the optical and catalytic functions of the hybrid nanomaterial and analyze the interaction between the two functions. Through experimental and theoretical studies of the optical properties of these nanostructures, we show that the flow of energy is strongly biased towards absorption (i.e. excitation of energetic charge carriers) in the thin Pt shell. We demonstrate the utility of these nanostructures for photo-catalytic chemical reactions in the preferential oxidation of CO in excess H₂. The reactor studies conclusively show that photo-excitation of these nanostructures results in photo-chemical reactions on the Pt surface. We describe the fundamental physical reasons for the observed directed flow of energy and discuss how these discoveries impact the field of plasmonic catalysis.

C Boerigter, R Campana, M Morabito, S Linic, Nature communications, 7, 2016
C. Boerigter, U Aslam, S Linic, ACS Nano 10 (6), 6108-6115, 2016
S. Linic, U Aslam, C Boerigter, M Morabito, Nature Materials 14 (6), 567-576
Andiappan, S. Linic Science, 339, 1590, 2013
D. B. Ingram, S. Linic, JACS, 133, 5202, 2011
Rotational spectroscopy is introduced as a new in situ method for monitoring gas phase reactants and products during chemical reactions. Exploiting its unambiguous molecular recognition specificity and extraordinary detection sensitivity, rotational spectroscopy at terahertz frequencies was used to monitor the decomposition of carbonyl sulfide (OCS) over an aluminum nanocrystal (AlNC) plasmonic photocatalyst. The intrinsic surface oxide on AlNCs is discovered to have a large number of strongly basic sites that are effective for mediating OCS decomposition. The strength of rotational spectroscopy is witnessed through its ability to detect and distinguish isotopologues of the same mass from an unlabeled OCS precursor at concentrations <1 nanomole or partial pressures <10 mTorr. These attributes recommend rotational spectroscopy as a compelling approach for monitoring gas-phase chemical reactants and products in real time.

11:00 AM *ET08.06.06
Sustainable Nanocatalysis—Plasmonic Silver Nanocubes and Cellulose Nanocrystals as Non-Innocent Support Audrey Moores; McGill University, Montreal, Quebec, Canada.

We explored the use of cellulose nanocrystals as a non-innocent support to generate metal/cellulose nanohybrids. We showed that, with Pd, we could afford active and enantioselective hydrogenation catalysts, while with Ru, extremely active and recyclable catalysts were accessed for the difficult reduction of aromes under mild conditions. These nanocrystals in suspension could allow the direct synthesis of silver nanoparticles without the use of any additional oxidizing or reducing chemical. Besides, we have employed silver nanocubes for hydrogen activation and hydrogenation of ketones and aldehydes via irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes. Exposure to other wavelengths, or absence of light failed to provide activity thus proving the plasmonic effect. Compared to other catalytic systems, the plasmonically activated catalyst provides access to primary and secondary alcohols using milder conditions, in a highly atom economical fashion. Plasmonic catalysis of the oxidation of aldehyde to carboxylic acid was also demonstrated.


11:30 AM ET08.06.07
Efficient Ammonia Synthesis via Light-Driven Thermal Gradients in Fixed-Bed Catalytic Reactors Xueqian Li1, Jie Liu1 and Henry O. Everitt1,2; 1Chemistry, Duke University, Durham, North Carolina, United States; 2Physics, Duke University, Durham, North Carolina, United States; 3Army AMRDEC, Huntsville, Alabama, United States.

When the temperature of exothermic chemical reactions increases, thermodynamic equilibrium shifts away from producing products and towards retaining reactants. Unfortunately, for reactions with high activation barriers, the reaction rate can be extremely slow at the lower temperatures that favor products. Scalable industrial processes require both high reaction rates and high product yields and balancing these two represents the art of chemical engineering. A prominent example is the industrial Haber-Bosch process, which requires optimized catalysts, high temperatures, high pressures, and several recycling steps to achieve practical reaction rates and yields of ammonia, but at the cost of consuming up to 2% of the global energy produced annually. Here, we demonstrate how light-induced plasmonic heating can produce a controlled thermal gradient in a conventional Ru-based catalyst that simultaneously achieves both high reaction rates and high conversion yields in ammonia synthesis. Using continuous wave light emitting diodes, ammonia is copiously produced under ambient conditions without any external heating. Our results suggest that the optical control of thermal gradients in catalysts may become a universal strategy for simultaneously increasing reaction rates and conversion yields of many exothermic reactions.

11:45 AM ET08.06.08
Electrocatalytic CO2 Reduction at Functionalized Cu Surfaces—Structure-Reactivity Relationships Between Organic Modifiers and Product Selectivity Aya K. Buckley1,2, Francisca Maria Toma1,2, 1Joint Center for Artificial Photosynthesis, Berkeley, California, United States; 2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

An efficient electrocatalyst for the reduction of CO2 (CO2R) would enable the conversion of a major contributor to global warming into valuable carbon-based products. Cu surfaces are unique in that they are the only single-metal system to catalyze the formation of multiconcat products from CO2. However, the lack of selectivity of these Cu surfaces necessitates investigation into how their catalytic behavior may be adjusted.

The complexity of the catalyst/electrolyte interface poses challenges in identifying how a change in an electrocatalyst affects the observed CO2R selectivity. Therefore, we employ a methodical experimental approach that focuses upon identifying which parameters play an important role in determining CO2R selectivity.

First, we examined the effect of a series of organic modifiers on the CO2R selectivity of Cu. Oxide-derived Cu surfaces were functionalized with molecular and polymeric modifiers featuring a wide variety of structural characteristics, including neutral and cationic species, protic and aprotic species, and species bearing various functional groups. The product distribution of these surfaces in the CO2R reaction was characterized at -0.7 V vs. RHE, focusing upon the selectivity between CO, formic acid and H2. This allowed classification of the organic structures based upon the promoted product. Finally, each class of modifiers was examined and key, common structural characteristics of the modifiers were identified.

Through this systematic study, we demonstrate that the CO2R selectivity of a non-precious metal catalyst may be improved for CO, formic acid or H2 by changing the organic modifier applied. Selectivities of up to 76% CO or 62% formic acid were observed, and H2 selectivity was tuned from 97% down to 2%. In this presentation, we describe the structural characteristics of these modifiers that are key to changing the observed selectivity. These common features offer insights into the mechanism by which organic modifiers influence CO2R selectivity at the metal surface. We expect that the identified structure-reactivity relationships will illuminate important design principles for novel, selective CO2R electrocatalysts and organic structures for CO2R devices.
1:30 PM  *ET08.07.01
**Quantitative Super-Resolution Imaging of Nanocatalysis** Peng Chen, Cornell University, Ithaca, New York, United States.

This talk will present our latest efforts in developing and using single-molecule super-resolution microscopy to map catalytic reactions on single nanoparticles at nanometer resolution and under operando conditions. Depending on available time, the topics may include: 1) cooperative communications within and between single nanocatalysts; 2) visualizing bimetallic effect within single nanocatalysts; and/or 3) mapping catalytic hotspots on plasmonic nanostructures.

2:00 PM  *ET08.07.02
**In Situ Characterization of Metal Surface Dynamics in Reaction Gas by Atomic Scale and Millisecond Resolution Environmental TEM** Seiji Takeda, Naoto Kamiuchi, Takehiro Tamaoka, Ryotaro Aso and Hideto Yoshida; Osaka Univ, Ibaraki, Japan.

Environmental transmission electron microscopy (ETEM) provides us with mostly static structural data of solid surfaces in reaction environments for a long time. However, given the recent advancement in TEM image detectors such as CMOS-based TEM cameras, the technique has started to progress in revealing the atomic dynamics that are correlated with catalytic reaction processes [1].

In this presentation, first we summarize the history of in-situ TEM in our research group briefly for the past decades. Second we show our recent time-resolved analyses with millisecond-resolution on the unexpected atomic dynamics on the surface of nanoporous gold (NPG) catalysts. The surface of NPG catalysts is structurally stabilized in pure oxygen environments, while the surface appears to be dynamically fluctuated with space and time in the reaction environment for the oxidation of CO at room temperature. Since the NPG catalysts inevitably include the residual impurity of Ag in addition to the majority of Au, it is concluded that the Ag atoms on the surface are oxidized to form stable Ag-O-Au atomic clusters in pure oxygen environment. It is also concluded that the self-activating atomic clusters are reduced and oxidized repeatedly in a reaction environment that, of course, includes both oxygen and CO. Hence, the catalytically active structure in the gold catalysts (supported Au nanoparticulate catalysts and NPG catalysts) can now be experimentally unified toward elucidating the fascinating catalysis mechanism of gold. We also show some recent challenges on the oxidation and reductions processes on the surfaces of related metals.

Though a chemical reaction is an extremely fast electronic phenomenon, the present study has clarified that the atomic dynamics occurring on the catalytically active surfaces can be observable by the advanced ETEM technique. Finally, to derive clearly the intrinsic natures of a specimen in a reaction environment by atomic scale and millisecond resolution ETEM, it is still indispensable to consider the influence of electron beam. We also discuss the related topics [2].


2:30 PM BREAK

3:30 PM  *ET08.07.03
**Investigation of Gas-Solid Reaction in Confined Space by In Situ TEM and Synchrotron X-Ray** Yuzi Liu; Argonne National Laboratory, Lemont, Illinois, United States.

The reaction between gas and solid is a great interest for material science. In more specific, materials transformation, gas molecules adsorption/desorption and chemical reaction on the surface are the most attractive topics. Here we use both transmission electron microscope (TEM) and synchrotron x-ray to study the gas-solid reaction with the material in gas environment in confined space (tween two SiN membranes with gap ~500nm) which allow the high energy electron beam and x-ray penetrating the system. Firstly, the conventional and gas flow TEM were employed to study how the AgCl transformed to AgOx at different O2 partial pressure. It was found that the high energy electrons help to generate Cl vacancies which drive the AgCl reduction to Ag. The Ag was further oxidized to Ag2O due to the high O2 partial pressure. Secondly, the reaction between Cu2O and CO2 was studied by integrated imaging through combination of environmental TEM and synchrotron x-ray. The multi-beam and detectors were employed to study the same object at different length scales. A cross-platform holder was used to guarantee the same nanoparticle was investigated by electron beam and hard x-ray nanoprobe to ensure that we get the complimentary information. In addition to the study on the single particles, the investigation on the assembly of Cu2O particles by high resolution synchrotron x-ray powder diffraction (HRXRD) also indicates the charge transfer between Cu2O and gas molecules adsorbed on certain facets.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

4:00 PM  ET08.07.04
**Resolving the Atomic Details of Gas-solid Interfaces in Catalytic Materials Through In Situ Neutron Total Scattering** Daniel Olds, Jue Liu and Kate Page; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanostructured and porous materials have widespread industrial applications in adsorption and catalysis, but experimental studies providing atomistic data regarding gas-sorbent interactions under application-relevant conditions are limited. Current analytical methods give information about either the crystal structure or the macroscopic kinetics involved in these processes, but not their interplay.

We present a new sample environment for interrogating materials under precise gas-flow conditions using time-of-flight neutron scattering. This capability allows for simultaneous measurements of stroboscopic, isotope-contrast neutron total scattering and Steady-State Isotopic Transient Kinetic Analysis (SSITKA), thus providing material insight into both structural and kinetic details. We anticipate this sample environment will be useful in studies of gas-
solid interfaces, hierarchical structure, molecular sieves, nanomaterials catalysis, and more.

The results of a commissioning study on nitrogen adsorption in calcium exchanged zeolite X will be presented. Together with theoretical considerations from Grand Canonical Monte Carlo simulation, we identify the location of a heterogeneous distribution of adsorption sites under operational conditions (1 atm, 300°C). We also highlight recent upgrades to the sample environment allowing for high-temperature studies (up to 800°C) of materials under gas flow, which is demonstrated with an in situ redox reaction study on ceria nanorods. This sample environment is presently available in the general user program on the NOMAD beamline at the Spallation Neutron Source (ORNL).

4:15 PM ET08.07.05
Mechanisms of Photocatalytic H2 Evolution on Co-Catalyst Loaded Semiconductors in the UHV Constantin A. Walenta1,2, Sebastian Kollmannsberger1, Carla Couto12, Rui Nuno Pereira1, Martin Stutzmann1, Martin Tschurl1 and Ueli Heiz1; 1Chemistry Department & Catalysis Research Center, Technische Universität München, Garching, Germany; 2Department of Chemistry & Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; 3Walter Schottky Institute & Physics Department, Technische Universität München, Garching, Germany.

Despite of intense research efforts in the last decade, photocatalytic processes for the generation of renewable fuels are still lacking the requirements for successful application on industrial scale. Research strategies have so far been focused on material screening due to the complexity of the underlying processes. However, a deep fundamental understanding will ultimately allow us to implement knowledge-based improvements towards enhanced photocatalytic efficiencies, selectivities and stabilities.

In this work, we examine the reaction mechanism of photocatalytic alcohol reforming on a model system (co-catalyst loaded rutile TiO2(110)). By judicious choice of surface preparation and catalyst loading, we are able to unravel the photochemical mechanism on an atomic scale. By changing the reaction conditions e.g. temperature, photochemical reaction steps of the isotopically labeled reactant can clearly be disentangled from chemical thermal reaction steps in the mechanisms. A detailed kinetic analysis reveals, that the photocatalytic reaction rate depends linearly on the photon flux, indicating that only one charge transfer of this two-step process is facilitated photochemically.

4:30 PM ET08.07.06
Ammonia Synthesis on the Fe(111) Surface—Reaction Mechanism and Kinetics Qi An1, Jin Qian2, Alessandro Fortunelli1,2, Robert Nielsen1 and William Goddard4; 1University of Nevada, Reno, Reno, Nevada, United States; 2Materials Science, Caltech, Pasadena, California, United States; 3Consiglio Nazionale delle Ricerche, Pisa, Italy; 4Chemistry, Caltech, Pasadena, California, United States.

The Haber-Bosch (HB) process converting nitrogen gas (N2) and hydrogen gas (H2) into the ammonia (NH3) consumes 1–2% of the world's energy supply and generates more than 300 million tons of carbon dioxide annually. It is essential to optimize the efficiency of HB process extensively to save energy and reduce CO2 production. However, the reaction mechanisms of HB process at industrial conditions are not fully understood. Here, we employed density functional theory to predict reaction mechanisms and kinetics for NH3 synthesis on Fe (111) surface which is more efficient for NH3 synthesis than other surfaces such as (100) and (110). First of all, the free energies of all steps are predicted under experimental condition of 673 K and 20 atm and industry condition of 730 K and 200 atm. Then we built the free energy diagrams into a kinetic Monte Carlo model to predict the steady state catalytic rates and compare with single-crystal experiments. We predicted a turnover frequency (TOF) of 17.7 s⁻¹ per 2 × 2 site (5.3 × 10⁻⁹ mol/cm²/sec) under condition of 673 K and 20 atm. This agrees very well with single crystal experiment of TOF = 10 s⁻¹ per site.

4:45 PM ET08.07.07
Spatial Tailoring of Dopant Position in Solids for Enhanced Visible Light Photocatalytic Performance Pragathi Darapaneni1, Natalia da Silva Moura1, Darrell Harry2 and James A. Dorman1; 1Louisiana State University, Baton Rouge, Louisiana, United States; 2Chemical Engineering, Southern University, Baton Rouge, Louisiana, United States.

Transition metal (TM) doped semiconductor materials are extensively employed for light harvesting and photocatalytic applications to increase the charge mobility for better performance. The position and site occupancy of the dopant dictate the physical properties of these materials such as light absorption, separation of charge carriers, and the surface reaction kinetics. Commonly used bulk characterization techniques are often indifferent to surface vs. bulk dopant occupancy. Therefore, this work addresses the phenomenon of spatially controlled dopant incorporation for controlled optical and photocatalytic properties.

In this work, highly doped TiO2: Ni²⁺ (15 mol%) nanoparticles are synthesized via sol-gel chemistry. The drying and annealing of the aged sol are shown to affect the segregation of NiO on the surface of TiO2. Specifically, it is possible to control the dopant position by varying the moisture exposure time, indicating that the ambient water layer on the surface of TiO2 plays an important role on surface energetics. The effect of moisture and annealing rate on the dopant position was systematically studied using steady-state and time-resolved methods (XRD, UV-Vis, Raman, TGA/DSC, and FTIR) to extract crystallization temperatures, optical absorption, bond formation, and surface hydroxyl concentration. XRD results show that the vacuum dried TiO2:Ni powders formed a doped anatase phase while the air dried powders formed segregated anatase and NiO phases upon annealing. Furthermore, rapid annealing of the air-dried TiO2:Ni powders formed a metastable anatase doped phase while slow annealing resulted in the segregation of NiO phase, which can also be observed in TGA/DSC. The annealing processes produce a shift from discrete peaks to a broad absorption based on the dopant position. The evolving local environment is probed via x-ray absorption spectroscopy (XAS) and High-Resolution TEM to elucidate the difference in the dopant local environment with photocatalytic performance using photoluminescence (PL) spectrometer. Moreover, the charge carrier recombination kinetics in these NPs can be investigated using time-resolved PL measurements to understand the modified reaction pathways. This ability to incorporate higher dopant concentrations while engineering the dopant position in nanostructures will assist in the development of improved photocatalytic devices. Finally, a similar trend of dopant segregation was observed with other first row TM doped TiO2 powders upon slow annealing, suggesting that the segregation of TM dopants in TiO2 is a function of the dopant size.
Selective Formation of Li₂O in a Lithium-Air Battery

Jelyn Lunger, Livvia Giordano and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Although current electric vehicles rely on lithium-ion technology, lithium-ion batteries cannot provide a sufficiently far driving range at low cost [1]. Lithium-air batteries offer a promising alternative to conventional lithium-ion batteries due to their high theoretical energy density, close to that of gasoline. Although lithium peroxide is the discharge product typically observed in lithium-air batteries, lithium oxide is the preferred product with a specific capacity 1.3 times greater than that of lithium peroxide [2]. In addition, many electrolytes have been found to react significantly with lithium peroxide and with the superoxide ion, whereas lithium oxide is less reactive with the electrolyte [3]. Because the free energies of reaction for lithium oxide and lithium peroxide are similar (-561 kJ/mol and -571 kJ/mol respectively), it should be possible to design a catalyst that selectively forms lithium oxide at room temperature. Additionally, it is important that such a catalyst also reduces ORR/OER potential losses, which currently inhibit lithium-air battery efficiency.

To design a catalyst selective for lithium oxide formation, it is necessary to understand the reaction pathways for the growth of lithium oxide and lithium peroxide. While the reaction mechanism describing electrochemical growth of lithium peroxide has been well studied [4], much less is known about the initial nucleation of lithium peroxide or lithium oxide on the surface of a catalyst. In this study, the initial nucleation pathways for both lithium peroxide and lithium oxide are identified using the ruthenium dioxide (110) surface as a model catalyst. The lowest energy interfaces between lithium peroxide and lithium oxide and the ruthenium dioxide (110) surface are identified by employing a lattice matching algorithm. Density functional theory is then used to identify the charge and discharge pathways which offer the lowest overpotentials. Initial growth of lithium oxide on ruthenium dioxide (110) is found to have a discharge overpotential of 0.58 V, rate limited by adsorption of lithium ions. The removal of the final layer of lithium oxide on ruthenium dioxide (110) is found to have a charge overpotential of 0.44 V, rate limited by the desorption of oxygen. The effects on the charge/discharge overpotentials due to straining and doping the ruthenium dioxide (110) catalyst are studied to identify design principles for a catalyst that is both selective for lithium oxide formation and offers low ORR/OER overpotentials.


ET08.08.02
Computational High-Throughput and Screening of Catalytic Mass Activities of Tailored Pt Electro catalysts for the Oxygen Reduction Reaction
Marlon Rueck and Alessio Gagliardi; Department of Electrical and Computer Engineering, Technische Universität München, Munich, Germany.

Tailored Pt electrocatalysts harbor great potential to enhance the catalytic mass activity for the oxygen reduction reaction (ORR) in fuel cells [1]. Due to elaborate experimental synthesis and innumerable variations of nanostructures, computational high-throughput screening may highly promote the search for promising electrocatalysts. In our present work, we computationally screen through a plethora of distinct Pt nanostructures where an optimization algorithm tweaks the fine adjustment on the atomic-scale. Precise characterization of tailored electrocatalysts within feasible timescales is the critical step in high-throughput screenings. To this end, we employ our recently developed model [2] which rapidly predicts the catalytic mass activities of the screened nanostructures in absolute units of A mg⁻¹ Pt. Our study discloses nanostructures with high mass activities up to 3.86 A mg⁻¹ Pt. To further support experimental synthesis, we analyze the size dependence of the nanostructures on the catalytic mass activity. Summing up, our work comprises the crucial steps from screening and characterization to size dependence of tailored Pt electrocatalysts aiming at experimental and theoretical collaboration in nanoparticle synthesis.


ET08.08.03
Advanced Structural Characterisation of La-Doped Ceria Nanocubes for Enhanced Redox Ability
Colm O'Regan¹, Alberto Casu¹, Andrea Falqui¹, Danilo Loche², Lucy Morgan², Gavin Mountjoy² and Anna Corrias²; 1King Abdullah University of Science and Technology, Thuwal-Jeddah, Saudi Arabia; 2University of Kent, Canterbury, United Kingdom.

Ceria nanomaterials possess an exceptional reactivity due to the ability of the cerium ion to switch easily between 3+ and 4+ oxidation states, via the formation of oxygen vacancies within the ceria fluorite structure. This effect is enhanced at the nanoscale, and can be tailored by changing both the size and the shape of nanoparticles. In order to further enhance the ceria redox ability, doping of ceria with another element, such as lanthanum, has proved effective via an increased mobility of the oxygen vacancies.

With this aim, powder X-ray Diffraction (XRD), and transmission electron microscopy (TEM) techniques have been used to study the solid miscibility of La in samples of ceria nanocubes with nominal lanthanum doping up to 10 mol%, and to study the effect of doping on the morphology of the lanthanum-doped nanocubes.

Low-magnification TEM imaging shows lanthanum-doped ceria nanocubes have cubic morphologies, and a more regular cubic shape with sharper facets than pure CeO₂ nanoparticles. This suggests the beneficial role of La on maintaining a well-defined cubic shape during nanoparticle growth, via stabilization of the oxygen vacancies, and formation of highly reactive <100> terminated facets.

Additionally, XRD and aberration-corrected High Resolution TEM (HRTEM) imaging confirmed the cubic (Fm3m) fluorite single crystalline structure of the lanthanum-doped ceria nanocubes. In particular, the results of 2D-Fast Fourier Transform (2D-FFT) analysis conducted on HRTEM data were always consistent with the pure CeO₂ structure, confirming that the introduction of La did not give rise to the local formation of secondary phases. A shift in the peaks of the XRD patterns was observed with increasing La content up to approximately 7 mol%, suggesting the latter value is approximately the limit of the La solid solubility. Indeed, this was further confirmed by Energy Dispersive X-Ray Spectroscopy (EDS) spatially resolved chemical analysis, performed with subnanometer resolution by Scanning TEM (STEM). This revealed that the largest observed lanthanum concentration is equal to 7 mol%, in the sample with 10 mol% nominal lanthanum doping. Chemical mapping carried out using STEM-EDS also showed the La was homogeneously distributed throughout the CeO₂ nanocubes for all investigated samples, thus proving the formation of an evenly La-doped structure.

Further characterisation is in progress to confirm that these lanthanum-doped nanocubes do enhance redox ability.

ET08.08.04
NH\textsubscript{3} synthesis by the electrocatalytic N\textsubscript{2} reduction reaction (NRR) under ambient conditions is regarded as an appealing alternative to the industrial method that requires high temperature and pressure. Finding a material that can efficiently catalyze electrochemical N\textsubscript{2} fixation at ambient condition is a subject of considerable current interest. Atomically dispersed catalysts with mononuclear metal complexes or single metal atoms anchored on supports would be a promising candidate, because of their maximum atom efficiency, unique catalytic performances, and the similarity of the metal coordination environment to the ligand fields in molecular catalysts. A series of cost-effective and optimized atomically-dispersed electrocatalysts for NRR will be reported. Our results show that the catalysts are featured with high density of single metal atoms supported on hierarchically porous carbon frameworks. They exhibited remarkable selectivity of NH\textsubscript{3} formation and high NH\textsubscript{3} yield rate at low applied potentials at room temperature. Moreover, the catalysts show negligible activity decay in an N\textsubscript{2} electrolysis as long as 30,000 s. On the basis of our results and the previously reported work, a possible mechanism for NRR on the catalyst will be proposed to provide a fundamental insight into the high-efficiency NRR.

ET08.08.05
Efficient Photocatalytic and Photoelectrocatalytic Generation of Hydrogen Peroxide by Organic Semiconductor Catalysts

Shili Zheng and Yi Zhang; 1Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China; 2Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut, United States; 3University of Chinese Academy of Sciences, Beijing, China.

Recently, the market for hydrogen peroxide is expanding in various industrial applications, with the increasing importance of green chemistry. At present, hydrogen peroxide is synthesized by the so-called anthraquinone process on a large scale. The in-situ synthesis of H\textsubscript{2}O\textsubscript{2} based on advanced technologies is attracting much interest as a simple H\textsubscript{2}O\textsubscript{2} production method. Among them, electrochemical methods are environmentally-friendly and effective for the direct generation of hydrogen peroxide with high production rate and simple process.

Hydrogen peroxide can be electrochemically generated by the two-electron oxygen reduction reaction (ORR) on the surface of electrocatalysts. Considerable attempts have been made to prepare appropriate and cost-effective cathode materials to enhance the ORR activity and current efficiency for H\textsubscript{2}O\textsubscript{2} electro-generation. For this purpose, there are various materials reported including carbon-based materials (g-C\textsubscript{3}N\textsubscript{4}, graphite, carbon nanotubes, graphene, graphite felt and carbon cloth), transition metal oxides (Nb\textsubscript{2}O\textsubscript{5}, CeO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, and Co\textsubscript{3}O\textsubscript{4}) and precious metal nanomaterials. Development of low-cost carbon-based metal-free catalyst with high ORR catalytic activity and low cost is emerged as an effective strategy for the replacement of precious metal.

As carbon-rich precursor, biomass has been used as raw material for the fabrication of carbon-based materials for a long time. With the choice of suitable activators, various works have reported that porous carbon derived from biomass can obtain well-defined micropore size distribution and an ultrahigh specific surface area. Activated carbon materials are applied as the development of catalyst in energy storage/conversion devices. Furthermore, considering the advantages of nitrogen doping for the enhancing of electrocatalytic activity, nitrogen-rich biomass and their derivatives have been recently chosen as promising precursors for nitrogen-doping carbon catalysts.

As a typical low-cost and easily obtained nitrogen-rich biomass resource, Ramie is widely distributed in the east and south of China as textile, feeding and paper raw materials. We developed nitrogen-doped powered activated carbon from Ramie biomass under appropriate temperature with high surface area from Ramie biomass as a highly efficient electrocatalyst for hydrogen peroxide production. Electrochemical characterizations revealed that the as-prepared catalyst showed superior ORR selectivity through a two-electron pathway and extraordinary long-term stability. The nitrogen atoms on the catalyst surface was derived from the biomass and decomolovated by XPS techniques, which is the important factor for the enhancement of photocatalytic electrocatalytic performance. The present work paves a way for the development of biomass-derived carbon material for electrochemical applications.
ET08.08.09
Mediated Photoelectrochemical Oxidation of Water on WO3 by Silver (II)  Tae-Hwa Jeon1, Damián Monllor-Satóca1,2, Gun-hee Moon1, Wooyul Kim1, Hyoun-il Kim1, Hyunwoong Park1 and Wonyoung Choi1; 1Division of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); 2School of Environmental Engineering, Kyungpook National University, Daegu, Korea (the Republic of); 3School of Engineering, Universitat Rovira i Llo, Barcelona, Spain; 4Department of Civil and Environmental Engineering, Yonsei University, Seoul, Korea (the Republic of); 5Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul, Korea (the Republic of).

Ag(I) is a common electron scavenger used in photocatalysis for promoting oxidative pathways through photogenerated holes, preventing deleterious electron-hole recombination. Albeit its straightforward reduction to metallic state (i.e., Ag(0)), it can also capture holes to generate the highly reactive Ag(II) species, provided the proper reactive conditions are given. In this contribution, we demonstrate, for the first time, mediated photoelectrochemical oxidation of water and concurrent oxygen evolution by the Ag(I)/Ag(II) redox cycle with high efficiencies. In the presence of Ag(I), photoelectrochemical (PEC) performance of WO3 electrodes was enhanced (biased at 1.23 V vs. RHE) in a mild acidic nitrate medium (pH 5) in terms of steady-state photocurrent (>4-fold), and O2 evolution (>4-fold) and its Faradaic efficiency (40% without Ag(I) vs. 75% with Ag(II)). During the PEC reaction, the electrolyte solution acquires a brown color, caused by the formation of Ag(II)NO3 complexes. Upon turning both potential bias and light off, photocurrent drops to zero whereas O2 evolution continues over ~10 h (homogeneous water oxidation) leading to the overall Faraday efficiency of 100%, and simultaneously the electrolyte is gradually bleached. This confirms the Ag(II) complex-mediated water oxidation which occurs during the PEC and the unbiased dark periods. This phenomenon is found neither in the Ag(I)-free PEC reactions nor in the photocatalytic (i.e., bias-free) reactions with Ag(I). The various spectroscopic analyses (UV-Vis, XRD, XPS, SEM/EDS, HR-TEM/EELS, etc.) suggest that Ag0/Ag2O core-shell structure and AgNO3 complexes play the heterogeneous and homogeneous water oxidation reactions, respectively.

ET08.08.10
Loading Effect of Various Metal Oxide Colloids as an Electron Mediator on Visible-Light-Responsive Photocatalyst Particles in Photocatalyst Panels for Z-Scheme Water Splitting  Hiromasa Tokudome1,2, Sayuri Okunaka1,2, Shingo Oozu1,2, Qian Wang1, Takashi Hisatomi1 and Kazunari Domen1,3,4; 1TOTO Ltd, Chigasaki-city, Japan; 2Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; 3Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Japan; 4Center for Energy & Environmental Science, Shinshu University, Nagano, Japan.

Photocatalytic water splitting utilizing abundant sunlight including visible light is an active area of research focused on providing a renewable hydrogen. In the past two decades, a lot of visible light responsive photocatalysts have been developed to oxidize and/or reduce water, but only a few were known to overall split water into H2 and O2 in the stoichiometric amount. On the other hand, Z-scheme system is known to realize overall water splitting using two kinds of visible light responsive photocatalyst particles, which were active for either H2 or O2 evolution, with/without appropriate mediators such as redox ions or conductive materials. We recently developed a Z-scheme-type photocatalyst panel consisting of mixed films of two visible-light-active photocatalysts (La, Rh-doped SrTiO3 and BiVO4 for H2 and O2 evolution) and a colloidal electron mediator (gold or indium-tin-oxide) on a glass substrate. It showed relatively high activity with a solar-to-hydrogen energy conversion efficiency of 0.1%–1.2%. In this study, we prepared a Z-scheme-type photocatalyst panel composed of BiVO4 and Rh-doped SrTiO3 loaded with various metal oxide colloids as a low-cost and scalable electron mediator and examined the water splitting activity.

Z-scheme-type photocatalyst panels were prepared by a screen-printing on borosilicate glass substrates using a viscous paste including Rh-doped SrTiO3 loaded with various metal oxide colloids by impregnation or adsorption method and BiVO4 particles. The panels produced hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation. The water splitting activity varied depending on the kind of the loaded metal oxide colloids. This result showed that the colloids acted as an electron mediator between the two photocatalysts.


ET08.08.11
Improvement of Z-Scheme Water Splitting Activity on Nano ITO-Mediated Printable Photocatalyst Panels by Loading Co-Catalyst Sayuri Okunaka1,2, Hiromasa Tokudome1,2, Qian Wang3, Takashi Hisatomi1 and Kazunari Domen1,3,4; 1TOTO Ltd, Chigasaki-city, Japan; 2Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; 3The University of Tokyo, Bunkyo-ku, Japan; 4Shinshu University, Nagano, Japan.

Photocatalytic water splitting has been widely investigated as a potential method to produce hydrogen from renewable solar energy. Although two types of semiconductor-based systems (heterogeneous system and photoelectrochemical system) have extensively been studied for photo-induced water splitting so far, it is necessary to develop a scalable, versatile and cost-effective system for the practical application. Photocatalyst panels, wherein semiconductor particles are fixed on substrates such as glass, have a potential to be employed as a cost-effective system on large scale. To utilize wide range of visible light, it is necessary to employ narrow bandgap materials and/or introducing Z-scheme mechanism. Recently, the authors’ group reported that the composite-type photocatalyst panels, which composed of La, Rh-codoped SrTiO3 as the hydrogen evolution photocatalyst (HEP), Mo-doped BiVO4 as the oxygen evolution photocatalyst (OEP) and gold (Au) indium-tin-oxide (ITO) nanocolloids as the electron mediator, for Z-scheme water splitting. These panels were prepared by using simple screen-printing method. The obtained printable panels evolved hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation and showed relatively high activity with a solar-to-hydrogen energy conversion efficiency (STH) of ca. 0.1%–1.2%.

In this study, we investigated the effect of co-catalyst loading on the photocatalytic water splitting activity of the printable ITO nanocolloids-mediated photocatalyst panels. The water splitting activity of these panels was changed by changing the metal species and loading amount of co-catalyst. By loading appropriate co-catalyst, the water splitting activity was greatly enhanced and achieving 0.4% STH, which is four times greater than photocatalyst panels without co-catalyst loading.

ET08.08.12
Real Time Imaging of Nucleation, Growth and Corrosion Behaviors of Electrocatalysts Hao Shan, Yanling Ma, Fenglei Shi, Tao Deng and Jianbo Wu; Shanghai Jiao Tong University, Shanghai, China.

The core-shell catalysts with atomic layered structure Pt through liquid phase atomic layer deposition has been proven to be one of the most promising oxygen reduction (ORR) electrocatalysts with high activity and low consume of Pt. It is important to directly observe how the atomic layers grow via in situ
spectrum and simultaneous hydrolysis catalyst (for nerve agent removal) and oxidation catalyst (for mustard removal) is fairly needed. In this work, an advancement forward of the current bounds of continuous hydrothermal synthesis for catalysts applications is reviewed.

Metal oxide nanoparticles have been studied at length for their catalytic properties in many industries including chemical manufacturing, energy-related applications and environmental remediation. Given these advances in their applications, the tunable synthesis is of great interest, especially regarding the re-deposition behaviors during the cyclic voltammetry in TEM. References:


ET08.03.13 A Double-Anionic Oxides Based Organic-Inorganic Hybrid Compound for Simultaneously Catalytically Oxidative and Hydrolytic Decontamination of Chemical Warfare Agent Simulants Jufang Hu1 2; 1Beijing Institute of Nanoenergy and Nanosystems, Academy of Sciences, Beijing, China; 2College of Optoelectronic Engineering, Shenzhen University, Shenzhen, China.

Rapid transformation of chemical warfare agents (CWAs) to environmentally benign products is a significant issue, and considerable efforts have been devoted to the catalytic removal of CWAs. Although many homogenous and heterogeneous catalysts for CWA removal have been developed, a broad-spectrum and simultaneous hydrolysis catalyst (for nerve agent removal) and oxidation catalyst (for mustard removal) is fairly needed. In this work, an organic-inorganic hybrid compound, $\text{(NH}_4 \text{CH}_3\text{O}_2\text{)}_2\text{V}_2\text{O}_5\text{(OH)}_2\text{Cl}_2\text{H}_2\text{O}$ (I), based on two different anionic oxide fragments (also known as polyoxometalates, primarily constituted by Mo, V, Nb centers and oxo ligands), was hydrothermally synthesized, structurally thoroughly characterized, and catalytically tested with the broad-spectrum reactivity in the decontamination of chemical warfare agents. Compound I crystallizes in the tetragonal I-4 space group and contains bicapped polyoxoniobate (PNb$_6$O$_{19}$(VO)$_3$) and tetranuclear polyoxovanadate, which are independent on each other, a complex scarcely seen in polyoxometalate chemistry. Interestingly, compound I effectively catalyzes both hydrolysis of the nerve agent simulant, diethyl cyanophosphonate (DECP), and selective oxidation of the sulfur mustard simulant, 2-chloroethyl ethyl sulfide (CEES) under mild conditions. In particular, in the oxidative decontamination system 100% CEES was transformed selectively to nontoxic 2-chloroethyl ethyl sulfoxide and vinyl ethyl sulfioxide using nearly stoichiometric 3% aqueous H$_2$O$_2$ with a turnover frequency (TOF) of 16000 h$^{-1}$. The catalytic performance is maintained even after ten runs and CEES is completely decontaminated in 3 mins without formation of the highly toxic sulfone by-product. The combination of polyoxoniobates and polyoxovanadates give this compound those noteworthy catalytic properties, and a three-step oxidative mechanism is proposed. References:


ET08.03.14 Continuous Hydrothermal Synthesis of Catalytic Metal Oxide Nanoparticles in Supercritical Water Elizabeth G. Rasmussen, Brian R. Pinkard, Justin Davis, John C. Kramlich, Per G. Reinhall and Igor V. Novosselov; Mechanical Engineering Department, University of Washington, Seattle, Washington, United States.

Metal oxide nanoparticles have been extensively studied, primarily to extend their catalytic properties in many industries including chemical manufacturing, energy-related applications and environmental remediation. Given these advances in their applications, the tunable synthesis is of great interest, especially regarding control of crystal structure. In this study iron oxide (Fe$_2$O$_3$) and zirconium oxide (ZrO$_2$) nanoparticles were synthesized using a continuous-flow supercritical water reactor. The products were characterized for both size and crystalline structure by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Additionally, Raman spectra samples taken showed a decreased presence of the toxic organic solvent Dimethylformamide (DMF) showing advancement in completely eliminating such reagents in final products. Thus, the present product can be used for green and sustainable technology in a way that reduces the total environment load. The optimization of this technique is discussed and its advancement forward of the current bounds of continuous hydrothermal synthesis for catalysts applications is reviewed.

ET08.03.15 Intermetallic Pt-Mn/C Nanoparticles as ORR Electro catalysts Mahdi Ahmadi and Héctor D. Abrau; Cornell university, Ithaca, New York, United States.

The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode remains as one of the main challenges for commercial viability of alkaline exchange membrane fuel cells (AEMFCs). It is therefore, of great interest to explore the development of electrocatalysts with superior activity and stability relative to the conventional carbon supported Pt nanoparticles (NPs). In this work we have studied the effects and evolution of structure and surface composition of Pt-Mn NPs on their electrocatalytic activity for the ORR in alkaline media. Pt-Mn NPs were synthesized using solvothermal methods and were supported on C via impregnation. An ordered intermetallic phase was obtained by heat treatment. We have investigated the crystalline structure of these NPs using X-ray diffraction (XRD) and their size, morphology and composition using TEM/STEM, EELS and EDX. Cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry were used to assess their...
electrocatalytic activity and stability. The Pt-Mn NPs were electrochemically dealloyed in acidic media, through potential cycling, leading to the formation of a ~1nm thick Pt shell on an ordered Pt-Mn core. Enhanced mass and specific activity resulted by such electrochemical dealloying. The stability of the electrocatalyst was tested after 4,000 potential cycles in alkaline media following the DOE protocol (0.6-1.0 V vs reversible hydrogen electrode). In alkaline media, Mn surface segregation ensued, leading to a lower electrocatalytic activity when compared to the freshly dealloyed catalyst.

Descriptors from scaling relations are at the forefront of theoretical studies in the search for effective catalyst design principles and in the prediction of catalytic activity from first principles. We propose an intuitive and widely applicable structural descriptor for transition metal oxides from first principles. We demonstrate that our descriptor can provide the bridge between the structural, the electronic, and the energetic properties for TMO surfaces. We then use it to accurately predict C-H activation energies with low deviations from DFT calculations. By building upon the compositional diversity of the perovskites, we further establish some descriptors to correlate with the key reaction steps of methane activation on the oxide surfaces. From the analysis of first and second C-H activation energies and their correlation with the hydrogen adsorption energy on a variety of ABO3 perovskites, general trends emerge that an optimal range of hydrogen adsorption energy strikes the right balance between easy first C-H activation and difficult second C-H activation energies to avoid further oxidation.

8:30 AM ET08.09.01
Descriptors for Transition-Metal Oxides and Implications in Selective Catalysis
Dechen Jiang; Department of Chemistry, University of California, Riverside, Riverside, California, United States.

Zeolites are nanoporous industrial catalysts (e.g. consisting of [AlO4] 4- and [SiO4] tetrahedra) with catalytically active sites located inside the channels and nano-cages, rendering them inaccessible for surface science measurements. Two-dimensional (2D) ultrathin (~0.5 nm) bilayer aluminosilicate films consisting of hexagonal prisms with acidic hydroxyl groups exposed on the surface have been synthesized on Ru(0001) surface as a zeolite model system to study gas molecule adsorption1 and chabazite (CHA)-based catalysts2,3. DFT studies were performed to investigate the dehydrogenation and monomolecular cracking of n-butane molecules over the acidic hydroxyl groups of aluminosilicate films. Intrinsic energy barriers of dehydrogenation, terminal and central C-C bond cracking on aluminosilicate films were found to be ~0.6 eV higher than those of the bulk CHA. We further investigated the effects of the zeolite channel and cage sizes on the n-butane adsorption and monomolecular cracking for six different 3D nanoporous zeolite frameworks (TON, MEI, VFI, FER, CHA, and MEL). We found that as the confinement of straight channels or nano-cages decreases, n-butane adsorption becomes weaker and intrinsic energy barrier for terminal C-C cracking increases. The 2D bilayer film surface, which may be considered as zeolite cages at the infinite cage size limit, has the smallest adsorption energy and highest intrinsic energy barrier. Comparison of the reaction pathway of n-butane terminal C-C cracking in 3D nano-cages and on bilayer aluminosilicate film surface revealed that the decrease of the intrinsic energy barriers in bulk zeolites is caused by the stabilization of the transition states in the 3D nano-cages.


Research is carried out in part at the Center for Functional Nanomaterials and the Scientific Data and Computing Center, a component of the Computational Science Initiative at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. This research used resources of the NERSC, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

9:15 AM ET08.09.03
Exploring Non-Oxidative Dehydrogenation of Alcohols Using Reaction of Ethanol Over Transition Metals and Bimetallic Catalysts
Fatima Jalid1,2, Tuhin Suvra Khan1 and Mohammad A. Haider1; 1Department of Chemical Engineering, Indian Institute of Technology Delhi, Delhi, India; 2Department of Chemical Engineering, National Institute of Technology Srinagar, Srinagar, India.

The selective dehydrogenation of alcohols to carbonyl compounds is an important class of reaction as aldehydes and ketones produced are essential intermediates in the chemical process industry. The process can be made environmentally sustainable by integrating it with the renewable biomass-derived feedstock and employing a non-oxidative process, which prevents catalyst inhibition due to water formation and suppresses over-oxidation of products. To gain insights into the non-oxidative dehydrogenation (NODH) of biomass-derived alcohols over transition metal catalysts, a microkinetic model (MKM) using ethanol as a model molecule has been developed. Previously, a similar study has been conducted to understand the hydro-deoxygenation trends1. The NODH of ethanol was first demonstrated by Church and Joshi in 1951, wherein Cu catalyst was employed with Co and Cr as promoters2. Since then, catalysts mostly based on Cu have been utilized for NODH of alcohols. The NODH of ethanol may proceed via the initial C-H, O-H, C-O or C-C bond scission leading to the production of acetaldehyde, hydrogen, ethane, carbon monoxide, water and methane. For the production of aldehydes and ketones, the process should be made selective for acetaldehyde and hydrogen production. At the reaction conditions of 473K and 10% reactant conversion, the activity trend for acetaldehyde production from ethanol followed the order; Pt > Cu > Pd > Co > Ni > Ag > Au > Rh > Ru > Re. At these conditions, Pt showed the highest activity (TOF ~ 10^3 s^-1), followed by Cu (TOF ~ 10^4 s^-1). As Cu is the cheaper metal, therefore, it is widely used for this process. Followed by acetaldehyde, ethane was the other major product formed. However, all the metals except Au and Ag were selective towards aldehyde production. From the coverage analysis done in the MKM, it was determined that the surface of Cu was covered with the intermediate, CH2=CH2O whereas
most of the metal catalysts viz. Pt, Pd, Co, Ni, Rh, Ru, Re were covered with the intermediate CH3CO, suggesting difficult C-H bond activation of CH2CHO on it. Inspired from this fact, a bimetallic catalyst was proposed where Cu was combined with Ni in a monolayer having low C-H activation barrier (such as Ni, Pd, Pt, Rh). These bimetallic alloys were found to show higher reactivity (TOF > 10³ s⁻¹) as compared to Cu for aldehyde formation. Earlier experimental studies on ethanol NODH over the bimetallic NiCu measured lower activation barrier of 45 kJ/mol, than that of Cu catalyst (Ea = 70 kJ/mol) and increased catalyst stability owing to lesser Cu sintering in the presence of Ni²⁺.

2. Church, James M., and Hanumant K. Joshi. Industrial & Engineering Chemistry, 43, 8, 1951,1804–11

9:30 AM ET08.09.04
**Nanoarray-Based Monolithic Catalysts for Propane Oxidation—Enhanced Activity by Copper Manganese Oxide and Co Dopant Effect**


With growing demands of fossil fuel, advanced technologies of exhaust treatment are getting more concern in order to control the deteriorating air pollution from vehicles and factories. A series of nanoarray-based manganese oxide catalysts were developed by one-pot hydrothermal synthesis to fabricate nanorod arrays on the cordierite honeycomb substrates. Compared to monolithic catalysts with a traditional alumina support, nanoarray-based monolith catalysts possess advantages, e.g., efficient open surfaces, reduced usage of porous supports, low pressure-drop, less agglomeration of nanoparticles. Copper manganese oxide (CuMn2O4) nanosheets were introduced to enhance the oxidative activity for hydrocarbons. The CuMn2O4 nanosheets coated nanoarray-based catalyst, NA-CuMn2O4, shows efficient 90% propane (C3H8) conversion at around 400 °C, which is 50 °C and 75 °C lower than CuMn2O4 wash-coated catalyst (WC-CuMn2O4) and Pd loaded catalyst (WC-Pd), respectively. The benefit of nanoarray morphology was demonstrated by correlating the variation of surface area to the reactivity. The incorporation of cobalt ions was found to increase the specific surface area and thus enhance C3H8 conversion of CuMn2O4. The CuMn2O4/MnO2 nanoarray-based monoliths are promising types of emission control devices.

9:45 AM ET08.09.05
**Selective CO Production by Photoelectrochemical Methane Oxidation on TiO2**

Da He, Wei Li and Dunwei Wang; Boston College, Chestnut Hill, Massachusetts, United States.

The inertness of the C–H bond in CH4 poses significant challenges to selective CH4 oxidation, which often proceeds all the way to CO2 once activated. Selective oxidation of CH4 to high-value industrial chemicals such as CO or CH3OH remains a challenge. Photocatalytic reactions hold great promise for practical applications but have been poorly studied. Existing demonstrations of photocatalytic CH4 oxidation exhibit limited control over the product selectivity, with CO2 as the most common product. The yield of CO or other hydrocarbons is too low to be of any practical value. In this work, we show that high selectivity production of CO by CH4 oxidation can be achieved by a photoelectrochemical (PEC) approach. Moreover, our results revealed that the selectivity toward CO also depends on the substrate types and applied potentials. Based on the experimental results, we proposed a reaction mechanism that involves synergistic effects by adjacent Ti on TiO2. Spectroscopic characterization and computational studies provide critical evidence to support the mechanism. Furthermore, the synergistic effect was found to parallel heterogeneous CO2 reduction mechanisms. Our results not only present a new route to selective CH4 oxidation, but also highlight the importance of mechanistic understandings in advancing heterogeneous catalysis.

10:00 AM BREAK

10:30 AM ET08.09.06
**Novel Inverse Oxide/Metal Catalysts for Cl Chemistry**

Jose A. Rodriguez; 1Brookhaven National Laboratory, Upton, New York, United States; 2Chemistry, SUNY Stony Brook, Stony Brook, New York, United States.

Inverse oxide/metal catalysts have shown to be excellent systems for studying the role of the oxide and oxide-metal interface in catalytic reactions. These systems can have special structural and catalytic properties due to strong oxide-metal interactions difficult to attain when depositing a metal on a regular oxide support. Oxide phases which are not seen or are metastable in a bulk oxide can become stable in an oxide/metal system opening the possibility for new chemical properties. Using these systems it has been possible to explore fundamental properties of the metal-oxide interface (composition, structure, electronic state) which determine catalytic performance in the oxidation of methane, the water-gas shift, and the hydrogenation of CO2 to methanol. Systematic studies have been performed for the deposition of nanoparticles of CeO2, TiO2, FeOx and MgO on surfaces of late transition metals. The nature of the metal substrate has a large effect on the physical and chemical properties of the supported oxide. Recently, there has been a significant advance in the preparation of oxide/metal catalysts for technical or industrial applications. One goal is to identify methods able to control in a precise way the size of the deposited oxide particles and their structure on the metal substrate.

11:00 AM ET08.09.07
**Pt/Sn-Based Nanoparticles in Ionic Liquids as Nanocatalysts for the Selective Hydrogenation of Cinnamic Aldehyde**

Christine Dietrich and Silke Behrens; Karlsruhe Institute of Technology, Karlsruhe, Germany.

Bimetallic nanoparticles have attracted a lot of attention because they show multiple functionalities and prominent catalytic activity, selectivity as well as thermal and/or chemical stability over their monometallic counterparts. Due to synergistic effects, modified electronic and/or geometric surface structures, high catalytic activities and selectivities have been achieved for chemical reactions even if one of the constituents is less or even inactive. Although the controllable synthesis of nanoparticles has developed rapidly over the recent years, more accurate control over nucleation and growth stages is needed for bimetallic nanocrystals. Since bimetallic nanocrystals are composed of different metal atoms, the composition and atomic distribution not only influences the final nanoparticle architecture but also the catalytic properties. The catalytic performance is highly sensitive to the nature of atomic ordering (i.e., random alloy, intermetallic compound) even if the overall composition and stoichiometry are the same. Here, we address the synthesis of bimetallic Pt/Sn-based nanoparticles with tunable composition and structure by exploiting the beneficial properties of ionic liquids (ILs). Small nanoparticles are obtained in a one-pot synthesis by reducing the metal salt precursors with triethylborohydride in the IL. The weakly coordinating IL anions and cations directly control particle nucleation and growth processes enabling nanoparticle synthesis without addition of stabilizing additives or strongly coordinating capping molecules. The nanoparticles form sols of very high colloidal stability in the IL, which is particularly interesting in view of their use as quasi-homogeneous catalysts. The composition and structure of the nanoparticles is tailored by the nature of the metals salt precursors, their initial molar ratio and the nature of the IL. Investigations by X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy reveal the formation of random-type alloy or intermetallic nanoparticles. The catalytic performance of the bimetallic nanoparticles is evaluated in hydrogenation reactions. The selective hydrogenation of cinnamaldehyde, for example, is used to probe the catalytic performance of the Pt/Sn nanoparticles, demonstrating the effect of tin alloying on the catalytic activity and selectivity to the α,β-unsaturated cinnamic alcohol. In general, the selective hydrogenation of α,β-unsaturated...
aldehydes is a critical step in the synthesis of various fine chemicals. As compared to their monometallic counterparts, both a higher catalytic activity and selectivity to the α,β-unsaturated cinnamic alcohol is achieved for the Pt/Sn-based nanoparticles.

11:15 AM ET08.09.08

Supported Transition Metal Catalysts for Methane to Methanol Oxidation Darinka Prime1,2, Julie Fornaciari1,2, Adam Z. Weber2 and Alexis T. Bell1,2; 1Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Methane is a relatively inexpensive, abundant resource, and its partial transformation to chemicals and chemical fuels presents attractive pathways for its utilization. Conventional synthesis of methanol involve a multistep process, which requires high energy input and high cost [1]. Alternatively, methane oxidation using a catalyst in an electrochemical cell is a promising single-step approach to achieve a direct conversion of methane to methanol at lower temperatures and low cost [2].

Catalysts need to be developed for this energetically challenging process. There specific electrocatalysts play a dual role: the activation of the relatively inert C-H bond enabling oxidative hydroxylation of methane, and simultaneously inhibit further methanol oxidation. To date, a variety of the catalysts, including supported metals (Pd, Ru, Au, Ag) and metal oxides (V2O5, Fe2O3, CoO, Mn2O3, MoO3, CrO), have been tested in electrochemical cell and shown promise for the direct oxidation of methane [2]. However, further systematic studies are essential for understanding the mechanism for methane oxidation, enabling the rational design of the catalysts. In this regards single atom catalysts (SAC) are particulars interesting [3]. In addition of showing potential for high methane conversion and methanol selectivity, these catalysts are able to overcome the complicated multiple components and are regarded as ideal model catalysts to identify active sites and facilitate understanding of the reaction process at a molecular level. In spite of great interest; however, it still remains challenging to achieve atomically dispersed metals in high loadings for efficient catalysis. Moreover, for electrochemical methane-to-methanol conversion it is concurrently of importance to develop supported SAC which provide active sites along with hierarchical porosity enabling optimal mass/electron transport.

In this study, first-row transition metal oxides as well as single atom catalysts, supported on carbon supports, have been investigated. The catalysts are synthesized with a ligand-based approach and subsequently characterized for electrochemical methane-to-methanol oxidation. In-depth structural and chemical analyses of catalysts using a combination of various spectroscopy techniques is used to establish structure-property relationship. These insights will provide valuable basis for a scientific-guided approach toward new metal oxide and supported single-atom catalysts for this challenging process.

References

11:30 AM ET08.09.09

Bifunctional Catalysts Based on Colloidal Nanoparticles in the Single-Step Synthesis of Dimethyl Ether Manuel Gentzen, Joerg Sauer and Silke Behrens; Karlsruhe Institute of Technology, Karlsruhe, Germany.

The development of new routes to base chemicals and fuels from renewable resources has drawn much attention worldwide. Synthesis gas (CO + H2) derived from renewable sources (e.g., biomass) and its conversion to dimethyl ether (DME) provides one attractive option with respect to a wide range of applications (e.g. as liquefied petroleum gas, intermediate product for base chemicals or as clean diesel substitute). In the conventional two-step DME process, synthesis gas is converted to methanol over Cu-based catalysts in the first stage, which is subsequently dehydrated to DME over an acidic catalyst in the second stage. Alternatively, DME can be manufactured from synthesis gas in a single-step in the syngas-to-dimethylether (STD) process with methanol as an intermediate [1]. The STD process has many technical and economic advantages and allows for higher CO conversions. The design of efficient bifunctional STD catalysts with balanced methanol and dehydration functionalities and long term stability, however, remains a crucial issue. In this context, model systems derived from well-defined nanoparticles contribute to a more fundamental understanding of structure-performance relationships, enabling the future more rational design of highly efficient catalysts. Herein, we present the synthesis of small, uniform nanoparticles via ruct制服rilization. The colloidal nanoparticles are deposited on the dehydration catalyst (i.e., different types of solid acids), and in this way, serve as the key building blocks for the methanol active component in bifunctional STD catalysts [2,3,4]. This strategy provides us with a flexible nanoparticle toolbox which reduces the influence of the catalyst preparation history and ensures a high comparability. The catalytic properties of the nanoparticle-derived, bifunctional catalysts are investigated in a single continuous-flow reactor, using a simulated biomass-derived, CO-rich synthesis gas and different reaction parameters. The bifunctional catalysts revealed high CO conversions and DME selectivities. The effect of the materials characteristics of the two catalytically active components on the overall catalytic performance is elucidated. Long-term studies of selected bifunctional catalysts displayed outstanding stability under the reaction conditions.

References

11:45 AM ET08.09.10

The Addition of La Via Double Flame Spray Pyrolysis and Its Effect on Catalyst Activity and Selectivity Towards the Dry Reforming of Methane Jonathan Horlyck, Emma Lovell, Jason Scott and Rose Amal; University of New South Wales, Sydney, New South Wales, Australia.

The active and stable catalysis of methane dry reforming relies upon the ability of the material to inhibit carbon formation. Central to this is the ability of a catalyst support to remove oxygen from the acidic carbon dioxide gas, storing or transporting this oxygen, before releasing it to oxidise an adsorbed CHx intermediate species (Djinnovic et al., 2012). For the first time, an aerosol method was used to mix lanthanum with cobalt/alumina materials to improve support basicity. Double flame spray pyrolysis was used to synthesise heterogeneous mixtures of cobalt oxide, alumina and lanthanum oxide. Lanthanum loadings of up to 15 wt% were investigated at two separate nozzle distances (11 and 18cm). The lanthanum content in the materials and the nozzle distance separating the flames were both found to have a key influence over material composition and properties.

The structure of the supported cobalt catalysts was characterised by high-resolution transmission electron microscopy, X-ray diffraction, XANES, carbon dioxide temperature programmed desorption, X-ray photoelectron spectroscopy and hydrogen temperature programmed reduction. Catalytic activity and
stability for methane dry reforming was determined via testing in a fixed bed reactor over a temperature range of 500-800 °C, while catalyst activity was determined at a fixed temperature of 700 °C for 48 hours. The addition of La to the system gave rise to the substitution of La⁺ into the Al₂O₃ lattice, as shown by high-resolution transmission electron microscopy and XANES. Hydrogen temperature programmed reduction showed that doping with La and increasing the nozzle distance limited CoAl₂O₄ spinel formation and facilitated the production of readily reduced Co species. The addition of La also resulted in an increase in material basicity, independent of nozzle distance, lending the catalysts a strong resistance to carbon formation.

Methane conversion and catalyst stability at 700 °C were enhanced via the addition of La. Maximum methane conversions of 89-93% were observed for the two samples with the greatest (15 wt%). This remarkable conversion is very promising when compared to the other Co-based dry reforming catalysts. Additionally, the catalysts with 15 wt% La loading showed no sign of catalyst deactivation or carbon formation, indicating high selectivity towards the desired reaction.

The reactive metal-support interaction (RMSI) offers electronic, geometric and compositional effects that can be used to tune catalytic active sites. Generally, supports other than oxides are disregarded as candidates for RMSI. In this presentation, we will discuss an example of non-oxide based RMSI between Pt and Nb₂C₅ MXene, a recently developed, two-dimensional (2D) metal carbide. The surface functional groups of the 2D carbide can be reduced, and a Pt-Nb surface alloy is formed at a moderate temperature (350 °C). Such an alloy exhibits weaker CO adsorption than monometallic Pt.

Water-gas shift (WGS) reaction kinetics reveal that the RMSI stabilizes the nanoparticles and creates alloy-MXene interfaces with higher H₂O activation ability compared to a non-reducible support or a bulk niobium carbide. This RMSI between Pt and the niobium MXene support can be extended to other members of the MXene family and opens new avenues for the facile design and manipulation of functional bimetallic catalysts.
An electrode is a compound in which electrons serve as anions. Due to the weakly bound nature of the anionic electrons, electrodes exhibit a variety of interesting properties, such as long work function, which enables any few electron donation to materials with high work functions. Therefore, recently, these materials have been successfully employed as promoters to catalyze for ammonia synthesis [1]. Importantly, the reaction bottleneck was shifted from the sluggish N₂ dissociation to NH₃ formation, providing an alternative route to synthesize ammonia beyond the industrial Haber-Bosch process. However only a few electrodes have been discovered so far and most of them are chemically unstable in the presence of air and water, so the exploration of new electrodes and the concept of electrode are urgent issues for both chemical interests and catalytic applications in the materials society.

In the present presentation, we show that LaScSi (TM=Sc, Mn, Fe, Co, Ru) are new electrode candidates and show robust chemical stability in ambient conditions. LaScSi contains multiple types of symmetry-distinct interstitial voids accommodating tiered electron anions. When loaded with Ru, it shows outstanding activity for ammonia synthesis under mild conditions (0.1 MPa, 400°C), with its turnover frequency (TOF~0.1 s⁻¹) one order of magnitude higher than those of oxide-based Ru catalysts. When Sc is replaced by Mn, Fe, Co or Ru, the transition metal atoms become activation centers and the compounds show a self-promotion behavior with high catalytic activity without loading additional metals. As with other electrodes, these compounds show reversible hydrogen storage ability, and electron anions (H vacancies) exchange with H anions rapidly, providing many activated H for the catalytic reactions. Importantly, the transition metal atoms, implanted into the lattice, are activated and work effectively to cleave the N₂ triple bond and modify the rate-determining step from the N₂ dissociation to NH₃ formation. The good catalytic performance will be interpreted on a basis of the electrode concept and a “hot-atom” mechanism by combining the experimental observations and theoretical simulations.

References

2:45 PM ET08.10.05 Developing Fe-Based Electrocatalysts for Ambient Ammonia Synthesis Lin Hu, Jun Wang and Xiaofeng Feng; University of Central Florida, Orlando, Florida, United States.

Considering the limited supply of fossil fuels, there is an urgent need to use renewable energy to drive NH₃ production, as the current Haber-Bosch process for NH₃ synthesis is energy-intensive and consumes 3–5% of the world’s natural gas production. Electrochemical NH₃ synthesis may provide a promising strategy, which can enable sustainable, distributed production of NH₃ when powered by solar- or wind-generated electricity. However, the development of such a process has been impeded by the lack of efficient catalysts for the N₂ reduction reaction (N₂RR) under ambient conditions. Many catalysts show a Faradaic efficiency <1% for N₂RR under ambient conditions. Here, we report the development of Fe-based electrocatalysts for N₂RR with a Faradaic efficiency of up to 8.29%. An Fe/Fe₃O₄ sample was prepared by in situ reduction of a pre-oxidized Fe foil in 0.1 M phosphate buffer solution (PBS). The resulting Fe/Fe₃O₄ catalyst shows greatly enhanced activity and selectivity for N₂RR under ambient conditions than the original Fe foil, achieving a Faradaic efficiency of 8.29% for NH₃ production at ~0.3 V vs RHE in the 0.1 M PBS electrolyte, which is around 120 times higher than that of the Fe foil. The high selectivity is enabled by an enhancement of the intrinsic N₂RR activity as well as an effective suppression of the undesired hydrogen evolution reaction. Comparisons with Fe/Fe oxide samples prepared at different pre-oxidation temperatures indicate that the N₂RR activity may depend on the ratio between Fe and Fe oxide. In addition, the N₂RR selectivity of the Fe/Fe₃O₄ catalyst is superior to that of the Fe, Fe/Fe₂O₃ and Fe/Fe₃O₄ nanoparticles, which provides new insights into the understanding and development of efficient, cost-effective electrocatalysts for ambient NH₃ synthesis.

3:00 PM BREAK

3:30 PM ET08.10.06 Catalysis for Petrochemical Production Deng-Yang Jan and Jeffery Bricker; UOP - Honeywell, Des Plaines, Illinois, United States.

Producing petrochemicals and fuels with minimal capital investment and operating costs requires maximizing the formation of target molecules, while minimizing the formation of unrecoverable side product under the economic operating conditions with uninterrupted operation. One approach to understand what is required to attain the theoretically attainable performance is to lay out the elementary steps of the systems and identify thermodynamic limitations and sources of deficiencies. In this presentation we show how the material and process approaches are adopted to help circumvent the thermodynamic limitations and improve efficiencies of the elementary steps and overall process in petrochemical production.

4:00 PM ET08.10.07 Highly Active and Stable Carbon Nanosheets Supported Iron Oxide Nanocatalysts for Fischer-Tropsch to Olefins Synthesis Yunyun Zhou1,2, Sittichai Natthasakawan1,2, Thuy Duong Nguyen Phan1,2, Douglas Kauffman1, Christopher Marin1, Huolin Xiu3, Eli Stavitski3, Klaus Attenkofer5, Yijie Tang6, Yisong Guo6, Iradwikanari Waluyo5, Amitava Roy7, Jonathan Lekse1, John Baltrus1, Christopher Matranga1 and Congjun Wang1,2; 1National and modify the rate-determining step from the N₂dissociation to NHₓ formation. The good catalytic performance will be interpreted on a basis of the concept of electride are urgent issues for both chemical interests and catalytic applications in the materials society.

In the present presentation, we show that LaTMSi (TM=Sc, Mn, Fe, Co, Ru) are new electrode candidates and show robust chemical stability in ambient conditions. LaScSi contains multiple types of symmetry-distinct interstitial voids accommodating tiered electron anions. When loaded with Ru, it shows outstanding activity for ammonia synthesis under mild conditions (0.1 MPa, 400°C), with its turnover frequency (TOF~0.1 s⁻¹) one order of magnitude higher than those of oxide-based Ru catalysts. When Sc is replaced by Mn, Fe, Co or Ru, the transition metal atoms become activation centers and the compounds show a self-promotion behavior with high catalytic activity without loading additional metals. As with other electrodes, these compounds show reversible hydrogen storage ability, and electron anions (H vacancies) exchange with H anions rapidly, providing many activated H for the catalytic reactions. Importantly, the transition metal atoms, implanted into the lattice, are activated and work effectively to cleave the N₂ triple bond and modify the rate-determining step from the N₂ dissociation to NH₃ formation. The good catalytic performance will be interpreted on a basis of the electrode concept and a “hot-atom” mechanism by combining the experimental observations and theoretical simulations.

References

2:30 PM ET08.10.04 Electrode Concept in Intermetallic LaTMSi (TM=Sc,Fe,Co,Ru) for Catalytic Ammonia Synthesis Jiazhen Wu, Yutong Gong, Junjie Wang, Masaaki Kitano and Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.

Fischer-Tropsch to olefins (FTO) synthesis has drawn significant attention due to the high demand of light olefins as building blocks for the chemical industry, the desire to reduce the dependence on petroleum cracking for these chemicals, and the need for improving environmental sustainability. Iron-based catalysts have emerged as promising FTO catalysts because of their low cost and excellent catalytic performances. We have designed a promising nanocatalyst of porous interconnected carbon nanosheets supported iron oxide nanoparticles for FTO synthesis. The catalysts demonstrate an extremely high iron time yield (FTY) of 1882 μmolCO/gFe₃ with 41% selectivity for light olefins and excellent stability (> 100 h on stream). Our FTY value is found to be one of the highest FTYs and in particular, is 50 to ~1300 times higher compared with those catalysts exhibiting similar light olefins selectivity reported in literature. Mössbauer characterization demonstrates the presence of catalytically active iron carbide species after FTO reaction. ex situ XAFS measurements reveal that the carbon nanosheets support stabilizes metallic iron during the initial catalyst reduction step, which leads to more carbon uptake.
under FTO reaction conditions to more efficiently form highly active iron carbide phase. In contrast, a control sample with carbon nanotubes as the catalyst support exhibits oxidized iron in the catalyst after removal from H₂ reduction pretreatment, suggesting nanostructurally reduced stabilizing effect of carbon nanotubes towards supported metallic iron nanoparticles. This results in inefficient formation of iron carbide species under FTO conditions. Additional EXAFS results further confirm the buildup of iron carbide phase as a function of time on stream in the carbon sheets supported catalysts, whereas a much smaller portion and negligible growth of iron carbide phase was observed in the carbon nanotube supported catalysts under the same reaction conditions.

4:15 PM ET08.10.08 Hydrocracking Catalyst Optimization for Upgrading Heavy, Polynuclear Oil Fractions Mark Kaminsky¹, Sarah Kobasiljà¹, Tatiana Pilyagina¹, Kareemuddin Shatkii², Lianhui Ding³ and Essam Al-Sayed³; ¹Aramco Services Co., Cambridge, Massachusetts, United States; ²Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia; ³Technical Services Dept., Aramco Services Co, Houston, Texas, United States.

Introduction
Changes in global supply and demand for fuels versus chemicals has increased the incentive to better control how much of each is produced from a barrel of crude oil. In addition, as the value of crude oil increases, there is incentive to improve the efficiency of upgrading a barrel of crude, in particular the bottom of the barrel resid. Such highly aromatic resid fractions, which used to end up in petroleum coke or asphalt, are being upgraded to more valuable products with new catalytic and process advances. This is partly driven by further restrictions on the burning of petroleum coke, which makes delayed coking less desirable. Hydrogen addition, via hydrocracking, avoids the production of such petroleum coke from the resid fractions, transforming them into more useful fuel and chemical products.

Discussion
This talk will describe two aspects of hydrocracking catalyst development to upgrade heavier crude oil fractions. In the first part, we will present results on the development of a multifunctional hydrocracking catalyst, comprising both homogeneous organometallic and heterogeneous zeolite components. The homogeneous components are oil soluble organometallic compounds of Mo or Fe that are designed to transform in situ into unsupported nanoparticle metal sulfides that hydrocrack the large asphalteneic molecules, which tend to foul heterogeneous zeolitic pores. The mesoporous zeolites will then more effectively hydrocrack the smaller products of the asphaltene salts and maltenes cracking, in order to make chemicals/fuels with less pore plugging. However, with time on stream, the nanoparticles might sinter and become less active. We will present results on the sintering rates of the Mo and Fe nanoparticles at various conditions in the presence of zeolites. Since the nanoparticles and zeolite crystals are both in the same hydrocracking reactor, it is important to understand their interaction under reaction conditions via characterization of the used catalytic materials. Such catalyst characterization will shed light on the interaction and deactivation mechanisms of these catalyst species.

In the second part of hydrocracking catalyst development we will present data on the synthesis of nano-sized Beta zeolite crystals and the effect of zeolite crystal size and shape on hydrocracking activity. Details of the synthesis method for preparation of the nano-sized Beta will be presented in addition to activity studies using a highly aromatic LCO (Light Cycle Oil) feedstock for the hydrocracking reaction.

4:30 PM ET08.10.09 Electroreduction of Oxygen at Nanostructured Methanol Tolerant Cathodes for Mixed-Reactant Direct Methanol Fuel Cells Juan C. Abrego¹, Youling Wang², Alonso Moreno-Zuría³, Francisco Cuevas-Muniz⁴, Luis G. Arriaga², Shuhui Sun¹ and Mohamed Mohamed³; ¹Energie, Materiaux et Telecomunications (EMT), Institut National de la Recherche Scientifique (INRS), Varennes, Quebec, Canada; ²Centro de Investigacion y Desarrollo Tecnologico en Electroquimica, Queretaro, Mexico.

Energy sources for all kind of electronic devices are under constant pressure to achieve higher efficiency levels by increasing the energy density and decreasing both volume and weight while reducing the cost of portable power sources at the same time [1]. Mixed-reactant microfluidic direct methanol fuel cells (MR-μDMFCs) represent a promising power supply alternative for electronic portable devices in the future, due to their simplicity of design, fabrication and operation. Theoretically, they can achieve higher energy density in comparison with other DMFCs. The main challenge arises from the need for selective electrocatalysts [2]. The synthesis of cathode materials with high mass specific activity towards the oxygen reduction reaction (ORR) and no activity towards the methanol oxidation reaction (MOR) is crucial for the development and commercialization of MR-μDMFC.

In the present work, we report a two-step synthesis by pulsed laser deposition (PLD) of two Pt-based catalysts having a layer onto layer structure. For the two catalysts, first an ultra-low loading Pt layer is deposited directly on carbon nanotubes and further coated with a porous Ag layer or a porous Mn₃O₄ layer, obtaining Ag/Pt/CNTs and Mn₃O₄/Pt/CNTs, respectively. According to the physicochemical characterization, these layers don’t present electronic interaction with each other. The resulting binary materials exhibit electrocatalytic activity similar to Pt towards the ORR in alkaline media. The RRDE studies reveal that the ORR on both Pt/CNTs and Mn₃O₄/Pt/CNTs, is carried out through a 3.9 electron transfer mechanism, while on Ag/Pt/CNTs, the transfer is about 3.7 electron. Interestingly, the bilayer cathodes show no activity for the MOR. Furthermore, those materials demonstrate to be tolerant to methanol concentration as high as 5 M. The results suggest that the superficial Ag and Mn₃O₄ components discriminate between the molecular volume of O₂ and MeOH. Lastly, in order to compare the performance of the methanol-tolerant cathodes in a fuel cell, the materials are tested in a passive, air-breathing MR-μDMFC in conditions close to real application.


4:45 PM ET08.10.10 Epitaxial and Atomically Thin Graphene—Metal Hybrid Catalyst Films—The Dual Role of Graphene as the Support and the Chemically-Transparent Protective Cap Ali Abdelhafiz and Faisal Alamgir; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Commercialization of polymer electrolyte membrane (PEM) fuel cell materials has been of a great interest over the past decade. At the cathode side, the oxygen reduction reaction (ORR) is the key reaction where sluggish kinetics is present, for which Pt remains the catalyst of choice. In order to leapfrog the current limits to Pt use, three main objectives have to be achieved. First, is a reduction of Pt loading; second, is an enhancement of the mass activity per Pt atom; and third is an increase the catalyst durability. Herein, we demonstrate the dual role of single graphene layer, both as a growth template and as a protective cap for 2D Pt monolayers catalysts, where all three objectives can be achieved.

Using iterative under potential deposition (UPD), atomic layers of Pt catalyst are grown on top of a single layer graphene. X-ray absorption spectroscopic (XAS) and scanning transmission electron microscopy (STEM) analyses show that Pt growth is dictated by the graphene-templated epitaxy. Pt/graphene intimacy induces a localized compressive strain on Pt monolayers ranges 3-10%, owing to structural defects, with an overall compressive strain of 3.5% according to extended x-ray absorption fine structure (EXAFS) analysis. In addition, cyclic voltammetry (CV) analysis shows fully-wetted Pt monolayers coverage of graphene under-layer with only a ~1 nm ultra-thin layer of Pt, while ripening was suppressed as shown through STEM images. Atomic Force Microscopy (AFM) analysis demonstrates that Pt monolayers prefer to follow Frank-van der Merwe growth (i.e. layer-by-layer growth mode) rather than
Volmer-Weber growth (i.e. island growth mode), where root mean square (rms) of surface roughness remains quite similar while increasing Pt loading is increased.

Pt/graphene hybrid catalysts show superior catalytic activity for ORR relative to the graphene-free counterparts or state of the art Pt commercial catalyst. A combination of the graphene-imposed compressive strain and electron transfer, push the Pt d-band center up, lowering the overpotential needed for ORR to occur. Furthermore, the graphene/Pt cap hybrid shows the graphene protecting Pt MLs from both dissolution and from ripening, with almost no Pt loss after 5000 fuel cell operating cycles. Our demonstration of a graphene-Pt hybrid opens the door for graphene/metal or metal/graphene architectures with potential applications in, and not limited to, energy, thermo-electric and electronics field.

SYMPOSIUM ET09

Materials for Chalcogen Electrochemistry in Energy Conversion and Storage
November 26 - November 28, 2018

Symposium Organizers
Marine Cuisinier, Qatar Environment and Energy Research Institute
Jun Lu, Argonne National Laboratory
Yuyan Shao, Pacific Northwest National Laboratory
Jiajun Wang, Harbin Institute of Technology

* Invited Paper

SESSION ET09.01: Li-S Batteries: Design and Mechanism
Session Chairs: Kisuk Kang and Hongzhang Zhang
Monday Morning, November 26, 2018
Hynes, Level 3, Room 301

8:30 AM *ET09.01.01
Designing Lithium-Sulfur Batteries with Practically Necessary Parameters Arumugam Manthiram; The University of Texas at Austin, Austin, Texas, United States.

Sulfur has become appealing as a cathode in recent years as sulfur is abundant, is environmentally benign, and exhibits an order of magnitude higher charge-storage capacity than the currently used lithium-ion battery oxide cathodes. However, lithium-sulfur cells suffer from a few formidable challenges: (i) poor electronic and ionic conductivity of sulfur and its discharge product Li2S, (ii) dissolution in the liquid electrolyte of the polysulfide intermediates and their shuttling between the cathode and anode, (iii) large volume changes occurring during charge-discharge cycling, and (iv) lithium-metal degradation during cycling due to continuous solid-electrolyte interphase (SEI) formation and electrolyte consumption. Efforts to overcome these difficulties around the world have shown enormous improvements in cycle life, but a vast majority of the published work has been with low sulfur content, low sulfur loading, and a high amount of liquid electrolyte, which will drastically reduce the practical energy density and make the lithium-sulfur technology uncompetitive with the current lithium-ion technology.

This presentation will focus on designing lithium-sulfur cells with practically necessary parameters to be competitive with lithium-ion technology. Innovative sulfur cathode architectures and novel cell configurations will be presented to realize the practically necessary parameters. For instance, lithium-sulfur cells with a coaxial-graphene-coated cotton-carbon as a substrate for sulfur cathode that display high performance with simultaneously a high sulfur loading (~ 50 mg cm^-2), high sulfur content (75 wt. %), and a low electrolyte/sulfur ratio (4.2 μL mg^-1) will be presented. Such a cell exhibits remarkably a high areal capacity (31 mA h cm^-2), high sulfur content (75 wt. %), and a low electrolyte/sulfur ratio (4.2 μL mg^-1) will be presented. Such a cell exhibits remarkably a high areal capacity (31 mA h cm^-2) and areal energy density (66 mWh h cm^-2) with a capacity-retention of 68% over 200 cycles, exceeding the areal capacity (4 mAh cm^-2) and areal energy density (10 mWh h cm^-2) of commercial LiCoO2 cathode. Besides the challenging cycle life, lithium-sulfur cells also suffer from rapid self-discharge. With novel cell configurations, self-discharge data collected over an extended period of one year will be presented. Moreover, the roles of the porosity, electrical conductivity, and chemical interaction with sulfur of various carbons used in lithium-sulfur cells will be presented, which will help to choose the appropriate carbons. Finally, the areas that need to be addressed in the future to make the lithium-ion technology practically viable will also be presented. In addition, a comparison of the lithium-sulfur technology with other metal-sulfur batteries will also be provided.

9:00 AM *ET09.01.02

Taken advantage of a high theoretical energy density of 2567 Wh kg^-1, lithium sulfur batteries (LSBs) have been considered promising candidates for next-generation energy storage systems. Tremendous efforts have been devoted to improving the battery performance by preparing smart nanostructures. However, detailed reaction mechanisms and the principles of tailoring reaction paths at nanoscale remain unclear. In-situ transmission electron microscopy (TEM) is a powerful technique to probe the dynamic processes of electrochemical reactions at a high spatial resolution and in real-time. Through in-situ TEM study with a solid cell (using Li/Li2O as lithium source and electrolyte, respectively), we find that carbon nanofibers activated at 550 °C encapsulating sulfur particles (PCNF/A550/S) present a low volume expansion of <35% and integrated structure upon full lithiation. In contrast, PCNF/A750/S prepared from carbon fibers activated at 750 °C shows a larger volume expansion of 61 % and overflowing of Li2S, due to the weak
mechanical property and large pores of the carbon host, providing a testament to their different electrochemical performance. Further, we develop in-situ TEM techniques with a graphene-based liquid cell (GLC), where liquid electrolyte and TiN-C/S nanoparticles are encapsulated between two graphene sheets. When exposed to the electron beam, the liquid cells undergo chemical reactions, showing that sulfur particles disappear gradually and Li$_2$S particles nucleates and grows at the conductive and polar TiN substrate during lithiation. An interesting inward growth of Li$_2$S particles is observed in the TiN-C/S cathode. Now, we are trying to establish in-situ TEM with flow liquid cells undergoing electrochemical reactions. It is believed that in-situ microscopic investigation of sulfur cathodes would not only shed new light on understanding of reaction mechanisms but also provide fundamental guidelines to design better LSBs.

9:30 AM ET09.01.03
Sulfur Interaction with Porous Carbon Marie-Vanessa Cougel, Loic Gourmelen and Renaud Denoyel; CNRS-Aix Marseille Univ, Marseille, France.

Sulfur is the most puzzling element in the chalcogen family, in the liquid as well in the solid state. It is the element of the periodic table with the highest number of allotropes in the solid state [1]. At the melting point (Tim= 115°C), the liquid is essentially composed of S$\_8$ rings and has a low viscosity. Around 159°C, a reversible polymerization transition is observed and the chain formation leads to an increase in the viscosity of almost four orders of magnitude [2]. At 445°C, the sulfur sublimates into vapor consisting of S$_n$ molecules (n = 2 - 10) in proportions depending on temperature and pressure.

Within the last decade, Sulfur has been considered as a promising component of electrode material for the next generation of Li-ion batteries since it would permit to obtain high energy density rechargeable batteries [3]. However, the main drawbacks remains in the poor electrochemical cycle stability of the sulfur cathode because of the insulating nature of sulfur and the formation of highly soluble lithium polysulfides leading to the so-called shuttle effect.

One of the methodologies to avoid those problems consists in reducing the polysulfide dissolution using barrier materials. Among the proposed methods, confinement of the sulfur into porous carbon materials is seen as a promising technique since the pores could retain the polysulfides. Various hosts are considered ranging such as mesoporous carbon [4], microporous carbon [5] or carbon nanotubes [6].

Our objectives are to understand the interaction between sulfur and porous carbon and the influence of confinement of sulfur thermodynamic properties. The confinement is realized using commercial porous carbon structures that differ from their specific surface area and pore-size distribution. Various carbon-sulfur composites are synthetized using different impregnation temperatures in the liquid (before and after polymerization) and in the vapor states. It is shown that sulfur loading in the porous carbon hosts is related to the impregnation temperature and to the pore-size distribution. The evidence for sulfur incorporation into the pores is demonstrated owning energy measurements. Using immersion calorimetry, the interaction energy between sulfur and carbon is evaluated for both meso- and microporous carbons. These results could make it possible to propose new ways of synthesis of the Li-S batteries in order to improve their capacities.

Li-S batteries featuring high areal capacity and high current density have been developed based on functionalized free-standing carbon nanotubes (CNT). Each Li-S battery can potentially deliver high energy density and power, the critical problems such as high loadings of sulfur, polysulfide shuttle, and lithium dendrite formation still impede practical Li-S batteries. Furthermore, the state-of-the-art high-performance Li-S batteries use nanomaterials, which requires scalable synthesis processes and manufacturing processes with binders, which further hinder the commercial application of Li-S batteries.

This study reports free-standing self-assembled CNT electrodes activated by functional groups and embedded nanoparticles. The nano-structure provides polysulfide-philic surfaces in the cathode to alleviate the shuttle problem and lithiophilic surfaces in the anode to lower lithium nucleation potential. The activated CNT sponge electrode tackles most critical problems on cathode and anode of Li-S battery. The reduced interfacial resistance and charge transfer resistance at cathode and anode improved the reaction kinetics and lowered the overpotential. A binder-free CNT sponge can be manufactured with a commercially viable roll-to-roll process and directly used as electrodes. The 3D connected CNT network are flexible, ultra-light weight, highly conductive, porous and low-cost. The meso-scale structure such as porosity and tortuosity was tuned to facilitate optimal accommodation of active material as well as fast electron and mass transfer. The functionalized CNT sponge demonstrated not only performance improvement of Li-S batteries, but also provided a commercially viable solution of nanomaterials that can be utilized in energy storage and beyond.

SESSION ET09.02: Energy Conversion and Storage
Session Chairs: Seok-Jin Kim and Ju Li
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 301

1:30 PM *ET09.02.01
Advancing Li-S and Li-O2 Batteries Through New Electrolyte and Electrode Design Linda F. Nazar, Quan Pang, and Chun Xia; University of Waterloo, Waterloo, Ontario, Canada.

Li-S and Li-oxygen batteries are both promising as alternatives to conventional lithium-ion technology due to the high energy density of their theoretical redox couples. For Li-S, extended battery life times have been demonstrated, but two notable challenges still exist to realize its full potential: overcoming the undesired high electrolyte/sulfur (E/S) ratio required for the catholyte-type mechanism that governs most cell configurations, and inhibiting Li dendrite growth and its parasitic reaction with the electrolyte that results in cell degradation. In this presentation we demonstrate that by tuning the electrolyte structure, the challenges at both electrodes can be tackled simultaneously. The sulfur speciation pathway transforms from a dissolution-precipitation route to a quasi-solid-state conversion in the presence of lowered solvent activity and an extended electrolyte network structure, curtailing the need for high electrolyte volumes. With such an optimized structure, the Li plates dendrite-free and shows 20-fold reduction in parasitic reactions with Li, avoiding electrolyte consumption and greatly extending the lifetime of a low E/S (5 µl/mg) sulphur cell. A new advanced electrolyte/electrode design for the Li-oxygen cell will also be presented that demonstrates exceptional Coulombic efficiencies of close to 100% with good cycle life.

2:00 PM *ET09.02.02
"Solid Oxygen" Cathodes Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

As the energy ceiling (~700Wh/kg) of conventional transition-metal oxide (LiMn2O4, M=Ni,Co,Mn) Li-intercalation cathodes has been approached, hybrid anion- and cation-redox (HAC) cathodes are being actively pursued, to compete with purely anion-redox Li-S and Li-O cathodes [Nature Energy 1 (2016) 16111] as candidates for the next-generation Li-ion battery. HAC cathode is a hybrid between traditional Li-ion (purely cation redox, intercalation-type) and Li-O (purely anion redox, conversion-type) cathodes. Here we show a scalable synthesis of new HAC material with energy density 858 Wh/kg at the end of the 100th cycle at 1C, compressed density 3.5 g/cm3, with very little oxygen release by differential electrochemical mass spectrometry and almost no voltage decay.

2:30 PM ET09.02.03
Neighboring Pt Atom Sites in 2D Ultrathin FePt Nanosheets as the High Performance Oxygen Reduction Reaction Electrocatalyst Wenlong Chen, Wenpei Gao, Hong Zhu, Tao Deng, Xiaoqing Pan, Hong Yang, and Jianbo Wu; 1Shanghai Jiao Tong University, Shanghai, China; 2University of California, Irvine, Irvine, California, United States; 3University of Illinois at Urbana–Champaign, Urbana, Illinois, United States.

The shape and morphology structure of catalyst can largely affect their reactive selectivity and activity. Recently, single atom catalyst and two-dimensional (2D) nanostructures have attracted much interests because of their optimized electronic structures and sufficient use of atoms. Generally, single atom catalysts show an improved cost efficiency because the abundant participate and exposure of the noble elements in the reaction. However, in some catalytic processes, such as the oxygen reduction reaction (ORR) in fuel cells, its fast four-electron reaction path usually required at least two neighboring Pt atomic sites to cooperate, which cannot be realized in the traditional isolated single Pt atoms catalysts. To this regard, the low loading of a single atom hinders the wide application in some catalytic reactions which need enough active sites for reactants or intermediates. The fabrication of densely dispersed single atom catalysts with adjacent atom sites available at the same time on a 2D metallic nanostructures matrix with a high surface area paves a feasible way but is still challenging and rarely studied. Here, we combined the advantages of 2D structure and single atom to fabricate 2D ultrathin FePt nanosheets (NSs) with 6.7 wt % neighboring Pt atomic dispersion. Different from the previous reported isolated Pt single atoms materials, these neighboring Pt sites in the ultrathin wrinkled FePt NSs showed a four-electron reduction pathway, a high electrochemical active surface area of 545.54 m² g⁻¹, and an improved 7 times mass activity than the commercial Pt/C in the ORR. The high performance to catalyze a fast ORR derived from the sufficient use and synergistically interaction of neighboring Pt atoms dispersed in a more packed spacing and exposed on the surface of ultrathin sheets. In conclusion, this “neighboring atom catalyst” not only reserves the advantages of the traditional single atom catalysts but also can synergistically cooperate to catalyze the reaction, which needs two or more nearby sites, contributing to a four-electron pathway of the ORR, which distinguished from the traditional isolated single Pt atom catalysts that usually showed a two-electron path to produce H₂O₂. Furthermore, we also proved its outstanding CO-tolerance performance in the ORR by the experiment and computational density functional theory (DFT) calculation method.

2:45 PM ET09.02.04

The need for inexpensive high-activity materials in electrocatalytic applications such as water splitting has driven substantial research into the surface chemistry of non-noble metal catalysts, especially metal oxides. Great progress has been achieved in optimization of oxide electroactivity by the use of
mixed metal oxides, which achieve the necessary physicochemical properties via controlled substitution of cation sites. Despite the obvious importance of the anionic partner in determining the catalyst electronic and surface structure, knowledge of the effects of anionic substitution in electrocatalysis is far less certain. We show that, by controlling the relative proportions of oxide and sulfide, the activity of cobalt oxysulfide nanoparticle electrocatalysts can be substantially increased. Cobalt oxide nanoparticles undergo anion exchange in the presence of ammonium sulfide at low temperatures, allowing access to thermodynamically unstable structures by preventing phase separation of immiscible oxides and sulfides. A lightly doped CoO,S0.18 prepared in this way exhibits a metastable, S-substituted CoO structure and is 2-3 times more active in the hydrogen evolution reaction than either end-member of the oxide-sulfide series. We explain this result using density functional theory calculations, which reveal that S-substitution of the CoO surface increases the bonding strength of H to the surface. This binding energy reaches an optimum value at a low doping level, consistent with our observations. These results show that mixed-anion catalysts are accessible under mild conditions and provide an important strategy for controlling the physicochemical properties of electrocatalyst surfaces.

3:00 PM BREAK

3:30 PM ET09.02.05
Efficient Anchoring of Polysulfides Using a Metal Oxide Interlayer in Li-S Rechargeable Batteries with High Mass Loading S-Cathodes Aninda J. Bhattacharyya and Subhra Gope; Indian Institute of Science, Bengaluru, India.

Over the last decade, there has been a paradigm shift towards usage of earth abundant and cost effective electrodes in rechargeable batteries. This strategy enhances the energy density by nearly one order of magnitude. The concept of sulfur as a positive electrode material was highlighted as early as 1962 by Herbet and Ulan. Sulfur delivers a high theoretical capacity of 1672 mAh g⁻¹, nearly one order higher compared to the intercalation oxide cathodes (IOC) used in conventional Li/Na-ion batteries. The high theoretical capacity originates from the possibility of two exchangeable Li-ions/Atom as compared to only one Li⁺ ion/formula unit of IOC. In addition to high storage, S is cheap, highly abundant and non-toxic in nature. Despite these advantages, the chemical reactions determining the mechanism and quantum of electrical energy storage in Li-S battery pose a formidable challenge mainly due to the various intermediate polysulfides formed during the reversible conversion of elemental S8 to Li2S. Bulk of the work related to Li-S rechargeable battery revolves around materials design strategies of a suitable carbon/non-carbon)-host matrix targeted towards the entrapment of S and prevention of leaching out of polysulfides into the electrolyte. This strategy however, limits the extent of S-loading and depending on the host may simultaneously increase the un-utilizable mass of S in the electrode. The presentation will discuss various hosts for the sulfur cathodes for rechargeable Li-S battery. Recently, usage of interlayers between conventional S/C composite cathode and separator has been demonstrated in Li-S batteries. This interlayer, mostly carbon or doped carbon, has been used to trap the polysulfides in between the interlayer and S-cathode. Instead of carbon, we demonstrate here an alternative and novel interlayer of metal oxide nanoparticles between cathode and separator to efficiently trap and arrest the polysulfides at the S-cathode. Oxide-based compounds exhibit superior ability to hold the lower order polysulfides towards the S-cathode by bonding interactions thereby, enhancing anode protection. In the presence of metal-oxide nanoparticle interlayer, an alternative pathway for S-reduction and oxidation takes place which simultaneously lead to a phenomenal reduction in the polysulfide shuttle effect, even at extremely high loadings of sulfur (up to 15 mg cm⁻²). The inhibition of the shuttle effect is studied by probing the battery separator and interlayer ex situ (cycled at various depths of discharge and charge). The conventional Li-S cell with S/C composite cathodes and metal oxide interlayers exhibits a remarkable improvement in cyclability and rate capability vis a vis the cell without any interlayer. The talk will also discuss some of our explorations in to other metal-sulfur chemistries viz. Na-S and Mg-S.

3:30 PM ET09.02.06
Modification of Back-Surface Contacts to Metal Chalcogenide Active Layers Using Carrier-Selective Thionated Perylene Derivatives Curtis W. Doiron, Alexander D. Carl, Emma Travassos and Ronald L. Grimm; Worcester Polytechnic Institute, Acton, Massachusetts, United States.

Sulfur-terminated organic functional layers were attached to TiO₂ surfaces through successive reactions of substrates with 3-aminopropyl triethoxysilane (APTES), perylene tetracarboxylic dianhydride (PTCDA), and Lawesson’s Reagent (LR). X-ray photoelectron spectroscopy (XPS) quantified coverages of APTES and thionated perylene species. IRRAS confirmed chemical attachment of PTCDA to the APTES surface through the formation of the imide, and thionation yields on the exposed anhydride group of PTCDA were estimated by C=O features and the presence of sulfur in the XPS. Throughout the surface modification process, UPS studies observed changes in the HOMO-LUMO levels of the organic species at the TiO₂surface that indicate the desired electron-transfer and hole-blocking characteristics for the modified perylene surface that could ultimately yield increased solar energy conversion efficiency in a tandem junction solar cell with deposited metal chalcogenides.

3:45 PM ET09.02.07
Encapsulation of Fe in 2D Fused Aromatic Networks as an Oxygen Reduction Electro catalyst Seok-Jin Kim¹, Javeed Mahmood¹, Changmin kim¹, Gao-Feng Han¹, Seong-Wook Kim¹, Sun-Min Jung¹, Guomin Zhu², James J. De Yoreo², Guntae Kim¹ and Jong-Beom Baek¹; ¹Energy Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); ²Physical Science Division, Pacific Northwest National Laboratory, Richland, Washington, United States.

For oxygen reduction reaction (ORR), nonprecious iron (Fe)-based materials, such as Fe–N–C and FeFe:C have gained considerable attention as electrocatalysts. However, the poor stability hindered their practical application because of the defective protection of unstable Fe nanoparticles. Here, a synthesis strategy of a stable iron-based electrode catalyst is introduced using a two-dimensional phenazine-based aromatic porous organic network (Aza-PON). The bifunctional Fe@Aza-PON catalyst exhibited promising electrocatalytic activity and practical performance in a hybrid Li–air battery cell. Moreover, the Fe@Aza-PON displayed void-free encapsulation of vulnerable metallic nanoparticles for improved stability and tolerance against contamination (methanol and CO poisoning). The new design and synthesis of indirect-contact catalysts is promising for various additional applications.
Alkaline electrolysis has been considered in commercial applications as a clean and efficient technology for the growing demand for hydrogen fuel in fuel cell technologies. To speed up the Hydrogen Evolution Reaction (HER), several matrices including precious metals with appropriate surface properties have been considered as catalyst. Difficulty in common synthesis of catalysts through chemical means with variations in morphology and higher economics brings the need for a more scalable and cost-effective approach. Natural molybdenum disulfide (MoS2) in the form of the crystalline Molybdenite has been extracted from mine waste tailings (Residue Impoundment Sludge) in FCF Minerals Corp, Nueva Viscaya, Philippines through Rougher-Cleaner route of Oil-Agglomeration Froth Flotation with 99.97% final recovery and final grade of 74.80% Mo from a low grade Mo source (1.052% Mo) with ultrafine particles with interference of organic matter and silicates, with SEM/EDX photomicrographs of probable fine and flaky molybdenite particles on a silicate matrix. MoS2, nanosheets were produced from exfoliation of Rougher (1st stage flotation) and Cleaner 2 (final stage flotation) concentrates in OAF flotation through high-shear milling in common household surfactant solution and the dispersion in varying concentrations of Ethanol (EtOH). Agglomeration due to the retained oil from OAF has no significant effect on particle size distribution of PBM Products (Head sample, Rougher concentrate, Cleaner 1 concentrate and Cleaner 2 concentrate) with average Cumulant diameters of 26.27±6.56 nm, 25.69±50.40 nm, 25.93±67.58 nm and 25.51±61.23 nm, respectively. Exfoliated and dispersed Rougher (50%EtOH) and Cleaner 2 (20%, 50% and 80% EtOH) products were drop-casted onto a conductive substrate (0.025cm² NiO film) to serve as a cathode of in an electrolytic cell with 1 M KOH as electrolyte, Pt counter electrode and sat’d Ag/AgCl as reference electrode. Voltage bias of 0.5V at 0.1V/s at a rate of -0.7 to 0.3V was applied to derive the Linear Sweep Voltammograms of each cathode at 4 trials. There was a significant difference between Rougher and Cleaner 2 (50%EtOH) cathodes with the former having a wider range of performance and instability with the progression of trials that may be due to the lower grade of Mo on the sample and unwanted reactions on the cathode surface. There was a significant difference in Cleaner 2 cathodes in varying EtOH concentrations. Best electrocatalytic performance among the three was found at 50%EtOH with the lowest average onset potential of -0.341V, while 20% and 80% EtOH having -0.354 and -0.352V, respectively. The higher onset potentials were due to the summative of either ineffective dispersion or lower MoS2 concentration. Results show that the dispersed MoS2 from OAF flotation of fine molybdenite from mine waste tailings is a viable source of HER electrocatalyst in alkaline medium.

**ET09.03.02**

**Synthesis and Determination of the Activity of Mesoporous Sulfoselenides for the Hydrogen Evolution Reaction**

Shayvin A. Cetegen¹, Biswanath Dutta² and Yang Wu¹;
¹Chemical Engineering, University of Connecticut, Storrs, Connecticut, United States; ²Chemistry, University of Connecticut, Storrs, Connecticut, United States.  

In this work, Lead oxide (PbO) was synthesized chemically at an elevated temperature from lead acetate and sodium hydroxide solution. As prepared powder was polycrystalline in nature having alpha phase tetragonal symmetry. The average crystallite size of 70nm with lattice constants a=3.97Å, b=3.97Å, and c=5.02Å was obtained from X-Ray Diffraction analysis. Direct band gap of the PbO powder was found to be 1.9 eV by Uv-visible spectral analysis. Raman analysis confirmed the presence of pure alpha phase. Photoactivity of the prepared PbO powder was studied by employing it as a photoelectrode in photoelectrochemical cell. Photocurrent density value of about 0.5mA/cm² could be achieved by photoactive microcrystallites in ferrocyanide electrolyte.

**ET09.03.03**

**Synthesis and Determination of the Activity of Mesoporous Sulfoselenides for the Hydrogen Evolution Reaction**

Shayvin A. Cetegen¹, Biswanath Dutta² and Yang Wu¹;
¹Chemical Engineering, University of Connecticut, Storrs, Connecticut, United States; ²Chemistry, University of Connecticut, Storrs, Connecticut, United States.  

Electrocatalysis of water provides a scalable and sustainable means of hydrogen (H₂) production. The drive for a clean energy future inspired us to develop a stable, readily producible, and highly active catalyst that can serve as a cheaper alternative to many pyrites. To achieve this, we adopt the approach of structural tuning by different metals/non-metals that has been found to be effective in several instances. We present one such effort by partial surface selenization of mesoporous metal sulfides produced by sulfurization of cobalt, iron, and nickel UCT-synthesized metal oxides. Using a variety of analytical techniques and electrochemical measurements, we analyze the morphology and demonstrate the enhanced electrochemical activity of these mesoporous sulfoselenides under acidic media, highlighting our catalysts superiority over most existing systems.

**ET09.03.04**

**Improving Performance of Facile Preparing Antimony Selenide Sensitized Solar Cells by Interface Modification**

Bowen Zhao, Xingzhao Liu and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

Sb₂Se₃ has received great attention for photovoltaic cells recently due to its excellent optical property, superior stability and eco-friendly nature. Herein, an efficient Sb₂Se₃ sensitized solar cell (SSC) is prepared for the first time through a solution-based successive ionic layer adsorption and reaction (SILAR) procedure which is flexible, low-cost and easy to access. Aiming to further improve the device performance, a novel approach based on TiCl₄ treatment on mesoporous TiO₂ has been introduced, which is found to optimize the growth condition of Sb₂Se₃ nanoparticles and improve the interfacial surface state, resulting in the better band alignment and the controlled recombination losses in Sb₂Se₃ SSCs. The TiCl₄ treated devices achieve the best photovoltaic conversion efficiency of 1.22%, which is much higher than that of 0.46% for the solar cells without TiCl₄ treatment.

**ET09.03.05**

**La₉₋₆Ca₃MnO₉ as Model Catalyst System for the Oxygen Evolution Reaction**

Raika Oppeermann, Christoph Richter, David Kröck, Viet A. Chu, Bjørn Luerben and Juergen Janek; Institute of Physical Chemistry, Justus-Liebig-Universität Gießen, Gießen, Germany.

The catalysis of the oxygen evolution reaction (OER) represents a key challenge in (photo)electrochemical water splitting, fuel cells and metal-air batteries. In nature, the large overvoltage of the energy-intensive reaction is circumvented through a calcium-manganese complex in photosystem II, which draws the attention to manganese oxides as earth abundant alternatives to the state-of-the-art catalysts such as IrO₂ and RuO₂.

One main issue of binary manganese oxide catalysts is the insufficient activity in OER due to their poor electric conductivity. Ternary perovskite materials like CaMnO₃ have shown a possibility to overcome this problem. Controlled defect formation due to doping or careful post processing under varying oxygen partial pressures led to increased electrocatalytic activities in OER.²³

We have systematically investigated the perovskite system La₉₋₆Ca₃MnO₉ (LCMO) as model nonstoichiometric electrocatalyst for OER in alkaline media. Powder samples over the whole composition range have been prepared by citrate route as well as the corresponding thin films by pulsed laser deposition (PLD). By varying the lanthanum to calcium ratio we could adjust the manganese oxidation state and the nonstoichiometry from an oxygen deficient to an
Lithium-sulfur (Li-S) batteries have high theoretical specific energy for portable and stationary storage application. However, Li-S batteries have many challenging issues at the materials level. Here I will present our recent progress on: 1) Nanoscale design of host and interface for Li metal anodes; 2) Discovery of sulfur cathode phase behavior, leading to new guidance to materials design.

8:30 AM ET09.04.01
Nanoscale Design for Lithium-Sulfur Batteries Yi Cui; Stanford University, Stanford, California, United States.

Lithium sulfur (Li-S) batteries have high theoretical specific energy for portable and stationary storage application. However, Li-S batteries have many challenging issues at the materials level. Here I will present our recent progress on: 1) Nanoscale design of host and interface for Li metal anodes; 2) Discovery of sulfur cathode phase behavior, leading to new guidance to materials design.

9:00 AM ET09.04.02
Stable Li Anodes Enabled by Interfacial Functionalization for Li-S Batteries Donghai Wang; The Pennsylvania State University, University Park, Pennsylvania, United States.

Li-ion batteries are promising high-energy storage devices due to high theoretical capacities of both the sulfur cathode and lithium (Li) metal anode. Considerable efforts have been made to improve sulfur cathodes. However, the issues associated with Li anodes such as low Coulombic efficiency (CE) remain unsolved due to poor stability of solid-electrolyte interphase (SEI) associated with excessive SEI accumulation and exacerbation of Li dendrite growth, leading to poor capacity retention and short cycling life of Li-S batteries. In this talk, I will present a strategy to reinforce the SEI with desired properties including good tolerance to the Li-based material volume change and efficient surface passivation against electrolyte penetration. The strategy works via introducing multiple functional components bonded to the Li-based material surface into the SEI. The SEI reinforced shows much better stability than the SEI reinforced by electrolyte additive strategy, which is the current state-of-art and commercially used solution to SEI stability issue. The durable SEI layer can suppress dendritic Li growth, enhance Li plating/stripping CE, and in turn, enable Li-S batteries with long cycling life and good capacity retention. We also demonstrate the reinforced SEI can improve Li metal efficiency in a carbonate-based electrolyte for Li-metal oxide batteries. This study provides a promising route to address the issues associated with Li metal anodes and promote the development of high-energy rechargeable Li metal batteries.

9:30 AM ET09.04.03

The worldwide consciousness of the low-carbon economy and sustainable energy concept greatly promote the progress of chemical power sources such as batteries and fuel cells. With the rapid development of portable electronic devices and electric vehicles, the demand for research on advanced energy-storage and conversion systems with low cost, high power density, long cycle life and high energy density has significantly increased to optimize the traditional devices. Therefore, electrocatalytic layered materials and host materials, which success the task of separators in battery application, attracted great attention. Layered two-dimensional (2D) transition metal dichalcogenides (TMDCs) materials, like tungsten or molybdenum disulfide, are receiving increased interest due to their high specific surface area and versatile electronic structure. The direct bandgap of these monolayered materials is located in the visible light or near infrared range, which also make them promising for efficient solar energy conversion, water splitting applications as well as semiconductor utilization.

In this context, a new class of chalcogenide based transition metal single-source precursors of the formula [MIV(SEtN(Me)EtS)2] were designed in this work which enable a highly efficient approach towards crystalline 2D-structured transition metal disulfides (TMDSs). To synthesize mono- or few-layered WS2 and MoS2, volatile single-source precursors [W(SEtN(Me)EtS)2] and [Mo(SeN(Me)EtS)2] were prepared based on the reaction of the chelating pincer type (HSEt)3NMe-ligand with the tetravalent metals tungsten and molybdenum. Chemical vapor deposition (CVD) on various substrates including fibrous structures resulted in the formation of homogenous thin films, which were subjected to atomic scale imaging and x-ray analysis to confirm the synthesis of crystalline WS2 and MoS2 materials. The advantageous properties of WS2 and MoS2 combined with the flexible, controllable and sustainable synthetic route, developed in this work, is expected to be of significant interest for various energy storage and conversion applications including lithium-oxygen batteries and photochemical water-splitting.

9:45 AM ET09.04.04
Effect of the Solvate Electrolyte on Lithium-Sulfur Battery Performance and Reaction Mechanism Heng-Liang Wu; National Taiwan University, Taipei, Taiwan.

Solvate electrolytes such as acetoni-trile-based solvate electrolyte have been proposed to suppress the polysulfide dissolution and enhance the capacity retention of lithium-sulfur (Li-S) batteries.(1-3) In this study, we report on our use of in situ spectroscopy including Raman and X-ray spectroscopy (X-ray diffraction and X-ray absorption spectroscopy) to investigate sulfur reaction mechanism and the interaction between polysulfide and electrolyte. Raman spectroscopy and cyclic voltammetry obtained from sulfur-carbon cathodes in the conventional ether-based electrolyte show that long chain polysulfides (S2n2+) are formed in the first reduction process at ~2.4 V vs Li/Li+ and short chain polysulfides such as S2, S4, and S4O42- are observed with continued discharge at ~2.3 V vs Li/Li+ in the second reduction process.(4-5) The elemental sulfur changes from orthorhombic phase to monoclinic phase in the
conventional ether-based electrolyte during the first cycle. In acetonitrile-based solvate electrolyte, in situ spectroscopy results show that short chain polysulfides are formed at the early stage of discharge process and the formation of soluble long chain polysulfides is suppressed. Elemental sulfur with orthorhombic phase is reformed in acetonitrile-based solvate electrolyte during cycling. These results suggest that solvate electrolyte changes the sulfur reaction mechanism. The effect of solvate electrolyte on Li plating/stripping process was also studied. We next propose different solvate electrolytes with low polysulfide solubility and high stability toward Li metal to enhance the capacity retention of Li-S batteries.

References:
(2) K. A. See et al., ACS Appl. Mater. Interfaces 2016, 8, 34360.
(5) H.-L. Wu et al., Nano Energy 2017, 32, 50

10:00 AM BREAK

10:30 AM ET09.04.05
From Insulating to Conductive, From Hard to Soft Materials—Sulfur and Chalcogenides (CuS, MoS2) in Metal-Sulfur and Solid-State Batteries Philippo Adelhelm1,2 1Institute of Technical Chemistry and Environmental Chemistry, Jena University, Jena, Germany; 2Center for Energy and Environmental Chemistry (CEEC Jena), Jena University, Jena, Germany.

Sulfur and chalcogenides are attractive materials for rechargeable batteries thanks to their generally high specific capacity. Other relevant properties such as conductivity, plasticity or volume expansion during lithiation/sodiation largely vary and depend on the specific compound of interest. Sulfur and the ideal discharge product Li2S or Na2S are insulating which requires a sophisticated electrode design with a porous carbon matrix. CuS, on the other hand, is both electronically and ionically conductive which generally benefits the reversibility of the cell reaction. Finally, MoS2 is very soft which may be of advantage considering the large volume expansion during lithiation/sodiation. In this presentation, we will discuss specific properties of sulfur in contact with a porous carbon matrix combined with results on room-temperature-sodium-sulfur cells. We also address the use of copper sulfide and molybdenum sulfide as electrode material for lithium/sodium solid state batteries which can show high capacity despite their large volume expansion during cell cycling.

11:00 AM ET09.04.06
Developing Air Cathodes Using ORR and OER Catalysts for Aqueous Lithium-Air Batteries Varun Rai and Daniel John Blackwood; National University of Singapore, Singapore, Singapore.

Lithium air batteries with aqueous acidic catholytes system have a high potential to attain theoretical energy density limits in energy storage devices because of high conductivity and solubility of discharge products along with low CO2 solubility [1,2]. Therefore, the role of low cost, active, durable and noble free ORR and OER catalysts are very critical in improving charging and discharging cycles followed to addressing the problem in achieving high energy density for practical storage applications. Catalysts suitability as efficient air cathodes are determined by its electronic conductivity, non-solubility in aqueous acidic catholyte, optimal porosity for fast oxygen diffusion and selective adjustments of hydrophobic in ORR and hydrophilic property in OER processes. Transition metal oxides [3] shows fairly low conductivity in comparison to noble metal however by introducing dopant centers and hetero atoms like N, S, F etc significantly improve electronic conductivity and favorable redistribution of positive charges in the lattice for oxygen ad-sorption than pristine oxides. We would be presenting carbon black supported catalyst for better ORR performance with high current. As Carbon black improves the electron transfer among substrate, catalyst and electrode tip.

References

11:15 AM ET09.04.07
Amorphous Superatom Molecular Cluster-Based Nanospheres for Electrochemical Energy Storage and Conversion Boyu Qie1, Andrew Pinkard2, Xavier Roy2 and Yuan Yang1; 1Applied Physics and Applied Chemistry, Columbia University, New York, New York, United States; 2Chemistry, Columbia University, New York, New York, United States.

Precisely tunable and programmable synthesis of materials that satisfy specific functions is one of the critical points of materials chemistry. One trend to design solid-state materials is using functional molecular clusters, so-called superatoms, to substitute single atoms in strategy design to create more applicable possibility like high porosity and novel nanomaterials. A rich library of different molecular clusters has been established in a variety of attractive properties, such as redox activity, large magnetic moments and luminescence. However, to our knowledge, there have been few attempts to use these building blocks to assemble new materials for energy purposes - alkali ion battery and water splitting. Here we report a new method to synthesize cobalt sulfides (CoSx) and selenides (CoSex) based on molecular cluster building blocks. The products presented amorphous micron-size spherical shape with high porosity and surface area (~360 m2/g of CoSx and ~130 m2/g of CoSex), considering which, they could provide more channels/rooms for ion transport, to have better kinetics and less volume change during battery cycling in high-capacity conversion reaction. We successfully utilized these micron-sized spheres into lithium and sodium-ion batteries with high specific capacities (~650 mAh/g for CoSx-Li-ion battery and ~450 mAh/g for CoSeS-Na-ion battery), impressive rate capability, and reasonable reversibility (17% lost for 300 cycles in Li-ion battery and 10% lost for 100 cycles in Na-ion battery). Moreover, we also found that the super-based materials are efficient catalysts for the hydrogen evolution reaction (HER) with reasonable overpotential (the highest -0.184V vs. SHE at 10 mA/cm2 in 0.5 M H2SO4 solution).
1:30 PM *ET09.05.01
High Capacity Cathodes Invoking Oxygen Redox Chemistry  
Peter Bruce; University of Oxford, Oxford, United Kingdom.

The energy stored by Li-ion batteries is limited by the cathode. State-of-the-art materials can deliver in the region of 180 mAh g\(^{-1}\) of charge storage capacity. Such materials, e.g. LiFePO\(_4\), are limited by storing electrons only on the transition metal ion (transition metal redox). It is now known that the oxide in so called lithium-rich transition metal oxides, e.g. Li\(_2\)Ni\(_{0.6}\)Mn\(_{0.2}\)O\(_{2}\) can store charge (oxygen redox). To harness the opportunity of increased charge storage that O-redox may offer it is important to understand the nature of O-redox processes and the factors that control them. O-redox in 3d transition metal oxides will be discussed, leading to a high capacity manganese based cathode that utilises the full capacity of the Mn as well as charge storage on oxygen.

2:00 PM *ET09.05.02
Catalyzing the Charging Process in Li-O\(_2\) Batteries Using Lithium Halides  
Graham Levericker, Michal Tulodziecki, Ryoichi Tatara, Shuting Feng and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Non-aqueous Li-O\(_2\) batteries have been the subject of intense research interest over the past decade or two, owing to their very high theoretical gravimetric energy density; potentially up to three times that of state-of-the-art lithium ion batteries. Despite this widespread effort, lithium oxygen batteries still suffer from a number of significant issues, including high overpotential on charge and poor cycle life. Part of this poor charging performance can be attributed to the insulating nature of the Li\(_2\)O\(_2\) formed on discharge, which makes direct electrochemical oxidation challenging. While a number of approaches have been taken to try and catalyze the charging process of a Li-O\(_2\) battery, soluble lithium halides, such as lithium iodide and lithium bromide, in particular, have shown very promising performance. Despite this promise, there has been serious ambiguities in literature relating to the influence of lithium iodide on both the discharge and charge processes. In this talk, strategies for controlling the thermodynamics of the chemical oxidation of Li\(_2\)O\(_2\) during the charging progress are discussed, based on controlling solvation energy through solvent-ion interactions and the addition of water to the electrolyte, as well as through the formation of halide-complexes. This work shows promise that the charging process of a Li-O\(_2\) battery can be optimized for both energy efficiency and effective oxidation of Li\(_2\)O\(_2\) through systematic electrolyte and redox mediator design.

2:30 PM ET09.05.03
Systematic Design of Bifunctional Hybrid Electro catalysts Comprised of 1T’ MoS\(_2\) and Fe, Co, Ni-Based Compounds for Overall Water Splitting  
Haoyi Li and Xin Wang; Department of Chemistry, Tsinghua University, Beijing, China.

Driven by the exigent demand for sustainable and renewable energy sources, a huge effort has been devoted to the development of efficient and accessible energy conversion technologies. Electrochemical water splitting – an environmentally-friendly and cost-effective technology for hydrogen production from electricity – has attracted great attention as a promising pathway to decrease social dependence on fossil fuels. The development of low-cost, high-performance electrocatalysts is necessary to enable water splitting as a functional and practical technology. As a means of lowering the driving overpotential and increasing the efficiency of catalytic water splitting, first, enhancing the intrinsic activity of catalytic sites in electrocatalysts requires an optimization of the adsorption free energy of reactants to speed the rate-determining step of the overall reaction. Second, the enhanced conductivity of electrode materials contributes to fast charge transfer, a requirement for which metallic materials have demonstrated superior ability. Third, the optimization of mass transfer properties has a tremendous effect on the ultimate efficiency of electrocatalysts. Innovative nanoarray and porous two-dimensional architectures can facilitate the dissipation of as-formed gas bubbles from the electrode surface. Finally, the increased density of catalytic active sites in the electrode material allows for the maximization of limited electrode surface area – porous nanostructures have a proven ability to facilitate increased surface area.

Herein we prepared the hybrid nanostructures integrating metallic 1T’ MoS\(_2\) with Fe, Co, Ni-based compounds for water splitting via integrated compositional and geometric structural design. Metallic 1T’ MoS\(_2\) was employed for its excellent electrode kinetics, fast charge transfer, and remarkable intrinsic electrocatalytic HER activity. Fe, Co, Ni-based compounds were utilized for their inherent and adjustable OER reactivity (a result of synergistic effects between metal ions). Lastly, nanotube-array and porous two-dimensional architectures were exploited for their porosity, high surface area, and uneven surface characteristics – a way to maximize catalytic active site density and facilitate mass transfer. Notably, the hybrid nanostructures deliver a current density of 10 mACm\(^{-2}\) at an overpotential of 38 mV for the HER and 184 mV for the OER while demonstrating outstanding durability (200 mACm\(^{-2}\) for 80-hour continuous operation). The low Tafel slopes of 37.5 mVdec\(^{-1}\) and 49.9 mVdec\(^{-1}\) for HER and OER demonstrate the fast reaction kinetics. AES demonstrates that the predominant failure mechanism is film cracking and delamination, which originates from initial film heterogeneity.

**SESSION ET09.05: Catalysis in Energy Conversion and Storage**

*ET09.05.04*
Developing Photoelectrochemical Water-Splitting Anodes with Iridium Oxide-Based OER Catalysts  
Micha Ben-Naim\(^{1}\), Alaina L. Strickler\(^{1}\), David W. Palm\(^{1}\), Drew Higgins\(^{2}\), Laurie King\(^{1}\), Adam Nielen\(^{1}\) and Thomas F. Jaramillo\(^{1,2}\); \(^{1}\)Chemical Engineering, Stanford University, Stanford, California, United States; \(^{2}\)SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Photoelectrochemical (PEC) water-splitting is a promising technology that uses solar radiation to split water into hydrogen and oxygen, providing a storable form of chemical fuel to pair with intermittent renewable electricity sources\(^{1}\). Silicon shows promise as a small bandgap absorber material (1.1 eV) to use in tandem PEC devices\(^{1}\). However, pairing catalysts with semiconductorss has proven difficult due to poor energetic alignments and interfaces as well as stability concerns, which are especially limited in acid\(^{2}\).

Many catalyst deposition techniques require high temperatures and complicated processing and are incompatible with some photoabsorber materials. Thus, we developed a spin coating procedure due to its inherently simple and versatile nature to synthesize amorphous iridium oxide and biphasic strontium iridium oxide. Material structure is probed by SEM, XPS, AES, and XRD, while electrochemical performance was measured under illumination and in the dark by cyclic voltammetry, chronoanodometry, and electrochemical impedance spectroscopy.

The addition of strontium to the catalyst gives 550 mV of photovoltage, a 100 mV improvement upon iridium oxide. By probing a facile redox couple, we show that the strontium iridium catalyst forms a more beneficial electronic interface with silicon. A comparison of the as-prepared and post-test anodes via AES shows that the predominant failure mechanism is film cracking and delamination, which originates from initial film heterogeneity.
Designing simultaneous activity and stability of a catalyst during electrochemical water splitting is a significant challenge on the way to efficient energy storage. The development and deployment of these large electrolyzer stacks will cultivate the large-scale application of a variety of renewable energy sources. Due to their high conversion rate and efficiency, electrolyzers have been extensively investigated at Giner. Advanced catalysts have been developed to enhance the conversion rate and boost the process efficiency. For example, the electrochemical production of ammonia from nitrogen and water has thus led to tremendous energy savings compared to the conventional Haber-Bosch process. The produced ammonia can be used as low-cost energy carrier for fuel cells. Some of these advances have been applied in our electrolyzer products, from single cell lab hydrogen generators to large stacks. The performance and efficiency of our electrolyzers are thus tremendously improved. The development and deployment of these large electrolyzer stacks will cultivate the large-scale application of a variety of renewable energy. Due to their high density and reduced cost, the electrolysis technologies may become strongly competitive and complementary to rechargeable batteries for renewable energy storage.

3:40 PM ET09.05.07
Activation of Ultrathin SrTiO3 with Subsurface SrRuO3 for the Oxygen Evolution ReactionAndrew Akbashev1, 2, Liang Zhang3, J. Tyler Mefford1, 2, William Chuah1, 2 and Aleksandra Vojvodic3; 1Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 2Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 3Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Designing simultaneous activity and stability of a catalyst during electrochemical water splitting is a significant challenge on the way to efficient energy conversion. A dream material for the oxygen evolution reaction (OER) should evince sufficiently high activity and maintain stability of the active surface. Although oxide materials hold great promise for the electrocatalysis applications owing to their high OER activity, their efficient operation is often hindered by structural instability. A core-shell design, where an active core catalyst is covered with a stable nanometers-thick shell, is an attractive solution to the problem of catalyst instability that is commonly employed in metal nanoparticles. However, the interaction between the core and shell of oxide materials during electrocatalytic reactions is not well understood. We hypothesize that the core material can act as a subsurface activator for the shell by introducing spatially accessible electronic states. We validate this hypothesis by studying single-crystalline oxide heterostructures (epitaxial thin films) as model core-shell architectures.

A highly OER-active SrRuO3 undergoes rapid dissolution under OER conditions, which makes it an ideal material for a model active layer. On the contrary, SrTiO3 is OER-inert and chemically stable and can serve as a shell material. We employ atomically-precise deposition to fabricate ultrathin heterostructures composed of bottom SrRuO3 and capping SrTiO3 layers.

We demonstrate that inserting as little as one unit cell of an active material (SrRuO3) under a shell layer (SrTiO3) activates the inert shell, while only two unit cells (1 nm) of SrTiO3 is enough to fully protect the inherently unstable SrRuO3 against dissolution. Using density functional theory calculations, we unravel the mechanism for the subsurface activation in oxide systems. Burying an active material under an ultrathin shell layer introduces new electronic states in the system, changing the electronic hybridization between the adsorbates and the shell layer and facilitating an easy transfer to the adsorbed intermediates.

Ultrathin heterostructures serve as a rigorous platform for screening core/shell nanoparticle combinations and thicknesses. Our study provides an insight into the role of atomic-level modification of the surface and subsurface layers of oxide electrocatalysts, opening up a rich playground for further discovery and design of active and stable materials.

4:45 PM ET09.05.08
Hierarchical Titanium Nitride Nanostructures as Stable Catalyst Supports for Low-Pt Content Fuel Cell Cathodes Andrea Perego1, 2, Giorgio Giuffreda1, 2, Piero Mazzolini2, Rosaria Brescia1, Dinesh Sabarirajan3, Iryna Zenyuk4, Andrea Casalegno3 and Fabio Di Fonzo2; 1Department of Energy, Politecnico di Milano, Milan, Italy; 2Center for Nano Science and Technology @PolMi, Istituto Italiano di Tecnologia, Milan, Italy; 3Istituto Italiano di Tecnologia, Genova, Italy; 4Mechanical Engineering Department, Tufts University, Medford, Massachusetts, United States.
To overcome the high cost of the catalyst in Polymeric Electrolyte Fuel Cells (PEMFC) technology, research is moving towards the reduction in the Pt loading in the electrodes by increasing the electrochemical surface area through a proper catalyst support. To date, the state of the art of catalyst supports is dominated by mesoporous carbon, which shows high activity but suffers from stability issues especially on long term operation. As shown in various works in the literature, titanium nitride (TiN) has a metal-like conductivity with an outstanding chemical stability, making it a possible candidate to replace carbon.

In this contribution, we report about Pt-TiN catalysts support with self-assembled, hierarchical mesoporous nanostructure, grown by Pulsed Laser Deposition. This approach controls the gas dynamics of the nanoclusters-inseminated supersonic jet in order to differentiate the resulting impaction deposition, affecting the growth of the film. We demonstrate that with our technique, morphology can be controlled at the nanoscale to tune the pore size to a mesoporous range, already proven to be effective in fuel cell electrodes. Platinum catalyst is deposited on the tree-like structures either by electrodeposition and atomic layer deposition, tuning the process to achieve ultra-low Pt loading (~0.1 mg cm⁻²).

Electrochemical characterization towards ORR is carried out and shows it is possible to reach good value of the ECSA while controlling the porosity and the morphology of the material down to the nanoscale, reaching good current values. Stability of the scaffold is evaluated according to DOE Accelerated Stress Test (AST) standard protocols, and the ECSA loss is registered to be around only 7% with respect to the 40% goal. The thin films fabricated this way are then transferred by decal method to a Nafion® membrane, to demonstrate their applicability to a fuel cell cathode. Despite the currents are fairly low, further optimization, focused in particular towards a better ionomer contact in the electrode, will improve the cell performance in the future.

Our results show the potential of a PVD based technique that opens the doors of the nanoscale to the fabrication of highly stable electrodes whose morphological and electrochemical properties are easily tuned. This approach holds promises for a high platinum utilization and lower costs for PEMFC technology.

SESSION ET09.06: Poster Session II: Energy Storage
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET09.06.01 Lithiated Metal Oxide Nanosheets Decorated Sulfur Microparticles for High-Performance Lithium-Sulfur Batteries Arnab Ghosh1, 2, Amlan Roy1, Manas R. Panda1, Mega Kar1, Douglas R. MacFarlane3 and Sagar Mitra1
1, 2Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai, India. 3University of Victoria, Victoria, BC, Canada.

Due to its high capacity and high energy density, lithium-sulfur batteries are considered as promising alternative to conventional lithium-ion batteries. Combining lithium and sulfur could yield as much as 2600 Wh/kg. However, some serious issues like dissolution of active sulfur and polysulfides into the electrolyte and their shuffling between the anode and cathode impedes the practical realization of lithium-sulfur batteries. In this work, lithiated metal oxide (LMO) nanosheets (with an average size of 100 nm) were decorated on the surface of sulfur microparticles of 50-80 μm. The LMO decorated sulfur shows lower rate of dissolution of active material sulfur as well as intermediate polysulfides into the ether-based electrolyte, leading to a low self-discharge rate and high cycling stability. The lithiated metal oxide (LMO) facilitates the transport of Li⁺ ion throughout the cathode scaffold, resulting higher utilization of active material. At a current rate of 200 mA/g, the LMO decorated sulfur cathode delivers an initial reversible capacity of 788 mAh/g at second cycle and retains a capacity up to 657 mAh/g (83.4% of initial capacity) after 100 cycles. During the meeting discussion, I will elaborate the synthesis procedure and highlight the electrochemical performance of lithiated metal oxide decorated sulfur microparticles as cathode material in lithium-sulfur batteries.

ET09.06.02 MoSe₂ Anchored with N, P Dual Doped rGO for High-Performance Sodium-Ion Batteries Amlan Roy, Arnab Ghosh, Ajit Kumar and Sagar Mitra; IIT Bombay, Mumbai, India.

Although lithium-ion batteries excel for its sheer performance, sodium ion batteries have attracted more attention to the scientific community because of its low cost-per-storage and their vast abundance in the earth’s crust. There is an immense need for the battery farms to store renewable energy like wind energy and solar energy, therefore, a suitable host material specifically anode is required, which can integrate large size of sodium cation (0.108 nm vs. 0.078 nm of Li⁺) throughout the cycle. Graphite is a commercially available anode material for Li-ion batteries (LIB) but their limited capacity against sodium due to the discrepant interlayer distance between graphite layers because of the radius of Na⁺ ion. Another anode material based on transition metals (TMD) has the unique 2D structure with excellent electronic property and high energy density as compared to graphite. Another most commonly used conversion based anode material MoS₂ for SIB has the interlayer distance of 0.62 nm, but major issues with this material are the utilization of less conductive S after full conversion of MoS₂. MoSe₂, the analogous structure of MoS₂, have large interlayer distance (~ 0.64 nm) with higher conductivity as compared to MoS₂. The major drawbacks with this TMD’s are large volume expansion and layers agglomeration while cycling. Here, we improved cyclic performance as well as the stability of MoSe₂ by incorporating the heteroatom doped reduced graphene oxide (N, P doped rGO) in between the layers of MoSe₂ (denoted as MoSe₂/NPr) through single step method at the high temperature in the inert atmosphere. In MoSe₂/NPr, N and P dual dope boosts the conductivity of rGO sheets which improves the Na⁺ion transportation throughout the active material compare to bulk MoSe₂ electrode. The MoSe₂/NPr composite delivers 337 mA h g⁻¹ at a current rate of 0.1 A g⁻¹ and stable up to 100 cycles whereas MoSe₂ shows 63.2 mA h g⁻¹ after 100 cycles at the same current density. Lastly, Sodium storage mechanism also investigated by several ex-situ physical and microscopic studies.

ET09.06.03 Nickel-Based Sulfide/Phosphide Electrocatalysts for Rechargeable Lithium-Oxygen Batteries Bobae Ju, Hee Jo Song, Gwang-Hee Lee, Hyunseok Yoon and Dong-Wan Kim; Korea University, Seoul, Korea (the Republic of).

Lithium-oxygen batteries are considered as another potential alternative to lithium-ion technology due to their high theoretical energy density of 3505 W h kg⁻¹. However, in spite of their high energy density, lithium-oxygen batteries are still faced with many issues such as sluggish O₂ redox kinetics and inferior Li₂O₂/cathode contact interface on cathode, resulting in high oxygen reduction/evolution reaction (ORR/OER) overpotential, low round-trip efficiencies, short lifetimes, and poor rate capabilities. To overcome these obstacles, it is required to develop an effective electrocatalyst which is capable of inducing a reversible reaction between lithium-ion and O₂ at the cathode. So far, although carbon-based materials or carbon-supported noble metals, metal oxides are investigated as effective electrocatalysts, there still remain several unresolved drawbacks. Thus, it is necessary to develop the new efficient electrocatalyst for lithium-oxygen batteries. Transition metal sulfide/phosphide are known to be used as a hydrogen evolution reaction, oxygen...
evolution reaction electrocatalyst. However, the use of these materials has rarely been addressed as ORR/OER electrocatalysts for lithium-oxygen batteries in detail. In this study, therefore, we develop the nickel-based sulfide/phosphide electrocatalysts (NiS$_2$ and Ni$_3$P) for high-performance lithium-oxygen battery cathodes. Nanostreamed Ni(OH)$_2$ precursors are prepared via hydrothermal process, and then they are transformed to NiS$_2$ and Ni$_3$P via sulfidation/phosphidation process. Their microstructural and electrochemical activities are systematically investigated. Both NiS$_2$ and Ni$_3$P show the long-term cyclic stability over 200 and 150 cycles, respectively, at a current density of 500 mA g$^{-1}$ and a fixed capacity of 1000 mA h g$^{-1}$ in voltage range 2.0-4.8 V. Also, both electrocatalysts exhibit overpotential of 1.6 V even at the 100th cycle.

ET09.06.04

High-Capacity WS$_2$ Nanosheets Derived from WO$_3$ Nanocolloids for Lithium-Ion Battery Anodes

In this study, uniform WS$_2$ nanosheets derived from WO$_3$ nanocolloids are successfully synthesized via underwater electrical wire explosion and subsequent sulfidation process. Firstly, to prepare WO$_3$ nanocolloids, a tungsten wire was exploded in deionized water as a surrounding medium at 320V, and then the obtained nanocolloids were freeze-dried. Secondly, the dried WO$_3$ nanocolloids were placed in an alumina crucible and underwent sulfidation at various temperatures from 400 to 600 °C. Thin uniform WS$_2$ nanosheets were successfully prepared without any residual WO$_3$ phase. These nanosheets exhibited an excellent Li-ion electroactivity, delivering of over 700 mA h g$^{-1}$ at a current density of 50 mA g$^{-1}$.

SESSION ET09.07: Nano and Catalysis

Session Chairs: Xinliang Feng and Tae Yang Son

Wednesday Morning, November 28, 2018

Hynes, Level 3, Room 301

8:15 AM *ET09.07.01

Functional Energy Materials Based on Multifunctional Polymers and Carbon Nanomaterials

In this talk, I will present some of our rational concepts for the design and development of functional conjugated polymers and multidimensional carbon nanomaterials for various energy-related applications, including polymer solar cells containing graphene nanosheets for improving charge transport, fuel cells and metal-air batteries with carbon nanomaterials as multifunctional metal-free catalysts, and supercapacitors with nanotube/graphene hybrid electrodes for energy storage.

8:45 AM *ET09.07.02

Carbon-Rich Electrocatalysts by Design and Nanostructure Engineering

For universal utilization of hydrogen energy, development of high-efficiency, low cost and sustainable energy conversion technologies, especially fuel cells and electrochemical/photocatalytic water splitting devices, is of paramount significance. In order to enhance the energy conversion efficiency of water splitting and fuel cell systems, earth-abundant and stable electrocatalysts are essential for accelerating the sluggish kinetics of hydrogen and oxygen reactions. Up to now, noble metal (e. g., Pt, Ir and Ru)-based materials still remain as the benchmark hydrogen and oxygen electrocatalysts. Unfortunately, high cost and scarce reserve of such noble metals seriously hinder their large-scale applications. Recently, intensive study on active centers and nanostructures of carbon-based materials have greatly advanced the rapid development of new classes of carbon-rich electrocatalysts, featuring defined electronic structures of active sites, for example, metal-free carbons, atomic metal-doped carbons, metal-organic frameworks (MOFs), as well as conjugated porous polymers. To explore earth-abundant and efficient carbon-rich electrocatalysts, it is pivotal to rationally design their active sites, electronic properties and nanostructures that can offer optimal active sites, abundant accessible surface area, and fast mass transport during the electrochemical processes.

In this lecture, we will present our recent efforts on the design and synthesis of carbon-rich nanomaterials as metal-free or noble-metal-free electrocatalysts for hydrogen and oxygen reactions, particularly including template-directed synthesis of metal-free and noble metal-free carbons, 2D metal organic framework nanosheets and Cu surface-mediated fabrication of carbon-rich nanofibers. We will highlight the great potential by tailoring active sites and nanostructures as well as to address the fundamental relationships associated with these carbon-rich electrocatalysts.

9:15 AM ET09.07.03

Cu$_2$BaSn(S$_2$Se$_2$)$_3$-Based Photocathodes for Hydrogen Production

In this study, we develop the nickel-based sulfide/phosphide electrocatalysts (NiS$_2$ and Ni$_3$P) for high-performance lithium-oxygen battery cathodes. Nanostreamed Ni(OH)$_2$ precursors are prepared via hydrothermal process, and then they are transformed to NiS$_2$ and Ni$_3$P via sulfidation/phosphidation process. Their microstructural and electrochemical activities are systematically investigated. Both NiS$_2$ and Ni$_3$P show the long-term cyclic stability over 200 and 150 cycles, respectively, at a current density of 500 mA g$^{-1}$ and a fixed capacity of 1000 mA h g$^{-1}$ in voltage range 2.0-4.8 V. Also, both electrocatalysts exhibit overpotential of 1.6 V even at the 100th cycle.
Photoelectrocatalytic cells (PEC) provide a prospective sustainable and environmentally benign route towards the generation of hydrogen and oxygen from water. Various chalcogenides (Cu(In,Ga)(S,Se)2, CdTe, Cu2ZnSn(S,Se)4) have been adopted as a photocathode for hydrogen evolution but several concerns and material limitation remain regarding scarcity/toxicity (e.g., In and Ga/ Cd) and Cu-Zn anti-site disordering in earth-abundant Cu2ZnSn(S,Se)4 chalcogenides. Recently, the Cu2BaSn(S,Se)4 (CBTSSe) system has attracted attention as an emerging chalcogenide semiconductor with desirable properties for solar energy conversion applications. The current study investigates how the introduction of Se into the parent compound, CBTSSe, influences its electronic and optical properties and overall photoelectrocatalytic performance.

It was found that the photocurrent of vacuum-processed CBTSSe photocathode increases significantly with increasing Se concentration due to larger grain size, reduced grain boundaries, and improved light absorption. In addition, the use of TiO2/CdS protective overlayers creates a desirable band alignment for efficient charge extraction at the hetero-interfaces. This significantly improves the PEC performance of CBTSSe films, yielding a photocurrent of 12 mA/cm² at 0 V/RHE, the highest value reported for CBTSSe-based PEC devices, as well as stable hydrogen evolution for 10+ hours. Ultimately, the study demonstrates that similar level of performance is achieved with high purity CBTSSe films synthesized in solution using inexpensive and commercially available precursors. The present results highlight the potential of CBTSSe materials as efficient, stable and low-cost photocathodes for solar water splitting.

References:

10:30 AM ET09.07.06
Effects of Electrochemical Potential on Aliovalent Dopant Segregation on Perovskite Oxides Through Elastic and Electrostatic Interactions Dongha Kim, Roland Blien and Bilge Yildiz, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

La-based perovskite oxides such as (La,Sr)CoO3 and (La,Sr)MnO3 have been extensively studied as cathodes in solid oxide fuel cells (SOFCs) due to their high oxygen reduction activity and good compatibility with the electrolyte materials. However, cathode performance is still regarded as one of the main bottlenecks in SOFC operation. In the case of perovskite cathodes, the activity for oxygen reduction and incorporation is impeded by the surface segregation of aliovalent dopants such as Sr. Our previous work assessed the role of temperature and oxygen pressure on segregation of dopants on perovskite oxide surfaces. The present study investigates the effect of electrochemical polarization on dopant segregation. This is important for electrochemical energy conversion applications because electrode material is under different electrochemical and oxygen chemical potentials when we run the system in electrolytic or fuel cell modes. In order to resolve the electrochemical potential effect systematically, we applied a potential gradient parallel to the surface of thin films, (La,D)MnO3 (D =
electron-beam evaporation, thus modifying the local bond strength of oxygen in the surface region. Similar doping has proven successful in a previous study on solution-based metal deposition on (La,Sr)CoO$_3$ \cite{6}. Here we demonstrate that this effect is not limited to one material and deposition method, but can be generalized to (La,Sr)MnO$_3$, an intrinsically different type of cathode material, modified using metal evaporation. Using in-situ ambient pressure photoelectron spectroscopy and X-ray absorption spectroscopy, we observe an improved stability under the influence of metals such as Hf and Ti. In combination with scanning probe microscopy and electrochemical performance measurements, we analyze the details of surface doping on structure and stability and explore its limitations. Identifying the nature of the surface phase and the changes due to metal deposition will provide a foundation for targeted approaches to inhibit segregation, facilitating the pathway towards higher long-term stability of doped perovskite oxide surfaces.

Highly active doped ternary oxides, including perovskites, are common functional materials in energy conversion, catalysis, and information processing applications \cite{1}. At elevated temperatures related to synthesis or operation, however, surface segregation of dopant cations is a common problem of state-of-the-art materials, such as the Sr-doped La-based transition metal perovskites (La$_{1-x}$Sr$_x$CoO$_3$), (La$_{1-x}$Sr$_x$FeO$_3$), and (La$_{1-x}$Sr$_x$MnO$_3$), used for example as solid oxide fuel cell cathodes. In these oxides, Sr segregation under operating conditions leads to degradation via the formation of an inactive surface oxide \cite{2,3}, blocking the oxygen reduction reaction \cite{4}. This dopant segregation occurs due to two driving forces: strain and electrostatics \cite{5}. While the size mismatch between Sr and La cations causes strain that can be released via segregation, the electrostatic driving force originates in the attraction of negatively charged dopants to the surface layer enriched in positively charged oxygen vacancies.

Here we relate the segregation in perovskite oxide cathodes to their surface properties, comparing the effects on surface structure and composition of as-grown thin films and metal-doped surfaces. We address the electrostatic driving force of segregation by depositing metals of different reducibility using electron-beam evaporation, thus modifying the local bond strength of oxygen in the surface region. Similar doping has proven successful in a previous study on solution-based metal deposition on (La,Sr)CoO$_3$ \cite{6}. Here we demonstrate that this effect is not limited to one material and deposition method, but can be generalized to (La$_{1-x}$Sr$_x$MnO$_3$, an intrinsically different type of cathode material, modified using metal evaporation. Using in-situ ambient pressure photoelectron spectroscopy and X-ray absorption spectroscopy, we observe an improved stability under the influence of metals such as Hf and Ti. In combination with scanning probe microscopy and electrochemical performance measurements, we analyze the details of surface doping on structure and stability and explore its limitations. Identifying the nature of the surface phase and the changes due to metal deposition will provide a foundation for targeted approaches to inhibit segregation, facilitating the pathway towards higher long-term stability of doped perovskite oxide surfaces.

Support by the Fonds zur Förderung der Wissenschaftlichen Forschung (FWF, project J4099) and the Air Force Office of Scientific Research (AFOSR) is gratefully acknowledged.

\begin{itemize}
\item \cite{1} N. Setter and R. Waser, Acta mater. 48, 151 (2000).
\item \cite{2} S.P. Jiang J. Mater. Sci. 43, 6799 (2008).
\item \cite{3} R. Bertacco, J.P. Contour, A. Barthélémy, and J. Olivier, Surface Science 511, 366–372 (2002).
\item \cite{5} W. Lee, J.W. Han, Y. Chen, Z. Cai, and B. Yildiz, J. Am. Chem. Soc. 135, 7909 (2013).
\item \cite{6} N. Tsvetkov, Q. Lu, L.Sun, E.J. Crumlin, and B. Yildiz, Nat. Mater. 15, 1010 (2016).
\end{itemize}
Although intercalation and conversion battery chemistries have their own advantages in either gravimetric or volumetric energy densities, it is very challenging to achieve both simultaneously. Here, we develop an “intercalation+conversion” hybrid cathode by introducing electrochemically-active Chevrel-phase MoS\textsubscript{2} with fast lithium intercalation reactions and high tap density to hybrid with sulfur to achieve high full-cell gravimetric-and-volumetric-energy-density simultaneously. The mechanically “hard” MoS\textsubscript{2} with fast Li-ion transport, decent capacity contribution and the dramatically enhanced affinity for LiPS after lithium intercalation, is an ideal backbone to immobilize “soft” sulfur species and “unlock” their high gravimetric capacity. This material combination is akin to the relation between primer and TNT in explosives, one fast acting, the other with high gravimetric energy content. The cell using the hybrid cathode paired with Li metal anode delivers very high full-cell gravimetric and volumetric energy densities with good cycling stability, surpassing both Li-S and Li-ion batteries. Our approach demonstrates the potential for such hybrid cathodes for high energy density applications.

**SESSION ET09.08: Li-Sulfur Batteries: Design and Applications**

*Wednesday Afternoon, November 28, 2018*

Hynes, Level 3, Room 301

**3:30 PM ET09.08.03**

**Design of a High Energy Lithium-Sulfur Battery**

Ning Kang\textsuperscript{2}, Li Yang\textsuperscript{1} and Mei Cai\textsuperscript{1}; \textsuperscript{1}General Motors, Warren, Michigan, United States; \textsuperscript{2}Optimal CAE, Plymouth, Michigan, United States.

Li-S batteries have a theoretical energy density of 2510 Wh/kg and 2740 Wh/L, which is one of the most promising candidates for the next generation rechargeable batteries \textsuperscript{1}. Despite the great merits of the Li-S batteries such as high energy density and low cost, challenges, including polysulfide anions redox \textsuperscript{2} and low lithium cycling efficiency, hinder its commercialization. There has been great research effort devoted to the optimization of sulfur electrodes, the formulations of electrolytes as well as the ratios of electrolyte to sulfur. In this talk, we will address the impact of sulfur electrode porosity on the energy density of Li-S battery and the influence of electrolyte/sulfur ratio on the Li-S battery performance.

Based on our preliminary results, the total sulfur concentration [S] in the electrode increases exponentially with the decrease of the porosity. The [S] is 15 M at 70% porosity but increase to 30 M at 50% porosity, which may explain the reason for the 2nd discharge voltage plateau decay of the Li-S cells.

**4:00 PM ET09.08.04**

**A Li-Li\textsubscript{2}S Battery with Improved Discharge Capacity and Cycle Life at Low Electrolyte/Sulfur Ratio**

Chao Shen\textsuperscript{1}, 2, Jianxin Xie\textsuperscript{1}, 3, Mei Zhang\textsuperscript{1}, 4, Petru Andrei\textsuperscript{1, 2}, M. Hendrickson\textsuperscript{1}, E.J. Plichta\textsuperscript{3} and Jim Zheng\textsuperscript{1, 2, 4}; \textsuperscript{1}Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, Florida, United States; \textsuperscript{2}Aero-Propulsion, Mechatronics and Energy Center, Florida State University, Tallahassee, Florida, United States; \textsuperscript{3}Industrial and Manufacturing Engineering, Florida A&M University and Florida State University, Tallahassee, Florida, United States; \textsuperscript{4}High-Performance Materials Institute, Florida State University, Tallahassee, Florida, United States; \textsuperscript{5}Army Power Division, RDER-CCA, Aberdeen Proving Ground, Maryland, United States; \textsuperscript{6}Center for Advanced Power Systems, Florida State University, Tallahassee, Florida, United States.

Rechargeable lithium-sulfur (Li-S) batteries with a theoretical specific energy of 2,500 Wh kg\textsuperscript{-1} are promising candidates to replace Li-ion batteries in many applications.\textsuperscript{1} Even though Li-S batteries possess a high theoretical specific energy, several major technical challenges must be overcome. Many of these challenges are closely related to the formation of soluble lithium polysulfide (LiPS) intermediates. For instance, the irreversible redistribution of LiPS inside the battery leads to degradation of sulfur cathodes and passivation of Li metal anode. The uncontrolled LiPS relocation further leads to severe active material loss and self-discharge behavior of the batteries.

Ultimately, the most critical question for Li-S batteries is whether their high theoretical energy density can be practically delivered. The practical specific energy of Li-S batteries greatly depends on the electrolyte/sulfur (E/S) ratio of the batteries. To increase the energy density of rechargeable Li-S batteries, the E/S ratio should be decreased as much as possible. However, when the E/S ratio is decreased, multiple issues arise that degrade battery performance such as discharge capacity, cycle life, and rate capability. Very importantly, our group has recently found that once the electrolyte becomes saturated with liquid phase high-order LiPS, the solid phase LiPS cannot be further reduced and consequently does not contribute to the capacity of the cells at normal discharge.
discharge rates. Therefore, the solubility of high-order LiPS can potentially lower the achievable specific energy of Li-S batteries to less than 500 Wh kg⁻¹, which becomes much less attractive for their commercialization.

To address the above mentioned challenges associated with conventional Li-S batteries, here we use the solid-state lower-order LiPS, i.e., Li₂S₄, as the cathode active material to construct a new type of Li-Li₂S₄ battery. By replacing the elemental sulfur with solid-state Li₂S₄ as the active cathode material, we avoid any solubility limitation previously encountered in the upper plateau of discharge. We found that in the lower plateau of discharge, the discharge capacity is not limited by the finite solubility of Li₂S₄ and much higher discharge capacity with a Li-Li₂S₄ cell is achieved under a higher sulfur content of 84% and a low E/S ratio of 4.4 ml g⁻¹. Moreover, the cyclability is also enhanced due to the reduced diffusion of high-order LiPS. We believe the reported results of our Li₂S₄ cathode open a new direction of cathode development for high energy density Li-S batteries.


4:15 PM ET09.08.05
Electrochemical Study of Novel MoTe2 Anode Based Lithium-Ion Full Cell Manas R. Panda1, 2, 3, Anish Raj K2, Arnab Ghosh2, Ajit Kumar2, Qiaoliang Bao1 and Sagar Mitra2; 1IITB Monash Research Academy, Mumbai, India; 2Energy Science & Engineering, IIT Bombay, Mumbai, India; 3Material Science and Engineering, Monash University, Melbourne, Victoria, Australia.

Lithium-ion batteries (LIBs) are capable power sources for the convenient power electronic device, electric vehicle and space applications during last few years. However, the specific power density at high rate electrochemical test is still too poor to satisfy the industry needs. Hence, the development of high-performance rechargeable lithium-ion batteries becomes increasingly important. Transition metal dichalcogenides (TMDs) are considered as a promising anode for high-performance lithium-ion batteries due to their availability, low-cost, structural stability and layered structure for easy movement of lithium-ion into the host structure. Among TMDs, layered molybdenum ditelluride (MoTe₂) has the highest interlayer spacing and electronic conductivity which are the two key factors to provide more Li-ion storage property. However, their comprehensive study in lithium batteries is limited. Henceforth in the present study, the polycrystalline MoTe₂ powder has been prepared by a simple solid-state synthesis and characterized using XRD, FESEM, EDS, and HRTEM techniques. The physiochemical characterizations of the material prove the phase purity and crystallinity of the material. When the same material used as a working electrode for lithium battery, it gives a high reversible specific discharge capacity ~280 mA h g⁻¹ in the potential window of 0.1 V–2.8 V at a current density of 1.0 A g⁻¹. The above results stimulated us to construct a lithium-ion full cell using our synthesized anode against commercial LCO cathode for the first time. The electrochemical analysis of the MoTe₂/ LCO full cell shows a competitive discharge capacity of ~140 mA h g⁻¹ at a current density of 500 mA g⁻¹ in the potential range of 1.75-3.75 V. The excellent cyclability of the full cell without capacity fading over 50 cycles was achieved with the coulombic efficiency ~100%. The obtained results positively open up the possibility of scaling up the technology for energy-storage applications.

SYMPOSIUM ET10

Redox Active Materials and Flow Cells for Energy Applications
November 26 - November 28, 2018

Symposium Organizers
Xianfeng Li, Dalian Institute of Chemical Physics
Susan Odom, University of Kentucky
Maria Skyllas-Kazacos, The University of New South Wales
Wei Wang, Pacific Northwest National Laboratory

Symposium Support
Joule | Cell Press
Pacific Northwest National Laboratory

* Invited Paper

SESSION ET10.01: Organic Nonaqueous
Session Chairs: Susan Odom and Wei Wang
Monday Morning, November 26, 2018
Hynes, Level 3, Room 309

8:00 AM ET10.01.01
Complexes with Redox Non-Innocent Ligands for Flow Battery Energy Storage Kathryn Toghill, Ross Hogue and Craig Armstrong; Lancaster University, Lancaster, United Kingdom.

Redox flow batteries (RFBs) are energy storage devices where solutions of electroactive materials are pumped to/from external tanks to the electrode interface for charging/discharging. As energy is stored externally in solution, capacity can be increased independently of the battery power, thus making RFBs promising candidates for grid-scale energy storage. Established RFBs utilise aqueous electrolyte solutions; however the voltage output is limited by the narrow (~1.5 V) electrochemical window of water. Instead, the development of non-aqueous RFBs, which use organic solvents with wide
Redox flow batteries (RFBs) are expected to play a critical role in the grid energy storage by facilitating the widespread adoption of intermittent renewable energy sources like wind and solar. However, the worldwide market penetration of RFB systems is still limited due to technical and economic challenges. A key advantage of transitioning from aqueous to non-aqueous systems is the possibility of achieving higher energy density through the wider windows of electrochemical stability associated with organic solvents. Despite this promise, non-aqueous flow batteries are a nascent concept and, to date, no redox chemistry has proven competitive due to a combination of low solubility and stability for redox couples and a lack of selective membranes/ separators.

When building energy dense RFBs, the solubility of redox couples in the neutral and oxidized/reduced form is critical as active species must remain soluble across all states-of-charge. Notably, recent reports have highlighted redox active compounds that are highly soluble in their neutral state but haltingly soluble in their charged form, frustrating practical implementation. To this end, we have been developing a series of phenothiazine derivatives to achieve a high solubility at their neutral as well as charged states (radical cation and dication) through simple and easy molecular engineering strategies. This presentation will focus on the synthesis of highly soluble radical cations/dications with strategic substituents on phenothiazine, their solubility in non-aqueous solvents, spectroscopic, and electrochemical analysis of the radical cation salts.

References

Recent progress in performance enhancement of high-stability mushroom-derived non-aqueous redox flow batteries.

Acetylpyridinium and cyclopropenium salts have recently been identified as promising catholyte and anolyte candidates for non-aqueous redox flow batteries (RFBs). Most early work on these systems focused on independently cycling the anolytes and catholytes in static electrochemical cells. In this work, we demonstrate the cycling of these molecules together in a laboratory-scale redox flow battery. Cyclic voltammetry experiments indicate that the two molecules should be compatible in a flow battery. However, initial cycling experiments showed a significant capacity fade resulting from a combination of both (1) crossover of these molecules through the membrane and (2) degradation of the anolyte in presence of the catholyte. This presentation will describe our work on the molecular tailoring of both the anolyte/catholyte structures as well as the membrane in order to address both of these challenges.

We recently reported a bio-inspired strategy that leverages biological evolution as a toolkit to address the problem of redox-couple instability that impedes commercialization of NRB.The approach led us to investigate Amavadin, a redox-active vanadium-containing-biometabolite found in mushrooms, for application as a stable NRB-active-material. An analogue of Amavadin, known as vanadium bis-hydroxyiminodiacetate (VBH), has been selected as a molecular scaffold as a new NRB active material due to its exceptional stability, redox reversibility and ease of synthesis. We will present the recent progress in performance enhancement of mushroom-derived NRBs. Fundamental and technical factors underpinning high area-specific resistance and low capacity fade during extended cycling are elucidated using in-situ and ex-situ electrochemical and spectro-electrochemical diagnostic techniques. The results of these analyses will be discussed for various operating conditions and flow cell components.

References:

2) K. Gong, Q. Fang, S. Gu, S. Li and Y. Yan, Energy & Environmental Science, 2015, 8, 3515–3530.
Therefore, it is essential to understand any mechanisms for molecular degradation in these systems. The performance of a quinone flow battery system is the stability of the quinone molecules, which is an important factor of overall battery calendar life. For renewable energy sources such as solar, wind, and hydroelectric to be effectively used in the grid of the future, flexible and scalable energy-storage solutions are necessary to mitigate output fluctuations. For systems that are intended for both domestic and large-scale use, safety and cost must be taken into account as well as energy density and capacity, particularly regarding long-term access to metal resources, which places limits on the lithium-ion-based and vanadium-based RFB development. Here we describe an affordable, safe, and scalable battery system, which uses organic polymers as the charge-storage material in combination with inexpensive dialysis membranes, which separate the anode and the cathode by the retention of the non-metallic, active (macro-molecular) species, and an aqueous sodium chloride solution as the electrolyte. In parallel, printable solid-state polymer batteries were developed allowing a new generation of metal-free batteries (e.g. with application possibilities for smart labels, internet of things or smart clothes).

Aqueous organic redox flow batteries (AORFBs) have emerged as an attractive alternative RFB technology because redox active organic molecule materials are synthetically tunable, sustainable, and potentially low cost. We have previously showed that positively charged viologen molecules are a class of viable anolyte materials for pH neutral anion exchange AORFBs with water soluble ferrocene and TEMPO catholytes. The presentation will cover our recent research efforts in developing sulfonate functionalized viologen molecules as anolyte materials for cation exchange AORFBs with low cost ferrocyanide and halide catholytes. The viologen based cation exchange AORFBs demonstrated outstanding battery performance including capacity retention up to 99.99% per cycle, energy efficiency up to 72% at 60 mA/cm², and a power density up to 120 mW/cm². Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow batteries for large scale and dispatchable renewable energy storage.


Redox flow battery is considered as a powerful technology for grid-scale energy storage because of the excellent scalability and design flexibility to meet the requirements for diverse grid applications. Inorganic-based flow batteries are the state-of-the-arts, but generally suffer from limited energy density and high chemical costs. Instead, redox-active organic compounds have demonstrated encouraging physico-chemical properties and electrochemical performance as attractive alternative materials for flow batteries, suggesting a promising avenue for developing next-generation flow batteries. Despite the current progress of organic flow battery materials, further improvements in energy density and cycle life are still urgently needed to demonstrate their potential for practical grid applications.

In this contribution, we will introduce the newly developed organic diquat herbicide materials for aqueous organic flow batteries. A series of diquat derivatives were designed and evaluated in flow cells to investigate the structural effects on the flow battery-relevant properties including solubility, redox potential, and chemical stability. A combination of electrochemical analysis, density functional theory (DFT) simulations and electron paramagnetic resonance (EPR) studies were performed to reveal important structure-property-activity insights to the diquat family, which also suggests further developmental needs for performance improvement. The diquat-based flow cell was capable of long cycling with low capacity fading.

Among the technologies available for large-scale storage of electrical energy, flow batteries have recently gained considerable interest. They are suitable for longer-duration storage because their energy capacity and power ratings are decoupled. With the aim of minimizing storage costs, researchers have designed electrolytes with synthetic redox-active organic molecules made from inexpensive and earth abundant materials. Quinones in alkaline solution have proved to be promising candidates. Various quinone derivatives have been reported with different substituents. One key criteria of evaluating the performance of a quinone flow battery system is the stability of the quinone molecules, which is an important factor of overall battery calendar life. Therefore, it is essential to understand any mechanisms for molecular degradation in these systems.
Using 2,6-dihydroxyanthraquinone (DHAQ) as the model system, we here present an analysis of the chemical stability and decomposition mechanism of this quinone in alkaline solution during cycling. High resolution LC-MS and advanced NMR techniques were used in elucidating the degradation pathway of DHAQ. This degradation pathway is independent of substituent groups on the anthraquinone, but the rate can depend on the substituent groups. We draw important implications for the rational design of more stable quinone molecules for alkaline flow battery systems.

Development of redox flow batteries (RFBs) for fast growing grid-scale energy storage is supported in part by the Advanced Research Projects Agency (ARPA-E), which funds high risk, high reward transformational research to reduce energy related emissions, reduce imports of energy from foreign sources, improve energy efficiency across all economic sectors, and ensure US technological lead in advanced energy technologies. Exergy flow batteries are attractive for grid energy storage, because the amount of stored energy can be scaled up or down for rated power depending on the customer’s need and also potentially low cost. The cost reduction, which is the major driver in current RFB development, can be achieved by increasing power density (decreasing the stack cost) and using inexpensive active materials and electrolytes (decreasing energy cost). The former approach was funded via GRIDS program and led to development of high power cells based on traditional vanadium chemistry and their transfer to a commercial product. The latter approach was funded via OPEN projects and focused on low cost materials for aqueous RFBs. All-iron RFB uses one of the cheapest and most abundant active materials. However, the cell chemistry includes iron electroplating accompanied by hydrogen evolution side reaction. It required the development of cell rebalancing techniques, which were successfully demonstrated. Iron electroplating was realized on stationary (hybrid RFB) and movable (true RFB) electrodes. Another group of potentially inexpensive active materials is redox active, water soluble organic compounds. Redox potential and solubility of such compounds can be tuned by targeted substitution to increase RFB energy density. Trade-off between these parameters and the active materials cost and membrane crossover will be discussed.

Development of novel ion-selective membranes for RFBs is also being funded via IONICS program. Future ARPA-E program targeting the long duration energy storage will be also discussed.

A redox flow battery (RFB) can store large amounts of energy with relatively high efficiency and low cost. We have shown in the past that membrane-less lead flow batteries can operate with ultra long cycle life, enabled by simple additives. Recently, we reported that riboflavin derivatives, such as alloxazine and the sodium salt of flavin mononucleotide (FMN), can be relatively stable active materials for RFBs. Side reactions, such as the base-catalyzed hydrolysis and dimerization of flavins, however, are problematic. I will discuss on a few effective ways to maintain a highly stable FMN-based RFB enabled by the use of complexing agents. While the cycling performance at high efficiency could be further improved, other challenges regarding redox flow batteries will be discussed.

Considering the great system scalability and operation flexibility, redox flow batteries create their own niche for the large-scale energy storage application. Unlike other rivals like lithium ion and lead-acid batteries, the redox flow battery stores energy in flowable liquid electrolytes other than in immobile solid electrode materials. One of the main obstacles of conventional redox flow batteries is the low energy density (~40 Wh/L) as a result of the limited solubility of redox species in electrolytes, which adds onto system footprint and capital cost. To exploit the high energy density of lithium ion battery in flow systems, various redox-targeting based flow batteries have been developed recently. The energy density of those systems is no longer associated with the concentration of redox molecules but the amount of solid materials stored in the tanks. Thus, by increasing the loading of solid energy storage materials in the tanks, a markedly increased energy density can be achieved without sacrificing the merits of the flow battery. However, most reported redox-targeting reactions resort to multiple redox mediators and rely on lithium ion as the charge balancing and host ion. The potential mismatch of the multi-mediator system would result in undesirable complexity and low voltage efficiency. In addition, the scarcity of lithium relative to other elements may one day be a barrier for large-scale applications. Here, with the single molecule redox targeting reaction, a sodium ion-based redox flow battery with high energy density (up to 259 Wh/L) is developed to address the above issues. With a NASICON-type (Na3V2(PO4)3) both as the anodic and cathodic energy storage materials, an all-organic redox targeting system is demonstrated. In addition, to further reduce the system cost and improve the power capability, aqueous flow systems using open-framework materials are explored for practical applications. In light of operando spectroscopic measurements, the factors dictating the operation of the system at high power are unambiguously disclosed and investigated.

Reference:
The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity generation from intermittent renewable energy sources such as wind and solar. Wide-scale utilization of flow batteries is limited by the cost of redox-active metals such as vanadium or precious metal electrocatalysts. We have developed high performance flow batteries based on the aqueous redox behavior of small organic and organometallic molecules, e.g. [1-8]. These redox active materials can be very inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling both low cost and large-scale energy storage at greatly reduced cost. We have developed new protocols for measuring capacity fade rates and have discovered that the capacity fade rate is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed [7]. We will report the performance of the very few chemistries with long enough calendar life for practical application in stationary storage.


3:30 PM ET10.03.05 Aqueous Redox Flow Battery with Novel Organic Electrolyte Alolika Mukhopadhyay, Jonathan Hamel and Hongli Zhu; Northeastern University, Boston, Massachusetts, United States.

Renevable energy sources such as wind and solar can supply a significant amount of electrical energy in the United States and all over the world. However, only a very efficient and consistent energy storage system can fully utilize the potential of the renewable energy sources because of their sporadic nature. Another critical aspect of electrical power storage is to reduce the power surges and balance overload to improve the robustness and efficency of the grid. The discharge time at peak power is too short for solid-electrode batteries to regulate the grid or solar power output fully. In contrast, flow batteries permit more economical long-duration discharge than solid-electrode batteries by using liquid electrolytes stored outside of the battery. Currently, commercialized flow batteries use precious transition metal ions in acidic solution, which impose challenges with cost, abundance, and environmental impacts. Herein, for the first time, we propose Lignin, the second most abundant nature derived biopolymer surpassed only by cellulose, as an anolyte for the aqueous flow battery. Lignosulfonate, a water-soluble derivative of Lignin, is environmentally benign, non-flammable and very inexpensive as it is the main component in the liquid waste of the chemical pulping and biofuel production process. Lignosulfonate utilizes the redox chemistry of quinone moiety to store energy and undergoes a fast two proton two electron reversible redox reaction. In this work, Lignosulfonate was paired with Br2/Br-, and the full flowcell runs efficiently with high power density. Also, the large and complex molecular structure of lignin considerably reduces the electrolytic crossover, which ensures very high capacity retention over several cycles. The promising results obtained from this economical organic-inorganic redox combination could be a breakthrough in grid-scale energy storage.

3:45 PM ET10.03.06 Two Electron Transfer TPA-Based Catholyte by Molecular Engineering for a Zinc Redox Flow Battery Xiaowei Wang1, Wei Tang2 and Kian Ping Loh3; 1NUS Graduate School of Integrative Science and Engineering, National University of Singapore, Singapore, Singapore; 2Electronic Materials (ELE) Department, Institute of Materials Research and Engineering, A-star, Singapore, Singapore; 3Department of Chemistry, National University of Singapore, Singapore, Singapore.

Redox flow battery (RFB) has been increasingly popular for grid-scale energy storage to meet high power demand due to the high capability and designable power. Nowadays, RFB has moved to the milestone of aqueous systems based on organic redox-active materials, in order to achieve sustainability (organic compounds), safety (aqueous electrolyte) and high energy density (redox with more electron transfer). However, possibly organic molecules are insoluble in water and their redox are irreversible in water. Therefore, apart from water solubility, it is important to engineer organic species with stable redox in aqueous ambiance by decoding the mechanism that attributes to redox instability. Triphenylamine (TPA) readily undergoes anodic oxidation to form TPA radical cation whose stability depends markedly on para-substitution due to radical transfer from N atom to C atom, leading to a dimerization in non-aqueous phase and radical quenching in aqueous system. Herein, we found that para-substitution by methoxy groups generates 4, 4′, 4′-trimethoxytriphenylamine (S3), which exhibits a reversible redox couple of 0.5/0.45 V (vs Ag/AgCl) with one-electron transfer in aqueous system. Moreover, an extremely rapid and reversible two-electron transfer reaction system 4, 4′, 4′-trihydroxytriphenylamine (P3) was also prepared with redox potential at 0.46±0.02 V and 0.53±0.01 V (vs Ag/AgCl), boasting a high kinetic rate constant of 1.1×107 cm2 s−1. The enol/keto redox couple of P3 exhibits fast and reversible kinetics as catholyte when paired with zinc negative electrode in aqueous RFB, yielding a high working voltage of 1.3 V with good cycling behaviour. This work aims to transform irreversible redox-active organic molecules into reversible ones by molecular engineering to broaden more possibility of redox-active materials for organic redox flow battery.

4:00 PM ET10.03.07 Benzothiadiazoles—Energy-Rich Anolyte Materials for Non-Aqueous Redox Flow Batteries Jingjing Zhang1, Jinhua Huang1, Lily A. Robertson2, Rajeev S. Assary1, Ilya A. Shkrob and Lu Zhang1; 1Argonne National Laboratory, Lemont, Illinois, United States; 2University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.
Redox flow batteries (RFBs) are among the most promising electrochemical storage technologies for grid electricity. Aqueous systems, which are currently making significant inroads into the commercial market, often display compromised cell voltages in typical aqueous solutions. Non-aqueous RFBs (NRFBs) enable a wider electrochemical window than the aqueous counterparts, but require high stability of redox-active organic materials (ROMs) in solution when charged. This is truly a difficult requirement to meet since charged ROMs exist as radical ions in solution. 2,1,3-Benzothiadiazoles (BzNSNs) that combine low redox potentials, high electrochemical stability, and excellent chemical accessibility are an exceptional class of analyte materials for NRFBs. Systematic investigations were conducted to elucidate the substitution effects on key properties including redox potentials, and stability of corresponding radical anions, and solubility. In terms of cyclability in RFBs, parasitic reactions that involve the sulfur loss and the oligomer formations were shown to restrict the long-term stability of these radical anions, yet the BzNSN molecules are among the leading energy-dense ROMs in performance found to-day.

4:15 PM ET10.03.08
Electrodes Modified with Redox Mediators for Improved Charge Transfer in Redox Flow Batteries Robert K. Emmett; Chemical Engineering, Clemson University, Clemson, South Carolina, United States.

Electrochemical performance of Iron RFBs was improved through incorporating iron redox mediators into the electrodes. Iron nanoparticles in the electrode create “hotspots” for faradaic charge transfer that reduces losses associated with kinetical, ohmic, and mass transfer resistances. Carbon nanotube electrodes are activated using cyclic voltammetry to initiate interactions between redox electrolytes and iron nanoparticles in the electrode. Modified electrodes experienced 152% increase in power density and a 50% increase in energy density in coin cell configurations. Economic value and ready availability of iron paired with enhanced performance makes iron RFBs a viable option for future RFB research. The highest peak power density reported for all-iron RFBs to the author’s awareness was accomplished at 178 mW cm\(^{-2}\) with iron-modified electrodes.

SESSION ET10.04: Electrode
Session Chairs: Xianfeng Li and Shohji Tsushima
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 309

8:00 AM ET10.04.01
Designing and Fabricating Engineered Electrodes and Flow Fields in Redox Flow Batteries Shohji Tsushima1, Takahiro Suzuki, Hidetoshi Matsumoto2, Kentaro Yaji1, Shintaro Yamasaki1 and Kikuo Fujita1; 1Osaka University, Suita, Japan; 2Tokyo Institute of Technology, Tokyo, Japan.

For further implementation of redox flow batteries for large scale electrical energy storage, high current density operation with less overpotentials is of great importance, leading to reduction of the system cost. In this talk, we will discuss minimizing energy loss by designing and fabricating porous electrodes and flow fields. We will present an approach to explore optimal material properties of carbon fiber electrodes, e.g. porosity, fiber diameter, thickness, etc. 2D or 3D cell simulations indicate renewed material properties to be fabricated to achieve high performance redox flow batteries [1,2]. We will show our recent progress on engineered porous electrodes fabricated for reduced fiber diameter and surface modification with emphasis on characterization of electrode, i.e. reaction kinetics and transport properties [3,4]. We also present an optimization of flow fields in redox flow batteries. We will discuss a potential of topology optimization for designing flow fields to achieve better cell performance with less pressure drop [5].


8:30 AM ET10.04.02
Unveiling the Redox Reaction Between Vanadium Electrolyte and Electrode via Electrochemical Analysis and Computational Method Chan Yong Choi, Hyungjun Noh, Soohyun Kim, Riyl Kim, Juhyuk Lee, Jiyoung Heo and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

To enhance the performance of vanadium redox flow batteries (VRFB) and design the durable electrode, it is quite important to understand the redox reaction mechanism of vanadium electrolyte exactly. In spite of its importance, the redox reaction mechanism between vanadium electrolyte and electrode has not fully been unveiled yet.

Here, we report the electrochemical impedance spectroscopy analysis of symmetric positive and negative single cells to understand the mechanism. The symmetric cell analysis allows the individual investigation of the positive and negative redox reaction in a practical single cell structure without any perturbation from crossover and any use of problematic reference electrode. The comparisons of charge transfer resistance \(R_c\) for heat-treated/un-treated carbon felt electrode and positive/negative symmetric cell elucidated the feature of the redox reactions.

In addition, we demonstrated the hydration structure between the vanadium ion and the water molecule by molecular dynamics (MD) simulation, enabling a deeper understanding on the redox mechanism. We believe that the contribution provides an important insight on electrode material design and can motivate further research on study of vanadium electrolyte and redox reaction mechanism.

8:45 AM ET10.04.03
Conductive Polymer Electrodes for Controlled Energy Conversion Processes in Redox Flow Systems Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Intermittent sunlight necessitates the storage of electricity, ideally in controlled chemical reactions analogous to photosynthesis. Many efforts have focused on the oxidation of water at metal oxide semiconductor surfaces, although light-driven electrochemical reactions at photoelectrodes continue to suffer from
sluggish half reactions. Alternatively, redox couples such as ferrocene and quinones used in redox flow systems offer more control over electrochemical kinetics through synthesis, with rates of electron transfer being several orders of magnitude larger than water splitting for improved storage capacity. This talk will focus on alternative electrodes for charge transfer to anolytes and catholytes in redox flow systems. The ideal electrode material should be low cost, compatible with industrial printing methods, and most critically, have predictable kinetics to maximize energy conversion processes in the context of convection and diffusion processes found in redox flow systems. The challenge with inorganic semiconductors continues to be the ability to control interfacial mid-gap states that undergo band bending when interfaced with the electrolyte. Conductive polymer electrodes offer the possibility to control redox properties through synthesis and processing, if critical structure-property relationships are understood. Importantly, these semiconductors demonstrate a hybrid electronic-ionic conduction mechanism, and thus, have unique electrochemical behaviors relative to classical inorganic semiconductor electrodes. This talk will provide new insights into the mechanism of charge transfer at conductive polymer/liquid interfaces. A mathematical framework will be demonstrated using a modified Marcus-Gerisher model that enables prediction of rate constants from simple film properties. Experimental evaluation of potential-dependent rate constants will be demonstrated. Results will be contextualized in electrochemical devices, with consideration to transport and nanoscale phenomena.

9:00 AM ET10.04.04
Biomass-Derived Electrodes for Vanadium Redox Flow Batteries
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Redox flow batteries (RFBs) offer a promising pathway towards the goal of widespread, commercially viable energy storage capable of meeting increasing energy demands, seamlessly integrating renewable energy sources into the electric grid, and improving overall grid reliability and resilience. A critical shortcoming of the state-of-the-art all-vanadium redox flow battery (VRFB) that must be addressed is the inherently sluggish kinetics of involved vanadium redox couples, which significantly reduces cell efficiency. This has spurred research and development of novel electrode materials that outperform current materials, achieved by surface treatments or other means[31]. In addition to superior electrochemical performance, it is desirable that these surface-modified materials can be produced using low-cost methods that are both environmentally-friendly and sustainable.

In this work, we demonstrate that biomass can be used to obtain potentially lower-cost, sustainable electrodes that also enhance vanadium kinetics through the introduction of surface functionalities imparted by the choice of biomass precursor. Unlike fossil-derived carbon precursors (i.e. polyacrylonitrile), the biochemical constituents of biomass (e.g. proteins, carbohydrates, lipids) enable the manufacturing of electrodes with chemical functionalities that are uncommon in current generation carbon electrode materials, while using a low-value, renewable carbon source. Activated carbon (AC) with a hierarchical porosity and high surface area is produced by first stabilizing the biomass via hydrothermal processing at 200-300 °C for 6 h to obtain hydrochar, which is subsequently converted into AC by thermal activation at 850 °C in an inert environment. Evaluation of the electrochemical properties via ex-situ cyclic voltammetry and impedance spectroscopy of the biomass-derived activated carbons compared to carbon black (Vulcan XC-72) reveals that the ACs are not only conductive and electrochemically active, but also are, in some cases, more active than carbon black. Furthermore, XPS (and other compositional characterization techniques) suggest that increasing N-containing content reduces charge-transfer resistance and improves activity. The revealed correlation between electrode elemental composition and function will aid in the design of next-generation electrode materials.


9:15 AM ET10.04.05
Functional Construction of the Carbon Fiber Electrode Used in the Vanadium Flow Battery
Xinzhuan Fan, Haoran Jiang, Jing Sun and Tianshou Zhao, Department of Mechanical and Aerospace Engineering, HKUST Energy Institute, Hong Kong, Hong Kong.

Vanadium flow battery (VFB) is a liquid energy storage battery based on VO$_2$/VO$^+$ and V$^{3+}$/V$^2$ pairs, whose energy is stored in the electrolyte. Compared with other energy storage technologies, VFB has lots of outstanding advantages such as the long cycle life, large scale, high safety and reliability. So VFB has become one of the preferred technologies for scale energy storage. VFB is composed of the bipolar plate, electrode, separator and electrolyte. As the place where electrode reactions occur in VFB, the electrode is one of the key materials that determines the battery performance and cycle life. In general, The electrode portion near the membrane side often refers to “catalyst layer”, which requires high electrochemical activity and good mass transfer property. While the electrode portion near the bi-polar plate side often names as “conductive layer”, which not only needs good conductivity, but also a large contact area to reduce the contact resistance between the electrode and bipolar plate. The function of the electrodes in different regions is different, so it is unreasonable to use the traditional homogenous electrode directly as the electrode of VFB, which also greatly affects the corresponding battery performance. In response to this problem, we have constructed a functional carbon fiber electrode for VFB. Firstly, the active layer needs an excellent electrochemical activity and preferable pore structure, so we should produced electrop spun fibers with smaller fiber density and fiber diameters between 1 and 4 μm. The smaller density and larger diameter determine that the electrode has a good electrolyte transmission channel; then the electrop spun fibers are pre-oxidized and carbonized to ensure that the electrode has rich oxygen-containing groups, and these oxygen-containing groups can not only ensure the hydrophilicity of electrode, but also provide good electrocatalytic activity. Secondly, the conductive layer needs excellent conductivity and large contact area, so we made electrop spun fibers with larger densities and smaller diameters between 200-800 nm. The larger density and smaller diameter determine the electrode has a larger contact area; then the electrop spun fibers are graphitized to ensure a higher conductivity. Finally, the conductive layer and the catalytic layer are stacked together as a functional composite electrode, and it could be used as a freestanding electrode of VFB. The functional carbon fiber electrode for VFB constructed by the above method not only solves the contradiction between the electrode activity and conductivity of the conventional electrode, but also effectively improves the mass transfer process of electrode, and greatly reduces the contact resistance between the electrode and bipolar plate.

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. T23-601/17-R).

9:30 AM BREAK

SESSION ET10.05: Materials and System I

Session Chair: Wei Wang
deviations from high efficiency operation. Our analysis will not take the form of a set of idealized calculations (though some will be included) but will
situations demanding high power density or current density vs. high energy efficiency and high efficiency vs. an operating mode that allows for occasional
offs in the real world. Furthermore, it is likely to be different for different flow battery types. In this contribution, we will provide some comparative
A general path to high performance flow batteries can be defined in terms of properties of cell components. Unfortunately, this path requires many trade-
in the real world. Furthermore, it is likely to be different for different flow battery types. In this contribution, we will provide some comparative
discussion of the material properties of electrolytes, electrodes and other components of various types of redox flow batteries including aqueous systems
such as all-vanadium RFBs, non-aqueous RFBs and RFBs in which metallic phases are used. Trade-offs in the needed properties will be considered for
situations demanding high power density or current density vs. high energy efficiency and high efficiency vs. an operating mode that allows for occasional
deviations from high efficiency operation. Our analysis will not take the form of a set of idealized calculations (though some will be included) but will

With the increasing penetration of variable renewable generation, energy storage is now becoming one of the hottest topics in the utility industry. The
commercial success of energy storage applications will depend on aligning the cost of a project with the benefits of the technology. Research on materials
and devices has increased cost effectiveness, cycle life and safety of these systems. Besides Li-ion batteries, flywheels, flow batteries, and advanced lead-
carbon batteries are being deployed. The presentation will discuss research on flow batteries as an example of consistent, device driven reduction in cost.
Markets are now gradually taking shape as changes in the regulatory framework result in more equitable valuation of storage benefits. The presentation will
discuss diverse monetized and unmonetized benefit streams, using multi-megawatt applications of a variety of energy storage technologies and highlight
outcomes and objectives of DOE supported energy storage deployments in California, Massachusetts, Washington, Oregon, and Vermont. As major
players begin deploying more storage projects, operators are recognizing their value for ancillary services. In particular, smoothing and ramping of wind
and solar PV are being addressed. Emergency preparedness through storage microgrids is another important development. There are now over 1700 storage
projects close to 200GW capacity listed in the Global Energy Storage Data Base, but with the continuation of the California mandate for 1.3MW of storage
and new emphasis in other states, we can expect an exciting upsurge in storage research and many new projects to be realized.

In this presentation, we will describe appropriate porous electrode theory and boundary conditions to estimate overpotential and current distribution within
physical and electrical properties of a slurry electrode to performance, and will explore effects of cell dimensions and flow operating conditions, such as
mechanisms of electronic conductivity. Finally, we will discuss some of the practical problems we have encountered in scaling-up a slurry iron flow battery
incorporated into a full flow cell and undergone flow cell optimization. An exemplary candidate, when coupled with the benchmark ferri/ferrocyanide
catholyte, delivers an OCV of 1.35 V at 50% SOC and achieves stable cycling over extended periods. References: 1. Zhang, M.; Moore, M.; Watson, J.S.;

Grid-scale battery storage devices have garnered increased attention for their ability to balance the intermittency of ever-expanding renewable energy
deployment and to mediate periods of peak power demand. The redox flow battery has emerged as a viable alternative to traditional solid state batteries.
With decoupled electrode and electrolyte storage vessels, the redox flow battery offers design flexibility where capacity and power may be independently
tuned. The current state-of-the-art flow battery systems utilize vanadium-based electrolytes, however, the high cost of vanadium has hindered wide-scale
deployment. The use of organic molecules as electrolyte materials has emerged as a potentially lower cost alternative. Presented will be our recent
efforts in developing aqueous-soluble phenazine derivatives as anolyte materials for redox flow batteries. The phenazine core structure has undergone
rational design to affect solubility and redox potential via the introduction of varying substituents on the parent molecule. Promising candidates have been
incorporated into a full cell form and undergone flow cell optimization. An exemplary candidate, when coupled with the benchmark ferri/ferrocyanide
catholyte, delivers an OCV of 1.35 V at 50% SOC and achieves stable cycling over extended periods. References: 1. Zhang, M.; Moore, M.; Watson, J.S.;

Slurry electrodes have many advantages in electrochemical devices and systems. They can be used to de-couple power and energy in energy storage, such
as with flow capacitors and with flow batteries involving deposition reactions. Examples are an iron flow battery with a slurry electrode and flow electrochemical capacitors. Slurry electrodes also have high active surface area for enhancing interfacial mass transfer and reaction kinetics making them applicable for recovering metals from dilute streams, for chemical synthesis, and for other electrochemical processes. Slurry electrodes can also be used as sacrificial electrodes and for mechanical regeneration of electrode materials.

In this presentation, we will describe appropriate porous electrode theory and boundary conditions to estimate overpotential and current distribution within
the slurry electrode, and describe predictions of electrode materials utilization, and electrode performance. The analysis will demonstrate the importance of
physical and electrical properties of a slurry electrode to performance, and will explore effects of cell dimensions and flow operating conditions, such as
flow rate. The presentation will address models of the effective electronic conductivity of a slurry electrode, and discuss our perspective about the
mechanisms of electronic conductivity. Finally, we will discuss some of the practical problems we have encountered in scaling-up a slurry iron flow battery
such as flow blockages caused by slurry solidification, and describe means found to mitigate, or at least reduce the effects of these problems.

Acknowledgments
This work is partially supported by the all iron flow battery project (DE-AR0000352) funded from ARPA-E program of Department of Energy (DOE) of the
United States.

Related Publications
N. Hoyt et al., J. Electrochem Soc. 2015, 162, A652.
N. Hoyt et al., Chemical Engineering Science 288.

Extracting Ideal Component Properties from Data for Various Flow Battery Types Thomas A. Zawodzinski1,2, Gabriel Goenaga1, Reed
Wittman1,2 and Jagjit Nanda2; 1University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2Oak Ridge National Laboratory, Oak Ridge,
Tennessee, United States.

A general path to high performance flow batteries can be defined in terms of properties of cell components. Unfortunately, this path requires many trade-
offs in the real world. Furthermore, it is likely to be different for different flow battery types. In this contribution, we will provide some comparative
discussion of the material properties of electrolytes, electrodes and other components of various types of redox flow batteries including aqueous systems
such as all-vanadium RFBs, non-aqueous RFBs and RFBs in which metallic phases are used. Trade-offs in the needed properties will be considered for
situations demanding high power density or current density vs. high energy efficiency and high efficiency vs. an operating mode that allows for occasional
deviations from high efficiency operation. Our analysis will not take the form of a set of idealized calculations (though some will be included) but will
instead consider the actual behavior of operating cells and how various components affect this behavior for the classes of materials mentioned.

Acknowledgements
We would like to gratefully acknowledge the current support of this work by the U.S. Department of Energy, Office of Electricity Delivery and Energy Reliability (Dr. Imre Gyuk).

SESSION ET10.06: Materials and System II
Session Chairs: Aaron Hollas, Vijayakumar Murugesan, Jagjit Nanda and Mike Perry
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 309

1:30 PM *ET10.06.01
New Materials to Accelerate the Commercialization of Redox Flow Batteries Mike L. Perry; UTRC, Glastonbury, Connecticut, United States.

A Redox Flow Battery (RFB) possesses several key advantages that make this technology potentially well suited for large-scale energy-storage applications. This is especially true of applications that require high energy-to-power requirements (i.e., multiple-hour discharge times at rated power) since the energy capacity can be increased by simply adding reactant solution without necessarily requiring (or negatively impacting) the power-delivery components. Despite this inherent scaling-factor advantage relative to conventional battery systems, the initial capital cost of flow batteries has been the major barrier to commercialization of RFB technology. Capital cost targets for grid-scale energy storage are challenging; battery systems for major grid-scale applications must cost less on a normalized basis (i.e., $/kWh) than those currently used for portable or transportation applications. One attractive path to cost reduction is the development of RFB cells with substantially higher power densities than conventional RFB cells, which UTRC has developed and demonstrated in complete all-vanadium RFB Systems, including 0.5-MW/3-MWh systems built by Vionx Energy. The focus of this talk will be on new materials that can potentially enable additional RFB-system cost reductions while maintaining the high performance levels required to be commercially-viable. This includes advanced cell materials (e.g., electrodes, separators/membranes) that can further improve the performance RFB cells, as well advanced RFB active materials. A brief review of the state-of-the-art of each of these major RFB components, along with future targets, will be presented. Some of the latest results developed by UTRC and our partners as part of an ongoing ARPA-E IONICS Program project will also be included. The major goal of this presentation is to help material developers identify potential opportunities to substantially improve RFB technology.

Acknowledgements
The author would like to thank his many flow-battery development colleagues at both UTRC and Vionx Energy. Portions of the work described here was supported by the U.S. Department of Energy (DOE), which includes these projects: ARPA-E’s Flow Batteries—New Designs, Chemistries and Cost Models (DE-AR0000149) and ARPA-E’s IONICS Program (DE-AR0001478), and the Joint Center for Energy Storage Research (JCESR), Office of Science, Basic Energy Sciences (DE-AC02-06CH11357).
Vanadium redox flow batteries (VRFBs) are promising energy storage devices for the integration of renewable energy sources in grid-scale stationary applications, compensating the intermittent nature of renewable energy sources such as, wind and solar. The key advantage of these systems is that power generation and energy storage capacity are decoupled. While the volume of electrolyte and the energy rating can be changed to obtain the required capacity, the size of the cell dictates power rating, providing flexibility and modularity. Despite these benefits, there are problems related to the long-term cycling of these batteries which limit the cycle life and affect the overall performance of the system. One of the main issues associated with the prolonged cycling is faradaic imbalance which is described as the shift of the average oxidation state of the battery from the ideal case of V^{3.5+}. Faradaic imbalance happens as a result of irreversible side reactions (e.g., hydrogen evolution). The side reactions seen in VRFB operation often cause a positive shift to the average oxidation state of the electrolyte, which results in the equilibrium potential of the positive half-cell to increase. This potential shift increases the possibility of exceeding the critical polarization potential at the positive half-cell, consequently leading to CO and CO₂ evolution, and related electrode/bipolar plate corrosion. Despite their importance, the issues of faradaic imbalance and corrosion of electrode/bipolar plate have not been widely recognized in the community. These issues not only restrict the performance of the battery, but also can lead to a significant damage to the flow battery system.

This study investigates the effects of faradaic imbalance and related electrode corrosion on the overall performance of a VRFB by conducting two experimental case studies: one with prepared imbalanced electrolytes with different imbalance ratios, and the other one with corroded positive electrode, prepared through an accelerated electrochemical corrosion process. We will separately demonstrate the performance characteristics of the flow battery for both mentioned cases, using various electrochemical characterization techniques such as charge-discharge cycling, polarization curve, and EIS measurements. Additionally, the correlation between the material characteristics of the cell components and the system performance will be discussed.
Development of electrochemical capacitors focuses today on the improvement of their energy density (or specific energy) and cyclability. The energy density might be improved by capacitance enhancement and operating voltage increase. To some extent, the relation between capacitance and voltage and their impact on the energy output reflects an interfacial character of charge storage mechanisms in capacitors; capacitance is intimately linked with the electrode material whereas the operating voltage is governed by the electrolyte applied. Of course, they cannot be considered separately, since the final performance is always a combination of various factors (e.g., electrode porosity – electrolyte viscosity, wettability, etc.). The electrolyte-related issues create an interesting pathway for investigations aiming at maximum voltage increase and energy density enhancement. Undoubtedly, organic media (based on acetonitrile or propylene carbonate) and ionic liquids are the optimal electrolytic solutions in terms of performance is always a combination of various factors (e.g., electrode porosity – electrolyte viscosity, wettability, etc.). The electrolyte-related issues create an interesting pathway for investigations aiming at maximum voltage increase and energy density enhancement. Although the neutral electrolytes might demonstrate a significant decomposition overpotential once applied to porous carbon electrodes and thus provide the operating voltage up to 1.8 V, the performance of water-based capacitors is still not satisfactory enough for a broad application.

Since the significant disadvantage of water-based solutions is attributed to the solvent decomposition, in our recent study, we decided to decrease the amount of water in aqueous electrolytes to the minimal level. Since the primary study has been done on LiTFSI salt, in our study, we have focused on the conventional inorganic salts, based on the well-known anions like NO₃⁻ or SO₄²⁻.

The paper will discuss the correlation between the pore size distribution of carbon electrodes, electrolyte viscosity, and capacitor performance. Elucidation of the energy/power characteristics as well as cyclability at various temperatures will give a novel insight into ‘water’-based electrolytes.

References:

ET10.06.08
Study of the Interactions at the Electrode/Electrolyte Interface in Concentrated Solutions
Ilona Acznik1, Katarzyna Lot1, Agnieszka Sierczynska1 and Krzysztof Piec2; 1Institute of Non-Ferrous Metals Division in Poznan, Poznan, Poland; 2Poznan University of Technology, Poznan, Poland.

ET10.07.01
Synthesis of Mesoporous β-Ni(OH)₂ Modified CdS Nano-Heterojunction Networks Showing High Visible-Light Photocatalytic H₂ Production Activity
Ioannis Vamvakasakis and Gerasimos S. Armatas; Materials Science and Technology, University of Crete, Heraklion, Greece.

Over the last years, photocatalytic hydrogen production through water splitting has attracted immense attention as a potential method for low-cost conversion of solar energy into chemical fuels. However, despite tremendous efforts on the development of various semiconductor-type catalysts, key challenges of obtaining catalysts with high activity and long-term stability still remain. Recently, the synthesis of highly crystalline mesoporous semiconductors has been the focus in the field of photo- and electrocatalysis. These materials combine the high reactivity of semiconductor nanocrystals (NCs) with mesoporous structure, offering new perspectives in designing novel photocatalysts with improved efficiency and reliability. Unlike to bulk-like microstructures and individual nanoparticles, 3D mesoporous networks of connected NCs can benefit from the large and accessible surface area within the assembled structure and enhanced light-harvesting efficiency arising from multiple scattering of light inside the pores.

Herein, we present the synthesis of 3D mesoporous β-Ni(OH)₂-decorated CdS nanocrystal assemblies (NCAs) and demonstrate their excellent performance for the visible-light photocatalytic H₂ production. XRD, high-resolution TEM, XPS, and N₂ porosimetry characterization results corroborate that the resulting materials consist of a porous network of linked β-Ni(OH)₂ and CdS nanoparticles (ca. 4–5 nm in size) and exhibit large internal surface areas (164–207 m² g⁻¹) and narrow distribution of pore sizes (ca. 6 nm). Catalytic studies along with UV–vis/NIR optical absorption, photoluminescence and electrochemical impedance spectroscopy measurements suggest that the p-type β-Ni(OH)₂ behaves as the oxidation active sites (hole collector), promoting efficient charge transfer and separation across the β-Ni(OH)₂/CdS nano-heterojunctions. Consequently, the Ni-modified CdS NCAs catalyst containing 5 wt % Ni reached an outstanding photocatalytic H₂-evolution rate of 1.4 mmol h⁻¹ with an apparent QY of 72% at 420 nm, while demonstrating good stability for at least 20 h in alkaline (5 M NaOH) ethanol solution (10% v/v). This work not only demonstrates the potential of the present p-n β-Ni(OH)₂/CdS photocatalytic system for sustainable hydrogen production, but also opens up new opportunities for the design and in-depth understanding of noble metal-free photocatalysts for efficient solar-to-chemical energy conversion.

References:
(3) I. Vamvakasakis, K.S. Subrahmanyan, M.G. Kanatzidis, G.S. Armatas, ACS Nano 2015, 9, 4419.
(5) We gratefully acknowledge financial support from the European Union and the Greek Ministry of Education (NSRF) under the ERC Grant Schemes (ERC-09) and the University of Crete–Special Account for Research Funds.
Carbon Nanotube/Carbon Nanofiber Hierarchical Composites with Cobalt-Manganese Layered Double Oxide for High-Performance Flexible Membrane Capacitive Deionization Electrodes Meng Ding, Shaohuan Huang and Hui Ying Yang; Singapore University of Technology and Design, Singapore, Singapore.

In this work, our freestanding carbon nanotube/carbon nanofiber (CNT/CNF) composites are prepared from the electrospun nanofibers. After the electrospinning process, the obtained CNFs were coated with Co-Mn layered double hydroxides (LDHs) as the precursors for CNTs. By pyrolysis, hierarchical CNTs are able to grow on the surface of CNFs. And the LDH precursors were converted to Co-Mn layered double oxides (LDOs). The obtained CNT/CNFs are of benefit from the great electrical conductivity of CNTs and high surface area of CNFs. The Co-Mn LDOs provide good chemical reactivity. The prepared composites exhibited excellent desalination performance in long-term operation. The carbon substrates improve the mechanical strength, good conductivity and cycling stability. The combination of CNT/CNF/LDO composites is a promising method for preparing flexible membrane capacitive deionization electrodes with enhanced desalination performance.

ET10.07.03
Thermochemical CO2-Splitting at High Conversion Efficiency Using Doped-Ferrites Jimmy Rojas, Shang Zhai, Nadia Ahlborg, Kipil Lim, Arunava Majumdar and William Chueh; Stanford University, Stanford, California, United States.

Two-step thermochemical CO2 splitting (TCDS) cycle has been long pursued for CO2 mitigation, but the need for high operating temperature (>1400°C) makes it incompatible with the chemical industry infrastructure. Moreover, low CO2-to-CO conversion makes such cycles far from economical. We designed and synthesized a new class of doped-ferrites and experimentally demonstrated O2 evolution at 1300°C followed by 7 mL-CO evolution per gram of ferrite at 700°C with CO2/CO = 100:1 (balance Ar) in purge gas, indicating high conversion efficiency. The mechanism of oxygen exchange is illustrated through various characterizations: Ex situ x-ray diffraction on quenched samples illustrates the phase transition behavior of doped-ferrites while resonant x-ray diffraction sheds light on cation distribution. Furthermore, Fe is shown to be redox active by ex situ x-ray near edge structure. The high CO2-to-CO conversion efficiency achieved by innovative doped-ferrites opens new opportunities of thermochemical redox chemistry.

ET10.07.04
Polydopamine-Graphene Oxide Derived 3D Nitrogen Doped Graphene@Ni2P for Efficient Oxygen Evolution Electrocatalysis Huizhu Xu and Dianxue Cao; Harbin Engineering University, Harbin, China.

The composite catalysts which has large specific surface areas, growing uniform particles and high activity are particular important for oxygen evolution reaction. Here we report a three dimensional(3D), nitrogen doped graphene aerogel with abundant Ni2P nanoparticles in suit. The approach used dopamine undergoes self-polymerization that can functionalize the graphene surface and produce a large volume of graphene hydrogel (PDA/rGO). The PDA/rGO is immersed in an aqueous solution of nickel acetate, which adsorbs nickel ions. The nitrogen doped graphene aerogel with Ni2P (NGA@Ni2P) is produced by freeze-drying, 1173K carbonization, 623K phosphatization. The NGA@Ni2P has a low applied external potential of 1.68 V at 10 mA cm-2 and the Tafel slope of 78 mV dec-1.

Polydopamine has the properties of reducing, adhesiveness and adsorption of metal ions. Introduce polydopamine in graphene, which not only increased the volume of graphene aerogel, added to the favorable nitrogen species, but the abundant hydroxyl and amino groups in polydopamine, allowing metal ions can be uniformly long on the graphene. In this case, we use polydopamine to adsorb Ni2P nanoparticles. Ni2P nanoparticles have metallic quality, so it has better oxygen evolution performance. The unique 3D structure, high surface areas, favorable nitrogen species and uniformly grown nanoparticles of NGA-Ni2P have good performance as electrode material for oxygen evolution reaction. This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

ET10.07.05
Natural Selection as a Molecular Design Toolkit—Bio-Inspired Flow Battery Active Materials Shyam Pahari1, Tugba Caren Gokoglan2, Andrew Hamel3, Ertan Agar2 and Patrick J. Capelliing4; 1Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts, United States; 2Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Modern electrical grids, especially those comprising energy from intermittent, renewable sources such as wind and solar, require storage. Non-aqueous redox flow batteries (NRFB) are a promising technology to meet this growing need. They have the potential to greatly exceed the energy density of their aqueous counterparts while maintaining key advantages over Li-ion systems. These advantages include decoupled power and energy ratings, thermal stability, benign chemical nature and the capability of long-duration storage (months or even years).

Despite the promise of NRFB, fundamental technical obstacles limit their application:
- active-material instability (low cyclability)
- active-material insolubility (low energy density)
- poor electrochemical performance (low power, low open-circuit voltage)

We will present a bio-inspired approach that addresses each of these problems using a family of molecules that is naturally occurring and produced biologically. These compounds are analogues of Amavadin, which is found in mushrooms of the *Amanita* genus. Biosynthesis of this molecule evolved over countless generations to bind vanadium selectively and with the highest stability ever reported, using a unique tetratdentate, bis-carboxylato-η5-hydroxyimino- binding motif. Ligand-substitution is suppressed, shutting down a major mechanism of decomposition. In this way, natural selection serves as a toolkit for molecular design, elucidating a scaffold for optimized NRFB active materials. We will present a suite of electrochemical and spectroelectrochemical data demonstrating that this Amavadin analogue, which we call VBH, is stable even in the presence of water, is oxygen tolerant and that bulk oxidation and reduction is tightly coupled to formation of the vanadium(v) and vanadium(iv) species, respectively.

Further, we will discuss the key thermodynamic factors used to improve VBH solubility and present recent progress, including stable electrolyte solutions with > 1 M active material and > 2 M supporting electrolyte in organic solvent.

Finally, we will present a detailed computational investigation of the effect of covalent modification of VBH on its open-circuit voltage and its chemical stability in all oxidation states, along with progress on the synthesis of these derivatives.

ET10.07.06
A Stable and Long-Lasting Concentration Cell Based on Reduced Graphene Oxide Membrane and Redox Electrolyte Zhe Wang1, Yi He2,3, Jing Zhang' and Lei Wei1; 1School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore; 2National University of Singapore, Singapore, Singapore; 3School of Defence Science & Technology, Southwest University of Science and Technology, Mianyang, China.
Concentration cell is a promising solution in developing sustainable energy device. Most of the reported concentration cells employed an ion-selective membrane to separate two half-cells with different solution concentration. Thus, the voltage will be generated because of the concentration gradient which follows Nernst equation. However, the concentration gradient is easily decreased due to continuous diffusion, resulting in short lifetime and low output voltage. Although graphene oxide membrane (GOM) has been developed for providing the two-dimensional confinement of electrolytes to reduce the diffusion, the drawback of the reverse electrodialysis still exists. Moreover, GOM is unstable in water and can easily disintegrate, which further limit its application area in energy conversion. Therefore, we demonstrate a long-lasting concentration cell based on natural source, humic acid (HA), and water-stable reduced graphene oxide (RGO) membrane. This cell develops a new mechanism based on redox electrolyte and reaches a high voltage of 0.21 V for more than 210 h, provides a new solution for long-lasting concentration cell.

GO dispersion with a concentration of 0.9 mg/mL is prepared by modified Hummer’s method. 50 mL GO dispersion is transfer into a glass petri dish and then dried under 323 K for 24 h. After that, GO membrane will be formed at the bottom of the dish. Then 10 mL hydriodic acid (HI) is used to reduce the GO membrane to RGO membrane under 373 K for 1 h. Freestanding RGO membrane is obtained by washed with deionized water and dried under 353 K. SEM images show that the thickness of the RGO membrane is ~4 micrometer with a layer distance of 0.36 nm. The FTIR spectroscopy of GO film and RGO film illustrate that the oxygen-containing groups are removed after reduction process. To fabricate concentration cell, the RGO membrane is fixed between two plastic tubes. Thus, one side of RGO membrane is exposed to 20 mL HA solution (1 mg/mL), while the other side is exposed to deionized water, forming a concentration gradient. An open circuit voltage of 0.21 V is measured which last for more than 210 h, indicating its long lifetime. After measuring the cell’s performance with different electrolytes, including KCl, Na2CO3, and HA, we find that good performance can only be achieved using HA as the electrolyte, indicating that this cell is based on redox reaction and the RGO membrane has no ion selectivity. At last, the cyclic voltammogram (CV) curves for HA solution is measured. Experimental result shows that HA is oxidized at the anode side while O2 is reduced to H2O at the cathode side. Thus, the redox reactions on both electrodes are clarified. This work reveals its promising application prospect in energy conversion area.

**ET10.07.07**

The Role of Carbon Surface on the Quinone-Based Molecular Electrochemistry for Energy Applications

Grazia C. Sedenho1, 2, Diana D. Porcellini2, Yan Jing1, Emily Kerr1, Roy G. Gordon1, 2, Frank N. Crespi1, 2 and Michael J. Aziz2, 3

1 São Carlos Institute of Chemistry, University of São Paulo (USP), São Carlos, Brazil; 2School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 3Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States.

Growing global energy demand has motivated interest in new technologies for energy conversion and storage, such as aqueous organic redox flow batteries (AORFB). Quinones are promising as redox-active molecules in AORFB. Many of these molecules are composed entirely by Earth-abundant elements and are nontoxic, nonflammable, and safe for use in energy storage systems. The performance of a quinone-based AORFB depends directly on quinone properties such as redox potential, solubility in water and stability. The number of aromatic rings and the positions and types of side groups affect the redox potential and solubility; this opens a new opportunity in molecular engineering. The electrochemical redox kinetics can also be very important, and the electrode surface can play a decisive role in battery performance. Here, we show that the electrochemical kinetics can be significantly affected by the presence of functional groups on quinone-based molecules. We pay special attention to carbon-based electrodes because they are widely employed in flow batteries due to high electron conductivity and low cost. Based on half-cell experiments, we propose that some candidates for active redox molecules may have their electrochemical kinetics improved or worsened according to the electronegativity of the crystallinity of the carbon electrode. This is shown for alizarin red S, which shows two redox couples that are dependent on the structure of the carbon electrode material. We also evaluated some benzoquinones, which are candidates for the positive electrolyte: commercially available BQDS (1,2-dihydroxybenzene-3,5-disulfonic acid), and several newly-synthesized functionalized benzoquinones. We have observed sluggish kinetics with amorphous carbon and glassy-like carbon electrodes for these molecules. In contrast, graphite electrodes with a high density of plane edges on the surface exhibited a nearly reversible redox response. Based on these results, it is possible to propose new carbon electrode materials based on graphic structures to be used in AORFB.

**ET10.07.08**

Quaternized poly(arylene ether benzonitrile) Membranes for Vanadium Redox Flow Batteries

Eun Joo Park, Sandip Maurya, Yu Seung Kim and Ragachary Mukundan; MPA-11, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Development of membrane separators is important to enhance efficiency and durability of vanadium redox flow batteries (VRFB). Desired properties of the membranes for the VRFB application include (a) selective ion permeability, (b) high conductivity and (c) good chemical and mechanical stability in acidic-oxidative environment. Our approach to satisfy these criteria is synthesizing cation-functionalized nitrile-containing polyamorastics, poly(arylene ether benzonitrile)s, for membrane separators for VRFB. A series of high molecular weight poly(arylene ether benzonitrile)s with pendant quaternary ammonium groups were synthesized via aromatic nucleophile substitution polycondensation. The chemical structures of the polymers were characterized by 1H NMR and FT-IR spectroscopy. The polymers were cast as transparent and flexible membranes, and the ion exchange capacity was varied from 1.8 to 3.1 meq/g. The presence of highly polar nitrile groups, incorporated in the polymer chain enhances the dimensional stability of the membranes. The VRFB single cell performance of the quaternized membranes was measured and compared to standard Nafion membranes. In this presentation, the membrane properties and the electrochemical performance of quaternized poly(arylene ether benzonitrile)s in terms of cycling efficiencies, vanadium permeation and membrane durability will be discussed.

Acknowledgement

This work is fully supported by Laboratory Directed Research & Development, Los Alamos National Laboratory.

**ET10.07.09**

Electrodeposition of Redox Active Layered Double Hydroxides for Energy Applications

Erika Scavetta, Isacco Gualandi and Domenica Tonelli; Univ of Bologna, Bologna, Italy.

At present, there is an increasing demand in the development of new highly efficient and low cost catalytic systems in the field of global energy issues. Layered double hydroxides (LDHs) are lamellar compounds whose structure consists of positively charged brucite-like layers with interlayer anions balancing the positive charge. LDHs containing transition metals are redox active and are very promising materials for several applications due to their versatility, tunable properties, wide range of compositions and low cost. Recently, these compounds are attracting much interest in the area of electrochemistry for applications such as batteries, supercapacitors, sensors, fuel cells and as efficient electrocatalysts for oxygen evolution reaction (OER). For all these applications, the active material must be well adherent to the conductive support, thus guarantying the formation of a mechanically stable coating.

Our group has proposed and optimized an electrochemical approach to coat any kind of conductive supports, of any shape and dimension, with LDH films. The synthesis is based on the electrochemical generation of hydroxides by cathodic reduction of nitrate ions and its optimization was achieved through a detailed study and understanding of the sequence of reactions involved. The features of the deposited LDH (amount, thickness and composition) depend on the applied potential, the length of cathodic pulse and the composition of the electrolytic solution; the adhesion of the coating to the surface can be enhanced through a proper pretreatment of the electrode support (1).
This contribution is aimed to describe the outstanding results obtained by our research group on the performance of LDH films containing Cobalt or Nickel as bivalent cation and Iron and Aluminum as the trivalent one for two important energy applications, i.e., as supercapacitors and as electrocatalysts for OER. In particular, our results show that LDHs containing Co as the bivalent metal can be considered a good candidate for supercapacitors development, especially when the trivalent metal is Fe: actually for Co/Fe LDH the redox process significantly involves also the inner surface of the LDH, giving a peculiar electrochemical behaviour, where the capacitance has both Faradaic and charge separation origin. This guarantees a wider window than the one displayed by the Al based LDH, making that material even more suitable for supercapacitor development.

As to OER electrocatalysts are concerned the best performances in terms of onset potential, current density at a fixed potential and turnover frequency (TOF) were obtained for iron-based LDHs both containing Ni or Co as the bivalent metal. Our results show that the presence of iron is crucial to significantly enhance the OER performances of LDHs.

REFERENCES

ET10.07.10
Investigating the Decomposition of Acylpyridinium Salts as Anolytes in a Redox Flow Battery Anuska Shrestha and Melanie Sanford; University of Michigan, Ann Arbor, Michigan, United States.

Acylpyridinium (AcPy) salts had been identified as promising anolytes for redox flow battery applications. These materials are extremely stable towards bulk electrolysis cycling as well as to cycling in a symmetrical flow cell (with AcPy on both sides of the cell). However, flow cell cycling of AcPy anolytes in combination with cyclopropenium or ferrocenium catholytes results in >50% fade in capacity over 72 h of cycling. A close examination of the solutions after the battery experiment showed that anolyte decomposition in presence of the catholyte is one of the major causes of the capacity fade. 1H NMR spectroscopic analysis of the spent solutions revealed that the anolyte is degrading into two products. The structures of these products as well as the degradation pathways leading to their formation will be described in detail.

ET10.07.11
Effect of Non-Uniformity of Functionalized Surface on the Two-Dimensional Transition Metal Carbides for the Hydrogen Evolution Reaction Fun Seob Sim and Yong-Chae Chung; Division of Materials Science and Engineering, Hanyang University, Seoul, Korea (the Republic of).

The MXenes, which are two-dimensional form of MAX phases, have been introduced as a potential candidate for hydrogen evolution reaction (HER) catalyst due to their high surface area and thermostability. Recent studies of MXenes as an HER catalyst have focused on interaction between hydrogen and the uniformly functionalized surface. However, synthesizing MXenes with uniformly functionalized surface is still remained as a main challenge in this field, which induces gap between experimental and theoretical results. In this study, to evaluate the activity of the HER, the adsorption properties of a hydrogen atom on the non-uniformly functionalized surfaces of Ti2C-based MXene were investigated using density functional theory (DFT). On the surface where fluorine and oxygen functional groups coexist, a hydrogen atom was turned out to be adsorbed on the top of oxygen functional group with slightly larger adsorption energy than the case on the uniformly oxygen functionalized surface. At the vicinity of oxygen vacancy, compared with adsorption energy of a hydrogen atom on the uniformly functionalized surface, much larger adsorption energy was obtained when a hydrogen atom interacted with the exposed transition metal while slightly smaller adsorption energy for the on top site of nearest oxygen from vacancy. The change of adsorption energy of a hydrogen atom affects Gibbs free energy difference of hydrogen, which was derived from ab-initio thermodynamics. Through these results, it could be inferred that non-uniformly functionalized surface condition influenced the HER activity of Ti2C-based MXenes. Therefore, this theoretical study will provide further insight into the design of MXenes as a catalyst for HER.

8:00 AM ET10.08.01
Membranes for Redox Flow Batteries Dirk Henkensmeier1,2, Sangwon Kim3, Ruiyong Chen4 and Yongchai Kwon4; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Energy & Environment Technology, University of Science and Technology, Seoul, Korea (the Republic of); 3KIST Europe, Saarbruecken, Germany; 4Seoultech, Seoul, Korea (the Republic of).

Membranes need to balance a low resistance and a low crossover of redox-active species, and they have to be chemically stable in the electrolyte. For vanadium redox flow batteries, this implies stability against sulfurous acid and stability against VO2+ ions. For many years, the latter criteria strongly limited the choice of membrane materials, and perfluorinated Nafion membranes became the state of the art.[1]

A very recent development is the use of polybenzimidazole membranes, which do not conduct ions in the pure form, but become proton conductive in contact with the sulfurous acid containing electrolyte. The positive charge on the protonated polymer backbone and the narrow size of the electrolyte filled voids between the polymer chains successfully repels vanadium ions in ex-situ permeability measurements. Most interestingly, we observed that both voltage efficiency and coulomb efficiency increase when the membrane thickness decreases. This probably is related to the average charging potential, which increases with the membrane thickness and thus a) enhances migration in the electric field, providing some vanadium ions with the energy to pass the energy barrier which hinders them from entering the membrane, and b) possibly enhances side reactions.

This result suggests that cells with thin PBI films would be very efficient in terms of both voltage and coulomb efficiency; the thinner, the better.[2]

Building up on this finding, we prepared porous Nafion membranes coated with a thin PBI layer[3] and porous PVDF membranes coated with a thin PBI layer.

Another way to improve the voltage efficiency of PBI membranes is to blend them with anion exchange ionomers.[4, 5] By alkyllating PBI membranes, a permanent charge can be fixed on the PBI backbone, turning the membranes into anion exchange membranes with a high IEC.[6] While the alkyl groups may be s starting point for degradation by VO2+, this type of anion exchange membranes can be used well in other types of
flow batteries.[7]

References

8:30 AM *ET10.08.02
Diversity-Oriented Approaches for Pairing Redoxmers and Porous Polymer Membranes for Long-Lasting Redox-Flow Cells
Brett A. Helms; Lawrence Berkeley National Lab, Berkeley, California, United States.

Here I will discuss emerging strategies for realizing multi-hour energy storage using redox-flow batteries. In particular, I will address design considerations and constraints in active materials, electrolytes, and membranes, which together in the flow cell constitute a highly interactive chemical system. With this new perspective, it becomes possible to design each component to respond to the others when the cell is driven to different states of charge. This collective behavior by the system can be used to prevent active-material degradation, capacity loss due to precipitation, and active-material crossover, all of which compromise the efficiency and integrity of the cell long-term. These insights elevate the prospects for macromolecular design to overcome longstanding challenges to flow-cell development, toward reliable solutions for grid stabilization.

9:00 AM ET10.08.03
Graphene Oxide Frameworks with Size-Modulated Pore Structure as Ion-Selective Layers on Hydrocarbon Membranes for Vanadium Redox Flow Batteries
Soohyun Kim, Junghoon Choi and Hee-Tak Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

The laminated structure of graphene oxide (GO) membranes provides exceptional ion separation properties, due to the regular interlayer spacing between laminate layers. However, a larger effective pore size of the laminate immersed in water (~1.1 Å) than the hydrated diameter of vanadium ions (> 6.0 Å) prevents its use in vanadium redox flow battery (VRFB). In this work, we report an ion-selective graphene oxide framework (GOF) whose size is tuned by cross-linking the GO nanosheets. Its effective pore size (~5.9 Å) excludes vanadium ions by size but allows proton conduction. The GOF membrane is employed as a protective layer to address the poor chemical stability of sulfonated poly(arylene ether sulfone) (SPEA) membranes against VO₂⁺ in VRFB. By effectively blocking vanadium ions, the GOF/SPEA membrane exhibits 4.2 times lower vanadium ion permeability and five times longer durability compared with the pristine SPEA membrane. Moreover, the VRFB with the GOF/SPEA membrane achieves an energy efficiency of 89% at 80 mA cm⁻² and a capacity retention of 88% even after 400 cycles, far exceeding Nafion 115, and demonstrating its practical applicability for VRFB.

9:15 AM ET10.08.04
Flexible Ceramic Membranes for Low-Cost Flow Batteries
Gregory Newbloom; Membrion, Inc., Seattle, Washington, United States.

Grid-scale power storage remains one of the largest challenges to wide-spread adoption of clean energy technologies with intermittent energy sources (e.g., solar, wind and tidal). Redox flow batteries (RFB) are an environmentally friendly and scalable technology with the potential to meet this need. However, ion exchange membranes that are crucial to battery performance are expensive, lack chemical stability in a strong oxidizing environment, and/or have poor ion selectivity which leads to electrolyte diffusion across the membrane and performance instability. These issues have limited commercial flow battery manufacturers to two options: 1) perfluorosulfonic acid membranes - which are chemically robust and moderately ion selective but very expensive, or 2) separators - which are cheap but chemically degrade over time and have poor ion selectivity. In this paper, we discuss the design and scale-up of a novel, nanoporous ceramic flow battery membrane that is chemically robust, ion selective and inexpensive enough to reduce the total production cost of commercial flow batteries by > 15%.

In this work, we investigate the use of a primarily inorganic membrane created using sol-gel processing of silicates without calcination or sintering. Silica is an advantageous material for membranes because of its excellent chemical stability and extremely low cost. Furthermore, the gelation process can be utilized to tune the pore size for effective size exclusion of electrolytes (i.e., good ion selectivity). In this study, small angle x-ray scattering (SAXS) was utilized to characterize the membrane pore structure. Model fitting can be utilized to extract the porosity as well as pore shape, size and size distribution. By varying the gelation conditions, average pore radii were found to be in the range of 0.4 – 2 nm. This pore structure is nearly ideal for vanadium-based RFBs given that pores must be able to effectively transport protons (radius of 0.25 nm) but not vanadium ions (radius of 0.5 nm).

Proton conductivity and vanadium permeability were also determined and shown to be identical to an industry standard perfluorosulfonic acid membrane membrane is employed as a protective layer to address the poor chemical stability of sulfonated poly(arylene ether sulfone) (SPEA) membranes against VO₂⁺ in VRFB. By effectively blocking vanadium ions, the GOF/SPEA membrane achieves 4.2 times lower vanadium ion permeability and five times longer durability compared with the pristine SPEA membrane. Moreover, the VRFB with the GOF/SPEA membrane achieves an energy efficiency of 89% at 80 mA cm⁻² and a capacity retention of 88% even after 400 cycles, far exceeding Nafion 115, and demonstrating its practical applicability for VRFB.

9:30 AM ET10.08.05
Scaling the Water Cluster Size of Nafion Membrane and Its Application for High Performance Zn/Br Redox Flow Battery
Riyul Kim, Seongmin Yuk, Juhuyak Lee, Changyong Choi, Soohyun Kim, Ijjun Heo and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

Nafion membranes have been widely used in many electrochemical device as a typical cation exchange membrane. However, it have been considered unsuitable for Zn/Br redox flow batteries (ZBBs) due to its cation selective transport ability. This work shows that pre-hydration treatment can scale the water cluster size of Nafion membrane, which leads to not only high ionic conductivity but also bi-ionic transport property. With increasing the pre-hydration temperature, the water clusters expanded, resulting in the increase of water uptake, ionic conductivity and anion transference number. The bi-ionic transport and low area specific resistance induced by the pre-hydration enable successful operation of ZBB with NRE-212 membrane. As we confirmed that properly pretreated Nafion can be used in ZBB, we present a void-free 16 μm-thick Nafion-filled porous membrane for ZBBs to lessen the cost issue of Nafion. As a result, the ZBB based on the Nafion/PP membrane exhibits a higher energy efficiency, demonstrating that ion exchange membrane can outperform the conventional porous membrane by reducing the membrane thickness with inexpensive porous substrate.

9:45 AM ET10.08.06
Mechanically Robust Poly(Ethylene Oxide) Sodium-Ion Conducting Membranes for Redox Flow Batteries

Guang Yang1, Rose Ruther2, Michelle Lehmann3, Ethan C. Steel1, Zhijiang Tang1, Chelsey Chen1, Frank Delsnick1, Thomas A. Zawodzinski1, Tomonori Saito1 and Jagjit Nanda2
1Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Energy and Transportation Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The advancement of sodium-based energy storage systems relies on the development of high performance sodium ion conducting electrolytes and membranes, which must meet several stringent requirements including high ionic conductivity, chemical and electrochemical stability over a wide voltage window, selectivity to minimize crossover, mechanical robustness, and processability. Poly(ethylene oxide) (PEO) based polymer is one of the most commonly used polymer electrolytes. However, simultaneously improving the mechanical properties and ionic conductivity is the major challenge in PEO based membrane or any polymer electrolytes. We will present two strategies to develop sodium-ion conducting membranes that address this challenge. A crosslinked PEO based electrolyte was developed that demonstrates high ionic conductivity, as well as excellent mechanical and thermal stability. The role of ethylene oxide (EO) complexation with sodium triflate (NaTf) salt and its effect on polymer segmental dynamics and ionic conductivity is elucidated with and without tetraethylene glycol dimethyl ether (TEGDME) as a plasticizer. Ionic conductivities up to 2.0 x 10^{-4} S/cm at 20 °C and 7.1 x 10^{-4} S/cm at 70 °C were achieved for the plasticized membrane, four orders of magnitude greater than that of the non-plasticized membrane. The storage modulus of the membrane was maintained at ~1 MPa from -20 °C to 180 °C even with the addition of plasticizer.

The second method involves the use of TEGDME to plasticize linear high molecular weight PEO based membranes to increase the ionic conductivity. The conductivity of plasticized PEO membranes containing NaTf is about 2 orders of magnitude higher compared to non-plasticized PEO membranes. Vibrational spectroscopy and differential scanning calorimetry (DSC) describe the coordination chemistry in these materials and elucidate the mechanisms behind the increased conductivity. The mechanical properties of the plasticized membranes is significantly improved through the reinforcement with carboxymethyl cellulose (CMC). Importantly, all the materials selected for the membrane (PEO, NaTFS, TEGDME, and CMC) are highly stable at very negative voltages (near Na/Na+), and therefore compatible with sodium metal anodes or strongly reducing redox couples. Such a membrane can enable high voltage, high energy density batteries for grid storage applications.

Acknowledgment
This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity Delivery and Reliability, Department of Energy. The spectroscopy effort is supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

10:00 AM BREAK

10:30 AM *ET10.09.01
Redox Processes and Design Strategies for High-Energy-Density Redox-Flow Batteries

Yi-Chun Lu; Chinese University of Hong Kong, Shatin, China.

Energy storage system is a critical enabling factor for deploying unstable and intermittent renewable power sources such as solar and wind power sources. Redox flow batteries (RFBs) offer unique advantages of high efficiency, low cost, scalability and rapid response for grid energy storage. One of the most critical bottlenecks of RFBs is their low energy density, which is strongly related to the cell voltage and the solubility of the active materials. In this presentation, we will discuss strategies to improve the energy density of aqueous and nonaqueous RFBs and spectroscopic investigation on the redox processes involved in these RFB systems. Design strategies including redox complexing agent (e.g. lithium iodide, lithium bromide), semi-solid approach (e.g. sulfur/C and organic molecules) and highly-concentrated organic molecules (e.g. ferrocene-based) will be discussed. The influence of flow rate and current density on the electrochemical performance under continuous/intermittent flow modes as well as the synergistic interplay between solvent and redox-active materials in solid and liquid phases will be discussed.

11:00 AM *ET10.09.02
Zinc Based Flow Battery for Stationary Energy Storage

Hongzhang Zhang and Xianfeng Li; Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, China.

Zn2+/Zn redox couple attracts more and more attention in flow battery due to its characteristics of high solubility, electrochemical reversibility and environmental friendly. Moreover, in aqueous electrolyte, a negative potential together with the abundant reverse in earth crust enable zinc-based flow battery with low cost and high energy density. Until now, many zinc based flow battery systems such as zinc-bromine2, zinc-nickle and zinc-iron2,3 etc. have been investigated, which have very promising prospect to be used in power grid, large energy storage, emergency power supply and other fields. Among them, zinc-bromine is one of the most successfully example of zinc based flow battery system, while zinc nickel and zinc iron systems have obtained tremendous developments recently. Many new zinc based systems such as zinc iodine have been proposed and demonstrated great advantages in some aspects such as energy density. However, secondary batteries that use zinc electrodes typically exhibit short lifetimes, because of problems with undesirable zinc morphology especially zinc dendrites, that form during charge. Hence, the challenge is to deposit a compact, uniform and free of dendrite layer that ensure a long cycle secondary negative electrode. Therefore, in this presentation we will introduce the research and development status of zinc based flow batteries at DICP.

11:30 AM ET10.09.03
Highly Efficient Monolithically Integrated Solar Flow Battery

Wenjie Li1, Hui-Chun Fu2, Yuzhou Zhao1, J-Hau He2 and Song Jin1
1University of Wisconsin-Madison, Madison, Wisconsin, United States; 2Electrical and Mathematical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The practical utilization of solar energy demands not only efficient energy conversion but also inexpensive large scale energy storage. Building on mature regenerative solar cells and emerging electrochemical redox flow batteries (RFBs), more efficient, scalable, compact and cost-effective hybrid energy systems are being developed. The core of our strategy is the monolithic integration of a redox flow battery with a coplanar plate solar cell. This hybrid device is able to achieve high efficiency due to the extended active material volume, where the electrodes are directly coated on the absorber layer of the solar cell. Consequently, the performance is improved, the material yield is optimized, and the overall device is simplified. In this presentation, we will introduce the key results achieved so far, such as the improved efficiency and stability of the device.
conversion and storage devices could be realized. Here we present an integrated solar energy conversion and electrochemical storage device by integrating regenerative solar cells in aqueous electrolytes with RFBs using the same pair of organic redox couples. In such an integrated solar flow battery (SFB) device, solar energy is absorbed by semiconductor electrodes and photoexcited carriers are collected at the semiconductor-liquid electrolyte interface and used to convert the redox couples in the RFB to fully charge up the battery (i.e. store the solar energy into the redox couples). When electricity is needed, the charged up redox couples will be discharged on the surface of carbon felt electrodes as one would do in the discharge of a RFB to generate the electricity. We demonstrated that such an integrated SFB device can be charged under solar illumination without external electric bias and deliver a high discharging capacity comparable with state of the art RFBs over many cycles. This integrated device can utilize solar energy efficiently — an overall direct solar-to-output electricity efficiency (SOEE) of 14% has been achieved with advanced performance optimization. With comprehensive mechanism study and deeper understanding of the operation principles of SFBs, we also propose a set of design principles for highly efficient integrated SFB devices.

The water-energy nexus presents new opportunities for redox flow systems to make a large impact on our energy economy. Current efforts to make redox flow batteries commercially viable have traditionally focused on lowering capital costs; an alternative strategy is to increase the revenues associated with battery operation by creating a valuable product like desalinated water. By placing one or more intervening water chambers, bounded by ion-selective membranes, between the anode and cathode of a traditional flow battery, the system becomes capable of simultaneous water desalination and electrical energy storage. A symmetric flow cell that uses the same redox couple at both electrodes is no longer able to store electrical energy, but enables lowered specific energy consumption for salt removal, as well as greatly lowered reactant capital costs relative to the storage mode. Certain cell designs can additionally be switched reversibly between both operating modes, thereby allowing the stack to be utilized even when a conventional flow battery would normally be idled. We present several examples of devices that use flow battery architectures to perform redox water desalination for energy storage applications as well as nontraditional novel applications with large energy savings.

1:45 AM ET10.09.04
Redox Desalination Using Flow Battery Architectures Eugene Beh, Michael Benedict, Divyaraj Desai, Elif Karatay, David Johnson and Jessy Rivest; Palo Alto Research Center, Palo Alto, California, United States.

The water-energy nexus presents new opportunities for redox flow systems to make a large impact on our energy economy. Current efforts to make redox flow batteries commercially viable have traditionally focused on lowering capital costs; an alternative strategy is to increase the revenues associated with battery operation by creating a valuable product like desalinated water. By placing one or more intervening water chambers, bounded by ion-selective membranes, between the anode and cathode of a traditional flow battery, the system becomes capable of simultaneous water desalination and electrical energy storage. A symmetric flow cell that uses the same redox couple at both electrodes is no longer able to store electrical energy, but enables lowered specific energy consumption for salt removal, as well as greatly lowered reactant capital costs relative to the storage mode. Certain cell designs can additionally be switched reversibly between both operating modes, thereby allowing the stack to be utilized even when a conventional flow battery would normally be idled. We present several examples of devices that use flow battery architectures to perform redox water desalination for energy storage applications as well as nontraditional novel applications with large energy savings.

SESSION ET10.10: New Technologies II
Session Chairs: Xianfeng Li, Yi-Chun Lu and Wei Wang
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 309

1:30 PM ET10.10.01

Hydrogen generation from water splitting is reaching a tipping point, with large scale electrolyzer systems being deployed for fueling and energy applications, and a growing number of projects under development. Still, the overall lifecycle cost makes widespread application challenging, due to both capital cost and operating cost of electricity. The oxygen evolution electrode is a significant driver in both capex and opex, since the high voltage and overpotential result in limited material choices for stable performance. Proton OnSite and Pacific Northwest National Laboratory have been developing a versatile electrochemical device capable of serving roles in large scale energy capture and conversion as well as fuel production. The concept involves replacing the high overpotential oxygen evolution electrode in a water electrolyzer cell with a more facile and lower voltage redox couple, enabling the system to operate at significantly higher efficiency. The system can operate in two modes: 1) as a pseudo-electrolyzer, it produces renewable H2 gas for industrial or energy applications including vehicle fueling and 2) as a hydrogen-redox flow cell, it is capable of high efficiency and low-cost grid scale energy storage. This talk will focus on the progress realized in this project, including materials and electrolyte development, incorporation of 30 bar hydrogen pressure into the system, and synergies and learnings that are applicable to water electrolysis.

2:00 PM ET10.10.02
Photocatalytic Oxidation of Formic Acid Using BiFeO3—Stability and Reproducibility Wegdan Ramadan1, Ralf Dillert2 and Detlef Bahnemann2, 3; 1Physics Department-Faculty of Science, Alexandria University, Alexandria, Egypt; 2Institut für Technische Chemie, Leibniz Universität Hannover, Hannover, Germany; 3Laboratory “Photoactive Nanocomposite Materials”, Saint Petersburg State University, Saint Petersburg, Russian Federation.

Iron based compounds are tempting; they are cost effective and introduce interesting physical properties like magnetism but could have stability issues as well. In this context, BiFeO3 (BFO) is a multiferroic that has a band gap ~2.3 eV enabling it to absorb light in the visible region. The conduction and valence band are located at 0.46 eV and 2.68 eV with respect to NHE making it a good candidate for water oxidation and oxidation of other organic pollutants like Formic acid (HCOOH). Under solar illumination and in the presence of BFO, as photocatalyst, redox reaction should take place such that holes created in the VB oxidize HCOOH to CO2 and protons (H+) and electrons in the CB should reduce H+ into H2. The CB position is more positive than the value required for H2 reduction. Mass spectrometer showed the formation of CO2 and less H2. Hence, what is the fate of the electrons if they are not consumed in protons reduction? To further elucidate this point, XRD and XPS were carried out for the photocatalyst before and after reaction with Formic acid. XRD of BFO after reaction with Formic acid, showed bleaching of most impurity peaks, Fe3O4, Bi2Fe4O9 and Bi25FeO40 and relief of the strained crystal lattice. The removal of the impurities under illumination is essentially a photocatalytic process requiring the presence of an electron donor like HCOOH as concluded from results obtained in absence of HCOOH. XPS showed the d/doublets of Bi 4f5/2 and 4f7/2 with 5.20 eV separation, indicating the formation of Bi-O bonds. On the other hand, Fe doublets, 2p1/2, and 2p3/2, could not be fitted to a single oxidation state but rather to mixture of Fe2+ and Fe3+ such that 14% of Fe is Fe2+ and 86% is Fe3+. These contents change such that Fe2+ increases to 36% and Fe3+ decreases 64% after reaction. To maintain charge balance in the system, electrons are transferred to H2O to form HO2. To further elucidate the effect of the observed changes of the BFO on its photocatalytic performance, BFO powder obtained after a first photocatalytic run was employed in a second run performed under the same experimental conditions.

The ratio between CO2 evolved in the second run to the first experimental run was found to be 0.87. The respective ratio for the amounts of H2 was calculated to be 0.46. This decrease in the evolved CO2 by 13% indicates a decrease of the activity of the photocatalyst. These results indicate that under the adopted experimental conditions BFO deviates from the standard definition of a photocatalyst and suffers some changes during the photocatalytic reaction. It is essential to ensure stability of photocatalyst, especially iron-based ones, if we are seeking long term stability and reproducibility.
Flow battery technologies (e.g., vanadium flow battery, iron-chromium, and zinc-bromide flow batteries) are being commercialized into the application of stationary electrical energy storage. However, the electrolyte materials of vanadium, chromium, and bromine are considered costly and more toxic. H_{2}/Fe \text{ (HyFe) flow battery has captured the great attention of the scientific community because it takes the advantages of low cost and environmental-friendly materials, high energy efficiency of > 90%, fast kinetics of hydrogen evolution/oxidation and facile Fe^{2+}/Fe^{3+} redox pair. However, the main problem of low power density of HyFe flow battery impedes the implementation of this battery technology. Our study demonstrates that the electronic conductivity of electrolyte solution, complex ligands of iron ions and iron ions diffusion kinetics are the dominant factors to affect the power densities of HyFe flow battery. The temperature effects on electronic conductivities of electrolyte solution, iron ion diffusion kinetics and electrochemical performance of HyFe flow battery are also investigated. The maximum power density of 375 mW/cm² was achieved in our HyFe flow battery.

Redox flow batteries are one of the most suitable electrochemical systems for large scale energy storage. The All Vanadium Redox Flow Battery (VRFB) technology invented at UNSW is being utilised on a global scale for stationary applications, but its low energy density is currently limiting its use in mobile systems. One promising approach to increasing energy density is the use of the oxygen reduction process for the positive half-cell. This forms the basis for the new Vanadium Oxygen Fuel Cell (VOFC) which eliminates the need for the positive vanadium electrolyte and removes the constraints associated with solubility limits of V(V) at elevated temperatures. Increasing the vanadium concentration from 2M to 4M for the negative electrolyte and the use of the oxygen reduction process for the positive half-cell can theoretically quadruple the specific energy density of the current VRFB from 25 Wh/kg to 100 Wh/kg allowing potential application in new transportation systems.

For long-term operation of the VOFC an important aspect is the regeneration of vanadium (II). The regeneration of V(II) can be performed externally to the cell, for example, at a recharging station for electric vehicles. In the present development project of the VOFC at UNSW, a separate regeneration cell has been designed and used to regenerate the vanadium (II) electrolyte. It is critical that the supporting electrolyte for the VOFC be carefully selected so as to avoid the potential generation of hazardous gas at the positive electrode during re-charge. This limits the use of halide-based supporting electrolytes such as HCl that could potentially be used to enhance vanadium ion solubility. The use of electrolyte stabilising agents has therefore been evaluated to allow the use of vanadium electrolytes with concentrations greater than 3 M at elevated temperature. Alternate non-noble metal electrocatalysts have also been studied to improve the performance of the oxygen reduction process without using platinum based catalysts that could potentially catalyse the evolution of hydrogen in the negative half-cell electrolyte. The design of single and multi-cell VOFC systems will be described together with details on the fabrication of membrane electrode assemblies that are utilised in this hybrid system.

Redox flow batteries (RFBs) are promising energy devices for grid-level applications due to their extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental due to the extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities.
collectors.

Recently, alkali metal and ammonium thiocyanates (SCN-) aqueous solutions have been successfully applied as electrolytes to ECs. The comparative study on the effect of salt concentrations depending on the type of current collectors has been presented. The cell operating with gold current collectors revealed a limited effect on charge propagation resulting from its high conductivity.

In this work, the addition of various nanoparticles (Au, Ag, carbon nanotubes) at extremely low concentrations to potassium thiocyanate solution (KSCN) is presented as an attractive way for electrolyte modification. Our previous work has shown that especially gold has a positive influence on SCN- based systems performance – better charge propagation, fast redox response and lower resistance has been observed. Furthermore, together with Au nanoparticles, these species could form complexes such as [Au(SCN)2]- and [Au(SCN)4]- and the redox equilibrium Au(I)/Au(III) might be established in the solution.

The investigated ECs were manufactured with 7 mol/L KSCN solution with gold nanoparticles and carbon electrodes made of high surface area carbon black, providing a suitable micro-to-meso pore volume ratio. The electrolyte solution displayed very high conductivity (372 mS/cm) and neutral pH (7.5). The systems with potassium thiocyanate and gold nanoparticles were characterized by a high operational voltage (1.6 V) and high capacitance, namely 168 F/g (@1 A/g). Moreover, high energy density has been retained at the whole range of applied current densities: 15 Wh/kg (@1 A/g) and 13.7 Wh/kg (@20 A/g).

The electrochemical characterization will be supported by several operando techniques - Raman spectroscopy, Quartz Crystal Microbalance and Scanning Electrochemical Microscopy, in order to provide a full picture of the interfacial phenomena.

4:15 PM ET10.10.07
Functionalised Graphene as High Surface Area ORR Electrodes in PEM Fuel Cells Theo Suter1, Noelia Rubio2, Mike Whiteley1, Milo Shaffer2 and Daniel J. Brett2; 1Department of Chemical Engineering, Electrochemical Innovation Laboratory, University College London, London, United Kingdom; 2Department of Chemistry, Imperial College London, London, United Kingdom.

Fuel cells are one of the keystones of the hydrogen economy but costs remain high, partly due to the high cost of the catalyst system.1, 2 Typically commercial electrodes are still based on platinum on a carbon black support.1, 2 Significant research has focused on developing new catalyst systems, with costs and scalability being two of the most important factors for success. Graphene has great potential as an catalyst support material due to its potential to be high surface area and carbon corrosion resistance replacement for carbon black.3, 4 Functionalising this graphene enables reduced platinum nanoparticle size and increased activity, thus reducing cost without comprising power output. However achieving this without damage and in a scalable manner is an active research area.

In this work we explore a scalable synthesis of functionalised graphenes and their use as high surface area ORR catalyst in fuel cells. The graphene was synthesised by a scalable method utilising layer charging with sodium naphthalene to allow exfoliation, allowing functionalisation of the resultant material. By reacting the charged graphene with particular functional groups/polymers we were able to develop a highly active graphene based electrode. This was characterised via SEM, TEM and XPS, as well as being tested for ORR activity in RDE and fuel cell systems showing improved performance.


**SYMPOSIUM ET11**

Emerging Materials and Device Concepts for Flexible, Low-Cost Photovoltaic Technologies
November 26 - November 30, 2018

**Symposium Organizers**
Lan Fu, Australian National University
Alexander Sprafke, Halle-Wittenburg University
Rao Tatavarti, MicroLink Devices, Inc.
Lin Zhou, Nanjing University

**Symposium Support**
IQE plc

* Invited Paper
8:00 AM ET11.01.01
Highly Flexible Perovskite Solar Cells with Low Cost Electrodes and Charge Selective Materials Peng Li and Zijian Zheng; The Hong Kong Polytechnic University, Hong Kong, China.

The organic-inorganic halide perovskite solar cells (PSCs) have witnessed efficiency soar from initial 3.8% to current-record 22.7% in the past less than ten years, representing one of the most promising active photo absorbent candidates to reduce the materials cost in the photovoltaic devices. It is however often overlooked that the majority of the materials cost in the PSCs come from transparent electrodes (e.g. ITO, FTO, etc), charge-selective carriers (e.g. PTAA, Spiro-MeOTAD) or metal contacts (e.g. Au, Ag), instead of the perovskite photo absorber itself. On the other hand, sufficiently thin perovskite film spontaneously inspires tremendous research interests and efforts in flexible application scenario in the emerging era of wearable electronics, imposing foldable, stretchable and even squeezeable photovoltaic devices in huge demand.

To tackle this, we propose a perovskite solar cell system employing ultrathin substrate, low-cost copper front and back electrodes as well as inexpensive metal oxides charge-selective materials to enable highly flexible PSCs. All the materials can either be prepared with affordable synthesis cost on avalanche quantity basis or readily obtained in the commercial market. To be more specific, Cu mesh hybridized with doped PH1000 serving as bottom transparent electrode replaces costly transparent conductive oxides while top Cu electrode further reduces metal cost. N-doped graphene as the hole transporting layer eliminates the use of expensive polymer PTAA yet maintains comparable high open-circuit voltage. Inorganic ZrO has partially and in principle could completely fulfill the role of fullerene type electron transporting material of PCBM. As such, the whole PSC system embraces dramatically reduced material cost in corresponding components by several order of magnitudes. More interestingly, the ultrathin polymeric substrate endows the perovskite solar cells with terrific flexibility and accordingly robust application potentials.

8:45 AM ET11.01.02
Flexible Crystalline Silicon Photovoltaics with Vertically Aligned Microwires Inchan Hwang, Han-Don Um and Kwanyong Seo; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Flexible photovoltaics (FPVs) are one of the most promising research fields in the solar energy industry because they can be utilized as a continuous power source for wearable and portable electronic devices. Thin crystalline silicon (c-Si) has attracted much attention as a potential means for FPVs because of its excellent flexibility while retaining the advantages of c-Si FPVs of high efficiency and stability. For highly efficient thin c-Si FPVs, it is important to maximize light absorption while maintaining the flexibility characteristics. In general, the conventional c-Si photovoltaics have increased light absorption by applying surface structures. However, the surface structures without consideration of the flexibility would limit the flexibility of the FPVs because induced stress during bending cannot be uniformly dispersed. In this study, vertically aligned microwires (MWs) on a 50 μm-thick thin c-Si substrate are designed for novel FPVs. Increasing the length of the MWs enhances the optical properties of the thin c-Si without affecting its flexibility. To maximize the efficiency of the thin c-Si FPVs with MWs, tapered MWs and a localized back-contact structure are devised. This device shows a maximum efficiency of 18.9%. In addition, the proposed thin c-Si FPV with MWs shows high stability without any change in efficiency, even with 1000 bending cycles with a bending radius of 12 mm. Thus, we successfully demonstrate battery-free flexible electronic devices integrated with our thin c-Si FPVs with MWs.

9:00 AM ET11.01.03
BIPV—A Bad Idea or Tomorrow's Mainstream Application? Sarah R. Kurtz; University of California, Merced, Merced, California, United States.

In 1994, PowerLight introduced a building-integrated photovoltaic (BIPV) product, touting it as saving money (avoiding the cost of installing a conventional roof) while introducing PV into an attractive roof. At the time it was introduced, the mainstream opinion was that the future of PV would be building integrated and that utility-scale applications were a non starter. Today, utility-scale PV accounts for more than half of the world PV installations and BIPV is a niche market (with most rooftop systems being “building applied” rather than “building integrated.”) Was BIPV a bad idea?, or was BIPV an idea whose time had/has not come? Many things have changed since 1994; could BIPV be poised to become a mainstream application? Tesla and other companies are introducing BIPV products today. Will they be more successful? The talk will review many things that have changed (including power electronics, products with lower temperature coefficients, demonstration of PV as an accepted technology so that it’s not such a risk to builders, the value of generating solar electricity near load centers, etc.), suggesting that there may be a new opportunity for BIPV. Then, the talk will review how a shift back to a goal of large-scale deployment of BIPV and related products changes the research agenda.

9:30 AM ET11.01.04
All Dielectric Light Trapping Scheme for Enhancing the Efficiency of Ultrathin Flexible Gr/Si Solar Cell Sonali Das1, Mohammad Jobayer Hossain1, Kristopher Davi2,3, and Tania Roy1,2,4,5; 1NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States; 2The College of Optics and Photonics, University of Central Florida, Orlando, Florida, United States; 3Department of Materials Science and Engineering, University of Central Florida, Orlando, Florida, United States; 4Department of Electrical and Computer Engineering, University of Central Florida, Orlando, Florida, United States.

Graphene/silicon (Gr/Si) Schottky junction solar cells have attracted much attention due to the ease and low cost of fabrication, along with the lucrative properties of high electron mobility, transparency and mechanical flexibility of graphene as a transparent conducting electrode. Utilizing its inherent mechanical flexibility, graphene can be integrated with thin flexible crystalline Si substrates opening up a new regime of applications in flexible and wearable electronics. Reducing Si absorber thickness below 50 um offers advantages of reduced material cost, along with mechanical flexibility and light weight. But Si at such thicknesses suffers from low photon absorption in the solar spectrum. To compensate for the low light absorption in such thin substrates, light management schemes become essential. Light trapping in Gr/Si solar cells is enabled by engineering the Si surface to form nanopillars, nanowires etc., which decreases the reflection loss and allows more light to couple in to the Si substrate. The structured Si absorber increases surface area and surface recombination, which is detrimental to the solar cell efficiency. Thus, it is imperative to use a light trapping scheme devoid of Si structuring to enhance the photoconversion efficiency.

We present an all-dielectric light-trapping scheme on planar Gr/Si Schottky junction solar cells with the use of bottom layer of titania spheres and top layer of silica spheres. An optimal Si thickness coupled with an optimized light trapping scheme leads to efficient electron-photon harvesting. The photoconversion efficiency of a 20um thick nanosphere-decorated Gr/Si solar cell improves to 9%, which is 1.3x higher than the pristine cell’s PCE of 7%. FDTD simulations are performed for optimizing the diameter of nanoparticles in each of the layers. The ratio of size of nanoparticles in the top to bottom layer plays a crucial role in advanced light management. An optimized structure of silica spheres, having diameter larger than that of titania spheres, suppresses reflection over wide angles of incidence and increases absorption in active Si layer over AM1.5G solar spectrum. The non-absorbing dielectric spheres can be easily realized by the well-known Steber technique. Additionally, the photovoltaic characteristic of the laminated solar cell shows negligible change after several bending cycles having bend radius ranging from 5 mm to 10 mm. After continuous bending and straightening, the ultra-thin solar cell can retain its performance, revealing the excellent stability and flexibility of the device. Such simple, low-cost light trapping schemes are universal in nature, devoid of recombination losses and are potentially viable for any solar cell technology.
the rear side can theoretically exceed 50% conversion efficiency owing to an increase in absorption and improved carrier collection in nanowire structures. III-V-on-Si multijunction solar cells using 1.75 eV GaAsP nanowires on the front side of bulk Si solar cell and 0.5 eV InGaAs nanowires on the backside. The resulting device configurations combine Si and III-V materials to allow flexible and cheaply encapsulated modules and high voltage (and current) material devices for monolithically integrated PEC-PV concepts. The results of various types of devices will be presented: a-Si:H/CIGS 2-junctions, a-Si:H/OPV 2-junctions, and a-Si:H/a-Si:H/OPV 3-junctions, nc-Si:H/c-Si 2-junctions and a-Si:H/c-Si 3-junctions. The general design rules of these hybrid PV devices to accomplish high conversion efficiencies are discussed, like tackling the crucial electrical and optical loss mechanism. First, a detailed study on a wide variety of tunnel-recombination junctions for hybrid devices will be presented. Secondly, to realize conditions close to current matching a wide variety of light management concepts are discussed, like: modulated surface textured substrates and interfaces to establish a compromise between ideal light trapping and processing of high quality PV materials; bi-functional intermediate layers that act as reflector layers and tunnel recombination junctions; and minimizing the parasitic absorption losses of supporting layers. The current state-of-the-art hybrid PV devices will be presented. Finally, examples of the application of these multi-junction devices in solar-to-fuel and water purification applications will be presented.

10:00 AM BREAK

SESSION ET11.02: Nano Technology Application to PV I
Session Chairs: Elisa Antolin and Huiyun Liu
Monday Morning, November 26, 2018
Hynes, Level 3, Room 304

10:30 AM *ET11.02.01
What Can Nano Really Do for Solar? Erik Garnett1,2, 1AMOLF, Amsterdam, Netherlands; 2University of Amsterdam, Amsterdam, Netherlands.

Over the past decade there has been extensive research into using nanostructures for solar cells. Although many interesting optical and electrical phenomena have been observed, nanostructured solar cells still have not exceeded (or even reached) the same efficiency level as their bulk counterparts. The goal of this talk is to describe the ways in which nanoscience can theoretically improve solar cells and outline the remaining fundamental and applied research necessary to realize such theoretical gains in practice.

The talk will consist of two parts. First, ways in which nanoscience can help reach the standard Shockley-Queisser efficiency limit (34%) will be discussed. In particular, new methods for making a variety of relevant monocrystalline nanomaterials will be presented along with the accompanying nanophotonic concepts. The results of various types of devices will be presented: a-Si:H/CIGS 2-junctions, a-Si:H/OPV 2-junctions, and a-Si:H/a-Si:H/OPV 3-junctions, nc-Si:H/c-Si 2-junctions and a-Si:H/c-Si 3-junctions. The general design rules of these hybrid PV devices to accomplish high conversion efficiencies are discussed, like tackling the crucial electrical and optical loss mechanism. First, a detailed study on a wide variety of tunnel-recombination junctions for hybrid devices will be presented. Secondly, to realize conditions close to current matching a wide variety of light management concepts are discussed, like: modulated surface textured substrates and interfaces to establish a compromise between ideal light trapping and processing of high quality PV materials; bi-functional intermediate layers that act as reflector layers and tunnel recombination junctions; and minimizing the parasitic absorption losses of supporting layers. The current state-of-the-art hybrid PV devices will be presented. Finally, examples of the application of these multi-junction devices in solar-to-fuel and water purification applications will be presented.

11:00 AM ET11.02.02
Design and Simulation of Bifacial III-V Nanowire Arrays on Silicon Anastasia Fedorenko, Mohadeshe A. Baboli, Parsian Mohseni and Seth Hubbard; Rochester Institute of Technology, Rochester, New York, United States.

Cost-competitive Si-based hybrid photovoltaic systems featuring high photocurrent conversion efficiency can be realized through multijunction designs by combining Si and III-V materials. The manufacturing cost of III-V-on-Si solar cells can be further reduced by transitioning from thin-film to nanowire-based devices. III-V-on-Si multijunction solar cells using 1.75 eV GaAsP nanowires on the front side of bulk Si solar cell and 0.5 eV InGaAs nanowires on the rear side can theoretically exceed 50% conversion efficiency owing to an increase in absorption and improved carrier collection in nanowire structures compared to the planar devices. Wide-bandgap GaAsP top nanowire array, however, can suffer from low short-circuit current density lowering the overall efficiency of the multijunction cell. Thus, an optimization of the dimensions of nanowires relatively to their spatial distribution in the arrays is the key to achieving absorption enhancement providing high short-circuit current output to promote current matching between the subcells. Finite-difference time-domain (FDTD) simulation was used to model the absorption in periodic arrays of GaAsP nanowires on Si substrates dependent on the diameter, length, and spacing (center-to-center distance, or pitch) of the nanowires. Based on this study, the highest ultimate efficiency of 26% of the top 1.5 μm-thick nanowire array was achieved for the array with the nanowire diameter of 300 nm and pitch of 500 nm, thus showing an enhancement by about 5% compared to the planar GaAsP absorber with the same thickness. The peak total absorption of the arrays with different pitch was found to be associated with the diameter-to-pitch ratio of 0.6. Distinct resonance modes were resolved in the low-dimension nanowires. Additionally, front-side nanowires were shown to exhibit waveguiding properties in the absorption range of the underlying cSiPV. The final presentation will include physics-based simulation of
Germanium is one of the promising semiconductors for photovoltaic applications such as solar cells, due to its high electron and hole mobility [1], and its high absorption in the infrared region. Several researchers have demonstrated Ge-based solar cells [2], in fact, Germanium-based solar cells already account for more than 80% of satellite applications [3]. Recently, good quality Ge-on-Si films fabricated using RF-PECVD (atT=600 °C) were demonstrated [4]-[6], paving the way for their use in photovoltaic applications. From optical perspective, Ge has a high refraction index and 60% normal incidence reflection which leads to high surface reflection and hinder its use in solar cells which leads to high anti-reflective coatings (ARC). The use of metal nanoparticles, such as silver, is a low-cost and viable alternative to other ARC materials to improve the optical and electrical properties of Ge-on-Si films for solar cell applications. Metal nanoparticles are strong scatterers of light at wavelengths near their resonant frequency [7]. This work studies the effect of spin coating of 40nm silver nanoparticle films on 700nm of Ge-on-Si films grown using RF-PECVD. The optical and electrical properties of the films after spin coating with 10ml and 20ml of 40nm silver nanoparticle colloidal solution are studied and compared to the film properties with no nanoparticles present. The concentration of silver nanoparticles in the aqueous buffer solution is 0.02mg/ml, provided by Sigma-Aldrich.

In this work, Ossila Spin coater was used for spinning 40nm silver nanoparticles on RF-PECVD deposited 700nm Ge-on-Si films [4]-[6], where the spinning was performed for 45 seconds at 2000rpm. Three samples of Ge films were used, one sample is left as a reference sample and the other two are coated with 10ml and 20ml of the silver nanoparticles colloidal solution, respectively, which was dispersed using a pipette. Using ImageJ software for image analysis the spinning led to the deposition of 480 nanoparticles/mm² (0.047%) surface coverage and 3280 nanoparticles/mm² (0.328%) coverage, the samples were then characterized for optical reflectance and sheet resistance.

The optical and electrical properties of Ge-on-Si films with and without silver nanoparticles were analyzed. The reflectance was measured using LAMBDA1050UV/Vis/NIR Spectrometer. Results showed that presence of nanoparticles reduced the amount of the reflected light due to plasmon effect which enhances the light absorption in the near-infrared region. The sample with no nanoparticles had the highest sheet resistance (200Ω/Sq) whereas the sample with 480 and 3280 nanoparticles/mm² appeared to have lower sheet resistance of 60 and 1.5Ω/Sq, respectively, which is >95% less than the reference sample, showing promising film properties for device applications. Moreover, this finding validates the potential of using spin coated nanoparticles as a low-cost alternative to conventional ARC layers for photovoltaic applications.

Greenhouse Effect in Photovoltaic Cells to Enhance Efficiency Beyond the Shockley-Queisser Limit

Andrei Sergeev, Harry Hier, Kimberly Sablon and Christopher M. Waits; Army Research Laboratory, Adelphi, Maryland, United States.

The fundamental Shockley - Queisser (S-Q) model assumes chemical equilibrium between photocarriers and emitted photons (the same chemical potentials) and establishes a maximum solar conversion efficiency, which is limited by endoreversible thermodynamics. In this work we propose and investigate a new converter design, which mimics the greenhouse operation and increases the conversion efficiency, potentially above the Shockley - Queisser (S-Q) limit, due to suppression of radiative emission.

To overcome the S-Q limit, at least one of the conditions (i-v) that lead to the S-Q limit should be modified: (i) All above-bandgap photons are absorbed; (ii) All below-bandgap photons are absorbed; (iii) Every above-bandgap photon excites one electron-hole pair; (iv) All photocarriers reach thermal equilibrium with the lattice; (v) Photocarriers and emitted photons reach the chemical equilibrium. While various solar cell concepts related to (ii) – (iv) conditions have been actively studied (intermediate band cell, multi-exciton generation, hot carrier solar cell), the PV devices with chemical nonequilibrium between photocarriers and emitted photons (condition (v)) were not considered yet.

The proposed photonic-enhanced PV converter device mimics the greenhouse effect. The converter has a reflective interference “greenhouse” filter placed in front of a semiconductor cell and a reflective mirror on the back of the cell. The front filter is transparent for high energy photons, but traps low energy photons emitted by photocarriers accumulated near the semiconductor bandgap. Thus, the high energy band-edge of the greenhouse filter establishes the photonic bandgap above the semiconductor bandgap. The photons with energy above the photonic bandgap are absorbed and create electron – hole pairs. Most of the excess energy is gained by the photoelectron, while the hole has energy close to the edge of the valence band. For this reason, the kinetics of photoelectrons is more manageable than the kinetics of photo-generated holes. To optimize the kinetics of photoelectrons, the semiconductor PV cell should be the n-p single junction diode with a p-doped base. In the optimized operating regime of the greenhouse converter, the chemical potential of photoelectrons near semiconductor bandgap can substantially exceed the chemical potential of photoelectrons established by the filter. Such chemical nonequilibrium may be realized due to strong interaction of photoelectrons with holes. As a result, the photoelectrons de populate the states with energies above the photonic bandgap. Reduced photoelectron population of states above the photonic bandgap reduces the emission and improves conversion efficiency above the S-Q limit, up to 44%.

The work was supported by U.S. Army Research Laboratory.

SiGeSn as a Candidate Material System for use in Thin-Film Multi-Junction Solar Cells

Phoebe Pearce1, Nicholas Ekins-Daukes2, 1 and Andrew Johnson1; 1Department of Physics, Imperial College London, London, United Kingdom; 2School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, New South Wales, Australia; 1QE, Cardiff, United Kingdom.

Materials with a circa-1 eV bandgap are necessary in the optimal design of multi-junction solar cells, with one of the optimal bandgaps in many designs for two, three and four junction cells being close to 1 eV. The lack of suitable high-quality photovoltaic absorbers with a circa-1 eV bandgap and lattice constant matching that of Ge, InGaAs and In,Ga,AIP, commonly used in multi-junction solar cells, has meant recent research interest in various candidate material systems which can meet these requirements, including dilute nitrides, antimonides and bismides. A novel material system for use for a 1 eV absorber is the ternary Group IV alloy silicon-germanium-tin (SiGe,Sn). By adding relatively small amounts of Si and Sn to Ge, both the bandgap and lattice constant can be tuned. With an Sn:Si composition of around 3.7:1, the lattice constant of the resulting alloy remains equal to that of Ge, while the bandgap can be tuned by varying the Sn and Si fractions in this ratio. It is possible to achieve a circa-1 eV direct transition at relatively low (x < 0.1) Si and Sn fractions. At these compositions, the material remains slightly indirect, with its indirect bandgap around 0.8 eV. It is expected that the Voc of solar cells incorporating SiGeSn will be reduced compared to a material with a fundamental direct gap at 1 eV, since carriers can thermalize to the lowest available band edge; however, current-matching considerations mean it is still beneficial to absorb primarily across the 1 eV transition, which also allows thin layers to be used. Single and triple-junction InGaP (1.9 eV)/InGaAs (1.4 eV)/SiGeSn (≈ 1 eV) devices incorporating SiGeSn have previously been
Optical upconversion that turns infrared light into visible light could improve the efficiency of solar cells by capturing sub-bandgap photons. A solid-state and reaction (SILAR) have not reached high solar energy conversion efficiencies hitherto, and have primarily been studied as sensitizers for photovoltaic applications.

Efficient Solid-State Infrared-to-Visible Upconversion Integrated in a Microcavity

Mengfei Wu, Ting-An Lin, Michelle C. Sherrott, Vladimir Bulović and Marc Baldo; Energy Frontier Research Center for Excitonics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Optical upconversion that turns infrared light into visible light could improve the efficiency of solar cells by capturing sub-bandgap photons. A solid-state
device consisting of a monolayer of lead sulfide colloidal nanocrystals and a thin film of rubrene with a luminescent dopant can convert infrared photons at $\lambda = 1 \, \mu m$ into visible photons at $\lambda = 610 \, nm$ via sensitized triplet-triplet annihilation [1]. Such a bilayer device, limited by low infrared absorption in the nanocrystals, requires 12 W cm$^{-2}$ of incident intensity at $\lambda = 808 \, nm$ to attain maximum upconversion efficiency [1]. Depositing a silver back reflector with an optical spacer on top of the active bilayer enhances the optical field, and hence absorption, in the nanocrystal layer due to interference, boosting the upconverted emission by an order of magnitude and lowering the threshold intensity to $1.1 \, W \, cm^{-2}$ when pumped at $\lambda = 980 \, nm$ [2]. Here, to further increase the optical field, we deposit the above interference-enhanced device on top of a distributed Bragg reflector (DBR). Such a structure places the nanocrystal layer in a microcavity whose resonance can be tuned to the pump wavelength by adjusting the thicknesses of the DBR layers and the optical spacer. We observe another order-of-magnitude increase in the upconverted emission, and a threshold intensity as low as $20 \, mW \, cm^{-2}$ at $\lambda = 980 \, nm$, similar to the flux available in the AM1.5 solar spectrum. The microcavity-integrated device demonstrates the possibility of efficient solid-state upconversion under sunlight and its application to solar cells.

High-performance polymer solar cells (PSCs) with thick active layers are essential for large-scale production. Polymer semiconductors exhibiting temperature-dependent aggregation property offer great advantages towards this purpose. In this study, three difluorobenzoxadiazole (PffBX)-based donor polymers, PffBX-T, PffBX-TT, and PffBX-DTT, were synthesized, which contain thiophene (T), thieno[3,2-b]thiophene (TT), and dithieno[3,2-b:2′,3′-d]thiophene (DTT) as the n-spacers, respectively. Temperature-dependent absorption spectra reveal that the aggregation strength increases in the order of PffBX-T, PffBX-TT, and PffBX-DTT as the n-spacer becomes larger. PffBX-TT with the intermediate aggregation strength enables well controlled disorder-order transition in the casting process of blend film, thus leading to the best film morphology and the highest performance in PSCs. Thick-film PSC with an average power conversion efficiency (PCE) of 8.91% and the maximum value of 9.10% is achieved using PffBX-TT:PC(61)BM active layer with a thickness of 250 nm. The neat film of PffBX-TT also shows a high hole mobility of 1.09 cm^2 V^{-1} s^{-1} in organic thin-film transistors. When PffBX-DTT and PffBX-T are incorporated into PSCs utilizing PC(61)BM as the electron acceptor, the average PCE decreases to 6.54% and 1.33%, respectively. The performance drop mainly comes from reduced short-circuit current, as a result of non-optimal blend film morphology caused by a less well controlled film formation process. A similar trend was also observed in non-fullerene type thick-film PSCs using IT-4F as the electron acceptor. These results show the significance of polymer aggregation strength tuning towards optimal bulk heterojunction film morphology using PffBX-based polymer model system. The study demonstrates that adjusting n-spacer is an effective method, in combination with other important approaches such as alkyl chain optimization, to generate high-performance thick-film PSCs which are critical for practical applications.

In this work, we report a multilayer cascade device architecture which increases Voc through the insertion of discontinuous interlayers between electron donor (D) and electron acceptor (A). We systematically study the influence of adding various interlayers in a sequentially deposited α-6T/interlayer/SubNc/SubPc cascade OSC, resulting in a Voc which increases from 0.98 V to 1.16 V. We show that this remarkable Voc increase of 0.18 V is due to the suppression of non-radiative recombination, as a consequence of a reduced physical contact between α-6T (D) and SubNc (A). The EQE of electroluminescence (EQE_{EL}) of 0.9 E-4 for our highest voltage device is one of the highest for OSCs and corresponds to non-radiative losses of 0.23 eV, which are the lowest reported for OSCs. Hence, we achieve Voc of 0.58 eV from the optical gap (E_{gap}) to Voc and 0.61 eV energy losses from the low energy peak of the EQE spectrum to Voc. Most importantly, the low energy (700 nm) EQE peak remains high at 79%, despite a minimal driving force for charge transfer of less than 10 meV.

Our work shows that low E_{gap} can be efficiently combined with a high EQE in organic photovoltaic devices.

**SESSION ET11.05: Thin Films I**

Session Chairs: Lincoln Lauhon and Rao Tatavarty
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 304

---

**8:30 AM ET11.05.01**

**2D Material-Based Layer Transfer to Revolutionize Photovoltaic Energy Generation**

Jeewhan Kim, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Because of substantially low cost of Si wafers, Si-based photovoltaics (PV) has been dominating although maximum power conversion efficiency of III-V solar cells is substantially higher than that of Si solar cells. To address this issue, wafer-reusing technique has been developed for the past few decades. However, the cost of recycling process has been much higher than that of the wafer. Thus, the room to improve levelized cost of energy has been limited. In today’s talk, I will introduce MIT’s novel wafer-reusing technique, so called a 2D material- based layer transfer process. We discovered that single-crystalline III-V PV layers can be epitaxially grown on graphene-coated III-V substrates, where the graphene is sufficiently thin such that crystalline orientation of III-V films can be guided by the substrate beneath graphene. The slippery graphene surface allows the III-V PV layers to be released from the substrate while the III-V substrate can be constantly reused. I will discuss how this technology revolutionizes photovoltaic technology by maximizing efficiency of solar cells while maintaining the production cost.

---

**9:00 AM ET11.05.02**

**Improved Light Harvesting with a Printed Light Guiding Nano-Structure to Increase the Performance of Flexible CZTS-Monograin Photovoltaic Modules**

Martin Ursprung, Lukas Plessing, Dieter Neess, Dirk Bontnick and Dieter Meissner, Crystalsol GmbH, Vienna, Austria; Materials, Institut für Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft mbH, Weiz, Austria; Allnex, Drogenbos, Belgium; Materials and Environmental Technology, TTÜ, Tallinn, Estonia.

Crystalsol has developed a novel PV-module structure and a manufacturing process for both, the semiconductor powder as well as the PV-modules. The core innovations are a light absorbing layer made of single-crystalline semiconductor powder and a low-cost and scalable roll-to-roll production process. The crystals are made of copper, zinc, tin, sulfur and selenium (CZTS) and are manufactured separately before module production. This unique technology combines the advantage of a single crystalline absorber with a vacuum free low cost printing process.

The weight of the membrane is about 0.5 kg/square meter up to 1 kg/square meter depending on the encapsulation used. It can be rolled with a radius of less than 5 cm and tailored to the customer’s needs. As a result of intense research an efficiency of 9.5 % has been reached. The crystalsol membrane layout is based on semiconductor grains, which are deposited as a monolayer. The photoactive material - the grains - covers about 80 % of the provided area thus incident light falling into the gaps between the grains, is not utilized.
In this paper a light-guiding structure is presented, which deflects the light towards the CZTS-grains enabling a higher share of incident light absorption and therefore an increase in photocurrent of up to 6.7 % which results in a 6.7 % gain in module performance. The foil deflects roughly 40 % of the incident light perpendicular to the line structure, whereby longer wavelengths show a wider deflection angle than shorter wavelengths. This structure was developed within the framework of the project Nano_Outside by JR (roll-to-roll-UV-nanoimprint lithography – R2R-UV-NIL), alkynes (UV-curable resins) and crystalsol (flexible PV-modules). The project is funded by the Austrian Research Promotion Agency (FFG). The concept was first tested with printed nanostructures and developed further by using R2R-UV-imprinting on a self-adhesive PET foil, which could easily be applied to the crystalsol modules. The UV-imprint-resin is based on urethane acrylates and designed to meet the requirements of the R2R-UV-NIL processes being strong adhesion to polymer substrates, high curing speed and imprint fidelity as well as excellent outdoor – i.e. abrasion and weathering – stability for the application on PV-modules.

The optimization of the nanostructure manufacturing, its impact on the PV-performance, as well as an outdoor stability assessment of the structure will be demonstrated.

9:15 AM ET11.05.03
Thermo-Mechanical Lift-Off of Thin-Film Photovoltaics—High Specific Power, Low Cost Deborah McGott1, 2, Mike Kempe2, Stephen Glynn2, Nick Bosco2, Colin A. Wolden1 and Matthew O. Reese2, 1Colorado School of Mines, Golden, Colorado, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Thin-film photovoltaics (PV), such as cadmium telluride (CdTe) and CuInxGa1-xSe2 (CIGS), offer extremely low manufacturing costs (< $0.50/Wp) and have achieved device and module efficiencies that rival multi-crystalline silicon. However, despite being comprised of just a few microns of active material, thin-film modules are among the heaviest due to their double glass construction. This increases costs and prohibits their use in applications where flexibility and specific power (power-to-weight ratio) are critical factors. One approach to overcome this issue is to synthesize the solar cells directly on flexible substrates such as stainless-steel foils or polyimide. While success has been obtained using this approach, it can often introduce additional weight (stainless steel) and/or processing steps (polyimide).

Here, we describe an innovative technique to lift off thin-film solar cells that are grown under standard processing conditions from their glass substrates in a reproducible manner. In this two-step process, we first laminate a commercially available polymeric backsheet to the solar cell, then submerge the stack in a cold bath (T ≤ -30°C) to thermally shock the system. This causes the polymer to contract quickly and pull the polycrystalline film cleanly off of a clean, reproducible manner. In this two-step process, we first laminate a commercially available polymeric backsheet to the solar cell, then submerge the stack in a cold bath (T ≤ -30°C) to thermally shock the system. This causes the polymer to contract quickly and pull the polycrystalline film cleanly off of its substrate at an interface that is weakened by a monolayer accumulation of 2-D material (CdCl2 in CdTe and MoS2 in CIGS). To enable clean lift-off of diverse thin-film architectures, a theoretical framework is developed and key process control parameters are identified. Focusing on CdTe devices, we show that the lamination temperature and device architecture control the quality of lift-off, while the rate at which the film stack is removed is controlled by the temperature of the cold bath.

Crack-free CdTe devices are removed and successfully re-contacted, recovering up to 80% of the original device efficiency. The areal density of these devices is ~0.4 kg m-2, a reduction of over an order of magnitude relative to their initial weight on glass. The broader applicability of this technique is then demonstrated by lifting off large areas (>50 cm2) of CIGS solar cells. The ability to lift these two major thin-film technologies off post-growth will allow for pre-existing high-volume manufacturing lines and their cost-structure to be leveraged, thus providing an alternative pathway toward inexpensive, flexible PV with high specific power.

9:30 AM ET11.05.04
Ligand Exchange of Copper Indium Gallium Sulfide Nanoparticles for Minimization of Carbonaceous Impurities in High Efficiency Solution Processed Photovoltaics Ryan Ellis, Jacob Fields and Rakesh Agrawal; Purdue University, West Lafayette, Indiana, United States.

Solution processing is an attractive method of producing high efficiency copper indium gallium sulfoselenide (CIGSSe) photovoltaics with significantly lower manufacturing costs, higher throughput, and greater large scale uniformity compared to traditional vacuum-based deposition technologies. A relatively benign colloidal nanoparticle route has shown great promise, reaching power conversion efficiencies up to 15%. However, further improvements are hindered by carbonaceous impurities originating from high boiling point organic ligands commonly used in nanoparticle synthesis. These ligands are difficult to remove via thermal treatment and often leave carbonaceous impurities in the final photovoltaic device as a distinct “fine grain layer” which can increase series resistance and could contribute to interfacial recombination. As such, the exchange of native ligands with volatile and non-contaminating ligands is of great interest to reduce carbonaceous impurities. For a successful ligand exchange for photovoltaic device fabrication, the exchange must remove the majority of native ligands, be thermally labile and not leave impurity elements, retain the stoichiometry of the as-synthesized nanoparticles, exhibit excellent colloidal stability at high mass concentrations, and not inhibit lead selenium assisted sintering of the absorber layer. In this work, we screen a wide variety of ligand exchange reactions for removal of native oleylamine ligands on copper indium gallium sulfide nanoparticles using a variety of amines, thiols, pyridines, and inorganic sulfide ligands to simultaneously meet the aforementioned criteria necessary for photovoltaic device fabrication. The screening revealed that alkylamines preferentially etched indium and gallium from the nanoparticles, thiols and functionalized pyridines were not readily thermally labile, and inorganic sulfides and pyridine were individually unable to remove the entirety of native ligands. Using these observations, a novel two-step ligand exchange was developed in which an initial microwave-assisted solvothermal ligand exchange was performed with pyridine to remove the bulk of native ligands, followed by an inorganic sulfide exchange to remove pyridine, additional native ligands, and to significantly enhance the colloidal stability of the nanoparticles in a variety of polar solvents. The two-step approach was uniquely able to meet all of the aforementioned criteria necessary for successful photovoltaic device fabrication. Along with the careful selection of solvents for ink formulation, ligand exchanged inks were employed for the fabrication of solution processed absorber layers, demonstrating high efficiency, fine grain free CIGSSe photovoltaics using a highly scalable and benign ink. The novel ligand exchange and subsequent photovoltaic device fabrication methods used hold wide applicability for the removal of carbonaceous impurities in nanoparticle based solution processed chalcogenide photovoltaics.

9:45 AM ET11.05.05
Effect of Solution pH and Post-Annealing on the Optical Bandgap of the Copper Oxide Thin Films Grown by SILAR Method Farhad Syed1, Alauddin Hossain2, Md. Abdul Majed Patwary3, Rumana Akter2, Nazmul Islam Tanvir4, Shanta Majumder2, Muhammad Shahriar Bashar4 and Mohammad Farhad Syed1, 1Department of Chemistry, Comilla University, Comilla, Bangladesh; 2College of Science and Advanced Technology, Dhaka University, Dhaka, Bangladesh; 3Optoelectronics Laboratory, Department of Science and Advanced Technology, Saga University, Saga, Japan; 4Institute of Fuel Research and Development (IFRD), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh.

Copper oxide is one of the most studied p-type materials for solar cell and other optoelectronic devices due to its direct band gap, high optical absorption in the visible region and suitable band alignment with its n-type counterpart materials such as ZnO, TiO2 etc. Cuprous oxide (Cu2O) thin films have been grown on both microscope glass slides and Fluorine-doped Tin Oxide (FTO) substrates by SILAR technique. The pH level of the bath solution and concentration of NaOH solution were systematically varied. The films were deposited in the pH range 3.45 - 7.35 as well as 1M and 2M NaOH solution to control the texturing and phase purity of the as-deposited films. The effect of post-annealing treatments (75-350 °C) on the as-deposited films was also demonstrated.
studied and found to be crucial to control the optical band gap and electrical properties of the films. The XRD measurement showed that the as-deposited films were single phase Cu$_2$O with (111) preferred orientation and found to be changing with increasing pH and annealing temperature. The (111) texturing of the annealed Cu$_2$O films were found to be increasing and stable phase up to 200 °C and completely converted to cupric oxide (CuO) phases when the temperature reached to 350 °C. The optical band gap and the sheet resistivity of the as-deposited and annealed samples were found to be in the range (2.35 – 1.43) eV and (154.22 –393.9) × 10$^4$ Ω/square respectively. The prepared film shows fiber-like and dense grain surface morphology observed from their SEM images. The performance of copper oxide films was tested by estimating LED modulated ON/OFF ratio into a photoelectrochemical cell and was found to be reasonable to integrate them into optoelectronic devices.

10:00 AM BREAK

SESSION ET11.06: Organic Photovoltaics II
Session Chairs: Lan Fu and Jia Zhu
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 304

10:30 AM ET11.06.01
Bio-Inspired Metallic Networks as Flexible Transparent Conductors—From Lab to Pilot Scale Jinwei Gao¹, Jun-Ming Liu¹ and Krzysztof Kempa¹; ¹South China Normal Univ, Guangzhou, China; ²Nanjing University, Nanjing, China; ³Boston College, Chestnut Hill, Massachusetts, United States.

Transparent conductors (TC) are critical materials for modern optoelectronic applications ranging from light emitting diodes, to displays (including touch-screen and flexible), to solar cells, to wearable electronics. In lighting and solar applications TC must be highly conducting in order to lower the ohmic losses. In display applications, microscopic transparency and lack of haze is required, as well as there is a need for mechanical flexibility in the case of flexible displays and wearable electronics. A chemical stability is also a must. These new requirements put pressure on the current standard material, indium tin oxide (ITO), which has overall good electro-optic performance and chemical stability, but is resistive, brittle and quite expensive. Recently, a new generation of TC materials emerged as a possible replacement for ITO, which can be tailored to satisfy all the above requirements. This talk will review such materials including our metallic networks, which have been inspired by nature. In one example, we developed the quasi-fractal hierarchical TC based on the self-cracking network combined with nanowires. This network TC has record high conductivity and simultaneously excellent transparency, and thus is ideal for lighting and solar applications. We have shown, that it is the plasmonic refraction of nanowires, which allows for the network increased transparency beyond the classic, shading limit. In addition, this network TC is mechanically flexible, and can be made inexpensively with wet chemical processing only. A version of this network can be used in displays, due to its low haze and low network visibility. We have very recently developed a roll-to-roll pilot production line of the self-cracking network on flexible plastic substrates with width of ~400 mm.

11:00 AM ET11.06.02
Exciton Binding Energy and Dielectric Effect in Small Molecular and Polymeric Photovoltaic Materials Ho-Wa Li, Liu Taili and Sai-Wing Tsang; City University of Hong Kong, Hong Kong, Hong Kong.

Owing to the low dielectric constant of organic materials, organic photovoltaic (OPV) is regarded as an excitonic solar cell that excitons are generated upon photo-excitation. Such intrinsic small dielectric constant ($\varepsilon$) in organic materials results in large exciton binding energy ($E_b$). That becomes a key detrimental factor limiting the further improvement in organic photovoltaic cells. Increasing the material dielectric constant seems to be a straight-forward strategy to reduce the strong coulombic attraction of the photo-generated electron-hole pairs. Despite the matter of importance, there are limited reports in measuring the $E_b$ and $\varepsilon$ in organic photovoltaic materials and the correlation between the dielectric constant and the exciton binding energy is unclear. Here, we extend our demonstration by using quantum efficiency measurement [1] and electro-absorption to access the transporting gap and exciton binding energy in pristine organic photovoltaic materials for polymeric donor, fullerene and non-fullerene small molecular acceptors. It is found that $E_b$ varies from 0.3 eV to 1.2 eV in those prototypical materials and it apparently follows a second power law with the inverse of the dielectric constant of the materials, i.e. $E_b \propto 1/\varepsilon^2$. Instead of widely assumed first-order dependence, this second order dependent relationship is firstly reported. Interestingly, we have also found that the binding energy is more dependent on the molecular-molecular interaction rather than the intrinsic properties of single molecule. In this presentation, we will also demonstrate how the higher dielectric material benefits the exciton dissociation at donor/acceptor interface.


11:15 AM ET11.06.03
Improving the Photovoltaic Performance and Mechanical Stability of Flexible All-Polymer Solar Cells via Tailoring Intermolecular Interactions Minjun Kim; Hong Il Kim, Seung Un Ryu, Cheol Woong Park and Taiho Park; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Naphthalene diimide (NDI)-based polymers are significantly promising electron accepting materials in all-polymer solar cells (all-PSCs) due to strong light absorption at the near infrared region and high electron mobility. Most NDI-based polymers have a large crystal structure through thermodynamically self-assembled aggregates, which lead to the low intermixing with polymer donor, resulting in large-scale phase separation in all-polymer blend films. The undesirable all-polymer blend morphologies cause inefficient exciton dissociation and charge transport between polymer donor and polymer acceptor, limiting the photovoltaic performance as well as mechanical resilience in all-PSCs. The low crystalline polymer acceptor with highly interconnected networks can provide an effective approach to high electron mobility and finely phase-separated blend morphology. Herein, we introduced a copolymer of NDI and (F)$\pi$-(3-fluorothiphen-2-yl)ethene (FTVT) (PNDI-FTVT) as a polymer acceptor with a low crystalline structure and high electron mobility ($\mu_e$). The blend film incorporating PNDI-FTVT exhibits well-mixed morphology without a large-scale phase separation. Moreover, PNDI-FTVT forms inter-junctions between polymer donor and polymer acceptor through strong $\pi-\pi$ stacking via fluorine induced dipole-dipole intermolecular interactions, improving the chain interconnectivity to construct better charge transport pathway. PNDI-FTVT based flexible all-PSC exhibited increased photovoltaic performance compared to PNDI-FTVT based flexible all-PSC (3.86% → 5.90%) and excellent mechanical stability in the flexible all-PSC, maintaining 72% of its initial performances (5.90% → 4.26%). This is the highest efficiency in the field of flexible all-PSCs and the first demonstration of the photovoltaic
Hybridised silicon nanospheres formed by simplified plasma-enhanced chemical vapour deposition (PECVD), without seed particle injection or microwave plasma, are fabricated in a variety of dimensions and with differing physicochemical properties, such as selective doping, via a modified Multi-Layer PECVD technique. Although the nanospheres can be directly incorporated onto a suitable substrate and within a dielectric during deposition, ex-situ processes have shown additional purpose can be ascribed to the nanosphere surface. By reducing the necessity of colloidal suspension or centrifugation steps, the nanospheres can be produced in functionalised states, for wavelength selection, light trapping and nanoscale dopant inclusion without negatively compromising the conductivity or passivation of the underlying structure. This can be attributed to the homogeneous H-Si distribution with no evidence for surface or bulk aggregation.

Suspension in poly-vinyl alcohol or ethyl acetate was utilised first for liquid phase analysis, then subsequently, for printing onto a selection of substrates, including crystalline silicon (c-Si) and semiconductor polymer. For silicon, monocrystalline with both planar and lightly textured surfaces were utilised. Semiconducting polymers based on naphthobisoxadiazole (PNOz4T), and Benzo[1,2-b:4,5-b’]dithiophene (BTD) incorporating thiene[3,4-c]pyrrole-4,6-dione (TPD) as a main chain and oligo(thiénylenevinylene) side chain were tested.

Non-peripherally alkyl-substituted phthalocyanines like octahexylphthalocyanine (C6PcH2) were examined as a top-layer for their higher carrier mobility compared to a-Si:H layers, and present a suitable matrix for allocation of the nanospheres, due to its hexagonal disordered columnar mesophase at approximately 170°C. An amorphous In2O3 front contact layer comprised of a transparent conducting oxide (TCO) and transparent oxide semiconductor (TOS) are shown to be effective in enhancing the short circuit current density of the assembled device.

When incorporated into the polymer-silicon membrane, the hybridised silicon nanospheres provide a solution to non-brittle light trapping or wavelength selection for flexible photovoltaic devices.
Flexible and Light Weight GaAs Solar Cells with Micro-Pattern and Back Reflectors

Kamran Forghani, David Rowell, Chris Stender and Raaqib Tatavarti; MicroLink Devices Inc., Niles, Illinois, United States.

Session Chairs: Jeehwan Kim and Kyle Montgomery
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 304

For large-scale implementation of photovoltaics, further improvement in the power-conversion efficiency is needed. Conventional silicon solar cells lose a large part of incident sunlight energy via thermalization of excited charge carriers. Singlet fission, a spin-allowed charge-carrier multiplication process which converts one singlet exciton into two triplet excitons is a promising way to reduce such thermalization losses. One way to harvest triplet excitons is by transfer of their energy into quantum dots that then emit photons into the silicon solar cell underneath. Thereby, the efficiency of the silicon solar cell can be increased by modulating the broadband solar spectrum.

We develop a model to simulate such a “photon multiplier”, and how it enhances silicon solar cells under realistic conditions. This model includes the relevant physical parameters such as the energy of the singlet and triplet exciton, the full width at half-maximum of the quantum dot emission, and losses due to parasitic absorption and non-perfect wave guiding of the emitted photons. We simulate the performance potential of a photon multiplier in comparison to an optimized perovskite/silicon tandem solar cell under realistic conditions. We find that the photon multiplier is more stable against changes in the solar spectrum than tandem solar cells. We furthermore find that the better the silicon base cell, the lower the efficiency gain of a tandem solar cell compared to the silicon solar cell alone, while the efficiency gain of a photon multiplier increases with increasing efficiency of the silicon solar cell. For current record silicon solar cells, the photon multiplier can boost the efficiency by up to 4.2% absolute under realistic conditions.

2:30 PM ET11.07.04
Flexible and Light Weight GaAs Solar Cells with Micro-Pattern and Back Reflectors

Kamran Forghani, David Rowell, Chris Stender and Raaqib Tatavarti; MicroLink Devices Inc., Niles, Illinois, United States.

III-V multijunction solar cells have the highest record efficiency for any type of photovoltaic devices: E.g. about 38% for AM1.5 1-sun and 33% for AM1.5 1-sun, as reported for 3 junction cells utilizing epitaxial-lift-off (ELO) [1]. Application of backside reflecting mirror for solar cells will enhance the performance by multiple photo-recycling events. The increase in optical absorption, not only helps to boost the performance but also helps to thin the cell, making them radiation-hard for space applications. We present our finding on back patterned GaAs solar cells. Single junction GaAs solar cells with two different configurations of up-right on rigid n-type substrate, as well as inverted flexible ELO cells were investigated. Several different patterns were applied and their effect on the overall cell short circuit current (Jsc) and quantum efficiency was studied. A more than 4% increase of the Jsc was observed in the backside patterned devices. The Jsc as function of light incident angle will also be presented, indicating an improved photo-response at smaller incident angles as compared to the planar control samples.


2:45 PM ET11.07.05
Epitaxial Growth of SiGe on Si Substrate by Printing and Firing of Al-Ge Mixed Paste

Shogo Fukami1, Yoshihiko Nakagawa1, Kazuhiro Gotoh1, Yasuyoshi Kurokawa1, Masahiro Nakahara2, Marwan Dhamrin2 and Noritaka Usami2; 1Nagoya University, Nagoya, Japan; 2Toyo Aluminium KK, Gamo-Gun, Japan.

The germanium substrate used for the bottom cell of tandem III-V solar cells is one of the most expensive components of this device structure. To make these devices cost-competitive with silicon, it is necessary to find an alternative material having a narrow gap which is suitable for the bottom cell. Silicon-germanium (SiGe) has a lattice constant and band gap close to Ge while also being relatively low cost and environmentally friendly. Also, because SiGe is an all-proportional solid solution whose composition can be freely controlled, its lattice constant and bandgap can be precisely controlled. However, conventional SiGe fabrication methods such as solid phase crystallization or chemical vapor deposition require long growth times or toxic gases. Thus, we focus on liquid phase epitaxial (LPE) growth utilizing the melting point depression phenomena of Ge and Si by Al [1]. In this paper, we investigated methods for LPE growth of SiGe on Si(100) substrate by printing and firing Al-Ge mixed paste and the influence of epitaxial growth by heat treatment under various conditions. We applied Al-Ge mixed paste which its thickness is about 30 µm on Si(100) substrate by screen printing and dried. LPE was performed using an Al-Ge mixed paste screen-printed on a Si (100) substrate and then annealing above Al-Ge eutectic temperature (420 °C) in the air or the Ar atmosphere. We annealed at 700, 800 and 900 °C to investigate the influence of annealing temperature on the growth of SiGe. After annealing, the residue at the top of the Si substrate surface was etched with a solution of phosphoric acid (H3PO4: CH3COOH: HNO3: H2O=16:1:1:2). The obtained SiGe was characterized by X-ray diffraction reciprocal space mapping (XRD-RSM), Scanning Electron Micrographs (SEM) and energy dispersive X-ray spectroscopy (EDX). From the SEM and EDX images, in case of annealing at 800 °C in the air, wave-like oxide film was confirmed at SiGe/Si interface. It is assumed that the oxide film interfered with the growth of SiGe. On the other hand, at 800 °C in the Ar atmosphere, we succeeded in forming abrupt heterointerface with thick SiGe. The results of XRD-RSM indicated that only the Si peak was observed before annealing. After annealing, a peak derived from SiGe appeared in addition to the Si peak. The SiGe peak shape was widely distributed since the composition distribution of SiGe occurred. The peak obtained from XRD-RSM by annealing at 700 °C in the Ar atmosphere showed that Ge fraction in SiGe was 7.56 %, which is higher than at 800 and 900 °C. It is assumed that Ge fraction in SiGe decreased by annealing at higher temperature due to more dissolution of Si substrate. These results suggest that the average composition and composition distribution in the SiGe can be controlled by changing paste composition and heat treatment history.


3:00 PM BREAK
and perovskite, but also on III-V compounds that have been made into flexible solar cells with potential for high efficiency and record power to mass ratio. As it turns, higher performance for solar cells goes with high power processing per unit volume, provided that absorption of incoming light is kept high. This is seen for instance in concentrated PV, but can also be done by reducing the thickness of the active material, provided efficient light management schemes are developed, such as the multi-resonant approach.

The presentation will highlight recent results obtained with high efficiency approaches to flexible solar cells, starting with thin film technologies and aiming at ultimate efficiencies such as III-V and Hot Carrier solar cells.

4:00 PM ET11.08.02
Investigation into the Selenization of Solution Processed Silver Zin Tin Selenide (Ag₂ZnSnSe₄) Thin-Film Solar Cells

Xianyi Hu, Dana Sulas, Steve Johnston, Darius Kuciauskas, Carol A. Handwerker, and Rakesh Agrawal.

Materials Engineering, Purdue University, West Lafayette, Indiana, United States; Chemical Engineering, Purdue University, West Lafayette, Indiana, United States; National Renewable Energy Laboratory, Golden, Colorado, United States.

Although CZTS solar cells have been fabricated with a maximum power conversion efficiency (PCE) of 12.6%, no further improvement has been demonstrated since 2013 due to intrinsic defects. It has been proven that the high density of Cu₂ZnSn(S,Se)₄ anti-site defects limits performance. These defects create band tails and dramatically decrease the open circuit voltage ($V_{oc}$) of devices. To eliminate these intrinsic defects, Ag has been used to substitute for Cu, which increases the formation energy of anti-site defects due to its larger radius and single valence. Our group did partial substitution of Cu with Ag and showed improved minority carrier life time. Gershon et al. developed photovoltaic devices based on an n-type Ag₂ZnSnSe₄(AZTSe) absorber layer by co-evaporation and achieved ~ 5% PCE, suggesting the potential of this material.

To establish a more cost-effective method for large-scale fabrication of AZTSe, compared with vacuum deposition, solution-processing is needed. Here, we report a systematic investigation into the selenization process from mixed AZT and ZnS nanoparticle films into large grain selenide films. We study key factors, such as selenization time, temperature, heating rate as well as Se vapor pressure utilizing a rapid thermal processor. Our results demonstrate that AZTSe has a narrow processing window to obtain phase-pure films with uniform composition and few pin-holes. We find that the heating rate plays an essential role in eliminating the formation of SnSe₂. Due to the fast sintering rate of the Ag-contained sulfide nanoparticles, selenization temperature and time have to be balanced to fabricate uniform, continuous, large grains. In addition, Se vapor condenses on the surface of nanoparticle film to enhance liquid-phase assisted grain growth of AZTSe films. To achieve a more uniform microstructure of AZTSe films and better adhesion between films and substrate, we deposit an intermediate layer on the surface of the film. We demonstrate that this layer helps with nucleation at the beginning of the selenization. We characterize the AZTSe films with photoluminescence and show a single, sharp peak at 1.3 eV was not a defect emission shoulder in contrast to CZTSe.

We propose a selenization mechanism based on the microstructure evolution and phase transformations that we observed and compared with CZTS. Ultimately, we establish a strategy to obtain AZTSe films consisting of continuous grains with uniform composition and few pin-holes, which is essential for the future production of AZTSe solar cells.

4:15 PM ET11.08.03
An Insight into the Effect of Band Alignment at Grain Boundaries on Photovoltaic Performance in CIGS and CZTS Thin-Film Solar Cells

Wenjie Li; Shenzhen Institute of Advanced Technology, Shenzhen, China.

The efficiency of CZTS solar cells is still not so high compared with other thin films such as CIGS. The underlying mechanism for the difference is a long-standing question that has remained elusive in spite of tremendous research efforts in the past. For polycrystalline thin film semiconductor, highly populated grain boundaries in the material will certainly have big influences on the photo-generated electron-holes. In this work, a conducting probe atomic force microscopy has been applied to study the electronic structure of CIGS and CZTS thin films with capability of nm-scale resolution. To exclude the surface effect, grain boundaries in the bulk were examined through cross-sectional SPM measurements and compared for both CIGS and CZTS. Different electronic structure of the grain-interior (GI) and grain boundary (GB) have been identified in both CIGS and CZTS thin films. We find that the band alignment of GI and GB in CIGS and CZTS is different, which can well explain the different device performance in two type of solar cells. With good Schottky contact between the AFM tip and semiconductor, a local electrical and photovoltaic performance can be measured and the conduction band overlap between GB and neighboring GI can be obtained. In CIGS, it is found that the conduction band has a larger overlap than in CZTS, which is consistent with the results of others. In CZTS, it is found that the conduction band has a smaller overlap than in CIGS, which is also consistent with the results of others. In CZTS, the GB and GI in CIGS behaves like a type-I hetero-structure that will trap both electron and hole inside the GB to produce strong recombinations.

Many experiments had demonstrated that air annealing process can improve the CZTS device efficiency with increased open-circuit voltage and fill factor. Our experiments of cross-sectional SPM measurements revealed that, for grain boundaries in the bulk, after air annealing, the downward bending valence band of GB turned to be upward bending, while the conduction band of GB turned from downward bending to upward bending. This resulted in the formation of electron and hole barrier at GBs which reduced the recombination, which can well explain the increased efficiency. However, the air annealing induced GB states behaved as barriers which can block the transport of electron and holes. Better GB passivation techniques are still in need.

4:30 PM ET11.08.04
Improved Voc Deficit in Kesterite Cu₂ZnSn(S,Se)₄ Solar Cells via Grain Boundary Passivation at the p-n Junction Interfaces

Cheng-Ying Chen, Naili Saidatin, Chih-Yang Huang, Ruei-San Chen, Jih-Shang Hwang, Kuei-Hsien Chen, and Li-Chyong Li.

Materials Engineering, Purdue University, West Lafayette, Indiana, United States; National Taiwan Ocean University, Keelung, Taiwan, Keelung, Taiwan; Graduate Institute of Applied Science and Technology National Taiwan University of Science and Technology, Taipei, Taiwan; Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan, Keelung, Taiwan.

Kesterite-based Cu₂ZnSn(S,Se)₄ (CZTSSe) have emerged as potential alternatives for CdTe and CIGSSe absorbers due to the use of non-toxic and earth-abundant elements and providing desirable optoelectronic properties similar to those of CIGSSe. To raise the performance of CZTSSe based solar cells, much effort has been applied to improving the quality of absorbers, band alignments/passivation at p-n junction, front and back interfaces/contacts. [1,2,3,4]

The present investigation mainly addresses the open circuit voltage (Voc) issue in kesterites based Cu₂ZnSn(S,Se)₄ solar cells by simply introducing an interfacial alkaline earth fluoride (several nm MgF₂) between the absorber (i.e., CZTSSe) and the buffer layer (i.e., CdS) after sulfo-selenization processes without post-annealing. In statistical studies (10 cells), the alkaline earth fluoride increases power conversion efficiency ($V_{oc}$) from 7.5% to 8.8%, short circuit current density ($J_{sc}$) from 30.7 mA cm⁻² to 32.6 mA cm⁻² and from 440 mV to 470 mV, possibly resulting from the MgF₂ induced electric field passivation at grain boundaries. [2] Finally, a 9.4% efficient CZTSSe solar cell with $V_{oc}$ of 470 mV, $J_{sc}$ of 32.96 mA cm⁻² and fill factor (FF) of 60.7% was obtained.
Two-dimensional transition metal dichalcogenides (2D TMDs) are promising candidates for ultrathin photovoltaics because they have direct bandgaps that lie in the visible range, their absorption coefficients are one to two orders of magnitude higher than conventional semiconductors, and their interlayer van der Waals interaction eliminates the constraint of lattice matching in heterostructure design. Our group has demonstrated high internal quantum efficiency in 2D TMD photovoltaics (1), high open-circuit voltage remains a challenge (2). Here, we study open-circuit voltage in 2D TMD photovoltaics by fabricating both vertical and lateral photovoltaic devices with monolayer TMD absorber layers and contacts with asymmetric work functions (e.g. silver and platinum). In both vertical and lateral geometries, we compare the effects of transferred and directly evaporated metal contacts on the device’s open-circuit voltage. To transfer metal contacts, we modify a procedure that has been shown to create contacts to 2D materials with atomically smooth interfaces and no Fermi level pinning (3). Metals are patterned onto a smooth sacrificial substrate (i.e. silicon dioxide) using photolithography, peeled off that substrate using polyvinyl alcohol (PVA), and transferred onto a TMD device using a viscoelastic stamp. The devices are characterized, then passivated by immersion in solutions of the superacid bis(trifluoromethanesulfonimide) in acetonitrile to achieve near-unity photoluminescence quantum yield, as previously reported (4,5). Using photoluminescence mapping, photocurrent spectroscopy, and Kelvin probe force microscopy, we characterize these devices to analyze the effects of 1) vertical vs. lateral device geometry, 2) superacid-treated vs. untreated absorber layers, and 3) transferred vs. evaporated metal contacts on the open-circuit voltage of our photovoltaic devices. Our results demonstrate a pathway towards high open-circuit voltage in 2D TMD photovoltaics, and we outline specific design considerations for future high-efficiency devices.

References:

SESSION ET11.09: Compound Semiconductors
Session Chair: Jeehwan Kim
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 304

8:30 AM ET11.09.01
Metalorganic Vapor Phase Epitaxy of Large CdTe Grains on 2D Substrates through Chemical and van der Waals Mixed Interactions
Xi Sun1, Dibhajyoti Mohanty1, Zonghua Lu2, Yu Xiang3, Yiping Wang4, Lihua Zhang5, Kim Kisslinger6, Jian Shi1, Lei Gao3, Morris Washington1, Gwo-Ching Jahelka1, Deep M. Jariwala1,2, Joseph S. DuChene1 and Harry A. Atwater1; 1California Institute of Technology, Pasadena, California, United States; 2University of Pennsylvania, Philadelphia, Pennsylvania, United States.

High-quality heteroepitaxy of CdTe is challenging due to lattice mismatches of CdTe with many substrates. Herein, we demonstrate the epitaxial growth of single crystalline CdTe films on mica using metalorganic chemical vapor deposition, regardless of large in-plane lattice mismatch between CdTe(111) and mica. X-ray and electron diffractions suggest that CdTe is epitaxially aligned with mica: out-of-plane CdTe[111]/mica[001] and in-plane CdTe [-12-1]/mica [010]. Full-width-at-half-maximum (FWHM) of X-ray rocking curve and FWHM of X-ray azimuthal in-plane angular dispersion of CdTe are shown to be 0.11° and 0.38°, respectively, better than most CdTe films reported. Electron backscattering diffraction shows that CdTe grains are tens of μm in size and, if twin boundaries are excluded, in excess of 250 μm in size. In contrast to the belief that overlayer growth on mica is purely through van der Waals interaction, our first-principles calculations unveil that van der Waals interaction only contributes to 20% of the total interfacial energy, and 80% of the interfacial energy comes from chemical interaction. Furthermore, we demonstrate that epitaxial CdTe films can be achieved on other 2D substrates, such as graphene. Compared to on mica, however, the films grown on graphene are characterized with larger orientation dispersions along out-of-plane and in-plane directions and smaller grains. Our first-principles calculations indicate a van der Waals interaction dominating interface between CdTe and graphene. We thus conclude that the nature of interface interactions dictates crystal quality of CdTe films on different 2D substrates. The demonstrated epitaxy of II-VI semiconductors on 2D van der Waals substrates suggests potential for flexible optoelectronic devices.

8:45 AM ET11.09.02
Effect of Stacking Disorder and Metastable Polymorph on Charge Conduction in Earth-Abundant Cu2ZnSn(S, Se)4-Based Solar Cells
Ji-Sang Park, Sunghyun Kim and Aron Walsh; Imperial College London, London, United Kingdom.

Cu2ZnSn(S, Se)4-based solar cells have attracted a much attention in achieving terra-watt scale photovoltaics. The solar conversion efficiency of Cu2ZnSn(S, Se)4 solar cells, however, is generally lower than CuIn, GaSe2 solar cells because of low open-circuit voltage, usually termed as the open-circuit voltage deficit. While the problem has not been solved yet, the spatial fluctuations of band edge have been suggested as the culprit which results in the band tailing and the lower efficiency. The spatial fluctuations can be caused by the formation of anti-site defect pairs which form electrostatic dipoles, or lower bandgap
Indeed the formation of the lower bandgap polymorph (e.g. stannite) can be understood as the periodic formation of anti-site defect complexes. In multication materials such as Cu$_2$ZnSn(S,Se)$_4$, the octet rule can be satisfied when anti-site defects are formed on two-dimensional planes in certain ways. Metastable polymorphs can be obtained from kesterite crystal structure by applying such operations globally, and the metastable polymorphs are shown to have lower band gap from the hybrid density functional theory (DFT) calculations [1]. If the operation is locally applied, then it results in the formation of so-called anti-site domain boundaries, and their formation has been experimentally proven in Cu$_2$ZnSnS$_4$ nanocrystal. In this work, we performed hybrid DFT calculations and found that these defects in Cu$_2$ZnSn(S,Se)$_4$ lower the conduction band locally, and thus act as electron donors [1].

On the other hand, studies of other solar cell absorber materials show that stacking faults are formed abundantly in zinc-blende-derived materials. We calculated the formation energy of the stacking faults (e.g. intrinsic stacking faults) and analyzed their effect on the electronic structure as well. We found that Stacking fault defects in Cu$_2$ZnSn(S,Se)$_4$ are more easily formed than the anti-site domain boundaries [2]. In contrast to the anti-site domain boundaries, the stacking faults increase the conduction band and thus electron barriers are locally formed, hamper the electron conduction.

References

Acknowledgement
J.-S.P. thanks the Royal Society for a Shooter International fellowship. The work at ICL received funding from the European H2020 Framework Programme for research, technological development and demonstration under grant agreement no. 720907. See http://www.starcell.eu.

9:00 AM *ET11.09.03
Nanowires for Tandem Junction Solar Cells Magnus Borgström; Lund University, Lund, Sweden.

Semiconducting nanowires have been recognized as promising materials for high-performance electronics and optics where optical and electrical properties can be tuned individually, where the nanowires due to excellent light absorbing properties [1] have been suggested for future high efficiency solar cells [2, 3]. Especially, the geometrical shape of the NWs offers excellent light absorption. In order to further optimize the performance of NWPV, and integrate them on Si in a tandem junction configuration, nanowires with dimensions corresponding to optimal light harvesting capability are necessary. We developed nano imprint lithography for patterning of catalytic metal particles with a diameter of 200 nm in a hexagonal pitch of 500 nm, for which synthesis was redeveloped since the metal particles were found to move during annealing, destroying pattern fidelity before nucleation. By use of electron beam induced current measurements we learn how to improve the photocurrent generation profile in the nanowires by reducing native defects incorporated during synthesis, either by tuning the V/III ratio or by compensation doping, resulting in a certified efficiency of 15 % for a 12 % surface coverage of nanowires. We intend to transfer these grown nanowires to a Si platform (existing PV), either by direct growth on Si PV, or by nanowire peel off in polymer, followed by transfer and electrical contacting, or by aerotaxy and alignment for transfer to Si. The optimal band gap in combination with Si is about 1.7 eV, where we identify GaInP and GaAsP as materials for development of nanowire pn junctions by doping, the heart in a solar cell.

4. Åberg et al, IEEE J. of Photov, 6, 185 (2016)

9:30 AM ET11.09.04
Tailoring the Defect Properties of Chalcohalide Systems for Photovoltaic Applications John Buckeridge, Alex M. Ganose and David O. Scanlon; University College London, London, United Kingdom.

Bismuth chalcohalides are promising new candidates for cheap, nontoxic and highly effective solar absorber layers in photovoltaic systems. The majority of those studied so far, however, have shown poor efficiencies well below industry standards. We investigate the suitability of these materials for solar energy applications using relativistic first-principles computational techniques, focusing on two of the most promising systems: BiSI and BiSeI. We find that both compounds possess desirable optoelectronic properties, with band gaps well within the visible range combined with strong optical absorption, resulting in high predicted device performance. Our analysis of their defect chemistry indicates that deep traps are likely to form, which may account for the observed poor performance of the materials. Nevertheless, we show that, by varying the experimentally accessible synthesis conditions, it is possible to avoid the formation of such killer defects, which would allow much higher efficiencies to be achieved. Furthermore, we apply similar analysis to study other III- (and V-) chalcohalides and determine their suitability for photovoltaic applications, building up a family of promising mixed-anion materials with similar optoelectronic properties.

9:45 AM ET11.09.05
Development of New High-Band Gap Photoabsorbers for Low-Cost Tandem Solar Cells with Different Thermal Budgets Andrea Crovetto, Brian J. Seger, Ole Hansen, Peter Vesborg and Ib Chorkendorff; Technical University of Denmark, Kgs. Lyngby, Denmark.

One of the current key challenges in both photovoltaics and solar-driven water splitting is to identify an efficient, stable, and low-cost material to be used as a high-band gap (1.6-2.0 eV) photoabsorber in tandem device configurations. In this contribution, we will report on our group’s development of three different emerging, inorganic, high-band gap solar absorbers with thermal budgets from 150°C to 1000°C, which may satisfy different applications. The first material is Bi$_3$I$_6$ (thermal budget of 150°C, record efficiency 1.0 %), which is straightforward to make and may be used for tandem solar cells on flexible plastic substrates [1]. The second material in Cu$_2$BaSnS$_4$ (thermal budget of 550°C, record efficiency 2.0 %), which is a promising alternative to the more extensively studied Cu$_2$ZnSnS$_4$, due to its more appropriate band gap for tandem solar cell applications and to its lower density of tail states [2]. The third material is La$_2$YS$_3$ (thermal budget of 1000°C, no efficiency reports). To our knowledge, La$_2$YS$_3$ the first chalcogenide perovskite to have been synthesized in thin film form, as well as one of the first photoabsorbers discovered by computational screening that were actually synthesized [3]. Those three materials are currently being investigated in our group. They share the following favorable optoelectronic properties: 1) appropriate band gap (1.7-2.0 eV) as a top absorber in a tandem solar cell; 2) strong photoluminescence, and 3) small shift between band gap energy and photoluminescence peak energy. We will present our results on alternative growth methods for the two previously synthesized absorbers (sodalization of metallic Bi for Bi$_3$I$_6$; sulfuration of...
oxide films for Cu$_2$BaSnS$_4$, as well as the main optoelectronic properties of the novel LaYS$_2$ absorber. Finally, we will discuss the solar cell performance obtained from the three absorber materials, with particular emphasis on the different device architecture limitations arising from the different thermal budgets of the three materials.


10:00 AM BREAK

10:30 AM *ET11.10.01 Interface-Enhanced Bulk Photovoltaic Effect in Metal Oxides Yun Liu; The Australian National University, Canberra, Australian Capital Territory, Australia.

Photovoltaic (PV) is a process converting light energy to electrical energy. A high efficient PV effect relies on two factors: (i) a high photocurrent and (ii) a built-in electric field enabling the separation of the photogenerated electrons and holes. In traditional PV devices, electron-hole pairs are generated by light absorption in narrow bandgap semiconductors, and then separated through the depletion field in the heterojunction. The maximum voltage of these devices, however, equals to their bandgap, and thus the power conversion efficiency is restricted by Shockley–Queisser limitation. To break this limitation and obtain higher voltage, ferroelectric (FE) materials, due to their non-centrosymmetric structures that can induce stable depolarization electric fields and generate much higher photovoltage than their bandgap (named as bulk PV effect), have received a renewed attention in the PV application. Despite the high voltage the FE materials can exhibit, the photocurrent of most of the FE materials is really low because of their wide bandgaps resulting in the low conductivity and the deficient absorption of the solar energy. In this talk, we will present several strategies to improve bulk PV effect of materials, especially focusing on structurally distorted and chemically varied narrow bandgap metal oxide semiconductors, in which high performance ferroelectric properties are achieved without significantly changing their intrinsic electronic and photoelectronic properties. It is found that such a very thin (<10nm) functional metal oxide layer, deposited on a strain layer, shows an excellent bulk photovoltaic effect with a photocurrent 10$^3$–10$^4$ times higher than that of conventional ferroelectric materials and comparable to state-of-the-art multilayered multiferroics.

11:00 AM ET11.10.02 Optimizing the Properties of Transparent Electrodes Based on Silver Nanowire Networks for Integration into Organic Solar Cells Joao A. Resende1, Thomas Sannicolo1, Afzal Khan2, Nicolas Charvin3, Ali Nourdine1, Dorina Papanastrausi1, Viethuong Nguyen1, 1, Sara Aghazadehchors1, 4, David Munoz-Rojas1, Carmen Jimenez2, Ngoc Duy Nguyen1, Lionel Flaudin1 and Daniel Beller1; 1LMGP, Grenoble, France; 2Department of Physics, Univ. of Peshawar, Peshawar, Pakistan; 3Univ. Grenoble Alpes, Université Savoie Mont Blanc, CNRS, Grenoble INP, LEPHI, Grenoble, France; 4Univ. de Liege; CESAM/Q-MAT, Liege, Belgium; 5Centre d’Etudes et de Recherche en Chimie Analysée et Moléculaire (CERMAC), Univ. of Peshawar, Peshawar, Pakistan.

The demand for low-cost and flexible photovoltaic systems is rapidly increasing, creating a need for a new generation of transparent electrodes. In the specific case of organic photovoltaics (OPV), flexible transparent electrode materials would allow the wide-spread of large-scale OPV, offering a technology with non-toxic, low-weight and flexible modules available in different shapes and colors. Although indium-tin-oxide (ITO) constitutes the state-of-the-art transparent conductive material for solar cells, it exhibits drawbacks such as brittleness, thus preventing its application in flexible devices. To replace ITO, metal-based nanowire networks have been considered as a promising alternative solution that exhibits high conductivity and the deficient absorption of the solar energy. In this talk, we will present several strategies to improve bulk PV effect of materials, especially focusing on structurally distorted and chemically varied narrow bandgap metal oxide semiconductors, in which high performance ferroelectric properties are achieved without significantly changing their intrinsic electronic and photoelectronic properties. It is found that such a very thin (<10nm) functional metal oxide layer, deposited on a strain layer, shows an excellent bulk photovoltaic effect with a photocurrent 10$^3$–10$^4$ times higher than that of conventional ferroelectric materials and comparable to state-of-the-art multilayered multiferroics.

11:15 AM ET11.10.03 Head-to-Head Linkage Containing 4-alkoxy-5-(3-alkylthiophen-2-yl)thiazole-Based Polymeric Semiconductors for Polymer Solar Cells with Small Voltage Loss Xin Zhou, Chen Peng, Jianwei Yu, Han Guo and Xugang Guo; Southern University of Science and Technology, Shenzhen, China.

Head-to-head linked bithiophene-type unit with advantages of good solubility and high planarity has been proven as a successful building block for polymeric semiconductors. However, since the strong electron-donating nature of alkoxy chain, bithiophene-based polymers suffer from elevated frontier molecular orbitals (FMOs), which are unfavorable to stability of semiconductors and lead to small open-circuit voltages ($V_{oc}$) in polymer solar cells (PSCs). Herein, we report the design, synthesis and characterization of a new head-to-head linked building block 4-alkoxy-5-(3-alkylthiophen-2-yl)thiazole
(TRTzOR). Compared to our previous work, 3-alkoxy-3'-alkyl-2,2'-bi thiophene (TRTzOR). TRTzOR retains high planarity through the intramolecular noncovalent S–O interaction, while its FMOs have been considerably lowered for the substitution of electron-deficient thiazole for the electron-rich thiophene. Copolymerized with the benzothiadiazole and its fluorinated derivatives, TRTzOR-based polymer showed a wider absorption range extending to 950 nm and tune FMOs down by 0.2–0.3 eV, versus TRTzOR-based analogous polymers. Thus, TRTzOR-based polymeric donor enlargers the $V_{oc}$ of polymer solar cells by 0.1 eV. Moreover, a much smaller energy loss as low as 0.61 eV was realized. Our study demonstrates thiazole substitution is an effective approach to tuning energy levels for higher open-circuit voltages in PSCs. The exceptional small energy loss indicates that head-to-head linkage TRTzOR motif is a promising building block for organic semiconductor.

11:30 AM ET11.10.04
IMPULSE–OPV—Integrated Molecular Plasmon Upconverter for Low-Cost, Scalable and Efficient Organic Photovoltaics Jonas S. Lissau and Morten Madsen; SDU NanoSYD, Mads Clausen Institute, University of Southern Denmark, Sønderborg, Denmark.

Upconversion of low-energy photons transmitted by traditional single-threshold solar cells is a promising approach to overcome their theoretical efficiency limit. Due to their relatively high-energy absorption threshold organic solar cells have a particular high loss of low-energy photons and consequently a high potential for improvement by photon upconversion.

In IMPULSE-OPV, we apply photon upconversion via triplet fusion in organic molecules to improve the efficiency of organic solar cells. This approach can be synthetically tuned to match the spectral requirements of the solar cell technology. In addition, molecular photon upconversion benefits from spin-allowed broadband absorbing transitions, which facilitates reasonable upconversion efficiency under solar flux [1].

Specifically, we investigate in this work systems based on palladium(II) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine as a triplet sensitizer and rubrene as a triplet-triplet annihilator. After light absorption and intersystem crossing the resulting triplet state is transferred to rubrene. The molecular upconverter is embedded in a polyurethane matrix which allows for efficient triplet energy migration via molecular diffusion. Two rubrene triplet states can annihilate (triplet fusion) to produce a high-energy singlet state which decays by emission of an (upconverted) high-energy photon.

To further boost the photon upconversion efficiency, metal nanostructures tailored for plasmon resonance at the absorption band of the upconverter are integrated. This work therefore provides a route for production of low-cost, scalable, and efficient organic solar cells via photon upconversion.


11:45 AM ET11.10.05
Metal Decorated Nano-Composite Effects to Enhance the Performance of Inverted Thin-Film Organic Solar Cells Genene T. Mola; University of KwaZulu-Natal, Pietermaritzburg, South Africa.

The efficient generation and transportation of charge carriers are the major factors that influence the performance of thin film organic solar cells (TFOSC). We have successfully synthesized and employed tri-metallic nanocomposite (Ag:Zn:Ni) in the preparations of TFOSC with the view to address some of the challenges with respect to charge generation and transportation. The nanocomposites were dispersed in the solution phase of the photoactive layer of the solar cells. As a consequence, notable influence of the nanocomposite was evident on the power conversion efficiency of the devices due to local surface plasmon resonance (LPSR). Several synthesis methods have been employed in the preparations of various bi and tri-metallic nanoparticles which include chemical, physical and biosynthesis methods such as chemical reduction, microwave and laser ablation [1,2,3,4,5]. Among these techniques, the chemical reduction method is the most preferred one because of its simplicity and low cost preparation. Moreover, the chemical reduction method offers the ability to control size and distribution of the nanoparticles by optimizing the experimental parameters. In this work, we have synthesized and characterized of silver:zinc:nickel (Ag:Zn: Ni) tri-metallic nanoparticles which are eventually explored for first time to influence the photovoltaic performance of bulk-heterojunction organic solar cells. The synthesis of the nanocomposite, device preparation and characterization are discussed in terms of changes in optical, electrical and morphological properties.

References:

SESSION ET11.11: Oxides
Session Chairs: Seth Hubbard and Aaron Ptak
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 304

1:30 PM *ET11.11.01
Interfacial Solar Steam Generations—Materials, Structures and Applications Jia Zhu; Nanjing University, Nanjing, China.

Nanomaterials with carefully tailored properties can be used to manipulate the flow of phonons, electrons and photons, to enable unconventional solution for solar energy conversion. In this talk, I will present our recent progress in interfacial solar steam generations.
We report a plasmon-enhanced solar desalination device. This most efficient and broad-band plasmonic absorber is fabricated through self-assembly of metallic nanoparticles onto a nanoporous template by one step deposition process. Because of its efficient light absorption and strong field enhancement, it can enable very efficient and effective solar desalination by using low cost aluminum nanoparticles. Inspired by the transpiration process in plants, we report an artificial transpiration device with a unique design of two dimensional water path. With efficient two dimensional water supply and suppressed heat loss, it can enable an efficient (80% under one-sun illumination) and effective (four orders salinity decrement) solar desalination device. The energy transfer efficiency of this artificial transpiration device is independent of water quantity and can be achieved without extra optical or thermal supporting systems, therefore significantly improve the scalability and feasibility of this technology. In addition, interfacial solar steam generations can enable effective sterilization and efficient generations of electricity.

2:00 PM ET11.11.02
Synthesis and Characterization of c-Axis Oriented Zinc Oxide Thin Films and Its Use for the Subsequent Hydrothermal Growth of Zinc Oxide Nanorods
Farhad Syed1, Nazmul Islam Tanvir1, Muhammad Shahriar Bashar2 and Munira Sultana3; 1Solar Energy Conversion and Storage Research Section, Industrial Physics Division, BCSIR Labs, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh; 2Institute of Fuel Research and Development (IFRD), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh.

Oriented ZnO seed layers were deposited by simple drop casting of zinc acetate dihydrate(ZAD) solution on glass substrates at room temperature followed by a post-heating treatment at 250 °C. X-ray diffraction (XRD) analyses revealed that ZAD solutions with concentration 0.0025 – 0.0100 M produced amorphous type thin films, whereas 0.020 M ZAD solutions produced ZnO seed layers with a preferential c-axis texturing. The Scanning Electron Microscopy (SEM) analysis evident that the morphology of ZnO seed layer surface is compact and coherently carpets the underlying glass substrate. ZnO nanorods were then grown by hydrothermal method atop the oriented ZnO seeded and non-seeded substrates. The presence of ZnO seeding layers was found to significantly affect the surface morphology and crystallographic orientation of the resultant ZnO NRs films. The optical band gap of ZnO seed and ZnO NR were estimated to be in the range of 3.40 – 3.95 eV and 3.20 – 3.25 eV respectively by using UV–VIS–NIR diffuse reflection spectroscopy. The room temperature photoluminescence analyses revealed that nanostructured ZnO films exhibit a sharp near-band-edge luminescence peak at ~380 nm consistent with the estimated optical band gap and the ZnO nanorod arrays are notably free from defect-related green-yellow emission peaks.

2:15 PM ET11.11.03
Slow Transient Photoconductivity in ZnO Explained from Light-Induced Trap Filling
Jason A. Rohr1, 2, Mohamed Abdelkhalik1, Liam Appelson1, Anna Cieslak1, Janusz Lewinski1, 3, Jacinto Sa1, 2 and Steven Konezny1, 2; 1Department of Chemistry, Yale University, New Haven, Connecticut, United States; 2Energy Sciences Institute, Yale University, West Haven, Connecticut, United States; 3Department of Chemistry, Uppsala University, Uppsala, Sweden; 4Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; 5Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland.

Zinc oxide (ZnO) nanoparticles have been studied extensively as gas sensors, as an alternative electronic transport material to titanium dioxide in dye-sensitized solar cells, and as a potential photocatalyst for solar driven water splitting. This is primarily due to their low cost, material abundance, potentially large surface area as mesoporous films, low toxicity, relatively large charge-carrier mobilities, and their capability to be doped either n- or p-type. However, important fundamental mechanistic questions remain unanswered. The chemical nature of charge-carrier traps, and the observed transient behavior of the conductivity of ZnO thin films after UV light exposure, also known as persistent photoconductivity, are still as much the subject of debate as it has been over the last three decades. We offer new insight based on a combination of temperature-dependent conductivity measurements, in the 8 to 310 K range, and mid-infra-red transient absorption spectroscopy measurements. Using these techniques we are able to isolate the effects from light and temperature. At low temperature, the conductivity increases as transport tends from being trap limited to trap filled when exposed to UV light as the fraction of filled traps increases. At higher temperatures, the dark current, post UV exposure, slowly decreases as it returns to trap-limited behavior as charge carriers are reemitted from the traps. At practical device temperatures and light conditions, the observed conductivity is governed by both trapping and detrapping kinetics that establish an equilibrium density of occupied trap levels. We show that the conductivity can be modeled within this framework by assuming a combination of inter-particle tunneling, light induced trap filling and temperature-dependent detrapping kinetics. This model can be used to extract the trap depths, which can be assigned to the defects limiting the transport. Our findings not only give insight into the conduction mechanism of ZnO particle films, but into any conduction mechanism exhibiting persistent photoconductivity, such as other nanostructured metal oxides and amorphous metal chalcogenides.

2:30 PM BREAK

3:30 PM ET11.11.04
Optical Properties of Magnesium-Zinc-Oxide for Thin-Film Photovoltaics Applications
Mohammed Razaeqi, Prakash Koirala, Adam Phillip, Geethika K. Liyanage, Michael Heben and Robert W. Collins; Department of Physics and Astronomy, and Wright Center for Photovoltaics Innovation and Commercialization, The University of Toledo, Toledo, Ohio, United States.

Magnesium-zinc oxide (MgZn1-xO; MZO) is a window layer material of great interest in thin film photovoltaics technologies such as CdTe and CuIn(x)Ga(2-x)Se2. Recent numerical modelling and experimental data have shown that replacing the CdS window layer in CdTe devices with an MZO layer improves the band alignment at the front contact, which in turn reduces recombination [1,2] and leads to improved solar cell open circuit voltage and fill factor [3]. Although the window layer performance is critically dependent on its optical properties, such characterization of MZO films after the various steps throughout device fabrication has not been reported to date. Specifically, information is lacking on the evolution of the optical properties as a function of time during thermal treatments in different environments. Whereas the SnO2 high resistivity transparent (HRT) layer traditionally used in CdTe devices is known to be thermally stable, it is not clear the extent to which the properties of as-deposited MZO are affected by subsequent device processing. Here, we use spectroscopic ellipsometry (SE) to determine the optical properties of the MZO at various stages of CdTe device processing and apply this information to guide device fabrication. In these experiments, MgZn1-xO films with Mg contents from x = 0 to x = 0.25 were sputtered at room temperature on soda lime glass (SLG). This provides a range in the MZO bandgap energy from Eg = 3.3 eV to Eg = 3.7 eV, respectively. The room temperature complex dielectric functions of the MZO films on SLG were measured immediately after deposition and again after heating for 4 hours at 250 °C, the same thermal cycle used for sputtering an overlying CdTe film. In subsequent studies, the optical properties of the annealed SLG/MgZn1-xO/CdTe. The capabilities of SE are explored in particular for determining the magnesium content x simultaneously with the film structure for correlations of both composition and thickness with the device performance.

References
Photon management can be used in III-V solar cells to increase absorption in the active region of the device. This can allow addition of low bandgap nanostuctures such as quantum wells, without the need for excessive strain balancing. It can also be used to harden space cells against high-energy, damaging particles. In this work, a model was first developed integrating simulations from electromagnetics and device physics software packages to evaluate absorption enhancement in, and performance of, III-V solar cells with both flat and textured back surface reflectors as well as front side scattering structures. Models predicted that a nanostructured GaAs cell with a pyramid-textured back surface reflector (BSR) could enhance absorption of in the nanostuctures by about 30% compared to a conventional upright design of the same thickness. The model also found that integrated light management could be used to radiation harden InGaP/GaAs/Ge space cells by thinning the GaAs subcell to less than half of the conventional thickness. In addition, simulation was compared to experiment focusing on the GaAs middle cell using combinations of textured back reflectors as well as partially reflective epitaxial DBR mirrors. For epitaxial DBR mirrors, internal and external quantum efficiency, as well as performance under 1-sun illumination shows nearly complete recovery of performance to optically thick conditions, while using half the thickness of GaAs absorber. As well, pyramidal and random back surface texturing has shown that optical path lengths much greater than 2 can be realized in practice. These results have been used to verify and refine the developed simulations and as well predict realistic end of life enhancements for typical space radiation conditions.

ET11.12.01
ZIF-67 Derived Nanostructures of Co/CoO and Co@N-Doped Graphitic Carbon as Counter Electrode for Highly Efficient Dye-Sensitized Solar Cells
Hongyu Jing, Suzhen Ren, Yantao Shi, Xuedan Song, Yonglin An and Ce Hao; State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China.

Here we present a facile one-step approach of using ZIF-67 as a sacrificial template for the synthesis of counter electrode (CE) catalyst of dye-sensitized solar cells (DSCs). Via controlling the carbonization temperature under N2 atmosphere, porous nanocomposites of Co, CoO and N-doped graphitic carbon are synthesized. Structural characterizations indicate that some cobalt nanoparticles are well embedded in an N-doped graphitic carbon matrix (a core-shell structure named as Co@NGC) while the other cobalt and cobalt oxide nanoparticles are exposed on the external surface (named as Co/CoO). Especially, the nanostructure of Co@NGC is more chemically stable than Co/CoO against etching of strong acid, for example, hydrochloric acid (HCl, 0.1 M). The performance of DSC using ZIF-67-850 (pyrolyzed at 850 °C) as CE yields a photoelectric conversion efficiency (PCE) of 7.92%, which is close to that of Pt CE (8.18%) in the liquid I3-/I- redox couple electrolyte. The excellent performance of ZIF-67-850 can be ascribed to the synergetic effects between the Co and CoO coupled with the nitrogen doped graphitic carbon. The cost-effective porous Co/CoO and Co@NGC nanocomposites show great potential for application in the field of high performance CE in solar cells.

ET11.12.02
Effect of Solvent and Substrate on the Surface Binding Mode of Carboxylate-Functionalized Aromatic Molecules
Janna Domenico1, Michael E. Foster2, Erik D. Spoerke2, Mark Allendorf3 and Karl Sohlberg1; 1Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, United States; 2Department of Materials Physics, Sandia National Laboratories, Livermore, California, United States; 3Department of Electronic, Optical, and Nano Materials, Sandia National Laboratories, Albuquerque, New Mexico, United States; 4Department of Energy and Transportation Technology Center, Sandia National Laboratories, Livermore, California, United States.

The efficiency of dye-sensitized solar cells (DSSCs) is strongly influenced by dye molecule orientation and interactions with the substrate. Therefore, understanding the factors controlling the surface orientation of sensitizing organic molecules will aid in the improvement of both traditional DSSCs and other devices that integrate molecular linkers at interfaces. Herein, we employ DFT calculations and ab initio molecular dynamics simulations to investigate the effect of substrate, solvent, and protonation state on the orientation of linker molecules relevant to DSSCs. In the absence of solvent, we predict that most carboxylic acid-functionalized molecules prefer to lie flat (parallel) on the surface, due to van der Waals interactions, as opposed to binding at a tilted orientation with respect to the surface that is favored by covalent bonding of the carboxylic acid group to the substrate. Once solvation effects are considered, however, most molecules are predicted to orient perpendicular to the surface. This approach can be extended to help understand and guide the orientation of metal–organic framework (MOF) thin-film growth on various metal–oxide substrates. Finally, a two-part analytical model is developed that predicts the binding energy of a molecule by chemical and dispersion forces on rutile and anatase TiO2 surfaces, and quantifies the dye solvation energy for two solvents. The model is in good agreement with the DFT calculations and enables rapid prediction of dye molecule and MOF linker binding preference on the basis of the size of the adsorbing molecule, identity of the surface, and the solvent environment. Results suggest that linker orientation can be controlled by choice of adsorbate, substrate, and solvent; this novel approach can be used to achieve a desired linker orientation and, by extension, MOF growth orientation in a MOF-based DSSC.

ET11.12.03
Solar Cell Degradation Due to Corrosion of Glass Substrates
Yuriy Kudriavtsev, Angelica Hernandez, Rene Asomoza-Palacio, Miguel Avendaño and Marcela Guerrero; CINVESTAV, Mexico City, Mexico.

Thin film solar cells meet a great interest because of their low price and a relatively high efficiency. Many technologists use glass substrates to deposit thin films forming a photo-diode structure. In the most popular configuration of solar cells, photons transmit through the glass substrate and a special transparent ohmic contact before arriving in a p-n junction region. It is evident that glasses with a highest possible transparency coefficient are necessary.
for the higher solar cell efficiency and the transmittance should be saved for the time of life of the cells. Borosilicate (b-s) and soda-lime (s-l) glasses are most popular substrates because of the mentioned reasons. In our previous studies, we demonstrated that interaction of atmospheric water vapor with silicate glasses results to their corrosion. A radical difference in the corrosion mechanisms was observed for s-l and b-s glasses. Hydration of a near surface layer occurs in s-l glasses, whereas hydrogenation - in b-s glasses. Both the hydration and the hydrogenation processes are stimulated strongly by the temperature. Typical solar cells work at elevated temperatures, which can reach 90-100°C in a sunny day, so the glass substrate corrosion for a working solar cell due to such glass surface corrosion looks very possible. We realized an experimental hydration of s-l and b-s glasses in a 100% water vapor atmosphere at 90°C for two months to simulate the glass substrate corrosion. Experimental samples were cut from commercial polished substrates. SIMS depth profiling analysis was performed to define the thickness of hydrated and hydrogenated layers, formed in the s-l and b-s glass samples, respectively. Optical transmittance coefficients were measured for the hydrated samples in comparison with the original ones. We concluded a radical decrease of the transmittance of the s-l glasses, caused by hydrated layer formation. An insignificant decrease of the transmittance coefficient was observed for b-s glass. We concluded that a special study should be realized directly to those of the glass substrates used for solar cell fabrication to avoid cells degradation due to glass surface corrosion.

**ET11.12.04**

**Origins of Voltage Deficit in Earth-Abundant Kesterite Thin-Film Solar Cells**

Samantha Hood, Sunghyun Kim, Ji-Sang Park and Aron Walsh

We realized an experimental hydration of s-l and b-s glasses in a 100% water vapor atmosphere at 90°C for two months to simulate the glass substrate corrosion. Experimental samples were cut from commercial polished substrates. SIMS depth profiling analysis was performed to define the thickness of hydrated and hydrogenated layers, formed in the s-l and b-s glass samples, respectively. Optical transmittance coefficients were measured for the hydrated samples in comparison with the original ones. We concluded a radical decrease of the transmittance of the s-l glasses, caused by hydrated layer formation. An insignificant decrease of the transmittance coefficient was observed for b-s glass.

**Reference**


**ET11.12.06**

**Coumarin-Based Europium Complexes for Luminescent Solar Concentrators**

Ahmad Alsaleh, Anita C. Jones and Neil Robertson; University of Edinburgh, Edinburgh, United Kingdom.

Solar energy is the most promising source to address the growing energy needs of the planet. Luminescent solar concentrators (LSCs) can collect light over a large area and concentrate it onto a small area of solar cells in order to enhance the performance of the solar cells. The light is absorbed by a transparent sheet containing luminescent dyes and the emission is transported by total internal reflection to the edge of the plate where photovoltaic cells are positioned. β-diketonate-based Europium (III) complexes are promising candidates for use as dyes in LSCs due to their high quantum yields, extended absorption window, minimal overlap between the absorption and emission spectra, and narrow emission band. We will report a study of β-diketonate coumarin-based Lanthanide complexes aimed at optimising their luminescence characteristics by ligand design. Coumarins are well-known organic dyes that have served as antennae for LSC applications. We will report the preparation and photophysical properties of two Europium complexes, [Eu(L)_3X_2] where, X=DPEPO, L=7-methoxy or 7-diethylamine coumarin derivative, and investigation of their incorporation in several polymer films.

**Acknowledgment**

We are grateful to Dr. álvaro Cañete M. (Pontificia Universidad Católica de Chile) for the gift of the coumarin ligands.

**References**


**ET11.12.07**

**Fast Hall™—A New Method for Measuring Low Mobility Thin-Film Materials**

Jeffrey R. Lindemuth; Lake Shore Cryotronics, Inc., Westerville, Ohio, United States.

The Hall effect is the primary method to measure carrier density, mobility and carrier type in materials. The most common method for measuring the Hall effect in semiconductors uses a DC magnetic field. The community has developed a well-defined protocol for removing spurious voltages in the measurement. Reversing the magnetic field and subtracting the measured voltages will remove any voltage that does not depend on the magnetic field. As research interest in studies of the transport mechanisms expands beyond semiconductors, with moderate to high mobility, the standard DC field method reaches its limit of applicability. We present a new measurement protocol based on the reverse-field reciprocity theorem. The reverse-field reciprocity theorem considers a four port network with current inputs and voltage measurements and an applied magnetic field. If a current is applied to two of the inputs (say 1 and 3) and a positive field B a voltage (V) is measured on terminals 2 and 4. This voltage can depend of the magnetic field V(B). If the current and voltage leads are interchanged, current on terminals 2 and 4, voltage measured between 1 and 3, V(1) and V(2). The theorem states that V(2) = V(1) - V(B). This is a very general result; the only requirement of the material is that it is electrically linear. This means that thermoelectric voltages require special treatment. In the above example, V(2) = V(1) - V(B) removes the offset voltage without physically reversing the magnetic field. Measurements using the Fast Hall™ method on InAs, IGZO, ZnO, pyrite, Graphene and GaAsSb have demonstrated excellent agreement between measurements using DC or AC field hall and Fast Hall. The Fast Hall method can preform up to 100 Hall measurements per second. The high speed of the measurements greatly reduces the
effects of thermal drift and self-heating of the sample during the measurement. Thermal drift is one of the major contributions to noise in hall measurements of low mobility and thin film samples. The Fast Hall method increases measurement speed, extends the range of mobility that can be measured using DC field methods. The method is applicable to both single carrier materials and multi-carrier materials.

**ET11.12.08**

Air-Processed Defect-Free ZnO Nano-Particles for Solution Processed Photovoltaic Cells **Yuhui Ma**, Xiwen Xu, Yuemin Xie, Menglin Li and Sai-Wing Tsang; Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

Solution-processed ZnO nanoparticles (ZnO-NPs) have been widely used as electron transporting layer (ETL) in developing high efficiency organic photovoltaic (OPVs) cells. However, the ZnO-NPs are known to be sensitive to oxygen and moisture in air with strong trap emission in the visible (400-700nm) region. Consequently, those reported high efficiency OPVs with ZnO ETL were fabricated in inert environment. This limits the large-scale industrial implementation of low-cost and high-efficiency photovoltaic cells. Here, we will demonstrate an approach to achieve defect-free ZnO NPs thin film processable in ambient air. It is found that the trap states in ZnO are rapidly induced by oxygen and moisture within a few seconds exposure in air. Interesting, this trap developing process is complete with the ultra-violet (UV) irradiation. There exists an operation widow that the trap states can be drastically reduced in very short period of UV irradiation time with less than 10s. However, they start growing gradually with continuous irradiation in longer time for more than 1min. Using the air-processed ZnO-NPs ETL with short time UV irradiation, it is found that different donor:acceptor OPVs can achieve high efficiencies comparable with those fabricated in inert environment. By eliminating the trap states, it mainly reduces the interfacial recombination with enhanced fill-factor and prolonged device lifetime. The un-encapsulated devices stored in ambient air can retain more than 80% of the initial efficiency.

**ET11.12.09**

Synthesis and Characterization of SnO2 and TiO2 Nanoparticles Doped with Li or Ni and Hybrid Composites **Antonio Vázquez**, María Taeño, David Maestre, Julio Ramírez-Castellanos and Ana Cremades; Física de Materiales, Facultad de CC. Físicas, Universidad Complutense de Madrid, Madrid, Spain; 1Química Inorgánica I, Facultad de CC. Químicas, Madrid, Spain.

Wide bandgap semiconducting oxides, such as SnO2 and TiO2, have demonstrated potential applicability in numerous fields such as optoelectronic devices, catalysis, gas sensing or energy storage, which can be improved by controlling the dimensions, morphology, doping and composition of these materials. Moreover, hybrid composites combining advantages of inorganic and organic compounds are emerging as low cost materials with promising application in photovoltaic and energy storage devices [1]. These hybrid composites can retain the advantages of their organic and inorganic counterparts and even exhibit new synergetic properties, hence gaining increasing research attention in the last years.

In this work, rutile SnO2 and anatase TiO2 nanoparticles have been synthesized by a co-precipitation method based on hydrolysis, using SnCl2·2H2O or Ti(OBu)4, respectively, as precursors. For the synthesis of Ni or Li doped nanoparticles, stoichiometric amounts of NiCl2·6H2O or LiCl, respectively, were added as precursors. Large amounts of nanoparticles with high crystallinity, good homogeneity and dimensions ranging from 8 to 10 nm are obtained with this method. These nanoparticles have been initially characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), Raman spectroscopy, X-ray absorption spectroscopy (XAS), photoluminescence (PL), and cathodoluminescence (CL). The presence of dopants induces changes in the dimensions of the nanoparticles, and in their structure of defects and optical and electronic properties. In this work, nanoparticles with reduced dimensions were achieved by Ni doping, while Li doping induces an enhancement of the luminescence, both for SnO2 and TiO2. Moreover, changes in the Raman signal, mainly in the Eg modes associated with O-Ti-O symmetric stretching vibrations in anatase TiO2, and vibrations of O anions along the c axis in SnO2 were observed.

In this work hybrid compounds made with PEDOT:PSS functionalized with the undoped or doped SnO2 or TiO2 nanoparticles, synthesized by hydrolysis, were deposited onto Si substrates at room temperature by spin-coating, thus involving low cost and rapidity, as compared with the commonly used vacuum-based techniques. The thickness of the composite layers fabricated in this work is around 120 nm, as measured by atomic force microscopy (AFM). The presence of inorganic SnO2 or TiO2 nanoparticles could add functionality to the hybrid composite and broaden its related applicability in photovoltaic devices [1], photocatalysis, optoelectronics and bioapplications, as some examples, due to charge transfer and variations in the local electronic structure of the hybrid material which can lead to improved performance.


**ET11.12.10**

Improving Charge Extraction from Bismuth Oxyiodide Photovoltaics with 2D Metal Dichalcogenide Transport Layers **Tahmida N. Huq**, Rosie Baines, Robert L. Hoyer, Pin-chun Shen and Judith L. MacManus-Driscoll; 1Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 2Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 3EPSRC Centre for Doctoral Training in Graphene Technology, University of Cambridge, Cambridge, United Kingdom; 4Research Lab of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Bismuth oxyiodide (BiOI) has recently been shown to be a promising lead-free alternative to halide perovskites for photovoltaics. BiOI replicates the electronic structure of halide perovskites, and is predicted to show tolerance towards anti-site and vacancy defects. Notably, BiOI thin films have been found to be at least two orders of magnitude more air-stable than methylammonium lead iodide. Although record external quantum efficiencies of 90% have been achieved, the power conversion efficiency (1.8%) is limited by inefficient hole extraction in an ITO|BiOI|ZnO|Au device stack. This is due to downwards band-bending of BiOI at the BiOI|ZnO interface caused by poor energetic matching of the BiOI (work function of 5.1 eV) with NiOx (work function of 4.8 eV). Higher work function materials are required to overcome this barrier. In this work, 2d molybdenum sulphide (MoS2) is investigated as an alternative hole transport layer due to its work function tunability. Through plasma treatment, the work function is increased to >5.1 eV. We use photoemission spectroscopy to probe the MoS2|BiOI interface, and our detailed studies reveal an upwards band-bending which can enable improved hole extraction. We explore the modification of chemical vapour transport BiOI growth conditions required as a result of the change in surface chemistry at the new hole transport layer interface. SEM microscopy and X-ray diffraction reveal that these modifications lead to an improvement in orientation and morphology (i.e. more compact and pinhole free) of the BiOI films, essential for shunt-free devices. Through these optimisations and subsequent characterisation, we are able to increase our understanding of the interfaces in the device stack which is crucial for achieving at least 4% efficient devices.


**ET11.12.11**

Tomographic Imaging of PbSe Quantum Dot Superlattices for PV Applications **Xiaolei Chu**, Hamed Heidari, Alex Abelson, Caroline Y. Qian, Matt Law and Adam J. Moulé; University of California, Davis, Davis, California, United States; 2University of California, Irvine, Irvine, California, United States; 3University of California, Irvine, California, United States; 4University of California, Irvine, Irvine, California, United States; 5University of California, Davis, Davis, California, United States; 6University of California, Irvine, Irvine, California, United States; 7University of California, Los Angeles, Los Angeles, California, United States; 8University of California, Los Angeles, Los Angeles, California, United States; 9University of California, Irvine, Irvine, California, United States; 10University of California, Los Angeles, Los Angeles, California, United States; 11University of California, Irvine, Irvine, California, United States; 12University of California, Los Angeles, Los Angeles, California, United States.
Ordered PbS and PbSe quantum dot (QD) arrays have demonstrated multiple exciton generation in response to photo excitation by high energy photons. This inherently quantum material demonstrates a pathway to photovoltaic efficiency above the Shockley limit if ordered and defect free super-lattices of these QDs can be fabricated. Here we use high-resolution tomographic imaging of PbSe super-lattices to study the material order resulting from self-assembly and ligand exchange. Quantum dots are synthesized using long chain ligands to ensure a narrow size distribution. Superlattice arrays of long-chain ligand QDs self-assemble at liquid-liquid interfaces into ordered superlattice films with hexagonal packing. After the film has formed, in-situ ligand exchange is used to reduce the distance between QDs, leading to recrystallization of the super-lattice to a distorted simple cubic array. This array has structural defects including twinning between domains, point defects, and bridging between some neighboring QDs, that leads to a heterogeneous energy landscape. The super-lattice order, seen at the top interface of the film, is accessible using SEM imaging and is often very different from the arrangement of particles in the center of self-assembled films. We use tomographic reconstruction of STEM images to determine the position of QDs with nm precision and bridging between particles. We show how defects in the superlattice structure effects the charge localization.

ET11.12.12
Layered Hexagonal Oxycarbides, M_{n=1}AO_{2}X_{n} (M=Sc, Y, La, Cr and Mo, A=Ca, X=C)—Novel Photovoltaic Ceramics
Zhenu Wang, Xin Chen and Chunming Niu; School of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China.

Solar energy is increasingly becoming an integrated part in energy spectra worldwide and promises to greatly relieve the world from the shackles of fossil fuels. Development of high performance solar cells depends on the discovery of new photovoltaic materials. The search for the new photovoltaic (PV) materials has been intensified since the invention of the perovskite solar cells. 1 The rapid development of computational methods and tools deepens our understanding of existing materials and provides an insightful guide for experiments. 2 And most importantly, it also makes more and more feasible to discover novel materials via computer simulations, such as solid state electrolytes, electrocatalytic materials, two-dimensional (2D) semiconductors, and perovskite solar cell materials.

In the recent years, advanced functional ceramics attract broad interests due to its outstanding mechanical properties, such as high strength and hardness, excellent wear resistance and good frictional behavior. 3 Given excellent dimensional stability as well as the ability to withstand corrosive environments, the applications of functional ceramics in the semiconductor industry is desirable.

A family of layered hexagonal oxycarbides and oxynitrides with the general formula, M_{n=1}AO_{2}X_{n} (MAOX) is discovered using first-principles DFT calculations, where \( n=1\), \( M \) is an early transition metal, \( A \) is an alkaline earth metal in Group IIA or a late transition metal in Groups IB and IIB, \( X \) is C and/or N. 4 The family can be divided into three sub-groups of 2121, 3122 and 4123 with \( n=1, 2 \) and 3, respectively. Thermodynamically, the MAOX phases are very stable. Tuning the composition, MAOX can be metals, semimetals or semiconductors. In this report, we discuss five 2121 oxycarbide MAOX semiconductors, \( M \) is Sc, Y, La, Cr and Mo. Their band gaps are from 0.39 to 1.14 eV. They have superior PV properties and their theoretical solar cell efficiencies are on par with GaAs. Particularly, the efficiency of \( Cr_{2}CaO_{4}C \) reaches 27.7% that is above 90% of the Shockley-Queisser (SQ) limit. Furthermore, amazingly, the five MAOX semiconductors possess outstanding strength and machinability, e.g., their Young’s moduli are comparable to ceramics and MAX phases, and Poisson’s ratios higher than MAX and even comparable to metals. MAOX semiconductors are promising multifunctional ceramics. The unique combination of the photovoltaic and mechanical properties suggests great potentials for advanced solar cell applications.


ET11.12.13
Nanostructured Hybrid Semiconducting Materials as Efficient Photodetectors
Dawit M. Gedamu1, Ivy Asuo2-3, Luis Felipe Gerlein4, Ibrahima Ka4, Riad Nechache1, Suchismita Basu1, Jaime Benavides-Guerrero1 and Sylvain Cloutier1; 1École de technologie supérieure, Montreal, Quebec, Canada; 2inrs-/emt, Varennes, Quebec, Canada.

Layered Hexagonal Oxycarbides, M_{n=1}AO_{2}X_{n} (M=Sc, Y, La, Cr and Mo, A=Ca, X=C)—Novel Photovoltaic Ceramics
Zhenu Wang, Xin Chen and Chunming Niu; School of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China.

Solar energy is increasingly becoming an integrated part in energy spectra worldwide and promises to greatly relieve the world from the shackles of fossil fuels. Development of high performance solar cells depends on the discovery of new photovoltaic materials. The search for the new photovoltaic (PV) materials has been intensified since the invention of the perovskite solar cells. 1 The rapid development of computational methods and tools deepens our understanding of existing materials and provides an insightful guide for experiments. 2 And most importantly, it also makes more and more feasible to discover novel materials via computer simulations, such as solid state electrolytes, electrocatalytic materials, two-dimensional (2D) semiconductors, and perovskite solar cell materials.

In the recent years, advanced functional ceramics attract broad interests due to its outstanding mechanical properties, such as high strength and hardness, excellent wear resistance and good frictional behavior. 3 Given excellent dimensional stability as well as the ability to withstand corrosive environments, the applications of functional ceramics in the semiconductor industry is desirable.

A family of layered hexagonal oxycarbides and oxynitrides with the general formula, M_{n=1}AO_{2}X_{n} (MAOX) is discovered using first-principles DFT calculations, where \( n=1\), \( M \) is an early transition metal, \( A \) is an alkaline earth metal in Group IIA or a late transition metal in Groups IB and IIB, \( X \) is C and/or N. 4 The family can be divided into three sub-groups of 2121, 3122 and 4123 with \( n=1, 2 \) and 3, respectively. Thermodynamically, the MAOX phases are very stable. Tuning the composition, MAOX can be metals, semimetals or semiconductors. In this report, we discuss five 2121 oxycarbide MAOX semiconductors, \( M \) is Sc, Y, La, Cr and Mo. Their band gaps are from 0.39 to 1.14 eV. They have superior PV properties and their theoretical solar cell efficiencies are on par with GaAs. Particularly, the efficiency of \( Cr_{2}CaO_{4}C \) reaches 27.7% that is above 90% of the Shockley-Queisser (SQ) limit. Furthermore, amazingly, the five MAOX semiconductors possess outstanding strength and machinability, e.g., their Young’s moduli are comparable to ceramics and MAX phases, and Poisson’s ratios higher than MAX and even comparable to metals. MAOX semiconductors are promising multifunctional ceramics. The unique combination of the photovoltaic and mechanical properties suggests great potentials for advanced solar cell applications.

chemical vapor deposition. Replacing the currently dominant, but expensive gold top electrode with transparent graphene not only reduces the cost of device fabrication, but also allows for illumination of the device through the top electrode. Our results have shown that this leads to increased density of photo-generated carriers, evidenced by >10% increase in $J_{SC}$.

**ET11.12.15**

*Improve the Photo-Stability of Polymer Solar Cells by Controlling the Chemical Structure of Photoactive Materials* Rasool Shafke1, 2, Vu Van Doan1, 2, Chang Eun Song1, 2, Hang Kun Lee1 and Won Suk Shin1, 2; 1Energy Materials Research Center, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Advanced Materials and Chemical Engineering, University of Science and Technology, Daejeon, Korea (the Republic of).

To commercialize the polymer solar cells many conditions should be satisfied such as efficiency, process and stability. Recently many scientists are interested in the stability of the polymer solar cells, but most of the researches are hovering at thermal stability. But real challenges are in photo-stability and the burn-in loss during exposed on the sun light is one of the biggest challenges to go to the market. Lost more than 40% of their initial efficiency in just 24 hours after exposing to 1 sun condition is common for polymer solar cell devices. This burn-in loss does not come from the decomposition of the photoactive materials but rather caused by the electro- and physical-properties of the photoactive materials. To overcome the burn-in loss, we tried two approaches. First one is inserting an appropriate interlayer for inverted solar cells. Second approach is design new photoactive materials which reduce the burn-in loss. Here we present the improved photo-stability results by applying elaborately designed photoactive materials.

**ET11.12.16**

*Hydrogen Motility at Reduced-Dimension Interfaces in Proximity to Near Semiconductor-Metal Boundaries and Dislocations* Jonathon Mitchell; National Institute of Advanced Industrial Science and Technology, Koriyama, Japan.

Understanding of the fundamental physical processes underlying key material properties in electronically active interfaces has increased importance with reduced-dimension devices like FET, MOS and photovoltaics. As in many of these devices, the inclusion of non-natives like Hydrogen, Nitrogen and Oxygen, are known to strongly affect the electronic and structural properties of many materials and have particular importance in semiconductors for binding defects, enhancement or suppression of electrical activity, long-term stability and operation. Acting as an isolated interstitial impurity, amphoteric hydrogen occupies different lattice sites and can counter the conductivity of extrinsic dopants. Nitrogen is largely impeded by an anomalous optical saturation effect, and similarly Oxygen can be impacted by variable voltage influencing dielectric permittivity and charge separation. However, the mechanisms involved are more complex than the simple application of a single hydrogen, nitrogen or oxygen to the semiconductor bond. Although tracking individual particles through the sub-lattice interface remains difficult, previous theoretical and simulation study of these interfaces has provided additional information which resolves current experimental observations. Utilising an adaptive moving-mesh in Eulerian space with Lagrangian point-aggregation for a large 904 site interface surface with bookkeeping in z-space, our model has compared the smoother particle hydrodynamics with real-time and cumulative particle transport solids. Essentially rendering a recursive output for predictive yield of electron charge transport at or near semiconductor-metal interfaces.

In this work we evaluated planar and also surfaces with sharp discontinuities from manufacture and handling, comparing the simulation to the intermediate and long-term interface properties. Non-Gaussian distribution agreed with the observed preferential diffusion probabilities and pseudo-sparse motilities according to discontinuities including mecha-mechanical shearing, grain orientation, and chemical orientation of defect alignment. New information is obtained concerning the intergranular properties thermal characteristics, as well as the presence of distinct profiles seemingly dependent to some extent on the binding algorithm of the semiconductor between the bulk and extending through the interface. For MOS-like devices (including photovoltaic), oxygen and hydrogen both introduced long-term parasitic conductivity, while the response for nitrogen and hydrogen was suppressed. This describes the suitability of nitrogen based environment during the semiconductor fabrication prior to encapsulation on the long-term performance and reliability of thin, flexible devices.

**ET11.12.17**

*Exploring γ-In$_2$(Se$_{1-x}$Te$_x$)$_3$ Alloys as Photovoltaic Materials* Wei Li, Tianshi Wang and Anderson Janotti; Materials Science and Engineering, University of Delaware, Newark, Delaware, United States.

γ-In$_2$Se$_3$ (hexagonal crystal structure, space group P6$_3$) has a direct band gap of ~1.8 eV with high absorption coefficients near the band edge. Alloying with Te could allow for tuning the band gap, widening the wavelength range in the absorption spectra, adding great flexibility to device design. Using density functional theory with the HSE06 hybrid functional, we investigate the electronic and optical properties of γ-In$_2$Se$_3$ and γ-In$_2$(Se$_{1-x}$Te$_x$)$_3$ alloys. The calculated band gap of 1.84 eV for γ-In$_2$Se$_3$ is in good agreement experimental data, and the absorption coefficient is found to be as high as that in direct gap III-V semiconductors. We also find that incorporation of Te, forming γ-In$_2$(Se$_{1-x}$Te$_x$)$_3$ alloys, is an effective way to tune the band gap from 1.84 eV down to 1.23 eV, thus covering the optimal band gap for single layer solar cells. We determined the band alignments between γ-In$_2$Se$_3$ and γ-In$_2$(Se$_{1-x}$Te$_x$)$_3$, and their band edge positions with respect to vacuum level. Our results indicate that γ-In$_2$Se$_3$ has a tendency for displaying n-type conductivity.

**ET11.12.18**

*Synthesis and Measurement of Optical and Transport Properties of Promising Metal Oxide Light Absorber CuBiW$_2$O$_8$ with 1.5 eV Band Gap* Lin Zhou, Guangjiang Li, Edan Bainglass, Pranab Sarker1, Lyubov V. Titova2, Muhammad N. Huda1 and Pratap M. Rao; 1Department of Physics, The University of Texas at Arlington, Arlington, Texas, United States; 2Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 3Department of Mechanical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Metal oxide semiconductors with moderate band gaps are highly desired for high-efficiency, low-cost, stable, and environmentally-friendly solar cells. CuBiW$_2$O$_8$ (CBTO) has been predicted by density functional theory (DFT) to be a promising metal oxide light absorber with band gap of 1.43 eV. However, this semiconductor has not been experimentally synthesized so far, and the optical and transport properties have not been measured. Here, CBTO was successfully synthesized for the first time by solid-state reaction in a Cu-rich environment, and identified by X-ray diffraction. The light absorption spectrum of CBTO was measured, and a light absorption edge of 820 nm (~1.5 eV) with absorption coefficient of 10$^4$ cm$^{-1}$ at 700 nm, was observed. Electron mobility in CBTO (~200 cm$^2$ V$^{-1}$ s$^{-1}$) was determined by time-resolved THz spectroscopy. This CBTO showed promising performance as a photocathode for photoelectrochemical water reduction. However, the photovoltaic performance of the CBTO solar cell is still limited by granular CBTO film quality and impurities introduced by inter-diffusion between CBTO and other layers in the cell. By modifying the synthesis methods, we believe CBTO with ~1.5 eV band gap and promising charge mobility can achieve higher efficiency than Cu$_2$O, which is the best-performing metal oxide photovoltaic absorber to date.

Reference:
Silver (Ag) has been incorporated at the copper sub-lattice sites in the quaternary compound Cu$_2$ZnSnS$_4$ (CZTS) which is being under intense investigation as an absorber material for the photovoltaic application. Thin films of the resulting quaternary compound (Ag$_x$Cu$_{1-x}$)$_2$ZnSnS$_4$ (0 ≤ x ≤ 1) show remarkable changes in their microstructure and electronic properties. With the increasing Ag content, the grain size increased from 0.13 to 2 μm which could be attributed to the liquid assisted grain growth mechanism. While the observed increase in the optical band gap from 1.5 to 2.0 eV could be attributed to the influence of d-orbitals of Ag atoms on the valence band edge of the CZTS compound. The charge carrier density decreased by two orders of magnitude with only 4 atomic % Ag (x = 0.04) incorporated in the films which indicate the strong influence of Ag$_{32}$ on the density of Cu$_{32}$ and V$_{Cu}$ point defects which are the major acceptors in CZTS. The reduction of these intrinsic point defects is also being reflected in the observed decrease in the Urbach energy from 336 meV (for x = 0.00) to 230 meV (for x = 0.21). This has been further correlated with the ordering-disordering detected by the near-resonant Raman scattering. These observed changes with increasing Ag content could possibly be used for tailoring the properties of CZTS for the better performance of CZTS based solar photo voltaics.

ET11.12.20 Structural and Electronic Properties of the Pentenary Compound (Ag$_x$Cu$_{1-x}$)$_2$ZnSnS$_4$ Synthesized via Solution Route Jitendra Kumar and Sarang Ingole; Indian Institute of Technology Kanpur, Kanpur, India.

Silver (Ag) has been incorporated at the copper sub-lattice sites in the quaternary compound Cu$_2$ZnSnS$_4$ (CZTS) which is being under intense investigation as an absorber material for the photovoltaic application. Thin films of the resulting quaternary compound (Ag$_x$Cu$_{1-x}$)$_2$ZnSnS$_4$ (0 ≤ x ≤ 1) show remarkable changes in their microstructure and electronic properties. With the increasing Ag content, the grain size increased from 0.13 to 2 μm which could be attributed to the liquid assisted grain growth mechanism. While the observed increase in the optical band gap from 1.5 to 2.0 eV could be attributed to the influence of d-orbitals of Ag atoms on the valence band edge of the CZTS compound. The charge carrier density decreased by two orders of magnitude with only 4 atomic % Ag (x = 0.04) incorporated in the films which indicate the strong influence of Ag$_{32}$ on the density of Cu$_{32}$ and V$_{Cu}$ point defects which are the major acceptors in CZTS. The reduction of these intrinsic point defects is also being reflected in the observed decrease in the Urbach energy from 336 meV (for x = 0.00) to 230 meV (for x = 0.21). This has been further correlated with the ordering-disordering detected by the near-resonant Raman scattering. These observed changes with increasing Ag content could possibly be used for tailoring the properties of CZTS for the better performance of CZTS based solar photo voltaics.

ET11.12.21 Band Alignment at the Back Contact of CdTe Devices—What Bands Need to Align? Adam Phillips, Geethika K. Liyanage, Fadhil K. Alfadhiili, Randy Ellingson and Michael J. Heben; University of Toledo, Toledo, Ohio, United States.

The deep valence band position of CdTe (~5.9 eV) makes it difficult to form an Ohmic back contact in CdTe devices. Back contact formation typically results in significant downward band bending in the CdTe that forms an energetic barrier to hole transport. Historically, the addition of Cu at the back of CdTe results in a doped interface region in which the width of the band bending is limited, effectively reducing the barrier. In addition to limiting hole transport, the band bending in the conduction band affects electrons to the interface. While the Cu doping reduces the width of the band bending, the achievable doping levels do nothing to repel the electrons from this interface. Addition of semiconducting buffer layers with a conduction band higher than that of CdTe have been incorporated into devices to prevent the electrons from recombining in the back contact and are often referred to as electron reflectors. Recent numerical modeling of CdTe devices has shown that band alignment of the conduction band at the front contact is critically important to device performance. In this case, the a modest 0.1-0.2 eV “spike” at the emitter/CdTe interface results in the best device performance even though, energetically, it would appear to restrict electron flow. Recently, we used numerical modeling to understand how the band alignment at the back contact affects device performance. We showed that in an ideal case, one in which the CdTe/semiconductor buffer interface is outside the depletion regions, band alignment of the valence bands plays a significantly larger role than band alignment of the conduction bands, and, in fact, the overall device efficiency is independent of the conduction band offsets at the back of the device. In this presentation, we will discuss these generalized results and how to apply these results to real world applications.


ET11.12.22 Modeling PV/TPV Devices Based on Exact Analytical Solution of the Generalized Shockley-Queisser Model Andrei Sergeev, Sunny Karnani and Christopher M. Waits; Army Research Laboratory, Adelphi, Maryland, United States.

Currently, interplay of electron and photon processes in the open-circuit regime is understood substantially better than that in the regime with optimal conversion of electromagnetic power. First, the open-circuit regime is well described by classical thermodynamics. Second, there is exact analytical solution for the open-circuit voltage as a function of photon flux characteristics. This analytical solution has been generalized to include other losses due to nonradiative recombination processes in terms of luminescence quantum yield. Therefore, analysis of the open circuit regime is very often employed for optimization of electron and photon processes related to PV conversion. The Shockley-Queisser limit is described by the endoreversible thermodynamics, which includes irreversible processes and entropy generation due to thermal energy transfer from the radiation source to the solar cell. Despite extensive theoretical research, the analytical expression for the maximal efficiency as a function of photon flux characteristics and electronic properties has not been reported yet.

For advanced modeling of PV/TPV devices with sophisticated photon management we obtained exact solution of the generalized Shockley – Queisser model and developed original modeling tool. Our modelling takes into account spectral absorption/emission characteristics, nonradiative recombination processes, and photon management. For noninteracting electrons and for electrons interacting via Auger processes we obtained exact analytical solution for photovoltaic efficiency, output power, and all other PV characteristics. The obtained solution provides mathematical base of PV conversion and endoreversible thermodynamics controlled by the chemical potential. We derive exact equations for useful energy, emission losses, and total thermal losses (electron-phonon relaxation and nonradiative recombination) per absorbed photon. The developed formalism is very convenient for analysis of analysis of photocarrier kinetics. In particular, we derived the universal relation between the optimal photocarrier collection time and the photogenerated electron lifetime with respect to all radiative and nonradiative processes. Let us highlight that due to the short photocarrier collection time with respect to the photocarrier lifetime, the photocarrier kinetic and transport processes in the optimal power regime may differ from the processes in the open circuit regime. Our preliminary analysis also shows that in traditional devices without photon management, it is not possible to realize simultaneously both high absorption and fast photocarrier collection, which is required by the optimal collection rate. In PV/TPV devices with enhanced photon trapping and recycling, the thickness of the base may be reduced below the characteristic value, at which the diffusion processes do not limit the optimal photocarrier collection.

ET11.12.23 Solution-Processed Vanadium Oxide as an Efficient Hole Injection Layer for Phosphorescent Organic Light-Emitting Diodes Deepak K. Dubey, Yu C. Lo, Rohit Ashok Kumar Yadav, Sujith Sudheendran Swamyprabha and Jwo-Huei Jou; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu City, Taiwan.

Organic light-emitting diodes (OLEDs) have attracted significant attention in both industry and academic research because of the increasing demand of flat panel displays for televisions, smartphones and tablets, etc., and solid-state lighting applications. With the development of highly efficient materials, innovative fabrication and out-coupling techniques, the power efficacy of OLEDs can reach as high as, >100 lm/W, meeting the requirements for flat panel display and lighting applications. Nevertheless, most OLEDs with high efficiency are fabricated by thermal evaporation, which is suffering from the high manufacturing cost and difficulties to realize large area devices. To address these issues, all or partly solution-processed OLEDs offer an opportunity to
significantly lower the fabrication cost and also enable the application of large area devices and flexible substrates, thanks to its compatibility to roll-to-roll processing. However, relatively low efficiency is often a challenge for solution-processed OLEDs. To achieve high efficiency, hole injection/transport layers (HIL/HTL) and the charge blocking layers are usually incorporated to maintain charge balance and to confine the excitons in the emitting layer. Most solution processed OLEDs use PEDOT: PSS (polyethylene dioxythiophene :polystyrenesulfonate) as a hole injection material because of its high transparency, high work-function and high conductivity. However, PEDOT: PSS exhibits an acidic and hygroscopic nature, which induces the corrosion of ITO electrodes, resulting in the decrease of device performance lifetime. Therefore, much effort has been devoted to finding a new substitute for PEDOT: PSS. In this work, we develop a solution processed vanadium pentoxide (V2O5) as an alternative. The proposed approach can be easily processed under the simple conditions of room temperature and a water-free and solution-based process, which distinguish this approach from vacuum thermal evaporation or temperature annealing processes. OLEDs fabricated with V2O5 HIL exhibit a current efficiency of 64.3 cd/A, a power efficiency of 57.4 lm/W and an external quantum efficiency of 19.2% at the brightness of 100 cd/m², which are respectively 21, 23 and 31% higher to those fabricated with a conventional PEDOT: PSS HIL. Moreover, by substituting the problematic PEDOT: PSS with the inorganic V2O5, the operating voltage and maximum luminance of the OLEDs is also substantially improved. Our study demonstrates that the presented new approach can serve as a new and simple route for the emerging technologies of low-cost and large-scale organic optoelectronic devices.

ET11.12.24
Solar Photo-Crystallization in the Production of Thin-Film Solar Cells
Jesus Canistran Martínez, Laura Guerrero Martínez, Perla Yoloxóchitl García Ayala, Alessandra Beauregard León, M.T. Sanhanta Murri Nair and P. Karunakaran Nair; Universidad Nacional Autonoma de Mexico, Temixco, Mexico.

We present an innovative method of crystallization under concentrated sunlight of antimony sulfide selenide thin films in solar cell structure: F-doped SnO2 (FTO)/CdS/Sb2S3-Se3-x/C. Here, CdS n-window thin film of 90 nm in thickness, as well as the p-absorbers of Sb2S3-Se3-x thin films of 300 nm in thickness are produced by chemical deposition at 80 °C. Colloidal graphite paste is applied on the absorber films so as to define cell areas of ~0.25 – 1 cm². The absorber films require heating at 250 – 300 °C to transform them to crystalline phase, which till now required heating in a vacuum oven under nitrogen atmosphere. We report that under clear-sky condition, concentrated sunlight (115 – 215 suns) directed toward the absorber film by a glass lens 8.5 cm in diameter helps achieve this crystallization. The approach has the added advantage that it is a rapid thermal processing technique as well, which minimizes loss of volatile components of the absorber film (S and Se) when heated in conventional way. The absorption of concentrated sunlight at the absorber-electrode interface helps increase the temperature toward the crystallization temperature. The acrylic-based graphite paint also encapsulates the cell, thereby eliminating the need for a vacuum environment to prevent degradation of the cell through oxidation. Solar cell produced this way has open circuit voltage of 0.46 V, short circuit current density of 16 mA/cm² and conversion efficiency of 3 % at this stage. The deposition technique as well as the cell processing described here are low-capital intensive. Hence it offers an accessible alternative in the preparation of this type of solar cells.

ET11.12.25
Functional Prototype Modules of Chemically Deposited Antimony Sulfide Selenide Thin Films
Laura Guerrero Martínez, Perla Yoloxóchitl García Ayala, José Diego Gonzaga Sánchez, Alessandra Beauregard León, M.T. Sanhanta Murri Nair and P. Karunakaran Nair; Universidad Nacional Autonoma de Mexico, Temixco, Mexico.

Functional photovoltaic modules of 7 cm² in active area and open circuit voltage 3.3 V and 20 mW power capable of lighting blue-light emitting diode (LED) were prepared by chemical deposition. For this R & D, first a chemically deposited CdS thin film of 100 nm in thickness was prepared on a commercial F-doped tin oxide coated glass (FTO) of sheet resistance 7 Ω. On this, a thin film (300-350 nm) of antimony sulfide selenide was prepared by chemical deposition at 80 °C in two successive depositions lasting 7-8 h from solution containing potassium antimony tartrate, triethanolamine, ammonia (aq), thiourea, thiourea and selenourea. Graphite paste in acrylic base was painted on area 1 cm²; a total of 7 such area painted on each FTO-coated glass cut to 2.5 cm x 7.5 cm. Antimony chalcogenide thin films obtained from chemical deposition are amorphous in nature and they require heating at 270 – 310°C to crystallize them. In this work the heating was done at 300°C during 30 min in nitrogen ambient at 20 Torr. After these, the FTO coating was scribed using carbonic acid point; and the cells were demarked by etching. Colloidal silver paint was applied on the graphite electrode and on the FTO coating along the periphery. Current-voltage characteristics of the cells were measured using solar simulator under standard conditions as well as under the sun (925 W/m²) near mid-day at 24 °C. Average values of the cell parameters are presented: Voc= 0.47 V; Jsc= 18 mA/cm² and conversion efficiency, 3.9%.

ET11.12.26
Spray-Deposited CdS/PbS Solar Cell
Nagendra Dhakal1, Seth Calhoun1, Robert E. Peale1, Saiful Khondaker1 and Isaiah Oladeji2; 1University of Central Florida, Orlando, Florida, United States; 2Siism Thinfilms LLC, Orlando, Florida, United States.

We demonstrate photovoltaic action for a thin-film CdS/PbS heterojunction solar cell fabricated by aqueous spray deposition using earth-abundant elements as a potentially flexible, low-cost solar-cell technology. The structure comprises borofloat glass substrate, fluorine-doped tin oxide as transparent current collector, CdS window layer, and PbS absorber layer. Gold is deposited as ohmic contact to the PbS and light is incident through the substrate. The current-voltage curves in the dark are diode like with threshold voltage ~0.6 V. Under 1 sun illumination with 1.5 air-mass filter, the short circuit current density is ~ 4 microAmp/mm², the open circuit voltage is 0.14 V, the maximum power is ~ 150 nW/mm², and the fill factor is ~30%. The efficiency of these unoptimized first cells is ~0.01%.

ET11.12.27
Green Route Synthesized Copper-Zinc-Tin-Sulphide Nanocrystals for Heterojunction Solar Cells on Silicon Platform
Sudarshan Singh1, Ajit K. Katiyar1, Arup Ghoria2, Anupam Midya, Dipak K. Goswami1 and Samit K. Ray1, 2; 1Indian Institute of Technology Kharagpur, Kharagpur, India; 2’S. N. Bose National Centre for Basic Sciences, Kolkata, India.

Recently, the kesterite Cu2ZnSnS3 (CZTS), comprising earth-abundant and environmental-friendly elements, has been widely considered as the most promising material among the chalcogenide-based semiconductors for thin films photovoltaic (PV) applications. The colloidal CZTS quantum dots and nanocrystals (NCs) are potentially attractive candidates for low-cost PV cells and modules owing to their compatibility with solution processing techniques [1]. A novel, facile and environment-friendly synthesis route, at a relatively low temperature, has been developed to synthesize the CZTS nanocrystals. Natural, edible olive oil containing mainly oleic acid has been utilized as a solvent, which also acts as a capping agent to control the growth of nanocrystals. The synthesis of CZTS NCs inks were prepared at various centrifugation speeds obtained using ultrasonic techniques, and studied by means of their structural and optical characteristics. For the device demonstration, the quaternary nanocrystals ink prepared with different sized NCs have been integrated on n-silicon substrates by spin coating to fabricate the CZTS NCs/Si heterojunctions. The photovoltaic characteristics of the fabricated p-CZTS/n-Si heterojunctions using the synthesized colloidal quaternary NCs are demonstrated in detail. The study reveals that the CZTS nanocrystals having smaller diameter exhibits higher power conversion efficiency in comparison to the nanocrystals having the larger diameter. An improved minority carrier lifetime has been observed in open circuit voltage decay measurement for the CZTS/Si heterojunctions fabricated with smaller sized nanocrystals. Optical reflectance measurements show that the enhanced light scattering in smaller nanocrystals plays an important role in improved power conversion efficiency.
The one-step environmental friendly procedure for the production of CZTS NCs along with the demonstration of CZTS/Si photovoltaic cells implying the potential of earth-abundant and non-toxic CZTS in the nanostructured form integrated with the existing Si solar cell technology.

References:

**ET11.12.28**

**Large-Area Flexible Perovskite Solar Cells with Outstanding Mechanical Durability**

Gunhee Lee1, Min-cheol Kim1, Yong Whan Choi2, Namyoung Ahn1, Daeshik Kang1, Hyun Suk Jung2 and Mansoo Choi1; 1Seoul National University, Seoul, Korea (the Republic of); 2Sungkyunkwan University, Suwon, Korea (the Republic of); 3Ajou university, Suwon, Korea (the Republic of).

With the development of wearable electronic devices, the importance of portable power sources has been highlighted. Recently, perovskite solar cells have become promising candidates for portable power sources due to their high power density, lightweight features and low temperature processing. However, there still exist problems in terms of performance and flexibility of large-area device, prior to practical uses of perovskite solar cells as a portable power sources. To improve flexibility of perovskite solar cells, many studies have previously been conducted to replace the brittle transparent conducting oxide (TCO) like indium tin oxide (ITO), but there was no deep understanding about the mechanical properties of perovskite materials themselves. In this work, we experimentally investigated their own mechanical properties and flexibility from cyclic bending test of perovskite-coated film, in which the applied stress is controlled depending on different thickness of the substrate and bending radius. By finding crack-free region of perovskite films, we successfully demonstrated flexible perovskite solar cells with high efficiency (17.03%) and the unprecedented flexibility, sustaining its initial power conversion efficiency (PCE) after 10,000 cycles of bending at 0.5 mm bending radius. Finally, we fabricated large-area flexible perovskite solar cells without TCO, leading to the best PCE of 13.6% (cell size, 1.2 cm²). The large-area device showed outstanding flexibility as well.

**SESSION ET11.13: Low Cost High Efficiency Solar Cells**

**Thursday Morning, November 29, 2018**

**Hynes, Level 3, Room 304**

8:30 AM *ET11.13.01*

**Bringing III-V Photovoltaics Down to Earth with Dynamic-Hydride Vapor Phase Epitaxy**


III-V semiconductors are the gold standard of photovoltaic materials. They have the highest demonstrated conversion efficiencies, and they can be very light, thin, and flexible. III-V devices are also straightforwardly extendable to multijunction structures for even higher efficiencies. What III-Vs are not, however, is cheap. Much of the cost of III-V deposition comes from the expensive precursors used in the incumbent metalorganic vapor phase epitaxy (MOVPE) process, the inefficiency with which they’re used, and the low-throughput of traditional batch-style growth reactors. This leads to costly devices that are only prevalent in somewhat niche markets, including space power.

Here, we describe our recent development of dynamic hydride vapor phase epitaxy (D-HVPE), an extension of the standard HVPE process that has been known for decades, but unlike traditional HVPE allows for the deposition of relatively complex heterostructures and devices. HVPE uses much less expensive elemental source material, lower hydride overpressures, and lends itself to high-throughput, in-line deposition. These features project to make III-V deposition costs by D-HVPE much lower than is possible today.

The challenge is to use this low-cost growth platform to create III-V devices that rival the excellent performance of MOVPE-grown solar cells. There is little point in cheap III-V devices if they don’t maintain the conversion efficiency advantage that makes them so attractive in emerging markets such as electric vehicles, device charging, and other space-constrained applications. Fortunately, D-HVPE produces bulk material and interface quality that is nearly identical to MOVPE-grown material. We will give a general overview of the D-HVPE development of single-junction GaAs and GaInP devices, tunnel-junction interconnects, and the world’s first HVPE-grown multijunction solar cells. We will also describe the next steps for this technology as we attempt to bring photovoltaics that are largely constrained to space applications down to Earth.

9:00 AM ET11.13.01

**Engineering Light Absorption, Carrier Collection and Recombination in Atomically-Thin Photovoltaics**

Joeson Wong1, Deep M. Jariwala1,2, Artur Davoyan1, Giulia Tagliabue1, Michael Kelzenberg1, Joseph S. DuChene1, Matthias H. Richter1, Kevin Tat1, Michelle Sherrott1,2, Alexandra Welch1, Wei-Hsiang Lin1 and Harry A. Atwater2; 1California Institute of Technology, Pasadena, California, United States; 2Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The class of layered van der Waals (vdW) materials, materials where their weakly-bonded layered structure provides intrinsically passivated surfaces along the basal plane, allows one to mechanically cleave these materials to produce a single monolayer of atoms. Graphene, cleaved from graphite, was the first member discovered in this layered two-dimensional (2D) family. The group of layered vdW materials now span nearly every material class imaginable, from insulators and semiconductors to superconductors and topological insulators. Furthermore, because of their weak out-of-plane van der Waals interaction, they can be mechanically stacked to form a high-quality heterostructure between the most disparate materials, allowing one to design arbitrary heterostructures with a vast array of unexplored properties and applications.

An interesting member of this 2D family for photovoltaic applications is the semiconducting transition-metal dichalcogenides (TMDCs), compounds of the form MX₂, where M is a transition metal and X is a chalcogen (e.g. sulfur, selenium, or tellurium). TMDCs have some of the highest absorption coefficients of photovoltaic materials, and in their monolayer form, can be passivated in a way to reach nearly perfect radiative efficiency. Moreover, they offer a wide range of bandgaps (~1.1 – 2.0 eV), which can be tuned through quantum confinement effects and chemical alloying. Combined with their inherent stability and use of earth-abundant metals, vdW heterostructures of TMDCs are therefore attractive candidates for photovoltaic applications.

A conventional photovoltaic device that has high efficiency must maximize three figures of merit: optical absorption, subsequent carrier collection, and high photovoltage. Through proper nanophotonic engineering and device design, we show that atomically-thin vdW materials can achieve these three...
First, we experimentally show that in ultrathin (~10 nm) transition metal dichalcogenides (TMDs), it’s possible to achieve near-unity (>90%) broadband absorption in the visible spectrum. We therefore utilize this optical geometry along with an optimized carrier collection scheme (IQE > 70%) to create a device with record photocurrent density (EQE > 50%) in these materials. Second, we modified the recombination dynamics in these materials through the use of carrier selective contacts, leading to record values of open circuit voltage (Voc > 700 mV). Lastly, we present an outlook for large-area integration and schemes to further enhance the efficiency in these atomically-thin devices.

9:15 AM ET11.13.02
Microscopy Reveals the Role of Boundaries in Single-Crystalline-Like GaAs Solar Cells Grown on Flexible Metal Substrates Jonathan Pohlawsky\(^1\), Pavel Dutta\(^2\), Wei Guo\(^3\), Harvey Guthrey\(^4\), Monika Rath\(^5\), Devendra Khattawar\(^6\), Carlos Favela\(^7\), Sicorn Sun\(^2\), Chuanze Zhang\(^2\), Bo Yu\(^2\) and Venkat Selvamanickam\(^2\); \(^1\)Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; \(^2\)University of Houston, Houston, Texas, United States; \(^3\)National Renewable Energy Laboratory, Golden, Colorado, United States.

Photovoltaic (PV) devices based on single-crystalline GaAs semiconductors hold the world record for the highest efficiency for a homojunction solar cell. However, the substrates used for these materials are expensive making GaAs based solar cells cost-prohibitive for mainstream terrestrial use, which limits the device applications. A unique method to grow GaAs devices has been developed using roll-to-roll processing on a flexible metal substrate. In addition to decreasing costs, this method allows for GaAs devices to be flexible, which is of interest when considering transportability. In addition to solar cells, GaAs devices made using this process can be used for many other applications. The power conversion efficiencies (PCE) of the flexible GaAs solar cells were measured to be approximately 10%. Although a 10% PCE is about three times less than the world record GaAs solar cell, this is a good preliminary device using roll-to-roll processing. To better understand the efficiency limits, films and devices with different doping concentrations were tested using a suite of microscopy techniques including electron backscatter diffraction (EBSD), electron beam induced current (EBIC), probe tomography (APT), and cathodoluminescence (CL). The films showed a unique property in that the mobility increases with increasing dopant concentration, which has been better understood after the microscopy experiments. The EBSD results show that the GaAs films are highly oriented in the [001] direction, however, there is evidence of slight orientation deviations (<1°) between ~1 μm-sized features. The degree of orientation deviation and the presence of twin boundaries between grains has been shown to increase with dopant concentration. Correlative EBSD and EBIC cross-sectional measurements show a decreased EBIC signal in the grain boundary (GB) regions. Higher rotational angles (still <1°) have been correlated to a lower EBIC signal, which is indicative of recombination centers that are detrimental to the device performance. CL measurements corroborate the EBSD results showing defect emission in the GB regions. APT has shown C accumulation in the GB regions, which is potentially responsible for recombination in these regions. Overall, the results suggest that the low angle GBs (<1°) do not benefit the device and may be detrimental in their current state. Post-deposition heat treatments (HT), such as the CdCl\(_2\) HT for CdTe based solar cells, have been shown to significantly improve other solar cell technologies by passivating or activating GBs. The microscopy results suggest that a GB passivating treatment needs to be developed for these flexible GaAs solar cells to significantly increase their efficiency. A process that removes carbon from the GBs may be a good starting point for improving these devices. This research was supported by ORNL’s Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

9:30 AM ET11.13.03
Epitaxy-Free GaAs Nanowire Photovoltaics Phillip Jabelka, Wen-Hui Cheng, Rebecca Glaudell and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

We report on an unconventional, epitaxy-free GaAs photovoltaic cell process, designed to enable scalable manufacturing of III-V solar cells. Scalability places constraints on both the overall cost per Watt at the cell level, and the fraction of cost that related to capital equipment expense (capex), which must be minimized for large-scale production. Thin-film III-V compound semiconductors are promising for next generation photovoltaics because of their ideal bandgaps, high radiative efficiencies and mature development. However, almost all previously proposed III-V photovoltaics utilize epitaxial growth to define the cell and the high capital equipment and supply costs of epitaxy currently preclude the economic viability of these cells. In order to leverage the mature development of III-V devices without incurring the capex penalty of epitaxial growth, we have developed epitaxy-free processes for synthesis of GaAs solar cells where III-V nanostack arrays are etched using liquid-phase anisotropic etching, and mechanically exfoliated from a bulk III-V crystal, enabling many cells to be generated from a bulk crystal source material. Electron and hole selective contacts and passivation materials are then grown using low-temperature, non-epitaxial techniques.

Because low cost, epitaxy-free designs do not permit use of standard epitaxially-grown III-V heterojunctions and window layers, we first developed a coupled optoelectronic model to understand the design space of the proposed solar cell using nontraditional heterojunction carrier-selective contacts. Using this model, we determined the optimal design to be a radial junction and discovered the absolute necessity of wide-bandgap carrier selective contacts due to the high density of photogenerated carriers throughout the nanowire. Simulations indicate the potential for an optimized GaAs nanowire solar cell using SnO\(_2\) and CuSCN heterojunction contacts to operate as a single junction cell with 32% efficiency with Voc = 1.13 V and Jsc = 32.3 mA/cm\(^2\).

We have also performed proof-of-principle experiments for each fabrication step of our epitaxy-free cell processes. For GaAs cells, we have developed a metal-free wet chemical etch for defining nanostructures, and have also exfoliated them from a host wafer in a polymer handle. In addition, we have demonstrated very high quality passivation of planar 100 GaAs, with external radiative efficiencies implying a planar Voc of 970 mV, near the theoretical limit of bulk GaAs.

We have also taken first steps to extend this approach to synthesis of epitaxy-free In\(_n\)P solar cells. Highlights to date for In\(_n\)P include developing a plasma etching recipe for defining In\(_n\)P nanowires and successful exfoliation and fabrication of complete nanowire cells from their substrates by embedding them in a polymer handle. In addition, a nanowire-on-wafer In\(_n\)PTiO\(_x\)heterojunction cell exhibits a 70% increase in photocurrent over its planar counterpart.

9:45 AM ET11.13.04
Interfacial Misfit Growth of GaSb on GaAs by MOCVD for Multijunction Photovoltaics Stephen Polly, Emily Kessler, George Nelson and Seth Hubbard; Rochester Institute of Technology, Rochester, New York, United States.

The long-standing leader in multijunction photovoltaic technology consists of a three junctions made from InGaP, (In)GaAs, and Ge all grown lattice matched to germanium. While convenient due to the relative ease of growth, the bandgaps of these materials are not ideally matched based on the detailed balance for absorption from the solar spectrum which can be improved through the use of a wider band gap bottom cell. One method of realizing a higher band gap material based on the III-V material design spaces through thick metamorphic grading from the Ge lattice constant to 1 eV InGaAs, which must be grown inverted to limit the effects of the inevitable higher threading dislocation density created by this method. In this work, an alternate method is used relying on the large lattice mismatch between GaAs and GaSb (7.8%) to induce an interfacial misfit array, locking 90° dislocations in a thin layer which do
not propagate in the growth direction. This method allows for direct heteroepitaxy of GaSb and related direct bandgap materials on GaAs and InGaP heterostructures without the need for a thick grading buffer, enabling a wider range of more cost-effective inverted multijunction photovoltaic devices. Solar cells were grown and fabricated investigating the growth of GaSb single junction solar cells on GaAs substrates using the IMF technique as a function of growth conditions including metalorganic precursor type. Device results including 1-sun light-IV, quantum efficiency, and minority carrier lifetime will be discussed and compared against GaSb homoepitaxial devices, as well as the integration and performance of multijunction devices using this method.

10:00 AM BREAK

SESSION ET11.14: Thin Films III
Session Chairs: Sarah Kurtz and Roger Welser
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 304

10:30 AM *ET11.14.01
Demonstrating the Hot Carrier Solar Cell—The Ultimate Thin Photovoltaic Device Nicholas Ekins-Daukes1, James Dimmock2, Paul Stavrinou3, Huiyun Liu3, Mattias Kauer4 and Jiang Wu4; 1School of Photovoltaic & Renewable Energy Engineering, University of New South Wales, Sydney, New South Wales, Australia; 2Sharp Laboratory Europe, Oxford, United Kingdom; 3University of Oxford, Oxford, United Kingdom; 4University College London, London, United Kingdom.

The hot carrier solar cell has the potential for high efficiency and has recently been demonstrated experimentally in using both semiconductor and metallic absorbers. The latter is particularly interesting from the viewpoint of thin solar cells since a metal layer of only a few tens on nanometers can almost completely absorb broadband sunlight. Experimental hot carrier IV data has been measured from a chromium absorber deposited onto a GaAs based tunnel diode. Importantly the data confirm that the photo current arises from a hot carrier population as opposed to internal photoemission; the distinction being important since only a hot carrier device can attain high power conversion efficiency. The prospects for the technology as a realistic PV device will be discussed together with alternative applications such as photon energy resolving photodetection.

11:00 AM ET11.14.02
High Efficiency Infrared PbS Colloidal Quantum Dot Solar Cells with 50% EQE at 1.55 μm Haibin Wang1, Shoichiro Nakao1, Takaya Kubo1, Hidenori Saito2, Shinichi Magaino2, Katsuhiko Takagi2, Tetsuya Hasegawa1, Jotaro Nakazaki1 and Hiroshi Segawa1; 1The University of Tokyo, Tokyo, Japan; 2Kanagawa Institute of Industrial Science and Technology, Kawasaki, Japan.

Colloidal quantum dots (CQDs) have attracted much attention as light absorbers and carrier transporters for next-generation solar cells because mainly of QD-size dependent bandgap tunability, solution process compatibility and so on. Among various types of CQD solar cells, hetero-junction CQD solar cells constructed by combining PbS CQDs and ZnO have been widely studied, and the record high efficiency of 12% was reported [1]. Fundamental studies on CQD solar cells based on a new concept such as multiple exciton generation, hot-carrier concept, and multi-junction concept are also carried out to overcome the single junction efficiency limit (~30% under one-sun illumination). In fact, III-V semiconductors based multi-junction solar cells only have achieved a power conversion efficiency well over the single-junction limit. However, the solar cells rely heavily on high cost solar cell technology, which makes it difficult for the solar cells to be susceptible of wider application. While the size-dependent bandgap tunability and solution process compatibility unique to CQDs are suitable properties to construct low-cost multi-junction solar cells.

Here we constructed PbS colloidal quantum dot/ZnO nanowire solar cells, with the aim of developing solution-processed bottom subcells for multi-junction solar cells. Spatially-separated carrier pathways formed by ZnO nanowires together with highly infrared-transparent conductive oxide (Ta-doped SnO2; TTO) electrodes were successfully used to enhance the spectral sensitivity in the infrared region [2, 3]. Junction solar cells. The TTO-solar cells reached an even higher EQE of 50% at 1.55 μm due mainly to high infrared-transparency of the TTO electrode. This EQE value is, to the best of our knowledge, the highest value ever reported on the solution-processed solar cells. The results that we have obtained indicate that the solution-processed PbS CQD/ZnO NW solar cells are one of the promising candidates for the bottom subcells to construct flexible, low-cost multi-junction solar cells.


11:15 AM ET11.14.03

Colloidal quantum dots are promising materials for flexible solar cells because they have a large absorption coefficient ranging from visible to infrared wavelengths, a band gap that can be tuned across the solar spectrum, and compatibility with solution processing. However, the performance of flexible solar cells can be degraded by the loss of charge carriers due to recombination pathways that exist at a junction interface as well as the strained interface of the semiconducting layers. Therefore, fundamental strategies for actively controlling the junction properties are required to boost charge extraction and reduce the recombination of photo-generated charges. In this regard, the modulation of charge carrier transport using the piezoelectric effect is one of the effective ways to resolve the inherent material and structural defects. Towards this end, we have employed a porous piezoelectric poly(vinylidenefluoride-trifluoroethylene), PVDF-TrFE) polymer layer between a zinc oxide (ZnO) ETL and a PbS QD heterojunction in a flexible QDSC. Through the active control of strain/stress of the flexible form factors, the inserted porous PVDF-TrFE layer generates a piezoelectric potential which modulates the junction properties and consequently changes the behavior of the charge carriers. As a result of the modulated electric field at the junction, the photo-generated charges are effectively extracted along with reduced radiative recombination, which results in a 38% increase in the current density and a concomitant increase of 37% in the power conversion efficiency of the flexible QDSC.

11:30 AM ET11.14.04
The cadmium telluride (CdTe) thin film solar cells have attained over 20% efficiency with low-cost fabrication. However, the high efficiency CdTe devices have been achieved by increasing the photo-generated current by changing the traditional window layer (CdS) of CdTe to a wider bandgap material with better band alignment. The open circuit voltage ($V_{oc}$) remains below the theoretical limit due to the barrier at the back of the device due to the deep valence band edge of CdTe (~5.7 eV). $V_{oc}$ can be increased by adding a buffer layer between CdTe and the back electrode due to a decrease in band banding and reducing carrier recombination at the back surface. Previous modelling work shows that adding a Tellurium (Te) layer at the back contact of CdTe reduces band banding, which leads to higher performance CdTe thin film solar cells. Recently, we developed a way to form a Te layer at the back surface of CdTe by interacting the surface of CdTe sample with methylammonium iodide (CH$_3$NH$_3$I, MAI) solution followed by a mild thermal treatment. The MAI treatment is more effective than evaporated Te at the back of CdTe due to reducing the interface defect states between CdTe and the Te buffer layer. This leads to increasing the efficiency up to 10% compared to standard Cu/Au back contact. To further reduce the carrier recombination at the back surface, we need to increase the barrier for minority carrier (electrons) and reduce the barrier for majority carrier (holes) at the back surface. This can be achieved by adding a higher bandgap layer to act as an electron reflector (ER). Here, we demonstrate the use of Zinc Telluride (ZnTe) as an electron reflector at the back surface of CdTe devices with a Te layer between CdTe/ZnTe and ZnTe/metal interfaces to break down the large Schottky barrier at the CdTe/metal interface into four smaller ones. We show that this is an effective method to reduce the carrier recombination at the back surface despite not using Cu. The $V_{oc}$ of Cu-free devices with Te/ZnTe/Au back contact are notably higher than the CdTe device fabricated with standard Cu/Au back contact.

**SESSION ET11.15: Organic Photovoltaics III**

**Session Chairs:** Thomas Unold and Jia Zhu

**Thursday Afternoon, November 29, 2018**

**Hynes, Level 3, Room 304**

**1:30 PM *ET11.15.01**

**A Novel Approach to Multi-Junctions—The Heterojunction Bipolar Transistor Solar Cell**

*Elisa Antolin, Pablo García-Linares, Marius Zehender and Antonio Martí*

**Instituto de Energía Solar, Universidad Politécnica de Madrid, Madrid, Spain.**

Conventional multi-junction solar cells achieve unparalleled efficiencies at the price of a complex structure, high fabrication cost and low spectral tolerance. Recently a new device has been proposed called three-terminal heterojunction bipolar transistor solar cell (HBTSC) which has the same efficiency limit of a double-junction solar cell but consists of a much simpler structure with no tunnel-junctions or isolating layers. Being a three-terminal device, it enables higher spectral tolerance than series-connected multi-junction cells through the engineering of module interconnection.

The HBTSC comprises only three main active layers. These layers may be called emitter, base and collector since they resemble the structure of an npn (or pnp) transistor. However, the operation of this device is antagonistic to the operation of a transistor. In the HBTSC the emitter and base terminals form the top sub-cell and the base and collector terminals form the bottom sub-cell. For the device to achieve a high efficiency it is necessary that the voltage of the top sub-cell exceeds the voltage of the bottom sub-cell even though they share the base layer. In this talk we will present the theoretical model of the device and will show how that situation can be realized if the emitter injection efficiency approaches zero. One of the most interesting aspects of the HBTSC model is that biasing one sub-cell can improve the conversion efficiency of the other sub-cell. We will analyze the impact of the base layer design on the HBTSC operation and its effect on how the sub-cell efficiencies are interrelated.

We have produced proof-of-concept HBTSC prototypes based on epitaxial AlGaAs/GaAs structures. We will show experimental proof that the two sub-cells can be operated at their respective maximum power points, with the voltage of the top sub-cell exceeding the voltage of the bottom sub-cell. The operation of five HBTSC assembled in a prototype module with two-terminal output will also be demonstrated.

Finally, we will describe possible architectures to implement the HBTSC concept with low-cost technologies. These proposals will include a design comprising a perovskite absorber and another one based on the use of nanowires.


**2:00 PM ET11.15.02**

**Enhancing the Performance of Polymer Bulk Heterojunction Solar Cells by Large Sized Gold Nanoparticles via Near- And Far-Field Plasmonic Coupling**

*Min Seok Lee, Dong Hyun Kim, Justin Jessuraj Periyayagam, Hassan Hafeez and Seung Yoon Ryu*  

**Korea University, Sejong city, Korea (the Republic of).**

Nobel metal nanoparticles are well-known to unveil plasmonic coupling with molecular excitons to enhance the performances of opto-electronic devices especially light emitting diodes and solar cells. The higher momentum associated with metal surface plasmons can alter the lifetime of molecular excitons, thereby the efficiency increased in respective devices. However, this kind of coupling is stronger within the near-field of surface plasmons and is highly dependent on distance between metal surface to exciton and also on the size of metal nanoparticles.

In this scenario, we have investigated the effect of incorporating large size gold nanoparticles (AuNPs) in polymer bulk hetero junction (BHJ) solar cells. In addition, we exclusively studied the near- (Localized surface plasmonic resonance; LSPR) and far-field (scattering) interaction of AuNPs plasmons with BHJ excitons through theoretical and experimental tools. To clearly understand the efficiency improvement tactics, we have fabricated three BHJ solar cells containing three different donor active materials with [6,6]-phenyl-C$_{61}$,1,3-butyric acid methyl ester (PC$_{61}$BM). AuNPs have been incorporated in BHJ solar cells through the poly(3,4-ethylenedioxithiophene):poly(styrene sulfonate) (PEDOT:PS) solution as hole injection layer (HIL). To understand size dependent behaviors, AuNPs with sizes 71, 80, 87, 103 nm were inserted in PEDOT:PS and employed as HIL for the two polymer solar cells containing PBDTT-T:C$_{60}$,PC$_{61}$BM and PTB7:PC$_{61}$BM. Interestingly, smaller size AuNPs (equal or less than 80 nm) very active in establishing near-field interaction with excitons, whereas bigger size (~80 nm) particles were found to produce superior far-field scattering. By monitoring the lifetime of the excitons through time resolved photoluminescence found to be beneficial to identify the near- and far-field coupling. In other words, the AuNPs (<87 nm) showing lifetime lesser than the reference were considered to demonstrate near-field (LSPR) effect and AuNPs (>87 nm) revealed longer lifetimes indicating far-field (scattering) effect. At 87 nm, AuNPs yielded a fair combination of near-field coupling along with far-field scattering resulting in enhanced absorption and dissociation of photons in BHJ. Therefore, 87 nm found to be an optimum (maximum) size for AuNP to attain superior efficiency in BHJ solar cells through the cultivation of near- and far-field interactions. Further, full-
wave simulation (COMSOL) investigations were employed to reveal the plasmonic interaction and electric field distribution of AuNPs respectively. These findings are coincided with the experimental results of BHJ solar cell performances.

2:15 PM ET11.15.03
Side Chain Engineering of Polymer Donors and Non-Fullerene Small Molecule Acceptors for Organic Photovoltaics Micaela Matta, Tobin J. Marks and George Schatz; Chemistry, Northwestern University, Evanston, Illinois, United States.

Organic bulk-heterojunction (BHJ) solar cells made of polymeric donors and small molecule non-fullerene acceptors (NFA) have been the subject of interest due to their record-high efficiencies.[1] Tremendous effort is being directed at the development of novel donor and acceptor building blocks, and the optimization of energetics and morphology of donor/acceptor systems.

In order to make these highly conjugated materials soluble and thus processable at low cost, the presence of side alkyl chains is fundamental. However, their role in determining key morphological and structural properties in both donors and acceptors has been often overlooked by the organic photovoltaics (OPV) community.

Our work investigates how the length of alkyl side chains influences the properties of some of the best performing donors and NFAs available to date. The polymer donor PBTZF4[2] was characterized using a combination of molecular dynamics (MD) simulations, X-ray scattering and spectroscopic techniques. MD provided a rationalization for the observed trends among a series of PBTZF4-R devices with alkyl chains R of different length, elucidating the subtle equilibrium between the conjugated backbone rigidity and the folding enhancement provided by longer alkyl chain substituents. The results established a relationship between the single polymer chain behavior, its aggregation in solution and the subsequent formation of domains in the BHJ.[3] This study shows how side chain engineering can be used to fine tune the BHJ morphology without significantly changing the HOMO-LUMO levels of polymer backbone.

Moreover, a series of ITIC-derived[4] NFA having alkyl chain substituents of different length[6] was also investigated by means of quantum chemical calculations, MD simulations, X-Ray diffraction and other spectroscopic measurements. It emerges that the alkyl chain length has a dramatic effect on OPV performances. Side chains effectively mediate intermolecular interactions by preventing excessive aggregation and crystallization of the acceptor while allowing efficient π-stacking in the amorphous and semi-crystalline domains.

In summary, this work highlights the importance of side chain engineering as a strategic tool for OPV morphology control, where MD simulations have been instrumental in providing a correlation between molecular-scale properties and device performances.

References

2:30 PM ET11.15.04
Enhanced Photovoltage and Short Circuit Current Density for the Polymer:Fullerene Solar Cells Using Individual Bis-PCBM Isomers Xueyan Hou1,2, Jun Yan1, Xingyuan Shi3, James McGregor1, Jenny Nelson2 and T. John S. Dennis1; 1School of Physics and Astronomy, Queen Mary University of London, London, United Kingdom; 2Physics and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 3SPECIFIC, Swansea University, Swansea, United Kingdom.

It has been a longstanding goal to enhance the power conversion efficiency (PCE) of polymer donor: fullerene solar cells by tuning the acceptor energy levels to raise the open-circuit voltage ($V_{oc}$). Previous work showed that replacing the most commonly used fullerene acceptor, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), with its bis-adduct raised the $V_{oc}$ of poly(3-hexylthiophene-2,5-diyl) (P3HT):fullerene solar cells by ~100 mV and increased the PCE. The increased $V_{oc}$ was assigned to the higher lying LUMO energy of the bis adduct. However, when combined with other polymers, higher fullerene adducts tend to reduce PCE via losses in short-circuit current density ($J_{sc}$) and fill factor (FF) due to poor electronic properties. This is assigned to a combination of (i) energetic disorder, which results from varying frontier orbital levels of the individual isomers in the mixture that is normally produced; (ii) poor molecular packing leading to lower electron mobility. Recently, we separated all 19 bis-PCBM isomers from the as-produced mixture by peak-recycling HPLC and identified their structures by a combination of 13C NMR, UV-Vis spectroscopy and HPLC retention time analysis. LUMOs of all isomers lie above that of PCBM, with the highest lying about 100 meV higher than that of the mixture and 200 meV above PCBM. The pure isomers should contain much reduced disorder due to the absence of multiple isomers and be capable of crystallising. Therefore, improved electronic properties and solar cell PCE may be expected.

In this work, I will present a comprehensive analysis of the solution- and film-based energy levels, solubility and crystallinity of different bis-PCBM isomers. I will present the performance of devices when blended with different polymer donors of different crystallinity together with an analysis of the $V_{oc}$, $J_{sc}$ and transport properties. For example, $V_{oc}$ as high as 1.13 V was observed for some isomers along with a net increase in PCE. The pure isomer with a certain molecular structure can help us understand the intrinsic electronic properties of the higher fullerene adducts more clearly without the disorder of an isomer mix. Finally, I will give some suggestions for the synthetic routes to achieve particular higher adduct fullerenes whilst avoiding the disorder due to multiple isomerism.

References
backsheet product produced through an alternative process to the traditional lamination process, which uses adhesives and solvents in the production of multi-layer backsheets. Instead, they use coextrusion technology to produce their novel multilayer polymeric backsheet. Their current product, PhotoMark®Reflections™, is a 5-layer film that does not contain PET or fluoropolymers, but rather a proprietary polyamide-ionomer alloy coupled with polyolefin and amide layers. The primary purpose of this research was to compare the performance of Tomark-Worthen’s coextruded backsheet films with the current industry standard films and determine modes of failure. Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used in order to: assess the severity of degradation and determine the mechanism degradation after extensive exposure to damp heat and ultraviolet (UV) radiation. Spectroscopy and microscopy results indicate high stability of PhotoMark®Reflections™after exposure to these severe accelerated weathering conditions. Since the layers of the backsheet are adhered in the coextrusion process as opposed to the traditional use of adhesives, the interlayer bond strength of various backsheet samples was tested via ASTM D903-98. The results obtained from ASTM D903-98 show that Tomark-Worthen’s PhotoMark®Reflections™coextruded films have an interlayer adhesion strength 6.5 times greater than that of the current industry standard. Additionally, several backsheet samples were exposed to harsh hydrolysis conditions in a Highly Accelerated Stress Test (HAST) common to the solar industry. Current industry standard and competitive films experienced dramatic degradation and loss in tensile properties as a result of the HAST, while Tomark-Worthen’s PhotoMark®Reflections™showed minimal degradation.

3:00 PM BREAK
This tutorial will be divided into two parts. In the first part, the instructor will introduce advanced synchrotron X-ray techniques, focusing on latest developments in coherent X-ray scattering to image defects in solids. In the second part, the instructor will introduce electronic-structure methods, focusing primarily on the latest advances in Quantum Monte-Carlo techniques, with concrete examples on computing different types of properties in solids, relevant for energy materials.

1:30 PM
Advances in Coherent X-Ray Scattering Techniques Dillon D. Fong; Argonne National Laboratory

Synchrotron X-ray methods allow observation of the structure and behavior of materials in their native environment or while undergoing transitions. The continuing advances in X-ray sources are leading to considerable improvements in the coherence of the beam and will eventually enable direct imaging of a material in a non-destructive fashion with atomic-scale resolution. In this tutorial, we will discuss the application of different synchrotron X-ray techniques to the study of materials, with a focus on imaging defects and investigating real-time defect behavior. Examples of current and future experiments exploiting coherence will be provided.

3:00 PM BREAK

3:30 PM
Advances in Quantum Monte Carlo Methods for Solids Luke Shulenburger; Sandia National Laboratory

Predicting properties of materials for energy applications, such as batteries, fuel-cells and photovoltaics, often stresses the capabilities of current electronic structure techniques, such as Density Functional Theory. This tutorial will initially give a broad overview of electronic-structure methods that are used to compute such properties, focusing on their strengths and weaknesses. It will then give a deep dive into the state-of-the-art of Quantum Monte-Carlo techniques as applied to the condensed phase. Concrete examples will be shown from recent calculations pertaining to the properties of functional materials.

SYMPOSIUM ET12

Harvesting Functional Defects in Energy Materials
November 26 - November 29, 2018

Symposium Organizers
Panchapakesan Ganesh, Oak Ridge National Laboratory
Marina Leite, University of Maryland
Annamaria Petrozza, Istituto Italiano di Tecnologia
Hua Zhou, Argonne National Laboratory

Symposium Support
Advanced Photon Source at Argonne National Laboratory

* Invited Paper
1:30 PM *ET12.01.01
The Versatility of Mesoscopic Solar Cells Anders Hagfeldt; ISIC, EPFL, Lausanne, Switzerland.

In our work on solid-state dye-sensitized solar cells (ssDSC) we have recently shown that copper phenanthroline complexes can act as an efficient hole transporting material. We prepared ssDSCs with a novel organic dye WS-72 and \([\text{Cu(tmbpy)}]_{2}^{2+}\) as redox system and achieved record power conversion efficiencies for ssDSCs of 11.7%. Our best DSC efficiency of 13.1% for a liquid Cu-complex electrolyte is achieved by the discovery that the PEDOT-based counter electrode can be directly contacted with the dye/TiO₂ photoanode. Thus, there is no space between the two electrodes minimizing diffusion limitations and fill factors up to 0.8 is achieved.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 22% with a mixed composition of iodide/bromide and organic and inorganic cations. With the use of SnO₂ compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20%. Through the compositional engineering larger perovskite grains grown in a monolithic manner are observed and reproducibility and device stability are improved. With regards to lifetime testing, we have shown a promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests.

2:00 PM ET12.01.02
Active Materials and Interfaces for Stable Perovskite Solar Cells Antonio Abate; Helmholtz Berlin, Berlin, Germany.

Halide perovskites are quickly overrunning research activities in new materials for cost-effective and high-efficiency photovoltaic technologies. Since the first demonstration from Kojima and co-workers in 2009, several perovskite-based solar cells have been reported and certified with rapidly improving power conversion efficiency. Recent reports demonstrate that perovskites can compete with the most efficient inorganic materials, while they still allow processing from solution as a potential advantage to deliver a cost-effective solar technology. Compare to the impressive progress in power conversion efficiency; stability studies are rather weak and often controversial. An intrinsic complication comes from the fact that the stability of perovskite solar cells is strongly affected by any small difference in the device architecture, preparation procedure, materials composition and testing procedure. In the present talk, we will focus on the stability of perovskite solar cells in working condition. We will discuss a measuring protocol to extract reliable and reproducible ageing data. We will present new materials and preparation procedures, which improve the device lifetime without giving up on high power conversion efficiency.

2:15 PM *ET12.01.03
Role of Functional Defects in Cu₂ZnSnS₄ Solar Cells Sai Gautam Gopalakrishnan, Kuang Yu and Emily A. Carter; Princeton University, Princeton, New Jersey, United States.

Cu₂ZnSnS₄ (CZTS)-based solar cells, which are based on the kesterite structure of CZTS, constitute an inexpensive, beyond-Si photovoltaic (PV) technology. However, practical CZTS cells often suffer from low open-circuit voltage and poor efficiency. In the first part of the talk, we explain the fundamental origins of poor performance in CZTS, namely disorder in the Cu and Zn sub-lattices caused by anti-site defects. Based on a cluster expansion model built on density functional theory (DFT) calculations, we find that a significant amount of lattice disorder can accumulate within the kesterite structure under typical synthesis conditions. Additionally, we find that Cu-vacancies can beneficially improve performance by reducing band gap fluctuations within bulk CZTS.

One pathway to reduce anti-site defect formation in CZTS is to employ isovalent dopants, such as Cd²⁺ and Ag⁺ for Zn²⁺ and Cu⁺, respectively, as suggested by previous experimental studies. Hence, in the second part of the talk, we focus on the effects of Cd- and Ag-doping within CZTS cells, based on our evaluation of the bulk stability, defect (and surface) energetics, and the electronic structure of doped CZTS using DFT-based simulations. Importantly, we find that Cd and Ag can increase efficiencies via contrasting mechanisms, depending on the dopant concentration and Cu-content available during synthesis. For example, we predict that Cd (Ag) stabilizes the lower (higher) band gap stannite (kesterite) structure at high concentrations. Similarly, we find that Cd does not influence the surface energetics of kesterite-CZTS, while Ag decreases the surface energies significantly, which would favor smaller particle sizes. Finally, we suggest the exploration of alternate abundant, non-toxic, isovalent dopants to improve the performance of CZTS.

2:45 PM ET12.01.04
Assessing the Role of Hydrogen in Fermi-Level Pinning in Chalcopyrite and Kesterite Solar Absorbers from First-Principles Calculations Joel B. Varley¹, Tadashi Ogitsu¹, Vincenzo Lordi¹, Kimberly Horsley², Alex DeAngelis² and Nicolas Gaillard²; ¹Lawrence Livermore National Laboratory, Livermore, California, United States; ²University of Hawaii, Honolulu, Hawaii, United States.

Understanding the impact of impurities in solar absorbers is critical to engineering high-performance in devices, particularly over extended periods of time. Here, we use hybrid functional calculations to explore the role of hydrogen interstitial (H⁺) defects in the electronic properties of a number of attractive solar absorbers within the chalcopyrite and kesterite families to identify how this common impurity may influence device performance. Our results identify that H⁺ can inhibit the highly n-type conditions desirable for several higher-band gap absorbers and that H⁺ incorporation could detrimentally affect the open-circuit voltage \(V_{OC}\) and limit device efficiencies. Additionally, we find that H⁺ can drive the Fermi level away from the valence band edge enough to lead to n-type conductivity in a number of chalcopyrite and kesterite absorbers, particularly those containing Ag rather than Cu. We find that these effects can lead to interfacial Fermi-level pinning that can qualitatively explain the observed performance in high-Ga content CIGS solar cells that exhibit saturation in the \(V_{OC}\) with increasing band gap. Our results suggest that compositional grading rather than bulk alloying, such as by creating In-rich surfaces, may be a better strategy to favorably engineering improved thin-film photovoltaics with larger-band gap absorbers.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and supported by the HydroGEN Advanced Water Splitting Materials Consortium, established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cells Technologies Office.

3:00 PM BREAK

3:30 PM *ET12.01.05
Defects in Polycrystalline Solar Cell Absorbers—Addressing the Materials Science Paradigm at the Nanoscale Mariana L. Bertoni; School of...
The behavior of solar cells is very often limited by inhomogeneously distributed nanoscale defects. This is the case throughout the entire lifecycle of the solar cell, from the distribution of elements and defects during solar cell growth as well as the charge-collection and recombination during operation, to degradation and failure mechanisms due to impurity diffusion, crack formation, and irradiation- and heat-induced cell damage. This has been known for a while in the field of crystalline silicon, but inhomogeneities are far more abundant in polycrystalline materials, and are the limiting factor in thin-film solar cells where grain sizes are often on the order of the diffusion length.

We will show that the high penetration of hard X-rays combined with the high sensitivity to elemental distribution, structure, and spatial resolution offers a unique avenue for highly correlative studies at the nanoscale. We will present results on CdTe and Cu(In,Ga)Se\(_2\)) where carrier collection is directly correlated to the compositional and structural properties of the material under a large variety of synthesis and operating conditions. The segregation of copper at the grain boundaries of both solar absorbers will be discussed in detail as well as the impact to carrier collection efficiency. Furthermore, the kinetics of copper segregation during growth and processing will be presented.

4:00 PM ET12.01.06
**Probing Defects in Solar Cell Materials Through Microscale-Resolved Tomography**

John M. Howard\(^1,2\), Elizabeth Tennyson\(^3,7\), Bernardo Neves\(^3,7\) and Marina S. Leite\(^1,2\); \(^1\)Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; \(^2\)Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States; \(^3\)Department of Physics, Federal University of Minas Gerais, Belo Horizonte, Brazil.

Our society’s pressing need for low-cost photovoltaics has triggered an incessant search for materials that can provide high-performance devices, with stable power conversion efficiency. From this class of materials, CIGS is a promising option, with world record efficiency > 22%. Yet, its open-circuit voltage is currently the limiting factor for higher performance. Here, we build a 3D tomography of the voltage response of CIGS solar cells by means of wavelength-dependent photovoltage measurements using confocal optical microscopy. Using only three wavelength-dependent photovoltage scans, we elucidate the spatial variation in the electrical behavior of CIGS devices and assign the voltage response to the top (10 nm thick), the middle (100 nm thick), and the bottom (1000 nm thick) of the thin film. We investigate four devices to compare the influence of their chemical composition and processing method on performance: CIS, Ag-CIS, CIGS with one-step deposition, and CIGS with 3-step deposition processes. We find that, in all cases, the middle section of the tomography map corresponds to the highest yield in voltage (~80% of the overall signal). The Ag-CIS device presents the highest voltage response (192 μV), in agreement with macroscopic measurements. These materials present photovoltage values that negatively contribute to the overall device performance, which is related to the non-radiative recombination centers caused by the boundaries composing the absorbing layers. Our paradigm paves the way for reconstructing the 3D electrical response (voltage and current) of a variety of energy harvesting systems, ranging from photoelectrochemical devices to nanostructured catalysts and perovskite solar cells.

4:15 PM ET12.01.07
**The Role of Hydrogenation on Defect Passivation and Enhanced Performance of GaInNAs Solar Cells**

Anmir Kaphle\(^1\), Gang R. Neupane\(^1\), Vincent R. Whiteside\(^2\), Collin R. Brown\(^2\), Khalid Hassain\(^1\), Mohamed A. Khalifou\(^1\), Mathieu Leroux\(^4\), Ian Sellers\(^2\) and Parameswar Hari\(^7\); \(^1\)Physics and Engineering Physics, Univ of Tulsa, Tulsa, Oklahoma, United States; \(^2\)Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma, United States; \(^3\)Amethyst Research Inc, Ardmore, Oklahoma, United States; \(^4\)CRHEA-CNRS, Valbonne, France.

In this study, we present recent results that show the enhanced performance of GaInNAs solar cells by passivating the defects using a UV-activated hydrogenation process. We have studied four cells, a reference cell with no hydrogenation and three cells with low (0.1×10\(^15\) atoms/cm\(^2\)), medium (0.5×10\(^15\) atoms/cm\(^2\)), and high (1.1×10\(^16\) atoms/cm\(^2\)) level of hydrogen incorporation. Previous work has indicated this process improves the performance of a GaInNAs solar cell by a factor of three through passivation of larger nitrogen-nitrogen related complexes and defects [1]. Here, the capacitance-voltage analysis is used to further understand the nature of this passivation in improving solar cell performance. It will be shown that hydrogenation is very effective in enhancing the depletion width and lowering the background doping concentration via the passivation of non-radiative centers in the absorber region. For the reference cell, a narrow depletion width of 206 nm and background doping concentration of 1.7×10\(^18\) cm\(^{-3}\) was measured. As the hydrogen passivation level is increased to high, the depletion width increased to 768 nm, and this resulted in a decrease in background doping concentration to 2.0×10\(^17\) cm\(^{-3}\). We also analyzed the density of trap states using admittance spectroscopy for different levels of hydrogenation. It was observed that hydrogenation is effective for passivating the trap concentration from 7.4×10\(^17\) cm\(^{-3}\) to 8.7×10\(^16\) cm\(^{-3}\). However, the trap energy is almost constant at 0.30 eV for all the level of hydrogenation. Impedance measurements at different applied biases were also performed. Imp to investigate minority carrier lifetimes. The minority carrier lifetime increased from ~ 2 μs to ~ 6 μs as hydrogen passivation level increased from low to high.


4:30 PM ET12.01.08
**Ab Initio Defect Characterisation of Candidate Solar Absorber Sb:Se**

Christopher Savory\(^1,4\), Laurie Phillips\(^2\), Jon Major\(^3\) and David O. Scanlon\(^1,3,4\); \(^1\)University College London, London, United Kingdom; \(^2\)University of Liverpool, Liverpool, United Kingdom; \(^3\)Diamond Light Source Ltd., Didcot, United Kingdom; \(^4\)Thomas Young Centre, London, United Kingdom.

As the world’s demand for energy increases, the need for technologies that can efficiently and sustainably generate energy are crucial to our society’s development. Photovoltaics are a rapidly developing renewable market, with capacity growing by a multiple of 57 from 2000 to 2015, to a total of 227GW, a higher rate than the growth in demand for electricity. While the price of silicon, the market leader PV material, has decreased in these recent years, the most cost-effective (S/W) absorber material remains CdTe, which only requires nanometre-thin films to absorb light efficiently. Nevertheless, the toxicity of Cd and low abundance of Te remain potential issues for global deployment of the technology.

In this study, we examine another potential thin-film absorber material, antimony selenide. In our ab initio calculations, we have found that Sb:Se has an ideal pseudodirect 1.3eV band gap and shows a spectroscopically limited maximum efficiency\(^2\) of 28% for a film thickness of 200nm, at which CdTe would have a value of 20% - demonstrating its extremely efficient absorption. Cell efficiencies for Sb:Se have, however, historically been low, at close to 5%. In the past 2 years, however, a number of reports have pushed this efficiency to 7%, and discussed potential resistance to the negative effects of grain boundaries, however measured \(V_{oc}\) are still low in comparison with the band gap of the material.\(^3,5\) Here, together with our experimental collaborators at the University of Liverpool, we attempt to characterise the deep defect levels within Sb:Se that could be limiting its performance. We calculate the transition levels for all intrinsic defect environments in the structure using hybrid Density Functional Theory, and compare them to DLTS measurements performed on a 7.9% efficiency cell to identify detrimental recombination centres. From our results, we can propose a strategy to minimize the impact of these deep defects, and identify potential methods to passivate them and so allow Sb:Se to reach cell efficiencies that could compete with other champion solar absorbers.
We use this new device model to explore the optimization of an intermediate band solar cell, showing how to optimize device performance given fixed material quality, elucidating important figures of merit and design rules. All efficient devices rely on careful design and modeling tools, but there are no existing device modeling tools for IB materials. We present for the first time a coupled Poisson and drift-diffusion device model with ability to simulate both standard semiconductors and IB materials, based on the finite element method (FEM), implemented using the FEniCS platform [5]. The model supports 2D and 3D devices. Semiconductor device models generally face challenges due to the large dynamic range needed to represent carrier concentrations and often need to use extended-precision arithmetic, implemented at the software level, to attain reliable results. We demonstrate high quality, well-converged results using standard 64-bit floating point numbers, allowing high-speed operation and efficient use of memory resources. Performance of the solver is demonstrated for standard semiconductors through comparisons with other simulation tools including TCAD Sentaurus.

We use this new device model to explore the optimization of an intermediate band solar cell, showing how to optimize device performance given fixed material quality, elucidating important figures of merit and design rules.

All efficient devices rely on careful design and modeling tools, but there are no existing device modeling tools for IB materials. We present for the first time a coupled Poisson and drift-diffusion device model with ability to simulate both standard semiconductors and IB materials, based on the finite element method (FEM), implemented using the FEniCS platform [5]. The model supports 2D and 3D devices. Semiconductor device models generally face challenges due to the large dynamic range needed to represent carrier concentrations and often need to use extended-precision arithmetic, implemented at the software level, to attain reliable results. We demonstrate high quality, well-converged results using standard 64-bit floating point numbers, allowing high-speed operation and efficient use of memory resources. Performance of the solver is demonstrated for standard semiconductors through comparisons with other simulation tools including TCAD Sentaurus.

We use this new device model to explore the optimization of an intermediate band solar cell, showing how to optimize device performance given fixed material quality, elucidating important figures of merit and design rules.

characterisation. (We emphasise that special low dose transmission electron microscopy (TEM) methods and dry, ion-free TEM specimen preparation is imperative if an undamaged structure is to be observed [1,2].)

We characterize and compare structure-property relationships in two photovoltaic systems: the mixed organic mixed cation perovskite MAxFAl−xPbI3 (with methylammonium, MA=CH3NH3+ and formamidinium, FA=NH2CH=NH2+) and x=0, 0.15, 0.5, 0.8, 0.9 and 1) [3] and the more structurally stable pure inorganic CsPbI1−xBrx (−x) [4].

We reveal the different crystal structures and defect structures induced by varying composition and identify how these in turn impact upon charge carrier recombination and device performance, providing insights into the structural environments necessary to optimise device performance.


9:00 AM ET12.02.03
Understanding Perovskite PV Materials from a Defect Perspective Yi-Yang Sun; Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Being a new class of materials achieving commercially competitive efficiency in an amazingly short period, the halide perovskites have set a new horizon for photovoltaic (PV) research. The success has been largely attributed to the unusual defect properties of the halide perovskites. In particular, the materials exhibit surprising defect tolerance even when synthesized by low-cost solution-based methods. The common understanding has been that the halide perovskites are “free” of deep defect levels which usually serve as efficient carrier recombination centers and are detrimental to the solar cell efficiency. While density functional theory calculations using semi-local functionals without including spin-orbit coupling (SOC) support this view, high-level calculations such as those using a hybrid functional including SOC suggest the existence of deep levels. Another puzzle is that the solution-produced halide perovskites exhibit high resistance suggesting an ultralow concentration of the shallow defects, which is at odds with the low formation energy of these defects. In this talk, we attempt to address these puzzles by a systematic comparison of the calculated defect transition levels and formation energies for hybrid halide perovskites, pure inorganic halide perovskites, as well as chalcogenide perovskites using different levels of methods. It is expected that the results will shine a light on the understanding of the role of defects in the perovskite PV materials.

9:15 AM ET12.02.04
Heterovalent Doping and Defect Formation in Metal Halide Perovskite Material Pabitra Nayak1, Michael Sendner2, Bernard Wenger1, Zhiping Wang1, Kavita Sharma2, Robert Lovricic3, P. K. Madhu1 and Henry Snaith1; University of Oxford, Oxford, United Kingdom; “TIFR Centre for Interdisciplinary Sciences, Hyderabad, India; “InnovationLab, Heidelberg, Germany.

Optoelectronic devices based on intrinsic Pb halide perovskites (HP) based semiconductors have shown wide applications in the recent past. There have been several attempts to introduce heterovalent metal ions (e.g., Li+, Bi3+, Sb5+) in the perovskites in an attempt to induce electronic doping and increase the charge carrier density in the semiconductor. It has been reported that inclusion of heterovalent metal such as Bi3+ decreases the bandgap of the material considerably. However, contrary to the earlier conclusions, despite a definite change in the appearance of the crystal as observed by eye, here we show that bandgap of MAPbBr3 crystals does not change due the presence of Bi3+ them. Formation of optically active defects states in the bad gap region and use of very thick samples for the transmission measurements erroneously give the impression of bandgap shift. Moreover, we find that all the claims regarding the bandgap narrowing in single crystals reported in many reputed journals in the past are also incorrect. Our finding also eliminates the ambiguity regarding the range of bandgap values reported for a single type of perovskite material. We find the bandgap values for the thin film and crystals of a MAPbI3 is same. In the Bi3+ doped crystals, we find that the microstrains and the density of sub-bandgap state (defects) increase due to the inclusion of Bi ions in the crystal. These bandgap states also act as non-radiative recombination centers in the crystals. Our findings give a clear indication of the impact of heterovalent (Bi3+) doping and also highlights the challenges which need to be resolved for this to be of real use. This latter aspect is of critical importance to reach the perovskite research community so that researchers can be mobilized to investigate how to dope HA materials effectively.

9:30 AM ET12.02.05
Passivation and Photo-Brightening in Metal Halide Perovskites Bernard Wenger, Julian Godding and Henry Snaith; University of Oxford, Oxford, United Kingdom.

Lead halide perovskites show impressive optoelectronic properties as demonstrated by their high radiative efficiencies and power conversion efficiencies in photovoltaic devices surpassing 20%. Since this is rather exceptional for materials synthesized directly from precursors in solution with simple coating techniques, the quality of semiconducting lead halide perovskites has sometimes been attributed to their “defect tolerance”. [1] However, substantial improvements of radiative efficiency can be obtained by various post-deposition treatments. The effectiveness of such passivation techniques demonstrates clearly that these materials do suffer from defects and, moreover, that these defects are likely to be localised at the surface of grains in polycrystalline films. In this contribution, we investigate several passivation strategies, compare them and also combine them for the model MAPbI3 perovskite as well as for high performing mixed cation, mixed halide perovskite such as FAxA-Cs1−xPbI3−yBry.

First, we discuss the effect of passivation by the addition of Lewis bases, such as pyridine and related organic molecules. Then, we investigate the effect of several monovalent cations salts (e.g. K+) which have been recently shown to improve massively the photoluminescence efficiency of triple cation (MA/FAS-Cs) perovskites and allowed for the fabrication of highly efficient thin film solar cells [2]. Finally, we compare (and combine) the addition of passivation agents with the photo-brightening effects obtained when exposing the perovskites to light in air in the presence of moisture.

Combining optical, electronic and materials characterisation techniques, we propose a detailed mechanism leading to passivation and demonstrate a new approach to further improve the radiative efficiency by a simple post-deposition treatment.

References
Defect Photochemistry of Lead-Halide Perovskites

Filippo De Angelis, CNR-ISTM, Perugia, Italy.

An outstanding property of lead-halide perovskites is the incredibly low band-gap to open circuit voltage loss, which in optimized devices is close to the thermodynamic limit (1.6 eV gap; 1.3 V voltage, loss 0.3 V).[1] The high open circuit voltage is extremely attractive for both photovoltaics and water splitting. These observations suggest an apparently low density of carrier traps in MAPbI3, contrary to the expected high defect density of a low-temperature, solution-processed material, suggesting that metal halide perovskites are inherently defect tolerant due to dominant defects introducing only shallow traps in the material band-gap.[2]

We present on overview of first-principles computational analyses devoted to understanding the outstanding optoelectronic properties of lead-halide perovskites. We show that despite the fairly high defect density due to Pb- and MA-related defects, less abundant iodine defects introduce deep electron and hole traps in MAPbI3.[3-5] The peculiar iodine redox chemistry leads, however, to kinetic deactivation of filled electron traps, leaving only short-lived hole traps as potentially harmful defects.[6,7] Hole traps can be eventually converted to electron traps under mild oxidizing conditions, clarifying the surprising material defect tolerance.

Exposing the material to light may initiate light-induced annihilation of iodine defects, that may explain the reversible enhanced PL quantum yield repeatedly observed. Under high irradiation intensity of short wavelength, however, bimolecular photochemical transformations of such iodine defects may start to prevail, leading to PLQ quenching and eventually to material degradation.[8]

Identifying the key factors underlying defect photochemistry in lead-halide perovskites may allow to further improve the material optoelectronic quality and can represent the basis for development of new materials with similar target characteristics, possibly avoiding the environmental risks posed by lead.

References
8. S. Motti et al., submitted for publication.

10:45 AM ET 12.02.07
Broadband Excitonic and Trap-Assisted Emission in Cs2Bi2I9 Nanocrystals
Giuseppe M. Paterno1, Nimai Misra2, Alex J. Barker2, Zhiya Dang3, Guglielmo Lanzani1, Liberato Manna1, Annamaria Petrozza4 and Daniele Cortecchia1; 1Nanochemistry, Istituto Italiano di Tecnologia, Genova, Italy; 2Center for Nanoscience and Technology, Istituto Italiano di Tecnologia, Milano, Italy.

In the recent past, lead-based perovskite nanocrystals (NCs) have received significant attention for their unique optical and electronic properties.1 This lead-based perovskite nanostructures with chemical formula APbX3 (A: Cs, CH3NH3 (MA), X=Cl, Br, I) have been reported with high PL quantum efficiency (PLQE), tunable quantum confined emission, large absorption cross section, and low-threshold for lasing. However, the toxicity of the lead2 and stability in air limits its practical application.3 Here, we present a study on ligands-capped lead-free Cs2Bi2I9 nanocrystals showing unprecedented structured and broadband (200 nm) emission. We attribute such features to the recombination of self-trapped excitons mediated by ligand vibrations and to the emission from trap-states. Given these interesting features, we envisage application of these materials in solid-state lightning.

References
8. S. Motti et al., submitted for publication.

11:00 AM ET 12.02.08
Tailoring the Broadband Emission Properties of 2D Perovskites Through Synthetic Design
Daniele Cortecchia1, Tetiana Borzda1, Stefanie Neutzner1, Benny Febriniay2, Jason England1 and Annamaria Petrozza2; 1Centre for Nano Science and Technology, Istituto Italiano di Tecnologia, Milan, Italy; 2Energy Research Institute @ NTU(ERI@N), Nanyang Technological University, Singapore, Singapore; 3Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Two-dimensional (2D) perovskites are attracting increasing interest in photonics and light emitting devices. These low dimensional structures are characterized by great synthetic versatility which allows the incorporation of a wide range of organic cations for the fine-tuning of their optoelectronic properties. The excitons confined in these quantum-well-like structures strongly interact with the highly polar perovskite lattice and determine their characteristic optical properties.1 [1] Through careful material’s engineering, it is possible to modulate the emissive properties from narrowband luminescence with high colour purity, to ultrabroad and highly Stokes shifted luminescence. Such broadband emission is generally attributed to trap states with wide energy distribution originating from exciton-self trapping phenomena.2 [2,3] Although recent progresses suggest that broadband emission is favoured in case of strong distortion of the inorganic lattice [2,4], a full understanding of the interplay between the material’s structure and defectivity/luminescence properties is still missing, urging the synthesis and analysis of a broader range of materials. In this work, we report the study of a series of novel 2D perovskites combining temperature dependent and time resolved spectroscopic measurements with structural characterization. We exploit the templating properties of different organic cations to control the structural arrangement of the inorganic motif and show that increased distortion of the octahedral coordination promotes the exciton self-trapping process enhancing the contribution of broadband photoluminescence. On the other hand, we demonstrate that optoelectronically active organic cations (e.g. naphthyl and pyrene based organic molecules) can be used to further tune the luminescence properties of the hybrid perovskite.

Our findings extend the understanding of the processes underpinning broadband luminescence in 2D perovskites and provide fundamental guidelines for the synthetic design of efficient emitters with tunable luminescent properties.
Investigation of Structural and Compositional Defects in Hybrid Organic-Inorganic Triple Cation Perovskite Films and their Effect on Optoelectronic Properties

An issue of critical importance in lead-based halide perovskites, much sought-after class of semiconductors in photovoltaics (PV) research, is defects; “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination[1], whereas impurity induced energy levels in the band gap could lead to increased absorption of sub-gap photons which can enhance efficiencies[2]. While experimental detection of defects is non-trivial and identification of the origin of defect states is usually impossible, density functional theory (DFT) calculations have been widely applied to accurately predict defect formation energies and transition levels[3]. In this work, we use DFT to study various intrinsic and extrinsic point defects in mixed bromide/chloride MAPbBr_{3-y}Cl_y perovskites (MA = methylammonium) with varying compositions (y = 0, 0.75, 1.5, 2.25, 3), where the calculated band gap increases from ~ 2 eV for y = 0 to ~ 2.6 eV for y = 3. We simulated all vacancy, self-interstitial and anti-site defects, as well as several transition metal substitution defects at the Pb site and calculated their formation energies in different charged states as a function of the chemical potential of relevant species and the Fermi level in the semiconductor as it moves from the valence band maximum (VBM) to the conduction band minimum (CBM). Our results revealed that in MAPbBr₃, vacancy defects (V₀, V₁, and V₂) are dominant acceptor and donor defects and only create shallow transition levels (i.e., close to the VBM or CBM), while higher energy defects create deeper levels; this is in good agreement with the computational literature[4]. The equilibrium Fermi level changes from inside the VB to the CBM (i.e., the highest level of intrinsic conductivity) on going from Br-rich to Pb-rich chemical potential conditions. Upon adding Cl to the system, it is seen that vacancy defects are again the lowest energy defects and the equilibrium Fermi level follows the same trend as in MAPbBr₃, but halogen vacancies (Vₙ and Vₓ) create deeper levels in the band gap the higher the value of y, indicating that in mixed Br/Cl or pure Cl perovskites, there is a danger of non-radiative recombination of carriers owing to deep defect levels. Further, several extrinsic substitutes like Sc, Y, Zr, Nb and Hf are shown to compensate for the dominant intrinsic defects in MAPbBr₃, MAPbBr₃Cl, and MAPbCl₃ by creating lower formation energy defects and shifting the equilibrium Fermi level towards the CBM, thus making the semiconductor conductivity more n-type. These substituents can not only help overcome the adverse effect of deep intrinsic defects, but their mid-gap states can potentially be exploited for optoelectronic properties of perovskite thin films.

In this talk we will detail a multiscale approach to determine 1) the nature of the defects, 2) their effect on the electronic properties of (MA,FA,Cs)Pb(IₓBr₁₋ₓ)₃ thin films and 3) how a number of the most promising passivation strategies modify defects on the nanoscale and subsequently reduce trap state densities. We spatially correlate high-resolution nano x-ray diffraction and nano x-ray fluorescence maps obtained on the I14 nanoprobe beamline at Diamond Light Source, with scanning electron diffraction, scanning transmission electron microscopy - energy dispersive x-ray, photoluminescence, and photoemission maps to reveal that strain related structural defects have a significant impact on the nanoscale and microscale optoelectronic properties of perovskite thin films. Our work reveals important information on the relevance of defects in the operation of state-of-the-art perovskite optoelectronic devices, which is critical to inform future defect engineering and passivation strategies. We also detail correlated multimodal characterisation techniques with nanoscale spatial resolutions that are applicable to a wide range of inherently beam sensitive materials.

REFERENCES


11:15 AM ET12.02.09

11:30 AM ET12.02.10

Compensation of Intrinsic Point Defects by Extrinsic Substitution in Lead-Based Mixed Halide Hybrid Perovskites

An issue of critical importance in lead-based halide perovskites, much sought-after class of semiconductors in photovoltaics (PV) research, is defects; “deep” defect levels can prove catastrophic for PV performance by causing non-radiative carrier recombination[1], whereas impurity induced energy levels in the band gap could lead to increased absorption of sub-gap photons which can enhance efficiencies[2]. While experimental detection of defects is non-trivial and identification of the origin of defect states is usually impossible, density functional theory (DFT) calculations have been widely applied to accurately predict defect formation energies and transition levels[3]. In this work, we use DFT to study various intrinsic and extrinsic point defects in mixed bromide/chloride MAPbBr₃Clₓ perovskites (MA = methylammonium) with varying compositions (y = 0, 0.75, 1.5, 2.25, 3), where the calculated band gap increases from ~ 2 eV for y = 0 to ~ 2.6 eV for y = 3. We simulated all vacancy, self-interstitial and anti-site defects, as well as several transition metal substitution defects at the Pb site and calculated their formation energies in different charged states as a function of the chemical potential of relevant species and the Fermi level in the semiconductor as it moves from the valence band maximum (VBM) to the conduction band minimum (CBM). Our results revealed that in MAPbBr₃, vacancy defects (V₀, V₁, and V₂) are dominant acceptor and donor defects and only create shallow transition levels (i.e., close to the VBM or CBM), while higher energy defects create deeper levels; this is in good agreement with the computational literature[4]. The equilibrium Fermi level changes from inside the VB to the CBM (i.e., the highest level of intrinsic conductivity) on going from Br-rich to Pb-rich chemical potential conditions. Upon adding Cl to the system, it is seen that vacancy defects are again the lowest energy defects and the equilibrium Fermi level follows the same trend as in MAPbBr₃, but halogen vacancies (Vₙ and Vₓ) create deeper levels in the band gap the higher the value of y, indicating that in mixed Br/Cl or pure Cl perovskites, there is a danger of non-radiative recombination of carriers owing to deep defect levels. Further, several extrinsic substitutes like Sc, Y, Zr, Nb and Hf are shown to compensate for the dominant intrinsic defects in MAPbBr₃, MAPbBr₃Cl, and MAPbCl₃ by creating lower formation energy defects and shifting the equilibrium Fermi level towards the CBM, thus making the semiconductor conductivity more n-type. These substituents can not only help overcome the adverse effect of deep intrinsic defects, but their mid-gap states can potentially be exploited for intermediate band PV applications[5].

REFERENCES


11:45 AM ET12.02.11

Polarization, Mixed Conductivity and Deep Level Defects in Organometallic Halide Perovskites

Understanding the type, formation energy and capture cross section of defects is one of the challenges in the field of organometallic halide perovskite (OMHP) devices. In more matured semiconductors like Si, the knowledge of defects was one of the major factor in successful technological implementation. This knowledge and its control can make a paradigm in development of OMHP devices. Yet there is limited information on the properties of defects in OMHPs and controversy on the nature and role of these defects. Several studies explained that main intrinsic defects are only shallow level...
defects leading to long carrier diffusion length and carrier life time coupled to efficient OMHP devices suggesting a class of materials with low concentration of defects and/or highly defect tolerance. Recently, it was revealed that the performance of OMHP devices is mainly limited by Shockley-Read-Hall recombination confirming that defects are dynamic elements and have a critical role in development of OMHP devices. Therefore, deep localized defects exist and limit the operation of highly efficient OMHP devices. It is crucial to fundamentally understand how deep levels can explain the long carrier life time and how this characteristic can be used practically in development of OMHP devices. The non-radiative defect assisted carrier recombination is particularly important in operation of solar cells for higher Voc and in detectors for high charge collection efficiency. In this work, we provide a profound insight into crucial electrical and transport properties of OMHPs based on single crystal MAPbBr3 device. The space charge dynamics associated with charged deep level defects was studied by time-of-flight technique (ToF) driven by pulse voltage bias. We have previously shown that current waveform (CWF) used in ToF technique is sensitive to space charge near the contacts, which deforms the electric field inside the device and enables evaluation of the space charge parameters. Such modification of ToF allows us to determine the effect of deep levels on material transport properties such as lifetime, carrier mobility, and electric field profile. Using CWF ToF measurements and polarization theory, we explored polarization dynamic and transport properties of MAPbBr3 single crystals. In order to determine deep level activation energy and capture cross section, for the first time photo-Hall effect spectroscopy (PHES) with enhanced illumination in both steady and dynamic regimes was used. Using these measurements with tunable photon energies, we revealed the inner-bandgap electrical structure of MAPbBr3 single crystals and the activation energy and capture cross section of deep level defects was estimated.

References:

SESSION ET12.03: Elucidating Roles of Defects in Operating Fuel Cell Materials and Devices
Session Chairs: Daniele Cortecchia and Panchapakesan Ganesh
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 313

1:30 PM ET12.03.01
Surface-Terminating Grain Boundaries as Active Sites for Oxygen Electrochemical Reactions Sossina M. Haile1, Ichiro Takeuchi2 and Robert E. Usuki3; 1Northwestern University, Pasadena, California, United States; 2Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 3Max Planck Institute for Solid State Research, Stuttgart, Germany.

Lanthanum strontium manganite is the canonical cathode for solid oxide fuel cells. It offers a valuable balance between electrochemical activity, chemical stability, and thermomechanical compatibility with the widely used electrolyte, yttria stabilized zirconia (YSZ). Despite its widespread implementation, questions regarding the reaction pathway for oxygen electroreduction on this material remain open. Here, a fundamental study of the reduction mechanism is carried using thin film methods. Libraries of (La0.8Sr0.2)0.98MnO3+δ thin film microelectrodes with systematically varied thickness or growth temperature were prepared by pulsed laser deposition, and a novel robotic instrument was used to characterize these libraries in automated fashion by impedance spectroscopy. All impedance trends are consistent with a reaction pathway involving oxygen reduction over the LSM surface followed by diffusion through the film and into the electrolyte substrate. The surface activity is found to be correlated with the number of exposed grain boundary sites, which decreases with either increasing film thickness (at constant growth temperature) or increasing film growth temperature (at constant thickness). These findings suggest that exposed grain boundaries in LSM films are more active than exposed grains towards the rate-limiting surface process, and that oxygen ion diffusion through polycrystalline LSM films is faster than several prior studies have concluded.

2:00 PM ET12.03.02
Dopant and Vacancy Distribution in Doped Ceria and Its Influence on the Oxide Properties—Theoretical Approach Natalia Skorodumova1, 2; 1Materials Science and Engineering, The Royal Institute of Technology (KTH), Stockholm, Sweden; 2Physics and Astronomy, Uppsala University, Uppsala, Sweden.

Transition metal oxides are often doped in order to tune their performance for particular applications. It is generally known that the properties of doped oxides are sensitive to the details of dopant distribution and its dynamics, however, reports demonstrating exact structure – properties relations are still rare. Here, taking Gd-doped ceria as an example, we show how the ordering of dopants and oxygen vacancies varies with temperature and concentration. The phase diagram for the Gd-doped ceria has been determined by means of a combined Density Functional Theory (DFT), cluster expansion and lattice Monte Carlo approach. In the thermodynamic equilibrium, we observe two transitions: an onset of oxygen-vacancy ordering at ~1300K~3300K for concentrations xGd = 30 – 100% and then, below ~1000 K, a phase separation into CeO2 and C-type Gd2O3 for the whole concentration interval (xGd = 0 – 100%). We also observe that the immobilization of cations below 1500 K does not prevent the oxygen-vacancy C-type order from forming. We demonstrate that this oxygen-vacancy ordering transitions noticeably influences the lattice parameter, bulk modulus and elastic moduli of Gd-doped ceria as well as its oxygen-ion conductivity.

2:30 PM ET12.03.03
Atomic-Scale Structure and Stability of Dopant-Defect Complexes at Misfit Dislocations in CeO2/MgO Heterointerfaces Pratik P. Dholabhai; School of Physics and Astronomy, Rochester Institute of Technology, Rochester, New York, United States.

Complex oxide heterostructures and thin-films have emerged as promising candidates for diverse applications, wherein interfaces play a critical role in influencing novel properties not present in individual components. In Solid Oxide Fuel Cells (SOFCs), the oxide thin films and heterostructures have found applications as advanced electrolytes. Lattice-mismatched epitaxial-growth of oxide films on substrates above a critical thickness lead to the formation of misfit dislocations, which influence vital material properties. We have employed atomistic simulations to investigate the influence of misfit dislocations on dopant-defect complexes at CeO2/MgO heterointerfaces. In this case, the experimentally observed [110]CeO2||(100)MgO interface orientation relationship has been utilized. For ionic conductivity applications, trivalent dopants are generally added to CeO2 as they have a net effective charge that affects the electrometallity condition, which lead to the formation of oxygen vacancies. In bulk electrolytes, at low temperatures, dopants and oxygen vacancies form complexes that influence ionic conductivity. However, at misfit dislocations, the role of dopant-defect complexes is not well understood. We find that the complexes shaped by trivalent dopants and oxygen vacancies have diverse features at the heterointerfaces. We have considered various scenarios...
Defect Engineering of Bulk Al\textsubscript{2}O\textsubscript{3} and the Al\textsubscript{2}O\textsubscript{3}/Al Interface to Enhance Its Hydrogen Permeation Barrier Properties

Compressive experimental study on how the deposition oxygen pressure and post-annealing control the brownmillerite phase formation and evolution and the formation process for the SFO films grown on LAO substrate, which is in good agreement with our experimental observation. Our results display a single crystalline films on LaAlO\textsubscript{3} (001) substrates by pulsed laser deposition. By tuning the deposition oxygen pressure and post-annealing, the orientation of the perovskite lattice sites. Such vacancies produce both oxygen-ion conduction and electronic conduction, and the former could be exploited in electrolytes in exchange at the surface is typically rate-limiting, tuning of the electrode surface is a key aspect in the development and optimization of materials for energy conversion applications. Sr-doped perovskite materials form passivating Sr-rich layers and particle on the surface due to segregation of the dopant strontium ions. This surface layer inhibits the oxygen exchange at the surface, thus increasing polarization resistance and reducing the energy efficiency of the SOFC.

Although the basic features of the LSM defect chemistry have been well-understood for at least 20 years based on experiments, the more detailed aspects (such as antisite defects and A/B ratio) and their possible implications for Sr segregation are not understood. Due to the large variety of defect species, the surface and bulk defect chemistry of LSM (as well as other perovskites) have not been explored in detail with computational methods in the past. As a consequence, there is little consensus in the literature about the nature and driving force of Sr segregation. We assess the stability of LSM over a wide range of T and p(O\textsubscript{2}) using a combination of DFT calculations on the GGA+U level and DFT-based thermodynamics. We apply these methods to examine the stabilities of the LSM(001) surface and the LSM bulk. We find the clean LSM(001) surface to be unstable and prone to reconstructions and defect segregation. Considering a wide variety of near-surface defects, as well as the growth of SrO as clusters, particles or homoepitaxial layers, we come to the conclusion that Sr segregation should be self-limiting because the surface dipole moment is removed by SrO overlayers that do not cover the entire surface. These surface terminations are stable and not prone to further segregation of Sr.

Experimental studies report the formation of SrO particles on the surfaces of Sr-doped perovskites after annealing, while our findings suggest that these large quantities of Sr cannot come from the surface. We considered the formation of a SrO phase as a new type of defect reaction in a new defect model for LSM that considers all of the defects mentioned above. We find that the equilibrium Sr content in LSM varies considerably within the relevant range of T and p(O\textsubscript{2}), which can effortlessly explain the experimentally observed formation of SrO under SOFC operating conditions, as well as the experimentally observed onset temperature of Sr segregation.

These results allow us to develop a knowledge-based doping strategy that prevents Sr segregation in LSM. Our modeling strategy and principle findings are transferable to other perovskite oxides.

Hydrogen is a promising clean fuel. A key bottleneck to its widespread utilization is the susceptibility of the materials used in hydrogen storage and transport infrastructure (typically steels) to embrittlement and failure. This necessitates the use of permeation barriers to prevent hydrogen ingress into the steel. Al\textsubscript{2}O\textsubscript{3} has been established as a popular hydrogen permeation barrier material, due to its low hydrogen solubility and diffusivity. The goal of this study is to further enhance the permeation resistance of Al\textsubscript{2}O\textsubscript{3} by two means: point-defect engineering of the Al\textsubscript{2}O\textsubscript{3} bulk, and space-charge engineering of the metal-H\textsubscript{2}O interface.
the Al₂O₃/Al interface, to reduce the overall hydrogen solubility and diffusivity of the system. To evaluate the performance of the Al₂O₃ bulk, a combination of first principle calculations and thermodynamic concepts were used to obtain defect concentrations in undoped and doped Al₂O₃. Our findings aid in the identification of suitable dopants that result in superior hydrogen permeation resistance of bulk Al₂O₃. Donor dopants like Ti, Si, Fe or Cr drastically reduce the concentration of free hydrogen interstitials (the primary diffusible defect under room temperature H₂ gas transport conditions) to negligible amounts, with majority of the total hydrogen concentration trapped at aluminum vacancy sites with high binding energy (~3 eV). Hydrogen is thus rendered immobile, with reduced diffusivity in Al₂O₃. In addition, Fe and Cr doping aid in decreasing the overall hydrogen solubility to 1/4 and 1/2 that of the undoped case respectively.

To evaluate the performance of the Al₂O₃/Al interface, first principles methods and continuum modeling were used to establish and tune the nature of the interfacial core and space-charge layer to lower the hydrogen solubility and diffusivity. Accounting for the interfacial band offset and variation in the local environment through defect segregation energies, Poisson’s equation is self-consistently solved to obtain the defect equilibria at the interface. Moreover, dopants have a large tendency to segregate to the Al₂O₃/Al interface, and thus are used to regulate the nature and extent of this space charge. This study thus aids in the atomic-level understanding of the impact of the Al₂O₃/Al interface on overall hydrogen permeability of the coating. This study also helps rationalize experimental findings that multilayer coatings of Al₂O₃/Al have superior permeation resistance than a single layer of Al₂O₃ of the same thickness. It is emphasized that the results of this study can also be extended to other systems where the metal/oxide interface (and interphase formation) affects device efficiency, such as the electrode/electrolyte interface in resistive switching devices and the metal/dielectric interface in MOS devices.

4:30 PM ET12.03.08
Discovery of Proton- Conducting Ceramic Fuel Cell Materials Using Genetic Algorithm Yeong-Cheol Kim¹, Ki-Yung Kim¹, Yurie Kim², Jason Kim³ and Jun- Yeong Jo¹; ¹School of Energy Materials and Chemical Engineering, KoreaTech, Cheonan, Korea (the Republic of); ²Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

BaCeO₃ and BaZrO₃ have been the most studied electrolyte materials for proton-conducting ceramic fuel cells for the last four decades. BaCeO₃ shows high conductivity and very sinterability, but poor stability under CO₂ atmosphere. BaZrO₃ shows good stability, but poor sinterability and low conductivity at grain boundaries. Mixing these two materials to take advantage of the merits of both materials have been a trend, and recently BaZr₀.₄Ce₀.₄Y₀.₁Yb₀.₁O₃ (BZCYYb4411) was introduced as a best electrolyte, replacing BZCYYb1711 [1]. Y and Yb are dopants to generate oxygen vacancies in the electrolyte materials. As researchers have increased the number of components to improve the material properties, they had to invest more time and money to investigate the vast materials composition space. We used genetic algorithm to save time and money in searching the vast structure space for better materials. We converted structures into chromosomes and applied crossover, mutation, and compensation to generate next-generation chromosomes. Based on the best chromosomes, we added water molecules to fill the oxygen vacancies. Genetic algorithm was applied again to find optimum configurations of protons in the structure. This technique was also applied to air electrode materials to find optimum solid solution configurations.

Reference

4:45 PM ET12.03.09
Controlled Oxygen-Vacancy Distribution and Intergranular Amorphous Phases to Boost the Ionic Conduction in Perovskite-Oxide Electrolytes Sung-Yoon Chang; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

ABO₃-type perovskites are one of the oxide families where various ionic defects can be created by changing the oxygen partial pressure and adding proper dopants. Among many notable physical properties and transport phenomena observed in perovskites, aspects of high proton conductivity have been intensively investigated in zirconates and cerates over the past three decades in efforts to elucidate the precise conduction mechanisms and further improve the ionic conductivity for real applications as electrolytes in solid-oxide fuel cells operated at intermediate temperature. In the first part of this presentation, we demonstrate that the proton conductivity can be notably enhanced by the association of acceptor dopants and oxygen vacancies in BaZrO₃ and BaCeO₃. The acceptor-vacancy clustering is verified to be remarkably efficient against proton trapping by theoretical DFT calculations and experimental measurements based on impedance spectroscopy along with atomic-scale direct visualization (Angew. Chem. Int. Ed. 55, 13499 (2016)). In addition to the impact of defect association, we clarify that a nanometer-thick amorphous phase at grain boundaries in proton-conducting BaCeO₃ polycrystals is responsible for substantial retardation of proton migration in the second part of the presentation. By a combination of atomic-scale chemical analysis and physical imaging along with consideration of straightforward phase equilibria, it is demonstrated that highly densified BaCeO₃ polycrystals (~98% in relative density) free of a grain-boundary amorphous phase can be easily fabricated by a conventional ceramic process and show sufficiently high proton conductivity (order of 10⁻² S/cm at 600°C) and significantly improved chemical stability (Nano Lett. 18, 1110 (2018)). These findings emphasize the value of direct identification of lattice defects and subsequent manipulation of their distribution in ion-conducting oxide polycrystals.
effects on organic solar cells.

Here, we investigated the characteristics of ZnO layer prepared in different humidity and then explored their effects on the actual devices of organic solar cells. Specifically, the humidity was adjusted from 15% to 80% to coat the ZnO layer. As a result of comparing efficiency of organic solar cell devices using these ZnO layer, it showed the highest efficiency of 8.30% at 25% of humidity. In order to confirm the effect on the efficiency change, the surface characteristics, optical characteristics and defects were analyzed. To investigate the effect of humidity on the thickness and roughness of the ZnO thin film, the Alpha step and AFM were analyzed and the optical characteristics were analyzed by measuring the transmittance. The defects in the organic solar cell were defective through XPS and PL because the charge recombination reduced the efficiency. From the efficiency of organic solar cell device and analysis results, it is thought that ZnO produced at 25% humidity is most suitable as ETL layer of organic solar cell.

ET12.04.02
Hydration of BaCe_{1-x-y}Zr_{y}Y_{y}O_{3-δ} Using Genetic Algorithm Ki-Yung Kim1, Yurie Kim2, Jason Kim2, Young-Bok Kim3, Jun-Yeong Jo1, Dong-Gung Shin1, In-Gyu Cho1 and Yeong-Chool Kim1; School of Energy Materials and Chemical Engineering, KoreaTech, Cheonan, Korea (the Republic of)1; Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of). Oxygene-coduting solid oxide fuel cells (SOFCs) have been actively studied as an alternative power source because they have high energy conversion efficiency and no use of precious metal catalysts. The high operating temperatures (800-1000°C), however, hinder durability and low fabrication costs of the SOFCs. Proton-conducting FCs is an alternative solution due to their low operating temperatures (400-600°C) [1]. Recently, BaCe_{1-x-y}Zr_{y}Y_{y}O_{3-δ} that can be fabricated by mixing BaCeO_{3} and BaZrO_{3} with Y and Yb as dopants was introduced as an excellent electrolyte material [2]. BaCe_{1-x-y}Zr_{y}Y_{y}O_{3-δ} can take advantage of the strong points of BaCeO_{3} and BaZrO_{3}; BaCeO_{3} shows high conductivity but low stability, while BaZrO_{3} shows good stability but low grain boundary conductivity [3]. The material, however, shows many different configurations of Ce, Zr, Y and Yb atoms in the B site of the ABO_{3} perovskite structure. In this study, we employed genetic algorithm and lattice dynamics to find an energetically favorable BaCe_{1-x-y}Zr_{y}Y_{y}O_{3-δ} solid solution structure. We also investigated the hydration process by adding water molecules to fill the oxygen vacancies that reside in the solid solution structure. The distribution of protons after hydration will be discussed based on the results of genetic algorithm and lattice dynamics.

References

ET12.04.03
Equilibrium Space Charges Effect at Halide Perovskite Interactions—The Role of the Ionic Charge Conductions Gee Yeong Kim, Alessandro Spena and Joachim Maier; Max Planck Institute for Solid State Research, Stuttgart, Germany.

Methylammonium lead iodide (MAPI) is the archetype of the halide perovskites that are currently in the focus of photovoltaic research not only because of high conversion efficiencies but also because of intriguing long-time behavior. In this contribution we discuss equilibrium space charge effects at MAPI interfaces and concentrate on the implications for MAPI/TiO_{2} and MAPI/Al_{2}O_{3} contacts. Irrespective of polarization phenomena building up under operation, already the equilibrium situation is dominated by space charge effects. While such space charge effects are only considered as a consequence of electronic charge carrier redistribution, we will apply a generalized picture that discusses both ionic and electronic redistribution. In fact, we will show that the space charges are ionically dominated, in a sense that ions dictated the space charge potential and electrons follow the established field (fellow-traveler effect). Our analysis is based on the measurement of electronic and ionic conductivities in MAPI-TiO_{2} and MAPI-Al_{2}O_{3} composites, a technique that has been successfully applied in solid states Ionics [1-3]. The results are corroborated by Hall effect experiments.

References

ET12.04.04
Fano Defect Induced Resonant Thermoelectric Transport in Metallic Nanowires Chumin Wang, Fernando Sanchez and Vicenta Sanchez; Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

Fano defects consist of atomic chains attached to a low-dimensional system and produce rich wave interferences in its conductivity spectra [1]. Recently, we have analytically proved the existence of a novel ballistic conduction state in two-dimensional belts with a non-periodic arrangement of atoms in both its cross section and along the Fano plane defect [2]. Moreover, enhancements to the ballistic alternating current (AC) conductivity are reported when quasiperiodically placed Fano defects are introduced to a periodic chain or nanowire [3]. On the other hand, the direct conversion between thermal and electrical energies by thermoelectric devices has become an important alternative for the clean energy generation. Low-dimensional materials seem to be promising candidates, whose efficiency is determined by the dimensionless thermoelectric figure-of-merit (ZT) that can be calculated by using the Boltzmann formalism. The inherent correlation between the thermoelectric quantities, such as electrical and thermal conductivities, makes difficult to improve the value of ZT.

In this work, we study the thermoelectric properties of metallic nanowires with periodic and quasiperiodically placed Fano defects by means of a real-space renormalization plus convolution method [4] developed for the Kubo-Greenwood formula, in which tight-binding and Born models are respectively used for the study of electric and lattice thermal conductivities [5]. We analytically demonstrate the existence of a significantly improved ZT due to the Fano defects [6]. In addition, the numerical results suggest that the quasiperiodicity could be another important ZT enhancing factor, since it highly diminishes the thermal conduction of long wavelength acoustic phonons, which are responsible of the phononic conductivity at low temperature and not easy to block their transmission since they do not feel local defects neither impurities [7].

This work has been partially supported by UNAM-DGAPA-IN106317 and CONACyT-252943. Computations were performed at Miztli of DTGC-UNAM.

References
SESSION ET12.05: Harvesting Functional Defects for Photoelectrochemistry  
Session Chairs: Joanne Etheridge and Hua Zhou  
Wednesday Morning, November 28, 2018  
Hynes, Level 3, Room 313

8:00 AM *ET12.05.01  
Effect of Surface and Bulk Defects on Hot Carrier Transport in Ultra-Thin Metallic Films  
Jeremy N. Munday; University of Maryland, College Park, Maryland, United States.

Photon absorption in metal films can result in the excitation of hot carriers, i.e. electrons and holes with kinetic energy in excess of their thermal distribution. For hot carriers generated within a diffusion length of the surface, opportunities arise for extraction of these energetic carriers, which can perform tasks not achievable by thermal electrons including modification of chemical reaction rates, charge injection into nearby semiconductors for current generation, etc. However, one of the key limitations on carrier transport and collection is defects. Both surface and bulk defects can cause carrier relaxation and forfeit their original benefits. Here we will discuss our recent work on excitation and collection of hot electrons and holes in thin metal films and our attempts to mitigate the harmful effects of defects. We will show energy conversion and photodetector devices that can operate over both the visible and near-IR based on injection of hot carriers either into semiconductors or across insulating barriers into an adjacent conductor. We will also discuss future applications of this work for tailoring photon absorption and carrier lifetime.

8:30 AM ET12.05.02  
Precise Design of Photocatalyst Heterostructure with Controllable Photo-Generated Carrier Behaviors for Solar to Fuel Conversion  
Kan Zhang; 1,2, 3Nanjing University of Science and Technology, Nanjing, China; 2Yonsei University, Seoul, Korea (the Republic of).

Solar-driven hydrogen (H2) evolution has been considered as a clean, green and efficient strategy to solve the energy shortage and ameliorate environmental pollution. Heterogeneous photocatalysts comprising an excitable semiconductor and a H2 evolution co-catalyst (HEC) are regarded as a standard configuration to drive efficient photocatalytic H2 reaction. However, photocatalytic H2 generation requires both efficient charge separation and redox steps to occur simultaneously. Loading a HEC on photocatalyst is an efficient means of extracting photogenerated charge carriers, host active sites for catalytic H2 evolution and improve stability by suppressing photo-corrosion. However, H2 generation in photocatalyst remains limited by the electron/hole mutual Coulomb interaction, which seriously inhibits spatial charge separation. When HECs are near the charge generation region of CdS, both electrons and holes can be localized via Coulomb interaction. This localization determines the wavefunction overlap with the HECs and trap states and retards the electron transfer rates. In this sense, generating a long-lived charge-separated state for delocalized electrons is crucial for efficient H2 evolution while accelerating hole consumption by hole scavengers. In this talk, I will discuss how to control photo-induced electrons that successfully deliver to HECs sights towards highly efficient solar hydrogen evolution through structure design of nanomaterials.

8:45 AM ET12.05.03  
Dispelling the Myth of Passivated Codoping in TiO2  
Benjamin A. Willianson1,2, Nicholas P. Chadwick1,3, Sanjayan Sathasivam1, Claire J. Carmalt1, Ivan P. Parkin1 and David O. Scanlon1,2,4; 1Department of Chemistry, University College London, London, United Kingdom; 2Thomas Young Centre, University College London, London, United Kingdom; 3Bio Nano Consulting, London, United Kingdom; 4Diamond Light Source Ltd., Diamond House, Didcot, United Kingdom.

Modification of TiO2 to increase its visible light activity and promote higher performance photocatalytic ability has become a key research goal for materials scientists in the past two decades. One of the most popular approaches to achieve this is “passivated co-doping”, whereby an equal number of donor and acceptor dopants are introduced into the lattice, producing a charge neutral system with a reduced band gap. From the multitude of codoped systems, [Nb+N] and [Ta+N] are widely regarded as the “archetypal” codoping pairs of doped anatase, however the literature results rarely claim 1:1 passivated codoping. Using state-of-the-art hybrid density functional theory, and using the [Nb+N] and [Ta+N] codoped systems as examples, we show that fully passivated TiO2 is unrealisable due to the inherent doping asymmetry of anatase or any other n-type photocatalysts. This research critically discusses the future of passivated codoping as a mode of band gap modulation.

9:00 AM ET12.05.04  
First Principles Modelling of Polaron Formation in TiO2 Polymorphs  
Razak Elmaslmane1, Matthew Watkins2 and Keith McKenna3, 1University of York, York, United Kingdom; 2University of Lincoln, Lincoln, United Kingdom.

We present a computationally efficient and predictive methodology for modelling the formation and properties of electron and hole polarons in solids. Through non-empirical optimization of the fraction of Hartree-Fock exchange (α) in a hybrid functional, we ensure the generalized Koopmans’ condition is satisfied and the self-interaction error is minimized. Our previous work in model systems has shown that accurate densities and energies can be obtained from such an optimization. The approach is applied to model polaron formation in known stable and metastable phases of TiO2 including anatase, rutile, brookite, TiO2(H), TiO2(R) and TiO2(B). Electron polarons are predicted to form in rutile, TiO2(H) and TiO2(R) (with trapping energies ranging from -0.02 eV to -0.35 eV). In rutile the electron localizes largely on a single Ti ion, whereas in TiO2(H) and TiO2(R) the electron is distributed across two neighboring Ti sites. Hole polarons are predicted to form in anatase, brookite, TiO2(H), TiO2(R) and TiO2(B). Electron polarons are predicted to form in rutile, TiO2(H) and TiO2(R) (with trapping energies ranging from -0.02 eV to -0.52 eV). In anatase, brookite and TiO2(B) holes localize on a single O ion, whereas in TiO2(H) and TiO2(R) holes can also be distributed across two O sites. We find that the optimized α has a degree of transferability across the phases, with α=0.115 describing all phases well. We also note the approach yields accurate band gaps, with anatase, rutile and brookite within six percent of experimental values. We conclude our study with a comparison of the alignment of polaron charge transition levels across the different phases. Since the approach we describe is only two to three times more expensive than a standard density functional theory calculation, it is ideally suited to model charge trapping at complex defects (such as surfaces and interfaces) in a range of materials relevant for technological applications, but previously inaccessible to predictive modelling.

9:15 AM ET12.05.05
Anomalous Conductivity Tailored by Domain Boundary Transport in Crystalline Bismuth Vanadate Photoanodes Wenrui Zhang1, Danhua Yan1, Jun Li1, Qiyuan Wu2, Jiajie Cen2, Lihua Zhang1, Alexander Orlov2, Huolin Xin1, Jing Tao1 and Mingzhao Liu1; 1Brookhaven National Laboratory, Upton, New York, United States; 2Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Carrier transport in semiconductor photoelectrodes strongly correlates with intrinsic material characteristics including carrier mobility and diffusion length, and extrinsic structural imperfections including mobile charged defects at domain boundaries, which collectively determines the photoelectrochemistry (PEC) performance. Here we elucidate the interplay between intrinsic carrier transport, domain-boundary-induced conductivity and PEC water oxidation in the model photoanode of bismuth vanadate (BiVO4). In particular, epitaxial single-domain BiVO4 and c-axis oriented multi-domain BiVO4 thin films are fabricated using pulsed laser deposition to decouple the intrinsic and extrinsic carrier transport. In addition to the low intrinsic conductivity that is due to the small polaron transport within BiVO4 domains, we identify anomalously high electrical conductivity arising from vertical domain boundaries for multi-domain BiVO4 films. Local domain boundary conduction compensates the inherently poor electron transport by shortening the transport distance for electrons diffused into the domain boundary region, therefore suppressing the photocurrent difference between front and back illumination. This work provides insights for engineering carrier transport through coordinating structural domain boundaries and intrinsic material features in designing modulated water splitting photoelectrodes.

9:30 AM BREAK

10:00 AM ET12.05.06
Tuning Catalytic Properties for Water Splitting with Functional Defects Xiaolin Zheng; Stanford University, Stanford, California, United States.

Defects, such as vacancies and dopants, offer rich opportunities to tune the catalytic properties of crystals. In this talk, we will present three examples on using defects to optimize the catalytic activity for water splitting and all examples are supported by density functional theory calculations and experimental results. The first example is related to the well-known hydrogen evolution reaction (HER) catalyst, MoS2. For MoS2, the perfect basal plane is chemically inert, but it can be activated by creating S-vacancies. In addition, the activity of the S-vacancy can be further tuned by either strain or transition metal modification. The second example is also related to another HER catalyst: WS2. I will explain how the basal plane activity of WS2 is activated and optimized by tuning Co doping configurations. The third example is switched to the water oxidation side for water splitting. I will demonstrate how rare earth doping enhances the activity, selectivity and stability of BiVO4 towards H2O2 production.

10:30 AM DISCUSSION TIME

10:45 AM ET12.05.08
Enhancing Water-Splitting Performance of Hematite Photoanodes via Hydrogenation Induced Defects Hariom Jani1, 2, Mengyuan Zhang3, Lydia H. Wong1, 4 and Thirumalai V. Venkatesan1, 2, 3; 1NanoCore, Singapore, Singapore; 2NUS Graduate School of Integrative Sciences and Engineering, National University of Singapore, Singapore, Singapore; 3ECE, National University of Singapore, Singapore, Singapore; 4Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore; 5School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore.

Hematite (α-Fe2O3), is a photoanode material candidate for Oxygen Evolution Reaction in a Photo-Electro-Chemical cell (PEC). It has an optical bandgap (~2.1eV) which straddles the water oxidation and reduction potentials, allowing it to drive water splitting by absorbing solar radiation. Its chemical resistance, non-toxicity and low cost, make it a promising material to manufacture hydrogen in an environmentally friendly way. Unfortunately, its poor electrical conductivity, carrier transport dynamics and absorptivity, yield low solar-to-hydrogen conversion.

In my talk, I will present how we have used a special hydrogen treatment to systematically enhance the bulk electronic transport in Hematite Nanorods. We observe that hydrogen doping increases the electronic conductivity of α-Fe2O3 without changing its optical bandgap or its structural properties. Consequently the PEC performance of treated photoanodes is much higher than their pristine counterparts.

The novel hydrogenated phase of α-Fe2O3 is characterised by X-Ray Diffraction, Raman and UV-Vis Spectroscopy, Electron Microscopy and Impedance Spectroscopy. The physics underlying the electronic changes are elucidated by Ultrafast Optical-Pump Probe techniques, X-Ray Absorption and Ab-Initio calculations. Our work paves way to utilizing novel hydrogen induced defect states to systematically enhance functionality of oxide photoanodes.

11:00 AM ET12.05.09
Minimizing the Grain Boundary Effect by Dopant Segregation on Hematite Photoelectrodes for Solar Water Oxidation Aryane Tofanello1, Andre Luiz M. Freitas2, 3 and Flavio L. De Souza1; 1University Federal-ABC, Santo Andre-SP, Brazil; 2University of California, Santa Cruz, Santa Cruz, California, United States.

This work describes the effect of nitrogen atmosphere and chemical addition of different metal transition elements (M = Sn, Ti or Mn) on the hematite surface electrode and its impact on the photoelectrochemical performance (PEC). For comparison, undoped [Air or N2-Fe2O3] and modified [Air or N2-M-Fe2O3] hematite electrodes were prepared by aqueous solution precursor method under hydrothermal condition at low temperature and at fixed synthesis time (2 hours). The as-prepared materials were subjected to additional thermal treatment at 750 ºC for 30 min in air and nitrogen (N2) atmosphere. The undoped electrodes obtained after 2 hours of synthesis exhibited the columnar morphology with thickness around 300 nm. In case of undoped electrodes, treatment in nitrogen atmosphere (N2-Fe2O3) promoted the oxygen vacancies formation (evidenced by X-ray photoelectron spectroscopy) leading to a better photocurrent response at 1.3 mA.cm-2 at 1.23 VRHE. The chemical addition of metal transition elements (M = Sn, Ti or Mn) followed by the thermal treatment and monitored by top-view scanning electron microscopy (SEM) shows significant changes in the morphology. Additionally, to the morphology changes the “dopant” insertion seems to drastically reduce the grain growth, which increases the number of interfaces and surface area. Although the surface area available for chemical reaction increases with the reduction of grain size, the increased number of interfaces or grain boundaries in hematite normally is a problem to the charge separation by acting as recombination sites. Surprisingly, the chemical addition of Sn and Ti, which was found to be segregated in the hematite grain boundaries, seems to reduce the energy in between grains facilitating the electron transport and enhancing the overall electrode performance. The impedance spectroscopy (Nyquist plot) data revealed that the combination of N2 atmosphere with chemical addition of Sn or Ti significant reduce the electrical resistance increasing the hematite performance for water oxidation assisted by sunlight independent of the final morphology.

11:15 AM ET12.05.10
The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Role of Fluorine Doped Tin Oxide Substrate-Hematite Electrodes Interface in the Solar Water Oxidation Performance

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis

The Effect of Defects Created in Microporous Vanadosilicate AM-6 Thin Films in Photocatalysis
as Zintl thermoelectrics (e.g. ZnSb), which are ubiquitously p-type. In this talk, I will present and discuss our recent efforts in modeling point defects in semiconductors, in particular in relation to understanding and predicting their dopability. The focus of the work is on establishing quantitative relationships between the dopability of semiconductors on one side, and their chemical composition and crystal structure on the other, with the main purpose to advance design and discovery of novel optoelectronic and thermoelectric materials. In addition, I will examine more closely our recent prediction of bipolar dopability in the metastable, high-pressure rocksalt phase of ZnO, and discuss significant prospects it implies to overcoming doping asymmetry of semiconductors through polymorphism.

The work is supported by the US National Science Foundation.

2:00 PM ET12.06.02
Predictive Design of Defects in Non-Ideal Ternary Nitrides—Off-Stoichiometry, Contamination and Disorder Ji-Sang Park1, Jacob Cordell1, Andriy Zakutayev1, Adele Tamboli1 and Stephan Lany1, National Renewable Energy Laboratory, Golden, Colorado, United States; 2Colorado School of Mines, Golden, Colorado, United States.

II-IV-V2 ternary nitrides offer many advantages in enhancing functionality for optoelectronic applications. For example, ZnSnN2 (ZTN) is a promising absorber material for photovoltaic (PV) applications and ZnGeN2 (ZGN) can be used in light emitting devices. However, the properties of multinary compounds strongly depend on the materials nonidealities, e.g., disorder, stoichiometry, and impurities. For example, in practice, the growth of ZTN thin film incorporates a non-trivial amount of oxygen. The excess amount of oxygen can lead to cation off-stoichiometry, i.e., Zn excess, and disorders in the material. The conventional dilute-defect model does not capture these non-ideal conditions. In this contribution, we present a predictive defect model of these complex ternary nitrides with disorder, off-stoichiometry, and oxygen contamination, e.g., Zn1-xSnxN2-2xO2x, and their effects on materials properties, such as band gap, carrier localization, absorption coefficients, and defect equilibria. The disordered structures were created by Monte Carlo (MC) simulation with simplified Hamiltonians, such as motif-Hamiltonian and cluster expansion. The MC generated structures were then passed on to electronic structure calculations for disordered and off-stoichiometric structures. These calculated changes in the band structure were then fed back to the materials property predictions, such as net doping, defect equilibria.

2:15 PM ET12.06.03
Effect of Extended Defects on Electrical Properties in Earth Abundant Inorganic Materials Ji-Sang Park1, Sunghyun Kim1, Maria K. Chan2 and Aron Walsh1, Imperial College London, London, United Kingdom; 2Argonne National Laboratory, Lemont, Illinois, United States.

In diamond and zinc-blende structure semiconductors, the stacking sequence can be altered by a missing layer or an additional layer and combinations of them. These extended defects, which is termed as stacking faults, can be regarded as local wurtzite phase in the zinc-blende host, and the material properties are affected accordingly. In a material with at least two types of cation, anti-site domain boundaries, which are periodic arrays of anti-site defects, can be formed as well. We have investigated the extended defects in Cu2ZnSn(S, Se)4 and Si to obtain a general understanding of the defects [1,2]. Cu2ZnSn(S, Se)4 based solar cells have attracted much attention for achieving terawatt scale photovoltaics. While the problem of the open-circuit voltage deficit has not been resolved yet, spatial fluctuations of the band edges by disorder have been regarded as the origin of the deficit. Our hybrid density functional theory calculations indicate that the extended defects also have a role in the lower photovoltaic efficiency [1]. The anti-site domain boundaries, another type of disorder, lower the conduction band. The fact that the anti-site domain boundaries act as electron capture can be understood by the formation of metastable polymorphs or Sn anti-site defects. On the other hand, stacking faults in the material act as electron barriers, while their formation is more likely than the anti-site domain boundaries which formation was experimentally observed. Cation substitutions can promote or suppress the formation of stacking faults.

We also found that the stacking faults affect the stability of point defects. It is known that stacking faults are formed in Si solar cells after the potential induced degradation of shunting type happens. Our calculation shows that the Na interstitials are more stable at the stacking faults where the Na becomes less mobile [2]. Based on the calculation results, we suggest that Na atoms are accumulated at the stacking faults after a long time of operation because of the segregation. Effect of the stacking faults on the device will be discussed.

References

Acknowledgement
J.-S.P. thanks the Royal Society for a Shooter International fellowship. The work at ICL received funding from the European H2020 Framework Programme for research, technological development and demonstration under grant agreement no. 720907. See http://www.starcell.eu. The work at ANL was supported by Laboratory Directed Research and Development (LDRD) funding under Contract No. DE-AC02-06CH11357. Use of the Center of Nanoscale Materials was supported under Contract No. DE-AC02-06CH11357.

2:30 PM BREAK

3:30 PM *ET12.06.04
Oxygen Vacancy in Complex Oxides—The Good, the Bad and the Ugly Ho Nyung Lee; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Functional ionic defects, such as oxygen vacancies, play a central role in the performance of many advanced information and energy materials. While of immediate benefit for low temperature energy production and storage devices and sensors, the ability to artificially control oxygen vacancy content in any environment is also crucial for variety of functional materials, such as high-temperature superconductors, colossal magnetoresistors, memristors, and spintronic devices. On the other hand, for some of functional materials, such as ferroelectrics, the formation of oxygen vacancies is highly detrimental for the performance and endurance of the ferroelectric polarization. However, achieving deliberate control of the oxygen stoichiometry in the oxide thin films has not been much studied, albeit critical for the performance. In this presentation, I will review a synopsis of the major developments and achievements in formation, control, and understanding of oxygen vacancies in correlated oxides. This includes the oxygen sponge SrCoO4 (Jeon et al., Nature Mater. 12, 1057 (2013), Petrie et al., JACS 138, 7252 (2016), Adv. Funct. Mater. 26, 1564 (2016)), oxygen diode formed in LaNiO3 (Guo et al., Adv. Mater. 2018, 1705904), strain control of oxygen kinetics in the Ruddlesden-Popper oxide La6-xSr4-xCuO12-x(Meyer et al., Nature Commun. 9, 98 (2018)), and metal-insulator transition by oxygen stoichiometry control in VO2 (Sharma et al., (unpublished)). Overall, these results summarize the role, importance, and challenge in film growth for the right stoichiometry as well as strain utilization for developing next generation energy and functional materials and devices.
This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

4:00 PM ET12.06.05
Dramatically Improved UV Photoluminescence from ZnO Nanowires by Selective Introduction of Surface Oxygen Vacancies Danhua Yan1, Wenrui Zhang1, Jiajie Cen2 and Mingzhou Liu1; 1Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 2Department of Materials Science and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States.

Zinc oxide nanowire arrays (ZnO NWs) have been extensively studied for their versatile applications in optical and optoelectronic devices, such as light-emitting diodes (LEDs), photodetectors, optical modulator waveguides, and photoelectrochemical anodes. Among various techniques that have been used to fabricate ZnO NWs, the wet-chemical approach becomes the most widely adopted method for its simplicity, as well as its capability to synthesize well-oriented single crystalline ZnO NWs. These devices require quality ZnO NW materials grown by the wet-chemical process usually feature a high density of defects, which suppress near band edge emission and contribute to broad defect state emission in the photoluminescence (PL) spectra.

Here, we demonstrate, counter-intuitively, that the near band edge emission may become dominant by selectively introducing surface oxygen defects to ZnO nanowires via surface engineering. Specifically, near band edge emission (NBE) is effectively enhanced after a thermal annealing that removes most bulk defects and a low pressure O2 plasma treatment that spurs off surface oxygen species to produce a reduced and oxygen vacancy-rich surface. Through a combined study by low-energy electron microscopy (LEEM) and ultraviolet photoelectron spectroscopy (UPS), we discover that the effect is attributed to the lowered surface valence band maximum of the reduced ZnO surface that creates an accumulative band bending, which screens the photocarriers at low carrier densities.

Using two Sn-based transparent conductive oxides as model systems, i.e. amorphous zinc tin oxide (a-ZTO) and polycrystalline tin oxide (SnO2), the origin of these subgap defects and routes for their passivation were studied. Previously we have demonstrated that in a-ZTO, the overall optoelectronic properties still provide free electrons maintaining the high conductivity of the film. This simple passivation scheme with SnO2 significantly improves the optical transparency in the visible spectrum range.

4:15 PM ET12.06.06
Passivating Defects in Sn-Based Oxides—SiO2 Replaces Thermal Treatments Monica Morales-Massie1,2, Esteban Rucavado1, Migle Grauzinyte1, Jose A. Flores-Livas1, Quentin Jeangros2, Federica Landucci2, Stefan Goedecker2, Aicha Hessler-Wyser1 and Christophe Ballif1; 1Ecole Polytechnique Federale de Lausanne, Neuchatel, Switzerland; 2MESA+ Institute of Nanotechnology. University of Twente, Enschede, Netherlands; 3Universitat Basel, Basel, Switzerland.

Tin (Sn)-based metal oxides have been of high technological importance for decades, with applications ranging from photovoltaics, sensors, displays and smart windows. For Sn-based oxides, oxygen deficiencies and undercoordinated Sn atoms result in extended densities of states below the conduction band edge. While shallow states provide free carriers necessary for electrical conductivity, deeper states inside the bandgap create absorption centers affecting the transparency of the films.

Using two Sn-based transparent conductive oxides as model systems, i.e. amorphous zinc tin oxide (a-ZTO) and polycrystalline tin oxide (SnO2) the origin of these subgap defects and routes for their passivation were studied. Previously we have demonstrated that in a-ZTO, the overall optoelectronic properties can be improved by defect passivation via annealing at high temperatures in oxygen-rich environments. Yet, the high thermal budget associated with such treatment is incompatible with many applications such as devices requiring temperature-sensitive materials or fabricated on polymer-based substrates. As an alternative low-temperature passivation route, we propose co-sputtering Sn-based TCOs with silicon dioxide (SiO2). In-depth optoelectronic characterization of the co-sputtered SnO2-SiO2(or a-ZTO-SiO2) films and density functional theory simulations indicate that the SiO2 contribution is twofold. First, oxygen from SiO2 passivates the oxygen deficiencies that form deep defects in SnO2 and a-ZTO. Second, the ionization energy of the remaining deep defect centers is lowered by the presence of silicon atoms. Remarkably, these ionized states do not contribute to subgap absorptance while still providing free electrons maintaining the high conductivity of the film. This simple passivation scheme with SiO2 significantly improves the optical properties without affecting the electrical conductivity, and it is independent of the microstructure of the films, hence overcoming the known transparency conductivity trade-off in Sn-based TCOs.

E. Rucavado et al. Journal of Physical Chemistry C, under consideration

4:30 PM ET12.06.07
Probing Defects in Au- and Te-Hyperdoped Si with Deep Level Transient Spectroscopy and Carrier Lifetime Measurements Shao Qi Lim1, Christopher Xiao-Kuan Lew2, Brett Johnson2, Philippe K. Chow1, Senali Dissanyake1, Meng-Ju Sher4, Quentin Hadspeth1, Jeffrey M. Warrender2 and Jim S. Williams1; 1Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, Australian Capital Territory, Australia; 2Centre for Quantum Computing and Communication Technology, School of Physics, University of Melbourne, Melbourne, Victoria, Australia; 3US Army ARDEC - Benet Laboratories, Watervliet, New York, United States; 4Physics Department, Wesleyan University, Middletown, Connecticut, United States.

Developing a technology that can allow Si to efficiently absorb light in the mid infrared region can open-up important applications in fibre-based communications as well as facilitating the fabrication of Si-based infrared (IR) imaging arrays. In this context, recently Mailoa et al. demonstrated that by hyperdoping Si with Au by ion implantation and pulsed-laser melting (PLM), a Si-based photodetector can absorb into the IR up to 2200 nm [1]. The thin Au surface layer (~150 nm) so produced contained up to 1 atomic % Au that was almost all in solid solution at concentrations far exceeding the solid solubility limit for Au in Si. Spectroscopic data suggest that the observed enhanced absorption was associated with the Au deep donor level in the Si bandgap [1].

Enhanced sub-bandgap absorption of Si hyperdoped (HD) with Ti, S, Se and Te [2-4] have also been demonstrated. However, despite considerable literature on the physical, optical and electrical characterization of HD Si, there is a lack of characterization of defect states that lie in the Si bandgap as well as the related carrier lifetime data of such materials. This study aims at using deep level transient spectroscopy (DLTS) and carrier lifetime measurements with THz spectroscopy [5] to investigate the nature of defects present in Au- and Te-HD Si and thus better understand how these defects contribute to the overall photodetector performance.

Several variations of the DLTS method was performed on the Au-HD Si photodiodes from [1], revealing the presence of defects as deep as 1-2 um from the surface, well beyond the HD region. The defect identities currently remain undetermined due convoluted hole and electron trap signals and other experimental complications. However, current efforts have been successful in overcoming such barriers, and concentration depth profiling of individual trap components via small-pulse DLTS will further elucidate the role of each type of defect in the Au-HD diodes. On the other hand, carrier lifetime measurements made on Te-HD Si reveal the presence of both short (picosecond) and long (microsecond) lifetime components. These DLTS and carrier
lifetime results will be discussed in terms of defects emanating from the PLM processing of HD Si, as well as its implications for photodiode properties.


4:45 PM ET12.06.08
Role of Vacancy-Type Defects in Au-Hyperdoped Si Fabricated by Ion Implantation and Pulsed Laser Melting Wenjie Yang1, Naheed Ferdous2, Philippe K. Chow3, James M. Gaudet4, Peter Simpson5, Austin Akey3, Jeffrey M. Warrender2, Michael J. Aziz6, Elif Ertekin2 and Jim S. Williams1; 1Australian National University, Canberra, Australian Capital Territory, Australia; 2University of Illinois at Urbana-Champaign, Champaign, Illinois, United States; 3U.S. Army ARDEC- Benet Laboratories, Watervliet, New York, United States; 4University of Western Ontario, London, Ontario, Canada; 5Harvard University, Cambridge, Massachusetts, United States.

Ion implantation followed by pulsed laser melting can produce hyperdoped Si with a highly non-equilibrium impurity concentration, giving rise to sub-band gap optical absorption that holds potential in Si-based photovoltaics and infrared light detection. [1, 2] In particular, a Si-based infrared photodetector has been successfully demonstrated on Au-hyperdoped Si, motivating a detailed study on the role of substitutional Au and other related defect complexes that arise from the non-equilibrium hyperdoping process. [3]

In this study, the atomic location of Au in hyperdoped Si is determined using Rutherford backscattering spectrometry combined with ion channelling (RBS/C) and triangulated angular scans. Additionally, the local lattice environment around the Au atoms is examined using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), high-resolution x-ray diffraction (HRXRD) and positron annihilation spectroscopy (PAS). Surprisingly, the incorporation of large Au atoms into the Si lattice appears to contract rather than expand the lattice. We show that vacancies trapped following pulsed laser melting, and, with the aid of density functional theory (DFT) calculations, propose that the vacancy trapping process is consistent with the local minimisation of lattice strain around the large Au atoms. Finally, we explore the thermal stability and sub-band gap optical activity of these vacancy-type defects. This vacancy trapping process may be global in other laser-melted hyperdoped Si systems with large-size impurities and may affect their efficacy as infrared absorbers.

References:
to increased alkaline layer distance. In this talk, we show the novel interplay between these TM ions and the charged point defects to modulate the electrochemical performance of Na,TM,VO$_2$ through unique ordering and disordering phases. A combined in situ (synchrotron) XRD, atomic resolution (scanning) TEM, neutron diffraction and density functional theory (DFT) simulation techniques are used to understand the coupled sodium, TM charge and magnetic orderings and disorderings. For the Fe containing mixed transition metal system of NaFeTM$_2$O$_2$, a novel disordered phase at high voltage was developed due to the unique electronic property of FeO$_x$ octahedrons, while at low voltage it goes reversibly back to the ordered phase. For NaMnO$_2$ a unique superstructure evolution mechanism related to the Jahn-Teller activity of Mn$^{3+}$ was found to dominate the electrochemical performance through the charged point defects in a special ordering pattern. The underlying connection between the two systems of Na(FeTM)$_2$O$_2$ and NaMnO$_2$ will be discussed to further facilitate the design of new battery cathode materials.

9:15 AM ET12.07.04
Defect-Enhanced Phase Transition Kinetics in LiFePO$_4$  
Ming Tang, Liang Hong and Kaiqi Yang; Rice University, Houston, Texas, United States.

Lattice defects such as antisite defects are commonly present in battery compounds and traditionally viewed as deleterious features. In this work, however, we use phase-field modeling and theoretical analysis to illuminate a mechanism of antisite defects accelerating phase transition and hence enhancing the rate performance of battery particles for compounds with strong ion diffusion anisotropy. Using LiFePO$_4$ as an example, we show that the inclusion of antisite defects can increase the phase boundary velocity by orders of magnitude in the surface-reaction-limited phase transition regime, which is closely related to the effect of antisite defects on reducing the Li diffusion anisotropy in LiFePO$_4$. As such, defect-rich LiFePO$_4$ particles can be (dis)charged much faster than defect-free particles especially at low overpotentials, where the metastable solid solution does not form. Based on the mechanistic understanding, criteria for optimizing the defect concentration are presented. This finding suggests defect engineering as a fruitful approach to enhance the rate performance of intercalation compounds.

9:30 AM ET12.07.05
Charge Storage and the Critical Role of Defects—Case Study of 2D Layered Delta MnO$_2$ and VO$_2$(B) Nanosheets  
Scott Misiurewicz, Peng Gao, Robert Koch, Madeleine N. Flint and Alec Ladonisi; Alfred University, Alfred, New York, United States.

It has recently become clear that defects may be of great importance in developing new electrochemical energy storage materials. Herein we focus on two model systems, 2-D layered delta MnO$_2$ and 2-D VO$_2$(B) nanosheets, with controlled defect contents, and investigate the atomic-scale mechanisms of charge storage. Using a combined approach of high energy X-ray scattering and X-ray spectroscopy, we find that MnO$_2$ nanosheets possess a peculiar out-of-plane Mn$^{3+}$ defect, forming a “surface Frenkel” defect. In our earlier work, we correlated the concentration of these defects (~20-30%) to the charge storage, where defects increase the overall capacitance from 200 to 300 F/g while decreasing the charge transfer resistance from ~15 to ~3 Ω. In situ XRD and X-ray PDF studies show that in-plane expansion and contraction occurs in the nanosheets upon charge and discharge. In situ XANES reveals a 31% change in the Mn oxidation state in the presence of 30% surface Frenkel defects, promoting ion intercalation and charge transfer. To test the hypothesis of charged defects controlling capacitance, Mm doping into layered VO$_2$(B) nanosheets has also been investigated. Addition of ~9 mol% Mn to the VO$_2$ results in 80% higher capacitance, as well as 2X smaller charge transfer resistance and 2X improvement in cyclability. PDF and X-ray scattering demonstrate distorted local structures with increased cation substitution, which may facilitate Na" intercalation. The formation of more V$^{4+}$ (≈13% higher by XPS) and oxygen vacancies by Mn doping can also help relieve electrochemical strain and increase electrical conductivity. Through these model systems, we provide insight into engineering defects for the next generation of transition metal oxide nanosheet electrochemical supercapacitors.

9:45 AM ET12.07.06
Guiding Principles for Designing Highly-Efficient Metal-Free Carbon Catalysts  
Li Peng Zhang$^1$ and Zhenhai Xia$^2$; 1 Beijing University of Chemical Technology, Beijing, China; 2 University of North Texas, Denton, Texas, United States.

Carbon nanomaterials are promising as metal-free catalysts for energy conversion and storage. To accelerate the search for the highly-efficient catalysts, it is necessary to establish design principles for the carbon-based catalysts. This review focuses on theoretical analysis and material design of metal-free carbon nanomaterials as efficient photo-/electro-catalysts to facilitate the critical chemical reactions in clean energy technologies, including oxygen reduction reaction (ORR) in fuel cells, oxygen evolution reaction (OER) in metal-air batteries, hydrogen reduction/evolution (HER) in water splitting, iodine reduction (IRR) in dye-sensitized solar cells, and carbon dioxide reduction (CO2RR) in artificial photosynthesis. Intrinsinc descriptors and design principles are analyzed and summarized, and future directions are discussed in development of efficient carbon-based catalysts for clean energy conversion and storage.

10:00 AM BREAK

10:30 AM ET12.07.07
The Role of Chemically Pretreated Cationic Species at the Interlayer Region of Layered Oxides in Electrochemical Energy Storage  
Ekaterina Pomerantseva; Drexel University, Philadelphia, Pennsylvania, United States.

Transition metal oxides with layered crystal structures favor reversible intercalation of ions at relatively high potentials and as a result are attractive for cathode application in lithium-ion batteries. However due to the concerns related to the abundance of lithium on Earth and a desire to reduce battery cost, the interest in developing beyond lithium ion energy storage systems fuel discovery of new electrode materials that would be efficient in reactions of intercalation of more abundant and therefore less expensive ions, such as Na$^+$ and K$^+$ ions. The larger size of these ions compared to that of lithium ion dictates the need for expanding the interlayer region of layered oxides to enable facile diffusion of the electrochemically cycled ions. This presentation will focus on new materials synthesis approach, called chemical pre-intercalation, which allows to tune the interlayer spacing of a model bilayered vanadium oxide phase from ~10 to ~30 Å. The effect of introducing inorganic and linear organic ions on charge storage properties in electrochemical systems with different charge-carrying ions will be discussed. Methods to control species in the interlayer region will be highlighted and correlated with functional properties of materials. This talk will also demonstrate that chemical pre-intercalation synthesis approach can be extended to synthesize new layered transition metal oxide phases beyond vanadium oxide. Overall, this presentation will shed some light on ways to chemically control interlayer content in layered oxides to modify their structure and chemical composition with the aim to achieve enhanced electrochemical properties in energy storage applications.

11:00 AM ET12.07.08
Tailoring Mobile Defects for Fast Ionic Conductors  
Yifei Mo; University of Maryland, College Park, College Park, Maryland, United States.

Fast ionic conductor materials are the key component in enabling a variety of electrochemical devices. It is crucial to understand why only a few materials exhibit faster ionic conduction than typical solids and how one can design fast ion conductors following simple principles. We perform ab initio modeling
on a range of novel fast ion conductor materials as model systems. In lithium super-ionics, we show that fast diffusion in super-ionics happens through unique concerted migration mechanism of multiple ions with low energy barrier in contrast to isolated ion hopping in typical solids. We elucidate that low energy barriers of the concerted ion diffusion are a result of unique mobile ion configurations and strong mobile ion interactions in these super-ionics conductor materials. Our theory provides a conceptually simple framework for guiding the design of super-ionics conductor materials.

Using first principles computation, we demonstrate this strategy by designing a number of novel fast ion conducting materials. In addition, our computational studies in other ionics conductors will also be discussed, and newly discovered design strategies will be presented.

11:30 AM ET12.07.09
Tuning Bifunctional Oxygen Electrocatayls and Changing A-Site Rare-Earth Element in Perovskite Nickelates
Le Wang1, 2, Kelsey A. Stoerzinger1, Lei Chang2, Junling Wang3 and Yingge Du4; 1Pacific Northwest National Laboratory, Richland, Washington, United States; 2Nanyang Technological University, Singapore, Singapore;

Perovskite-structured (ABO3) transition metal oxides are promising bifunctional electrocatalysts for efficient oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). In this paper, we investigate a set of epitaxial rare earth nickelates (R(NiO3) thin films with controlled A-site isovalent substitution to correlate their structure and physical properties with ORR/OER activities. The ORR activity is shown to decrease monotonically with decreasing the A-site element ionic radius which lowers the conductivity of the R(NiO3) (R = La, La0.5Nd0.5, La0.2Nd0.8, Nd, Nd0.5Sm0.5, Sm, Gd) films, with LaNiO3 being the most conductive and active. On the other hand, the OER activity initially increases upon substituting La with Nd and is maximal at La0.2Nd0.8NiO3 in which oxygen vacancies (Vo) start to form. Moreover, the OER activity remains comparable within error through Sm-doped NdNiO3. Beyond that, we cannot reliably measure activity due to the potential voltage drop across the film. The improved OER activity is ascribed to the partial reduction of Ni4+ to Ni3+ as a result of Vo, which increases the average occupancy of the eg antibonding orbital to more than one. Our work highlights the importance of tuning A-site elements as an effective strategy for balancing the ORR and OER activities of bifunctional electrocatalysts.

11:45 AM ET12.07.10
Lifting Electrocatayltic Activity in LaNiO3 Perovskite Films with Helium Jonathan Petrie1, Thomas Zac Ward1, Anthony Wong1, John w. Freelander2, Valentino Cooper1 and Ho Nyung Lee1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

Complex oxides, such as ABO3 perovskites, can catalyze oxygen reduction and evolution reactions essential for fuel cells, metal-air batteries, and other energy-related devices. Similar to noble metal films such as Pt, in-plane compressive strain was recently reported to generate significant enhancements in the electrocatalytic activity of LaNiO3 (LNO) perovskite films epitaxially grown on different substrates. Greater amounts of in-plane compression induced by the substrate increases the out-of-plane (c) lattice parameter via the oxide’s Poisson relationship. The increased tetragonality in turn improves the catalytic activity due to strain-induced splitting of the eg orbitals in the film’s NiO6 octahedral units. However, this sole reliance on in-plane epitaxial strain to facilitate uniaxial changes in the c-parameter limits our ability to optimize the activity.

Recently, low energy helium (He) ion implantation was demonstrated as a means to directly control uniaxial c-axis lattice expansion in epitaxial perovskite oxides. Here, we show that this “strain doping” process presents an additional avenue towards manipulating catalytic activity in LNO films coherently grown on STO substrates. Through the introduction of controlled amounts of interstitial He atoms into the film, we can continuously adjust the c-axis lattice expansion that drives changes in the eg orbital asymmetry essential for greater catalytic activity. Consequently, we can use these He point defects to raise the activity of LNO films by over an order of magnitude. Furthermore, the LNO activities seen surpass any yet found through straightforward substrate-induced epitaxial strain. The considerable enhancement in oxygen activity through the tailored incorporation of He into LNO demonstrates the emerging power of this ‘defective’ dial to enhance oxide functionality.

SESSION ET12.08: Mastering Functional Defects for Energy Efficient Ionic and Electronic Materials
Session Chairs: Xin Li and Hua Zhou
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 313

1:30 PM ET12.08.01
Designing Dopants for Higher Performance TCOs
David O. Scanlon; University College London, London, United Kingdom.

The combination of electrical conductivity and optical transparency in a single material gives transparent conducting oxides (TCOs) an important role in modern optoelectronic applications such as in solar cells, flat panel displays, and smart coatings. The most commercially successful TCO so far is tin doped indium oxide (Indium Tin Oxide – ITO), which has become the industrial standard TCO for many optoelectronics applications; the ITO market share was 93% in 2013. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other TCO; resistivities in ITO have followed by in situ atomically resolved imaging with scanning tunneling microscopy (STM) and subsequently with ex situ x-ray diffraction (XRD).

2:00 PM ET12.08.02
Controlling Surface Mobility and Step Barrier Heights in Oxide Film Growth
Arthur P. Baddorf1, Alexander Tselev1, Rama K. Vasudevan1, Anthony Gianfrancesco1, 2, Liang Qiao1, Tricia Meyer1, Ho Nyung Lee1, Michael Bielajewski1 and Sergey V. Kalinin1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Control of defects during nonequilibrium growth requires an understanding of surface mobilities and diffusion barriers, such as step barrier heights. We have explored these parameters and their influence on structure in epitaxial La0.5Ca0.5MnO3 thin films grown with pulsed laser deposition by varying laser fluence, oxygen pressure, and substrate-induced strain. Films were examined in operando using reflective high-energy electron diffraction (RHEED) followed by in situ atomically resolved imaging with scanning tunneling microscopy (STM) and subsequently with ex situ x-ray diffraction (XRD).
Regardless of the laser fluence, RHEED intensity oscillations were observed, characteristic of layer-by-layer growth. For SrTiO$_3$ substrates (and not the better lattice matched NdGaO$_3$) the envelope of the oscillations first drops with film thickness, then increases. Such RHEED behavior can be interpreted as first roughening of the film surface, then a decrease of the roughness and eventual conversion to a stable layer-by-layer growth. STM images confirm this interpretation. Remarkably, this indicates that the suboptimal layer-by-layer growth involving multiple exposed layers evolves into a nearly ideal layer-by-layer growth with the prototypical three exposed layers. At intermediate film thicknesses, atomically resolved images show that the surface consists of both A$\chi$- MnO$_3$ and B-site, (La, Ca, O)$_3$ terminations with (12$\times$2$\times$8$\times$2) reconstructed surfaces. The A-site termination is clearly more highly ordered. As the film thickness increases, the less ordered B-site domain dominates and by 250 layers is the sole termination. This surface morphology is largely independent of the laser fluence, but layer-by-layer growth could be delayed by reducing the growth pressure. Rough growth is frequently associated with an Erlich−Schwoebel barrier for adatoms to descend steps resulting in a reduction of the downhill flux. This interpretation is confirmed by atomically resolved images with a high concentration of adatoms along the terrace edges. Image analysis and Monte Carlo simulations estimate the height of the Erlich−Schwoebel barrier to be 0.18 ± 0.04 eV for deposition at 750 °C. Similarly, the evolution of adatom mobility can be inferred from STM images based on adatom island sizes and spacing. In the layer-by-layer regime, an increase in the adatom mobility with increasing thickness is accompanied by an increase in the out-of-plane lattice parameter. STM images reveal a pattern of extended stoichiometric surfaces, which can be ascribed to subsurface defects created during growth.

Research was sponsored the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and the Office of Science Early Career Research Program. Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2:15 PM ET12.08.03 Non-Stoichiometry-Induced Metal-to-Insulator Transition in Nickelate Thin Films Grown by Pulsed Laser Deposition Jongmin Lee$^1$, Kyoung Soon Choi$^2$, Tae Kwon Lee$^3$, Il-Seok Jeong$^4$, Sangmin Kim$^5$, Jaesun Song$^6$, Chung Wung Bark$^7$, Joo-Hyoung Lee$^8$, Jong Hoon Jung$^9$, Jouhahn Lee$^{10}$, Tae Hoon Kim$^{11}$ and Sanghun Lee$^{12}$.

The chemical stoichiometry in transition-metal oxides influences their physical properties due to the multi-valent nature of the transition-metal element. In perovskite rare-earth nickelates (RNiO$_3$, except for $R$ = La), which undergo metal-to-insulator phase transitions (MITs) with the decreasing temperature, the oxidation state of the transition-metal Ni$^{3+}$ ion is very sensitive to the stoichiometry and the transport property becomes different relying on the Ni valence state. Thus, it has been extensively studied how off-stoichiometry in either bulk or thin-film RNiO$_3$ modifies the Ni oxidation state and then, affects the MITs eventually. However, the detailed study of the non-stoichiometry effect has been rare due to a difficulty in the systematic control of cation and oxygen contents. Herein, we manipulate the cation stoichiometry in RNiO$_3$ bilayer films (NdNiO$_3$/LaNiO$_3$ on SrTiO$_3$ (001)) epitaxially grown by a pulsed laser deposition technique. Through a training process by laser irradiation, we can systematically control the RNi compositional ratio in RNiO$_3$ target. Interestingly, a Ni-excess RNiO$_3$ bilayer film shows MITs at around ~ 50 K. In contrast, a stoichiometric RNiO$_3$ bilayer film is metallic at all temperatures. Based on the first-principle calculations results, the possible origin of the non-stoichiometry-dependent transport behaviors will be discussed in conjunction with x-ray reflection (XRR) and x-ray photoemission spectroscopy (XPS) analyses.

2:30 PM ET12.08.04 Machine Learning Guided Design of Functional Materials with Targeted Properties Prasanna V. Balachandran, Department of Materials Science and Engineering & Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia, United States.

Computational strategies that enable identification of predictive design rules have the potential to rationally design materials for targeted applications. In this talk, I will discuss some of our recent works that have rationally guided experiments and computational codes (eg., density functional theory) towards promising regions in the vast design space of functional materials. The uniqueness of our approach lies in the integration of machine learning methods with experimental design in an adaptive feedback loop. The role of machine learning is two-fold: (i) to establish a relationship between the features and property of interest and (ii) to quantify uncertainties. Experimental design, on the other hand, uses the machine learning outcome to recommend the next experiment or simulation. I will demonstrate examples showing the efficacy of these approaches to design novel complex oxides and alloys with improved properties.

3:00 PM BREAK

3:30 PM ET12.08.05 Neuromorphic Computing Based on Dynamic Control of Dopants in Organic and Inorganic Materials A. A. Talin; Sandia National Laboratories, Livermore, California, United States.

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. In my talk I will describe a non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, based on the concept of reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the control of Li vacancy concentration in Li$_2$CoO$_2$ through reversible Li-ion intercalation. Li vacancies act as positive dopants, resulting in linear, highly symmetric, and low voltage switching between hundreds of analog conductance states and achieving high classification accuracy when implemented in neural network simulations. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and utilizes the proton as the mobile ion to control the polaron carrier density in the channel. Plastic NVRMs are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems. (1) Fuller, E. J.; El Gabaly, F.; Leonard, F.; Agarwal, S.; Plimpton, S. J.; Jacobs-Gedrim, R. B.; James, C. D.; Marinella, M. J.; Talin, A. A. Li-Ion Synaptic Transistor for Low Power Analog Computing. Advanced Materials 2017, 29, 1604310. (2) van de Burgt, Y.; Lubberman, E.; Fuller, E. J.; Keene, S. T.; Faria, G. C.; Agarwal, S.; Marinella, M. J.; Talin, A. A.; Salleo, A. A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing. Nature Materials 2017, 16, 414.
which are responsible for the plasmonic response. However, electronic state modification can be further amplified via strain engineering which is limited to film/substrate lattice mismatch and deposition pressure. An alternative approach to induce strain within these systems is through size confinement and morphology control. This work focuses on utilizing wet-chemical processes to control defects (oxygen vacancies and dopant) to tune the optical response of a host nanocrystal (SrTiO3, STO) doped with Nb ions, Sr1-xTixNb1-yO3+δ (STNO).

STNO nanoparticles were synthesized via a two-step co-precipitation/pressure-controlled molten salt technique. This low-pressure synthetic route limits available oxygen during the crystallization process allowing for systematic control of oxygen vacancies and dopant incorporation. The resultant particles have been identified as highly doped, cubic STNO nanostructures via TEM, EDX, and XRD. The average strain on the host matrix due to different dopant concentrations and oxygen pressures was calculated to be ~1%. Additionally, it is possible to induce the expected optical response by controlling the oxygen partial pressure and subsequent annealing processes. This optical response was confirmed to be due to the formation of Nb5+, as opposed to the more stable Nb3+ state, in the STO lattice using X-ray photoelectron and X-ray absorption spectroscopy. These results on low dimensional Nb-doped SrTiO3 nanoparticles demonstrate a capacity for infrared light harvesting which has the potential for applications in optical communication, remote sensing, spectroscopy, and thermal imaging.

4:15 PM ET12.08.07
Exploring Defect-Coupled Polarization Dynamics in Ferroelectrics via Multimodal X-Ray Imaging Qian Li1, Ben Xu2, Bo Wang3, Joshua Agar4, Hua Zhou1, Nouamane Laanait1, Lane W. Martin1, Long-Qing Chen1, Sergei V. Kalinin2 and Haidan Wen1; 1Advanced Photon Sources, Argonne National Laboratory, Lemont, Illinois, United States; 2School of Materials Science and Engineering, Tsinghua University, Beijing, China; 3Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; 4Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 5Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

It is broadly acknowledged that oxide ferroelectric materials inherently contain significant amounts of defects, such as oxygen vacancies, that form during fabrication due to thermodynamic defect equilibria. These defects are also known to interact with ferroelectric polarization, though in many cases leading to adverse effects such as polarization fatigue. It is thus crucial to understand the configuration and dynamical behavior of defects in order to enhance the functional properties of ferroelectric materials. Diffuse scattering is one of a few widely applicable methods that gives microscopic insights about defects, with its quantitativeness, nondestructiveness and high sensitivity. Here at the Advanced Photon Source, we have developed a new materials characterization instrument which combines scanning probe microscopy (SPM) in-situ with nano-focused X-ray diffraction imaging (XDM). We have devoted the initial application of this development to an examination of the defect-coupled polarization dynamics in Pb(Zr,Ti)O3 ferroelectric epitaxial thin films. This model system has been found to show mechanical switching behavior, that is, the polarization can be switched under mechanical pressure exerted by an SPM tip. We have performed XDM around such mechanically written regions and observed remarkably enhanced diffuse scattering in these regions, which nonetheless preserve the pristine average structure. Defect scattering modeling based on the classical Huang theory and phase-field modeling based on the Landau-Ginzburg theory, both informed by atomistic simulations of the defect (oxygen vacancy) configuration, have been performed to obtain a deep understanding of the pertinent dynamic processes. Altogether, they lead to a coherent picture that the tip pressure drives a redistribution of ionized oxygen vacancies in the films due to the Vegard strain coupling; slave to this process, the polarization switching occurs due to the electrostatic coupling. While our discovery substantially challenges the prevailing belief that flexoelectricity drives the mechanical switching, it points to a fundamentally different route to manipulate ferroelectric polarization at the nanoscale and prompts a rethinking of the functional roles of oxygen vacancies. Beyond ferroelectrics, this methodology may well be applied to a wide range of condensed matter systems where oxygen vacancies and the-like ionic defects modulate electronic transport, magnetism and other physical properties.

This work is supported by U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

4:30 PM ET12.08.08
Mapping Potential Energy Landscapes via Electron Beam Induced Atomic Impurity Dynamics Maxim Ziatdinov1, Ondrej Dyck1, Feng Bao2, Ali Yousefzadi Nobakht3, Rick Archibald1, Kody Law4, Stephen Jesse1 and Sergei V. Kalinin1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Department of Mathematics, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States; 3The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 4The University of Manchester, Manchester, United Kingdom.

Atomic fabrication of materials remains the ultimate goal of nanotechnology. The modern-day scanning transmission electron microscope allows to simultaneously image and manipulate matter at the atomic scale and is therefore considered one of the most promising tool for building new forms of matter from the atom up. Accomplishing this goal requires detailed understanding of the mechanisms of beam-induced transformations. Here we show that moving atomic impurity under beam excitation can be used to map atomic scale potentials in solids and determine beam-induced effects on chemically-relevant time scale. We first used stochastic reconstruction of molecular dynamic simulations to extract information on the random force exerted by the beam on Si dopant in graphene (arxiv:1804.03729). We then extended our approach to recover the potential along step edge of graphene nanohole with multiple impurities and to study cooperative effect between substrate reconstruction and 1D crystallization-like behavior under electron beam irradiation. Our study paves the way towards controllable electron beam induced transformations of matter.

SYMPOSIUM ET13
Materials for Multifunctional Windows
November 26 - November 28, 2018

Symposium Organizers
Arun Gupta, University of Alabama
Paul O'Brien, University of Manchester
Luminescent solar concentrators (LSCs) are envisioned to reduce the cost of solar electricity by decreasing the usage of more expensive photovoltaic (PV) materials and diminishing the complexity of multi-cell PV modules. The LSC concept can also enable unconventional solar-energy conversion devices such as PV or “solar” windows that can be especially useful in highly populated urban areas. Due to their high emission efficiencies and readily tunable emission and absorption spectra, colloidal quantum dots (QDs) have emerged as promising LSC fluorophores. The focus of this presentation is on both fundamental studies of luminescent concentration exploiting nearly ideal LSC characteristics of engineered QDs [1, 2] as well as practical, high-performance devices demonstrating commercial viability of a QD-LSC approach [3]. Specific topics of discussion will include practical concentration limits tested using nearly perfect QD emitters with >95% quantum efficiencies [1], various approaches to Stokes-shift engineering [4, 5], single- and double-layer LSC architectures, as well as cost/efficiency considerations for QD-LSCs [3, 6]. The overall conclusion of the reviewed studies is that engineered QDs represent a promising materials platform for realizing inexpensive, high-efficiency sunlight collectors applicable as both semi-transparent building-integrated solar windows and stand-alone, large-area LSC-PV modules.

regarding the use of near infra-red lead sulphide (PbS) quantum dots (QDs) as in planar LSCs. The results of this study indicated that PbS LSCs generate nearly twice the photocurrent in silicon cells compared to a traditional dye and cadmium selenide QDs, achieving an integrated optical efficiency $\eta_{opt}$ of 12.6%. This was primarily due to the broadband absorption of PbS, and a smaller overlap between the absorption and emission spectra, which reduces SA. However, despite the superior performance, PbS also exhibits a gradual and permanent photo-oxidation, which decreases the photocurrent at the rate of 0.1% per minute. Tuning the device architecture led to some improvements in PbS-based LSCs, as we demonstrated next, fabricating solid and hollow cylinders from a composite of QDs in polydimethylmethacrylate. The experimental results were in good agreement with theoretical calculations, with hollow LSCs having a higher absorption of incident radiation and lower SA compared to solid cylindrical and planar geometries with similar geometric factors. In addition to optical efficiency almost thrice that of planar LSCs, these also exhibited improved photo-stability under both laboratory and ambient conditions. Most recently, we have begun exploring the suitability of organic–inorganic hybrid perovskite (PVSK) thin films as the active medium in planar LSCs. PVSK compounds are at the forefront of photovoltaic research, and their high refractive index, broad absorption spectrum, and superior QY make them theoretically ideal candidates for LSCs. In practice, however, the possibility of high self-absorption in a continuous film, coupled with the inherent instability of PVSK materials, have hindered their use. Our results display an impressive $\eta_{opt}$ in the range 15%–29% despite high SA losses, and the devices remain operational for up to seven weeks in ambient conditions. We attribute this to the high QY and refractive pushed the efficiency to 34.7%. Further, using 3D Monte Carlo simulations that incorporate our experimental results, we have demonstrated the possibility of scaling these LSCs up to almost 100 cm, thereby providing a route toward optimizing thin film PVSK materials for these and other optoelectronic and photovoltaic applications. This work was supported by funds from the National Aeronautics and Space Administration grant no. NNX15AQ01A.

10:30 AM ET13.01.04
Light Scattering in Poly(methyl methacrylate) Doped with Functionalized Si Quantum Dots Samantha Hill1; Ryan Connell2; Vivian Ferry3 and Uwe R. Kortshagen1; 1Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; 2Chemical Engineering & Materials Science, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

The near-infrared emission and large effective Stokes’ shift of Si quantum dots (Si QDs) are attractive properties for light-management technologies like downshifting layers on photovoltaics or luminescent solar concentrating windows. In the case of the latter, the Si QDs must be finely dispersed in a transparent matrix, like a polymer, in order to achieve high light concentration factors. Our Monte Carlo models show that increasing the average light scattering length from 1 mm to 1 m in a 1 m2 device would provide a 4-fold increase in collected light for devices using Si QDs with a quantum yield of 50%. This gain only increases in the case of more efficient Si QDs. However, obtaining low-scattering dispersions of Si QDs in relevant, cost-effective polymers remains a challenge, and few reports of Si QD/polymer composites exist. Here, we studied the effect of surface ligand choice on the light scattering properties of Si QDs incorporated within mass polymerized poly(methyl methacrylate). Nanocomposites were made using Si QDs capped with a typical, nonpolar ligand or an ester-ended analog. We find the two surface treatments lead to significantly different dispersion characteristics in methyl methacrylate: either a primarily singly dispersed mixture is achieved, or agglomeration produces strongly scattering Si QD clusters at least 10 times larger than a single QD diameter. Fully polymerized nanocomposites exhibit increased light scattering corresponding to the agglomeration state in the monomer, especially at higher QD loading fractions. UV-Vis measurements of these composites indicate that choosing ligands similar in structure to the composite monomer can help reduce scattering losses within the nanocomposites. These results offer a strategy to improve Si QD luminous solar concentrator performances in a low-cost, structural polymer suitable for window applications.

10:45 AM ET13.01.05
Flexible Bragg Reflectors for Efficient Deformable Luminescent Solar Concentrators Mark Portnoi1; Christian Sol, Tom S. Robbins, Johannes Schlaefer, Clemens Tummler and Ioannis Papakonstantinou2; Electronic and Electrical Engineering, University College London, London, United Kingdom.

Structural flexibility of photovoltaic devices can lead to an expanse of applications such as wearable technologies, flexible electronics, self-powered sensors and roll-to-roll manufactured smart facades. Luminous solar concentrators (LSCs) composed of flexible host matrices such as polydimethylsiloxane (PDMS) have been proposed as a means of providing this flexibility. The elastomer sheets doped with luminophores can be fabricated in a range of sizes, transparencies, colours and rigidities to the designer’s needs.

This additional functionality can come at a cost to efficiency. Curvature results in increases in both reabsorption and escape cone losses. In this work we explore how curvature affects these losses and propose a solution for their mitigation. We investigate the effect of curvature on LSC efficiency by means of an experimentally verified Monte-Carlo model (MCM) for curved LSCs. We show that for large scale devices, the optimal concentrations of fluorophore concentrations at fixed thicknesses required to achieve the highest external optical efficiency differ for curved and flat LSCs.

To mitigate escape cone losses, we propose flexible distributed Bragg reflectors (DBRs) consisting of alternating PDMS and PDMS-titanium composite thin films with a refractive index contrast of ~0.3. These DBRs are designed to have omnidirectional reflectivity in the spectral region of the emission of the luminophores but high transmission in the absorption region. We fabricate prototype DBRs and compare reflectance to transfer matrix model (TMM) calculations. Combining our MCM and TMM into a hybrid package we optimise the application of such DBRs to Lumogen Red 305 doped flexible LSCs and demonstrate the DBR effect on their efficiency. We then use the model to predict the full potential of this pairing.

This work will pave the way for efficient and deformable LSCs. We plan to incorporate these into devices for use in everyday life.

11:00 AM ET13.01.06
Powering Future Cities with Quantum Dot-Tinted Glass Luminescent Solar Concentrator Windows Hunter McDaniel; Matt Bergren, Karthik Ramasamy, Aaron Jackson, Nikolay Makarov, Andres R. Velarde and Nicolai C. Archuleta; UbiQD, Inc., Los Alamos, New Mexico, United States.

In urban settings where demand (and price) for electricity is high, the space available for solar modules is minimal. Tall buildings utilize vast amounts of electricity that is transmitted from remote power stations on lossy transmission lines. Emerging competing sunlight-harvesting window solutions are expensive and have poor aesthetics. Competing quantum dot (QD) technologies are costly, toxic, and/or unstable. UbiQD invokes proprietary methods for low-cost manufacturing of stable, high performance, non-hazardous QD composites that are utilized in luminous solar concentrators (LSCs). Partially transparent LSCs provide a simple method of harvesting sunlight wherein absorbed light is effectively redirected to small solar cells hidden in the frame of a window. The company has achieved a certified record performance for solar windows, and is close to its target of 50 W/m2 of power output at 50% visible light transmittance, enough to turn an 80-story skyscraper into a >1GWh/yr urban power station. In this talk I will provide an overview to the market opportunity for solar windows, competitive landscape, and how our QD LSC technology compares. I will also provide a status update on UbiQD's best performing prototypes to date, and other recent milestones at the company.
Single junction photovoltaic devices exhibit a bottleneck in their efficiency due to incomplete or inefficient harvesting of photons in the low- or high-energy regions of the solar spectrum. This can be overcome through the retrofitting of a spectral converter to the device, which is used to convert solar photons into energies that are more effectively captured by the solar cell through a photoluminescence process. However, while a lumophore may show seemingly ideal optical characteristics for spectral conversion in an ideal solution (high emission quantum yield, strong absorption), disappointment frequently awaits its translation to the solid-state, where aggregation and quenching effects lead to significantly reduced photoluminescence yields.

In an effort to overcome this limitation, our research focuses on the bottom-up design of integrated lumophore-host materials for solar spectral converters, in which materials chemistry design strategies are used to control the packing, orientation and placement of p-conjugated lumophores in solid-state host materials. Since the electronic properties depend explicitly on the arrangement and packing of the p-conjugated species, this approach provides a means of modulating the optical properties. In this talk, we will report our recent results on the design of II-conjugated composite materials that utilise a family of organic-inorganic hybrid polymers known as the ureasils as the host. Ureasils are comprised of a siliceous skeleton that is chemically-grafted to poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) chains through urea cross-linkages, the number of which depends on the degree of branching in the organic polymer precursor. Ureasils are intrinsically photoluminescent, exhibit high refractive indices and function as optical waveguides. Through judicious selection of the degree of branching and length of the organic backbone and the incorporation method (grafting vs immobilization vs permeation), we can control the packing, orientation and placement of the II-conjugated species in the ureasil host. This in turn provides a means of modulating the optical properties. For example, a dramatic enhancement in the emission quantum yield to >60% is observed due to exciton localization at isolated nanodomains of a conjugated polyelectrolyte entrapped within the ureasil host. Similarly, Förster resonance energy transfer from the ureasil to embedded or grafted conjugated lumophores can be exploited to tune the emission color and even obtain white-light emission. These characteristics can be exploited to improve light-harvesting and trapping within the integrated material, which can be used to develop highly efficient LSC’s to enhance the performance of silicon solar cells.

High performance QDs, dispersing agents, and controlled resin curing are all important for manufacturing successful LSC materials and solar windows. Our CIS QDs have high QY and are stable in air at high temperatures. This allows formulation and curing of QD resins in air with minimum QY reduction. The high temperature stability also opens future opportunities for extrusion processes. In fact, we demonstrate that our CIS QDs can withstand 190°C for more than 10 minutes with minimal QY reduction. We incorporate QDs into windows as part of an interlayer in a glass laminate configuration where the laminate is made by a casting manufacturing technique. The glass has minimal surface defects which allows highly efficient TIR. Typically, the hydrophobicity of the QDs limits QD resin formulations to low viscosity, low adhesion, and low concentration formulations. However, by using dispersing agents and controlled curing techniques, we are able to formulate our resins with functionality similar to commercial polymers. For example, our resins use a variety of viscosity modifiers, plasticizers and adhesion promoters that allow scalable manufacture such as roll-to-roll coating and polymer casting. With these complex formulas, our QD LSCs with a VLT of 50% allow solar windows to be made with 29W/m² as certified with testing at NREL.
Luminescent solar concentrators (LSCs) appear as an intriguing way to cope with the mismatch between the photovoltaic (PV) cells absorption and the solar spectra, with the additional advantage of urban integration of photovoltaics [1,2]. We present LSCs based on bundles of triangular hollow-core plastic optical fibers (POFs) filled with amine-functionalized organic-inorganic hybrids (di- and tri-ureasils) doped with Rhodamine 6G, Rhodamine 800 or an Europium b-diketonate complex with visible-to-NIR tunable emission. The LSCs are characterized by optical conversion efficiency values up to $h_{opt}=5.3\%$ and when coupled to commercial Si PV cells yield maximum power conversion efficiency values of PCE=0.74% [3].

Aiming at following a sustainable route for the designing novel LSCs, photosynthesis was an inspiring natural mechanism and chlorophyll-based LSCs were processed and optically characterized. The chlorophyll molecules were extracted from Spirulina maxima which is an abundant cyanobacteria and an attractive natural source. To enable the easy and controlled processing of planar LSCs, the chlorophyll molecules were incorporated into di- and tri-ureasils with the added advantages of avoiding the formation of non-luminescent dye-aggregates, enhancing quantum yield and photostability. The chlorophyll-based LSCs were coupled to a Si-based PV device, revealing $h_{opt}$ and PCE values $~3.70\%$ and $~0.10\%$, respectively, demonstrating the huge potential of nature-inspired LSCs for sustainable PV energy conversion [4].


**3:45 PM ET13.02.06**
Advances and Challenges in Luminescent Solar Concentration for Building Integrated Photovoltaics Francesco Meinardi; Department of Materials Science, University of Milano-Bicocca, Bicocca, Italy.

Luminescent solar concentrators (LSCs) could facilitate the green architecture revolution by enabling the realization of semi-transparent photovoltaic (PV) systems, which could potentially convert the façades of urban buildings into distributed electrical power generators. LSCs were first proposed in 1976 as cost-effective alternatives to silicon solar cells. However, only after the recent breakthroughs in the realization of new classes of colloidal semiconductor nanocrystals, which combine suppressed reabsorption with broadband spectral coverage, the performances of the LSCs have been boosted to such a degree that they become the most promising technology for the next generation of PV glazing units. The LSC technology is now set on a clear path to become a PV technology that can be “irresistibly” integrated into the built environment without detrimental effects to the aesthetics of the building or the quality of life of the inhabitants in the form of colorless and electrodeless solar windows or as other semi-transparent architectural elements. Nevertheless, this final integration step, and in particular the optimization of the power efficiency for devices on the meter scale, will require scientists and engineers to face new emerging challenges.

This talk will review the successful strategies that have allowed this historical change of pace, examining and comparing the different types of developed nanomaterials, and discuss the issues that remain to be investigated for further progress. On the materials side, the realization of high-quality optical waveguides will be the most demanding task. It will require a perfect pattern of the nanocrystals inside the waveguide matrix to avoid detrimental light-scattering losses and, probably, also the adaptation to LSCs of highly transparent polymers or glass variants currently used in photonics and telecommunications will be necessary to produce very large LSCs. Finally, the optical-to-electrical conversion by the PV cells at the LSC edges will have to be suitably designed and optimized. This last step in the luminescent solar concentration process has not yet been fully investigated because of the challenges in the realization of highly performing optical waveguides. Together with the role of the waveguide absorption, this will soon be at the forefront of research into LSCs for real-world applications.
Encouraged by the commercial utility of organic molecular electrochromes in electrochromic windows and mirrors, we are developing scalable and solution processable conjugated electrochromic polymers (ECPs), which provide a unique encompassing set of structurally tunable colorimetric and redox properties, stable over thousands and tens of thousands of redox switches. Processing of these materials is carried out using a variety of solution methods including spin-coating, spray-coating, blade-coating, slot die coating, and ink jet printing. In this lecture, we demonstrate how the optical absorbance spectra of ECPs can be tuned to yield materials of all colors that can be switched to highly translucent forms as desired for absorptive/reflective (display type) and absorbive/transmissive (window type) devices. We will show how random copolymerization has been used to broaden spectral absorption yielding a family of black-to-transmissive ECPs. We have also developed a set of fast switching, high contrast, black and brown ECP blends, where the precise hues are readily tunable. We use these brown blends to showcase a practical application of ECPs in color changing eyewear. In addition to their yielding a family of black-to-transmissive ECPs. We have also developed a set of fast switching, high contrast, black and brown ECP blends, where the aesthetic qualities, their optical memory in both the colored and colorless states allow these devices to be run at low power. Photo-oxidative stability will be addressed using encapsulated films and ECDs. Finally, we combine our ECP and OPV technologies into possibilities for solar powered electrochromic windows.

9:00 AM ET13.03.02
Digitally Inkjet Printed Electrochromic and Electrofluorochromic Polymer for Dual-Mode Display Applications
Manuel Pietzsch1, 2, Johannes Zimmermann1, 2, Tobias Rödlmeier1, 2, Stefan Schlüske1, 2, Carlos Romero-Nieto3 and Gerardo Hernandez-Sosa1, 2, 1LTI, Karlsruher Institute of Technology, Karlsruhe, Germany; 2KIT, InnovationLab GmbH, Heidelberg, Germany; 3OCI, Ruprecht-Karls-University Heidelberg, Heidelberg, Germany.

Electrofluorochromic devices (EFCD) receive increasing attention in investigation in the past years, because they offer the possibilities for dual-mode display devices, which combine the advantages of reflective and emissive displays. Besides that, the low power consumption, the low voltage requirement and simple device architecture (i.e. electrochemical cell) provide the opportunity for low-cost display devices. To provide a cost-effective method with the freedom of design necessary for smart windows and display applications, inkjet printing can be used as a suitable method with high throughput, low material waste and upscaling capabilities to industrial fabrication. Here, we report the synchronous electrochromic and electrofluorochromic switching of polyindenofluorene-8-tryarylamine (PIF8-TAA). The investigated devices consisted of a layer of PIF8-TAA and a polymer electrolyte gel (PEG), using poly(methyl methacrylate) (PMMA), tetrabutylammonium hexafluorophosphate (TBA PF6) and propylene carbonate (PC), sandwiched between two indium tin oxide (ITO) electrodes. In its neutral state the polymer is transparent in the visible range and changes its color to deep red upon oxidation. Simultaneously, the blue colored fluorescence intensity is quenched. Besides its high stability in ambient conditions, the devices showed switching times of <2s, a coloration efficiency of 542±10 cm2/C at 395 nm, a fluorescence contrast ratio of 4,1±0,3 and an electrochromic contrast of 50±4% in the visible spectrum. These figures of merit ranking in the upper range of literature values make it a promising material for dual-mode display applications. Furthermore, by changing the working electrode to inkjet printed poly(3,4-ethylenedioxythiophene) (PEDOT) we demonstrate the fabrication of an electrofluorochromic device with independently addressable pixels to demonstrate the functionality of inkjet printed, structured EFCDs. Thus demonstrating the potential of these devices in display and smart window applications.

9:15 AM ET13.03.03
Polymer Dispersed Liquid Crystal Optimization for Low Power DC Field Application
Caitlyn Cook, Elaine Lee, Brian Giera, Herbert Wakefield, Andrew Pascall, Marcus A. Worsley and Joshua Kuntz; Lawrence Livermore National Laboratory, Livermore, California, United States.

Polymer dispersed liquid crystals (PDLC) have been heavily researched for applications such as smart windows in buildings, displays, and automobiles. A large focus on improving smart window production is in the reduction of production cost and required power. Here, the developed PDLC provides transmittance contrast ratios up to 30, with required power on the order of micro-Watts. Our smart PDLC windows can maintain a steady state of high transparency in DC field application and does not require high power (milliWatt), high frequency AC fields like conventional PDLCs with similar contrast ratios. When using commercially available pre-polymer, significant relaxation of the transparent state back to a translucent or opaque state occurs when holding a voltage at a steady state for a few seconds. This phenomenon occurs increasingly so at lower voltages (10V), as determined via UV-VIS (transmission) and custom color difference quotient (reflection) characterization techniques. To further understand and improve relaxation with DC voltage application, a series of photosensitive acrylate-based pre-polymer chemistries similar to PN393 were formulated and tested. Each formulation component has been systematically modified and characterized via the aforementioned characterization techniques in conjunction with scanning electron microscopy and UV-Rheology in a trend towards decreasing the power requirements and reducing electro-optical relaxation with DC field application. With polymerization induced phase separation speeds completing within two seconds in response to 365 nm light, such a formulation can be incorporated into a roll-to-roll production method and thus can be utilized for flexible electronics. Prepared by LLNL under Contract DE-AC52-07NA27344.

9:30 AM BREAK

10:00 AM ET13.03.04
Transparent Intelligence—Progress in Chromogenic Materials and Devices for Glazing
Claes-Goran Granqvist; The Ångström Laboratory, Uppsala University, Uppsala, Sweden.

This paper outlines the essential properties of the radiation around us, and uses this information to specify a number of requirements for energy efficient glazing. Spectral selectivity, angular dependence, and time variability stand out as important concepts. Focus is then put on novel results for thermochromic and electrochromic materials and devices. In particular, I present a number of strategies for boosting the cycling stability of electrochromic thin films of tungsten oxide and nickel oxide by electrochemical pretreatment or post treatment in lithium-ion-conducting electrolytes, or by intermixing of several
oxides.

10:30 AM ET13.03.05
Stretchable Array of Active-Matrix Based Poly-(3-methylthiophene)/Prussian Blue Electrochromic Devices with Low Power Consumption

Dong Sik Kim, Heun Park and Jeong Sook Ha; Korea University, Seoul, Korea (the Republic of)

We report on the fabrication of low power operated, stretchable array of active-matrix based electrochromic devices (ECDs). ECD consists of poly(3-methylthiophene) and prussian blue grown on indium tin oxide coated polyethylene terephthalate film, and mixed gel electrolyte of acetonitrile, poly(methyl methacrylate), propylene carbonate, and LiClO4. Upon application of a bias voltage at -1, 0, and 1 V, the ECD displays red, green, and blue colors, respectively. For the operation of the ECD, low powers of 373 μW/cm² at -1.0 V and 378 μW/cm² at 1.0 V are consumed but with a high coloration efficiency of 201.6 cm²/C at 1.0 V.

On a stretchable Ecoflex substrate, 4x4 array of ECDs with corresponding 4X4 n-type FETs as active-matrix elements for preventing the cross-talk, are integrated using patterned liquid metal, GanSn interconnections. Such fabricated ECD array exhibits a mechanical stability by biaxial stretching by 30% and bending deformation. Finite element method analysis of the strain distribution also confirms that the strain is only concentrated onto the Ecoflex area between the active devices of ECD and FETs. This work demonstrates the high potential of our fabricated stretchable ECD array in the application to full-color display associated with stretchable electronics, wearable devices, and electronic skin.

10:45 AM ET13.03.06
Hybrid Organic-Inorganic Materials for Multifunctional Window Application

Elsa John and Aswani Yella; Indian Institute of Technology-Bombay, Mumbai, India.

Hybrid lead halide based perovskites have gained much interest as an absorber material in solar cells owing to its low cost, easy processing method and suitable optoelectronic properties like broad absorption, small exciton binding energy, long lived photogenerated carriers and ambipolar charge transport. The wide variety of the organic and inorganic moiety that can be incorporated into these perovskites not only make the structure very flexible but also enable fine tuning of the material specific to the application. Within a few years of its inception in the solar cells, the certified power conversion efficiency of these perovskite solar cells have increased from 3.8% to 22.1%, making it one of the most explored material in the field of photovoltaics. The most common general formula for these halide perovskites is ABX₃, where A is a large monovalent cation (methylammonium CH₃NH₃⁺, formamidinium CH(NH₂)₂⁺), B is usually Pb²⁺ and X is a halide ion. Three dimensional corner-sharing PbX₆ octahedra with the central site occupied by organic cations form the structure of these perovskites. Although these materials have most extensively been used in the solar cells, they have also garnered significant interest in other fields such as field effect transistors (FET), light emitting diodes (LED), laser diodes and photodetectors. Changes in the structure of these hybrid materials induced by electrochemical changes bring about a change in the optical property making it a suitable material for multifunctional windows. This work highlights the structural changes in the material brought out by electrochemistry and the underlying phenomenon. The change in optical property is studied to optimize the device performance for window application, making it an environmentally sustainable material.

11:00 AM ET13.03.07
Designing Tunable On/Off Electrochromic Bragg Stacks

Sungyeon Heo, Ankit Agrawal and Delia Milliron; Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Dynamic tuning of Bragg stacks with wide spectral range and reflection is desired for efficient energy-saving windows, camouflage platforms, and military purposes. Especially for window applications, color neutrality and efficient heat blocking can be achieved via visible or near-infrared reflection compared to dominant approach that utilizes light absorption. Previous approaches of designing dynamic electrochromic Bragg stacks used optical constants of thin films from ex-situ ellipsometry measurement. However this ex-situ method doesn’t reflect dynamic reflection measurement condition and predicted reflection with simulation was missing. Moreover significant reflection at both charged and discharged states compromises its window applications, which is generally expected to show transparency in the discharged state. Here, we designed nanocrystals (NCS)-based Bragg stack films consisting of WO₃ and ITO NCs, and demonstrated their on/off reflection tuning over visible and near-infrared ranges. We provide a complete analysis with a combined approach of in-situ ellipsometry and transfer matrix simulation to rationalize and predict the optical behavior of the Bragg stacks. Combining our novel processing approach with judicious material design, we show how an optimized 1-D Bragg stack can be implemented for electrochromic applications. First, Bragg stacks on the ITO-PET flexible substrates without any annealing process were demonstrated with the advantage of ligand stripped NCs. The Bragg stacks with annealing process gave more enhanced reflectance, predicted by the in-situ ellipsometry analysis. By adjusting the ITO film thickness, the reflectance was changed from visible to near-infrared range, and the each film’s reflectance and peak position were tuned by changing the potential, matched with simulation. We expect this approach with simulation will guide us to rationally design the more enhanced NCs-based Bragg stack for efficient energy-savings in windows.

SESSION ET13.04: Chromomergens and TCOs
Session Chairs: Vivian Ferry and Hunter McDaniel
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 303

1:30 PM *ET13.04.01
Smart Materials Based on Multifunctional AIEgens

Benzhong Tang; The Hong Kong University of Science and Technology, Hong Kong, China.

Chemists are always seeking new methods to obtain artificial smart materials with multiple on-demand functionalities. Although the responsive process of these smart materials can be monitored by various methods, such as NMR, IR, MS and electron microscopy, etc., a problem associated with these methods is that they are all invisible to our naked eye. Fluorescence shows rich advantages such as superior sensitivity, high selectivity, fast response, and simplicity. More importantly, it can provide high spatiotemporal resolution for precise visualization into complicated processes in a noninvasive way. Another thing that need to be considered is that most of the smart materials function in the condensed phase which show notoriously ACQ effect to result in compromised sensitivity. Diametrically opposed to conventional luminophores, AIEgens are nearly non-luminescent in the isolated state but luminesce...
strongly in the aggregate/clustered state. Based on different AIEgens, we have fabricated various intelligent materials which can respond to different stimuli, such as force, temperature, moisture, pH, electric, and light. These smart materials show fascinating applications in sensors, actuators, and biological processes.

References

2:00 PM ET13.04.02
Phase Transformation and Photophysical Properties of Silver Doped Copper Indium Sulphide Colloidal Quantum Dots for Solar Cell Applications Shanna-Kay Spencer1, Richard A. Taylor1, Paul Menautarg2 and Paul O'Brien2; 1Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago; 2Chemistry and Materials, University of Manchester, Manchester, United Kingdom.

Ternary chalcopyride silver doped copper indium sulphide (Ag-CIS) quantum dots are currently being explored as promising materials for photovoltaic applications. Quantum dots <10 nm have been synthesized via a hot injection colloidal method using a unique combination of precursors and capping agents over a range of temperatures. Those synthesized at 140, 180 and 210 °C show quasi-spherical morphology with fairly narrow size distribution (5.6 ± 1 nm) exhibiting predominantly chalcopyrite structure. However, nanoparticles synthesized for 10 minutes at 180 °C have the narrowest size distribution with a wurzite structure instead of chalcopyrite. Furthermore, structural data confirm a change from wurzite to chalcopyrite structure as the annealing temperature increases up to 200 °C. The Ag concentration in CIS nanoparticles increases with temperature and with an increase in Ag concentration the Ag ions substitute Cu sites in the CIS lattice. The photoluminescence (PL) peak peak of as-synthesized Ag-CIS quantum dots is at 660 nm. The PL peak redshifts significantly as the temperature of annealing increases from 180 °C to 210 °C. The Ag-CIS nanoparticles over a range of temperatures up to 600 °C but there are no reports to the best of our knowledge which employs the use of dopants or show an influence of synthesis duration on phase transformation.

These findings suggest an attractive route to tune structure and optical properties and an effective means for possibly enhancing photovoltaic performance. To this end, we will be focused on making a plausible and crucial connection between the effect of synthesis duration and dopant content on phase transformation in colloidal Ag-CIS nanoparticles. Further we will discuss the effect of dopant concentration on the photo-physical properties including time-dependent luminescence and the role of the dopant Ag ion in these CIS quantum dots for tunable photovoltaic effects.

2:15 PM ET13.04.03
Chemical Solution Deposition Process of Advanced Multifunctional Transparent Thin Films—Inorganic Octahedral Metal Cluster and Electrophoretic Deposition Process Fabien Grasset1, 2, Ngan T. Nguyen2, 1, Adele Renaud3, Maxence Wilmet4, 1, 5, Marion Dubernet3, 1, Noee Dumait3, Yann Moillard3, Marian Amelia-Cortes4, Stephane Cordier4, Naoki Ohashi2, 1 and Tetsuo Uchikoshi2, 1; 1UMI 3629 LINN, National Institute for Materials Science, Tsukuba, Japan; 2RCFM, National Institute for Materials Science, Tsukuba, Japan; 3UMR 6226 ISCR, Université de Rennes 1, Rennes, France; 4Saint-Gobain Recherche, Aubervilliers, France.

Transparent thin films or coatings, with thickness ranging from nanometers to few tens micrometers are playing a very important and indispensable role in daily life [1]. Recently, the demand of new robust, low cost and friendly-environmental functional hybrids thin films with high transparency for optical applications is increasingly growing. The main targeted applications are lightening and color design [2], self-cleaning [3], photovoltaic luminescent solar concentrators [4-6] or window solar control [7-9]. Moreover, the use of solution processes are highly desirable in order to reduce the cost and waste and that can enable fabrication method for large area and even flexible devices.

This presentation will summarize our very recent works on the synthesis of multifunctional nanocomposites thin films or coatings on glass by chemical solution deposition processes (CSD) [10-18]. CSD processing of inorganic nanocolloidal solutions is generally acknowledged to be highly flexible in terms of precursor composition, targeted substrate and processing procedures (dip-spin coating, electrophoretic deposition process (EPD)...) in ambient pressures, and thus can be faster and less expensive than vapor based deposition routes while providing materials with matching or even superior properties. In this study, the EPD appears as an efficient process to fabricate highly transparent and functional nanocomposite thin films on glass for optical and energy applications. Several octahedral atom clusters were used to prepare thin films with high transparency in the visible. Several octahedral atom clusters were used to prepare thin films with high transparency in the visible. Each octahedral atom cluster were used to prepare thin films with high transparency in the visible. Each octahedral atom cluster was used to prepare thin films with high transparency in the visible. Each octahedral atom cluster was used to prepare thin films with high transparency in the visible. Each octahedral atom cluster was used to prepare thin films with high transparency in the visible. Each octahedral atom cluster was used in the aggregate/clustered state. Based on different AIEgens, we have fabricated various intelligent materials which can respond to different stimuli, such as force, temperature, moisture, pH, electric, and light. These smart materials show fascinating applications in sensors, actuators, and biological processes.

References
2. N. Vogel et al., Nat. Comm. 2013, 4, 2176
4. F. Meinardi et al., Nat. Photonics, 2017, 11, 177
7. Y.V. Bestero et al., Nano Lett., 2018, DOI: 10.1021/acs.nanolett.8b00764
12. T.K.N Nguyen et al., Coatings 2017, 7, 114
15. A. Renaud et al., ChemistrySelect, 2016, 1(10), 2284
18. T. Aubert et al., Part. P art. Syst. Charact., 2013, 30, 90

2:30 PM ET13.04.04
Transparent Electrodes for Multifunctional Windows—A Brief Overview Daniel Bellet; LMGP, Grenoble Institute of Technology, Grenoble, France.

Both energy and material consumption of buildings are and will remain a major concern for the next decades. In every buildings, either residential or
commercial, the overall energy use can significantly be lowered through optimization of heat accumulation and heat loss of façades and windows. This leads to research devoted to novel materials for smart windows which can be conceived as affordable multifunctional systems that offer enhanced energy control. Therefore development of materials for multifunctional windows is of huge importance. For instance electronically switchable windows, called as well smart windows, enable the alteration of their optical transparency thanks to an applied electric field. Generally speaking the topics of multifunctional windows concerns materials which can be photochromic, electrochromic, piezoelectric, transparent/semi-transparent etc. Very often these technologies required two parallel and opposite transparent electrodes: this is for example the case for creating an electric field to actuate an electrochromic material as well as for transparent/semitransparent photovoltaics to collect the photo-generated carriers. Therefore transparent electrodes should as well be thoroughly understood and optimized for an efficient integration into multifunctional windows.

The present contribution focuses on the different technologies associated to transparent electrodes. The various studied materials are for instance the classical transparent conductive oxides (TCO) and more recently metallic nanowire networks. We will describe and compare the main structural, optical and electrical properties of the different materials developed for transparent electrodes in multifunctional windows. The main scientific challenges associated with transparent electrodes for improving performance of multifunctional windows, as well as their stability, will be discussed. Stability can indeed be a crucial issue, involving optical and thermal aspects, ageing and chemical degradation.

Some references of our team related to the study of transparent electrodes:


2:45 PM BREAK
ET13.05.01
Thermal Insulation via the Photothermal Effect of Chlorophyll Thin-Film Coating—An Energy Efficient “Green Window” Yuan Zhao and Donglu Shi; Dept of Mechanical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio, United States.

One of the critical components in energy saving is thermal insulation, especially for large-area high-rise public building windows in cold climates. The conventional approach mainly relies on optimization of the thermal insulators and window designs (double-pane). It has remained a great challenge, however, to implement single-panes due to conflicting intrinsic materials properties (i.e. thermal insulation vs. transparency). In this study a new concept is developed to prevent heat loss without any insulating medium such as gases within double-panes and low-e coatings. A “Green Window” has been designed for single-pane applications that meet the U-factor specifications of Department of Energy for colder regions of the United States. The “Green Window” is structurally composed of a thin film window coating of naturally occurring chlorophyll that exhibits pronounced photothermal effect, while remaining highly transparent. Upon collecting solar light, considerable heat is created, effectively raising the window surface temperature, leading to a reduced U-factor less than 1.7 W m-2 K-1, even below the values of double-panes. As such we demonstrate of new concept in “thermal insulation” via optical means instead of sole dependence on thermal insulators. This concept lifts the dependence on insulating materials making single-pane window highly plausible.

ET13.05.02
Joule-Heating-Induced Infrared Switching in Flexible VO2 Nanoparticles Film Nan Shen and Chun Cheng; Southern University of Science and Technology of China, Shenzhen, China.

As a typical metal-insulator transition (MIT) material, vanadium dioxide has attracted much attention due to its distinct infrared and resistive switching characteristics. However, the relatively high phase transition temperature and uncontrollable thermally driven phase transition of VO2 inhibited its practical applications. In our work, we fabricated flexible VO2 nanoparticles films using a scalable printing method and investigated joule-heating-triggered infrared switching of VO2 films by applying voltages. Well-matched luminous transmittance (Tlum=57.3%) and solar energy modulation ability (∆Tsol=13.8%) of VO2 films can be achieved at 2.0 wt.% solid content. The infrared switching of VO2 nanoparticles films is well controlled by input voltages and exhibits high stability. A quite small increase (6.8%) after 10000 bending cycles is observed for normalized Tlum and ∆Tsol of VO2 samples, reflecting excellent flexibility. Our results provide an alternative strategy to regulate the infrared switching performance of flexible VO2 films, which would significantly promote the development of thermal-sensitive VO2 devices.

ET13.05.03
Ladder-Structured Polysilsesquioxane/Al2O3 Nanocomposites for Transparent Wear-Resistant Windows Min Seon Kim1, Yejin Ahn1, Sunyoo Kim2, Ji Ho Youk2 and Bong-Gi Kim1; 1Department of Organic and Nano System Engineering, Konkuk University, Seoul, Korea (the Republic of); 2Department of Chemical Engineering, Inha University, Seoul, Korea (the Republic of).

As a protective layer for deformable displays, we synthesized ladder-type polysilsesquioxanes (LPSQs) containing cyclic epoxy as a curable unit. The mechanical properties after photo- and thermal-curing of LPSQs with a small amount of added Al2O3 nanoparticles were compared with those of the pure LPSQs. The prepared LPSQ-Al2O3 nanocomposites and the pure LPSQs exhibited comparable optical transparencies and thermal stabilities. In addition, the degree of conversion of the applied epoxy units in LPSQs and the resulting mechanical properties, as monitored by Fourier transform infrared spectroscopy and nanoindentation tests, indicated that the addition of nanoparticles to LPSQs moderately enhanced the epoxy conversion rate and remarkably improved the wear resistance, including hardness, after photo-thermal-curing processes. The LPSQ-Al2O3 nanocomposites achieved higher wear resistance than epoxy-silica nanocomposites containing similar curable functional groups and reinforcing fillers (silica). The excellent mechanical properties of the LPSQ-Al2O3 nanocomposites could be attributed to three-dimensionally interconnected networks of organic-inorganic hybrid-type chemical structures in the LPSQ as well as additional reinforcement from amine-functionalized Al2O3 nanoparticles covalently interconnected with the LPSQ. We believe that the devised LPSQ-Al2O3 nanocomposites could serve effectively as a wear-resistant platform for deformable display windows.

ET13.05.04
Low Temperature Growth of Conductive SrVo3 Thin Films on Various Substrates by RF Sputtering Deposition Daeho Jung, Hosun Lee, Hyeon Seob So and Sangbin Hwang; Kyunghee Univ, Yongin-si, Korea (the Republic of).

It is very important to improve the performance of transparent conducting oxide (TCO) for display applications. Recent studies have suggested a novel method of making transparent conductors. Perovskite metal oxides have correlated electrons, and become transparent in the visible spectral range due to the carrier mass renormalization. The effective mass becomes heavier, by the interaction between the electrons. To have high electrical conductivity and to be transparent in the visible light region, absorption and reflection of light must be minimized in the visible region, and high carrier concentration and small carrier scattering are required. Particularly, strontium vanadates (SrVO3) have been intensively studied due to high electrical conductivity as well as high optical transparency in the visible range.

SrVO3 thin films were grown on various substrates using RF magnetron sputtering deposition with a commercial SrVO3 target as low as at 400°C with a mixed gas of H2 and Ar. Film thicknesses varied between 40 and 90 nm. We used (LaAlO3)0.5( Sr2AlTaO6)0.5 (LSAT), LaAlO3, SiO2/Si, a-c-m- and r-plane sapphires as substrates. The structural and morphological properties of SrVO3 films were studied using grazing-incidence-angle X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoemission spectroscopy (XPS). The electrical properties of all samples were measured using Keithley 4200.

SrVO3 films grown on LSAT substrates showed crystalline peaks of cubic phase SrVO3 films at 53.3° (210) using GIXRD. SrVO3 films grown on SiO2/Si showed crystalline peaks of cubic and orthorhombic phases as well as Sr3V2O7 phase. SrVO3 films showed grain boundaries with the average grain size between 100 nm and 150 nm according to SEM. High-resolution TEM images of SrVO3 thin films grown on LSAT showed high crystallinity and a well-ordered cubic phase.
We found the binding energy for multivalence state of \(V_{2p}\) from \(V^{4+}\) (516.8 eV) to \(V^{5+}\) (516.3 eV) for SrVO\(_3\) thin films on LSAT with increasing film thickness. We note that the insulating phase of SrV\(_2\)O\(_3\) (in \(V^{5+}\) state) films can be changed to SrVO\(_3\) (in \(V^{4+}\) state) films as the growth times increased due to \(H_2\) gas-induced reduction phenomenon. The resistivity of the SrVO\(_3\) films on LSAT was lower than other substrates because SrVO\(_3\) films were nearly latticed-matched to LSAT substrates. XRD, TEM, and XPS depth profiles showed a good crystallinity of SrVO\(_3\) thin films grown on LSAT substrates. The transmission spectrum of SrVO\(_3\) films with various film thicknesses grown on LSAT substrate were measured between 300 nm and 1000 nm of photon wavelength. The transmission was measured to be about 60% and 97% for film thickness of 40 nm and 70 nm, respectively, in the visible range. This work demonstrates that high-quality cubic phase of SrVO\(_3\) films can be grown using RF magnetron sputtering deposition with growth temperature as low as 400°C.

**ET13.05.05**

**Electrochromic Perovskite Nickelate Windows**

Yifei Sun\(^1\), Zhaoyi Li\(^2\), Nanfang Yu\(^2\) and Shiriram Ramanathan\(^1\); \(^1\)Purdue University, West Lafayette, Indiana, United States; \(^2\)Columbia University, New York, New York, United States.

Electrochromic windows are of interest in energy efficient adaptive architectures as well as various tunable optical devices. In this work, we present a class of correlated perovskite nickelate thin films (such as SmNiO\(_3\) (SNO) and NdNiO\(_3\) (NNO)) as promising next generation electrochromic materials. We will discuss results from electrochromic devices comprising indium doped tin oxide (ITO) coated glass as transparent electronic conductors, NNO thin film as electrochromic layer and salt solution as liquid ionic conductor exhibiting quick response and excellent stability upon coloring and bleaching cycles. The mechanism of color change in perovskite nickelates is distinct from conventional electrochromic materials which are based on redox reactions and become more conductive upon electron doping. During ion intercalation, a colossal phase transition in nickelate occurs that is an effect of strong electron-electron correlation, which makes them highly insulating and transparent due to charge carrier localization. We further show that the nickelate films allow for continuous and large tuning of optical transmissivity across the entire visible, near-infrared and mid-infrared spectra, which is of interest for control of sunlight transmission and variable emissive coatings.

**ET13.05.06**

**High Transparency and Self-Healing Liquid-Infused Surfaces for Optical Devices**

Meiling Zhang\(^1\), Qi Liu\(^1\), Jun Wang\(^1, 2\) and Rongrong Chen\(^3\); \(^1\)Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin, China; \(^2\)Institute of Advanced Marine Materials, Harbin Engineering University, Harbin, China.

High transparency is one of the basic requirements for optical devices, such as smart windows, solar cell panels and optoelectronic devices, to function well. However, frequent exposure of these devices to different outdoor environments, inevitably stains their outermost surfaces, which might diminish their performance. Superhydrophobic surfaces have anti-adhesion properties with water contact angle greater than 150° and slide angle below 5°. However, during the process of droplet condensation on a rough surface, the droplets on the surface can transform from the Wenzel-Cassie state to the Wenzel state, leading to the failure of superhydrophobic effect. Aizenberg et al. [1] first proposed the concept of a slippery liquid-infused porous surface (SLIPS). They poured lubricating oil into the porous surface for the preparation of super-slippery surfaces, along with the formation of a dynamic oil film, solving the problem of super-hydrophobic failure efficiently. Silica is often chosen as the alternate material because of its low refractive index and low absorbance of visible light. Herein, we propose to use tube-like SiO\(_2\) textures for trapping a lubricant liquid inside, and choose this liquid for allowing a drop of another liquid to float on this mixed substrate. A micro-mesoporous hollow tubular material with a wall thickness of about 100 nm and an inner diameter of about 1 \(\mu\)m was prepared successfully. Inspired by Yao Lu et al. [2], they use glue to make the coating robust on the surface, in this paper, glutaraldehyde was chosen as an adhesive to adhere the porous hollow tube-like SiO\(_2\) on the glass substrate and then a lubricant oil is poured into the surfaces after modification with FAS. As a consequence, these surfaces have remarkable slip properties: drops hardly pin on them, which makes them roll off readily and continuously retract as evaporating, contrasting dramatically with usual solids. It should be a promising candidate for long-term transparent optical devices.

**Keywords:** transparency surfaces; self-healing; SiO\(_2\); mechanical robust

**Acknowledgements**

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

**References**


**ET13.05.07**

**Composition and Structural Characterization of Photochromic Gd-Based Oxy-Hydrides Thin Films**

Giorgio Colombi\(^2\), Steffen Cornelius\(^2\), Alessandro Longo\(^1\), Herman Schreuders\(^2\), Fahimeh Nafizarefi\(^2\) and Bernard Dam\(^1\); \(^1\)Institution Netherlands Organization for Scientific Research (NWO), The European Synchrotron, Grenoble, France; \(^2\)Chemical Engineering, Delft University of Technology, Delft, Netherlands.

On average 30-40% of the energy consumption in the developed world is in the building sector. In this context, smart energy saving windows are envisaged to play an important role in bringing this number down and help with the urban air-pollution that is typical of the warm season. The recently discovered Rare Earth-based metal oxy-hydrides (MH\(_x\)O\(_y\)) are a particularly promising class of inorganic materials which show photochromic properties under ambient condition. The optical transmittance in these materials can be decreased reversibly by exposure to sunlight. The largest contrast change is observed between 400 and 1000 nm, however, the photochromic contrast extends up to the MID-IR region. Therefore these materials are not only suitable for the light-modulation in the visible range (where the darkening is colour-neutral) but they also act as a barrier to the heat irradiated by the sun at longer wavelengths. Despite the efforts of the last years, the darkening and bleaching mechanism is still under debate and it remains unclear which parameters affect its amplitude, speed and persistence upon several illumination cycles. In the interest of this open question, this work attempts to tackle the somehow elusive chemical nature of this materials.

The focus is given to Gd-based oxy-hydrides, a case-study chosen for its high optical contrast and for its sensitivity to several scattering techniques. Phase purity, Gd lattice and long-range order are probed by XRD, while XAS gives information on the local coordination of the Rare Earth and on the position of the lighter atoms within the lattice. The hydrogen to oxygen ratio and the exact composition are measured by RBS and ESR. These compositional and structural information can serve in future computational works to depict the band structure of the material: a first step to shed

```
light on the chemical interplay of oxygen and hydrogen and on their effect on the electronic structure of the Gd oxy-hydrides.

**ET13.05.08**

**Reversible Responsive Multifunctional Porous Particle by Chemical Vapor Deposition**

Wenny Wenny and Hsien-Yeh Chen; Chemical Engineering, National Taiwan University, Taipei, Taiwan.

A challenging fabrication of porous particle with reversible responsive functions is being approached by chemical vapor deposition (CVD). The compatible poly-para-xylylenes are utilized to cloak chemicals without changing their characteristics. Solidified droplets of solution is carried out to undergo the process of sublimation and used for the vapor deposition. The sublimation process also allows the polymer to go through vapor deposition. Remarkably, it is able to imitate the shape of the droplets and maintaining their specialties such as reversible magnetic, temperature responses, etc. This study is demonstrated by ferroferric oxide (Fe3O4), which is well known for its magnetic response and poly(N-isopropylacrylamide) (PNIPAM), that is renowned for its temperature response. It is capable to be applied in biomedical materials to support chemicals with specific roles and expectantly may lead to an excellent drug carrier with detection, targeting and delivering abilities.

**ET13.05.09**

**Field Effect Smart-Glass for Near Infrared Reflection and Transmission**

Mark C. Altweege, Iulian Gherasoiu and Harry Efistathiadis; SUNY Polytechnic Institute, Albany, New York, United States.

We report the development of a versatile and robust, metamaterial that can reflect near infrared heat radiation (NIR) in the range 0.7-2.5 μm while transmitting more than 90% of the visible light intensity. Metal oxides can be used to manage the light reflectance over the long wavelength range. However, to obtain high reflectivity starting at shorter wavelengths, the doping concentration of the metal oxide must be increased above the level of 1x10^{21}/cm^3. At these concentrations the dopant incorporates not only substitutionally, but large amounts will also be found interstitially. Interstitial dopants have been shown to produce carriers with heavier effective mass, decreased mobility, and deeper donor states that significantly decrease the transmittance. Ultimately substitutional dopants degrade the crystallinity of the host material, generating compensating defects that limit the achievable carrier density. To circumvent the need for excessive dopant incorporation we deposited a multilayer structure that alternates insulating and conducting layers of silicon dioxide (SiO2) and silicon doped zinc oxide film (ZnO:Si). This structure is deposited by RF magnetron sputtering from Si and ZnO targets at low temperature. The structure uses the electric-field enhancement of carrier density to regulate the bandwidth of the NIR and in turn the amount of heat reflected. This is achieved through the formation of a quasi 2-dimensional electron gas in a thin layer at the dielectric/ZnO:Si interface. In this paper, the synthesis conditions as well as the results of the electro-optical and structural characterization of the device, through Hall effect measurements, x-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), atomic and conducting force microscopy (AFM/CAFM), Rutherford Back Scattering (RBS), as well as transmittance measurements in the range from 0.3μm to 1.3 μm are presented. The fabrication challenges are discussed and a path for improving the performance of the device is outlined.

**ET13.05.10**

**Hydrothermal Synthesis and Characterization of Mn-Doped VO2 Nanowires**

Gen Long, Mostafa Sadoqi, Asher Suissa and David Matatov; Saint John's University, Jamaica, New York, United States.

Monoclinic VO2 is a known polymorph of vanadium dioxide that has received much attention due to its layered structure, high energy storage capacity, moderate work potential and promising applications in functional windows. VO2 can usually be obtained through a hydrothermal method under high pressure. In this work we report a study of synthesis and characterization of VO2 doped with Manganese using a rapid single-step hydrothermal process with V2O5, Mn- Acetate and citric acid as precursors. Different syntheses were carried out in which the concentration of V2O5 and citric acid remained constant whereas the concentration of Manganese (II) Acetate was varied. The reactants underwent a stirring phase for 30 minutes before being loaded into a hydrothermal reactor for 2.5 hours at 200°C. The resultant was washed three times to remove the residual precursors. Imaging and spectroscopy characterizations such as TEM, SEM, XRD, EDS and UV-VIS-NIR have been performed on different doping concentration and the results display a dependence on doping concentrations. The successful doping of Mn in VO2 provides another possible approach of tuning (through magnetic field) in the relevant applications.

**ET13.05.11**

**A Novel Viologen-Based Electrochromic Device Containing All-in-One Self-Healing Polymer Electrolyte**

Yi Wang, Rongzong Zheng and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

Electrochromism refers to a phenomenon where materials undergo electrochemical reactions accompanied by the change of their optical characteristics from a bleaching to a coloration state through the manipulation of potential biases. This technology enables several useful applications, including smart windows, antiglare rear view mirrors and electrochromic (EC) displays. The efforts in recent years were mainly focused on development of various EC materials, while less attention has been paid to the problems arises in practical application of these ECDs. These devices not only require excellent EC performance, but also reliability and resistivity against various external forces (such as repeated bending) and irreversible physical damages unavoidable during practical applications. Hence, excellent self-healability and renewability are important for the development of ECDs aiming for extending lifetime and lower cost of materials and devices. Here, a novel viologen derivative has been synthesized to perform as chromophores and dissolved in the self-healing polymeric electrolyte for the fabrication of ECDs. The self-healing polymer electrolyte has been synthesized containing acrylic acid, 1-vinylimidazole and vinyl hybrid silicone nanoparticles copolymerizing. A type of hybrid ECDs was fabricated containing the self-healing electrolyte with viologen EC materials and polyaniline film counter electrode. The devices shown higher optical contrast (over 45%), fast switching time (2.0 s for coloring and 1.8 s for bleaching), coloration efficiency (406.96 cm2/C) and cycling stability (~5000 cycles). The self-healing polymer electrolyte shows excellent mechanical properties (tensile strength 11 kPa, elongation at break 210%), and noticeable self-healing performance with healing efficiency of 90.5% within 20 min. This work highlights the important of self-healing property for the ECDs and opens up a new strategy for manufacturing ECDs to further development of the devices for advanced smart windows.

**ET13.05.12**

**Microcapsule Display Based on Polyurethane Acrylates**

Jihong Bae, Kyung Seok Kang, Chanhyuk Jee, Hyo Jin Jung, WonBin Lim, Byeongjoo Kim and PilHo Huh; Pusan National University, Busan, Korea (the Republic of).

The different molecular weight of polyurethane (PU) prepolymer were successfully prepared using polycaprolactone diol (PCL) and Isophorone diisocyanate (IPDI) as soft segment of prepolymer, dimethylolbutanoic acid (DMBA) as emulsifier, and trimethylamine (TEA) as neutralizer. Synthesized prepolymer and liquid crystals (LC) were stirred at the constant rate. And de-ionized water (DI) containing bishexamethylenetriamine (BHMT) was added
in the reaction mixture for the polyurea reaction. LC contains photo-curable acrylate, which allows to have a certain oriented direction in the micro droplet by UV irradiation. Generally, the study of polymer isolated liquid crystal (PILC) are founded on the combination of UV epoxy and liquid crystal or the mechanical dispersion using membrane filters. The most problem of these studies is the lack of capsule size control and the aggregation of polymer. In this study to control the microcapsule size by the molecular weight of the prepolymer in the waterborne polyurethane form. We measured the molecular weight and the peak of the functional group of the polyurethane through the GPC and FT-IR. Various properties to apply as opto-electronic device were also evaluated the response time, contrast ratio and voltage-transmittance curves. These microcapsule LC research using polymer matrix is being applied to the variety fields of next-generation display such as 3D printer material, smart window and flexible display.


Recently, colorful and semitransparent organic photovoltaic (OPVs) are growing due to their demand in aesthetically power generating windows. Traditionally, different colors in OPVs has been fabricated by employing different active layer materials exhibiting distinct absorption spectra, while semitransparent OPV mainly focus from less opaque top electrodes. Thus, this will complicate the process of fabrication and cause deviations in device performance among differently colored OPVs. Herein, colorful semitransparent OPVs with a single active layer material are demonstrated using Ag–TiO2–Ag Fabry-Perot resonant cavity color filters (CFs) electrodes. Thermal evaporation of Ag layer and spin coating technique of solution process TiO2 layer will help to restore the active layer material from damage. The CF enables the OPV to transmit spectrally pure colors with peak transmission efficiencies surpassing 25% average transmission for window application, and allows the colors to be freely tuned by changing the thickness of TiO2 layer. Besides being effective color electrode, this CF works as a mirror to reflect the absorption light thus enhance the short-circuit current. It is shown that when compared to a transparent OPV consisting of the same active layer material and thickness, CF-integrated OPVs generate more short circuit current. With this current result, simple and convenient fabrication technique is needed to achieve pure color, high transmission and higher efficiency compare to only semitransparent OPVs.

ET13.05.15 Phonon and Magnetoelastic Coupling in Multiferroic A\textsubscript{6}Ga\textsubscript{5}FeO\textsubscript{3} Karuna K. Mishra, Alvaro Instan, Mohan K. Bhattacharai, Sita Dugu and Ram Katyar; University of Puerto Rico, San Juan, Puerto Rico, United States.

Multiferroic materials that exhibit coexistence of both magnetic and ferroelectric order parameters are of research interest because of the intriguing coupling phenomena among spin, phonon, and charge degree of freedoms. A\textsubscript{6}Ga\textsubscript{5}FeO\textsubscript{3} (ALF) is a lead-free multiferroic exhibits ferrimagnetism near room temperature. We report phonons and magnetic ordering in ALF using our experimental findings involving temperature dependent Raman scattering and magnetization measurements. A single phase polycrystalline sample was prepared by solid-state reaction method and its phase purity was confirmed from the XRD analysis. Energy dispersive X-rays analysis and X-ray photoelectron spectroscopic results indicate nearly stoichiometry of the elemental compositions. Temperature dependent magnetization studies in both field-cooled and zero-field-cooled conditions identify the Neel’s temperature T\textsubscript{N} around ~220 K. ALF stabilizes in orthorhombic (Pna2\textsubscript{1}) phase with eight formula units which translate into a total of 117 Raman active optical phonons. However 30 modes are experimentally observed in our measured Raman spectra. The temperature dependence of phonon frequencies are analyzed based on the standard anharmonicity model in the paramagnetic phase. In the low temperature ferromagnetic phase, a large departure of phonon frequencies from the extrapolated theoretical curve which essentially represents the normal phonon behaviors, suggests the existence of spin-phonon coupling in this system. In addition to lattice modes, several bending modes of octahedral are found to be strongly affected by the magnetic ordering. Further studies on ALF thin films are in progress. The detail experimental results will be presented in the meeting.

SESSION ET13.06: Dye and Perovskite Solar Cells
Session Chair: Richard Lunt
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 303

8:30 AM *ET13.06.01 Electrical Control of Photoluminescence in Hybrid Perovskite Films Juan Bisquert; University of Jaume I, Castello, Spain.

The development of organic-inorganic lead halide perovskites with very high efficiency requires us to understand the operation of the solar cell. These materials have excellent semiconductor and optoelectronic properties, but they are ionic as well as electronic conductors. The motion of ionic defects can regulate the number of nonradiative recombination centers, hence electrical control of planar devices with lateral contacts can give a switch of PL. This property may be exploited to extract information on transport and recombination and for the realization of new of new applications. Finally we adress new methods of characterization of the optical by means of light modulated spectroscopy.

9:00 AM ET13.06.02 Hybrid Nanowires and 3D Nanoflowers on a Large Scale for Dye-Sensitized and Perovskite Solar Cells Jose Rajan\textsuperscript{1}, Zinab Bakr\textsuperscript{1}, Bhupender Pal\textsuperscript{1}, Naveen Kumar Elumalai\textsuperscript{2} and Mashtiah Mohd Yusoff\textsuperscript{2}; 1Faculty of Industrial Sciences & Technology, University of Malaysia Pahang, Kuantan, Malaysia; 2School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Optical transparency and workability at low light conditions enable the dye-sensitized solar cells (DSSCs) and the perovskite solar cells (PSCs) as desirable choice as smart windows in modern buildings for adding aesthetics with diverse choice of colours while producing clean electricity so as to realize zero-energy buildings. In both of these solar cells, the photoactive material is chemically developed from solutions on a wide bandgap material, known as photoelectrode. The photodetector influence the performance of the solar cells in many ways as they are either the charge separation medium or the charge transport medium or both. Commercially available mesoporous TiO2 has been a widely investigated material, but its sluggish charge kinetics due to the surface states and intrinsic poor electrical conductivity triggered an intensive search on new materials worldwide. As a result many materials and materials architectures are developed with superior properties than the commercial choice; however, most of new materials are hardly scalable to the industrial levels. Among them, nanowires and 3D nanostructures such as flowers offer many advantages such as anisotropic charge dynamics, large surface area, and high crystallinity. Again, most of the materials synthesized thereby are through hardly scalable chemical processes. We have now developed nanowires and 3D nanoflowers as a composite of two binary wide bandgap metal oxide semiconductors (SnO\textsubscript{2}–TiO\textsubscript{2}) in large quantities (100 g scale) using multineedle electrospinning technique by controlling the nucleation and growth of inorganic species in a polymeric nanofibrous growth vessel. In the conventional
electrospinning to synthesize inorganic nanowires, the metal precursor dispersed in the polymeric fiber is allowed to nucleate and grow at appropriate
conditions—which took place at equilibrium conditions, i.e., the growth vessel (the polymeric fiber) is large enough to accommodate all the nuclei. On the
other hand, to synthesize composite nanofilaments a non-equilibrium situation is produced such that the nuclei developed could not be located within
the growth vessel such that growth requires an expansion of space. The electron microscopic investigations show that this strategy is successful and the large
scale electrospinning could be applied to produce the two type of materials architectures. The composite formation, surface properties, and electrochemical
properties of the composite materials are systematically investigated and compared with their single component counterparts. Finally, DSSCs and PSCs
were fabricated using the composite nanowires and 3D nanoflowers. The devices fabricated using the 3D nanoflowers showed superior photovoltaic
properties than those of the nanowires; the best performing device in this study is a perovskite solar cell with a photo conversion efficiency of 17.25%.
open circuit voltage of ~1 V, short circuit current density of ~23.73 mA/cm² and fill factor 73.07%.

9:15 AM DISCUSSION TIME

9:30 AM BREAK

SESSION ET13.07: Other Windows
Session Chair: Richard Taylor
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 303

10:00 AM **ET13.07.01
Highly Transparent Solar Cells for Distributed Applications Richard R. Lunt; Michigan State University, East Lansing, Michigan, United States.

Solar energy offers a viable solution to our growing energy demand, but adoption has been hindered by cost, aesthetics, and difficulties with integration.
Excitonic materials offer new opportunities for unique solar harvesting science and applications that can help accelerate solar deployment in new areas
previously inaccessible. In the first part of this talk I will introduce our work on developing highly transparent photovoltaics (TPVs) that can maximize the
product of the transparency and efficiency for seamless solar harvesting around buildings, automobiles, mobile electronics, and greenhouses. These devices
are enabled by the manipulation of excitonic semiconductor materials with selective harvesting in the invisible components of the solar spectrum. I will
describe key photophysical properties, outline the thermodynamic and practical limits for a range of TPVs, and discuss their commercial impact for a
variety of applications. I will also discuss new figures of merit necessary to characterize and test TPVs. In the second part, I will describe the development
of several new classes of materials for TPV integration including: 1) organic salts that allow selective photosresponse beyond 1600nm; 2) luminescent
nanoclusters with massive downconversion; and 3) halide perovskites with ideally tuned bandgaps and transparencies above 70%. TPVs ultimately represent
a new paradigm for solar energy harvesting that could generate nearly half of the US electricity demand when deployed at full-scale, while also creating
additional functionality in managing solar heat.

10:30 AM ET13.07.02
100 cm² Dynamic Windows Based on Reversible Metal Electrodeposition with Sub-Minute Switching Speeds Michael Strand1, Tyler S. Hernandez1,
Christopher Barile2 and Michael D. McGehee1, 3, 4; 1Stanford University, Stanford, California, United States; 2University of Nevada, Reno, Reno, Nevada,
United States; 3University of Colorado Boulder, Boulder, Colorado, United States; 4National Renewable Energy Laboratory, Golden, Colorado, United
States.

While the demand for optically tunable windows is paramount in today’s residential and industrial communities, traditional electrochromic windows have
not yet been commercialized on a large scale. Dynamic windows based on reversible metal electrodeposition (RME) have emerged as an exciting,
developed class of electrochromic devices poised to overcome the challenges inherent to conventional technologies. Metals are ideal light-modulators for
dynamic windows because they can be color-neutral, inert, IR-reflective, and opaque at 20-50 nanometer thicknesses. Our team has demonstrated metal-
based dynamic windows that boast cheap processing, fast switching, and stable performance over thousands of cycles on the 25 cm² scale.

Several technical challenges hinder further scalability of the technology. Common transparent electrode materials like indium tin oxide (ITO) have
relatively high sheet resistance. By Ohm’s Law, maintaining a uniform current density through resistive electrodes necessitates a voltage drop proportional
to the electrode area. Large-scale dynamic windows must be engineered with a tolerance to the non-uniform potential distribution across the electrode
surface in order to maintain optical uniformity during switching. Additionally, undesired side reactions like the hydrogen evolution reaction (HER) set
strict limits on the potentials that may be applied in aqueous electrolytes. The ideal system will enable uniform nucleation and growth of metal films over
the potential range set by side reactions inherent to aqueous electrolytes, and the voltage drop inherent to transparent conductors. Prudent design of electrode structure enables uniform and reversible electrodeposition over large areas. Using a scalable process, we fabricate transparent
electrodes coated with Pt nanoparticles for dynamic windows. The Pt nanoparticles serve as preferred nucleation sites for the electrodeposition reactions.
By controlling the nanoparticle surface density, we have direct control over the active site density for nucleation, and thus the subsequent growth of the
metallic film. This nucleation control enables transparent electrodes that exhibit uniform transmission versus time relationships over a large range of
applied potentials.

Finally, we demonstrate 100 cm² dynamic windows based on reversible metal electrodeposition that switch uniformly despite the voltage drop across the
working electrode. The devices switch reversibly from a clear state (60% transmission) to a color-neutral, opaque state (~5% transmission) in less than one
minute.

10:45 AM ET13.07.03
Dynamic Windows with High Contrast, Neutral Color and Excellent Durability Using Metal Electrodeposition and Dissolution Christopher Barile1,
Michael McGehee2, Shakirul Islam3, Tyler S. Hernandez1, Michael Strand1, 2 and Daniel Slotcavage1; 1University of Nevada, Reno, Reno, Nevada,
United States; 2University of Colorado Boulder, Boulder, Colorado, United States; 3University of Colorado Boulder, Boulder, Colorado, United States.

Optoelectronically tunable windows have applications in buildings, automobiles, and switchable sunglasses. By controlling solar lighting and heating,
dynamic windows significantly improve the energy efficiency, comfort, and aesthetics of spaces as compared to traditional window technologies. The
majority of research on switchable windows over the last several decades has focused on transition metal oxides and polymers as the optically-active
materials. In contrast, we are developing dynamic windows based on the reversible electrodeposition and dissolution of metals. These windows display
clear-to-black transitions with ~80% optical contrast in 1 minute. 25 cm² device prototypes cycle thousands of times without significant deterioration.
Applications

11:00 AM

Electrolyte and Electrode Engineering for Dynamic Windows Based on Reversible Metal Electrodeposition

Tyler S. Hernandez, Michael Strand, Christopher Barile, Dan Slotcavage, and Michael D. McGehee;
Stanford University, Menlo Park, California, United States; University College London, London, United Kingdom.

In recent years vanadium dioxide (VO$_2$) has generated a broad range of interest due to its heat-mediated structural phase transition from a semiconductor to a metallic state at living temperatures. In many parts of the world, this entails the use of both heating and cooling during daylight hours depending on ambient temperatures. Optically tunable dynamic windows demonstrate many advantages over static lighting controls, such as blinds and shades. This technology allows users to control both heat and light flow into and out of buildings, without sacrificing their comfort or view. Despite both the aesthetic and energetic appeals of these reversibly tinting windows, existing electrochromic technologies have yet to perform ideally. Dynamic windows based on reversible metal electrodeposition (RME) offer an exciting alternative to traditional electrochromic technologies. The use of metals is an attractive option for electrochromic applications due to their high optical extinction coefficients, color neutral metallic state, chemical inertness, and high solubility in aqueous electrolytes. Our group has recently designed 25 cm$^2$ RME dynamic windows that demonstrate color-neutral, fast switching speeds over thousands of cycles with minimal degradation.

These windows operate by the reversible, electrochemical movement of metallic ions from a transparent conducting electrode to a metal counter electrode frame through an aqueous electrolytic medium, usually consisting of Bi$^{3+}$ and Cu$^{2+}$ ions. Despite a promising initial design, indium tin oxide (ITO) working electrodes degrade under the acidic environments necessary for aqueous Bi-Cu halide electrolytes. Furthermore, the counter electrode frame design will be problematic at a larger scale due to the voltage drop associated with increasing ionic diffusion lengths. We address both the durability and scalability issues associated with these initial devices by designing RME dynamic windows with an acid stable working electrode, a halide-free Bi-Cu electrolyte, and a plane-parallel counter electrode.


11:15 AM ET13.07.05

Color Degradation of Organic Semiconductors in Power Generating Windows

Bharati Neelamraju, Michael Anderson and Erin L. Ratcliff;
The University of Arizona, Tucson, Arizona, United States.

Organic Photovoltaics (OPVs) have incredible prospects for next-generation, flexible opto-electronic energy harvesting and storage devices. Their unique properties of being semi-transparent, flexible, light-weight, low cost and scalable with customizable color perception makes them an ideal candidate for energy generating windows technology for buildings and green houses. Their tunable transparency and color selectivity gives them an aesthetic edge over conventional technology while maintaining the power conversion efficiencies. In green houses, this tunable wavelength approach of OPVs allows maximum usage of the photosynthetically relevant light to reach the plants, while using the unused wavelengths for generating electricity. Yet challenges still exist in terms of degradation of organic semiconductors in these devices which could affect both the efficiency and the color of the OPVs in the long run for use in power generating windows. This effort considers the following “How does degradation of organic semiconductors effect the color and power conversion efficiency (PCE) of the OPV devices in a given architecture”. Electronic properties and color measurements in CIE coordinates are analysed using spectroscopy and correlated with density of states. Transport properties are analyzed using mobility, conductivity and PCE measurements. Collectively, these measurements allow us to design organic semiconductor systems with controllable behaviors for next-generation of organic photovoltaic technologies.

SESSION ET13.08: Thermochromic and Photochromic Windows

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 303

1:45 PM ET13.08.01

A Combined Experimental and Theoretical Study into the Performance of Multilayer Vanadium Dioxide Nanocomposites for Energy Saving Applications

Christian Sol, Johannes Schlaiser, Tao Li, Ivan P. Parkin and Ioannis Papakonstantinou;
University College London, London, United Kingdom; Chemistry, University College London, London, United Kingdom.

In the built environment there is a increasing issue of heat management, with buildings expending significant energy resources to maintain comfortable living temperatures. In many parts of the world, this entails the use of both heating and cooling during daylight hours depending on ambient temperatures. Due to the variation in the desired temperature control classical solutions can become counter productive in their aim of maintaining comfortable temperatures, therefore it is important to employ adaptive solutions that vary their functionality based on circumstance. In recent years vanadium dioxide (VO$_2$) has generated a broad range of interest due to its heat-mediated structural phase transition from a semiconductor to...
Invited Paper

Fabrication and Spectral Properties of Textured Phase Change VO2 Nanostructures Obtained via Oxidation of Thermally Evaporated Metallic Vanadium Films

We demonstrate the growth of highly textured VO2 nanocrystals via annealing of amorphous e-beam deposited metallic V. Temperature dependent ellipsometry results reveal the pronounced reflection near the IR spectrum above the transition and an almost temperature independent weak reflection in the visible spectrum. The infrared reflection displays a strong hysteresis during heating and cooling near the transition temperature at 68°C, indicating a first order transition and a strain-free structure. Our work demonstrates the feasibility to obtain high quality phase change nanostructures that transmit the visible spectrum but reflect infrared and is suitable for large scale fabrication.

2:00 PM ET13.08.03
Interdependence of Molecular Precursors, Morphology and Phase Transitions in Thermochromic VO2 Nanostructured Thin Films

In recent years, monoclinic/rutile vanadium dioxide VO2 (M1/R) has attracted attention as a promising candidate for energy saving window applications due to its unique thermochromic reversible metal-insulator transition (MST) at 68°C. Phase selective chemical vapor deposition of nanostructured vanadium dioxide (VO2) on a glass substrate and use the simulations to guide the fabrication process. The design makes use of coherent interference within the multi-layered structure to suppress reflection of visible light and improve the reflective component of solar modulation. In doing so, we are able simultaneously improve the visible transmission and solar modulation of the film above what would be possible with a single layer film. Additionally, the use of thin film VO2 also acts to reduce the detrimental transition hysteresis typically seen in small domain sized nanoparticulate VO2 films. The multilayer structure is fabricated via spin coating of sol-gel based precursors and subsequent annealing. After which the structure is optically characterised and results are compared with simulation along with standard single layer VO2 films and other nanoparticulate based VO2 films.

2:15 PM ET13.08.04
Fabrication and Spectral Properties of Textured Phase Change VO2 Nanostructures Obtained via Oxidation of Thermally Evaporated Metallic Vanadium Films

We demonstrate the growth of highly textured VO2 nanocrystals via annealing of amorphous e-beam deposited metallic V. Temperature dependent ellipsometry results reveal the pronounced reflection near the IR spectrum above the transition and an almost temperature independent weak reflection in the visible spectrum. The infrared reflection displays a strong hysteresis during heating and cooling near the transition temperature at 68°C, indicating a first order transition and a strain-free structure. Our work demonstrates the feasibility to obtain high quality phase change nanostructures that transmit the visible spectrum but reflect infrared and is suitable for large scale fabrication.

SYMPOSIUM ET14/BI01/NM04
TUTORIAL: Life Cycle Analysis from an Industrial Perspective
November 25 - November 25, 2018

* Invited Paper

TUTORIAL Life Cycle Analysis from an Industrial Perspective
Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 200

Environmental issues keep steadily increasing, thus there is a strong urge to discuss how materials scientists could more rapidly respond to the worldwide concerns. This joint tutorial effort would be organized by the three symposia together. To ensure the success of such synergistic efforts it is also urged a close dialogue with society so to establish guidelines for policymakers, thus this tutorial will incorporate both the societal and the engineering aspects of life cycle analysis (LCA) would be covered. The main objective of this tutorial is to explore communications pathways between companies and materials researchers that further elevate the profile and challenges of sustainability that represents a societal necessity and a viable and critical topic for research.
Materials are not simply the product of an engineering discipline, Materials Science, but also "social constructs" that have entertained a close relationship with society all through the historical timeline and remain a core element of our modern world, what is called a Key Enabling Technology. How this can be analyzed by parallel approaches of hard and soft sciences will be explained in the class as well as the tryptic of economic, environmental and social values of materials. Examples reported in the 13 past SAM conferences will be used as examples.

The instructor will provide an overview on all the aspects considered in a life cycle analysis aimed to the engineering design of an industrial process. A part of the tutorial will involve the interaction with the audience in order to apply some of the concepts described in the first part of the tutorials to common objects.

The symposia organizers will divide the participants into groups and a sustainability challenge will integrate the concepts presented by the instructors so to review and facilitate networking among participants and instructors.

A large class of strong-base anionic exchange resins with quaternary ammonium ions as the fixed cationic charge and carbonate, bicarbonate or hydroxide for mobile anions exhibit equilibria with gaseous CO2 that are strongly affected by the presence of water. At room temperature, changing the relative humidity of air over the resin from 20% to 100% changes the equilibrium pressure of CO2 in the gas phase for a fixed dissolved inorganic carbon loading of the resin five hundredfold. This novel phenomenon is of interest for capture of CO2 from ambient air as it can support novel sorption/desorption cycles driven by moisture rather than temperature or pressure changes. It can support novel membranes where a concentration gradient in moisture can pump CO2 against a chemical potential across the membrane. The impact of water on CO2 sorption is so large that it cannot be explained through simple competition for sorption sites. Instead, theoretical analysis suggest that the effect is mediated through changes in the hydration states of the ions present in the resin. The emergence of superacids in nano-droplets as was described by Colussi and his group provides an analogy. The analysis suggests that the process is...
complicated and goes to the heart of the nature of water and its behavior in confined spaces and its interactions with ions. A better understanding and more detailed experimental analysis would be extremely valuable. There are a number of unanswered questions a more detailed research program would need to answer: how does the interaction of water with ions affect the ionic equilibrium; how does the nature of the polymer structure of the resin impacts this behavior, in terms of equilibrium conditions, but also transport conditions. The nature of the cation is also of great interest. If indeed the simple models which suggest that the nature of the cation and the polymer structure are of secondary concern proves correct under experimental scrutiny, then one can focus on cost, and long-term stability in choosing among different polymer structures and cations. Answers to these questions would open a new field of sorbent technologies that could have impact well beyond the immediate application in direct air capture.

9:00 AM ET14.01.02
Nano Porous Polymeric Composite Membranes—Excellent Carbon Dioxide Separation Performance and with Processible Membrane Properties
Ali Sekyzkardes1,2, Saurendra Venna1,2, Victor Kusama1,2 and David Hopkinson1; 1National Energy and Technology Laboratory (NETL), U.S. Department of Energy, Pittsburgh, Pennsylvania, United States; 2AECON Pittsburgh, Pittsburgh, Pennsylvania, United States.

Nano porous polymers such as polymers with intrinsic microporosity (PIMs) have attracted great interest in Materials Science to applied as gas separation membranes. PIMs are constructed by contorted monomer backbones and given its inefficient polymer chain packing, PIM-1 possesses an intrinsic micro porosity with an unprecedented amount of free volume for a polymeric membrane. The unique polymer structure of PIM-1, however, constirates two major drawbacks: Average pore size of PIM-1 (~1nm) is too large, hence permeate most of small gas molecules such as H2, N2, CO2, CH4 and consequently PIMs show lower gas selectivity properties compared to other polymeric membranes. The second drawback is weak mechanical properties for PIM due to the lack of sufficient hydrogen bond capability between polymer chains, affording brittle film formation. Here we study novel composite membrane fabrication and characterization by incorporation of flexible in house synthesized polymer (NETL-PE) and porous organic fillers in PIMs. PIM/NETL-PE membranes show distinct improvement in brittle film properties of PIM-1 by greatly improving low strain to failure (~ 1%) of PIM-1 to as high as 10.5%, which is indicative of a very flexible and durable film formation. The resultant membranes showed an excellent CO2/N2 selectivity of 40 while maintain high CO2 permeability of up to 2500 barrer. Comparing these membranes with reported polymeric membranes above the 2008 Robeson upper bound shows that these membranes are one of best materials for CO2/N2 separation applications while having good mechanical properties. Fabrication and characterization of the membranes with pure and mixed gas permeation tests will be presented.

9:15 AM ET14.01.03
Quaternary-Ammonium Grafted Macroporous Resin for Direct Air Capture of CO2
Yusong Wu, Chenglong Hou, Xinru Wang, Tao Wang and Mengxiang Fang; Zhejiang University, Hangzhou, China.

Global warming, believed to be triggered by the emission of CO2, has become the focus of the sustainable development of human society nowadays. It is imperative and urgent to take some effective actions to reduce the global CO2 emission. Considered to be one of the key technologies to achieve the negative CO2 emissions, Direct Air Capture (DAC) has attracted worldwide attention since 2000. After decades of fundamental research on DAC sorbents, the low sorption kinetics, higher energy consumption for regeneration, and the insufficient stability become the major obstacles for DAC application in practical processes. Aiming to solve the problem above, this paper proposed a novel resin sorbent synthesized by chemical grafting the quaternary ammonium groups onto the nonpolar macroporous resins. Three different support materials (XAD-4, XAD-16, D101) with preferred porosity were selected as supports and the CO2 adsorption performance were demonstrated with isothermal experiments. The structure-activity relationship of the sorbent were further revealed with multiple characterization methods including FESEM, FTIR, MIP and elemental analysis. Results indicated that the CO2 adsorption isotherms of quaternary- ammonium grafted resins were in line with the classic Langmuir model. Quaternized XAD-16 sample, with a moderate pore size, had the highest CO2 adsorption capacity of 0.42 mmol/g, and the quaternized XAD-4 and D101 samples were only 0.28 mmol/g and 0.21 mmol/g, respectively. Combined with the results of elemental analysis and pore analysis, it was inferred that the macropores in the resin are conducive to the grafting density of quaternary ammonium groups, while the quaternary ammonium groups confined in the micropores could reach a higher CO2 adsorption efficiency. The adsorption kinetics of the optimized adsorbents could be one magnitude higher than commercial resin at 400 ppm CO2. The stability of the adsorbents were verified with a cyclic adsorption-desorption test based on moisture swing technique, showing no evident decline in working capacity in 10 cycles under 25 C. Owing to higher kinetics and the energy-efficient moisture swing process, it can be suggested that the quaternary-ammonium grafted macroporous resin could be a promising and cheap material for direct air capture.

9:30 AM DISCUSSION TIME

9:45 AM BREAK

10:15 AM ET14.01.04
Carbon Dioxide Capture in Diamine-Appended Metal-Organic Frameworks
Rebecca Siegelman1,2, Phillip Milner1,2, Jeffrey Martell1, Alex Forse1,2, Miguel Gonzalez1, Eugene Kim1, Tomce Runceski1, Jarad Mason1,2, Thomas McDonald1,2,3, Jeffrey Reimer1,2 and Jeffrey R. Long1,2; 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Mosaic Materials, Inc., Berkeley, California, United States.

Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications. In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for potential use as solid adsorbents in post- and pre-combustion CO2 capture, and for the separation of O2 from air, as required for oxy-fuel combustion. In particular, MOFs with diamine-functionalized surfaces have been demonstrated to provide high selectivities and capacities for the adsorption of CO2 over N2 under dry flue gas conditions. Thermogravimetric cycling and multicomponent adsorption measurements now further show that compounds of this type remain highly effective in the presence of water, while calorimetry data reveal a low regeneration energy compared to aqueous amine solutions. Most significantly, as determined by in situ nuclear magnetic resonance, infrared, x-ray absorption spectroscopy experiments, crystal structure determinations, and computational simulations, the unusual stepped CO2 adsorption isotherms exhibited by these materials arise from a unique cooperative insertion mechanism to form one-dimensional chains of metal-bound ammonium carbamates. A detailed understanding of this mechanism now enables us to design new materials for the low-energy separation of CO2 from a wide variety of key gas mixtures, including flue gases, air, biogas, and natural gas deposits.

10:45 AM ET14.01.05
Nano Fabricated Polybenzimidazoles with Chemically Robust Membrane
Jung Ji Hye, Moon Ki Jeong and Sang Yong Nam; Gyeongsang National University, Jinju, Korea (the Republic of).

Polybenzimidazole is well known for its superior heat resistance and good mechanical properties. Due to an excellent various property, PBI has been used
in a lot of fields such as gas separation, OSN and secondary battery membrane. This work is focused on fabrication of meta-Polybenzimidazole(m-PBI) and control of morphology according to concentrations or manufacturing conditions. The membranes were prepared via the phase inversion method from casting solutions with predetermined amounts PBI, dimethylacetamide (DMAc) and tetrahydrofuran (THF). The polymer solutions were cast on a clean glass plate by using casting knife. The membrane was immersed in IPA to remove the residual solvent and dried in vacuum oven for 24 h. The membrane was crosslinked by α, α’-Dibromo-p-xylene. Also, this membrane can be prepared by electro-spinning. Electro-spinning can make highly porous non-woven fabrics consisted of nanofibers with the small diameters and overall porous structure. Also, electrospun fabrics have high specific surface area. To observe morphology, Scanning electron microscope (SEM) was used. In case of gas transport properties, H2, CO2 Permeability and selectivity of this membrane was measured via pure gas.

11:00 AM ET14.01.06
Ultra-selective Defect-Free Interfacially Polymerized Molecular Sieve Thin-Film Composite Membranes for H2 Purification and Carbon Capture Zain Ali, Federico Pacheco, Ingo Pinnau and Yingge Wang; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H2 purification and carbon capture Purification is a major bottleneck towards generating low-cost commercial hydrogen from syngas mixtures. According to reports published by United States Department of Energy (USDOE), reduction is hydrogen purification costs can immediately increase the hydrogen market by 10-fold promoting its use in desulfurization, hydrotreating, chemical manufacture, power generation and use as a potential energy carrier. In this work, inexpensive high-performance H2 separating membranes were fabricated by modifying the commercially successful reverse osmosis membrane production method. Defect-free thin-film composite membranes were formed that demonstrate unprecedented mixed-gas H2/CO2 selectivity of ≈ 50 at 140 °C with H2 permeance of 350 GPU, surpassing the permeance/selectivity upper bound of all known polymer membranes by a wide margin. Coupled with excellent H2/CH4 separation properties, given the targets specified by the USDOE, the membranes are excellent candidates for pilot-scale testing aimed at hydrogen purification from syngas while simultaneously promoting capture of accompanying CO2. Fortunately, these ultra-high-performance membranes can be produced by making only small changes to existing commercial membrane manufacturing processes. Therefore, their fabrication cost should be similar to standard RO membranes – only ≈ 1 – 2 $/ft², which would lower the membrane cost by 50-100-fold based on the USDOE target value of 100 $/ft². This study demonstrated that varying fabrication parameters can tune permselectivity to meet the needs of specific processes. A few simple modifications to a time-tested commercial membrane production process can produce membranes that meet a key industrial need. These membranes also demonstrated remarkable selectivity for O2/N2, CO2/CH4, H2/N2 and CO2/N2 separations. With rapidly developing economic and environmental pressures to increase efficiencies for separation processes, such highly-selective, low-cost, commercial barrier materials fabricated as ultra-thin films show potential for a paradigm shift to streamline industrial use of membranes for a large number of gas separation applications, including but not limited to hydrogen separations, air separations as well as a number of liquid-bases separations. The combination of exceptional separation performance and low manufacturing cost makes interfacially polymerized thin-film composite molecular sieves excellent candidates for cost-effective hydrogen purification from steam cracking and similar processes.

11:30 AM ET14.01.07
Tailoring Molecular Architecture of Graphene Oxide for CO2-Selective Membrane Jae Eun Shin, Jun Kyu Jang, Inho Park and Ho Bum Park; Hanyang University, Seoul, Korea (the Republic of).

Graphene Oxide (GO) has been extensively investigated as a membrane material for CO2 separation due to their high CO2 sorption properties and 2-dimensional nanosheets structure for membrane formation. Although GO membrane is considered as one of promising membrane, it has a limitation to apply for practical application because of low gas permeability. In general, gas molecules are passed along the layered structure, which lead to increase of diffusional pathway and resistance to oxygen functional groups on the basal plane of GO. As such, in this study, we prepared modified GOs to reducing the diffusional pathway and increasing structural stability by adjusting the architecture of GO using the following methods; (1) surface porosity and interlayer distance control by sol-gel reaction, (2) tailoring sp2-graphitic and sp3–oxidized regions with mild hydrothermal treatment, (3) creating and decorating pores on the basal plane of GO nanosheets without thermal reduction. Finally, we fabricated membranes to confirm gas transport behaviors. From these results, the CO2 permeability was significantly increased up to 30 times compared to the pristine GO membrane and CO2/N2 selectivity was increased up to as high as 30. These results have the potential to open up new approaches for an improvement in the transport properties of two-dimensional membrane materials for use in next-generation membrane for CO2 separation.

11:45 AM DISCUSSION TIME

SESSION ET14.02: DAC/CCS by Sorption in Materials II
Session Chair: Klaus Lackner
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 305

1:30 PM *ET14.02.01
Design of CO2-Sorbing Materials and Their Compatibility with Practical, Scalable Direct Air Capture Processes Christopher W. Jones; Georgia Institute of Technology, Atlanta, Georgia, United States.

A variety of classes of materials have been established for CO2 adsorption from gaseous mixtures. One particular challenge that has emerged in recent years is the design of materials that bind CO2 suitably strongly and selectively that they can efficiently extract CO2 from ultra-dilute mixtures, such as ambient air (400 ppm). Such materials and processes will play an important role in future climate mitigation strategies if society chooses to try and limit global climate change, being one of the only highly scalable approaches to achieve negative CO2 emissions. In this contribution, I will discuss various classes of materials that have been proposed for use in such “direct air capture” technologies, highlighting strengths and weaknesses of assorted compositions in these applications, as well as critical research challenges that the field should address.

2:00 PM ET14.02.02
Fabrication of Large and Free-Standing Nanomembranes Preferential CO2 Separation Under Atmospheric Pressure Shigenori Fujikawa, Toyoki Kunitake and Roman Selyanchyn; WPI-ICNER, Kyushu University, Fukuoka, Japan.

Biological lipid bilayer membrane is an ideal example for precise and efficient molecular separation. One of its characteristics is a free-standing property
with molecular thickness, and molecular scale phenomena become dominant in the direction of the membrane thickness. Thus, artificial membrane with a free-standing properties and nanometer thickness would be a unique property different from conventional thicker membrane. Especially in membrane separation, the thickness plays an important role for the efficient separation. Based on this idea, we have developed free-standing nanomembranes (thickness: 100 nm or less) with preferential CO₂ permeation ability even under low partial pressure difference of CO₂ across a membrane. Our developed nanomembranes showed very high CO₂ flux (about ~10,000 GPU, 1GPU ≈ 7.5 × 10⁻¹² m²/ Pa), without losing CO₂ selectivity which is identical to that of thicker membranes. This unique feature of free-standing nanomembranes, high CO₂ flux with preferential CO₂ separation, would be beneficial to capture CO₂ from the air, so-called "direct air capture". Indeed, our free-standing nanomembrane showed preferential CO₂ separation even under very small pressure difference.

2:15 PM ET14.02.03
Techno-Economic Analysis of Membrane-Supported \( H_2O \) Splitting with CO₂ capture Xiao-Yu Wu, Yu-Dong Chen and Ahmed F. Ghoniem; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In this presentation, we show the techno-economic analysis of an advanced hydrogen production technology: membrane supported water splitting with CO₂ capture. Oxygen permeable membranes such as \( La_0.9Ca_{0.1}FeO_3_\delta \) (LCF) [1,2] and \( BaCo_xFe_yZr_zO_3_\delta \) (BCFZ) [3, 4] are used to in \( \textit{ situ} \) separate the water splitting products. On the feed side of the membrane, \( H_2O \) splitting occurs and high purity hydrogen is produced. On the sweep side, methane oxidation takes place to consume the permeated oxygen and to maintain the oxygen potential gradient across the membrane. CO₂ produced from methane oxidation is ready to be captured at high pressure.

First, we built a thermodynamic model to compare the membrane reactor with the conventional methane reforming for high purity hydrogen production. Results show that membrane reactors have higher efficiency (as high as 8 percent points), especially when renewable heat source, e.g., solar and geothermal energy is incorporated into the system. The energy cost of hydrogen production with CO₂ capture is lower for the membrane reactors.

Secondly, a high-fidelity reactor model is built to simulate a monolith membrane reactor with 100 kmol/h \( H_2 \) production rate. The dimensions and operating conditions are similar to the solid oxide fuel cell stacks, and 90% methane conversion is achieved. Two well-studied perovskite membrane materials, i.e., LCF and BCFZ are compared. Results show that BCFZ membrane can produce more hydrogen per unit surface area, so the required LCF membrane surface area is 5.3 times larger than the BCFZ membrane area.

As the BCFZ membrane contain critical minerals, e.g., cobalt and zirconium, the membrane reactor cost can be impacted by the fluctuating mineral prices. Based on the quoted prices from Alibaba website on April 2018, the raw materials to produce the BCFZ membrane is 2.3 times more expensive than those for the LCF membrane. However, as the required LCF membrane surface area is larger, the cost for the LCF membrane reactor is 2.4 times more expensive than that for the BCFZ reactor. Sensitivity analysis shows that if cobalt price increases by 2.82 times, the cost for the BCFZ reactor can be more expensive.

Furthermore, it has been showed that BCFZ membrane is susceptible to performance instability due to the cobalt segregation [5], while LCF membrane can perform stably under both oxidizing and reducing environments [1]. Life-cycle analysis will be carried out to compare the costs of these two membrane reactors for a hydrogen plant designed with 20-year operating life.

Reference:

2:45 PM BREAK

SESSION ET14.03: CO₂ Fixation by Biological Systems
Session Chair: Edda Aradottir
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 305

3:15 PM ET14.03.01
Nano-/Microscopic Design for the Hybrid Biological | Inorganic System of Electricity-Driven CO₂ Reduction Chong Liu; University of California, Los Angeles, Los Angeles, California, United States.

A hybrid biological | inorganic (HBI) system combines the benefits of both inorganic and biological catalysts and leads to high energy efficiency of electricity-driven CO₂ reduction to commodity chemicals. However, the reactor throughput and the versatility of chemical feedstock may not be optimal yet, as biocatalysts can be kinetically slow and have stringent requirements of substrates and liquid environment. In this talk, we will discuss some design strategies at micro-/nanoscopic scale to address these questions.

3:45 PM ET14.03.02
Photocatalyst-Biocatalyst Integrated Artificial Photosynthesis System for Highly Selective Solar Fuel Production from CO₂ Jin-ook Baeg; KRICT, Daejeon, Korea (the Republic of).

The natural photosynthetic process has fascinated chemists for long due to its high specificity in solar energy conversion to sugar. However, given the structural and functional complexity, it is a challenge to mimic this natural process. In recent years, these efforts have intensified due to increasing emphasis on the development of emission-zero systems/technologies for production of solar fuel/chemicals. Utilizing the natural photosynthesis as blueprint, a number of covalent, and non-covalent donor-acceptor conjugate dyes have been studied as systems for CO₂ fixation. Although capable of efficient photoinduced intra- and intermolecular electron transfer(ET), they suffer from low conversion efficiency, poor product selectivity and lack of
Rising atmospheric carbon dioxide levels make CO₂ an abundant source of carbon for synthesis of commodity chemicals. One of the most promising methods of CO₂ reduction developed in recent years is the use of a hybrid biological inorganic system that couples an electrochemical cell and CO₂ reducing microbes to simultaneously split water and fix carbon dioxide. While this system is highly energy efficient, the low solubility of the redox carrier, H₂ gas, in aqueous environments is hindering the scale-up of the hybrid biological inorganic system. We propose that bio-compatible perfluorocarbon nanoemulsions can serve to increase the H₂ gas solubility to overcome this kinetic limitation. We discovered that perfluorocarbon nanoemulsions not only increase the average concentration of H₂ generated from electrochemical water splitting, but also accelerated the local H₂ transfer rate in proximity to the microbes. Both factors contributed to an average 20% (n ≥ 3) enhancement in overall device efficiency with high device throughput. We believe that our improved hybrid system could be used at point sources of CO₂ emissions to generate important chemical building blocks while reducing atmospheric CO₂.

**4:15 PM *ET14.03.04**
**Carbon Negative Production of Living Biofertilizers** Daniel G. G. Nocera and Daniel Loh; Harvard University, Cambridge, Massachusetts, United States.

Global soils store 2-3 times more carbon than the atmosphere, acting as a massive reservoir for carbon sequestration. Increasing soil carbon reservoirs by 0.4% per year would completely halt the increase of atmospheric CO₂ levels from human activity. These efforts to sequester carbon simultaneously enrich agricultural soils, supporting soil biology and reducing the need for synthetic fertilizers, a production system responsible for >245 million tons CO₂/year. To both sequester atmospheric CO₂ and replace synthetic fertilizer production, we have developed a living, CO₂-negative biofertilizer. This work adapts the rate in proximity to the microbes. Both factors contributed to an average 20% (n ≥ 3) enhancement in overall device efficiency with high device throughput. We believe that our improved hybrid system could be used at point sources of CO₂ emissions to generate important chemical building blocks while reducing atmospheric CO₂.

**4:45 PM ET14.03.05**
**Photosynthesis-Mimicking Cell with 15.6% Solar-to-CO Efficiency** Junlang Liu, Yuhang Wang and Gengfeng Zheng; Fudan University, Shanghai, China.

The vigorous growth of atmospheric CO₂ level has posed a threat on sustainable development of our blue planet. The solar-energy-driven electrochemical CO₂ conversion into various value-added chemicals (namely artificial photosynthesis) is regarded as one of the most promising solutions to alleviate this urgent environment pressure and energy crisis. Compared to the other configurations of artificial photosynthesis systems such as photocatalysis and photoelectrochemical conversion, electrocatalysis powered by photovoltaics has shown the highest solar-to-fuel efficiency to date, which has achieved over 10-fold enhancement compared to natural photosynthesis. Nonetheless, the operation of all artificial photosynthesis systems still strongly relies on sunlight illuminations, which are altered significantly over time of a day, weathers and regions. Thus, designing artificial photosynthesis devices capable of CO₂ reduction reaction (CO₂RR) under different sunlight conditions is of crucial significance.

Delighted by the temporary energy storage function of ATP and NADPH in green plants, we propose that a redox medium can be introduced between oxygen evolution reaction (OER) and CO₂RR. The redox medium forms a loop with OER electrode to store the photogenerated electrons in the step of light reaction, as the charging of battery. These photogenerated electrons can be released spontaneously to reduce CO₂ in the following artificial carbon fixation step, as the battery discharge.

Therefore, we develop a green-plant-mimicking artificial photosynthesis-battery system, by introducing Zn/Zn(OH)₂⁺ redox pair as the energy transfer medium between artificial light reaction and carbon fixation to simulate ATP/ADP: Nano-Au and NiFe hydroxides were employed as electrocatalysts for CO₂RR and OER, respectively. A GaAs solar cell was utilized to drive oxygen evolution reaction and store electrons in Zn/Zn(OH)₂⁺. The further release of electrons proceeded without light and led to an unassisted CO₂ electroreduction. The solar conversion efficiency of artificial light reaction is 28.7%. During carbon fixation, the unassisted electrochemical CO₂ reduction achieved a record-high solar-to-CO efficiency peaking at 15.6% under 1-sun intensity at the current density of 10 mA/cm². By tuning CO₂ electroreduction current density in the range of 2 to 10 mA/cm², a tunable and light-independent selectivity of CO₂ production was realized.

Our two-step, artificial photosynthesis-battery design possesses high efficiency, tunable selectivity, excellent stability and flexibility to various sunlight conditions even in the dark, owing to the mutual independence of light reaction and carbon fixation. Combining with further robust electrocatalysts as well as new redox media able to provide higher potential difference for carbon fixation, our design actually suggests new opportunities in anthropogenic manufacture of fossil fuels from CO₂ and sunlight with such a green-plant-mimicking approach.
Increasing atmospheric carbon dioxide and sulfur dioxide emissions from combustion of fossil fuels, such as coal and oil, are considered as a globally alarming environmental issue. Hence, the quest for an immediate solution for sequestration and storage of carbon dioxide and sulfur dioxide is warranted. Recently, amine and ionic liquid based absorption process have attracted widespread attention to capture these gases but this process passes several disadvantages such as severe corrosion, highly energy intensive, and low contact area. One viable alternative is adsorption technology, which is recognized to be attractive to replace current absorption technology. Therefore, development of novel porous carbon based materials has become one of the hot areas due to their extensive applications in gas storage and separation. In this regard, first we have modeled an experimentally observed 3-D porous structure of graphene sponge (GS) using molecular dynamics simulations (MD). The initial structure is composed of randomly distributed graphene flakes and inclusion particles of variable dimensions following the lognormal distribution. [1] MD simulations are performed using Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential to mimic the synthesis of 3-D graphene sponge. Further, we have used this graphene sponge as an adsorbent to capture CO2/SO2. We have performed Grand Canonical Monte Carlo (GCMC) simulation to get adsorption isotherm and to examine selectivity for CO2 and SO2 in graphene sponge. Our simulation results show that graphene sponge obtained using smaller size inclusion particles have large uptake capacity at post combustion conditions. We first tested pure component flue gas adsorption capacity in graphene sponge then we moved on for more realistic ternary mixture (CO2/SO2/N2) of flue gas adsorption. Pure component adsorption results show that SO2 adsorbs preferably over CO2 and N2. At 1 bar, extent of excess adsorption of SO2 and CO2 in GS of 10 Å pore size are found to be 13 mmol/g and 2.6 mmol/g, respectively. Upon increasing pore size to 20 Å excess amount decreases by 56 % and 38 % for SO2 and CO2 respectively. In case of ternary mixture, we have found that adsorption follow the same order as in the pure component flue gas adsorption but adsorption amount decreases significantly. Selectivity analysis of adsorption show that adsorption selectivity of SO2 over N2 is highest followed by selectivity of CO2 over N2 and SO2 over CO2. Thus, our results indicate that graphene sponge obtained using smaller size inclusion particles is a promising material for treatment of flue gas at post combustion conditions.

References

ET14.04.02
Determining the Role of the Ionic Radii of Interlayer Cations for CO2 Capture in Synthetic Smectite Clay Kristoffer W. Humble1, Leide Cavalcanti2, Matthias Daub3, Barbara Pacakova4, Paolo H. Brito5, Kenneth Knudsen6, Josef Breu7 and Jon O. Fossom11; 1Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway; 2Institute for Energy Technology, Kjeller, Norway; 3Lehrstuhl für Anorganische Chemie, University of Bayreuth, Bayreuth, Germany.

Large amounts of clays are found in cap-rock formations and act as pressure barriers in storage sites for anthropogenic CO2 [1,2]. Clays are also relevant as capture/recovery elements for combustion gases, such as methane or CO2. Recent experiments and simulations have shown that CO2 (like H2O) can intercalate in smectite clays, both in the supercritical (scCO2)[3], and in the gaseous/liquid phase[4]. Understanding how clay swells and adsorbs CO2 interacts with clay capture elements for combustion gases, such as methane or CO2. Recent experiments and simulations have shown that CO2 (like H2O) can intercalate in smectite clays, both in the supercritical (scCO2)[3], and in the gaseous/liquid phase[4]. Understanding how clay swells and adsorbs CO2 interacts with clay is vital for CCS and capturing applications. The group has previously demonstrated that CO2 intercalates into dry synthetic (Na, Ni and Li)-Fluorohectorite (Fh), with Li-Fh clay being able to retain CO2 (0.23 ton of CO2/m3 captured) up to a temperature of 35°C, at ambient pressure, and that the captured CO2 can be released by heating above this temperature. Na+ showed much slower intercalation dynamics than the Ni2+ and Li+, which might relate to its larger ionic radii, and thus a lower ability polarize CO2:[5]

We have studied (Li, Ca, Ba, Ni)-fluorohectorite [6] with a capillary based high-pressure cell with synchrotron X-ray powder diffraction. Here we show that dehydrated Ni-Fh is able to adsorb CO2 at higher temperatures range than Li-Fh, and that dehydrated Ca-Fh and Ba-Fh is not able to adsorb CO2:


ET14.04.03
Efficient CO2 Conversion to CO Catalyzed by Metal Nanoclusters Hong Seong, Yongjin Lee and Dongil Lee; Department of Chemistry, Yonsei University, Seoul, Korea (the Republic of).

Significant progress has been made recently in the electrochemical CO2 conversion to value-added products. Various polycrystalline metal electrodes have been investigated as electrocatalysts for electrochemical CO2 conversion, but they typically require high overpotentials and show relatively low catalytic activities. In this paper, we present that atomically precise metal nanoclusters, such as Au132(SR)130, where SR is thiolate ligand, can efficiently catalyze the CO2 conversion to CO with high selectivity. The electrochemical CO2 reduction was studied with Au132 nanoclusters immobilized on gas diffusion electrode in CO2-saturated aqueous solution containing KHCO3 and KCl. We found that Au132 nanoclusters can catalyze the CO2 conversion to CO with high selectivity (>90%) at high current density of nearly 100mA cm-2. Additional studies on the effects of compositions and pH of the media on the electrocatalytic activities reveal the key factors controlling the catalytic activities of the nanoclusters. To further circumvent CO2 mass transport limitations in aqueous solutions, we explored the possibility of using flow electrolyzer that supplies continuous CO2 stream at the electrode-electrolyte interface. The electrocatalytic activity of the Au132 nanoclusters was found to be drastically enhanced with high CO selectivity when the electrocatalysis was conducted with the flow electrolyzer.

ET14.04.04
Electrochemical CO2 Reduction Catalyzed by Atomically Precise Copper-Hydride Nanoclusters Yongjin Lee1, Woogjun Choi1, Dongil Lee1, Qing Tang2, De-En Jiang3, Dai-Ying Li1 and Chen-Wei Liu1; 1Department of Chemistry, Yonsei University, Seoul, Korea (the Republic of); 2Department of...
Electrochemical CO₂ conversion into valuable fuels and feedstocks has been the focus of recent research in electrocatalysis. In particular, copper-based electrocatalysts have received much attention because they can catalyze the formation of significant amounts of hydrocarbons at high reaction rates. However, the mechanistic understanding of CO₂ reduction on nanostructured Cu catalysts has been lacking. In this poster, we show that the atomically precise Cu-hydride nanoclusters, such as Cu₃H₂₆L₁₂, where L is di(thiophosphate) ligand, offer unique selectivity for electrocatalytic CO₂ reduction at low overpotentials. Density functional theory (DFT) calculations have predicted that the presence of the negatively charged hydrides in the copper cluster plays a critical role in determining the selectivity of the reduction product, producing HCOOH over CO at lower overpotential. To confirm the DFT prediction, Electrochemical CO₂ reduction was performed on the Cu₃H₂₆L₁₂ loaded electrode in aqueous media. Analysis of the reaction products demonstrated that HCOOH was indeed produced with 89% selectivity at low overpotential, while H₂ production occurred at higher overpotential. The unique selectivity observed in this system can be understood by the lattice-hydride mechanism offered by the unique Cu-hydride nanocluster.

ET14.04.05
Gas Separation Membrane of poly(ethylene glycol)-polyimide Copolymer for Separating Carbon Dioxide Sang Yong Nam, Jin Woo Jo and Ji Hyun Kim; Gyeongsang National University, Jinju, Korea (the Republic of).

The study of polymer separation membrane for carbon dioxide separation for global warming is drawing attention. Among various polymer membranes materials, Polyimide (PI) has excellent thermal and mechanical properties, good chemical stability and high gas transport property. Many researchers have studied gas transport property of polyimide membrane for gas separation. However, polymer membrane still have low performance compared with ceramic membrane and absorption process. Many researchers have been studied to complement this weak point, and can improved permeability of membranes by controlling diffusivity and solubility. Poly(ethylene glycol)(PEG), rubbery polymer, can improve solubility. The moieties with high fractional free volume (FFV) such as cardo fluorene and durene group can improve diffusivity. In this work, Diamines containing cardo fluorene and durene group were used to obtain polyimide having the high FFV. we synthesized PI-PEG copolymer to improve solubility. Finally, chemical structure, thermal property (thermal degradation and glass transition temperature) were investigated and PI-PEG copolymer membrane formed via immersion precipitation process and then membrane morphology was observed and gas transport property of PI-PEG membrane was investigated.

ET14.04.06
Hydrogen Production by Methane Decomposition Over Carbon Catalysts with Different Structures Dai Miyamoto1, Haruki Nishii2, Yoshito Umeda3, Hiroaki Hamaguchi1, Masashi Suzuki1, Toru Hariga1, Tsuyoshi Tanimoto1, Hirofumi Takikawa1 and Sada Yoshiyuki1; 1Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Japan; 2Toho Cryogenics Co., Ltd, Nagoya, Japan; 3Aichi Center for Industry and Science Technology, Toyota, Japan.

Thermo-catalytic decomposition (TCD) of methane is an attractive hydrogen production process to mitigate CO₂ emissions commonly associated with the conventional processes (such as steam methane reforming). However, the problem of the process is catalyst deactivation by carbon deposition [1]. The purpose of this study is to investigate the relationship between the catalysts structure and the catalytic activity of produced carbon during TCD of methane by using four types of carbon catalysts with different structures.

Four types of carbon catalysts were tested in the TCD of methane: activated carbon (AC), mesoporous carbon (MC), carbon black (CB), and carbon nanofiber (CNF). Experiments were carried out in a fixed-bed reactor using 1.7 g of the catalysts with space velocity of 360 h⁻¹, at a reaction temperature of 1173 K. The produced gas was analyzed by a hydrogen detector and gas chromatography. Carbon catalysts before and after the experiments were analyzed by Raman spectroscopic analysis. The methane conversion ratio was derived from the hydrogen concentration obtained by gas analysis. Temporal change of methane conversion ratio of each catalyst is evaluated by the concentration ratio of produced hydrogen and methane. Methane conversion ratios of all the tested catalysts eventually reached about 25%. We also investigated the temporal change of the intensity ratio of the G band and the D band in Raman spectrum (I_D/I_G) of the produced carbon. I_D/I_G is used to evaluate the degree of graphitization of carbonaceous materials [2]. After 600 min elapsed, I_D/I_G of the produced carbons of all the tested catalysts was about 1.5. Therefore, we found that the produced carbon shows the same activity and degree of graphitization regardless of the structure of catalysts. We also found that Raman spectroscopy is an effective method for evaluating initial catalytic activity for methane decomposition.

References
process is not currently competitive (economically) with fuels refined from fossil hydrocarbon sources. The capex of required supply chains is too high and CO2 emission penalties are not effective. The optimal geographic location for sufficient levels of low-cost solar electricity generation may not coincide with the location of sufficient point sources of carbon emissions required by a commercial scale solar fuels production facility. The viability of solar fuels depends on a continual decline in the cost of renewable power and on realizing disruptive performance improvements in direct air CO2 capture and conversion technologies.

Electrochemical routes, such as Co-electrolysis of H2O and CO2 to CO, may offer a competitive alternative for CO2 conversion compared to "standard" catalytic technologies, both in terms ofCAPEX and OPEX. An overview of Shell’s current co-electrolysis program will be presented along with an industrial view of what targets needs to be improved to make the “solar e-refinery” concept a success. Some examples of current projects designed to achieve these targets will be presented.

9:00 AM ET14.05.02
E-Refinery—Towards the Sustainable Electro-Refining of Chemicals and Fuels from Renewable Resources

Wilson Smith; Delft University of Technology, Delft, Netherlands.

Electrification is a key enabler towards reducing CO2 emission. The availability of renewable electrical energy does however not remove the demand for fuels, chemicals and other materials. In addition, the variability of nature calls for electricity storage to safeguard continuous electricity supply. Electrosynthesis is a promising approach to electrify the manufacturing of fuels, chemicals and materials and to contribute to energy storage. Given the Dutch strategic position in the international chemical, renewable energy and transport sectors, TU Delft sees exciting opportunities to establish a national consortium taking the first steps towards industrialscale ‘e-refinery’ systems to convert electricity into molecular bonds. Flexible energy storage in the form of chemicals produced by using electrical energy offers prospects for the energy sector to deal with the growing challenge of demand versus supply mismatch. The large-scale production of synthetic fuels, for example for heavy long-distance transport and aviation, platform chemicals and other materials using electrical energy from renewable sources addresses sustainability demands and is a decisive step towards creating a circular economy. In this presentation, we explore the challenges that lie ahead, dividing them according to the three scales involved: the micro scale (Materials, Catalysts, Electrochemistry), the meso scale (Transport phenomena, Reactor Engineering & Process Intensification, Energy Technology & System Engineering) and the macro scale (Process and System Integration, Societal Embedding). We envision a national consortium and a long-term (10+ years) research and development programme to tackle these challenges, in line with the recent advice by the Electrochemical Conversion and Materials (ECCM) committee to the Dutch Top Sectors HTSM, Energy and Chemistry. TU Delft started the e-refinery initiative and is motivated to play a key role in such a national activity. Across all the disciplines involved, from fundamental research to societal implementation, TU Delft has the expertise to pioneer the topic of large scale electrosynthesis of chemicals and fuels from renewable feedstock. A systems integrated approach to CO2 electroreduction will be given as an example of how process integration and intensification can provide relevant reaction conditions at the micro and nanoscale that differ significantly from current areas of academic research. Therefore, materials science and chemistry research can benefit from understanding the 'big picture', and lead to more rapid technological development.

9:15 AM ET14.05.03
Fe-Doped Carbon Spheres Architecture as a Catalyst for CO/CO2 Methanation

Arturo Reza Ugalde, Hani E. Naguib, Pin Tsung Liao and Olivia Kesler; University of Toronto, Toronto, Ontario, Canada.

The CO2 is one of the greenhouse gases with higher impact in the global warming. Although a natural cycle regulates the CO2 concentration by the photosynthetic organism, the large-scale burning of fossil fuels has increased considerably the concentration in the atmosphere producing an unbalanced carbon cycle. Nowadays, the only solution available is the underground storage of the CO2, however, this method is extremely expensive and require continuous monitoring. An alternative solution is the sequestration and utilization of the CO2, where the greenhouse gas is captured and reduced into different products (mainly hydrocarbons), which then can be used to produce energy. With this system, the cycle of CO2 can be completed reducing the environmental impact. Among the post-capture treatments of CO2, the catalytic hydrogenation into methane is one of the most studied routes, nevertheless, the lack of a durable and cost-efficient catalyst is still a problem. This work presents the fabrication process (through nitration and impregnation) of a Fe-doped carbon spheres architecture as the electrocatalyst for CO2/CO methanation via hydrogenation. Through a thermodynamic analysis, we studied the degradation of carbon during the methanation process to ensure the longevity and stability of the carbon spheres. Furthermore, the selectivity and activation of the Fe and its transition into Fe2+ and Fe3+ were considered to guarantee the catalyst efficiency.

9:30 AM DISCUSSION TIME

9:45 AM BREAK

10:15 AM ET14.05.04
C2CNT—The Inexpensive, Efficient Direct Transformation of Atmospheric or Emitted CO2 to Valuable Carbon Nanotubes by Molten Electrolysis

Stuart Licht; George Washington University, Washington, District of Columbia, United States.

”C2CNT” (CO2 to carbon nanotube) is a Carbon XPRIZE technology for transforming CO2 to the most valuable product. An incentive to remove CO2 is provided by a low energy, low cost, high yield conversion to valuable products such as carbon nanotubes. Displaying superior strength, conductivity, flexibility and durability, carbon nanotube (CNT) applications had been limited due to their cost intensive their synthesis. An inexpensive source of CNTs made from CO2 will facilitate its adoption as an important societal resource for building, transportation, renewable energy, sporting and consumer electronics, while concurrently consuming CO2. We present an inexpensive, high-yield and scale-able synthesis of CNTs. A new chemistry for the effective capture of CO2 and its high yield, low energy transformation is via dissolution in a molten carbonate electrolyte and electrolytic splitting to CNTs and O2.\textsuperscript{1-10} The CO2 reactant is directly absorbed from air (without the need for pre-concentration), or can be used and removed from industrial emissions. CNTs are a compact, stable storage for the removal of anthropogenic CO2. We show that common metals act as CNT nucleation sites in molten media to efficiently drive high yield electrolytic conversion of CO2 dissolved in molten carbonates to CNTs. The CNT structure is tuned by controlling the electrolysis conditions, such as nucleation sites, composition of the electrolyte, and the control of temperature and current density. Upward scalability of the process is demonstrated over several orders of magnitude. Our goal is to transform CO2 from a pollutant to a desired resource. Molten carbonate electrolysis production is significantly less expensive than contemporary CVD to produce CNTs, and uses CO2 as the reactant. An inexpensive source of CNTs has demand as a preferred, lighter weight, stronger replacements to metals and plastics, which can provide a large market to mitigate anthropogenic CO2.

C2CNT publications:

\textsuperscript{1}One-pot synthesis of carbon nanofibers from CO2, \textit{Nano Letters}, 15, 6142 (2015).
11:30 AM DISCUSSION TIME

1:05 AM ET14.05.05
Selective Electrochemical CO₂ Reduction to CO on Ultrathin MXene Nanosheets

Data on … CNTs made directly from CO₂ by molten electrolysis, Data in Brief, 14, 593 (2017).
Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection CNTs, J. CO₂ Utilization, 18, 335 (2017).

Anthropogenic release of CO₂ is believed to be a leading cause of global climate change. An attractive proposed strategy to limit this change is to capture CO₂ after production and if possible to electrochemically convert it into value added chemicals using renewable energy. Research is presented that investigates the catalytic activity of Mo₆C and Ti₂C MXenes towards the electrochemical CO₂ reduction reaction (CO₂RR) as a cheaper alternative to precious metals that are known to catalyze this reaction. The metallic nature, large surface area of the 2D nanosheets and the ability of these MXenes to spontaneously bind CO₂ are key factors that make them attractive materials for the CO₂RR. We report very high faradaic efficiencies, ~90% for the reduction of CO₂ to CO at low overpotentials, ~300 mV, in acetonitrile/ionic liquid electrolytes on Mo₆C MXene. Ti₂C MXene shows ~65% FE at an overpotential of ~600 mV for the cathodic half reaction. The use of ionic liquid 1-ethyl-2-methylimidazolium tetrafluoroborate suppresses the competing H₂ evolution reaction and also acts as the electrolyte. High selectivity and high FE of CO₂ reduction to CO makes these MXenes, which are composed of earth abundant elements, an attractive non-precious metal electrocatalyst for the CO₂RR.

11:00 AM *ET14.05.06
Indirect Ocean Capture of Atmospheric Carbon Dioxide

Negative emissions technologies (NETs) are needed to limit the increase in average global temperature to less than 1.5 °C. In this talk, I will present the design, prototype performance characterization, and techno-economic analysis for a new negative emissions technology (NET) termed indirect ocean capture (IOC). IOC removes carbon dioxide gas from the atmosphere by leveraging both air-ocean gas exchange and the pH sensitivity of the ocean’s carbonate buffer system. I will present the predicted net cost per ton of removed carbon dioxide for multiple scenarios, including co-location with desalination plants, and discuss the tradeoff between minimizing cost and maximizing impact. Finally, I will explain the results of a techno-economic sensitivity analysis to highlight the research and development areas that hold the most promise for future cost reduction.

11:30 AM DISCUSSION TIME

SESSION ET14.06: CO₂ Petrification
Session Chair: Matthew Eisaman
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 365

1:30 PM *ET14.06.01
CarbFix – Reducing Emissions by Rapidly Petrifying CO₂ in the Subsurface with Added Economic, Social and Economic Value

Global emissions must be put on a permanent downward trend by 2020 if severe consequences of global warming are to be prevented. CarbFix involves capturing otherwise emitted CO₂, dissolving it in water and injecting it into basaltic geological formations. There, the CO₂ is turned into rock in less than two years and is thereby permanently removed from the atmosphere. The CarbFix team has developed the method from scratch over the past twelve years; moving from laboratory-scale and numerical simulations, through pilot-scale field injections, to stage-wise build-up of industrial-scale capture and injection. Innovative equipment and methods for capturing, injecting, and monitoring have been designed and built. The annual CO₂ emissions of Hellisheidi geothermal power plant, the home of CarbFix, were reduced by 34% since industrial scale CCS operations began in 2014 until 2017. The CarbFix team, in collaboration with the Swiss company Climesworks, is currently running a pilot demonstration of a conjugated direct air capture and subsurface CO₂ mineral storage through support of the EU’s H2020 framework program. Large worldwide potential lies in joint application of direct capture of CO₂ from ambient air and CCS technologies in favorable rock formations, as this allows for rapid, permanent removal of CO₂ from the atmosphere.

The CarbFix method provides a safe and efficient alternative to conventional CCS methods in which CO₂ is stored in less reactive rock formations as a supercritical phase. It only takes two years to petrify the injected CO₂ in CarbFix, whereas mineralization happens on the scale of hundreds to thousands of years in conventional CCS. Risks of leaks are also eradicated in CarbFix as the injected phase is denser than the surrounding groundwater and therefore...
CarbFix checks all three pillars for sustainability, providing added environmental, social and economic value. The method imitates and accelerates processes already happening in nature and is, as such, environmentally benign. Added social value from CarbFix e.g. involves dissemination of knowledge, training of next generation students, on-site access to facilities, and raised awareness of available climate solutions in mass media. Added economic value can be achieved by using the method to co-capture and mineralize other environmentally important gases. At Hellisheiði power plant, the method was used for co-capturing CO₂ and H₂S. Significant savings on both capital and operational expenses were achieved compared to conventional gas removal methods. The value of those savings is over US $100 million for this single power plant.

2:00 PM ET14.06.02
Controlled Synthesis of MgO with Diverse Basic Sites and Its CO₂ Capture Mechanism Under Different Adsorption Conditions Wanlin Gao and Qiang Wang; College of Environmental Science and Engineering, Beijing Forestry University, Beijing, China.

Mesoporous MgO adsorbents with diverse basic sites were prepared via a urea hydrolysis synthesis method for CO₂ capture. With elevated hydrolysis temperatures, the phase transition process made great contributions to the morphological changes of the precursor architectures. In situ DRIFTS analysis demonstrated that various carbonate surface species including bicarbonate, bidentate, and unidentate carbonates were formed on the obtained MgO during interaction with CO₂. Furthermore, the main component of adsorbed CO₂ surface species swings from bicarbonate to bidentate and unidentate carbonates with increase of adsorption temperature. The highest CO₂ uptake of 1.22–1.99 mmol g⁻¹ was attained for MgO sample at the lowest calcination temperature in a wide temperature range of 60–300 °C. High specific surface area (372.0 m² g⁻¹), large pore volume (0.38 cm³ g⁻¹) as well as diverse basic sites of the synthesized MgO make it an eligible candidate for CO₂ capture, with a nearly 20-fold enhancement of the commercialized light MgO. Additionally, the results of CO₂ uptake studied under diluted and wet (H₂O containing) CO₂ conditions for the as-prepared MgO adsorbent also suggested good prospect in practical applications.

2:15 PM ET14.06.03
Technoeconomics of Electrochemical Carbon Dioxide Conversion on the 100-kW Scale Stafford W. Sheehan; Catalytic Innovations, Adamsville, Rhode Island, United States.

Key discoveries in the last century have demonstrated the breadth of products that could be made electrochemically from carbon dioxide, including carbon monoxide, formic acid, methanol, ethylene, and others. We conducted an economic assessment of both beachhead market opportunities and bulk commodity chemicals that use each of these compounds as feedstock material, with a focus on value propositions unique to products made from carbon dioxide (on-site production, cost tied to electricity prices, and use of renewable feedstock). Our findings identify pathways to implementation of electrochemical carbon dioxide conversion technologies across diverse industries that have been under-explored until now, and we identify technological roadblocks that remain for economically viable implementation.

2:30 PM DISCUSSION TIME
2:45 PM BREAK

SESSION ET14.07: Materials Science and CCUS—So What?
Session Chairs: Christopher Jones and Klaus Lackner
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 305

3:15 PM ET14.07.01
Materials Science Facing Global Warming—So What? Jenny G. Vitillo; University of Minnesota, Minneapolis, Minnesota, United States.

More than the cost. Carbon capture, as any technology, is not free of costs, as evaluated in different ways: money, energy and carbon dioxide production itself. Unlike others, it is a technology that does not have a one-to-one correspondence with the person or the group paying for it, being the benefits of its application spread on a global scale. This is a problem because it makes less appealing to invest in it, unless driven by humanitarian or environmental interests. Nevertheless, it is clear from purely economical projections that investing in technologies aimed to the mitigation of the global temperature rise to 1.5 °C will allow significantly saving with respect to the cost to pay for the impact of climate change in terms of money.¹ And if extreme weather events are considered the cost to be paid will be not be restricted only to that.² Several studies will be presented during the symposium giving different perspectives on the solutions envisaged for the reduction of the CO₂ concentration in the atmosphere and its possible use.

This presentation will summarize and compare the results presented along the symposium, trying to give a more general background to the conclusions made. A discussion involving the speakers, the organisers and the audience will be stimulated trying to understand which among the different technologies are the most mature working tools to face the global warming. The possibility to size down a direct air capture technology and the benefits/drawbacks of this will be envisaged, in order to evaluate if the large sensitization of the general public on this theme can be exploited through its direct involvement (person-sized DAC devices) or indirect involvement (carbon tax or carbon credits) and then centralized carbon capture centers are more viable solutions.

References
2. King, D. A., Climate Change Science: Adapt, Mitigate, or Ignore? 2004, 303, 176-177.

3:45 PM DISCUSSION TIME
4:00 PM CLOSING REMARKS
An Integrated Strategy for Defense Waste Immobilization

Kevin Fox; Savannah River Nat Lab, Aiken, South Carolina, United States.

The US Department of Energy is actively retrieving, treating, and immobilizing defense nuclear wastes at multiple sites. The Savannah River Site employs borosilicate glass and saltstone to immobilize high-level and low-activity wastes, respectively. The Hanford Site will use borosilicate glass for both of these waste streams. An integrated strategy is needed to guide the multiple unit operations necessary for the success of these operations. This strategy must bring together aspects of the feed streams, requirements of the final product, and manufacturing technologies in a manner that maximizes both waste throughput and operational flexibility. DOE’s waste immobilization efforts will take decades to complete; therefore, advances in technology are needed to reduce mission schedule and cost. Recent advances include improved property/composition predictive models for glass waste forms, higher waste loading concentrations in cementitious waste forms, accelerated salt waste decontamination, reduced need for feed pretreatment, facility lifetime extension, and more economical disposal systems. Each of these advancements must consider impacts to the overall flow sheet, both up- and down-stream, to maintain an integrated processing strategy.

What Has Been the Evolution and Structure of the Scientific Basis for Nuclear Waste Management?

Francois Diaz-Maurin1, 2, Hilary C. Sun3 and Rodney C. Ewing1, 4; 1Center for International Security and Cooperation (CISAC), Stanford University, Stanford, California, United States; 2Amphos 21 Consulting S.L., Barcelona, Spain; 3Computer Science Department, Stanford University, Stanford, California, United States; 4Department of Geological Sciences, Stanford University, Stanford, California, United States.

Nuclear waste management is at the interface between the technologies of the nuclear fuel cycle and the natural hydrologic and geochemical cycles of geologic repositories. Yet, despite its clear interdisciplinary scope, nuclear waste management, as practiced, is not a unified scientific field. Subdisciplines continue to work in relative isolation from one another: materials science dealing with the immobilization of nuclear waste; engineering science dealing with the design of the waste package and engineered barriers; geoscience dealing with the long-term behavior of host rocks and the hydrology; health science dealing with the effects of radiation; social sciences dealing with the issues of trust, risk and ethics. Each one of these fields is just one way of looking at the same issues. Defining a unified scientific basis of nuclear waste management requires working at the interfaces of these subdisciplines. Based on a comprehensive review and analysis of the scholarly and scientific literature, we discuss the evolution and structure of research in nuclear waste management between 1940 and 2017. We performed a corpus analysis and a citation network analysis based on the Elsevier B.V.’s Scopus® database aiming to identify the main themes, methods and authors for each one of the relevant disciplines dealing with nuclear waste management issues. We also analyzed the level of interdisciplinarity for each of the subdisciplines by exploring their citation patterns and impact on the other subdisciplines. Using the proceedings published on the MRS Online Proceedings Library Archive, we also analyzed papers in the MRS symposia “Scientific Basis for Nuclear Waste Management” held since 1978 as a reference case and compare its structure and evolution with those of the main academic corpus. Based on this study, we suggest the framework of the scientific basis for nuclear waste management as a unified discipline.

Uncertainty in Safety Assessments of Geological Repositories—Quantitative Performance Assessment vs the Safety Case Approach

Francois Diaz-Maurin1, 2 and Rodney C. Ewing1, 4; 1Center for International Security and Cooperation (CISAC), Stanford University, Stanford, California, United States; 2Amphos 21 Consulting S.L., Barcelona, Spain; 4Department of Geological Sciences, Stanford University, Stanford, California, United States.

Quantification of uncertainty is one of the key issues in analyzing the safety of geological repositories for the disposal of radioactive waste. In the U.S., quantitative performance assessments have been adopted as the standard method used in repository licensing. Quantitative performance assessment relies on the quantification of both stochastic (i.e., aleatory) and subjective (i.e., epistemic) uncertainties on parameters and models used as inputs to the models for the total system performance analysis. In this approach, both the random variations of aleatory uncertainties and the subjective variations of epistemic uncertainties are treated with the same mathematical methodology. Yet, although these “treatments” can be mathematically computed, the value of
quantitative performance assessments has been challenged. In repository design, epistemic uncertainties arise when projecting coupled geophysical and geochemical processes involved over large scales. These uncertainties can be qualitatively characterized by expert judgment, but they limit the ability of the analysts to predict—the long-term behavior of the repository because of the unavoidable lack of knowledge about future geological conditions. Because of the large uncertainties in such assessments, one has to expect public skepticism of statements that a repository is “safe enough.”

The “safety case” concept has been proposed as an appropriate method for analyzing the safety of a geologic repository. The safety case approach relies on the quantification of parameter variations and on scenarios that capture uncertainties in conceptual models and changing boundary conditions. Similar uncertainty quantification is still performed for stochastic parameter variations and uncertainties in projection models. But, the quantification of epistemic uncertainties will only be performed for guiding a qualitative argument (i.e., a “safety case”) about the possible long-term behavior of the repository. This hybrid approach to the safety analysis of geologic repositories thus seeks to address uncertainties for which the quantification poses epistemological constraints on the safety analysis of geologic repositories.

We discuss the use of uncertainty quantification in the safety case approach. Based on the methods of value of information and sensitivity auditing, we show simple examples of how to incorporate both quantitative and qualitative judgements in a performance assessment. In doing so, we seek to develop an analytical framework that better acknowledges the existence of unavoidable uncertainties in the assessment of the long-term performance of geologic repositories and better defines the safety case concept for its introduction in the US repository development program.

9:30 AM ET15.01.04
Reducing Risk and Uncertainty Associated with Nuclear Waste Processing and Disposal—A Hanford Tank Waste Case Study

Carolyn J. Pearce1, David K. Peeler2, Rolf Sjöblom2, Mark B. Triplet1, Kirk J. Cantrell1, Robert C. Moore1, Michael J. Schweiger1, Vicky L. Freedman1, Matthew S. Fountain1, Sue B. Clark1 and Albert Kruger1;

1Pacific Northwest National Laboratory, Richland, Washington, United States; 2The University of Sheffield, Sheffield, United Kingdom.

The Department of Energy’s Environmental Management cleanup effort is focused on developing and implementing innovative and high impact technologies and solutions that positively impact the overall mission lifecycle by: (1) reducing lifecycle costs; (2) accelerating lifecycle schedules; (3) mitigating mission uncertainties, vulnerabilities, and risks; and (4) minimizing the mortgage associated with long-term, post-closure and post-completion stewardship. Pacific Northwest National Laboratory and its partnering institutions, are focused on reducing risk and uncertainty across the integrated flowsheet which includes safe waste storage, retrieval, pretreatment, immobilization, disposal, and tank closure. In this presentation, an overview of the major Hanford flowsheet unit operations will be provided and examples of specific projects focused on reducing risks and uncertainties will be explored. For example, a key issue of Hanford tank waste processing and disposal is that, although radionuclides (e.g., technetium) drive the disposal risk for the low-activity flowsheet, the presence of ‘benign’ elements (e.g., aluminum) dictate processing limits or rates in both retrieval and pretreatment unit operations and have other potential downstream negative impacts. Thus, safe, cost-effective, and efficient waste processing depends on a fundamental understanding of aluminum chemistry in high strength, highly alkaline solutions where water activity is low. Once the waste has been retrieved, processed, and immobilized, controlling the behavior of risk driving elements (e.g., Tc and/or I for low-activity waste) in the waste form and the environment becomes essential for waste form disposal or tank closure. With respect to low-activity waste form disposal, material solutions must demonstrate that the risk driving radioactive elements can be contained in a manner wholly consistent with statutory requirements. Modelling future performance remains a challenge for performance assessment (PA) formalism. An appealing option is to perform an inverse PA (IPA) and look far into the past. Archeological artifacts, analogous to wasteform materials (i.e. glass and concrete) that have been left by our ancestors and exposed to the environment for thousands of years can be used to check for comprehensiveness as well as to validate and refine predicted wasteform durability. An IPA describes the features, events and processes that have influenced the corrosion of a material over time and can help establish the most likely scenarios that should be included in PA for the future. An IPA for ancient glass from a hillfort at Broborg, Sweden (ca. 400-575 AD), used to fortify the fort walls will also be one of the key focal points of this presentation.

10:00 AM BREAK

SESSION ET15.02: Ceramics for the Safe and Secure Immobilization of Actinide Wastes

Session Chairs: Clémence Gausse and Daniel Gregg

Monday Morning, November 26, 2018

Hynes, Level 3, Room 308

10:30 AM ET15.02.01
Ceerrium Substitution in Zirconolite Ceramic Waste Form

S. K. Sundaram and Braeden M. Clark; Alfred University, Alfred, New York, United States.

Compounds with the formulae Ca2(1-x)Ce(x)Ti2O7 with x = 0.1-0.5 were synthesized by solid state reaction. Cerium was used as a surrogate for actinide elements. Sintering was carried out via spark plasma sintering (SPS), during which the perovskite phase (Ca0.6Ce0.4TiO3) was stabilized due to the reducing conditions of this technique. A transition from the 2M polymorph to the 4M polymorph (expanded unit cell due to cation ordering) in zirconolite was observed with increasing cerium content. In 2M-zirconolite, trivalent Ce co-substituted on both the Ca and Zr sites, while both trivalent (Ca and Zr sites) and tetravalent (Zr sites) Ce substituted into 4M-zirconolite. Conversion of 4M-zirconolite to perovskite and 2M-zirconolite occurred during the SPS process due to the reducing environment. This was due to the reduction of Ce4+ into Ce3+, where the 2M-zirconolite was charge balanced by co-substitution of Ce0+ on the Ca and Zr sites and the perovskite formed due to the partial reduction of Ti4+ to Ti3+ leaving excess Ca and Ti to react with the trivalent Ce to form perovskite. The presence of both trivalent Ce, contrary to formulation, was confirmed using X-ray absorption near edge spectroscopy (XANES), suggesting substitution on both Ca and Zr sites. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) revealed that the 2M polymorph was dilute in Ce content in comparison to the 4M-zirconolite. High temperature X-ray diffraction (HTXRD) was used to detail the kinetics of perovskite to zirconolite transition. It was found that CaCeTi2O7 (cubic pyrochlore) forms as an intermediate phase during the transformation. CaCeTi2O7 formed as an intermediate phase up until 1300°C, and 4M-zirconolite began at 1350°C. The re-oxidation of Ce3+ and Ti3+ to their tetravalent states allowed the original phase assemblage to be attained. The transformation to 4M-zirconolite was slow, but complete conversion to the original phase assemblage was achieved with a 24h heat treatment in air. Our results showed that a transition from 2M- to 4M-zirconolite occurred with increasing Ce content and the transition could be controlled by adjusting the P02 and the heat treatment temperature.

10:45 AM ET15.02.02
Immobilisation of Chlorine Contaminated Plutonium Residues in a Zirconolite-Glass Ceramic

Neil Hyatt1, Stephanie Thornber2, Lucy Mottram2, Martin Stennett2 and Amber Mason2;

1National Nuclear Laboratory, Sellafield, United Kingdom; 2The University of Sheffield, Sheffield, United Kingdom.

The Department of Energy’s Environmental Management cleanup effort is focused on developing and implementing innovative and high impact technologies and solutions that positively impact the overall mission lifecycle by: (1) reducing lifecycle costs; (2) accelerating lifecycle schedules; (3) mitigating mission uncertainties, vulnerabilities, and risks; and (4) minimizing the mortgage associated with long-term, post-closure and post-completion stewardship. Pacific Northwest National Laboratory and its partnering institutions, are focused on reducing risk and uncertainty across the integrated flowsheet which includes safe waste storage, retrieval, pretreatment, immobilization, disposal, and tank closure. In this presentation, an overview of the major Hanford flowsheet unit operations will be provided and examples of specific projects focused on reducing risks and uncertainties will be explored. For example, a key issue of Hanford tank waste processing and disposal is that, although radionuclides (e.g., technetium) drive the disposal risk for the low-activity flowsheet, the presence of ‘benign’ elements (e.g., aluminum) dictate processing limits or rates in both retrieval and pretreatment unit operations and have other potential downstream negative impacts. Thus, safe, cost-effective, and efficient waste processing depends on a fundamental understanding of aluminum chemistry in high strength, highly alkaline solutions where water activity is low. Once the waste has been retrieved, processed, and immobilized, controlling the behavior of risk driving elements (e.g., Tc and/or I for low-activity waste) in the waste form and the environment becomes essential for waste form disposal or tank closure. With respect to low-activity waste form disposal, material solutions must demonstrate that the risk driving radioactive elements can be contained in a manner wholly consistent with statutory requirements. Modelling future performance remains a challenge for performance assessment (PA) formalism. An appealing option is to perform an inverse PA (IPA) and look far into the past. Archeological artifacts, analogous to wasteform materials (i.e. glass and concrete) that have been left by our ancestors and exposed to the environment for thousands of years can be used to check for comprehensiveness as well as to validate and refine predicted wasteform durability. An IPA describes the features, events and processes that have influenced the corrosion of a material over time and can help establish the most likely scenarios that should be included in PA for the future. An IPA for ancient glass from a hillfort at Broborg, Sweden (ca. 400-575 AD), used to fortify the fort walls will also be one of the key focal points of this presentation.

10:00 AM BREAK
The immobilisation and disposal of fissile materials from civil and defence nuclear programmes requires compatible, passively safe and proliferation resistant wasteforms. In this study, we demonstrate the application of an albitic glass – zirconomelite ceramic material for immobilisation of chloride contaminated plutonium oxide residues in the United Kingdom. The chlorine solubility limit in the albitic glass phase was determined to be 1.0 ± 0.1 wt. %, above the maximum envisaged chlorine inventory of 0.7 wt. %. Cl K-edge of X-ray absorption Near Edge Spectroscopy (XANES) was exploited to confirm partitioning of Cl to the glass phase, speculated as the chloride anion, with exsolution of crystalline NaCl above the chlorine solubility limit. Combinatorial fitting of Cl XANES data, utilising a library of chemically plausible reference spectra, demonstrated the association of Cl with Na and Ca modifier cations, with environments characteristic of the aluminosilicate chloride minerals. The partitioning of Cs, as a Pu analogue, within the glass-ceramic was not adversely impacted by incorporation of Cl. The significance of this research is in demonstrating the compatibility of the glass-ceramic wasteform toward Cl solubility at the expected incorporation rate, below the determined solubility limit.

11:00 AM ET15.02.03
Synthesis and Sintering of Th-Based Cheralites from Rhabdophane-Type Precursors
Danwen Qin, Adel Mesbah, Stéphanie Szenknect, Nicolas Ducheux and Nicolas Clavier; ICSR, CEA, CNRS, ENSCM, Univ Montpellier, Bagnols/Cèze, France.

Monazite-type ceramic wasteforms have been investigated for long for the specific conditioning of actinides. Indeed, they are known to provide high weight loadings in actinides, good sintering capability and strong resistance to aqueous corrosion and radiation damages. The incorporation of tetravalent actinides generally processes through coupled substitutions, leading to monazite-cheralite solid solutions with the general formula MIIxAnIVxLn1-2xPO4. Nevertheless, the preparation of such samples was mainly achieved using dry chemistry methods, which can lead to heterogeneities in the solid and to the degradation of the properties of interest.

The incorporation of thorium in CaxThxNd1-2xPO4 solid solutions (0 ≤ x ≤ 0.15) was then investigated through wet chemistry processes based on the initial precipitation of rhabdophane-type precursors. A multiparametric study was undertaken to specify the operating conditions (starting stoichiometry, temperature, heating time) leading to single-phase CaxThxLn1-2xPO4.nH2O powdered samples. Particularly, the excess of calcium appeared to be a prevailing factor, with a suggested initial Ca:Th ratio of 10:1. Similarly, the recommended heating time should exceed 4 days while the optimal temperature of synthesis lies around 110 °C.

The transformation of rhabdophane-type precursors into highly durable CaxThxLn1-2xPO4 cheralites was further studied. TG analyses showed that the conversion first proceeded with a dehydration step occurring around 210-220°C, this temperature increasing linearly with the thorium content in the sample. Additionally, the phase transition between anhydrous rhabdophane and cheralite was determined by dilatometric measurements and varied from 700°C to about 820°C depending on the chemical composition considered. After heating at high temperature (i.e. typically at 1100°C), XRD analysis revealed the formation of single phase cheralite-monazite solid solutions without any trace of side products such as α-ThP2O7 or Th4(PO4)4P2O7.

Finally, first insights concerning the sintering of CaxThxLn1-2xPO4 wasteforms directly from the shaping and heating of low-temperature precursors were obtained. Full densification (i.e. > 95%TD) was achieved after 4 hours of heating at 1400°C for all the samples investigated. Nevertheless, the chemical composition was found to strongly influence the sintering process and the final microstructure. Indeed, thorium incorporation was found to slightly enhance the densification temperature determined by dilatometry, while the presence of small amounts of calcium in excess can drastically increase the final grain size.

11:15 AM ET15.02.04
Microstructure Control of Gd:TiO2 Pyrochlore by Spark Plasma Sintering and Its Dissolution Behavior
Yachun Wang and Jie Lian; Rensselaer Polytechnic Institute, Troy, New York, United States.

Pyrochlore, with a chemical composition of A2B2O7 (A and B are metals), shows great potentials as advanced waste forms for effective nuclear waste immobilization due to its capability to incorporate wide range of radionuclides, exceptional radiation tolerance, and desirable chemical stability. Those properties can be profoundly affected by microstructure features. However, the effect of grain size, particularly of nanometer length scale, on the dissolution behavior of pyrochlore has not been studied yet. This study explored the connection between grain size of Gd2Ti2O7, a type of Pyrochlore, and its chemical durability in acidic condition. Specifically, bulk Gd2Ti2O7 pellets with different grain sizes were fabricated by spark plasma sintering (SPS) and post sintering annealing. Subsequently, we focused on the dissolution behavior of different grain sized Gd2Ti2O7 pellet under aqueous condition (with isotope tracer 18O, at high temperature (90 °C) and acidic conditions (pH=1 and 2)). Dissolution rate of Gd and Ti were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Elements depth profile in dissolution alternated layer probed by secondary ion mass spectrometry (SIMS) showed the formation of a surface passivation layer enriched by O18, providing new insights into the dissolution mechanism of Gd2Ti2O7. The results highlighted the great potential for nano grain sized Gd2Ti2O7 with enhanced dissolution resistance for nuclear waste immobilizations.

SESSION ET15.03: Rational Design, Synthesis and Modelling of Framework Architectures for Radionuclide Sequestration
Session Chairs: Theo Cordara and Josef Matyas

Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 308

1:30 PM *ET15.03.01
New Engineered Forms of Zeolites for the Selective Removal of Cs and Sr from Effluent
Joe Hriljac, Ryan George, Mohamed Karmaoui and Tzu Yu Chen; University of Birmingham, Birmingham, United Kingdom.

Aluminosilicate zeolites, such as clinoptilolite and chabazite, are the traditional inorganic materials for removal of water-soluble radioactive cations such as 137Cs+ and 90Sr2+. In addition to the need for excellent selective ion exchange properties, the materials need to be available in a physical form that is suitable for use in a gravity flow column. Use of very fine-grained powders will often cause problems due to a slow liquid flow causing blockage. Synthetic zeolites and other ion exchangers such as the titanosilicate CST used in IONSIV crystallise as submicron to a few micron sized powders. Therefore they are unsuitable for column use unless produced in an engineered form such as IONSIV R9120-B where the CST is blended with an inert binder material into a pellet form. We are investigating alternative means of producing new forms of ion exchange materials and in this talk I will discuss two of those. The first is the production of zeolite monoliths via 3D printing methods for use in traditional gravity flow columns. The second is producing magnetized systems which can be separated from effluent via magnetic trapping after use.

2:00 PM ET15.03.02
Sequestration of Radionuclides in Metal-Organic Frameworks from First Principles Calculations
Shubham Pandey, Zhilin Jiu, Brian Demaske, Ekaterina Dolgopolova, Natalia Shustova, Wahyu Setyawan, Chuck J. Henager and Simon R. Phillpot; Department of Materials Science and
Metal-organic frameworks (MOFs) could lead to development of novel class of hybrid materials emerging as potential wasteforms to sequester nuclear waste. Density Functional Theory (DFT) calculations were used to determine the favorability of substitution of relevant radionuclides in various parent MOF clusters. The radionuclides of interest are U, Th, Am, Cm and Tc. Results from various levels of treatment of the exchange-correlation functional are compared to establish the robustness of the results. We find that Tc incorporation is energetically well-favored in all of the MOFs considered. The electronic structures of both the actinide-based MOFs and radionuclide substituted MOFs are analyzed and correlated with experimental data. We also study the effect of the electronic properties tunability as a function of transition metal incorporation.

This work was supported by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC) funded by the United States Department of Energy Office of Basic Energy Sciences through Award DESC0016574.

2:15 PM ET15.03.03

Synthesis and Ion Exchange Properties of Zirconogermanates Ryan George and Joe Hriljac; School of Chemistry, University of Birmingham, Birmingham, United Kingdom.

The synthesis of novel ion exchange materials for uses in nuclear waste management and environmental remediation is a key area of research. The established methodology for the removal of caesium and strontium from effluent in the UK involves the use of a natural zeolite material clinoptilolite1, but future waste streams and POCO activities may be better tackled with other systems. Much effort is being placed in designing materials with better selectivity and ion exchange capacity than clinoptilolite.

One family of materials which have been widely investigated are mixed octahedral and tetrahedral framework metal silicates due to potentially interesting ion exchange properties as well as better chemical and radiation stability than aluminosilicate zeolites. One of these types of materials, a natural zirconosilicate mineral umbite (K$_2$ZrSi$_3$O$_9$.H$_2$O), has been synthesised as have related materials with both Sn and Ti as the octahedral component replacing some or all of the Zr, for which the ion exchange properties have been explored in the literature2. The variation of the tetrahedral (Si) component has been explored in this work with the successful synthesis of a germanium derivative of the mineral umbite (K$_2$ZrGe$_3$O$_9$.H$_2$O).

Subsequent ion exchange results show both caesium and strontium uptake by Ge-Zr-umbite (K$_2$ZrGe$_3$O$_9$.H$_2$O) but at low levels. This is substantially improved by chemical modification of the umbite structure with the incorporation of up to 25% Nb/Sb for Zr at the octahedral site. High resolution synchrotron X-ray powder diffraction data shows complex structural behaviour of these doped materials when they undergo caesium exchange. Further attempts at doping higher levels for Zr results in mixed phases with the formation of pharmacosiderite phases (HK3Ge$_7$O$_{16}$.4H$_2$O and HK$_3$Ti$_4$Ge$_3$O$_{16}$.4H$_2$O), with these also showing interesting ion exchange properties. The thermal decomposition products of the pharmacosiderite phases have all been analysed for potential wasteform candidates.

References

2:30 PM BREAK

SESSION ET15.04: Corrosion in the Near Field Context of a Geological Repository
Session Chairs: Claire Corkhill and Stefan Neumeier
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 308

3:00 PM *ET15.04.01

Nuclear Waste Form Corrosion Gerald S. Frankel*, John Vienna†, Jie Lian‡, John R. Scully§, Seong Ho Kim∥, James Saal¶, Joseph Ryan∥, Stephane Gin∥, Wolfgang Windl*, Jincheng Du†, Jianwei Wang‡, Christopher Taylor§, Jenifer Locke∥ and Daniel Perea¶; 1The Ohio State University, Columbus, Ohio, United States; 2Pacific Northwest National Laboratory, Richland, Washington, United States; 3Rensselaer Polytechnic Institute, Troy, New York, United States; 4University of Virginia, Charlottesville, Virginia, United States; 5The Pennsylvania State University, State College, Pennsylvania, United States; 6QuesTek Innovations, Evanston, Illinois, United States; 7French Alternative Energies and Atomic Energy Commission, Marcoule, France; 8University of North Texas, Denton, Texas, United States; 9Louisiana State University, Baton Rouge, Louisiana, United States.

This talk will summarize the activities of WastePD, an Energy Frontier Research Center focused on the performance and design of nuclear waste forms. The Center has 13 PIs from 9 institutions and comprises three thrusts based on materials classes: waste glass, crystalline ceramics, and metals. Commonalities in the degradation of these materials and synergies between the thrusts have led to new understanding of the environmental degradation processes. A framework for the design of materials with improved corrosion resistance was developed, called Science of Environmental Degradation of Materials, SEDMat. Existing approaches for design for corrosion resistance are largely empirical and based on qualitative models and experimental data. The ultimate goal is to develop a fully descriptive synthesis of detailed models of all of the elementary processes. While working toward that goal, calculable parameters are being combined to generate expressions with predictive capabilities. Examples of the scientific findings of each of the materials thrusts will be presented including state of the art characterization of the gel alteration layer on waste glass using flash freezing, cryo-processing of samples, and cryo atom probe tomography. New corrosion-resistant high entropy metallic alloys will be described, as well as studies of ceramic degradation in aqueous environments.

3:30 PM ET15.04.02

Lead/Lead-Based Alloy Canister for High Level Nuclear Waste and Used Nuclear Fuel Revisited—Insight from Advances in Lead Solution Chemistry Yongliang Xiong*, Yifeng Wang**, Sungtae Kim*** and Greg Roselle†; 1Sandia National Laboratories, Carlsbad, New Mexico, United States; 2Brigham Young University-Idaho, Rexburg, Idaho, United States.
The canister for high level nuclear waste (HLW) and used nuclear fuel (UNF) is important for the safe disposal of such wastages, as a canister serves as the first line of defense in the multiple engineered barrier systems. The lead and lead-based alloy canisters were proposed in several countries’ repository designs. For instance, in the Argentine repository design, the containers for reprocessed and vitrified wastes have a thick intermediate layer made of lead with a 10 cm width, owing to its excellent radiological protection and corrosion resistance. In Russia, lead and lead-based alloys are also considered as prospective matrices for containers for used nuclear fuel, and are being used for conditioning spent sealed radioactive sources at radioactive waste disposal facilities. Lead containers are also used in the Brazil repository design.

In this presentation, we revisit the lead and lead-based alloy canister for HLW and UNF, based on the insights from the recent advances in lead solution chemistry including lead corrosion experiments in corrosive, high ionic strength solutions, and recent archaeological studies on ancient lead artificial products.

In environments where dissolved sulfide and oxygen are absent or poor, the corrosion products of lead are likely to be lead oxide (litharge, PbO) or lead carbonate (cerussite, PbCO₃). Archaeological studies have indicated that litharge was formed when lead was corroded under anoxic conditions. In our corrosion experiments with lead in high ionic strength solutions at P_{CO2} > 10^{-12} atm, we observed cerussite and tamowskitize [[(Cu, Pb)CO₃] as corrosion products.

The solubility of lead corrosion products is a key to the performance of a lead container, as the corrosion products usually behave as a protection layer. We have developed the thermodynamic model for lead solution chemistry valid to high ionic strengths, which can accurately describe solubilities of various lead solid species under various conditions. In this presentation, we evaluate lead solubilities in various repository designs by applying our thermodynamic model. The repository designs include those in granites, shales, crystalline rocks, salt formations, and sedimentary basins.

A This research is funded by the WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.  b Sandia National Laboratories is a multimission laboratory operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s Nuclear Security Administration under contract DE-NA-0003525. SAND2018-5657A

3:45 PM ET15.04.03 The Corrosion of Copper Nuclear Waste Containers in Sulphide-Containing Groundwaters David Shoesmith, Jian Chen, Taylor Martino, Mengnan Guo and James Noel; University of Western Ontario, London, Ontario, Canada.

The Canadian/Scandinavian concept for the permanent disposal of high level nuclear waste is to seal it in a container with an outer copper coating/shell and bury it in a deep geologic repository. While the container could experience a number of corrosion processes, the most likely long term corrosion process will be the reaction of Cu with sulphide present in the groundwater. The nature of this corrosion process and the morphology of damage distribution will eventually determine the time to failure of the copper coating/shell.

We have been studying these processes using electrochemical, corrosion science and surface analytical techniques. With a particular emphasis on the nature of the corrosion product deposits (copper sulphides) and the morphology of the corroding copper/deposit interface. This latter feature will determine the local loss of wall thickness required to define the required copper coating/shell corrosion allowance.

Using electrochemical impedance spectroscopy (EIS), we have shown the corrosion product deposit to be porous at the low sulphide concentrations anticipated in a repository, and to vary in morphology depending on the sulphide concentration, groundwater ionic type and concentration (in particular chloride), and the transport conditions prevailing at the copper surface. Using EIS and voltammetry techniques we have demonstrated that passivation of the copper surface, which could potentially lead to pitting, will not occur. Based on SEM images recorded on focussed ion beam cut cross sections, some localization of corrosion can be observed due to micro galvanic coupling of the copper substrate to the electrically conducting chalcocite (Cu₇S₈) deposit. This localization is facilitated by the transport of copper, as either soluble complexes or neutral clusters (Cu₅S₄) from the corroding anodic locations to the cathodic locations were copper sulphide deposit occurs.


The presence of H₂S in underground water is a factor that has to be considered in the safety assessments of deep geological repositories (DGR) for spent nuclear fuel because H₂S drives the corrosion of many metal. The canister material that is planned to be used in the Swedish DGR, copper, is no exception to this and the formation of copper sulfide films has been observed in experiments where the metal was exposed to H₂S(aq). In order to understand the phenomenon at the atomic-scale, we performed density functional theory (DFT) investigations of the molecular and dissociative adsorption of H₂S and of its dissociation products, HS and S₂, at perfect and defective Cu(110) surfaces described using large supercells with c(6x6) periodicity. For single and pairs of adsorbates, we investigated the adsorption at a diversity of sites such as pits, terraces and holes. For the perfect surfaces we scanned through all possible binding sites for the adsorbates, studied the interactions between adsorbates as a function of their distance, and investigated electronic structure effects such as the formation of surface dipoles in order to develop a rationale for the construction of models for the growth of thick layers of surface products.

We found that the adsorption modes and energies of the products of dissociation of H₂S are largely dependent on the presence of defects and that for high coverages, H₂S forms stacked half-monolayers that interact with each other via a complex hydrogen bond network. The surface perturbation induced by S₂ can be explained by the charge transfer model, H₂S leads to a perturbation that arises mostly from Pauli exclusion effects, while HS shows mixed: charge transfer-Pauli exclusion effects. These effects have a large contribution to the long range adsorbate-adsorbate interactions observed. We considered then two models for the growth of a layer of S-atoms at the surface: the formation of islands vs the formation of more homogeneous surface distributions of S-atoms. For coverages lower than 0.5 ML, S-atoms cluster as islands that evolve to stripes with increasing coverage. At 0.5 ML a homogeneous distribution of S-atoms becomes more stable than the formation of stripes. For the coverage equivalent to 1 ML, the formation of two half-monolayers of S-atoms that disrupt the Cu-Cu bonds between the first and second layers is more favorable than the formation of 1 ML homogeneous coverage of S-atoms. Here the S-Cu bond distances and geometries are reminiscent of pyrite, covellite and to some extent chalcocite. The small energy difference of ≈0.1 eV that exists between this structure and the formation of 1 ML suggests that in a real system at finite temperature both structures may coexist leading to a structure with even lower symmetry.

4:30 PM ET15.04.05 Anoxic Corrosion of Low-Carbon Steel at Elevated Temperatures—Effects of Chloride and Sulfide Charlotte Sisk Scott; Jonathan Icenhower, Chase Kicker, Cassie Mars, Leslie Kirkes and Praveen Sirirama; 1 Repository Performance, Sandia National Laboratories, Carlsbad, New Mexico; 2 Sandia National Laboratories, Albuquerque, New Mexico; 3 Sandia National Laboratories, Livermore, California.
Anoxic experiments were carried out on low-C steel coupons in dilute solutions and simulated brines with and without sulfide to determine gas generation rates, iron-release rates, and secondary corrosion phases. Corrosion rates were determined in a flow-through system (90°C) and a static apparatus (70°C) at pH (25°C) = 9. The experiments comprised of two sets of solutions, consisting of either Simplified Generic Weep Brine or deionized water. Each of the sets had substrates containing sulfide in the form of NaHS. Polished coupons of steel were reacted in the flow-through experiments whereas unpolished cylinders were reacted in the static experiments. Dissolution rates were quantified by analysis of Fe released to solution (Fe^{2+} and total Fe) and by liberation of H_{2}. In the case of the flow-through experiments, H_{2} was collected in-stream and analyzed by GC-TCD. In the static experiments, the increase of pressure was monitored and H_{2} was collected and analyzed by GC-TCD at experiment termination. Steel coupons and cylinders, and the secondary corrosion products, were analyzed post-test and ex-situ by Raman, SEM and XRD. In sulfide-free SGWB at 90 °C the calculated surface retreat rate based on the Fe-release rate, measured in the flow-through system, was ~3.1±1 μm/yr. In contrast, the retreat in sulfide-bearing SGWB was measured to be 0.02 μm/yr, a factor of ~160 slower. In deionized water, the average surface retreat rate was measured to be 0.08 mm/yr. In the static experiments, the highest gas generation rate based on H_{2}(g) production was 0.4 mol/m^{2}·yr. Examination of the secondary phases by Raman spectroscopy indicated the presence of Fe(OH)_{2} and magnetite in sulfide-free SGWB and DIW and mackinawite and pyrrhotite as reaction products in sulfide-bearing solutions. Green rust was also identified as a reaction product in sulfide-free SGWB experiments.

SANDia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of SANDia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy. SAND2018-6307A
as they form complex eutectic mixtures during early stage melting. In LAW melting, this alkali salt phase can preferentially incorporate radioactive Cs, halides, and peroxoanions. During melting of the feed, some oxoanions sequentially break down during melting, such as some carbonates, sulfates, and other inorganic acids. Alkali-salt phases can form gases, or partially volatilize, such as some halides. Sulfates, however, tend not to volatilize but have limited solubility in the final borosilicate glass waste form. Excess salts, usually related to high concentrations of sulfate, form a water soluble salt phase on the cooled glass surface compromising the waste form long-term chemical durability. To better understand these low temperature processes, a scoping study was undertaken to synthesize melts of equimolar ratios of K₂SO₄-ZnSO₄ (a known glass-forming system) with added nitrates, halides, carbonates, or various halides. Some of the materials formed single phase glasses and some underwent more or less crystallization upon quenching. Characterization of these quenched materials, including thermal analysis, vibrational spectroscopy, and diffraction, will be discussed.

ET15.05.04 Effect of TiO₂ Doping on Crystallization of Alkali and Alkaline-Earth Molybdate Phases in an Improved High Level Waste Glass-Ceramic Prashant Rajbhandari1, Kristian Barnsley1, John Hanna1, John S. McCloy2, Russell Hand3 and Neil Hyatt1; 1University of Sheffield, Sheffield, United Kingdom; 2Washington State University, Pullman, Washington, United States; 3University of Warwick, Coventry, United Kingdom.

The incorporation of high molybdenum and rare earth elements in the conventional borosilicate glass can induce liquid-liquid phase separation and that is followed by crystallization of alkaline-earth molybdates CaMoO₄ (water-durable) and alkali molybdates Na₂MoO₄ (water-soluble). The resistance against water attack can be significantly reduced due to the formation of water-soluble crystalline phase (Na₂MoO₄) during the melt cooling. In this work, the impact of small amount of TiO₂ (1-4 mol%) on the crystallization of Molybdate phases on simplified Mo-containing borosilicate glass is investigated. The differential thermal and XRD analysis were implemented to study the thermal behavior of the compositions and nature of the crystalline phases. The results indicated that the addition of TiO₂ significantly reduced the formation of water-soluble Na₂MoO₄ phases. The morphology and structural modification of the material were investigated by implementing SEM and solid state NMR analyses respectively.

ET15.05.05 Multinuclear NMR Methods for Characterising Precipitates During Simplified MW25 Glass Dissolution Rui Guo and Ian Farman; Univ of Cambridge, Cambridge, United Kingdom.

The presence of Mg in the UK high-level waste glass MW25 has shown to increase the aqueous reactivity when compared with Mg-free glasses like SON68 (the inactive analogue of French R77 high-level waste glass)[ii]. The exact mechanism by which Mg reduces the aqueous durability of glasses is not clear, but it has been concluded that the effect is not a primary one in which changes induced in the glass structure (and composition) by the addition of Mg alter the initial dissolution rate[iii].

The accepted mechanism of passivation in glass dissolution is that an altered layer forms on the surface of the underlying glass by in-situ mechanisms of hydrolysis and re-condensation of the glass network. This retards further dissolution by acting as a diffusion barrier or molecular sieve[iv]. A significant degree of re-incorporation of Mg, Al, Si had been observed during Mg-containing glasses dissolution in our experiments. Thus, it was proposed that the “passivating” altered layer formed on Mg-containing glasses have an inferior retarding efficacy because of the secondary co-precipitations that might alter the “conventional” passivating mechanisms.

Multinuclear (²⁵Mg, ¹⁷O, ²⁷Al, ¹H) NMR methods have been exploited to determine the atomic speciation of the precipitates (and altered layer) in question. In addition, first-principle electronic structure calculations combined with GIPAW to calculate NMR parameters on several Mg-silicate/silicate structures have been conducted to constrain the type of local atomic environments in support of interpreting experimental results.

and-ilw-glasses-the-effect-of-magnesium;
The accident at the Fukushima Daiichi Nuclear Power Plant (1F-NPP) occurred following the Great East Japan Earthquake on 11 March 2011, and led to the release of volatile radionuclides, which were deposited on the environment in the Fukushima prefecture and the surrounding areas. After the short-lived I-131, radiocaesium such as Cs-134 and Cs-137 have controlled radiation dose rate. The authors derived the apparent diffusion coefficients ($D_a$) of some radionuclides such as Cs-134 and Cs-137 based on time variation of the depth profiles of respective radionuclides in soil obtained in field investigations in earlier studies. Almost all $D_a$-values were of order 10^{-14} (m^2/s) and well consistent with distribution coefficients ($K_d$) obtained from batch experiments. Whilst, field investigations for the relaxation mass depths of Cs-137 in soil by a scraper plate method were conducted at totally 85 locations over a period of nearly 6 years in Fukushima Prefecture, south part of Miyagi Prefecture and north part of Ibaraki Prefecture from December 2011 to October 2016, and time variation of the relaxation mass depths was recently reported. Consequently, the relaxation mass depths of Cs-137 showed a tendency to linearly increase with an increase of elapsed time. This indicates that radiocaesium gradually moves to the deeper part of soil with time. In this study, $D_a$ based on Fick’s diffusion equation was derived based on time variation of the relaxation mass depths of Cs-137 in soil. In order to calculate $D_a$ based on Fick’s law, correlation between relaxation depth and square root of elapsed time was derived from the correlation between relaxation mass depth and elapsed time (where, relaxation depth is defined as the depth of 1/e of radioactivity concentration at the ground surface and can calculate by relaxation mass depth/soil density). The calculated $D_a$ of Cs-137 was of order 10^{-12} (m^2/s), which was about 2 orders of magnitude higher than $D_a$-values that we previously reported as described above. Considering that almost all relaxation depths of Cs-137 were shallow within 2cm in depth from the ground surface and near the surface layer of soil is unsaturated, it is considered that $D_a$ derived in this analysis includes the effect of dispersion by advection (by flow in the vertical direction of rainwater).

8:30 AM *ET15.06.01
Hot Isostatic Pressing of Advanced Nuclear Waste Forms Daniel Gregg, Eric Vance, Rohan Holmes and Gerry Triani; Australian Nuclear S&T Org, Sydney, New South Wales, Australia.

ANSTO Synroc Technologies has a significant focus on the use of hot isostatic pressing (HIPing) technology to fabricate tailored candidate glass–ceramic and ceramic waste forms for different types of actinide, high- and intermediate level wastes. Such advanced waste forms can offer performance and economic benefits for the immobilisation of different types of waste which are problematic for glass matrices or existing vitrification process technologies. The HIP technology itself offers several advantages such as increased density, minimum grain size and removes the need for costly and bulky off-gas systems. In addition, it has been demonstrated that glass, glass-ceramic, ceramic and metal encapsulated waste forms can all be produced using this one flexible process technology.

The industrial demonstration of Synroc technology will be achieved at ANSTO with the first of a kind Synroc Waste treatment Facility (SyMo) to treat waste arising from molybdenum-99 production. Construction of this facility commenced in 2018. Hot isostatic pressing is a key process for this facility, with significant technical challenges being addressed for industrial implementation. ANSTO Synroc’s approach has been to employ a multidisciplinary team which uses systems integration and risk mitigation to nuclearize waste treatment processes. The plant delivery model has been to develop the process chemistry and the process engineering including mock up and full scale demonstration to mitigate integration risks. This paper will discuss the engineering principles behind the development of the SyMo facility for the treatment of Mo-99 wastes as well as the application of ANSTO Synroc Technology as an advanced waste form and technology platform for many other intractable nuclear wastes.

9:00 AM ET15.06.02
Vanadinite Ceramic Waste Forms by High Energy Ball Milling and Spark Plasma Sintering for Chlorine Confinement Penghui Lei1,2, Tiankai Yao1, Guang Ran2 and Jie Lian1; 1Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; 2College of Energy, Xiamen University, Xiamen, China.

Apatite structure type, with a typical chemical composition of A$_2$(BO$_4$)$_6$C$_2$ (e.g., A=Ca, Na, Pb, rare earth, fission product, actinides; B=P or V; C=F, Cl, I) shows tremendous potentials as advanced waste forms for effective nuclear waste management. A wide range of radionuclides can be incorporated into its crystal structure by coupled substitutions at both cation and anion sublattices. Pb$_3$(VO$_4$)$_2$Cl$_3$, a potential waste form for long-lived CI-36 immobilization, is used to confine highly volatile chlorine. In this work, Pb$_5$(VO$_4$)$_3$Cl powder samples are synthesized by solid state reaction at room temperature by using High energy ball milling (HEBM). Low-temperature consolidation of dense vanadinite pellets by spark plasma sintering(SPS) at various temperature (753K, 783K, 793K, 823K, 843K, 873K) were performed. Microstructure analysis indicates a nanocrystalline ceramic with an average grain size less than 200nm at 723K. No significant chlorine loss was identified by HEBM and during densification SPS process. The effects of sintering on microstructure, density, thermal stability and mechanical properties were investigated. These results highlight the immense potential of SPS combining with HEBM as an advanced materials fabrication technology for immobilization of volatile radionuclides including radioactive chlorine.

9:15 AM ET15.06.03

High level waste (HLW) waste form containers shall take no aqueous durability credit when considering non-spent fuel HLW. Yet immobilisation of spent power plant fuel currently will rely strongly on metal encapsulation, particularly for the highly soluble fission products that do not inhabit UO$_2$. This is probably due to the absence of widely accepted waste form candidate phases other than a very low waste loaded glass at the time relevant research on spent fuel immobilisation began. More recent work however, has demonstrated relevant tailored waste form options with acceptable waste loadings. Here we propose a pyrochlore glass-ceramic made by hot isostatic pressing at ~1250°C/100MPa as a strong candidate wasteform for spent fuel. It is also as an ILW waste form for 99Mo production waste produced from irradiation of UO$_2$ targets. The U oxide and rare earth fission products would be incorporated in the pyrochlore and the fission products in the glass. We have put forward the pyrochlore mineral phase before for the ILW but have more recently favoured a glass-ceramic containing around 50-80 wt% pyrochlore plus 20-30 wt% borosilicate glass. Depending on the redox conditions in calcination and the addition of Ti metal to the canister for HIP, the pyrochlore phase is sensitive to redox conditions with slightly oxidising conditions favouring brannerite as...
an extra ceramic phase and perovskite and UO₂ as extra phases being favoured by highly reducing conditions. Optimisation of the phase assemblage is discussed.

9:30 AM BREAK

SESSION ET15.07: Management and Long Term Behaviour of Spent Nuclear Fuel I
Session Chairs: Olivia Roth and David Shoesmith
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 308

10:00 AM *ET15.07.01
Dissolution of Uranium Dioxide and Associated Solid Solutions in Nitric Acid—Impact of Fission Products and Microstructure Nicolas Dauchoux, Theo Cordara, Thomas Dalger, Florent Tocino, Laurent Claparede, Stéphane Szenknect, Nicolas Clavier, Adel Mesbah and Renaud Podor; IC3M, CNRS, CEA, ENSCM, Univ Montpellier, Bagnoles sur Ceze, France.

The dissolution or leaching of the spent nuclear fuels (SNF) is a key step either in the field of their reprocessing or their long-term storage in underground repository. Their structure and microstructure become very complex due to the formation of actinides and Fission Products (FP). In order to discriminate the role of several parameters on the chemical durability, a large variety of sintered materials were prepared from hydroxide or oxalate precursors then submitted to multiparametric dissolution tests.

The impact of actinides incorporation was examined through the study of U₁₋₅,Th₂O₃ solid solutions dissolution in nitric acid. Uranium mole loading clearly impacted the chemical durability. Indeed, for the lower uranium incorporation rates (x₅<0.5), the dissolution was mainly controlled by surface-controlling reactions at the solid/solution interface involving the adsorption of protons on reactive sites. On the contrary, for uranium enriched materials (x₅>0.5), oxidation of uranium (IV) into uranyl at the solid/solution interface became clearly preponderant (leading to the decrease of the chemical durability, as shown for pure UO₂). Partial order related to the proton concentration as well as apparent activation energy associated to the reaction of dissolution were affected by this change. The role of nitric acid on the normalized dissolution rate of U₁₋₅,Th₂O₃ was particularly examined.

The impact on the chemical durability of several FP (lanthanides or PGM’s) within the structure of UO₂ was also studied. Thus, several samples incorporating 1 to 20 mol.% of a mixture of lanthanide elements (13% La; 7.4% Y; 25.6% Ce; 12% Pr; 42% Nd) or 0.6 to 3 mol.% of PGM’s (55% Ru; 9.6% Rh; 35.4% Pd) were prepared through oxalate or hydroxide precipitation, respectively, then sintered.

The presence of lanthanide elements in UO₂ did not affect significantly the normalized dissolution rates in concentrated nitric acid solutions (C > 1M). On the contrary, the effect was more important in less concentrated solutions (e.g. a factor of 100 compared to pure UO₂ observed in 0.5M HNO₃) when the role of surface-controlling reactions on the overall dissolution became predominant. Moreover, the chemical durability of UO₂ samples doped with PGM’s was significantly lowered compared to pure UO₂. This effect was strengthened in less acid media; a factor of 4500 being observed after 175 days of leaching in 0.1M HNO₃.

Such a macroscopic description of the ceramics dissolution was connected to operando monitoring of the evolving solid/solution interface (including reactive surface area, composition) during dissolution tests. Preferential dissolution was observed within Ln-enriched UO₂ grain boundaries or near the UO₂/PGM’s interface, indicating different progresses of the dissolution at the solid/solution interface. Moreover, variations in the distribution of cations also affected the chemical durability of heterogeneous U₁₋₅,Th₂O₃ pellets through a clear incongruent dissolution.

10:30 AM ET15.07.02
Effect of Nuclear Fuel Additives on the Spent Nuclear Fuel Reprocessing Dissolution Step Theo Cordara, Hannah Smith, Claire L. Corkhill, Martin Stennett and Neil Hyatt; Department of Materials Science and Engineering, University of Sheffield, Sheffield, United Kingdom.

Nuclear power producers are seeking to lower the cost of generating electricity through the development and application of new fuels that are capable for being “burnt” for longer within the reactor. One of the main limitations for how long fuel can remain in the reactor is the ability of the fuel to accommodate fission products, especially fission gases like Kr, Xe, He, etc. The build-up of these gases can lead to a swelling of the fuel and to cladding failure, resulting in downtime of the reactor. The solution to this issue is to improve the UO₂ fuel by promoting the growth of larger grains and increasing the rate of diffusion of fission products to the grain boundaries during fission. This is achieved by doping UO₂ with additives; the most extensively applied are Cr₂O₃, Al₂O₃ and a mixture of Cr₂O₃-Al₂O₃.

In this presentation, we describe the synthesis and characterisation of Cr, Al and Cr+Al-doped-UO₂ materials, containing between 100 and 1,500 ppm of dopants. Samples were prepared by dry (oxides mixing) and wet (oxalic or nitrate precipitation) synthesis routes. Oxide powders thus obtained were pelletized and sintered at 1,700°C during 8h under a reducing atmosphere. SEM images and pycnometer measurements have respectively highlighted an increase of the grain size and of the densification rates in presence of additives. XRD patterns confirmed that the fluorite structure (space group Fm3m), the characteristic crystalline structure of UO₂, was retained when the samples were doped. Further characterisations (e.g. HR-XRD and EXAFS) were performed to further determine the solubility limit of Cr and Al within the UO₂ lattice, the lattice parameter and the Cr-coordination in these materials. Finally, pellets produced through the above methods were compared to those obtained using hot-isostatic pressing (HIP), which is a sintering method where the pellet is heated at the same time as the application of gas pressure.

10:45 AM ET15.07.03
Long Term Structural Stability During Storage of Self-Damaged Nuclear Spent Fuel Simulant Oliver Dietze, Thierry Wiss, Emanuele de Bona, Jean-Yves Colle, Ondrej Benes, Dragos Staica and Rudolph J. Konings; JRC, Karlsruhe, Germany.

The plutonium together with the minor actinides will be responsible for the long term radiotoxicity of spent nuclear fuel, and for the medium term heat loading of the fuel in open nuclear fuel cycles. As these transuranic elements present on the nuclear waste are mainly alpha-emitters, increasing amounts of alpha-damage and helium during spent fuel storage and in the repository will be generated. Most of the defects produced by alpha-decays are generated through elastic energy losses from the recoil of daughter nuclei. In addition, when the alpha-particle comes to rest it becomes a helium atom that can alter the microstructure of the material, e.g. by forming microscopic bubbles. The fluorite structure, shared by all actinide dioxide, is known as being a radiation damage resistant crystal configuration. However, high alpha-dose can have detrimental effects on the long term stability of materials envisaged as fuels. To be able to predict the behavior of the spent fuel on the very long term storage, surrogates are being used to simulate the high alpha damage that will be accumulated on the waste after millennials of storage and beyond.

In the present work we report on experimental observations of alpha-damage effects on samples with high content of ²³⁹Pu that serve as surrogates for very
old spent fuel by transmission electron microscopy (TEM), energy loss electron spectroscopy (EELS), x-ray diffraction (XRD) and thermal diffusivity, among others.

11:00 AM ET15.07.04
Dissolution of Uranium Thorium Mixed Oxides—The Role of Nitrous Acid

Laurent Claparede1, Thomas Dalger2, Stéphanie Szenknect3, Philippe Moisy3 and Nicolas Dacheux1; 1ICSM, University of Montpellier, Bagnols sur Cèze, France; 2ICSM, Commissariat à l’énergie atomique et aux énergies alternatives, Bagnols sur Cèze, France; 3DMRC, Commissariat à l’énergie atomique et aux énergies alternatives, Bagnols sur Cèze, France.

Mixed actinide dioxides (MOX) are currently used as fuels in Gen III reactors. MOX-fuels with higher plutonium loading stand as potential candidates for several concepts of Gen IV fast reactors. In this field, the reprocessing of actinides coming from spent nuclear fuel is considered, but the hydrometallurgical processes need to be optimized. In particular, the dissolution step appears to be one of the main issues concerning the recycling of Gen IV MOX fuels. Although dissolution of MOX fuel in nitric acid is already used in industrial processes, the role of several nitrogen based species such as NO3− and HNO2 in the oxidative mechanism of uranium-based mixed oxides remains unclear.

In this study, dissolution tests were performed on sintered pellets of U0.75Th0.25O2 in various acid solutions (from 10−3 M to 4 M) under dynamic conditions. Therefore, a multiparametric study of the kinetics of dissolution was achieved in order to quantify the influence of several species of interest. In aerated hydrochloric acid solutions, the kinetics of the overall dissolution reaction appeared to be controlled by adsorption and desorption of protons at activated surface sites. The dissolution rate determined in aerated sulfuric acid solution was enhanced compared to hydrochloric acid solution of the same acidity. This result was interpreted in terms of formation of sulfate ions surface complexes that favor the detachment of the actinides from the mixed oxide solid solution. In nitric acid solutions, the dissolution of the ThO2.5U0.5O2 pellets followed several successive steps. During this first steady state period, the kinetics of the overall dissolution reaction appeared to be controlled by the oxidation of U(VI) by HNO3 at the solid/solution interface. A rate law was established by adding a redox contribution to the proton-promoted surface contribution defined for aerated hydrochloric acid solutions. Then, an increase of the normalized dissolution rate was observed, which was attributed to the simultaneous increase of the specific surface area of the pellet and of the HNO3 concentration in solution. Therefore, the monitoring of the solid/liquid interface by ESEM during dissolution allowed to discriminate the impact of these phenomena on the normalized dissolution rate.

11:15 AM ET15.07.05

Dirk Boubach, Felix Brandt, Martina Klinkenberg, Victor Vinograd, Juliane Weber and Guido Deissmann; IEE-6, Forschungszentrum Jülich, Juelich, Germany.

The waste containers emplaced in geological disposal facilities for nuclear wastes built in crystalline rocks or clay formations will inevitably come into contact with ground water post-closure, after re-saturation of the repository. Even in repositories in salt rocks, the presence of water cannot be completely ruled out for less probable scenarios, for example, an early failure of shaft seals and plugs. As a consequence, after container failure due to aqueous corrosion, radionuclides can be released from the degrading waste forms into the near-field water and subsequently migrate into the geo-/biosphere via the water pathway. The mobility of radionuclides released from the wastes into the repository near- and far-field is controlled by various processes such as sorption onto minerals and colloids (e.g. by surface complexation or ion exchange), precipitation/dissolution of solid phases, as well as entrapment in, or solid solution formation with other minerals. However, the aspect of solid-solution thermodynamics and the effects of solid-solution formation on radionuclide solubility and mobility are considered only rarely in specific cases in long term safety assessments for nuclear waste repository systems at present.

Here, we present and discuss the development and application of thermodynamic models for solid solution – aqueous solution systems and their relevance to nuclear waste management and safety assessments for deep geological repositories, emphasizing the significance of complementary experimental and state of the art computational approaches (e.g. atomistic modelling). Using the uptake of radium by barite (BaSO4) as an example, it is demonstrated that an improved mechanistic understanding of solid solution thermodynamics and its consideration in performance assessments leads to a more realistic and scientifically corroborated picture on release, solubility, and subsequent migration of safety relevant radionuclides in the repository near- and far-field.

Thermodynamics of mixing for the binary (Ba,Ra)SO4 and ternary (Ba, Sr, Ra)SO4 solid solution system were determined on the basis of first principles calculations and experimentally validated by batch type Ra uptake experiments. The Ra uptake experiments yield homogeneous solid solutions via dissolution and re-precipitation within 1000 days at room temperature and also at elevated temperature up to 90 °C. These thermodynamic data allow for a full quantitative description of solid solution – aqueous solution equilibria. Application of state-of-the-art micro- and nano-analytical methods (FIB, TEM, APT) provided a mechanistic understanding of the relatively fast Ra uptake and the fact that a homogeneous solid solution forms. This Ra uptake was established via internal micro- and nano-porosity opening the possibility to form a chemically homogeneous mixed phase at room temperature via dissolution and re-precipitation (excluding solid state diffusion).
scales that are not accessible to experimentation. After describing the basic principles that have guided how these reactive transport models are constructed, their usefulness will be exemplified on the modelling of clay-concrete interaction. The modelling of a ten years in-situ experiment will illustrate the complexity of the multiphase and temporal-scale issues that must be taken into account.

2:15 PM ET15.08.02
Thermal and Thermophysical Behavior of Bentonite Investigated by Means of Thermal Analysis Techniques
Ekkehard Post, NETZSCH Geraetebau GmbH, Burlington, Massachusetts, United States.

Bentonite clay was investigated with regard to its potential application as a sealing material for nuclear material storage. Bentonite is a clay with high swelling ability under humid conditions. Due to this behavior and its chemical and physical properties, bentonite is widely used, e.g., in the oil drilling industry for sealing the bore hole. In nuclear waste management, in some countries it is considered or even used as a sealing material in repositories or waste containers. Depending on the water content, the volume and density of bentonite (consisting mainly of montmorillonite) can vary considerably. Below a certain temperature, water loss and uptake are reversible, this means this material contracts during water loss, but also expands again in a humid atmosphere. In this contribution, bentonite clay was investigated by means of TGA-DSC, dilatometry/TMA, LFA and evolved gas analysis. The results for the thermal stability and thermal expansion in dry and under wet conditions and the thermal diffusivity will be discussed.

2:30 PM BREAK

SESSION ET15.09: Processing and Performance of Vitrified Wasteforms I
Session Chairs: Kevin Fox and Daniel Neuville
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 308

3:00 PM *ET15.09.01
Raman and X-Ray Absorption Spectroscopic Studies of Hydrothermally Altered Borosilicate Nuclear Waste Glasses
David A. McKeeown, Isabelle Muller, Andrew Buechele and Ian L. Pegg, Catholic Univ of America, Washington, District of Columbia, United States.

Raman spectroscopy and X-ray absorption spectroscopy (XAS) are used to characterize structural changes that take place in a variety of hydrothermally altered borosilicate glasses used in durability studies of these materials for nuclear waste storage. The glasses investigated range from simplified five component (Na,K)-alumino-borosilicates to complex composition borosilicates that include more than 20 components to more closely model actual nuclear waste glasses. The hydrothermal experiments, or vapor hydration tests (VHT), were performed on glass wafers up to 30 days from 200 to 238°C to simulate and accelerate long-term alteration processes that may occur in a nuclear waste repository. Raman spectra indicate two major glass structure changes that take place during alteration: one, partial depolymerization of the alumino-borosilicate network, and two, introduction of water or OH in the altered layers that can approach 10 wt.%. Raman, as well as supporting X-ray diffraction and scanning electron microscopy (SEM) evidence indicate analcime and other tectosilicate crystals at or near the altered sample surface with some altered layers containing intergrowths of amorphous silicate gels with zeolites and fine-grained clays. More localized information from XAS show expanded Na environments in the VHT samples with longer Na-O distances and more nearest-neighbor oxygen atoms, compared with the original glasses, which may be due to hydrous species introduced into the Na-sites. Changes in Si K-edge also show some depolymerization of the network in the VHT altered samples, consistent with the Raman trends. SEM profiles indicate diffusion of many elements across the alteration layers, where one example, Tc, is enriched toward the altered sample surface. XAS measurements of the same samples show that much of the original oxidized Tc(VI) pertechnetate in the glass reduces to Tc(IV) species in six-fold coordination in the VHT altered sample. Latest Raman profiles and map images of VHT altered sample cross-sections will be presented to illustrate distributions of the different crystalline and amorphous phases within the altered layers, as well as how water is incorporated into the glass at different stages of the alteration process.

3:30 PM ET15.09.02
On Alteration Rate Renewal Stage of Nuclear Waste Glass Corrosion
Michael I. Ojovan, IAEA, Vienna, Austria.

The four generically-accepted stages of glass corrosion are reviewed with focus on fourth stage termed alteration rate renewal (or resumption) stage when the glass may start corroding with the rate similar to that at the initial stage. It is emphasised that physical state and physical changes that occur in the near-surface layers can readily lead to effective increases of leaching rate similar to alteration rate renewals. Corrosion of glass in a geological repository is typically considered to occur into four stages [1, 2]: Stage I: Upon initial contact by water alkali cations are extracted by interdiffusion. The process of interdiffusion is followed by two simultaneous reactions: hydration and dissolution of the glass network. Stage II is when glass corrosion rate becomes dependent on the solution saturation state. Unlike the rate of ion exchange, the dissolution rate of the glass network decreases. Stage III: The solution becomes saturated and secondary minerals begin to form; the alteration phase is often a simple clay mineral, such as a smectite or chlorite. Stage IV: Alteration rate renewal may occur depending on the type of alteration phase formed. Experimental data on long-term (during few decades) corrosion of radioactive borosilicate glass K26 designed to immobilise NPP radioactive waste evidence on resumptions of radionuclides (129I,131Cs) leaching [3]. The cause of that was however related not to chemical changes in the leaching environment but rather to physical state of glass surface. Formation of small cracks on the surface results in new fresh-glass areas in contact with water. Both experimental and molecular dynamic simulations prove that the freshly formed glass surfaces are enriched in alkali elements including 137,134Cs [3,4]. Because of that the leaching of radionuclides is not monotonic and has distinct step-like additives at the times of cracks formation which resembles resumption of initial stages of glass leaching. This paper emphasises that not only alteration phase formed can lead to an increased rate of corrosion and return to the forward rate, and that physical state and physical changes that occur in the near-surface layers can readily lead to an effective alteration rate renewal. Nuclear waste glass corrosion in the disposal environment is of primary importance for ensuring safety of nuclear waste disposal therefore the research programmes focused on long-term behaviour of glasses [5, 6] should account for both chemical and physical effects.


3:45 PM ET15.09.03
A glass-ceramic waste form is being considered for immobilization of waste streams of alkali (A), alkaline-earth (AE), lanthanide (Ln), and transition metals generated by transuranic extraction for reprocessing used nuclear fuel. Benefits over an alkali borosilicate waste form are realized by the partitioning of the glass-insoluble fission product fraction into a suite of ceramic phases through controlled crystallization, including AEMO$_3$ (powellite) and (Ln,AAE)$_2$Si$_6$O$_{26}$ (oxyapatite). In this study, a simplified 8-oxide system was used, 33.5 SiO$_2$ - 21.9 Nd$_2$O$_3$ - 9.6 CaO - 8.9 Na$_2$O - 8.2 B$_2$O$_3$ - 6.6 Al$_2$O$_3$ - 6.4 MoO$_3$ - 4.9 ZrO$_2$ (in mol%).

In-situ neutron diffraction experiments were attempted to capture crystallization upon cooling from 1300°C. The combination of high temperatures and reactivity of borosilicate glass with typical containers such as vanadium and niobium prevented their use, so methods using sealed thick-walled silica ampoules were developed. Unexpectedly, high neutron absorption (despite isotope substitution with B-11), low crystal fraction, and high silica container background made quantification difficult for high temperature measurements. Proof of concept measurements were then performed on different potential high-temperature container materials, emphasizing crystalline materials so that residual glass in the sample could be more easily analyzed. Room temperature measurements were conducted with a crystallized sample in ‘ideal’ containers stable at low temperatures (vanadium and thin-wall silica capillaries) and compared to the same in containers stable at high temperatures (platinum, single crystal sapphire, and thick-walled silica ampoules).

Results suggested that sapphire is probably the best choice if suitably sealed to prevent contamination from the sample after neutron activation. Companion experiments are suggested for high-temperature in-situ x-ray diffraction measurements. With high energy x-rays, levitation experiments might be possible despite sample volatility, since collection times are much shorter at synchrotrons than those required for neutron experiments. Additionally, wire heater methods using a very small amount of sample are also possible with x-ray interrogation. Other possibilities for obtaining in-situ crystallization data upon cooling from molten glass are suggested.


The UK is currently in the process of adopting a modified seven-oxide base glass (ZnCa MW), containing ZnO and CaO for the vitrification of high level waste at a molar ratio of ZnO/CaO 40:60 in the nominal Mixed Windscale (MW) formulation. Previous studies have given an insight to how Zn and Ca may influence glass dissolution, however the dual role of Zn and Ca remains poorly constrained.

This investigation studied a series of six ZnCa MW compositions with different ZnO/CaO ratios, with the aim of understanding how the varying ratios influence the structure of the glass and how this relates to the aqueous durability in all stages of glass corrosion. Structural analysis using 26Si and 11B NMR has been utilised to determine the relative influence of Zn and Ca on the borosilicate glass network and on the altered glass post-dissolution. Dynamic flow-through (SPFT) and static (MCC-1 and PCT-B) batch dissolution experiments give insight to the behaviour of the various ZnO/CaO ratios, whereby dissolution rates and formed altered layers were sensitive to small compositional changes.

Waste-loaded ZnCa MW formulations with varying ZnO/CaO ratios and varying waste loads (20, 28 and 35 wt.%) were developed and subjected to static dissolution (MCC-1 and PCT-B) in clay, granite and saline groundwaters under conditions relevant to geological disposal. From these studies, optimised glass formulations have been suggested in terms of their long-term aqueous durability.

4:15 PM ET15.09.05 Probing the Temperature Dependence of Aqueous Glass Dissolution Mechanisms Thomas J. Gould1, Edward Tipper1, Sambuddha Misra1, Madeleine Bohlin1, Rui Guo1, Aleksy Sadekov2,3 and Ian Farrat1; 1University of Cambridge, Cambridge, United Kingdom; 2Centre for Earth Sciences, Indian Institute of Science, Bengaluru, India; 3School of Earth Sciences, The University of Western Australia, Crawley, Western Australia, Australia.

Countless simulants nuclear waste glass dissolution experiments have taken place at 90 °C to accelerate glass alteration. It is implicitly assumed that the dissolution mechanisms occurring at 90 °C would be the same as those in a deep geological disposal facility post-thermal pulse, which would be at around 40 °C. Accurately predicting vitrified package lifespans within a repository therefore requires a comprehensive understanding of the dissolution mechanisms occurring at both temperatures; by extension an assessment of whether dissolution rates measured at 90 °C can be applied to repository conditions. Elemental releases and images of surface alteration alone from variable temperature experiments provide limited insight into the underlying dissolution mechanisms at each temperature, simply investigating whether glass dissolution rates follow an Arrhenius-type temperature dependence.

Static batch experiments conducted on a simultaneous UK Magnox waste glass at temperatures of 40 °C, 60 °C, 70 °C, 80 °C and 90 °C investigated the temperature dependence of the concentrations leached into solution and the kinetics of alteration product formation, but could not discern the dominant dissolution mechanism at each stage of dissolution. Consequently, more evidence was required to provide a complete picture of glass alteration and complement the concentration and surface alteration results. Based on the significant differences in the morphology of the altered glass as predicted by conflicting models of glass alteration, it was expected that different magnitudes of isotopic fractionation for mobile glass species leached into solution would be observed depending upon the extent and structure of the altered layer and the dominant dissolution mechanism. Through preliminary proof of concept experiments on a simplified simulant Magnox waste glass analogue leached at 90 °C and a simulant Magnox waste glass leached at 40 °C and 90 °C, we observed systematic temperature-dependent isotopic fractionation which was consistent with the mechanisms and altered layer morphologies described in interdiffusion models of glass dissolution which arise from a highly passivating altered layer structure.
Self-radiation damage from the decay of radionuclides can affect microstructural evolution, phase stability, and thermodynamic properties in ceramic nuclear waste forms. The principal sources of radiation are beta-decay of the fission products and alpha-decay of the actinide elements. In general, beta-decay of the short-lived fission products is the primary source of radiation and heat generation in high-level waste forms during the first 600 years of storage; however, there is no evidence of significant long-term effects of fission product decay on the physical properties of nuclear waste forms. Because of the long half-lives of the actinides and their daughter products, alpha-decay is dominant over very long timescales. Alpha decay produces energetic alpha particles (4.5 to 5.5 MeV) and recoil nuclei (70 to 100 keV), which result in both radiation damage and the accumulation of helium. The evolution of radiation damage due to alpha-decay has been studied using short-lived actinides, such as $^{238}$Pu and $^{244}$Cm, in several candidate ceramics for the immobilization of actinides. Ion beam irradiations of candidate ceramics are more frequently employed due to decreased costs, shorter irradiation timescales and the non-radioactive nature of the irradiated materials. Ion irradiations are performed over a wider range of irradiation conditions to implant helium, study radiation damage kinetics, understand the separate and combined effects of alpha particles and alpha recoils, and benchmark against alpha-decay damage due to short-lived actinides. At ion energies typically used to study alpha-decay damage in nuclear waste ceramics, the electronic and nuclear energy losses are both important, and local ionization along the ion path can affect damage production and evolution. For heavy ions used to mimic radiation damage from alpha recoil nuclei, the spatial coupling of electronic and nuclear energy loss can lead to reduced or enhanced damage production along the ion trajectory. The athermal annealing induced by electronic energy loss of heavy ions can significantly impact the evolution kinetics of radiation damage. While alpha particles are much less damaging than alpha recoils, the electronic energy loss from the alpha particles can also cause athermal annealing of heavy ion damage (i.e., alpha-recoil damage) that can impact the evolution of radiation damage. Helium implantation studies have shown that the accumulation of helium and heavy ion damage leads to the formation of helium bubbles above a threshold helium concentrations. These results have significant implications for interpreting and modeling the radiation response of nuclear waste ceramics in accelerated testing using MeV ion irradiation.

This work was supported by the U.S. DOE, BES, MSED.

9:00 AM ET15.10.02 Molecular Dynamics Simulation of Ballistic Effects in Simplified Nuclear Waste Glasses Anręen Iau1, 2; Jean-Marc Delaye1; Sebastien Kerisit3 and Stephane Gin4; 1CEA Marcoule, Bagnols-sur-ceze, France; 2Geochemistry, Pacific Northwest National Laboratory, Richland, Washington, United States.

Immobilization of High Level Waste (HLW) in borosilicate matrix and further disposal into geological repository has been regarded as one of the best way for long term isolation of HLW from biosphere. Radionucleides are expected to stay confined until glass matrix has been breached by water and it begins to alter. Recently, an increase in glass alteration rate was observed in irradiated samples (with dominant ballistic dose) as compared to non-irradiated samples. Other studies using doped glasses, external irradiation techniques and molecular dynamics have now confirmed that ballistic effects caused by recoil nuclei, on alpha decay, will be the dominant source of irradiation damage on the long term. Ballistic effects have been observed to induce macroscopic and microscopic structural changes e.g. swelling, decrease in hardness, increase in fracture toughness and structural disorder and depolymerisation in the glasses. Thus, it becomes necessary to study such changes and their impact on the physical and chemical durability of this glass. In the current study, molecular dynamics simulation of ballistic effects have been investigated in simple sodium borosilicate [$Na_2O:SiO_2-B_2O_3=1$] and sodium alumino-borosilicate [$Na_2O:Al_2O_3-SiO_2-B_2O_3=1$]glass compositions, by exposing such glasses to series of displacement cascades, wherein heavy projectiles cause atomic displacements by elastic collisions and progressively damage the bulk glass. The accumulated pressure or stored energy inside the glass was found to saturate with deposited energy. Furthermore, structural analysis of the irradiated glasses revealed a decrease in density, depolymerisation, increase in intermediate, short range disorder and randomness. The magnitude of damage was found to depend on the glass composition and, in general, alumino-silicate glasses were found to be slightly less damaged, after irradiation, as compared to borosilicate glasses. An ongoing study on, impact of such structural evolutions under irradiation, on alteration of glass will also be discussed.

9:15 AM ET15.10.03 Investigation of the Structural Behavior of YSZ Under Ion Impact—Effect of Grain Size, Temperature and Specific Energy Loss Parswajit Kalita1, Santanu Ghosh1 and Divesh K. Avasthi2; 1Indian Institute of Technology Delhi, New Delhi, India; 2Amity University, Noida, India.

A crucial issue regarding the use of nuclear energy is the safe management of radioactive plutonium and minor actinides since they are unavoidable byproducts of nuclear energy generation using the conventional uranium fuel technology. A possible solution to this problem might be the ‘inert matrix fuel’ (IMF) concept, which is based on ‘uranium free’ plutonium or minor actinide compounds embedded in an inert material matrix. Since these fuels are being contemplated to burn plutonium or minor actinides instead of uranium, they have the dual advantage that they do not breed plutonium or higher actinides during burn-up and that the existing stockpiles of plutonium and minor actinides can also be reduced. Amongst many different potential materials, the oxide ceramic yttria stabilized zirconia (YSZ) is considered to be very promising for application as the inert matrix material.

Now, the materials employed in nuclear reactors are prone to un-desirable damages (amorphization, point defect clustering, volume swelling, etc.) since they are subjected to an extremely harsh environment consisting of extensive radiation (fission fragments that create damage via electronic energy loss, alpha recoil particles that create damage via nuclear energy loss, neutrons etc.) and high temperatures (~ 1000 K). Accumulation of such radiation damage over a period of time may lead to material failure ultimately resulting in catastrophic nuclear accidents. It is therefore vital to understand the behavior of YSZ under such extreme conditions, before using it as the inert material matrix in IMFs, for the design of safe, durable and efficient nuclear energy systems.

A number of factors, such as: (i) Specific energy loss (electronic energy loss ($S_e$) & nuclear energy loss ($S_N$)) of the energetic particles (ii) Grain size of the material (iii) Temperature of the environment (irradiation temperature) etc., needs to be taken into consideration for an in-depth understanding of the radiation induced damage.

Motivated by this, YSZ pellets having different grain sizes (ranging from tens of nano-meters to few microns) were irradiated with different ions (single beam irradiation with low energy ions or single beam irradiation with high energy ions or simultaneous dual beam irradiation with low and high energy ions) at different temperatures (room temperature and 1000 K) in an attempt to understand the dependence of radiation damage on the above mentioned factors. The low energy and high energy ions were chosen so as to simulate the damage produced by alpha recoil particles and fission fragments respectively, while the irradiations at 1000 K helped to better simulate a typical nuclear reactor environment. We will show that the irradiation damage depends critically, and in a complex manner, on the crucial interplay between the specific energy loss/type of irradiation (single beam or simultaneous dual beam), grain size (grain boundaries) and environmental temperature.

9:30 AM BREAK
Role of Volatiles Elements, Halogen and Noble Gases in Glass and Melt

Volatiles elements in glass and melt can induce very strong changes both in properties and structure. They can play a fundamental role during glass making, glass processes, and also in Earth Sciences since they can change drastically the dynamism of some eruptions, in particular during degasifying processes. In detail, volatile elements, such as chlorine and fluorine, have a significant role in the generation, dynamics, and evolution of magmas as they influence the solubility of minerals as well as the melts viscosity and thermodynamic properties. This results, for example, in a strong control of the main volatile element that is water on the extraction rate of magmas from the upper mantle and crust. At surface, the amount of water and CO2 dissolved in magmas influence the dynamics of volcanic eruptions. Furthermore, other elements such as SO2 and iodine also affect the melt properties as well as on their geochemical signature. Fluorine and chlorine can also produce very big disasters especially during andesitic volcanic eruptions.

Therefore, volatile elements influence in various ways the geologic dynamic of the Earth and play important role in materials science. Therefore, we need to quantify the proportion and understand the speciation of dissolved volatiles in silicate melts. In order to tackle such challenging subject, we propose to investigate glasses, including natural magmatic compositions and industrial glasses, which contain dissolved CO2, H2O, SO2, I2, F, and Cl by using Raman spectroscopy, a powerful and non-destructive technique.

Glass Structure and Crystallization in Boro-Alumino-Silicate Glasses Containing Rare Earths and Transition Metals

Nuclear wastes generated from reprocessing of used nuclear fuel tend to contain a large fraction of rare earth metals (RE e.g., Nd), transition metals (TM e.g., Mo, Zr), alkali metals (A e.g., Cs), and alkaline earth metals (AE e.g., Ba, Sr). Various strategies have been considered for immobilizing such waste streams, varying from nominally crystal-free glass to glass-ceramic to multi-phase ceramic waste forms. For glass and glass-ceramic waste forms, the added glass-forming system is generally alkali-alumino-earth-alumino-boro-silicate (i.e., Na-Ca-Al-B-Si oxide).

In this US-UK collaborative project, we investigate the glass structure and crystallization dependence on compositional changes in simulated nuclear waste glasses and glass-ceramics. Compositions ranged in complexity from 5 oxides to 8 oxides. Specifically, the roles of Mo and lanthanides are investigated, since a proposed glass-ceramic waste form contains crystalline phases such as powellite [(AE,A,RE)MnO4] and oxyzapatite [(RE,AE,Al)2SiO5], and the precipitation of molybdenum phases is known to be affected by rare earth concentration in the glass. Additionally, the effects of other chemical additions have been systematically investigated, including Zr, Ru, P, and Ti. A series of studies was also undertaken to ascertain the effect of the RE size on glass structure and on partitioning to crystal phases, investigating similarities and differences in glasses containing single RE oxides of Sc, Y, La, Ce, Nd, Sm, Er, Yb, or Lu. Finally, the effect of charge compensation was investigated by considering not only the commonly assessed peralkaline glass, but also metaluminous and peraluminous compositions.

Glass structure and crystallization studies were conducted by spectroscopic methods (Raman, x-ray absorption, nuclear magnetic resonance, optical absorption, x-ray photoelectron spectroscopy), microscopy (scanning electron microscopy, transmission electron microscopy, electron probe microanalysis), x-ray and neutron diffraction, small angle measurements, and physical characterization (scanning calorimetry, viscosity, density). This talk will give an overview of the research program and some characteristic results.

Alkali-Silica Gel Reaction in Glasses Dissolved at High pH—Implications for Co-Disposal of Vitrified and Cementitious Nuclear Wastes

International consensus is that vitrified nuclear waste should be disposed of underground where it can safely undergo radioactive decay, isolated from the environment and future populations. Cement will be ubiquitous in all disposal facility concepts. For example, cement will be used to line vaults, in seals and plugs, as buffer material and in general construction. It is expected to play a key role in the Belgian and UK deep geological disposal concepts for high- and intermediate-level vitrified waste, respectively, and possibly also for the shallow disposal facility at Hanford site in the USA. The interaction of cement with vitrified waste is a key issue, since the generation of a hyperalkaline plume could accelerate glass dissolution mechanisms, thereby enhancing radionuclide release from the vitrified waste.

Here, we discuss the results of investigations developed to elucidate the mechanisms and kinetics of sodium aluminoborosilicate glass dissolution in the presence of simplified, buffered high-pH alkali solutions (K2SiO3, Na2SiO3, CaSiO3, MgSO4, and H2SiO4), synthetic cement leachates, including a young cement water (K, Na-rich; pH 13.7), an evolved cement water (Ca, Na-rich; pH 12.5) and an old cement water (Ca, Na-rich, pH 11.8), and also real cement leachates (containing mixed alkalis; pH ~13). The surfaces of glass powders and monoliths were characterised using SEM, TEM, EDX, XRD and NMR. The rate of degradation of the glass in these solutions was found to be the result of two key mechanisms: i) the formation of a porous alkali- or alkaline-earth silica gel, where mean pore diameter was governed by pH, and the type of alkali or alkaline-earth element retained depended on the relative abundance of K, Na, Ca or Mg, the hydrated ionic radius and the ΔG of hydration of the alkali or alkaline-earth species; and ii) the precipitation of crystalline phases—including zeolite (e.g. phillipsite-K), phyllosilicate (e.g. rhodesite) and clay (e.g. smectite)—that, depending on the combination of glass composition, solution chemistry and the phase, either formed a dense layer, impervious to solution species, that protected the surface from further dissolution or, conversely, promoted the ongoing dissolution of the glass through continual consumption of dissolved silica and re-precipitation of Si-bearing phases. These results highlight the complex, but significant effects of high pH, cementitious solutions on the dissolution of nuclear waste glasses, which should be included in future models of vitrified waste disposal in a cement-containing geological disposal facility.
Researchers in many fields are interested in the understanding of iodine behavior in solid and molten materials, however, only a few data on iodine solubility and speciation are available in the literature. Iodine is the heaviest stable halogen element, and in spite of its low natural abundance, it is interesting in Geosciences, mainly because of its link to xenon since most of the iodine isotopes become xenon isotopes by β radioactive decay. In the framework of the Comprehensive Nuclear-Test-Ban Treaty, the atmospheric radioxenon analyses provide the only distinctive signature of a nuclear explosion. \[1\] It is of particular concern because it will be a major contributor to the radioactivity released by a geological repository site for nuclear wastes, but previous studies show that iodine mobility is strongly dependent on the redox.

For all these reasons, it is important to understand the mechanisms related to the solubility of iodine depending on the composition of the glass and to analyze its solubility, redox state, and distribution in a glass network.

We investigated the iodine solubility, speciation, and the influence on properties and glass structure, depending on bulk chemistry, temperature and pressure. Iodine redox state studies were carried out both by Raman and X-ray Absorption Spectroscopy. Our studies on silicate glasses show that iodine could be stabilized with different valences (as $I^-$, $I_3^-$ and $I_5^-$) and with concentrations up to 3.3 wt.\% when B is introduced.

\[1\] Technical Strategic Plan 2016, 2016, Nuclear Damage Compensation and Decommissioning Facilitation

SESSION ET15.12: Managing Corium and Degraded Nuclear Fuels from Severe Accidents

Session Chairs: Nicolas Clavier and Claire Corkhill

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 308

2:00 PM ET15.12.01

Synthesis, Characterisation and Preliminary Corrosion Behaviour Assessment of Simulant Fukushima Nuclear Accident Fuel Debris Clémence Gausse1, Martin Stennett1, Neil Hyatt1, Charilaos Paraskevoulakos1, Mahmoud Mostafavi1, Tomooki Shiba1 and Claire Corkhill1; 1University of Sheffield, Sheffield, United Kingdom; 2Japan Atomic Energy Agency, Tokai-mura, Japan; 3University of Bristol, Bristol, United Kingdom.

The earthquake and the tsunami that occurred on the 11th March 2011 at the Fukushima Daiichi Nuclear Power Plant (NPP) induced a loss of coolant accident and the partial meltdown of boiling water reactor Units 1 to 3. The temperature within the reactor rose in excess of 2000°C causing melting and reaction of UO2 pellets with the steam-oxidised zircaloy fuel cladding, forming nuclear accident fuel debris (NFD) and, where melting of other reactor components occurred (e.g. concrete, steel from the pressure vessel), corium. We present results of an investigation aimed at simulating NFD and corium, including an assessment, by μ-focus XAS methods, of the distribution of simulant fission products (Ce as a surrogate for Pu and Nd to represent trivalent rare earth fission products), which is an important prerequisite to fuel debris retrieval from the Fukushima reactors, due to commence in 2021. Synthesis of materials in the $U_xZrO_2$ solid solution was performed by wet and dry chemistry routes, and materials in the $U_xLn_2O_3$ ($Ln = Ce$ and/or $Nd$) solid solutions were mixed with $Zr$ metal and heated >2000°C by oxyfuel processing. Selected phases were further melted with concrete and steel to synthesise simulant corium materials. Analysis of each phase was performed by techniques including XRD, SEM/EDX, XPS and Raman spectroscopy.

After the accident, continuous filtered water injection (firstly seawater, followed by Fukushima NPP ground water and filtered water) has been used to cool the NFD and corium, and reduced the temperature below 100°C. \[1\] In this so-called stable cold shutdown situation, analysis of coolant water effluent evidenced the presence of Pu, indicating the fuel debris is dissolving. Since the aqueous alteration of fuel debris is expected to alter its chemical and mechanical properties, and may also result in the formation of secondary alteration products, we here present preliminary results of leaching experiments of the above materials in relevant solution compositions.

\[1\] Technical Strategic Plan 2016, 2016, Nuclear Damage Compensation and Decommissioning Facilitation

2:15 PM ET15.12.02

During the tsunami-caused 2011 meltdown at Fukushima Daiichi nuclear power plant, melted nuclear fuel (corium) was exposed to emergency cooling aqueous media, especially borated and sea water, which may have an effect on the stability of the fuel. The corium consists of solidified melt of nuclear fuel, fission products, cladding, control rods and other structural materials. Up to 600 tons of corium debris lies in Fukushima damaged units. It is important to provide data on stability of corium in these aqueous media in order to provide indications about potential radionuclide release mechanisms and their environmental impact and science-based advice for the decommissioning and remediation of the damaged sites.

In order to assess the stability of corium in aqueous cooling media used in Fukushima, experiments were carried out at JRC-Karlsruhe in collaboration with CRIEPI (Japan) using genuine irradiated corium samples taken from the TMI-2 accident.

Static leaching experiments were performed in air and at hot-cell temperature in deionized water and in water containing 2g/L of boric acid. In all cases the solution was continuously stirred and renewed several times during the experiments. The results are compared with similar experiments carried out on LWR spent nuclear fuels (with average burnups of 54 and 60 GWd/tHM), carried out in deionized water and boric acid water, but also in sea water and simplified groundwater (1 mM NaHCO3 and 19 mM NaCl).

After approximately one year of experimental campaign, the releases of matrix elements such as uranium, neptunium, cerium, the instant release fraction of elements like caesium as well as the release of less soluble elements like zirconium in water containing boric acid do not differ significantly from the releases observed in deionized water. The results reveal no significant effect due to the origin of the sample, core or crust, and to the presence of boric acid on the mobility of the radionuclides in the studied samples. As partial exception, the amount of silver found in solution was higher in experiments carried out with core samples. The presence of heterogeneously distributed silver metallic spheres in TMI-2 corium samples (originating from control rod material) has been previously reported and is most probably responsible for this specific effect. Chemical analysis to determine the inventory of the samples will be used for normalisation and comparison.

A detailed comparison between corium samples and undamaged irradiated fuel samples is complicated because of the different morphology of the fragments. The results of surface area determination by SEM image analysis will be reported.

The present experimental results are part of a programme dedicated to the analysis and the management of LWR after severe accidents. In particular, they will be useful in support to defining the decommissioning and remediation strategies of the Fukushima Daiichi nuclear power plant.

2:30 PM BREAK

Session Chairs: Felix Brandt and Michael Ojovan
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 308

3:00 PM ET15.13.01
Tc-99 and I-129 Immobilization by Ettringite Formation in Cementitious Waste Forms Sarah Saslow1, Sebastien Kerisit1, Tannas Varga2, Matthew Asmussen1, Wooyong Um1, Gary L. Smith1 and Reid Peterson1; 1Pacific Northwest National Laboratory, Richland, Washington, United States; 2Pohang University of Science and Technology, Pohang, Korea (the Republic of)

Immobilization of technetium-99 (Tc) and iodine-129 (I) at the Hanford site in Washington State, USA, is a persistent challenge that can be assisted by using cementitious waste form (CWF) technologies. In response to the dynamic compositional range of Tc- and I-containing low activity waste (LAW) and secondary waste streams generated by LAW vitrification, the development of alternative CWF formulations is required to address composition-specific challenges related to contaminant immobilization. For example, sulfatic acid neutralization of highly alkaline waste streams generates a high-sulfate liquid waste that cannot be immobilized by the baseline Cast Stone CWF formulation (8% ordinary portland cement (OPC)/47% blast furnace slag (BFS)/45% fly ash (FA)). At the anticipated sulfate concentrations in these waste streams the Cast Stone CWFs are less likely to cure and prolonged formation of ettringite [Ca6Al2(SO4)3(OH)12●26(H2O)] will lead to expansion and subsequent cracking that increase risk of contaminant release.1-2 Recently, some of these challenges were overcome by increasing the calcium content in the waste form through substitution of hydrated lime (HL, Ca(OH)2) for FA, providing a sink for excess sulfate during the early curing period.2 However, the most striking observation came from contaminant leach tests, where Tc effective diffusivity decreased by two orders of magnitude as ettringite-growth continued relative to previous testing campaigns.3 This suggests that ettringite may aid contaminant retention throughout the CWF life cycle. Here, the mechanism for Tc and I incorporation into ettringite is explored using X-ray diffraction and X-ray absorption spectroscopy techniques combined with ab initio molecular dynamics simulations. Evidence for TcO4- and IO3- substitution for Cl- and SO4- is observed. Molecular dynamics simulations provide insights into the radiation and chemical effects of Tc and I incorporation into ettringite, which can be used to predict the performance of CWFs in field conditions.


4:00 PM ET15.13.02
Establishing Radiation Effects in Silica Based Waste Forms Laura Levy, Aaron Daubney and Alex J. Potts; University of Manchester, Moor Row, United Kingdom.

In order to fully understand the performance of a nuclear waste form, the effects of radiation must be understood. Silica based materials can be used to treat waste; glass is the material of choice for HLW immobilisation and geopolymers are now being considered as an alternative to cementitious grouts for ILW. These materials are both comprised of an amorphous network of silica modified by elements such as Al or B as well as cationic species such as Na or K. This represents a complex system where the effects of network reorganisation and ion migration must be understood. In addition, mechanisms of energy transfer to an aqueous phase in contact with this material, and the radiolysis effects, must also be considered. Ongoing experimental studies into radiation effects using external radiation sources such as gamma and heavy ion acceleration are underway. Here we present some preliminary finding and invite further discussion into irradiation effects in amorphous silica based waste forms.

4:15 PM ET15.13.03
Solidification of HyBRID Waste Using Metakaolin Based Geopolymer Waste Form Jinmo Ahn1, Seongye Kwon1, Won-Seok Kim1, Seonbyeong
The hydrazine based reductive metal ion decontamination (HyBRID) process is recently developed for decontamination of primary coolant system of nuclear power plant and considered as an attractive process because of no organic chelates used. The HyBRID sludge waste is the final product of HyBRID process formed through BaSO₄ precipitation, containing high content of sulfate. The presence of sulfate in HyBRID sludge waste may cause defective cement waste forms due to the potential formation of sulfate bearing mineral such as ettringite \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_2(\text{OH})_12\cdot 26\text{H}_2\text{O})]\). Therefore, instead of cement waste form, geopolymer waste form was developed in this study for solidification of HyBRID sludge waste. Metakaolin was used as geopolymer precursor and the two types of alkaline activators were prepared to test: sodium hydroxide solution with fumed silica and potassium hydroxide solution with fumed silica. Geopolymer waste forms were formulated with desired molar ratio of Si/Al (1.6-2), (Na⁺ or K⁺)/Al (0.8-1), and H₂O/Al (5-7.8). All geopolymer pastes were poured into cylindrical mold (23 mm in diameter x 46 mm in height) and cured for 7 days at room temperature. Geopolymer waste forms with waste loading (>30%) were successfully synthesized to meet the acceptance criteria (>3.45 MPa). Potassium-based geopolymer has better waste loading than sodium-based geopolymer. Moreover, geopolymer waste forms with 1 (Na⁺ or K⁺)/Al molar ratio showed higher compressive strength than geopolymers formed with 0.8 (Na⁺ or K⁺)/Al molar ratio, where the absorbance band of amorphous silica was detected. This suggests that amorphous silica was not fully dissolved when geopolymers were formed with 0.8 (Na⁺ or K⁺)/Al ratio. Besides, the result of FT-IR spectra showed that the absorbance band at 964-976 cm⁻¹ indicated the vibrations of Si-O-Si and Si-O-Al groups of the geopolymer gel network. The each geopolymer waste forms were characterized by X-Ray diffraction (XRD) and scanning electron microscopy with X-ray energy dispersive spectrometry (SEM-EDS): (1) XRD results revealed that there was no change in the crystalline structure of HyBRID sludge after geopolymerization process. (2) Elemental mapping results indicated that there was no change in the crystalline structure of HyBRID sludge after geopolymerization process.

Cementitious materials are widely applied in nuclear waste management in particular due to their capability for radionuclide retention and immobilization. However, the mechanisms governing the immobilization of various safety relevant radionuclides in these materials on the molecular scale are still not completely understood. Here we present experimental and computational studies to enhance the mechanistic understanding of radionuclide uptake and retention in cementitious materials. To obtain a more detailed understanding of the radionuclide uptake by the different constituents of hardened cement pastes and concretes, a bottom-up approach is applied by investigating radionuclide interactions with various synthesized cement model phases like calcium silicate hydrates (C-S-H), monosulfate (AFm) and ettringite (AIF₆) phases, as well as hardened cement pastes made from ordinary Portland and low pH cement. Batch-type sorption experiments under anoxic conditions were performed to analyze the sorption kinetics and the effects of solution composition and solid to liquid ratio on radionuclide uptake. We observed a strong retention of Ra by C-S-H phases with a distinct dependency of the distribution coefficients on the Ca/Si ratio of the C-S-H and the alkali content in solution. TRLFS studies on the uptake of Eu by C-S-H phases indicated two different Eu(III) species in the C-S-H structure, in addition to the formation of a surface precipitate (probably Eu(III)-hydroxide). In order to interpret the experimental data and to obtain closer insights into the incorporation mechanisms, we constructed a set of structural models for the Ra and Eu uptake in C-S-H phases with different Ca/Si ratios based on modified tobermorite structures suitable for ab initio calculations. Using density functional theory (DFT) simulations we computed the energetics of the uptake of Ra and Eu species into the C-S-H phases, comparing in particular the incorporation of the Ra and Eu cations on different crystallographic sites. We found that, in addition to Ra sorption on surface sites, Ra can be exchanged also for Ca in the C-S-H interlayer, in particular at low Ca/Si-ratios, which is in line with the experimental findings on Ra uptake. The calculations of Eu uptake give a slightly different picture, confirming the possible Eu uptake on both interlayer and Ca intralayer positions, consistent with the experimental observations. We will discuss the importance of atomistic modeling studies for the interpretation of radionuclide uptake mechanisms and further possible developments for such joint experimental and computational studies on cementitious materials.

Influence of Mineral Salts Solubility on Bituminized Wastes Products Leaching Behavior in Free Swelling Conditions Jean-Baptiste Championniet, Rémi Blinder3, Arnaud Leclerc4, Armel Guillermo5, Michel Bardet6 and Arnaud Poulesquen7; 1CEA Marcoule, Bagnols-sur-Cèze, France; 2Univ. Grenoble Alpes, CEA, INAC; 3Grenoble, France; 4Univ. Grenoble Alpes, CEA, CNRS, INAC; 5SYMMES-UMR 5819, Grenoble, France.

During the last decades, some nuclear wastes of low/intermediate activity level were incorporated into a bituminous matrix. The behavior under water-induced leaching of the resulting bituminous waste products, which were elaborated by extrusion process and composed of approximately 60 wt % of bitumen and 40 wt % of various salts, has to be evaluated in the prospect of their acceptability into a deep geological disposal. This work aims at assessing the influence of the solubility of the incorporated salts on the water uptake, by studying the leaching behavior of simplified bituminized waste products (containing only one type of salt).

In order to model bituminized waste products, a series of simplified bituminized waste products was elaborated by incorporating 40 wt % of mineral salts of increasing solubility ranging from 2.5 10⁻³ to 912 g / L, by using barium, strontium, calcium, magnesium, sodium sulfates and sodium nitrate. The amount of water uptake was monitored for each sample as a function of time by using gravimetric measurements. In addition, the ingress of water was simultaneously monitored by using ³H-nuclear magnetic resonance and the corresponding samples morphology was evaluated with environmental scanning electron microscopy. Gravimetric measurements show that the higher the solubility of the incorporated salt, the higher the amount of uptake water. Simultaneously, it was observed that the lower the solubility, the lower the mean diameter of pores, and the deeper the water ingress. These results were of particular interest to discuss the leaching behavior of industrial bituminized waste products that incorporated many salts with a similarly wide range of solubilities.
Technetium is a high yield fission product with 22 isotopes all of which are radioactive. Due to its long half-life ($t_{1/2}=211,000$ years), Tc-99 requires immobilisation in a suitably robust host matrix prior to final disposal in a GDF. Iron phosphate glasses are an attractive solution as they can accept a wide range of ions in the glass network and have sufficient aqueous durability. The inherent difficulty of working with technetium and its compounds necessitates prior investigation using analogues before beginning investigations proper. A series of 40:60 iron phosphate glasses doped with rhenium were produced and characterised by Raman spectroscopy, powder X-ray diffraction, scanning electron microscopy and Mössbauer spectroscopy to determine the effect of rhenium addition on the glass network and iron redox. The results of this investigation provide useful insight as to the possible influence of technetium on iron phosphate glasses.

8:45 AM *ET15.14.02
Strategies for the Capture and Immobilization of Radioiodine Josef Matyas; Pacific Northwest National Laboratory, Richland, Washington, United States,

To support the revival of nuclear energy, advanced materials and processes are needed to capture and safely store radioiodine released during reprocessing of spent nuclear fuel. During this process, about 94-99% of the total iodine is volatilized to the dissolver off-gas, with the rest partitioned among off-gas streams from the vessel ventilation, cell, and melter. The iodine is primarily present in the form of $I_2(g)$ with small concentrations of organic iodides (e.g., $(Na,Li,Ca)_{0.5}(Al,Fe,B,P)SiO_4$, we sought to study the effects of substitution in the nepheline based glasses on the resulting crystallization. We summarize

9:15 AM ET15.14.03
Durability Testing of Iodine Waste Forms Matthew Asmussen, Joseph Ryan, Jarrod Crum and Nancy Avalos; Pacific Northwest National Laboratory, Richland, Washington, United States.

The release of radioiodine would need to be controlled in the off-gas management system during the dissolution of used nuclear fuel. Several material classes have been investigated for the capture of radioiodine including solid sorbents. Two examples are silver mordenite (AgZ), which is considered the benchmark material and silver functionalized aerogels (SFA), which have higher iodine capacity than AgZ. Both materials capture iodine through the formation of silver iodide (AgI). Due to the long half-life of I-129 (15.7 million years), this captured inventory of iodine must be safely managed for disposal in a repository. While AgI has low water solubility ($K_{sp} = 8 \times 10^{-17}$) it can have deleterious interactions with the environment; examples being pH changes in the near field, redox processes that destabilize the AgI, and interference from species such as sulfide. Thus, a durable waste form will be required to ensure containment of the radioiodine upon the disposal of these AgI-laden materials. However, limited work to date has been performed to assess the durability of iodine waste forms. This presentation will provide an overview of recent corrosion testing efforts carried out on iodine waste form materials. Two samples systems were investigated: iodine-loaded AgZ material processed with hot isostatic pressing (HIP) and iodine-loaded SFA material with spark plasma sintering. These materials were assessed using aqueous corrosion methods including single-pass flow-through testing (SPFT), the product consistency test (PCT), dilute reactor analysis (DRCA), and electrochemical analyses. The results from these tests were supplemented with characterization of the microstructure to track the progression of corrosion on the surface using scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction, and optical profilometry. It was generally observed that corrosion attack was most prominent in areas of low Si for SFA and at low Si and Al for the AgZ samples. As well the boundaries between Si- and Al-rich particles in the remaining matrix experienced general inward attack.

9:30 AM *ET15.14.04
Compositional Dependence of Nepheline Crystallization in High Level Waste Glasses Ashutosh Goel1, Ambar Deshkar1, Ping Lu1, Yaqoot Shaharyar1, José Marcial2, Mostafa Ahmadzadeh3, Paul Bingham3 and John S. McClay2; 1Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 2Washington State University, Pullman, Washington, United States; 3Sheffield Hallam University, Sheffield, United Kingdom.

Owing to high concentrations of Al$_2$O$_3$ from dissolved fuel cladding and Na$_2$O from basification of the waste, about half of the high-level waste by volume at Hanford, Washington, USA is rich in both Na and Al. Formulations of high waste-loading glasses result in lower amounts of SiO$_2$, which often leads to undesirable precipitation of nepheline (NaAlSiO$_4$). Nepheline crystallization can be affected by both framework and non-framework cations which are present in the glass network. At Hanford, Washington USA, nepheline has been identified in the near field, redox processes that destabilize the AgI, and interference from species such as sulfide. Therefore, a durable waste form will be required to contain the radioiodine upon the disposal of these AgI-laden materials. However, limited work to date has been performed to assess the durability of iodine waste forms. This presentation will provide an overview of recent corrosion testing efforts carried out on iodine waste form materials. Two examples systems were investigated: iodine-loaded AgZ material processed with hot isostatic pressing (HIP) and iodine-loaded SFA material with spark plasma sintering. These materials were assessed using aqueous corrosion methods including single-pass flow-through testing (SPFT), the product consistency test (PCT), dilute reactor analysis (DRCA), and electrochemical analyses. The results from these tests were supplemented with characterization of the microstructure to track the progression of corrosion on the surface using scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction, and optical profilometry. It was generally observed that corrosion attack was most prominent in areas of low Si for SFA and at low Si and Al for the AgZ samples. As well the boundaries between Si- and Al-rich particles and the remaining matrix experienced general inward attack.

10:00 AM BREAK

SESSION ET15.15: Materials for Nuclear Safeguards
Session Chair: Daniel Bailey
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 308

10:30 AM *ET15.15.01
Microparticle Production as Reference Materials for Particle Analysis Methods in Safeguards Stefan Neumeier, Philip Kegler, Martina Klinkenberg, Irmgard Niemeyer and Dirk Bosphach; Forschungszentrum Juelich GmbH, Juelich, Germany.

The International Atomic Energy Agency (IAEA) implements technical measures, or safeguards, in order to verify the compliance of member states their international legal obligations to use nuclear material and technology only for peaceful purposes. Predisposal and geological disposal of high-level radioactive waste and spent nuclear fuel, if declared as waste, is also subject to safeguards. One of the technical measures used are analytical measurements...
of samples taken during inspections of nuclear facilities. The application of this measure goes hand in hand with the development and advancement of analytical measurements and of reference materials for quality control purposes.

To this end, a two-step process has been developed and established at Forschungszentrum Juelich which is capable to produce microparticles intended as source material for certified reference materials for particle analysis methods applied in safeguards. The first step is an aerosol-based particle production process. A monodisperse particle size distribution as well as the single phase UO2 structure was confirmed by SEM, mass spectrometry and μ-X-ray methods. Mass spectrometry analysis performed on single uranium microparticles confirmed consistency of the uranium isotopic ratios in comparison to the initial precursor solutions. In the second step the particles are transferred into suspensions for which the stability of the particles in suspension was investigated with respect to dissolution. It turns out that ethanol is a suitable medium for the storage of particles over a period of several months. Our results from systematic particle analyses by SEM/EDX demonstrate that the two-step process developed at Forschungszentrum Juelich enables the reproducible production and homogeneous distribution of monodisperse microparticles and particle mixtures on several types of substrates, such as quartz discs and cotton swipes. Hence, it allows for a very flexible and time-saving preparation of various types of test samples suitable as reference materials for particle analysis methods applied in safeguards.

11:00 AM ET15.15.02
Wet Chemistry Route to Uranium Oxide Micropheres as Reference Materials for Nuclear Safeguards Nicolas Clavier1, Jerome Maynadie1, Victor Trillaud1, Jerome Manaud1, Laure Sangely1, Thippatai Tranpaphan1 and Nicolas Dachere1; 1ICSM, Bagnols, France; TAE, Vienna, Austria.

The preparation of morphology-controlled uranium oxide particles is currently attracting a growing interest, notably due to its importance in the field of nuclear safeguards. Particularly, provided certain homogeneity and stability requirements, such particles could act as reference materials for microanalytical methods. In this framework, several protocols have been already tested, but frequently required specific equipment and cannot be easily implemented in standard chemistry labs. On this basis, we developed from several years original wet chemistry routes aiming to precipitate directly morphology-controlled actinide oxides from mixtures of solutions. Such methods are mostly based on the hydrolysis of tetravalent actinides which leads to the formation of amorphous An(OH)3 samples, finally aging to AnO2.nH2O.

In this aim, hydrochloric solution containing tetravalent uranium (natural isotopic composition) was first mixed with aspartic acid, used both as complexing and shaping agent, to yield an amorphous uranium(IV) aspartate precipitate. Solid phase and supernatant were then transferred in a Teflon-lined autoclave and placed under mild hydrothermal conditions (T = 160°C). A multiparametric study was then undertaken, in order to evidence the impact of pH, aspartic acid concentration, or mechanical stirring. On the one hand, acid concentration was found to be the most critical parameter, as microspheres were only obtained for pH values close to 2. On the other hand, the size dispersion of the particles produced could be improved by using a large excess of aspartic acid during the initial precipitation step. Finally, the addition of a mechanical stirring during the hydrothermal treatment step allowed us to control more accurately the size of the particles produced in the range 100 nm – 1 µm. For all the compounds prepared, further XRD analysis attested the formation of UO2.nH2O samples, while TG experiments revealed the presence of residual organics. Nevertheless, additional heating treatments performed up to 600°C led to produce anhydrous and carbon-free dense particles without altering their initial morphology.

Finally, preliminary tests of these samples as reference materials for nuclear safeguards were performed. In this aim, UO2 microspheres were first deposited on carbon planchets after dispersion and dilution with ethanol. The number of particles deposited, the spacing between them, the cleanliness of the areas not intended for particle deposition and the absence of uranium background between the particles was found to be satisfying. Also, first LG-SIMS experiments aiming to determine the isotope composition of uranium led to very good results, the behaviour of the particles under the IMS beam being comparable to typical field sample particles.

SESSION ET15.16: Management and Long Term Behavior of Spent Nuclear Fuel II
Session Chairs: Dirk Bosbach and Laurent Claparede
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 308

1:30 PM ET15.16.01
Leaching of Spent Nuclear Fuels—Influences of Sample Preparation and Matrix Composition on Radionuclide Release Patterns Olivia Roth1, Anders Paranen1, Daqing Cui1, Alexandre Barreiro Fidalgo1, Lena Evins2 and Kasriost Spahiu2; 1Studsvik Nuclear AB, Nyköping, Sweden; 2SKB, Stockholm, Sweden.

The rate of release of the radionuclide content from spent nuclear fuel during water contact is a central issue to the safety assessment of spent nuclear fuel repositories. Although the area has been subject to studies for several decades there are still issues to be resolved. The general trend among reactor operators is to increase the burn-up of the fuel. There are also new fuel types on the market where additive or dopants have been added to the fuel matrix in order to enhance the in-reactor fuel performance. Both these factors alter the spent fuel matrix and can be expected to influence the leaching behavior. Many spent nuclear fuel deep repository designs involve large amounts of iron in the disposal canister and canister cladding gap, the samples have been prepared in different manners. Furthermore, the effect of fuel matrix dopants on the hydrogen effect has been studied by performing leaching of Al/Cr doped fuel both in aerated conditions and under hydrogen atmosphere and comparing the results with results from leaching of standard UO2 fuel.

2:00 PM ET15.16.02
Electrochemical Simulation of the Influence of Radiolytically-Produced Hydrogen on the Corrosion of Uranium Dioxide Nazhen Liu1, Fraser King2, David Shoesmith1 and James Noel1; 1University of Western Ontario, London, Ontario, Canada; 2Integrity Corrosion Consulting Ltd, Nanaimo, British Columbia, Canada.

The ability of hydrogen to inhibit the corrosion of uranium dioxide has received considerable attention since this process has the potential to suppress radionuclide release from spent fuel exposed to groundwater inside a failed nuclear waste container emplaced in a deep geologic repository. A number of mechanisms have been proposed to explain this inhibition. Hydrogen oxidation on the noble metal particles present in spent fuel leading to
the prevention of oxidation of the galvanically-coupled uranium dioxide matrix has been clearly demonstrated. However, the direct reaction of hydrogen on the uranium dioxide surface also appears capable of preventing fuel corrosion and radionuclide release by consuming the OH radicals produced by hydrogen peroxide dissociation on the oxide surface. In addition, the combination of radiation (gamma) and hydrogen can be shown to suppress the corrosion potential of uranium dioxide to values below which the oxide should be thermodynamically immune to oxidation. This suppression appears to be partially irreversible suggesting a chemical reduction of the oxide matrix by H radicals. In this study, we have attempted to simulate this influence of radiation by generating H atoms via water/proton reduction on the oxide surface. A similar suppression of the corrosion potential is achieved and, on removing the radiation field, only a partial recovery of the corrosion potential, towards the value which prevailed before irradiation, is observed. By conducting a series of electrochemical experiments on oxides with various degrees of non-stoichiometry, it is shown that the oxide matrix is reduced with the extent of reduction depending on the degree of non-stoichiometry of the oxide. Also, by performing similar experiments in solutions with a range of pH values, it was shown that the extent of oxide reduction increases at low pH when the generation rate of H atoms is increased.

These studies indicate that a combination of radiation and hydrogen can lead to the direct reduction of the oxide matrix via a reaction with absorbed H atoms.

2:15 PM ET15.16.03
Powder Leaching Study for Grain Boundary Inventory of Two High Burnup Fuels Alexandre Barreiro Fidalgo1, Olivia Roth1, Anders Puranen1, Lena Evins2 and Kastriot Spahiu2; 1Studsvik Nuclear AB, Nyköping, Sweden; 2SKB, Stockholm, Sweden.

In the context of a deep geological repository safety assessment, the Instant Release Fraction (IRF) is defined as the fraction of radionuclides in spent fuel which rapidly dissolves in contact with water. The IRF is sourced both from the pellet-cladding gap and the grain boundary. It is however uncertain how much the grain boundary inventory contributes to the IRF. Commonly, the IRF is determined by using short-term dissolution experiments, which does not distinguish between these two fractions. However, a few experiments have been performed to specifically investigate the grain boundary fraction through simultaneous grinding and leaching experiments [1-2].

For this study, the main goal is to establish the closed grain boundary inventories of two Swedish fuels with high burnup (local burnup 58 and 65 MWd/kg). In addition, the results will be compared to those already obtained for another high burnup fuel (local burnup 75 MWd/kg) [3].

The experiments are performed on fuel fragments without cladding. The selected fragments are samples that have already been leached in previous campaigns and therefore the IRF of exposed grains and matrix dissolution behavior under aerated conditions have already been established [4-5].

The fuel fragments were exposed to an initial leaching period under aerated conditions in 10:10 mM NaCl:NaHCO3 solutions for 3 months. The main objective of this initial step is to wash away any pre-oxidized phases formed during humid-air storage in cell.

After the washing step, the fuel fragments are placed in a mill together with simplified groundwater (10:2 mM NaCl:NaHCO3 solution) under oxidizing conditions (air) at room temperature. The grinding and simultaneous leaching is performed in similar conditions as tested in a previous campaign [3]. The solutions are analyzed with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and gamma spectroscopy. Additionally, the grinded fuel is taken for Scanning Electron Microscope (SEM) analysis.

The preparations, experimental setup as well as the experimental results will be presented and discussed in the conference presentation.

References

2:30 PM BREAK

3:00 PM ET15.16.04
Radionuclides Present at Inner Cladding Surfaces of Irradiated PWR Fuel Rod Segments in the Context of Safety of Extended Dry Storage of Spent Nuclear Fuel Michel Herrn, Ernesto González-Robles, Nikolaus Müller, Tobias König, Kathy Dardemne, Jörg Rothe, Dieter Schild, Ron Dagan and Volker Metz; Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

In the German waste management concept, spent nuclear fuel (SNF) is designated for direct disposal in a deep geological repository available by 2050 at the best. However, considering the delay in the site selection process so far as well as the time needed for exploration, construction, and commissioning of a repository for high-level waste, start of waste emplacement is expected by the end of this century. Thus, a prolonged dry interim storage of SNF assemblies is inevitable.

Integrity of the irradiated Zircaloy cladding after 50 to 100 years of dry interim storage is of importance e.g. to ensure a safe reloading of fuel assemblies from storage casks to final disposal casks. However, cladding integrity is affected by various processes during reactor operation and beyond, e.g. fuel cladding chemical interactions. Moreover, inner cladding surfaces exposed to precipitates of fission/activation products released from fuel pellets are possibly prone to corrosion processes. In particular, the presence of cesium, iodine, tellurium, and chloride at the fuel-cladding interface and their impact on the integrity of the cladding are analyzed.

Irradiated Zircaloys-4 specimens, currently under investigation, are sampled from the plenum section as well as cladding tube in contact with SNF of an UO2 fuel rod segment (50.4 GWd/kg). Experiments with irradiated cladding in contact with MOX fuel (38.0 GWd/kg) have been started recently.

Composition of agglomerates found on the inner surface of the plenum cladding and fuel-cladding interaction layers were analyzed by means of SEM-
The microstructure, in particular grain size, grain orientation and dopant distribution (i.e. either in solid solution within the UO₂ matrix or segregated on dissolution behaviour e.g. regarding the larger grain size in doped fuels and contributions of grain boundaries, the model material pellets were synthesized free of any grinding steps to be applicable in a dedicated glove box line. Process optimization was achieved by a systematic investigation of various process to mimic fuel ages between 1,000 and 10,000 years, later in DISCO. Syntheses were performed by co-precipitation and wet-coating methods and had to be pellets, Cr-doped UO₂ as well as Cr- and alpha doped (238Pu) pellets. A wet chemical route was favored due to the very low doping levels of 238Pu required reactor (LWR) fuels such as Cr-, Al-, and Si-doped UO₂ fuels. For these modern types of LWR fuel it is still not known, whether their performance in a deep geological waste repository will be similar to conventional spent LWR-fuels. Corrosion experiments with spent nuclear fuel (SNF) cannot unravel all alteration model will be presented.

In a deep geological repository, the fate of spent UO₂ fuel and the associated release of radionuclides depend on UO₂(s) corrosion kinetics, precipitation kinetics of secondary phases as well as on thermodynamic constraints. These processes are influenced by a variety of factors such as the radiation field, the resulting dose rate, the availability of oxidizing radiolytic products, the groundwater composition and the redox potential. As a result of numerous studies it turns out that corrosion of spent UO₂ fuel is strongly inhibited under hydrogen overpressure. In contrast to earlier results, radiolysis driven fuel corrosion appears to be less relevant for most repository concepts. Even though the protective hydrogen effect on corrosion of spent UO₂ fuel has been evidenced in many experiments open questions remain related to the exact mechanism.

Using batch-type corrosion experiments with depleted UO₂(s) under gamma-irradiation, we studied alteration of the UO₂(s) surface under H₂ overpressure. Prior to the corrosion experiments, a series of UO₂(s) samples were annealed at 1150°C in Ar/H₂ gas stream. Immediately after cooling of the samples to ambient temperature, surfaces of one sample were characterized by XPS. The other UO₂(s) samples, annealed in the same batch, were placed in autoclaves with aqueous near neutral pH solution. The autoclave experiments were irradiated for several months in the GB77 Co-60 source at Institut für Oberflächenmodifizierung, Leipzig. The mean gamma-dose rate at the position of the autoclaves were measured with a Fricke dosimeter and was below 600 Gy/h. Surfaces of UO₂(s) samples recovered from the autoclave experiments were analyzed by means of SEM-EDS, Raman spectroscopy, and XPS techniques. A UO₂(s) reference sample (CBNM#106, EC Reference Material no. 106) was fractured in ultra high vacuum of our XPS device, to provide baseline measurements for uranium oxidation states. Solely 4f elemental lines and respective satellite signals were detected in the reference sample with a UO₂.0 stoichiometry. Similarly, the depleted UO₂(s) sample measured immediately after annealing in Ar/H₂ gas stream contained solely U(IV). After storing the annealed UO₂(s) under dry conditions in a glovebox with Ar atmosphere (containing < 1 ppm O₂) for one year, both U(IV) and U(V) were detected on the sample surface. We detected metaschoepite and Na-diuranate type precipitates on the UO₂(s) samples recovered from the gamma-radiolysis experiments. Besides layers of U(VI) secondary phases, U(IV) was detected at these samples when precipitates were removed. Experimental results and conclusions with respect to the spent UO₂(s) matrix alteration model will be presented.

The current efforts to improve fuel performance in nuclear power generation resulted in an increased utilization of a variety of new types of light-water reactor (LWR) fuels such as Cr-, Al-, and Si-doped UO₂ fuels. For these modern types of LWR fuel it is still not known, whether their performance in a deep geological waste repository will be similar to conventional spent LWR-fuels. Corrosion experiments with spent nuclear fuel (SNF) cannot unravel all of the various concurring dissolution mechanisms entirely due to the chemical and structural complexity of SNF and its high beta- and gamma radiation field. Technical restrictions allow only for a very limited number of experiments. Therefore, within the EU-DISCO project (www.disco-h2020.eu) experiments on irradiated modern fuels are complemented with systematic dissolution studies carried out with synthesized and well characterized, simplified UO₂-based model materials. A bottom up approach is followed to understand how the addition of Cr-oxide into the fuel matrix affects SNF dissolution behavior under repository relevant conditions.

Here, we show recent results on the development and optimization of the process steps for a wet-chemical route to produce nominally pure UO₂ reference pellets, Cr-doped UO₂ as well as Cr- and alpha doped (238Pu) pellets. A wet chemical route was favored due to the very low doping levels of 238Pu required to mimic fuel ages between 1,000 and 10,000 years, later in DISCO. Syntheses were performed by co-precipitation and wet-coating methods and had to be free of any grinding steps to be applicable in a dedicated glove box line. Process optimization was achieved by a systematic investigation of various process parameters such as calcination temperature and pressing forces. In order to provide insights into the effects of the material's micro structure on the dissolution behaviour e.g. regarding the larger grain size in doped fuels and contributions of grain boundaries, the model material pellets were synthesized. The microstructure, in particular grain size, grain orientation and dopant distribution (i.e. either in solid solution within the UO₂ matrix or segregated on grain boundaries) in the model materials were characterized using various complementary methods e.g. SEM, EBSD, and XRD. First results of accelerated dissolution studies with UO₂-based Cr-containing model systems were performed using H₂O₂ to mimic the oxidative radiolysis species to study the effect of micro structure and Cr-doping upon the dissolution rate.

**SYMPOSIUM NM01**

Carbon Nanotubes, Graphenes and Related Nanostructures
November 26 - November 30, 2018

Symposium Organizers
How the Microstructure of the Alumina Layer Can Lead to Full Growth Reproducibility of Millimeter-Tall Forests of Carbon Nanotubes

Gilbert D. Nessim and Eti Teblum; Bar Ilan University, Ramat Gan, Israel.

The chemical vapor deposition (CVD) synthesis of millimeter-tall carbon nanotube (CNT) forests using iron catalyst on alumina underlayer has now become established. Many studies have elucidated the role of precursor gases and water vapor, catalyst coarsening, and possible models for growth termination. However, it is well-known to the practitioners that the synthesis is not always fully reproducible and can be affected by tiny amounts of carbon or water vapor present in the reactor, by laboratory temperature or humidity, etc. To solve this problem, we assumed that the key issue is the interface between the catalyst and the alumina underlayer and the subsurface diffusion of iron (catalyst) into alumina (underlayer). We focused on tuning the microstructure of the alumina underlayer and studied how different microstructures would affect CNT growth, keeping all the other process and material parameters constant. We postulated that the issue was the grain size of the underlayer and thus the amount of grain boundaries. Since the iron catalyst subsurface diffusion into the alumina underlayer will strongly be affected by the amount of grain boundaries, with grain boundary diffusion being much faster compared to lattice diffusion, we decided to control the grain size of the alumina. Using electron-beam evaporation, we prepared samples where we heated the substrate at 350 °C during deposition and slowly evaporated the alumina with the goal to obtain large grains in order to minimize the amount of grain boundaries. We also prepared samples where we evaporated the alumina at a fast rate to obtain small grains and to maximize the amount of grain boundaries.

References:
Carbon nanotubes (CNT) had received broad attention in the past decades due to its dramatic physical and chemical performance of individual tubes and became a powerful candidate of future star materials. As synthesis determined the future, in this talk, I will focus on the controlled growth of SWNT arrays with ultra-high density, high ratio semiconducting properties and special chiral angles. For the SWNTs arrays with ultra-high density, Trojan catalysts (released from substrate) was developed and the density can be as high as 150 tubes/µm. For the SWNTs arrays with semiconducting properties, oxides catalysts with oxygen vacancy, bimetal catalysts and uniform Mo$_2$C catalyst were used to grow semiconducting SWNTs arrays and ratio of semiconducting tubes can be higher than 95%. For the SWNTs arrays with special chiral angles, it is based on a consideration of nanotube/catalyst interfacial thermodynamics determined by symmetry, and the kinetic growth rates set by the number of kinks. Using these strategies, horizontally aligned metallic ((12, 6), abundance >90%) and semiconducting ((8, 4), abundance >80%) SWNT arrays with an average density higher than 20 tubes/µm and 10 tubes/µm, respectively, were successfully obtained on uniform solid catalysts.

References:

10:45 AM NM01.01.06
Locally Controlled Growth of Single Lambda-Shape Carbon Nanofibers

Christian Lutz, Tobias Loritz, Julia Syurik, Sharali Malik, C.N. Shyam Kumar, Christian Kübel, Michael Bruns, Christian Greiner, Michael Hirtz and Hendrik Hoelscher, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Since first studies of branched carbon nanotubes (CNTs) with L-, Y- and T-shapes were published in the mid of the 1990 various approaches were presented to grow such structures. Branched carbon nanotubes are of high interest due to their unique electrical properties making them a promising material for advanced nano-electrical devices. However, SWCNTs are not easy to grow in a defined way. Therefore, Y-shaped MCNTs or CNTs are also of interest as a material mimicking hierarchical nanostructures found in nature.

In general, the growth of branched or non-branched CNFs or CNTs is conducted with an elaborate infrastructure relying on a certain amount of process gases and considerable energy input. We present an approach to grow inverted V-shaped or Y-shaped CNFs in an open ethanol flame. Due to their resemblance to the Greek letter lambda we named them Λ- or λ-shaped CNFs depending on their actuals shape. Λ-shaped CNFs consist of two CNFs attached to the substrate with one end and connected to each other with the other end resulting in a free standing lambda-shape. An additional CNF can be grown from the connecting point of the first two CNFs with increasing growth time resulting in λ-shaped CNFs. Our experiments suggest that the connecting point of the lambda-CNFs is the nickel catalyst and that the third CNF growth from that center. The exact growth position of the overall structure on the substrate can be determined through microchannel cantilever spotting (µCSP) or dip-pen nanolithography (DPN) via the locally controlled deposition of nickel catalyts. Down-scaling to a spot size that results solely in one single lambda-shaped CNF is demonstrated.
Single-walled carbon nanotubes (SWCNTs) are one-dimensional materials exhibiting unique properties, so they have been anticipated for various electronic devices in future. Presently, catalyst-assisted chemical vapor deposition (CVD) are widely used to obtain high-yield SWCNTs, where alumina buffer layers are used to enhance the catalyst activity. However, the enhancement mechanism of catalyst activity by the alumina buffer layers remains poorly understood. In this study, we performed SWCNT growth at 600°C by alcohol catalytic CVD using Rh catalysts on different types of alumina buffer layers prepared using different processes, and the effects of oxidation and crystallinity of alumina buffer layers on catalysts activity were investigated. Five kinds of alumina buffer layers were used to support Rh catalysts; native oxidation of Al layer deposited by electron beam (EB); thermal oxidation of Al layer deposited by EB; EB deposition of Al2O3 powder; native oxidation of Al layer deposited by rf-sputtering; thermal oxidation of Al layer deposited by rf-sputtering. After deposition of Rh catalysts (nominal thickness ~ 0.2 nm) on them, we carried out SWCNT growth by alcohol catalytic CVD [1]. The grown SWCNTs were characterized by Raman measurements, FESEM and TEM. The alumina support layers were analyzed by XPS, XANES, AFM, TEM and ellipsometry. Rh particle sizes and subsurface diffusion were characterized by TEM and depth profile using XPS.

Although Rh nanoparticles were formed on all alumina layers, SWCNTs were not grown on the alumina buffer layer in which metallic Al was contained. Deposition profile showed that the large inward diffusion of Rh catalysts occurred on the "metallic" alumina buffer layer, resulting in the reduction of SWCNT yield. For the alumina buffer layers prepared by thermal oxidation, disordered-type alumina polycrystals were formed and that Ostwald ripening of Rh catalysts was enhanced on them, leading to small SWCNT yields. Conversely, on the amorphous alumina layers, Ostwald ripening was suppressed and Rh particles suitable for SWCNT growth were formed. Additionally, the inward diffusion of Rh catalysts was suppressed on the diaspore-type amorphous layers with higher densities. Our results demonstrated that amorphous alumina support layers with high densities are suitable for suppressing both Ostwald ripening and inward diffusion of catalysts, making them favorable for high-density SWCNT growth.


11:15 AM NM01.01.08
Hyperspectral Raman Spectroscopy—A Powerful Method to Investigate Plasma Treatments of Graphene Films
Pierre Vincion1, Germain Robert Bigras1, Xavier Glad1, Charlotte Allard2, Richard Martel2 and Luc Stafford1; 1Physique, Université de Montréal, Montréal, Québec, Canada; 2Chimie, Université de Montréal, Montréal, Québec, Canada.

Raman spectroscopy is an efficient tool giving distinctive features for pristine, damaged and even doped graphene. Typical Raman methods are however limited by their intrinsic microscopic nature, only allowing to probe the area exposed to the laser beam (~1 μm). Hence, Raman mapping is often used to assess a broader region of graphene samples. Nonetheless, especially when graphene is grown on a polycrystalline substrate, strong discrepancies may appear on a scale larger than the available mapping area (~ tens or hundreds of μm). Moreover, in the case of plasma irradiation of graphene, it is essential to understand the impact of the small heterogeneities in pristine graphene (local defects, grain boundaries, etc.) on the resulting graphene structure after treatment. In this context, recent advances in laser technology combined with increased efficiencies of Charged-Coupled Devices (CCD) and the development of efficient Bragg filters opened the road to new Raman imaging methods with reasonable integration time. In particular, hyperspectral Raman Spectroscopy or RIMA (Raman Imaging) is a very powerful method to obtain qualitative as well as quantitative Raman data on a macroscopic scale [1]. In this work, RIMA was used to examine plasma-induced modification of CVD-grown graphene films. Experiments were realized in a low-pressure inductively-coupled plasma. This method is a commonly used post-processing technique to alter materials properties and thus, is a good candidate to tune graphene films. It is however difficult to decouple doping and damage mechanisms. In damage studies of graphene, ions beams are operated at energy above a few tens of eV [2] while ions energy in our plasma conditions is below the energy threshold for atom displacement (T.dis = 15-20 eV) [2]. Yet, defects generation by such plasmas are reported in few studies [3] but are not clearly understood.

Graphene films were exposed to an argon plasma and RIMA measurements were performed on different areas to study the sample homogeneity. These results reveal how the initial state of graphene films is a key factor to understand plasma irradiation effects. In addition, the very large number of Raman data (>10^6) was used to establish links between doping, strain and damage types in both as-grown and plasma-processed graphene films. To further understand plasma-graphene interactions, plasmas conditions were adjusted as to vary ion energy and fluence of plasma-generated species.


11:30 AM NM01.01.09
Chirality Distributions of SWNTs—Experimental Evaluation versus Thermodynamic Modeling
Annick Loiselle1, Frédéric Fossard1, Yann Magnin1,2, Hakim Amani1, François Ducastelle1, Esko Kauppinen1,2,3,4 and Christophe Bichara1; 1LEM, CNRS-ONERA, Chatillon, France; 2MultiScale Material Science for Energy and Environment, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 3CNRS-Université Aix Marseille, CINAM, Marseille, France; 4Department of Applied Physics, Aalto University School of Science, Aalto, Finland.

Although significant progress has been made since 25 years, one major obstacle to realization of Single-walled carbon nanotubes (SWNTs)-based nanotechnology has been the lack of control for designing selective synthesis conditions. This is partly due to the incomplete understanding of the physical and chemical effects driving the kind of tubes able to nucleate and grow under given experimental conditions [1].

A way to address this basic question is to consider SWNT growth from a thermodynamic point of view. To that aim, we have developed a statistical thermodynamics model, valid in the case of a perpendicular growth [2], which has been experimentally proven to yield a near-armchair selectivity [3]. This model relates the stable (n,m) tube structures to the tube/catalyst interfacial energies for zigzag and armchair edges and the temperature [4]. Taking the configurational entropy of the tube edge into account is a central point that explains how chiral tubes become stable at finite temperature, while ground state structures are either zig-zag or armchair. Exploring the parameter set enables one to display temperature dependent chirality maps, locating the most stable tube structure. More precisely, for each set of interfacial energies and temperature, this model yields a probability distribution of (n,m) SWNTs.

With this model in hand and thanks to a scrupulous analysis of our previous results and data of the literature, we will compare in this talk experimental measured and model chirality distributions facing two difficulties. A first notorious difficulty is the experimental evaluation of the chiral distribution of tubes produced in a CVD process, as most of characterization techniques might fail either in the identification of the different kinds of tubes present in a sample or in determining their relative fractions. On the other hand, the model, being purely thermodynamic, does not take into account kinetics and experimental conditions which may impact the tube selectivity such as a possible preferential etching of metallic tubes.

These limits given, we will show the efficiency of the model in understanding the origin of the frequently reported near-armchair selectivity and for
accounting for chirality distributions observed under given synthesis conditions. Finally we shall evaluate the potential of the model for providing guidelines for catalyst design and growth condition optimization.


11:45 AM NM01.01.10
Large-Scale Dynamic Energy Driven Assembly of Two-Dimensional Layered Materials on Polymer Substrate
Dong Zhou and Bo Li; Villanova University, Villanova, Pennsylvania, United States.

Two dimensional layered materials (2DLMs) are important candidates of flexible electronics applications, used for health monitors, displays, batteries, and sensors. Despite the significant progress being made in synthesis technologies and in the prototyping of 2DLM flexible electronics, the work in the scalable integration of 2DLMs with flexible polymer substrates has proven, thus far, to be minimal and limited to several specific 2DLMs and polymer substrates. In this work, we demonstrated directly assemble wafer-scale 2DLM film on a polymer substrate through a dynamic energy driven assembly (DEDA) method seamlessly integrating a liquid exfoliation and a new assembly strategy. The DEDA method includes three steps: exfoliation of 2DLM in a designated solvent using sonication, and submerge polymer substrate to process the assembly, and take out the assembled substrate to dry. The principal innovation of DEDA is to control the relative interfacial energy among solvent, 2DLM and polymer substrate such that a relative low-energy 2DLM-polymer interface and a relative high-energy solvent-polymer interface will enable effective assembly of 2DLM on the polymer. Unlike the traditional assembly strategies, which start with a stabilized solution and emphasize good wetting among all components, DEDA theory suggests poor-wetting solvent is the key that determines the assembly quality. As a proof-of-concept, we have successfully used DI water, a non-toxic but poor wetting solvent for PDMS, to exfoliate and then assemble different 2DLMs (graphene, h-BN, and MoS2) on a PDMS substrate. A uniform film can be formed as short as 10 seconds after immersing PDMS substrate in the solution and by adjusting the solution concentration and assembly time, the thickness of the assembled film can be easily tuned from several nanometers to hundreds of micrometers. It is also interesting to notes, adding 2-propanol into water decreases the assembly efficiency dramatically. This results matching the prediction from DEDA theory where improved wetting between the solution and PDMS diminish the driving force of assembly. In summary, the unique features of this DEDA method are (1) a new interfacial energy driven assembly strategy that has the potential to be generalized broadly to arbitrary 2DLMs and polymers, (2) the usage of the non-equilibrium 2DLMs solution for rapid assembly, and (3) high controllability of the assembly through simple concentration and assembly time controls. This study not only creates a new assembly method for the scalable and hierarchical fabrication of 2DLM flexible electronics but also advances knowledge in nanomaterials assembly and will promote the field of nanomanufacturing.

SESSION NM01.02: Synthesis and Characterization II
Session Chairs: Don Futaba and Naoyuki Matsumoto
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Republic AB

1:30 PM *NM01.02.01
Evaluation Methods for Quality Control of Carbon Nanotubes and Graphene Toshiya Okazaki; AIST, Ibaraki, Japan.

Due to their extraordinary electrical and mechanical properties, carbon nanotubes (CNTs) and graphene are widely regarded as very attractive nanomaterials. For example, CNT production capacity has rapidly increased worldwide. For commercialization of CNT and graphene-based products, the qualities of CNTs and graphene must be controlled. In this talk, we will show effective methods for quality evaluation of CNTs and graphene.

First, the lengths of CNT are estimated by far-infrared (FIR) spectroscopy. Based on the plasmon resonance model, the length of the clean channel qualities of CNTs and graphene must be controlled. In this talk, we will show effective methods for quality evaluation of CNTs and graphene.


2:00 PM NM01.02.02
Efficient CVD Growth of Single-Wall Carbon Nanotube Carpets Using Industrial Gaseous Waste as a Feedstock
Haider Almkhelfe1, Xu Li1, Rahul Rao2, and Placidus B. Arnma1; 1Tim Taylor Department of Chemical Engineering, Kansas State University, Manhattan, Kansas, United States; 2Materials & Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio, United States; 3UES, Inc., Dayton, Ohio, United States.

A gaseous product mixture from Fischer-Tropsch synthesis (FTS-GP) has been utilized as an efficient feedstock for growth of high-quality, well-aligned, single-wall carbon nanotube (SWCNT) carpets of millimeter-scale heights on Fe and (sub) millimeter-scale heights on Co catalysts via chemical vapor deposition (CVD). Growth conducted at optimal temperatures for Co and Fe catalysts yielded predominantly SWCNTs that are largely free of carbon impurities. Growth on Fe is characterized by a growth rate of ~50 μm/min and catalyst lifetime that is longer than 90 min, with the catalyst showing no decay of activity. In contrast, growth on a Co catalyst shows a lifetime of ~60 min, with a slower growth rate of ~7μm/min. Resulting area densities of SWCNT carpets grown on Fe and Co catalysts, determined by the weight-gain method, were 1.0 × 1012 and 6.0 × 1012 cm2, respectively. The catalyst
lifetime and area densities of SWCNTs are among the highest achieved on standard catalysts. Unlike SWCNT carpet growth involving conventional feedstocks (such as $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and CO), growth rate and density of SWCNTs on Fe are less sensitive to the FTS-GP fraction and thus allow for relatively easy optimization and scale-up.

2:15 PM NM01.02.03  
**Defect-Free Graphene Growth at Low Temperatures via Plasma Enhanced Chemical Vapor Deposition**  
Bilge Bekdüz, Yannick Beckmann, Jan Mischke, Jonas Twellmann, Wolfgang Mertin and Gerd Bacher; University of Duisburg-Essen and CENIDE, Duisburg, Germany.

Plasma enhanced chemical vapor deposition (PE-CVD) is the method of choice to fabricate graphene films at temperatures well below 1000°C. Low growth temperatures are of interest e.g., to decrease the production cost, to make the process suitable for roll-to-roll implementation or to facilitate the growth of graphene on other non-catalytically substrates. Although few groups showed nearly defect-free PE-CVD grown graphene at low temperatures, a detailed understanding of the growth mechanism is still missing [1].

In order to study the growth mechanism in PE-CVD we used a commercially available 4" cold wall reactor to fabricate graphene on electrochemically polished high-quality copper foils [2]. A cost-effective DC plasma is applied to dissociate the precursor methane. To suppress unintended vertical graphene growth and ion acceleration to the substrate we introduced a sacrificial Cu foil into the growth chamber. The growth temperature was systematically varied from 1020°C down to 600°C. By varying the growth time at different temperatures two types of samples were prepared: graphene flakes and graphene films. By analyzing the flake areas the growth rate could be determined in dependence of growth time and growth temperature.

Almost defect-free graphene with negligible ($\mu_{\text{eff}} < 0.1$) contributions of the D peak in Raman spectroscopy could be prepared even at 600°C. Compared to thermal CVD we found that the activation energy for the growth rate decreases from 4 eV down to 1.8 eV in PE-CVD, indicating efficient precursor dissociation in the plasma. From our studies we conclude that the carbon attachment step is the limiting factor for the PE-CVD growth. During the early stage of growth, we observed crystalline graphene grains surrounded by amorphous carbon in Raman spectroscopy. With increasing growth time graphene flakes grow at the expense of amorphous carbon and eventually merge into an almost defect-free graphene film with a sheet resistance down to 470 $\Omega$/sq.

References

2:30 PM NM01.02.04  
**Layer Number Determination of Graphene on Nickel Substrate Using EELS Spectra with Scanning Auger Electron Spectroscopy**  
Masahide Shimizu1, Hiroki Kato1, Kota Shihomatsu2 and Yoshikazu Homma2; 1JEOL Ltd., Tokyo, Japan; 2Tokyo University of Science, Tokyo, Japan.

Graphene is one of the atomic layered materials which has interesting physical properties such as mechanical strength, optical transparency, electron and thermal conductivity. The identification of a layer number is necessary for graphene based technology, because these properties strongly depend on a number of layers. Optical microscopy, Raman spectroscopy, scanning electron microscopy and other microscopic techniques are used to image a map of graphene layer. SEM has superior character among these various techniques for its high spatial resolution and large field of view. In order to observe graphene using scanning electron microscopy, it is necessary to detect electrons emitted by the interaction between electron beam, graphene and substrate. When the graphene on substrate are observed with SEM using secondary electrons emitted from not only graphene but also the substrate. In the present study, the effect of graphene layers on the secondary electrons including elastic and energy loss peaks were investigated using Auger electron microscopy. A carbon-doped poly crystalline nickel foil was heated (up to 900 degree or more) by electrical current supply and cooled rapidly. Through the thermal process, graphene having different number of layers was precipitated on the nickel surface by segregation. SEM observation and reflection electron energy loss spectroscopy (REELS) measurement was performed using a scanning Auger electron microscope (JAMP-9510F, JEOL Ltd.). The accelerating voltage was 1.5 kV. The full width at half maximum of the back scattered electron peak was about 0.9 eV. The angle between the SEM column and electron analyzer was 60 degree. The sample tilting axis of the sample stage was perpendicular to the plane made by SEM beam axis and analyzer collection direction, so called sagittal plane. Therefore, the sample could be set in specular geometry such as the incident and outgoing angle of electrons were the same, by tilting 30 degree. All experiments in this report were performed in the specular condition to get highest intensity for zero-loss and energy loss spectra. At the first, the sample was observed with SEM using out-lens secondary electron detector. The SEM image shows that various layer graphene segregated from the nickel foil. There was the same foil region near at the center of the foil ribbon because the center was highly heated by the DC current feed through. The SEM image shows that the layer number of graphene increased along the ribbon.

The result of REELS measurement is that the intensity of zero-loss peak monotonically decreased depending on the layer number of graphene and the shape of energy loss spectra has specific feature of each layer number of graphene on any kinds of substrate can be determined by using the elastic peak and energy loss spectra.

2:45 PM NM01.02.05  
**Scalable CVD Manufacture and Heterostructure Integration of Graphene and h-BN with Domains Size, Alignment and Layer Control**  
Ruizhi Wang1, Robert Weatherup1,2, Stephan Hofmann1 and Oliver Burton1; 1University of Cambridge, Cambridge, United Kingdom; 2University of Manchester, Manchester, United Kingdom.

Chemical vapor deposition (CVD) has emerged as the most promising method for scalable growth of two-dimensional materials (2DM), such as graphene and hexagonal boron nitride (h-BN). To improve growth, the focus has mainly been on fine-tuning the deposition process using a copper (Cu) catalyst. Notable progress has been made in understanding the nature of the as-grown 2DM. However, the high vapour pressure of Cu is a source of reactor contamination and its low melting point sets a challenging limit for any process optimization. Furthermore, 2DM are prone to contamination by trace Cu, which is a constraint for CMOS integration.[1] Here we present a holistic approach for CVD of 2DM starting with the choice of the catalyst. Based on considerations including accessible CVD parameter space, ease of CMOS integration, feasibility of growth and strategies for transfer, we have determined platinum (Pt) as the optimal catalyst for growth of graphene and h-BN.

The growth of graphene on Pt is critically dependent on the supply and removal of carbon from the catalyst surface by bulk diffusion. By tuning this kinetic process, it is possible to grow graphene isothermally, by precipitation or through both mechanisms. By careful tuning of the growth conditions, we can achieve continuous single-layer graphene with large domains (>0.1 mm), isolated bi-layer graphene domains (>0.05 mm) and continuous bilayer graphene.

Layer Number Determination of Graphene on Nickel Substrate Using EELS Spectra with Scanning Auger Electron Spectroscopy  
Masahide Shimizu1, Hiroki Kato1, Kota Shihomatsu2 and Yoshikazu Homma2; 1JEOL Ltd., Tokyo, Japan; 2Tokyo University of Science, Tokyo, Japan.

Graphene is one of the atomic layered materials which has interesting physical properties such as mechanical strength, optical transparency, electron and thermal conductivity. The identification of a layer number is necessary for graphene based technology, because these properties strongly depend on a number of layers. Optical microscopy, Raman spectroscopy, scanning electron microscopy and other microscopic techniques are used to image a map of graphene layer. SEM has superior character among these various techniques for its high spatial resolution and large field of view. In order to observe graphene using scanning electron microscopy, it is necessary to detect electrons emitted by the interaction between electron beam, graphene and substrate. When the graphene on substrate are observed with SEM using secondary electrons emitted from not only graphene but also the substrate. In the present study, the effect of graphene layers on the secondary electrons including elastic and energy loss peaks were investigated using Auger electron microscopy. A carbon-doped poly crystalline nickel foil was heated (up to 900 degree or more) by electrical current supply and cooled rapidly. Through the thermal process, graphene having different number of layers was precipitated on the nickel surface by segregation. SEM observation and reflection electron energy loss spectroscopy (REELS) measurement was performed using a scanning Auger electron microscope (JAMP-9510F, JEOL Ltd.). The accelerating voltage was 1.5 kV. The full width at half maximum of the back scattered electron peak was about 0.9 eV. The angle between the SEM column and electron analyzer was 60 degree. The sample tilting axis of the sample stage was perpendicular to the plane made by SEM beam axis and analyzer collection direction, so called sagittal plane. Therefore, the sample could be set in specular geometry such as the incident and outgoing angle of electrons were the same, by tilting 30 degree. All experiments in this report were performed in the specular condition to get highest intensity for zero-loss and energy loss spectra. At the first, the sample was observed with SEM using out-lens secondary electron detector. The SEM image shows that various layer graphene segregated from the nickel foil. There was the same foil region near at the center of the foil ribbon because the center was highly heated by the DC current feed through. The SEM image shows that the layer number of graphene increased along the ribbon.

The result of REELS measurement is that the intensity of zero-loss peak monotonically decreased depending on the layer number of graphene and the shape of energy loss spectra has specific feature of each layer number of graphene on any kinds of substrate can be determined by using the elastic peak and energy loss spectra.

2:45 PM NM01.02.05  
**Scalable CVD Manufacture and Heterostructure Integration of Graphene and h-BN with Domains Size, Alignment and Layer Control**  
Ruizhi Wang1, Robert Weatherup1,2, Stephan Hofmann1 and Oliver Burton1; 1University of Cambridge, Cambridge, United Kingdom; 2University of Manchester, Manchester, United Kingdom.

Chemical vapor deposition (CVD) has emerged as the most promising method for scalable growth of two-dimensional materials (2DM), such as graphene and hexagonal boron nitride (h-BN). To improve growth, the focus has mainly been on fine-tuning the deposition process using a copper (Cu) catalyst. Notable progress has been made regarding the quality of the as-grown 2DM. However, the high vapour pressure of Cu is a source of reactor contamination and its low melting point sets a challenging limit for any process optimization. Furthermore, 2DM are prone to contamination by trace Cu, which is a constraint for CMOS integration.[1] Here we present a holistic approach for CVD of 2DM starting with the choice of the catalyst. Based on considerations including accessible CVD parameter space, ease of CMOS integration, feasibility of growth and strategies for transfer, we have determined platinum (Pt) as the optimal catalyst for growth of graphene and h-BN.

The growth of graphene on Pt is critically dependent on the supply and removal of carbon from the catalyst surface by bulk diffusion. By tuning this kinetic process, it is possible to grow graphene isothermally, by precipitation or through both mechanisms. By careful tuning of the growth conditions, we can achieve continuous single-layer graphene with large domains (>0.1 mm), isolated bi-layer graphene domains (>0.05 mm) and continuous bilayer graphene.[2] While high-quality graphene alone is sufficient for certain applications, most require a van der Waals (vdW) heterostructure, where graphene is embedded within layers of h-BN. Currently, h-BN is mainly obtained through exfoliation of bulk crystals due to lack of clean methods of transferring CVD grown h-BN. Here, we present an approach to grow high quality h-BN on Pt, with domain sizes exceeding 0.5 mm, and to transfer these layers using a delamination-based process, which avoids the contamination associated with traditional transfer methods. These layers can then be used to sequentially pick up additional layers of h-BN or graphene for scalable fabrication of vdW heterostructures. To demonstrate the feasibility of our approach, we have fabricated devices that outperform existing devices relying on CVD 2DMs.[3]

Based on the in-depth understanding of the CVD growth mechanism and the subsequent integration pathway, we present a new approach to scalable
fabrication of 2DM. Instead of additional process optimization, we show how by choosing the optimal catalyst, it is possible to offer solutions to some of the pressing challenges for the scalable manufacture of 2DM. We demonstrate the growth of both graphene and h-BN, with control over layer number, domain size and alignment, and show how these layers can then be cleanly assembled to form vdW heterostructures.

References
[2] R. Weatherup & R. Wang et al., In Submission
[3] R. Wang et al., In Submission

3:00 PM BREAK
process through molecular dynamics simulations. The combined approach of in situ experimental work and theoretical studies paves the way to design suggested which of the generated species are stable at synthesis conditions, showed the geometrical structure they form, and followed the nucleation species, and (c) the catalyst. Different morphologies were obtained by controlling the dimension of the catalyst particles. Our theoretical calculations led us to design an experimental set-up that allows the control of three important factors for the formation control; namely (a) B species, (b) N structured of the BNNTs that formed later. Magnesium, a component of the precursor, was found to play a vital role that served to generate the formation. At the early stages of production large amounts of nanospheres were formed possessing tail-like structures and these were found to be the seed BNNTs in large quantities, the fundamental science particularly the nucleation and growth of BNNTs must be first understood.

Herein, we report

Swart2 and Nicole Grobert1; 1Department of Materials, University of Oxford, Oxford, United Kingdom; 2ICREA and IQCC, Universitat de Girona, Girona, Spain.

SESSION NM01.04: Poster Session I
Session Chairs: Jeffrey Fagan and Esko Kauppinen
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM01.04.01
In Situ Experimental and Theoretical Studies of the Nucleation and Growth Towards Controlling the Morphology of Boron Nitride Nanotubes Using Chemical Vapour Deposition Techniques Jesus A. Acapulco1, Seyyed Shayan Meysami1, Vitaliy Babenko1, Koen Evers1, Ruth S. Jones1, Marcel Swart1 and Nicole Grobert1; 1Department of Materials, University of Oxford, Oxford, United Kingdom; 2ICREA and IQCC, Universitat de Girona, Girona, Spain.

Structurally analogous to carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) exhibit similar mechanical and thermal properties. However, BNNTs offer additional features such as greater thermal and chemical properties, electrical resistance, and they absorb radiation. Because of these properties BNNTs have attracted much interest due to the wide range of potential applications in which they could enhance, for instance, fuel efficiency particularly in space applications, thermal management for batteries and devices1, as tissue engineering scaffolds in biomedical applications, and in applications where strong, lightweight and thermally conductive but electrically insulating materials are required. To date, the exploitation of BNNTs in applications has been hampered by their limited availability. Although few teams were able to reach yields of up to ca. 20g, the final morphology of the up-scaled BNNT suffers from massive entanglement turning the BNNTs into a felt-like material. Only a very limited number of reports investigating the actual formation of BNNTs are available. In order to produce BNNTs in large quantities, the fundamental science particularly the nucleation and growth of BNNTs must be first understood.

Herein, we report in situ short time reaction studies revealing the formation mechanism of BNNTs and show the nucleation and embryonic stage of BNNTs formation. At the early stages of production large amounts of nanospheres were formed possessing tail-like structures and these were found to be the seed structured of the BNNTs that formed later. Magnesium, a component of the precursor, was found to play a vital role that served to generate the intermediate species and medium for the diffusion of BN species essential for the formation of BNNTs. Our findings led us to design an experimental set-up that allows the control of three important factors for the formation control; namely (a) B species, (b) N species, and (c) the catalyst. Different morphologies were obtained by controlling the dimension of the catalyst particles. Our theoretical calculations suggested which of the generated species are stable at synthesis conditions, showed the geometrical structure they form, and followed the nucleation process through molecular dynamics simulations. The combined approach of in situ experimental work and theoretical studies paves the way to design
efficient production lines for the up-scaling of BNNTs and therefore provides a practical route to the efficient exploitation of BNNTs.


NM01.04.02
Use of Refractory-Metal Diffusion Inhibitors to Slow Ostwald Ripening of Catalytic Metal Particles—A Route to Ultra-Long Carbon Nanotubes (CNTs) Michael J. Bronikowski and Melissa J. King; University of Tampa, Tampa, Florida, United States.

Growth of Carbon Nanotubes (CNTs) to lengths useful in many materials applications is currently limited by a number of factors, the most important of these being Ostwald ripening and subsequent deactivation of the metal catalyst particles from which the CNTs nucleate and grow. Here is proposed and demonstrated a novel method for overcoming this limitation. It is shown that inclusion of refractory, high-melting-point metals in the metallic catalyst used for CNT growth can substantially enhance the lifetimes of the particles of catalytic metals, enabling growth of CNTs to much greater lengths than possible using the pure catalytic metals. This lifetime enhancement occurs because the refractory metal inhibits the surface diffusion of the catalyst metals, slowing the Ostwald ripening of the catalytic particles and allowing them to grow CNTs for greater times, resulting in longer CNTs. This effect has been demonstrated for several catalyst/diffusion-inhibitor systems, and results are presented and discussed here.

NM01.04.04
Computational Study on Optimization of Sheet Conductance of Carbon Nanotube Transparent Films Masaki Tsukuda and Takahiro Yamamoto; Department of Electrical Engineering, Tokyo University of Science, Katsushika, Japan.

Although Carbon nanotube (CNT) thin films are expected as flexible transparent conductive films, the physical origin of their high electric performance remains to be clarified yet due to complexity of nanotube network. This is because that individual variations in nanotube length and chirality are involved in nanotube network and its electrical conductivity also depends on geometrical network structure such as nanotube density and alignment. Therefore, understanding various properties of CNT thin film has been the subject of controversy over the last few years.

In order to understand various properties of CNT thin film, it is essential to understand relation between the network structure with the nanotube densities, alignment, length and diameter, and their electrical transport property. We thus theoretically explored how nanotube alignment affects electrical transport properties of CNT thin films, using a numerical stick-percolation-based model. In the present study, we investigate electric properties of a CNT films consisted of metallic CNTs. First, we generated two-dimensional random networks in a film. Nanotubes are distributed in a film with the fixed values of the film length of L=5 μm, the film width W=5 μm, nanotube length l_{CNT}=0.5 μm and the chirality of a nanotube as (10,10) and the angle between the axis of nanotube and x-axis as Θ. The value of Θ takes a uniformly random value in the range Θ_{max} < Θ < Θ_{min}, where Θ_{min} < Θ < 90° (we define Θ_{max} as nanotube alignment). CNT network is transformed into effective resistor network composed of the resistance R_{CNT} along an individual CNT and the junction resistance R_{j} between CNT pairs, using ref [1]-[2]. Then, we apply a nodal analysis method to calculate a current value flowing in a film and calculate the sheet conductance in the film by changing the value of angle alignment Θ_{max} for several different nanotube area densities σ.

Our simulation reveals two characteristic of CNT thin films. First, when exceeds the percolation threshold, the sheet conductance increases, depending on the increase of when Θ_{max}=90°. Sheet conductance at σ=200 tubes/μm² is 37.6 kΩ/sq, which is in good agreement with the previous experimental work (40.0 kΩ/sq)[3]. Second, when, the sheet conductance exhibits a maximum at a certain nanotube alignment angle while there is a drop of the sheet conductance caused by the function of junction resistance of the (10,10) - (10,10) CNT. This is because of the competition between the decrease in the number of junctions and lengths of the electrical conducting paths. These results would be helpful for understanding electric transport properties of complicated nanotube network structure.


NM01.04.05
Behavior of Graphite and Graphene Under Mechanochemical Activation with Hematite and Magnetite Nanoparticles Monica Soreesco and Mark Allwes; Duquesne University, Pittsburgh, Pennsylvania, United States.

Graphite-doped hematite and magnetite nanoparticles systems (~50 nm) were prepared by mechanochemical activation for milling times ranging from 2 to 12 hours. Their structural and magnetic properties were analyzed by 57Fe Mossbauer spectroscopy. The spectra corresponding to hematite milled samples were analyzed by considering two sextets, corresponding to the incorporation of the carbon atoms into the iron oxide structure. For ball milling time of 12 hours a quadrupole split doublet has been added, representing the contribution of ultrafine particles. The Mossbauer spectra of graphite-doped magnetite were resolved considering a sextet and a magnetic hyperfine field distribution, corresponding to the tetrahedral and octahedral sublattices of magnetite, respectively. A quadrupole split doublet was incorporated in the fitting of the 12-hour milled sample. The recoilless fraction of all samples was determined using our previously developed dual absorber method. It was found that the recoilless fraction of graphite-doped hematite nanoparticles decreases as function of ball milling time. The f factor of graphite-containing magnetic nanoparticles for the tetrahedral sites stays constant, while that of the octahedral sublattice decreases as function of ball milling time. These findings reinforce the idea that carbon atoms exhibit preference for the octahedral sites of magnetite.

Graphene-hematite and graphene magnetite nanoparticles systems were synthetized using mechanochemical activation for time intervals of 2-12 hours. Their structural and magnetic properties were analyzed by Mossbauer spectroscopy. For ball milling times of 2-12 hours, the least-squares fitting revealed the presence of a sextet for hematite (50.84 T), a sextet for carbon-substituted hematite (46.57 T), a broad sextet for iron carbides (29.34 T) and a quadrupole split doublet for iron-containing carbon nanoclusters (0.73 mm/s). Similarly, the Mossbauer spectra of ball-milled graphene and magnetite were consistent with the occurrence of two sextets for the tetrahedral and octahedral positions of magnetite (49.26 and 46.12 T) and the formation of iron carbides (29.5 T) at long milling times (8 and 12 hou ). Also, the appearance of the doublet representing the iron-containing carbon nanoclusters (0.73 mm/s) was manifest at the longest milling times employed. The recoilless fraction was determined from the Mossbauer spectra using our dual absorber method and it could be evidenced that the recoilless fraction exhibits maxima for the occurrence of additional phases at long milling times. If we relate the present results with the previous ones regarding milling graphite and iron oxide nanoparticles, we should note the additional appearance of the iron carbide phases and the occurrence of carbon nanoclusters. This means that graphite is not merely a source of carbon, but exhibits its own reactive properties during mechanochemical activation.

NM01.04.06
Laser Scribed Graphene Carbon “Grass” Establishing a Highly Selective, Sensitive and Low Detection-Limit, Point-of-Care Dopamine
A range of novel carbon nanomaterials, including 0D fullerene, 1D carbon nanotubes, 1D carbon nanofibers, 2D graphene and graphene oxide, and 3D carbon aerogels, has attracted considerable interest and investments from across the scientific society. Due to their excellent performance, the carbon nanomaterials have contributed significantly towards the development of miniaturized integrated point-of-care biological and chemical sensors. Graphene, as a sensing and signal transducing material is well established, and the recently developed method of “laser scabbing” has already been demonstrated as a facile approach for manufacturing graphene electronics for highly selective, sensitive biological sensing devices [1, 2]. Inspired by the different morphologies and derivatives of the carbon nanomaterials that have been fabricated, including carbon nanowalls, graphene nanoribbons, vertically aligned CNTs and laser induced graphene fibers, we first fabricated laser scribed graphene (LSG carbon grass) with a novel 3D vertical aligned tree-like morphology. We have then used the LSG carbon grass in the application of dopamine detection by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical anodic peaks of dopamine (DA), ascorbic acid (AA) and uric acid (UA) using LSG carbon grass electrode were well resolved, where UA and AA were considered as interference. The sensitivity of LSG carbon grass for DA sensing was highly improved compared to normal LSG. The fabricated LSG carbon grass sensor exhibits a sensitivity of 0.299 μA/μM and detection limit of 1 μM. The outstanding performance for dopamine detection using LSG carbon grass is a reflection of the promising future of carbon nanomaterials with interesting high surface area morphologies.

References

NM01.04.07 Electrochemical Tunneling through Atomically-Flat Hexagonal Boron Nitride Matej Velicky1, 2, 3, Sheng Hu4, Andre K. Geim2 and Robert A. Dryfe1; 1Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States; 2School of Physics and Astronomy, University of Manchester, Manchester, United Kingdom; 3School of Chemistry, University of Manchester, Manchester, United Kingdom.

Two-dimensional (2D) materials hold promise for a range of electrochemistry-related applications, including energy storage/conversion and sensing. The tunability of the electronic structure of these materials by their thickness or external stimuli such as electric field or strain suggests a range of opportunities in optoelectronics, electrochemical switching, and photocatalysis [1]. Here, we demonstrate electrochemical tunneling across monolayer and few-layer hexagonal boron nitride (hBN), a wide-gap insulator that has gained interest in device encapsulation and solid-state tunnel field-effect transistors [2]. The electrochemical behavior of tunneling devices based on ~5 μm diameter ultramicroelectrodes is studied using reversible redox mediator systems. Optical microscopy, Raman spectroscopy, and atomic force microscopy, are used to characterize the devices. We show that the tunneling current, electron transfer kinetics, and the breakdown voltage depend on the number of hBN layers between monolayer and bulk. We compare our results to other well-studied tunneling systems, such as alkylthiol chain monolayer or thin-layers of solid-state dielectrics.

Our findings show that varying the thickness of the hBN yields a tunable electrochemical response, which provides fundamental insight into the electrochemical tunneling behavior across atomically-flat insulating materials and could be exploited in applications such as electrochemical switching or surface passivation.


NM01.04.08 Electrochemical Supercapacitors from Hybrid Porous Graphene-Based 3D Structures Decorated Carbon Nanotubes-Nanoparticles Neftali L. Carreno, Jose H. Alano, Bruno Noremberg, Ricardo Marques Silva, Guilherme Maron and Lucas Rodrigues, University Federal-Pelotas, Pelotas - RS, Brazil.

The search for new supercapacitors materials is extreme importance for the development of the future of the energy sector. This is due to the fact that the technology evolution, which demands increasingly alternative devices, fast load, high power and great storage. Thus energy storage devices are currently the focus of several studies, both in the academic and industrial sector, the energy sector depends strongly on the development of the new materials. At the forefront of the materials used for electronic devices, the carbon-based materials such as graphene hybrid system with oxide (GO), carbon nanotubes (CNT) could be significant modified by chemical methods and morphology. These materials are widely used due to low density, high surface area and high hold capacity. Thus, the objective of this work is to obtain a composite on porous graphene-based 3D structures (like sponge) decorated with nanoparticles like chalcogenides (ZnS, MoS2), transition metal (Ag, Fe, Ni), nickel cobaltite (NiCo2O4), metal oxides (In2O3, SnO2, ZnO), each nanoparticles system were previously grew homogeneously and well dispersed on the multiwalled carbon nanotubes (MWNTs), under microwave-assisted hydrothermal synthesis (MHS). These hybrid composite display interesting morphology and appropriate electrochemical properties to be applied as electrodes for supercapacitors.

NM01.04.09 Temperature Dependence of Photoluminescence Spectra from a Suspended Single-Walled Carbon Nanotube with Water Ad sorption Layer Yuichiro Tamaka1, Yuta Saito1, Kazuki Yoshino1, Akiko Ora1, Shohei Chiashi1 and Yoshikazu Honma2; 1Tokyo University of Science, Shinjuku, Japan; 2The University of Tokyo, Bunkyo, Japan.

Thermal property of the single-walled carbon nanotube (SWCNT) has been intensively studied because the SWCNT is expected to be an excellent heat transport material. Many measurement methods of thermal conductivity of SWCNTs have been proposed and photoluminescence imaging spectroscopy is one of the powerful methods [1]. In this method, a suspended SWCNT is irradiated by laser, and the spatial distribution of the PL emission energy (E11) along the SWCNT axis is measured by a near-IR 2D camera, which is converted to the temperature distribution. The thermal conductivity is obtained from the temperature distribution. Thus, the accurate conversion of E11 emission energy to temperature is crucial in this method. The temperature dependence of E11 is simply expressed by Varshni’s equation independent of SWCNT chirality (n,m) when SWCNTs are in vacuum. On the other hand, when SWCNTs are located in the ambient air, water molecules adsorb on the outer surface of SWCNTs and they affect the energy of E11 [2]. Elucidation of the temperature dependence of E11 of SWCNTs with water adsorption layer is necessary to measure the thermal conductivity of SWCNTs in the ambient air. In this study, we measured the temperature dependence of the E11 in suspended SWCNTs with water adsorption. Suspended SWCNT was synthesized by
chemical vapor deposition method on a quartz pattern substrate. PL spectra were measured from suspended SWCNTs with different chirality under controlling temperatures (220 to 300 K). SWCNTs were exposed to water vapor at 300 K and the water adsorption layer was formed. It was found that the energy shifts of E11 exhibited a complicated temperature dependence depending on chirality in the case of SWCNTs with the adsorption layer. The energy shift was understood as the summation of intrinsic temperature dependence of the band-gap, the strain effect and the change of the dielectric constant of the adsorption layer. When the temperature decreased, axial strain due to the adsorption layer occurred in SWCNT. The strain changed E11 and the change clearly exhibited type-dependence [3]. The dielectric constant of the adsorption layer simply increased with decreasing temperature. Although the interaction between SWCNT and the water adsorption layer is weak, the adsorption layer drastically affected the optical properties of SWCNTs. By taking those effects into account, we could accurately determine the temperature along the tube axis.

1) K. Yoshino et al., ACS Omega 3 4352 (2018).

NM01.04.10
Multifunctional Graphene Nanocomposites for 3D Printing Applications
Maria Soria Sanchez and Gerard Tobias Rossell; Solid State Chemistry, Institute of Material Science of Barcelona, Barcelona, Spain.

In a relatively short time, 3D technology has become a new method for manufacturing prototypes and is occupying a first place in terms of research in multiple universities across the world, as well as the searching of new materials with advanced properties suitable for the development of prototypes with 3D printing. In this sense, layered graphene represents one of the most impressive materials for this purpose, due to the combination of its properties like high electrical and thermal conductivity or high mechanical strength. The main objective of the present research work is to study the impact that graphene has over the properties of the selected polymer when they are integrated in a unique compound forming a nanocomposite. In order to facilitate the integration of both components, graphene and polymer, chemical and structural modification of the layered graphene has been necessary. These modifications of the graphene lead to an improvement in the dispersion of both components, which has shown to be a critical parameter for the stress transfer from the nanoparticles to the matrix. In this way, modified graphene has been synthesized through different chemical processes, what first includes the synthesis of graphene oxide (GO) from graphite and its subsequent chemical reduction with different chemical reducing agents to obtain the reduced graphene oxide (rGO), which has similar properties to graphene. Lyophilization of the resulting graphene samples has been also carried out in order to increase the distance between graphene layers and improve the dispersion. Two different strategies has been employed during the synthesis of the nanocomposites: direct integration of the reduced graphene oxide (rGO) into the matrix of the polymer through solution in proper solvents (DMF and THF), and reduction in situ of the graphene oxide already integrated into the polymer structure. In both cases it is necessary the complete elimination of the solvent to ensure that the electrical and mechanical properties of the nanocomposite are not affected by the presence of traces of solvent. Polymers most commonly used in 3D printing have been used in this work, including ABS, PCL and PLA filaments. Nanocomposites were prepared with several loads of graphene between 3% and 15%, in order to compare the mechanical and electrical properties before being used in 3D printing. Graphene loading is also an important factor to take into account since too much loading could hinder the printing process due to the formation of graphene agglomerates. Characterization techniques employed to evaluate the samples have shown that the mechanical reinforcement of the polymeric structures is possible by addition of both GO and rGO. It also been establish that a well dispersed rGO into the matrix not only improves properties in relation to strength and fracture toughness, but also electrical conductivity of the nanocomposite, which is not possible to get by adding only GO.

NM01.04.12
Mesoscopic Simulations of Cross-Linked Carbon Nanotube Materials—Quasi-Static Mechanical Loading, Wave Propagation and Shear Lag Effect
Md Abu Horaira Banna, Arun B. Thapa and Alexey N. Volkov; University of Alabama, Tuscaloosa, Alabama, United States.

Individual carbon nanotubes (CNTs) are one of the strongest materials in nature. Networks of pristine CNTs, however, do not show similar superior mechanical properties due to weak load transfer between individual CNTs via van-der Waals interaction. Shear load transfer between CNTs can be improved by introducing covalent cross-links between nanotubes by means of ion or electron beam irradiation or chemical functionalization. The goal of this work is to quantify the effect of cross-links on quasi-static and dynamic mechanical properties of CNT network materials like CNT films, fibers, and aerogels in large-scale mesoscopic simulations. In our mesoscopic computational model, every nanotube is represented by a chain of stretchable cylinders. Mesoscopic force field accounts for stretching, bending and buckling of individual nanotubes, van-der Walls interactions, and cross-links between nanotubes. In order to account for the load transfer on individual CNTs, we developed a novel effective bond model. This model is parameterized based on results of atomistic simulations of pulling out of a central CNT from a seven-tube bundle performed in a range of CNT diameters and cross-link linear densities. The developed model is first applied to study the shear load transfer in long CNT bundles. The simulations reveal extremely strong shear lag effect, which sets limits on the ability of cross-links to reinforce nanotube bundles. Next, we perform simulation of quasi-static and dynamic wave loading of CNT films, aerogels, and fibers. The equilibrium networks structures in these materials are obtained in preliminary mesoscopic simulations as a result of self-assembly of dispersed nanotubes into networks of entangled bundles. The cross-links are distributed inside these in-silico generated CNT material samples in order to simulate the process of irradiation or chemical functionalization of pre-existing networks of nanotubes. The simulations show that the dominant mechanisms of non-reversible structural changes in CNT networks under an applied mechanical load strongly depend on the deformation rate. The elastic and inelastic properties of CNT materials, as well as the acoustic speed, are found for materials with various degrees of anisotropy, density, CNT length, and density of cross-links. This work is supported by the NSF CAREER award CMMI-1554589 and NASA Early Stage Innovations program (project NNX16AD99G).

NM01.04.13
The Interaction of Carbon and Boron Nitride Nanotubes with Metals
Christoph Rohmann1, 2, 3, Zwolak Michael1 and Searles Debra1; 1Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2The Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States; 3Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland, Australia.

The interaction of carbon and boron nitride nanotubes with metals is significant for a wide variety of applications. For example, the binding of tubes to transition metal nanoparticles plays a role in their catalytic growth, as well as in their nucleation. Similarly, the strength of nanotube-metal composites crucially depends on the interaction strength between the tube and the metal matrix. We performed quantum chemical calculations to investigate the binding strength and geometry of a variety of metals with carbon and boron nitride nanotubes. We examined both, binding by individual metal atoms and the interaction with metallic surfaces to identify possible candidates for the creation of novel metal matrix composites.
Ricin (MW~64 KDa) is one of the most toxic proteins, with LD₅₀ varying from 10 μg to 20 mg/kg depending on the uptake pathway. Being soluble in water, it's quite easy to extract from castor bean seeds. Ricin belongs to Ribosomal inhibiting protein (RIP) family and was classified by CDC (Centre of disease and control and prevention) as a category B bioterrorism agent. Detection of Ricin before or even after being assimilated may be critical to survival, as there is no efficient counter-measure against its poisoning. Ricin is composed by two chains, one bearing the enzymatic activity (chain A, RNA glycosidase) and the other one acting as a recognition/transportation moiety (chain B, galactose-binding lectin). Current methods for its detection are essentially based on SPR, ELISA, colorimetric and Raman (SERS) techniques.¹

SALDI-MS (surface assisted laser desorption ionization mass spectrometry) concerns the use of nanostructured materials (mainly carbon and semiconductive ones) that will absorb energy from UV laser helping the desorption/ionization of the analytes (with no use of organic matrix in the contrary to MALDI) followed by their subsequent detection by MS. Among their known properties, they should be anti-reflective, have low photoluminescence and low thermal conductivity. They have been shown to be very salt tolerant and highly sensitive to small compounds.² Recently, we have demonstrated that vertically aligned boron doped graphene sheets (known as carbon nanowalls, CNWs) are suitable nanomaterials for SALDI-MS detection of various small compounds including carbohydrates, lipids, peptides etc.³ However, detecting larger compounds by SALDI-MS such as proteins is still challenging. Indeed, only few examples of protein detection by SALDI-MS have been reported so far.⁴

Here, we propose, for the first time, to use CNWs for the SALDI-MS detection of the Ricin B chain (32 KDa) from buffered solutions and blood serum. A systematic study was conducted to optimize our interface by varying the dimensions of the nanowalls and the boron doping level. Other important parameters such as thermal conductivity, electrical resistivity, morphology, internal energy deposition, optical properties were also studied and discussed in correlation with the protein detection performances. Finally, the detection of Ricin was achieved and a limit of detection (LoD) found to be 8 ng/0.5 μL, meaning that for an average person weighting 70 kg, the lowest ricin’s LD₅₀ can still be detected. The ability of our CNWs to detect proteins via SALDI-MS paved the way and opened new opportunities to matrix-free LDI-MS, still limited to small compounds detection so far.

References:

NM01.04.15
Micro-Fabricated Individual CNT Point Cathode Field Emission Electron Source for Focused Electron Beam Applications
Xiuyuan Shao, Amit Banerjee and Anjam Khursheed; Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore.

There is remarkable interest and potential for field emission technology for the development of cold field emission sources for ultra-high-resolution scanning electron microscopes, lithography and other applications. However, some inherent problems have prevented the widespread practical usability of these sources, e.g. inherent ultrahigh vacuum condition requirement (10⁻¹⁰ torr), relatively poor current stability and rapid emission decay. The current report presents a cold field emission electron source which overcomes these problems based upon using a resist-assisted patterning process fabricated carbon nanotube (CNT) electron emitters. The CNT emitter was grown on a silicon (Si) substrate by direct current plasma-enhanced chemical vapor deposition (DC-PECVD), using nickel (Ni) catalytic layer patterned by a conventional photolithography process, which provided several micron-scale CNT seeds and photoresist required for CNT growth. The patterned sample was formed at 600°C over 30 min under ambient argon (Ar) in DC-PECVD. The resulting CNT emitter featured unique structural properties and the geometry is determined by the temperature, total pressure, gas ratio, and in optimized process conditions for one individual CNT emitter growth. Preliminary experiments on one free-standing CNT emitter electron beam properties with tip radii ranging from 5 nm to 60 nm demonstrate to be promising in terms of current stability, high brightness, coherence, low energy spread, and small virtual source sizes, comparable to state-of-the-art conventional cold field emission sources. The freestanding CNT emitter cold-cathode electron sources have promising application possibilities to a variety of electron microscope or lithography devices, fabrication of compact glass-sealed x-ray tubes and cold cathodes for high-resolution imaging.

NM01.04.16
Towards Pure and Large-Scale Hexagonal Boron Nitride 2D Layers—A Unique Combination of PDCs Route with SPS Process
Yangdi Li,¹ ² Catherine Journet-Gautier², Bérangère Toury², Vincent Garnier¹ and Philippe Steyer¹; ¹MATEIS, INSA Lyon, Villeurbanne, France; ²LMI, Université Lyon, Villeurbanne, France.

Since graphene's properties are strongly linked to the substrate on which it is deposited, it is clear that the promising future development of practical graphene devices will necessarily go through the development of insulating substrates on which graphene can be deposited without changing its intrinsic properties. As one of the most suitable substrates, hexagonal boron nitride nanosheets (BNNSs) are promising 2D materials for their exceptional chemical and thermal stabilities together with electrical insulating properties. These capabilities make it interesting as support for graphene in devices and also as clean, flat insulating environment for materials of heterostructure. However, in order to make h-BN relevant for real world applications, scalable synthesis routes are needed. As a consequence, the development of a novel source for highly crystallized h-BN crystals, suitable for a further exfoliation, is a prime scientific issue. We have developed a promising approach to synthesize pure and highly-crystallized h-BN crystals, which can be further exfoliated into high quality, ultrathin, uniform BNNSs. This new accessible production process represents a relevant alternative source of supply in response to the increasing need of high quality BNNSs. The synthesis strategy is based on a unique combination of Polymer Derived Ceramics (PDCs) route with Spark Plasma Sintering (SPS) process. Through a multi-scale chemical and structural investigation, it is clearly shown that obtained layers are large, defect-free and well-crystallized, which are key-characteristics for a subsequent exfoliation into relevant BNNSs.

NM01.04.17
Ultralow Platinum Carbon Electrodes by Cathodic Polarization Treatment for Efficient Hydrogen Peroxide Sensing
Muhammad Adil Riaz and Yuan Chen; School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, New South Wales, Australia.

Hydrogen peroxide (H₂O₂) is a widely used oxidizer, bleaching agent, and disinfectant in many fields, such as food processing, medicine, and environment. Thus, detecting the trace amount of H₂O₂ is essential for many industrial and biological applications. Electrochemical H₂O₂ sensors, especially nonenzymatic ones, have attracted significant interests because of their relatively simple operation, low cost and fast response. Platinum (Pt) based Electrochemical H₂O₂ sensors demonstrate superior sensing performances, i.e., higher sensitivity, wider detection concentration range and lower detection limit. However, the high mass loading and cost of Pt limits their practical applications. Here, we develop a cathodic polarization treatment method to deposit ultralow mass loading of Pt nanoparticles on a high surface area (385 m²/g) porous carbon composite substrate comprised of reduced graphene oxide (rGO) and carbon nanotubes (CNTs). Using multiple cyclic voltammetry (CV) cycles at the specific potential window (-0.8-0 V vs. standard caramel electrode) in 0.5 M H₂SO₄ electrolyte without Pt precursors, about 3.89 wt.% of Pt nanoparticles were anchored on the rGO-CNT composites with a
narrow size distribution around 1–2 nm from a Pt mesh anode. Furthermore, different Pt mass loadings on rGO-CNT composites were obtained by varying the CV cycles and their morphological and physicochemical properties were characterized by SEM/EDS, TEM, and XPS along with H$_2$O$_2$ sensing performance to understand the synthesis-structure-property relationships. The optimized Pt/rGO-CNT composite obtained at 3000 CV cycles shows superior H$_2$O$_2$ sensing performances with a detection limit of 10 µM, a wide linear range up to 15 mM, and the sensitivity of 2027 µA/mM·cm$^2$, which are one of the best among recently reported Pt/carbon composites and commercial 20 wt.% Pt/C catalysts. Further, the Pt/rGO-CNT sensor can also detect trace amount of H$_2$O$_2$ in milk and juice samples, demonstrating their excellent practical application potentials.

NM01.04.18
Selenium-Functionalized Graphene Oxide that Can Modulate the Balance of Reactive Oxygen Species Jiahao Xia and Huaping Xu; Department of Chemistry, Tsinghua University, Beijing, China.

Graphene oxide (GO) is an important two-dimensional material since it is water soluble and can be functionalized to adapt to different applications. Diselenide bond is a dynamic covalent bond and can respond to both redox condition and visible light irradiation in a sensitive manner. In this work, by combining the stimuli response of diselenide bond and the oxidative/radical attackable nature of GO, we achieved the in situ covalent functionalization of GO simply by stirring GO with diselenide-containing molecules in aqueous solution. The covalent functionalization was proven by FT-IR, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Atomic Force Microscopy (AFM), etc. And the functionalization mechanism was deduced to involve both redox reaction and radical addition reaction according to the XPS, Atomic Emission Spectroscopy (AES), etc. Moreover, we found the selenium-functionalized GO could modulate the balance of reactive oxygen species (ROS). Specifically, GOSe could decrease ROS level by accelerating the reduction of peroxides when the ROS concentration is high while boosting the ROS level by in situ generating ROS when its concentration is relatively low.

NM01.04.19
High Aspect Ratio Nanomaterials in Corrosion Protection Composite Coatings David W. Johnson1, Alex Borak1, Carmen Espejo2, Simon Gibbon1, Steven Gourlay1, David James3, Jennifer MacKay3 and Jonathan Moghal1; 1Centre for Process Innovation, Sedgefield, United Kingdom; 2Crown Technology, Wantage, United Kingdom; 3Akzo Nobel, Northallerton, United Kingdom; *Akzo Nobel, Birmingham, United Kingdom; Thomas Swan, Consett, United Kingdom.

Anti-corrosion coatings are ubiquitous with an expected market value of $20 billion by 2025. Current innovation is being driven by both demand and regulatory restrictions. (Global Market Insights 2016) A promising option is the incorporation of high aspect ratio nanomaterials (HARNs), such as graphene and boron nitride, as polymer composite coatings. (Liu, et al. 2016)

It has previously been shown that platelet like materials can improve the performance of anti-corrosion coatings. This is typically thought to be due to the creation of a "tortuous path" in which corrosive media (typically water, electrolytes and oxygen) must follow a long path through a network of impermeable filler to reach the metal substrate. (Zheng, et al. 2017) This effect is maximised when the platelets are high aspect ratio and aligned parallel to the metal substrate.

While the concept of such a system is simple there are several complex factors to consider in the production of a working coating. In producing HARNs it is challenging to control morphology and achieve both the large lateral dimensions and the thin sheet sizes desired. Dispersing HARNs in resin also presents challenges as aggregates reduce the effective aspect ratio and risks creating porous structures through which electrolytes can penetrate. Once dispersed the nanomaterial must remain wetted by the resin throughout the cure process to avoid generating voids and an associated decrease in performance. Finally, the coating must remain adhered to the substrate and not delaminate.

In this work we present data on the effect of HARN morphology and surface energy on the barrier performance of a protective coating. Consideration is given to how these variables may affect nanomaterial dispersion quality, porosity and interaction with the metal substrate. Initial results indicate that dispersion quality and HARN surface chemistry both influence performance.


NM01.04.20
Heterogeneous Metal Oxide-Graphene Porous Single Fiber Derived from Engineered Graphene-Tunicate for Sensitive Chemiresistor Ji-Soo Jang and Il Doo Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Graphene oxide liquid crystal (GOLC) behavior is very intriguing and powerful phenomenon, especially for simply achieving graphene-based fibers, which have ordered graphene alignments in fiber. Taking advantages of graphene based fiber such as high mechanical strength, electrical conductivity, and supercapacitive behavior, various applications such as energy storage, photovoltaic cell, and chemical sensing have been explosively exploited. Although graphene based fiber have opened up great opportunities for various researches, high graphene density in graphene based fiber is disadvantageous for the creation of pores on graphene based fiber. This effect is maximised when the platelets are high aspect ratio and aligned parallel to the metal substrate.

In this work, we propose a facile synthetic route for providing high density of pores in graphene based fiber by employing tunicate cellulose nanofiber (TCNF) engineering. For the first time, by using the liquid crystal (LC) behavior of graphene oxide (GO)-TCNF composite, we successfully develop the ultra-porous GO fibers due to the random distribution of TCNF in GO fiber. Furthermore, by using the super-hydrophilicity of TCNF, TCNF in GO fiber is also used as seed layer for growth of WO$_3$ nanorods (NRs), leading to formation of porous WO$_3$ NRs-GO thorn-bush like composite single fiber. Due to its high porosity and heterogeneous junction effect (WO$_3$ NRs-GO), porous WO$_3$ NRs-GO showed reversible NO$_2$ detection capability even at 1 ppm level of NO$_2$ chemicals.
Design of Microwave Absorption Structures Based on Magnetite Multi-Granule Nanocluster–Multiwall Carbon Nanotube Composite Materials

Boo Hyun An1, Bum Chul Park2, Sahith R. Madara1, Hamad Al Yass1, Jung-Rae Park4, Jong E. Ryu1, Mihai Sanduleanu1, Young Keun Kim1 and Daniel S. Cha1; 1Kaifila University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Korea University, Seoul, Korea (the Republic of); 3Amity University, Dubai, United Arab Emirates; 4Minotech, Charlton, Massachusetts, United States; 5North Carolina State University, Raleigh, Indiana, United States.

Recently, reduction and cancellation technique of microwave has been widely studied in military and civil areas for various applications such as radar absorption, electromagnetic interference (EMI) shielding, reduction of electromagnetic wave pollution, and wireless communication fields. Research on microwave absorption materials is widely conducted by adopting dielectric and magnetic powder material to conductive matrix, because the conductivity, dielectric constant and permeability of the materials are contributing to the microwave absorption efficiency of the materials. [1-3]

Carbon nanotubes (CNT) are good candidate materials for the conductive matrix of microwave absorption composite structures due to their high electrical conductivity, light weight, and easiness to form thin layers. Ferrite nanostructures are generally used for microwave absorbing materials due to their magnetic and dielectric property. The electromagnetic properties of ferrites are different depending on microstructural and physical properties of the ferrites such as chemical composition, crystal structure, crystallite size, particle size. Such properties can be controlled by synthesis techniques and our novel synthesis method of multi-granule nanocluster (MGNC) of magnetite (Fe3O4) by controlling the cluster and granule size with the modified hydrothermal polyl process was previously reported [4].

In this study, we fabricated Fe3O4 MGNC – multiwall CNT (MWCNT) composites by using the surface-engineered tape-casting (SETC) method with various granule and particle size of MGNCs. The microstructural and microwave absorption properties in X-band (8.2 GHz – 12.4 GHz) with different granule size of the nanoclusters are investigated. Design and three-dimensional (3D) printing of the 3D metamaterials based on the nanocomposite materials made up of MGNC and MWSNT are also in progress.

Reference
Designing a Catalyst for Carbon Nanotube Growth by \textit{Ab Initio} Molecular Dynamics with Respect to the Carbon Source Molecule Dissociation Process Satoru Fukuhara1, Masaaki Misawa2, Fuyuki Shimjo2 and Yasushi Shibuta3; 1Department of Materials Engineering, The University of Tokyo, Tokyo, Japan; 2Department of Physics, Kumamoto University, Kumamoto, Japan.

For the application of carbon nanotubes (CNTs), a synthesis method which can control its property (e.g. length, diameter and chirality) is required. Catalytic chemical vapor deposition (CCVD) method is the standard way to produce CNTs. In this method, the quality and quantity of CNTs largely depends on the combination of the catalyst and the carbon source. For example when using ethanol as the carbon source, which C-O bond or C-C bond dissociates have effect on CNT growth. In order to develop a better catalyst, it is required to know the mechanism of the dissociation process. In this research, we clarify the difference of carbon atom dissociation reaction mechanism by catalysis element from the atomistic viewpoint, using the \textit{ab initio} molecular dynamics method (AIMD method) and clarify the advantages of using the alloy catalyst and give guidance to new catalyst design. The dissociation process of ethanol and carbon monoxide on Fe, Co, FeCo alloy catalyst is investigated by AIMD. 30 ethanol molecules and 30 carbon monoxide molecules are placed around the Fe12, Co12, Fe6Co6 clusters, respectively. The dissociation process of 5 ps for ethanol molecules and 2 ps for carbon monoxide molecules is analyzed at 1500 K. C-H bond and C-O bond of ethanol have been observed to dissociate on each catalysts, but C-C bond dissociation is only observed on Fe6Co6 catalyst. Regarding the calculation of carbon monoxide, C-O bond dissociation is only observed on Fe catalyst.

We have clarified that bond formation of oxygen and metal atoms is important in dissociation reaction mechanism. Specifically, strong bonds with oxygen as seen with Fe atoms are disadvantageous in C-C bond dissociation but are necessary for C-O bond dissociation in ethanol and CO molecules. From these results, it is possible to design a catalyst that dissociates both C-C bonds and C-O bonds by alloying elements that form strong bonds with oxygen.

The Effect of Heat Treatment on the Structural Development and Mechanical Properties of Carbon Fibers Jeong-Fum Lee, Sojeong Hae, Kyeonghun Choi, Sang-Ha Hwang, Youngho Eom and Han Gi Chae; Ulisan National Institute of Science and Technology, Ulisan, Korea (the Republic of).

Carbon fibers have been of great interest in many industrial applications due to their high specific mechanical properties. The tensile strength of the polyacrylonitrile (PAN)-based commercial carbon fiber is as high as 7 GPa, and the highest tensile modulus is about 600 GPa although the theoretical properties of carbon fibers are known to be 150 GPa and 1000 GPa, respectively. The property discrepancy is attributed to the defective structures including voids and structural heterogeneity. In addition, carbon fibers are often subjected to extreme environment such as high stress and high temperature, which may change their microstructure and properties. In this study, we have heat-treated commercial carbon fibers as high as 2400 °C without applying external stress, and traced the changes in microstructure using Raman spectroscopy, wide-angle X-ray diffraction, and X-ray photoelectron spectroscopy. The tensile testing and nano-indentation experiment were also conducted to examine the correlation between the microstructural variation and corresponding mechanical properties. The structure-property relationship of carbon fibers upon high temperature heat treatment will be presented.

Using Cell Membrane Models to Investigate the Toxicity of Carbon-Based Nanomaterials Juliana Cancino1, 2 and Valtencir Zucolotto3, 2; 1University of Sao Paulo, Sao Carlos, Brazil; 2Nanomedicine and Nanotoxicology Group, University of Sao Paulo, Sao Carlos, Brazil.

Single-wall carbon nanotubes (SWCNTs) and polyanidoamine dendrimers (PAMAM) have been proposed for a variety of biomedical applications due to their unique physico-chemical properties. However, toxicological studies have shown that these nanomaterials may exhibit high toxicity in biological environments. In this study we used C2C12 murine cells and membrane model systems to understand the interactions occurring at the bio-nano interface, as well as the possible toxicity exhibited by SWCNT-PAMAM conjugates against mamalian cells. The results showed that SWCNT-PAMAM and PAMAM inhibited the proliferation and caused DNA damage in C2C12 cells. Flow cytometry analyses revealed a less toxicity in C2C12 cells exposed to SWCNT compared to the other nanomaterials. The toxicity of SWCNT, SWCNT-PAMAM, and PAMAM in C2C12 cells are strongly correlated with the charge of the nanomaterials. The membrane model studies revealed a pronounced incorporation of SWCNT-PAMAM through dipalmitoylphosphatidylcholine (DPPC) monolayers even at high surface pressure values, ~30 mN/m. Therefore, the results confirm that the presence of the nanomaterial affects the packing of the synthetic membrane monolayers. The methodology introduced here may be of great importance for further nanotoxicity studies.

Detection of Acute Kidney Injury Biomarker Using Reduced Oxide Graphene Transistors Fabricio Santos1, 2, Nilton C. Vieira1, Naiara Zambianco1 and Valtencir Zucolotto1, 2; 1University of Sao Paulo, Sao Carlos, Brazil; 2Institute of Science and Technology, Federal University of Sao Paulo, Sao Jose dos Campos, Brazil, Brazil; 3Nanomedicine and Nanotoxicology Group, University of Sao Paulo, Sao Carlos, Brazil.

The early detection of biomarkers of renal damage is important because the glomerular filtration rate is reduced before the onset of the signs of renal failure. Cystatin C is a protein that has been identified as the most promising biomarker to acute kidney injury diagnosis in early stages. Here, we introduce a papain-modified graphene oxide field-effect transistor (rGOFET) for the detection of Cystatin C with enhanced sensitivity. The rGOFETs were fabricated using the layer-by-layer (LBL) technique, employing oppositely charged rGO onto interdigitated gold electrodes. Detection of Cystatin C occurred via electrical measurements upon monitoring output and/or transfer curves of rGOFETs. The detection mechanism is based on changes of the charge balance at the electrode surface after the formation of papain/cystatin C complex. Cystatin C could be detected at a concentration range from 5 ng/mL-1 to 100 ng/mL-1 with 0.13 mV/nmL-1 sensitivity, suggesting that the system may useful for clinical purposes.

Enhanced Conductivity and Thermal Stability of Carbon Nanotube Yarns via Densification and Chemical Doping Karen Soule1, 2, Colleen C. Lawlor1, 2, Andrew R. Bucoissi3, Cory D. Cress, Ivan Puchades1, 2 and Brian Landi1, 2; 1Nanopower Research Laboratory, Rochester, New York, United States; 2Electronics Science & Technology, U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Carbon nanotube (CNT) based conductors are candidate light-weight and robust alternatives to conventional metal conductors for a variety of space, defense, and power transmission applications. Although the conductivity of bulk CNT materials is still an order of magnitude less than copper conductors, these demanding applications can benefit from the reduction in weight, increased flexure tolerance, and corrosion resistance provided by CNT conductors. Previously, CNT conductors have been produced from commercially available CNT sheet material, which is rolled into wires of varying diameter. Radial densification and chemical doping with aqueous KAuBr4 has been used to increase the conductivity of these rolled conductors by an order of magnitude.
These works demonstrated the possibilities of CNT conductors along with the effects of densification and chemical doping, but these techniques are limited in scalability due to the batch nature of CNT sheet production. Recently, continuous processes have allowed for the production of CNT yarns available in kilometer lengths, a breakthrough needed for the practical implementation of CNT conductors. With the synthesis of scaled CNT conductors, the operational stability of these materials along with the accompanying chemical doping procedures needs to be explored.

NM01.04.30
Polyacrylamide Covalent Grafted on Graphene Oxide (GO) Surface for Extraction of Chromium(VI) Pei P. Yang1, 2, Ruimin Li1, 2 and Jun Wang1. 2, 3, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, China; 4, Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin University, Harbin, China.

With the rapid growth of industrialization, water pollution caused by heavy metals has become one of the most serious environmental problems, and attracted considerable attention. Heavy metals are non-degradable and can accumulate in living tissues, so they must be removed from wastewater. Extraction of heavy metals from wastewater embraces reverse osmosis, chemical precipitation, electrodialysis, organic−inorganic ion exchange, and adsorption. Among these methods, adsorption plays a significant role due to its simple operation and cost-effectiveness. Thus far, the most efficient adsorbent for the adsorption of heavy metals have not been suitable for application at wastewater pH. Currently, the design of a suitable wastewater adsorbent shows more promise for the extraction of heavy metals. In this report, we report a facile approach to construct a suitable wastewater pH and large surface area material that polyacrylamide (PAM) covalent grafted onto the surface of GO nanosheets. In the progress, transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used to determine the effectiveness of the synthesis of GO-PAM composites. Meanwhile, the GO-PAM composites were investigated for adsorption of Cr(VI) from aqueous solution. It is clear that the GO-PAM composites have a high adsorption capacity (qm = 398.2 mg g⁻¹, t=298.15 K) at a suitable wastewater pH with a high removal rate (~90%). Based on the FTIR spectroscopy, Zeta potential, and X-ray photoelectron spectroscopy (XPS), a possible adsorption mechanism of Cr(VI) onto GO-PAM composites is revealed. Finally, the result also exhibited outstanding adsorption efficiency and adsorption capacity under the operating conditions for the adsorption-desorption of Cr(VI) from aqueous solution, which indicated a promising potential in the application of the absorbent in wastewater. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

NM01.04.32
Are Carbon Nanotubes Intrinsically Hydrophilic? Grzegorz Stan1, Damian Łukawski2, Filip Lisiecki3 and Dawid Janas1; 1, Silesian University of Technology, Gliwice, Poland; 2, Faculty of Technical Physics, Poznan University of Technology, Poznan, Poland; 3, Institute of Molecular Physics, Polish Academy of Sciences, Poznan, Poland.

Although carbon nanostructures such as carbon nanotubes (CNTs) and graphene have shown promising properties on the electrical [1], thermal [2] and mechanical [3] fronts, their implementation is somewhat restricted because they are incompatible with the most of traditional polymer matrices. The problem is commonly explained by the nature of their surface, which has been considered as highly hydrophobic for many years. The employed main-stream solution is focused on chemical functionalization to introduce certain functional groups to make the surface hydrophilic. We have recently shown that carbon nanotube networks can have unexpectedly high hydrophilic character without any grafting if the films are briefly annealed at high temperature, which does not need to involve oxidation [4,5]. In this contribution, we would like to present an explanation of this effect and mark what are the most immediate applications of this high-performance material.

References:

NM01.04.33
Enhancement of X-Ray Shielding Properties of PVDF/BaSO4 Nanocomposites Filled with Graphene Liliane A. Silva1, Adriana M. Batista2 and L.O. Faria3; 1Engenharia Nuclear, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil; 2Anatomia e Imagem, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil; 3Materials, Development Center of Nuclear Technology, Belo Horizonte, Brazil.

Carbon nanotubes (NTCs) and graphene-based nanocomposites have been reported to enhance the X-ray shielding effects, for photons with energy below 17 keV [1,2]. The mechanisms behind this anomalous behavior cannot be interpreted by the already established X-ray absorption theory. In this work, we report additional evidences of the improvement of X-ray attenuation efficiency by the addition of a very small amount of reduced graphene oxide (4.0 wt %) in polymer composites made of poly(vinylene fluoride) (PVDF) homopolymer and barium sulfate (BaSO4) nanoparticles. The investigation was performed by using polycrystalline spectra produced by an X-ray tube energized with 20, 30, 40, 60, 80 and 100 kV. For the lowest voltage (20 kV), the beam attenuation for pure PVDF/BaSO4 nanocomposite (50%/50%) and the one with the addition of 4.0 wt % of rGO was found to be 9.14% and 24.56%, respectively. The respective linear attenuation coefficients (μ) were 39.9 cm⁻¹ and 54.4 cm⁻¹, respectively. The X-ray attenuation gradually decreases until 6.71% and 17.62%, respectively, for the highest energy spectrum (100 kV). Fourier transform infrared data revealed that, due to the lack of the bending vibration modes of CF₃ molecule at 656 cm⁻¹, 688 cm⁻¹, 723 cm⁻¹, 776 cm⁻¹ and 796 cm⁻¹, characteristics of the γ-crystalline phase of PVDF, the nanocomposites casted from solution are mostly in the β-ferroelectric phase of PVDF, besides the γ-paraelectric phase. SEM micrographs were used to
evaluate the dispersion state of graphene sheets and the BaSO4 nanoparticles into the polymeric matrix. UV-Vis spectrometry and Differential Scanning Calorimetry were also performed in order to complement the structural analysis. The results confirm that the addition of graphene sheets in PVDF polymer-based nanocomposites enhances the X-ray features. The phenomenon is discussed in terms of the reported anomalous negative thermal expansion coefficient of graphene sheets [3].

References


NM01.04.34
The Stability of Humidity Sensor Response in Graphene by Low Damage Plasma Chung-Huan Lin Lin1, Mingshiu Tsai1, Weitong Chen1, Chihsien Huang2, Weiyen Wong1 and Chiting Lin1; 1Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan; 2Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan; 3Physics, National Central University, Jangli, Taiwan.

Graphene has been recognized as a promising material for sensing applications, such as gas detection and biomolecular sensor. Although it has been demonstrated to have good sensitive characteristics, some essential aspects such as stability need to be improved for further applications. To conquer these obstacles, different kinds of surface functionalization, for example particle doping, chemical modification, and UV irradiation are used to demonstrate improvements of repeatability and stability with the cost of sensitivity degradation. Following surface functionalization idea, in this work, we used a low-damage oxygen plasma to functionalize a bilayer graphene sheet without high-energy ion bombardment and UV irradiation damage on the graphene structure. This leads to an improved stability of the developed bilayer graphene humidity sensor. Based on the experimental observation of Raman spectroscopy, the D/G ratio showed the result of the low-damage plasma functionalization and the integrity of graphene structure. Utilizing XPS spectra, at the same time, we found the fact that the compositional ratio of C-OH is increased with modified time. Similar observations can also be indicated by wettability enhancement by contact angle measurement. According to these experimental characterizations, one possible scenario is that the upper layer of the bilayer graphene is the one of the functionalization and the lower layer of the bilayer graphene keeps its original 2D structure. Then the developed low-damage bilayer graphene can be experimentally demonstrated as a humidity sensing material. Compared with traditional graphene humidity sensors, the developed low-damage bilayer graphene humidity sensor has less drifting. The drifting result is followed from the x electron adsorption, which can easily adsorb molecules, including the water molecule and the other air molecules. These adsorbed molecules are difficult to be desorbed from the surface and cause sensor degradations. In our low-damage bilayer graphene, there are high surface ratio of O-H bond introduced by the low-damage oxygen plasma. As a result, the surface with less x-electron help water molecule to be desorbed from the surface. This results in a stable sensitive response to humidity. This work raises a method which potentially helps to functionalize graphene-based sensing materials.

NM01.04.35

In this work, a partially reduced graphene oxide (GO) biosensor is presented. Mild thermal treatment is used to reduce GO drop-casted on a SiO2 substrate, after hydrophylization and functionalization. As a result of the reduction, the graphene sp2 lattice of GO is gradually restored and its electrical conductivity is enhanced. At the same time, the GO retains functional groups during the course of the reduction, thus facilitating the immobilization of proteins on its surface. To confirm this, Biotinylated Bovine Serum Albumin (b-BSA) was used as a model molecule in protein immobilization experiments. The immobilization of b-BSA was affirmed by inspecting the GO drops under a fluorescence microscope after reaction with the fluorescently labeled streptavidin. Reduced GO biosensors were then constructed by first drop-casting GO on APTES functionalized SiO2 substrates followed by a mild thermal treatment (heating for 1 h at 180°C) in order to achieve both protein immobilization and a conductive state. Silver paint conductive adhesive was then used to contact the GO drops. To test the sensor in the detection of b-BSA immobilization, a plastic frame was placed around the GO drops in order to contain the reaction fluids and prevent short-circuiting while resistance measurements were taken using the following procedure: a) inserting buffer solution in the frame and over the GO, b) adding different concentrations of b-BSA and monitor its immobilization, c) adding BSA blocking, and d) adding streptavidin at various concentrations. Using this procedure the sensor was capable to detect b-BSA concentrations down to 200 pM. Based on these initial results the sensor was then used in a medically relevant application which involves the detection of BRCA1 gene. For this experiment the characteristic gene sequence of BRCA1 is amplified and tagged during amplification with a biotin molecule at its end using Recombinase Polymerase Amplification (RPA) at 37°C for 30min. RPA was chosen as it possesses many advantages over other amplifications methods in terms of speed, portability, accessibility, sensitivity and specificity. Next, the GO sensor was prepared by drop-casting and immobilizing streptavidin over the reduced GO through non-covalent binding. Upon insertion, then, of the amplified DNA the biotin end interacts with the immobilized streptavidin. Using this scheme DNA concentrations down to 200pM was detected. These findings thus demonstrate the ability of the proposed sensor to detect on the one hand the immobilization of biotin on the sensor as well as its usefulness in a real world application. Further work will focus on further optimizing the sensor by introducing DNA probes for label free detection.


NM01.04.36
Doping of Boron or Nitrogen to Multilayered Graphene Grown on Copper by Simultaneous Thermal Chemical Vapor Deposition of Methane and the Vapor of Phenylboronic Acid or Melamine Ryoko Furukawa, Yuno Yamamoto, Yoji Nabe and Shunji Bandow; Meijo University, Nagoya, Japan.

Either boron or nitrogen doping was carried out while growing of graphene on a copper foil. For the boron doping, mixture of methane and the dopant vapor of phenylboronic acid, which was generated by heating between 393 and 433 K, was introduced to the furnace kept at 1273 K where the Cu foil was placed. For the nitrogen doping, we used the vapor of melamine generated at 473 K. Prior to grow of the doped graphene on Cu, the Cu foil was annealed at 1273 K for 8 hours under flowing of 20 sccm H2 at 3 kPa in order to improve the flatness of surface. Growth of the doped graphene was carried out for 2
hours at 1173-1273 K at the pressure of 3 kPa with a total flow of 100 sccm of the mixture of PR gas (10% CH₄ in Ar) and Ar gas for carrying phenylboronic acid or maleimide vapor by adding 2 sccm H₂. After growing the doped graphene, gas flow was switched to the mixture of 5 sccm H₂ and 50 sccm Ar at 3 kPa, then cooled. Cooling rate was ca. 40 K/min by 1073 K.

It was found that low pressure annealing of Cu foil was drastically improved the flatness of the surface, which would be a great benefit for growing graphene. From the Raman scattering, the number of the layers of the doped graphene was found to be excess of 5 layers which was evaluated by the intensity ratio of G'/G. Doping amount was evaluated by XPS, which was taken by an Al-Kα excitation, and was found to be in the range of a few at% for both B and N. In addition, rate of substitutional doping of B for C was increased when low level of phenylboronic acid vapor was mixed with methane by decreasing a vaporizing temperature of the dopant by 393 K. For the nitrogen doping, substitutional doping of N for C (quaternary N) was enhanced as decreasing growth temperature of graphene by 1173 K. In case of high temperature doping at 1273 K, pyridine-like (or pyrrole-like) N accompanying with atomic defect at the next of N became a major component for N-doped graphene. Electric conducting feature of B-doped and N-doped multilayered graphene would be opened as the results of sample characterization.

Acknowledgement: This work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, and by the National Science Foundation. Computational resources have been provided by DOE at Lawrence Berkeley National Laboratory, Berkeley, California, United States.

SESSION NM01.05: Structure and Properties II
Session Chairs: Jeffrey Fagan and Hua Jiang
Sheraton, 2nd Floor, Republic AB

8:30 AM "NM01.05.01 Strategies for the Chirality Control During Carbon Nanotubes’ Growth Feng Ding1, 1; 1Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2Center for Multidimensional Carbon Materials, Institute for Basic Science, Ulsan, Korea (the Republic of).

The formation of the cap structure determines the chirality of the consequent SWCNT and the addition of the last pentagon can turn the SWCNT into one with any possible chiral angle. Therefore, the random formation of the last pentagon during SWCNT nucleation explains the even distribution of chiral angles in most SWNT samples. During the cap formation, an external bias that affects the addition of the last pentagon may lead to the chirality-selected SWCNT growth. Detailed theoretical and experimental study suggests that the growth of (2n,n)-rich SWNT samples can be achieved by catalyst surface symmetry control. Besides the nucleation stage, varying the chirality during SWNT growth is predicted to be another route towards the chirality-specific SWNTs synthesis. Such a predication has been successfully realized by experimental studies and the synthesized SWNTs show exact chirality distribution as predicted theoretically.

9:00 AM NM01.05.02 Theory of Topological Phases and Topological Band Engineering of Graphene Nanoribbons Ting Cao1, 2, Fangzhou Zhao1, 2 and Steven G. Louie1, 2, 1Department of Physics, University of California, Berkeley, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Topological insulators (TIs) are an emerging class of materials that host highly robust in-gap boundary states while maintaining an insulating bulk. While most notable scientific advancements in this field have been focused on TIs and related topological crystalline insulators in 2D and 3D, we have shown that 1D symmetry-protected topological phases exist in graphene nanoribbons (GNRs) [1]. Using first-principles and model Hamiltonian calculations, we discover that semiconducting GNRs of different width, edge shape, and terminating unit cells can belong to electronic topological classes characterized by different values of an Z₂ invariant. Interfaces between topologically distinct GNRs characterized by different Z₂ are predicted to support robust in-gap topological interface states which can be utilized as a tool for material engineering.

The experimental realizations of these predictions and rational design of a topologically-engineered GNR superlattice synthesized from molecular precursors have been achieved [2,3]. Such GNR superlattice hosts a 1D array of topological interface states, which generates novel robust electronic bands with desirable properties. We present here the theoretical basis and calculations for these states. The band width and band gap of the topology-induced bands are tunable by the coupling between the adjacent topological interface states, which may be varied for example by varying the segment lengths. This novel manifestation of 1D topological phases presents a new route to band engineering in 1D materials based on precise control of their electronic topology, and is a promising platform for future studies of 1D quantum spin physics.


Acknowledgement: This work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, and by the National Science Foundation. Computational resources have been provided by DOE at Lawrence Berkeley National Laboratory's NERSC facility. Collaboration with the experimental groups of Professor Michael Crommie and of Professor Felix Fischer is gratefully acknowledged.

9:15 AM NM01.05.03 One-Third-Hydrogenated Graphene—The Fabrication and Anisotropic Electronic Properties Yuyang Zhang1, Hui Chen1, De-Liang Bao1, Shixuan Du1, Sokrates T. Pantelides3 and Hong-Jun Gao1, 1Chinese Academy of Sciences, Beijing, China; 2Vanderbilt University, Nashville, Tennessee, United States.

The hydrogenation of graphene is a powerful tool to change the carbon hybridization from sp² to sp³, which introduces a finite band gap and generates magnetic moments to make graphene functionalized. Large-scale periodically-hydrogenated graphene, namely with hydrogen atoms chemisorbed in a uniformly-periodic manner, can also be viewed as new kinds of two-dimensional (2D) crystalline materials, e.g. graphene, graphone, and 2D CₓHₙ. These new 2D crystals have been predicted to exhibit unique electronic structures beyond graphene, such as large band gap (graphane) and ferromagnetism (graphone). In hydrogenated graphene, however, the electronic properties strongly rely on the distributions of hydrogen atom. Thus, the fabrication of large-scale, periodically-hydrogenated graphene is critical important as the first step towards potential applications.
Here, in a combined investigation of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low-energy electron diffraction (LEED), Raman spectroscopy, and density-functional theory (DFT) calculations, we present the formation and anisotropic electronic properties of the single-crystal, millimeter-scale, one third hydrogenated graphene (OPTH) on Ru(0001) substrates. Monolayer graphene (MLG) was firstly synthesized on Ru(0001). The as-fabricated monolayer graphene was then exposed to atomic hydrogen generated by a radio-frequency (RF) atom source for 20 minutes and subsequently annealed to ~1200 K for 20 minutes. After four cycles of hydrogen exposure and subsequent annealing, the sample was characterized by STM and LEED. STM images show that the sample exhibits a moiré pattern with a periodicity of ~2.6 Å. Based on atomic-resolution STM images and LEED pattern, a double-sided 3√3×3√3R30° hydrogen-adsorbed structure was proposed. Simulated STM images show excellent agreements with experimental observed STM images validating the atomic model. The size and uniformity of the fabricated OPTH were checked by taking LEED patterns and STM images on different locations of the sample. We demonstrate that the single-crystal OTHG sample has areas up to 16 mm² (the size of the Ru substrate). Raman spectra and STS measurement indicate that the interaction between the fabricated OTHG and Ru substrate is weak. DFT calculations using a high-level hybrid functional show that for the new 2D material, OTHG, there are Dirac cones at Fermi level along only one high-symmetry (Γ-M) direction. Edge states with energy gaps (~0.6 eV) are opened along other two Γ-M directions due to the hydrogenation, leading to an anisotropic electronic structure. Considering the significant anisotropic electronic structure, novel anisotropic physical properties, such as anisotropic Fermi velocity and directional conductance are expected in OTHG[1].

References:

9:30 AM BREAK

10:00 AM *NM01.05.04 Structural and Environmental Factors for Tuning Photoluminescence Properties of Carbon Nanotube sp3 Defects S. Dong1, Avishhek Saha1, Xiaowei He1, Brendan Gifford2,3, Geyou Ao4, Ming Zheng4, Kirill Voltzhanin1, Sergey Toetjaki1,3 and Han Hoon1; 1Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Theory Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 4Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Photoluminescent defect states introduced by low-level covalent functionalization of single wall carbon nanotubes (SWCNTs) are of growing interest as routes to enhanced photoluminescence (PL) quantum yields and new functionality.1,2 In particular, exciton localization in deep traps at the defect sites gives rise to single photon emission at room temperature that is tunable to telecom wavelengths.3,4 Control over defect-state emission wavelengths and dynamics is essential for advancing potential applications of these unique emitting states. We present results exploring the role of nanotube structure in determining the range of binding configuration that can occur for functionalizing agents. We show that functionalization occurs at ortho-only binding configurations and that nanotube structural symmetry can lead to a 3-fold decrease in emission wavelength bandwidth for zigzag structural types. Strategies for tailoring the SWCNT environment to extend defect-state PL lifetimes (to nanoseconds) and optimize linewidths will also be presented. Environmental impacts on dephasing times will also be discussed, along with temperature dependent effects on relaxation dynamics.


10:30 AM NM01.05.05 Concentric Dopant Segregation in CVD-Grown Nitrogen-Doped Graphene Single Crystals Jinjun Lin1, Roland Yingjie Tay1, Hongling Li1, Lin Jing1, Shi Hon Tsang2, Asaf Bolker1, Cecile Sagny2 and Edwin Hang Tong Teo3; 1Nanyang Technological University, Singapore, Singapore; 2Solid State Institute, Haifa, Israel; 3Space Environment Department, Sorqeq NRC, Yavne, Israel.

Heteroatom doping in graphene leads to bandgap opening and tunable electronic, magnetic and optical properties, which are important for graphene-based electronics applications. In recent years, scalable fabrication of nitrogen-doped graphene (NG) by chemical vapor deposition (CVD) has been extensively studied because of its potential for practical application. A phenomenon that occurs exclusively for CVD-grown NG films is the segregation of doping concentration. However, most studies to date are conducted using highly polycrystalline NG films comprising N depleted regions as determined by Raman spectroscopy. Supported by scanning tunneling microscopy experiments, we propose that the segregation of N dopants is caused by a competing N attachment mechanism to either zigzag or Klein edges during growth; where the former should result in higher N concentration and the latter with lower N concentration. This work provides critical insights into the growth mechanism of CVD-grown NG and enables new opportunities to engineer the properties of graphene by fabrication of lateral heterostructures.

10:45 AM NM01.05.06 Symmetry Breaking in the Plastic Deformation of Coiled Carbon Nanotubes Under Torsional Stress/Strain Socrates O. Dantas1,2, Cristiano F. Woellner1, Alexandre F. Fonseca2 and Douglas S. Galvao1; 1Universidade Federal de Juiz de Fora, Juiz de Fora, Brazil; 2Applied Physics Department, State University of Campinas, Campinas, Brazil; 3Departamento de Fisica, Universidade Federal do Paraná, Curitiba, Brazil.

Since the discovery of carbon nanotubes (CNTs) [1], other carbon allotropes and/or morphologies were observed. One of these morphologies are coiled carbon nanotubes (CCNTs) [2]. It has been a continuous evolution in the study of the structures as well as properties (electrical, mechanical or thermal) of addition of nanostructured carbon materials (NCMs) to polymers and other host materials, forming all sort of composites. However, the molecular scale mechanisms by which the NCMs interact with the hosts are still not fully understood. Previous studies [3-5] used theoretical simulations to address the interaction of NCMs with polymers, and a recent review also illustrated the use of simulations on the study of graphene and hexagonal boron nitride polymer nanocomposites [6]. Inspired by these studies, we investigated the mechanical properties of pristine CCNTs as well as composites formed with CCNTs and hexagonal-shaped monolayer NG single crystals of ~20 µm on Cu substrates. The NG single crystals exhibit discrete concentric hexagonal rings comprising N depleted regions as determined by Raman spectroscopy. Supported by scanning tunneling microscopy experiments, we propose that the segregation of N dopants is caused by a competing N attachment mechanism to either zigzag or Klein edges during growth; where the former should result in higher N concentration and the latter with lower N concentration. This work provides critical insights into the growth mechanism of CVD-grown NG and enables new opportunities to engineer the properties of graphene by fabrication of lateral heterostructures.

References:
to the one for pristine systems, but as expected, at different deformation rates and/or ranges. 


11:00 AM NM01.05.07 Covalent Molecular-Nanotube Heterostructures for Photonics Applications Antonio Setaro1, Mohsen Adeli1, Antoine Godin2, Mareen Glaeske1, Timo Bisswanger1, Rainer Haag3, Laurent Cognet2 and Stephanie Reich1; 1Department of Physics, Freie Universität Berlin, Berlin, Germany; 2LP2N - Institut d'Optique, Université de Bordeaux, Bordeaux, France; 3Institute of Chemistry, Freie Universität Berlin, Berlin, Germany.

Single-walled carbon nanotubes have outstanding electronic and optical properties including ballistic transport and tunable infrared light emission. These properties arise from the delocalized π electrons of the sp² carbon structure and confinement effects around the nanotube circumference. There has been a long-standing need to controllably tailor single-walled nanotubes through the covalent attachment of functional groups. We recently introduced a novel way of nanotube functionalization using triazine anchors that preserves the π electrons of single-walled carbon nanotubes. [1] Infrared light emission from the optically active E₁₁ exciton was observed even at high degree of functionalization (4%) of the carbon atoms).

Here, we present functional hybrids that are built using the triazine groups to anchor functional units on single-walled carbon nanotubes. We show how our platform provides routes toward controlled doping in carbon nanotubes. Nanotube luminescence is tailored by the attachment of molecular switches and enhancing plasmonic gold nanostructures. The molecular switch spiropyran reproducibly introduces blinking in single-walled carbon nanotubes after switching into its open merocyanine form. This makes carbon nanotubes that are covalently functionalized with merocyanine promising markers for ultra-high resolution imaging in the infrared.


11:15 AM NM01.05.08 Capillarity-Driven Water-Holey-Graphene Interactions Yanbin Wang, Kunal Ahuja, Shayandev Sinha, Parth Rakesh Desai, Haoyuan Jing and Siddhartha Das; University of Maryland, College Park, Maryland, United States.

Holey graphene (HG) is a particular form of structurally defective nanoporous graphene where the holes are introduced during the fabrication process. A HG matrix is a vertical stacking of multiple HG sheets with inter-stack separation of several nanometers. This structure affords generation of a massive ion-accessible graphene surface area and has been employed for applications such as fabrication of supercapacitors, oxygen reduction, nitrogen adsorption, Li-ion batteries, etc. Here we would present our research on the use of molecular dynamics (MD) simulation to probe the capillarity-driven interaction of a water drop with the HG. We consider appropriate functionalization of the edges of the holes of the HG. We recover highly interesting transportation behavior of water through the HG matrix where in presence of an applied force water is transported faster in HG with hydrophobic functionalization of the hole edges and Darcy’s law is violated at a weak force where capillarity dominates. Secondly for cases where the force is applied for a duration less than that needed to make the water escape the HG matrix, our simulations reveal a development of novel transient and equilibrated water-graphene wetting states that ensure an attainment of enhanced water-graphene wetted area in a most facile manner. Finally, we study the motion of ion-rich drop through the HG matrix, only to reveal that an appropriate analysis would necessitate addressing the hitherto unprobed problem of the role of ions in modifying the capillary waves at the air-water interface.

11:30 AM NM01.05.09 Pulsed Laser Synthesis and Optical Properties of High Quality Quantum Dots of Nitrogen Doped Graphene Quantum Dots Muhammad Shehzad Sultan1, Muhammad Sajjad2, Vladimir I. Makarov3, Frank Mendoza3, Wojciech M. Jadwiszczak2, Brad R. Weiner4 and Gerardo Morell1; 1Department of Physics, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States; 2Department of Physics, Western Kentucky University, Bowling Green, Kentucky, United States; 3School of Electrical Engineering and Computer Science, Ohio University, Athens, Ohio, United States; 4Department of Chemistry, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States.

The graphene quantum dots (GQDs), a zero-dimensional graphene quantum structure, have triggered an intense research worldwide. GQDs possess unique optical, chemical and physical properties as compared to conventional quantum dots (QDs), such as low toxicity, biocompatibility, optical stability, chemical inertness, high photostability and good water-solubility and therefore hold great application potential in biomedical, optoelectronics and energy storage devices. The doping of GQDs with heteroatoms is one of the most effective ways to tune their photoluminescence emission and to increase quantum yield. In this study, we developed a novel approach to synthesize high-quality Nitrogen-doped graphene quantum dots (N-QGDs) with high quantum yield, via irradiation of s-triazene in a solution with benzene by using pulsed laser. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. To observe optical properties of as synthesized N-QGDs, the UV-vis and Photoluminescence measurements were carried out. The as-synthesized NQGDs exhibit high quality crystalline structure of graphene with an average size of about 3.7 nm. A high quantum yield was exhibited by the obtained N-QGDs as compared to the pristine GQDs. The obtained N-QGDs with oxygen-rich functional groups exhibit a strong emission. These outcomes result in an ample opportunity for the biomedical and optoelectronic applications.

11:45 AM NM01.05.10 Studying the Growth of Single-Walled Carbon Nanotubes by Optical Means Vincent Jourdain1, Léonard Monniello1, Huy-Nam Tran4, Hugo Navas1, Matthieu Picher2, Théry Michel3, Rémy Vialia3, Said Tahir3, Eric Anglaret1, Amandine Andrieux-Ledier2, Frédéric Fossard2, Annick Loiseau2, Akinari Kozawa1 and Takahiro Miura1; 1University of Montpellier, Montpellier, France; 2Laboratoire d'étude des microstructures (ONERA/CNRS), Châtillon, France; 3Meijo University, Nagoya, Japan.

Controlling the structure and arrangement of single-walled carbon nanotubes (SWCNTs) directly during their growth constitutes a central bottleneck for the applications of SWCNTs in numerous fields including optics and microelectronics. Catalytic chemical vapor deposition (CCVD) is currently the most popular method for synthesizing SWCNTs because it offers more defined and versatile growth conditions, thus allowing to grow SWCNTs with a better control of their structure, orientation, surface density and purity. Although many groups reported catalyst systems and growth conditions yielding high
selectivity for specific diameters or chiralities, a profound understanding of the processes impacting the structural distribution of SWCNTs is still missing. Two main reasons can explain the difficulty to experimentally isolate growth mechanism and structural features: 1) monitoring the growth of individual SWCNTs still remain very challenging, 2) determining SWCNT structure is usually complex and requires a combination of methods.

In this contribution, we will show how optical methods of spectroscopy and microscopy can help addressing this issue. First, we will present in situ and ex situ Raman measurements used to study the dynamics of the different populations of SWCNTs during their growth by CCVD [1]. Importantly, this study reveals that the nanotube diameter distribution strongly evolves during SWCNT growth but in dissimilar ways depending on the growth conditions. The origins of these evolutions will be discussed. Second, we will show how polarization-based optical methods can be used to monitor the growth of individual SWCNTs on substrates [2]. We will notably show that individual SWCNTs on substrate can be imaged during their growth with time resolution of 5-50 ms. Third, we will propose a general modeling of the polarized optical spectra of individual SWCNTs including the influence of the multi-layer substrate and of coherent and non-coherent depolarization by the optics. We will show that this model allows one to extract both the real and imaginary parts of the nanotube susceptibility and to improve the methodology of chirality assignment [3].

References

SESSION NM01.06: Structure and Properties III  
Session Chair: Jeffrey Fagan  
Tuesday Afternoon, November 27, 2018  
Sheraton, 2nd Floor, Republic AB

1:30 PM *NM01.06.01  
Toxicity and Degradation of Carbon Nanotubes After Uptake by Macrophage Minfang Zhang1, Mei Yang2, Hideaki Nakajima2, Masako Yudasaka1, Sumio Iijima1, 2, and Toshiya Okazaki2; 1Meijo University, Nagoya, Japan; 2National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

The public concern regarding possible toxicities of carbon nanotubes (CNTs) has attracted many attentions. Because CNTs would be mainly entrapped by macrophages when CNTs entered into the living body, the investigation of the degradation of CNTs and the resulted cytoxicity after uptake by macrophage would be crucially important. In this study, we quantitatively investigated the intracellular degradation of CNTs by macrophages using an optical absorption method [1] and studied the toxicity changes of CNT during degradation. We have found that the intercellular degradations of CNTs by both primary cells and cultured macrophages were happening in the beginning 3 days after uptake and almost no degradation by the longer period incubation. The cell viability and cell total protein amount did not change during the degradation, and the amount of ROS generated by macrophage decreased with the degradation. These results indicated that the degradation of CNTs by macrophages followed the oxygen-depended mechanism and the residues of un-degraded CNTs persisted in macrophages without toxicity. In addition, through investigation of over 8-types of CNTs, we have found that the degradation rates of CNTs were dependent on their diameters, which would be helpful to predict the degradation characteristics of CNTs from their physical and chemical properties.


2:00 PM NM01.06.02  
Electronic Structure of Electron-Irradiated Graphene and Effects of Hydrogen Passivation Asanka Weerasinghe1, Ashwin Ramasubramaniam2 and Dimitrios Maroudas1; 1Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Defect engineering through irradiation processes and chemical functionalization of graphene are promising routes for fabrication of carbon nanostructures and 2D metamaterials with unique properties and function. In previous computational studies, we reproduced experimentally observed structures of electron-irradiated graphene sheets through introduction of random distributions of vacancies in the graphene lattice and proper structural relaxation. We found that a vacancy-induced amorphization transition in graphene occurs for an inserted vacancy concentration between 5% and 10%. This order-to-disorder transition is accompanied by a brittle-to-ductile transition in the fracture mechanism upon uniaxial tensile straining as well as a transition in the lattice thermal transport mechanism in these irradiated graphene sheets.

Here, based on molecular-dynamics (MD) simulations in conjunction with first-principles density functional theory (DFT) calculations, we report results for the electronic structure of irradiated and irradiation-induced amorphized graphene. We find that localized states appear at the Fermi level upon irradiation and the corresponding local density of states increases with increasing inserted vacancy concentration. Furthermore, electronic band structure calculations show that band flattening occurs due to electron localization in the vicinity of irradiation-induced defects and reduces the charge carrier mobility. This band flattening effect becomes stronger with increasing vacancy concentration inducing an increasing number of flat bands near the Fermi level. Moreover, we present electron wave functions (as frontier orbitals) and charge density distributions, which provide clear evidence of carrier localization near the irradiation-induced carbon dangling bonds. Passivating these bonds with hydrogen atoms leads to delocalization of the charge density, hence increasing the carrier mobility, which also is seen in the reduced density of states observed at the Fermi level and the increased band dispersion with increasing inserted vacancy concentration. We find these spatially localized states to be spin polarized, which gives rise to a net local magnetic moment. We will show how polarization-based optical methods can be used to monitor the growth of individual SWCNTs on substrates [2]. We will notably show that individual SWCNTs on substrate can be imaged during their growth with time resolution of 5-50 ms. Third, we will propose a general modeling of the polarized optical spectra of individual SWCNTs including the influence of the multi-layer substrate and of coherent and non-coherent depolarization by the optics. We will show that this model allows one to extract both the real and imaginary parts of the nanotube susceptibility and to improve the methodology of chirality assignment [3].

References
scaling limits are completely unknown. In this talk, I will illustrate the electroburning approach for sub-5 nm nano-gap fabrication and subsequently define the fundamental limits to scalability. The phonon based nano-gaps which is associated to a carbon chain filamentation process (electric field driven formation of carbon chains). Using a phase change material in the nanogap as a demonstrator device, fabricated using a self-alignment technique, I will demonstrate that for gap sizes approaching 1 nm the switching is dominated by such carbon chain formation, creating a fundamental scaling limit for potential devices. These findings have important implications, not only for fundamental science, but also in terms of potential applications.

2:30 PM NM01.06.04
Defects Enable Dark Exciton Photoluminescence in Single-Walled Carbon Nanotubes
Amanda Amori1, Jamie Rossii, Zhentao Hou1, Brian Landi1 and Todd Krauss1
1University of Rochester, Rochester, New York, United States; 2Rochester Institute of Technology, Rochester, New York, United States.

Single-walled carbon nanotubes (SWCNTs) are fundamentally interesting and technologically relevant materials with size-tunable absorption and emission across visible and near infrared wavelengths. However, several important aspects of SWCNT photophysical properties defy even simple physical explanation. For example, we found using variable temperature photoluminescence excitation spectroscopy that a sideband located approximately 130 meV away from the bright S1 exciton peak relating to the K-momentum dark exciton state, called X1, decreased in intensity five-fold as the nanotubes were cooled. Direct optical excitation of this dark state is nominally forbidden, thus calling into question how the state is populated, why it is so prominent in the photoluminescence spectrum, and what causes its strong temperature dependence. Interestingly, the ratio of the integrated photoluminescence intensities of X1 to S1 scales with a Boltzmann factor completely unrelated to the phonon that is thought to be responsible for depopulating the K-momentum dark exciton state: an in-plane transverse optical phonon, A′. Furthermore, photoluminescence spectra from individual nanotubes show that only a small fraction exhibit the X1 feature, with varying oscillator strength, thus suggesting that intrinsic processes such as phonon scattering are not responsible for populating the dark state. Alternatively, we suggest that populating the K-momentum dark exciton state requires scattering from defects, which is consistent with the increased magnitude of the X1 feature for samples with increased sample purification and processing. Thus, the presence of an X1 peak in photoluminescence is an extremely sensitive spectroscopic indicator of defects on single-walled carbon nanotubes.

2:45 PM NM01.06.05
Thermoacoustic Generator from a Free-Standing Single Walled Carbon Nanotubes
Stepan Romanov1,2, Ali Aliev3, Albert Nasibulin2 and Boris Fme3; 1Skolkovo Institute of Science and Technology, Moscow, Russian Federation; 2University of Texas at Dallas, Dallas, Texas, United States.

Recent advances in material science provoked a new wave of researches in a thermoacoustic process induced by Joule heating. Mainly due to very low heat capacity per unit area (HCPUA) of the modern materials. Here, we present the state-of-the-art performance of free-standing single walled carbon nanotubes (SWCNTs) thin films as thermoacoustic sound generators. The SWCNT films synthesized by an aerosol chemical vapor deposition (CVD) method showed record sound pressure level of 101 dB with a frequency of 100 kHz at the distance of 3 cm and the input power of 1 W. Such performance was caused by extremely low HCPUA of the films 0.35 * 10^-3. The research was performed with the films of different thicknesses in the sound range from 1 kHz to 100 kHz. The importance of aerogel structure of the materials for thermoacoustic generator researches theoretically and with experiments of densification and vacuum annealing. Full theoretical model of thermoacoustic free-standing films, which included effects of diffraction and finiteness of heat capacity per unit area was derived. Theoretical model was checked numerically in 3D by solving full system of coupled Linearized Navier Stokes and Helmholtz differential equations. This work was supported by Skoltech NGP Program (Skoltech-MIT joint project).

3:00 PM BREAK

3:30 PM *NM01.06.06
Thermoelectric Materials Consisting of Doped Carbon Nanotubes
Yoshivuki Nonoguchi1,2; 1Nara Institute of Science and Technology, Nara, Japan; 2JST PRESTO, Kawaguchi, Japan.

Carbon nanotubes have recently been used as the building blocks of thermoelectric materials that enables the construction of wearable electronics and power modules. In this context, air- and thermally-stable doped, i.e. n-type materials are highly desired not only for the development of practical PN series thermoelectric modules but also for the optimal tuning of thermoelectric transport. In this presentation, I will talk about the preparation of air- and thermally-stable p- and n-type carbon nanotubes and their application in thermoelectric transport studies [1-6]. Supramolecular (electro-)chemistry is introduced to improve, and quantify doping efficiency and stability. A recent progress on the power factor enhancement is also presented.


4:00 PM NM01.06.07
Interlayer Charge Transport in 2D Molecular Structures
Elad Koren; Materials Science and Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

Weak interlayer coupling in 2-dimensional layered materials such as graphite gives rise to rich mechanical and electronic properties in particular in the case where the two atomic lattices at the interface are rotated with respect to one another. A lack of crystal symmetry leads to anti-correlations and cancellations of the p6 orbital interactions across the twisted interface, which gives rise to low friction behavior and low interlayer electrical transport. Using our recent nanomanipulation technology1, based on atomic force microscopy, we studied the interlayer electrical conductivity as a function of twist angle between two misoriented graphene layers with unprecedented angular resolution of ~0.1 deg. The angular dependence indicates that the electrical transport across the interface is dominated by a phonon assisted channel which conserve the momentum of conduction band electrons, tunnelling across the twisted Dirac bands. Most intriguingly, the conduction is significantly enhanced within a narrow angular range of less than 0.5 deg at pseudo-commensurate angles of 21.8 and 38.2 degrees. This provides the first experimental evidence for the existence of a 2-dimensional interface state originating from the coherent coupling of electronic states in the twisted sheets due to commensurate superlattices2. Finally, we show that combined electro-mechanical characterization techniques of mesoscopic graphite structures can be uniquely address open fundamental question related to the dielectric interlayer interactions and electronic charge transport through stacking faulted structures3.
The physics governing the adsorption of ions onto metallic or semimetallic surfaces underpins future technological developments in many areas. Specifically for graphene-based technology new emerging applications for example in energy storage or water filtration require a precise understanding of the relative stability of ions at the graphene surface and surface wetting properties. [1] However, many questions about the atomic structure of the electrolyte/graphene interface remain challenging to answer since the characterization of the interface proved to be elusive largely because the experimental techniques have not allowed direct observation of the behaviour of the ions. [2]

The driving force for the ion interfacial adsorption is a complex mix of enthalpic and entropic contributions, but molecular dynamics (MD) simulations of the electrolyte interface with both air and unstructured hydrophobic surfaces have demonstrated that it is mainly related to the stability of the ion’s solvation shell and its propensity to dehydrate. [3] For a semi-metallic surface, such as graphene, the proximity of an ion induces a further effect associated with polarization of the surface itself, which strongly affects the interfacial attraction/repulsion of the ions. In order to capture these important phenomena, we recently developed a novel molecular model that can include the polarizability of all the species involved and allow the prediction of the specific relative adsorption of ions on the graphene surface for electrolyte concentrations comparable to the experimental ones. [4]

In this talk we will show that this new model predicts that in a 1 M electrolyte solutions, cations are adsorbed onto the graphene surface with a trend (Li+ < Na+ < K+ ) opposite to that predicted by the gas-phase calculations and different than from that obtained from the single-ion simulations and with an energy of adsorption now validated by microscopy and electrochemistry experiments. [5] We will discuss how these findings are relevant for the graphene exfoliation process and wetting properties of the surface.

References


4:30 PM NM01.06.09
Contactless Detection of Opto-Electronic Anisotropy and Real-Time Atmospheric Doping in Single Walled Carbon Nanotube Films

Maxwell Jundt, Adam B. Phillips, Rajendra R. Khanal, Michael J. Heben and Nikolas Podraza; Physics & Astronomy, University of Toledo, Toledo, Ohio, United States.

Thin films of single-walled carbon nanotubes (SWCNT) have many attractive opto-electronic features such as tunable conductivity and visible light transmission that make them of interest for a variety of applications. We present a characterization method that employs multi-angle spectroscopic ellipsometry spanning a wide spectral range from the ultraviolet to the terahertz (210 nm – 3 mm) that is capable of simultaneously determining a variety of opto-electronic properties in a contactless manner. In particular, SWCNT films are prepared in both “de-doped” (i.e. heat treated) and heavily nitric acid doped states and measured in both ex-situ and in-situ modes. The ex-situ measurements fully leverage the wealth of spectral features present in the wide spectral range while the in-situ mode allows for tracking of changes in real time as the film properties change due to atmospheric exposure. This frequency domain spectroscopic measurement is one of the only known techniques sensitive to the optical effects arising from electrical anisotropy between the in-plane and out-of-plane directions. Comparison to direct electrical measurements sampling the in-plane electrical properties confirms accuracy. Such electrical anisotropy arises from the fact that, despite no intentional alignment of the nanotubes being made, the nanotubes tend to lie flat on the substrate surface. Nitric acid doping is shown to decrease the film resistivity by factors of ~4 and ~100 in the in-plane and out-of-plane directions, respectively. This capability of determining electrical anisotropy is particularly relevant for incorporation of SWCNT films into devices where the desired direction for conduction is a consideration. Measurement of real-time changes to the film through the in-situ measurements are of interest for SWCNT films used in sensor applications. Additionally, the influence of doping on optical features arising from metallic and semiconducting transitions is determined.

4:45 PM NM01.06.10
Gapped Graphene Nanoribbons with Spatial Symmetries as One-Dimensional Topological Insulators

Kuan-sen Lin1,2 and Mei-Yin Cheu1, 3
1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 3School of Physics, Georgia Institute of Technology, Atlanta, Georgia, United States.

The Berry phase is a geometrical phase that is known to provide the essential physics behind several intriguing materials properties such as the electric polarization, anomalous Hall effect, orbital magnetization, etc. It is expected that this geometrical phase also reflects the intrinsic topological properties of one-dimensional (1D) insulators, because the 1D Brillouin zone (BZ) integral forms a natural loop in the k-space. In this work, we study the system of gapped graphene nanoribbons (GNRs) with spatial symmetries (e.g., inversion) and show that a symmetry-protected Z2 topological phase exists. Although the Berry phase turns out to be -quantized in the presence of the chiral symmetry, it does not provide the correct Z2 correspondence as expected. It is found that only the origin-independent part of the Berry phase gives the correct bulk-boundary correspondence by its -quantized values, with the relevant Z2 invariant dependent on the choice of the bulk unit cell (namely, ribbon truncation) and connected to the symmetry eigenvalues of the wave functions at the center and boundary of the BZ. Using the edge-dressed GNRs as examples, we demonstrate the existence of localized states at the end of some GNR segments and at the junction between two GNRs based on topological analysis. The current results are expected to shed light on the design of electronic devices based on GNRs as well as the understanding of the topological features in 1D systems.

References

Novel nanocarbon-metal composites called covetics have the potential to improve significantly upon the mechanical, thermal, and electrical properties of common metals and alloys, including Al. Electric current applied to the melt containing a C precursor is believed to ionize carbon atoms and cause nanoscale graphitic ribbons and chains to form within the resulting Al lattice. Despite the potential of nanocarbon incorporation to improve desirable properties of Al alloys, critical for aerospace, structural, and power transmission applications, the atomic-scale mechanism is not yet completely understood.

In this work, the effects of current density and residence time on the uniformity and extent of carbon conversion to nano-graphite are explored in order to provide further insight into the conversion process. We characterize the structural and chemical features of nanocarbon-Al covetics using Raman spectroscopy, TEM imaging, electron energy loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPS). Raman and EELS spectra are localized to within a few μm of a selected region of interest, as guided by fiducial marks milled using a focused ion beam tool before collection of the spectrum images (SIs). The Raman and EELS SIs are subjected to nonlinear iterative fitting and hyperspectral decomposition using machine learning techniques to reveal features indicating nanocrystalline graphite embedded within the Al lattice. The Raman G and D peak intensities and shifts are found to depend on the current parameters, with greater exposure corresponding to greater graphitic order. Evidence of sp2 carbon bonding and Al-C bonding is seen by EELS and XPS. Local mechanical (nano-indentation) and electrical conductivity measurements will also be taken and related to processing conditions and local structure.

This work is based upon work supported by the U. S. Department of Energy under Award No. DE-EE0008313. Dr. David Forrest is the Project Technology Manager and Debbie Schultheis is the Project Officer/Manager.

NM01.07.03
Interfacial Detection with Carbon Nanotube Pipette Laden Graphene Quantum Dots Electrode
Hayley Richardson, N.N.N. Ahamed and K.S.V. Santhanam; School of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, New York, United States.

Single cell analysis is an emerging technology that can provide a mechanistic understanding of the complex biological systems and cell heterogeneity. (1) Any disruption of its activity can be monitored through interfacial bioelectrochemistry. In this emerging technology it is necessary to have high spatial and temporal resolution over an extended period of time that has been seldom achieved in the adopted analytical measurements. This problem has been solved in the present work by using an electrochemical technique such as differential pulse voltammetry (DPV) carried out with carbon nanotube pipette electrode that is laden with graphene quantum dots (20 nm-50 nm) (2). This modification gives rise to a sensitive electrode material for high temporal resolution through idealizing the DPV parameters. The in-vitro experiments carried out in understanding oxidative stress produced by p-aminophenol (PAP) that
results in membrane disruption suggest that molecular attachment of PAP to graphene is higher than the pipette electrodes (amorphous carbon) as indicated by the signal strengths being several orders of magnitude higher than with amorphous pipette electrode. The shape and features of the current-voltage curves that are recorded can be idealized as nanotube electrode arrays acting as an ensemble in harmony. As the electric field known to influence the cells, the electric field produced during the detection of an electroactive species by this ensemble has been simulated for practical usage for in-vivo studies. The new electrode opens up an approach at observing the electroactive neurotransmitter during its functioning in chronic diseases.


Electrochemical (re)activity of graphene and graphene-based ‘hybrid’ nanomaterials is crucial for food, energy and water sustainability applications, which requires delicate control over its geometric and electronic structures. We demonstrate that precise control of the density of defects, hierarchical porosity, and topological interconnectedness, invoked in hydrothermally synthesized graphene aerogel integrated with multi-walled carbon nanotubes that can finely tune mesoporosity and enhance the electrochemical heterogeneous electron transfer rate (kTST). We prepared range of three-dimensional solid network of graphene-based ‘hybrid’ scaffolds (i.e. aerogel) and their nitrogenated counterparts with varying graphene-carbon nanotube compositions using two schemes (approach 1 and approach 2). This study allows us to correlate quantitatively between number defect density determined (via Raman spectroscopy; RS) and heterogeneous electron transfer rate (via scanning electrochemical microscopy; SECM). RS provides nanoscale phononics characterization revealing collective atomic/molecular motions and localized vibrations. The first- and second-order phonon modes are analyzed in terms of Raman intensity, band position (intrinsic mechanical strain) and intensity ratio (structural disorder, number defect density), distinct localized n electronic states were found in photoluminescence excitation (PLE) spectra reflecting carbon atoms around oxygenated and nitrogenated species. The role of carbonyl (C=O), epoxy (C-O-C) and nitrogen (pryridinic-N and graphitic/pyrrolic-N) surface functionalities and corresponding bonding configurations besides hierarchical mesoporosity are emphasized in view of understanding the improved physicochemical properties for electrochemical energy, water desalination and sensing applications. The engineered defect density induced increase in finite electronic density of states (DOS) near Fermi level revealed using density functional theory (DFT) calculations and decrease in room temperature electrical conductivity, heled in establishing optimal defect density for moderate heterogeneous rate as a critical state such that the whole system becomes electronically activated while maintained structural integrity. Moreover, it enlarges the overlap between DOS for graphene aerogels and redox probe couple, which signifies the experimental correlation estimates.

Fabrication of Bilayer Graphene Based Films as Hygromorphic Actuators Omkar S. Bhatkar, Sheikh Rasel, David Smith and Reza Rizvi; Mechanical, Industrial and Manufacturing Engineering, University of Toledo, Toledo, Ohio, United States.

Extensive research is being conducted on graphene-based composite films to explore their potential in actuation mechanisms stimulated by electrical, thermal, mechanical or optical energy sources owing to its extra-ordinary electrical and mechanical properties. In this study, we report the use of all graphene based functionally graded, bilayer free-standing films as mechanical actuators triggered by adsorption of moisture at the film interface. The bilayer films were fabricated by a single-step doctor blade coating technique and dried at controlled temperature and humidity conditions. The reduction mechanism of Graphene Oxide into rGO was implemented through metal substrate-assisted reduction, which involves coating GO paste on an active metal like Aluminum that possess a high oxidation potential. The internal architecture of the films was tuned as per requirement by changing the initial process parameters like the concentration and pH of GO and the surrounding humidity and temperature. Selective reduction of Graphene Oxide into desired intricate patterns was also demonstrated, through usage of masks during film coating and deposition. The functional grading of the films, where one side is electrically-conducting GO while the other being insulating rGO was confirmed by SEM, Raman, XRD, FTIR and XPS analyses. SEM revealed an overall understanding of the porous nature of the film throughout the cross section whereas Raman Spectroscopy showed an increase in (ld/lg) ratio from GO to rGO face, denoting gradual reduction of sp² hybridized hexagonal carbon structure. XRD, FTIR and XPS results also confirmed the functional grading throughout the thickness of the film post-reduction. The bilayer film, which is composed of Graphene Oxide and Reduced Graphene Oxide on either side, is shown to exhibit selective bending mechanism in humid environments, due to the affinity of Graphene Oxide towards polar molecules like water. Reduced Graphene Oxide being immiscible in water shows repulsive nature towards humidified surroundings, thus triggering a differential bending mechanism in the individual bilayer film. The Hygromorphic behavior exhibited by the robust and flexible functionally graded graphene films, can intrigue a variety of applications in mechanical actuation, robotics and gas sensing systems.

References:

Mechanics of Triply Periodic Minimal Surfaces of Three-Dimensional Graphene Foams GangSeob Jung and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The mechanics of triply periodic minimal surfaces (TPMSs) with three-dimensional (3D) graphene foams are systematically studied to understand the effects of structure and size on the mechanical properties, e.g., elasticity, strength, and fracture. The design of lightweight open-shell porous solid materials with TPMSs has shown excellent and tunable load-bearing properties. However, subtle mechanics and their relations with surface topologies are largely unknown. Utilizing reactive molecular dynamics simulations, here we investigate the elastic and fracture properties of three different surface topologies with 3D graphene foams: P (primitive), D (diamond), and G (gyroid). Models with different lattice sizes are utilized to derive power laws, which can connect the properties along different sizes to shed light on the multiscale mechanics of 3D graphene with TPMSs. Our study provides a systematic understanding of the relation between TPMS topologies and their mechanical properties, including failure mechanisms of graphene foams, opening
opportunities to explore designable complex structures with tailored properties.

NM01.07.07
Thermal Conductivities of Triply Periodic Minimal Surfaces of Three-Dimensional Graphene Foams  
GangSeob Jung and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Graphene has excellent mechanical, thermal and electrical properties. However, there are limitations in utilizing monolayers of graphene for mechanical engineering applications due to its atomic thickness and lack of bending rigidity. Synthesizing graphene aerogels or foams is one approach to utilize graphene in three-dimensional bulk forms. The structures of graphene foams can be idealized with the triply periodic minimal surface (TPMS):P (primitive), D (diamond), and G (gyroid). Here, we investigate the thermal conductivity of three different surface topologies with 3D graphene foams by using full-atom molecular dynamics simulations. We derive a scaling law showing how the different TPMSs have different trends. Our analysis shows that the trend of the thermal conductivities can be attributed to defects and curvatures of graphene. Our study shows that three-dimensional porous graphene has potential that may be utilized in designing new lightweight structural materials with low and density-insensitive thermal properties and superior mechanical strength.

NM01.07.08
Enhancing the Thermal Conductivity of PBAT/Graphene Composites via Applying PLA as a Second Phase Reorganizer  
Xianhao Zuo, Yuan Xue, Miriam Rafailovich and Yichen Guo; Stony Brook University, Stony Brook, New York, United States.

In this study, we have designed and engineered polymer blends as an improvement of the thermal diffusion structure for polymer materials. In our system, poly (lactic acid) (PLA) was used as a second phase reorganizer of the Poly (butylene adipate-co-butylene terephthalate) (PBAT)/graphene composites. Two different types of graphene, H-5 and C-750, were used in this study to guarantee the thermal conductivity of the composites. According to the contact angle measurements and the calculation of the interfacial tension between polymers and graphene, we observed that graphene will be more stable in the PBAT phase than in the PLA one. Therefore, in our blends system, PBAT was designed as the polymer matrix, while the PLA was considered as the minor phase with a comparatively lower concentration. Because the size of H-5 (average around 5 nm) is larger than the PLA domain size (around 3 nm), H-5 can disperse perfectly in PBAT matrix and form continuous thermal diffusion paths. With 20% of graphene H-5, the thermal conductivity of PBAT/PLA blend can achieve a 26% enhancement, as compared with the sample without PLA. Moreover, we discovered that the incorporation of C-750, unfortunately, failed in promoting the thermal conductivity of the PBAT/PLA blend. Since the PLA domain size is much larger than the size of C-750 (average around 750 nm), it can hardly help drive the dispersion of the C-750 in a preferential orientation in the PBAT matrix and makes the formation of the thermal diffusion path even harder.

NM01.07.09
Quantifying Defects in Graphene for High Performance Conductive Ink  
Md Akibul Islam1, Sheikh Rasel1, Derek Keith Messer1, Wai Mak2, Reza Rizvi1,2 and Richard B. Kaner1; 1Mechanical, Industrial and Manufacturing Engineering, University of Toledo, Toledo, Ohio, United States; 2Chemistry and Biochemistry, University of California, Berkeley, Los Angeles, California, United States.

Over the past decade, comprehensive investigations have been conducted to develop graphene based two-dimensional (2D) materials to harness their excellent and unprecedented properties such as high electrical conductivity, optical transparency, mechanical strength, and flexibility. To fully utilize these functionalities, a number of methods including chemical vapor deposition, liquid shear exfoliation, sonication, ball milling, electrochemical exfoliation and polymerization can be used to produce high-performance conductive ink from exfoliated graphene. However, these methods can introduce significant defects during exfoliation into the graphene crystal structures that have a strong influence on their properties. This study is designed to compare the defect and flake quality between CFE and bath or probe sonication process for producing high-performance conductive ink from exfoliated graphene. In our CFE process, graphene is rapidly jetsonned through a small orifice using high-pressure gases without the need for any time-based treatment, unlike other shear-based liquid processes. Shear-induced exfoliation occurs due to the high velocities that expanding and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate (>$10^5$ s$^{-1}$) experienced by the graphite particles. In contrast, in the sonication methods, an ultrasonic transducer is used to induce unstable cavitation bubbles in a liquid medium, which upon their inevitable collapse emulate a shock wave. The energy of this shockwave is sufficient to fragment nearby bulk graphite powders into smaller lengths as well as thickness along the weak, secondary c-axis. But when the bulk particle is fragmented into smaller flakes, a good number of edge and basal plane defects are introduced into the flake. The defect population increases as the time for sonication rises. The occurrence of a disorder-activated D peak at 1330 cm$^{-1}$ in the Raman spectra of graphene is indicative of defects, in particular, those which disrupt the sp$^{2}$ hybridization. Such defects can be interpreted to be the creation of new edges, vacancies or substitutions, with the ratio between the peaks intensities of the D to G peak ($I_{D}/I_{G}$) providing a qualitative indication of their population. In our study, we found the ratio of D peak to G peak is significantly less in CFE than that of bath sonicated graphene ($I_{D}/I_{G}$=0.66 for CFE graphene and $I_{D}/I_{G}$=1.1 for bath sonicated graphene. In contrast, the bulk graphite powder had $I_{D}/I_{G}$ ratio of 0.62. The increased quantity of defects in bath sonication may be attributed to the prolonged sonication time which is well known to be responsible for reducing the flake length and hence, introducing more edges. The flake quality of exfoliated graphene was also verified using atomic force microscope (AFM) and transmission electron microscope (TEM).

NM01.07.10
3D Knitted Carbon Nanotube Fabric as Smart Textiles  
Javad Foroughi; University of Wollongong, Wollongong, New South Wales, Australia.

Highly stretchable, actuatable, electrically conductive knitted textiles based on Spandex (SPX)/CNT (carbon nanotube) composite yarns were prepared by an integrated knitting procedure. SPX filaments were continuously wrapped with CNT aerogel sheets and supplied directly to an interlocking circular knitting machine to form the three-dimensionally electrically conductive and stretchable textiles. By adjusting the SPX/CNT feed ratio, the fabric electrical conductivities could be tailored in the range of 870 to 7092 S/m. The electrical conductivity depended on tensile strain, with a linear and largely hysteretic-free resistance change occurring on loading and unloading between 0 and 80% strain. Electrothermal heating of the stretched fabric caused large tensile contractions of up to 33%, and generated a gravimetric mechanical work capacity during contraction of up to 0.64 kJ/kg and a maximum specific power output of 1.28 kW/kg, which far exceeds that of mammalian skeletal muscle. The knitted textile provides the combination of strain sensing and the ability to control dimensions required for smart clothing that simultaneously monitors the wearer’s movements and adjusts the garment fit or exerts forces or pressures on the wearer, according to needs. The developed processing method is scalable for the fabrication of industrial quantities of strain sensing and actuating smart textiles.

NM01.07.11
Electronically Tunable SPR Biosensor with Reduced Graphene-Oxide Thin Films as Functional Layers  
Xiaolong Liu1,2, Pavel Damborský1, Walid-Madhat Munief2, Jessica Ka-Yan Law4, Vivek Pachauri1,2, Jens-Uwe Neurohr6, Samuel Grandthyll6, Karin Jacobs6, Frank Müller6, Jaroslav Katrlík3, Xianping Chen5 and Sven Ingebrandt1; 1Department of Informatics and Microsystem Technology, University of Applied Sciences Kaiserslautern, Zweibruecken, Germany; 2Department of Informatics and Microsystem Technology, University of Applied Sciences Kaiserslautern, Zweibruecken, Germany; 3Department of Glycobiotechnology, Slovak Academy of Sciences; 4Department of Chemistry, The Chinese University of Hong Kong, Hong Kong; 5Department of Electrical Engineering, RWTH Aachen University, Aachen, Germany; 6Department of Chemistry, Technical University of Denmark, Lyngby, Denmark.
Academy of Sciences, Bratislava, Slovakia; 2R·AGroupDEGmbH,Zweibruecken,Germany; 3KeyLaboratoryofOptoelectronicTechnology&Systems,ChongqingUniversity,Chongqing,China; 4ExperimentalPhysics,SaarlandUniversity,Saarbruecken,Germany.

Graphene is bustlingly exploited as a linker layer in surface plasmon resonance (SPR) biosensing for advanced biomolecule-recognition due to its intriguing plasmonic properties. However, the chemical nature of pristine graphene limits the binding of receptor biomolecules to physisorption and π-π stacking. Therefore, chemically exfoliated graphene oxide (GO) and reduced graphene oxide (rGO) are used instead for covalent immobilization of receptor biomolecules, since they possess various functional groups on the carbon basal plane and concurrently preserve the carbon-lattice as pristine graphene within nanoscale size. In this work, we investigated the sensing performances of Au/glass SPR chips with GO and rGO thin films as functional layers. As a proof-of-concept we applied a lectin Concanavalin A (ConA) binding assay with prostate cancer-specific antigen (PSA) as receptors. The results demonstrated stronger surface plasmon resonance effects for biomolecule recognition with rGO functional layers, whilst the average intensity of surface plasmons and signal-to-noise ratio were 1.7 and 3 times higher compared to the GO as functional layers. More remarkably, taking advantage of the bipolar property of the rGO thin films, it was possible to further enhance the surface plasmon intensity by applying bias voltages to the rGO thin films. The limit of detection ConA target molecules was 0.01 μg/mL. Such tunable SPR platforms based on rGO thin films lighten up a wider road for diverse surface functionalization, adjustable sensing regimes and improved sensitivity in the field of SPR biosensing.

**NM01.07.12**

**Vertically Aligned Single-Walled Carbon Nanotube Growth from Ir Catalysts by Alcohol Gas Source Method**

Takuya Okada, Takahiro Saida1,2; Shigeya Naritsuka1 and Takahiro Maruyama1,2; 1Applied Chemistry, Meijo University, Nagoya-shi, Japan; 2Nanomaterials Research Center, Meijo University, Nagoya-shi, Japan; 3Materials Science and Engineering, Meijo University, Nagoya-shi, Japan.

Single-walled carbon nanotubes (SWCNTs) have been anticipated for applications in a lot of future nanodevices. However, there still remain several problems for realizing the SWCNT devices, and one of the most significant issues is high-yield growth of semiconducting SWCNTs. So far, to grow SWCNTs with high-yield, Al2O3 buffer layers are widely used, because they prevent migration of catalysts on the substrate surface at growth temperature and aggregation of catalyst particles are suppressed [1]. In this study, we attempted to grow SWCNTs using Ir catalysts without Al2O3 buffer layers, which have never been used as catalysts in SWCNT growth. After deposition of Ir catalysts on SiO2/Si substrates, SWCNT growth was carried out using alcohol gas source method in a high vacuum [2]. Growth Temperature and growth time were set at 800°C and 1 h, respectively. The ethanol pressure was varied between 1×10⁻¹⁰ and 1×10⁻⁹ Pa. The grown SWNTs were characterized by FE-SEM, TEM and Raman spectroscopy. SEM and Raman results showed that, as the ethanol pressure increased, the SWCNT yield became higher and the SWCNT diameter became narrower. When the ethanol pressure was 1×10⁻⁹ Pa, high-density vertically aligned SWCNTs were grown, whose lengths were about 2 μm. Raman measurement showed that SWCNT diameter were distributed between 0.83 and 1.13 nm. In addition, Raman spectra showed that semiconducting SWCNTs were dominantly grown from Ir catalysts. This study is the first report to grow SWCNTs from Ir catalysts, and our results indicated that Ir catalysts are effective to obtain high-density vertically aligned and small diameter SWCNTs using no Al2O3 buffer layers.


**NM01.07.13**

**Band Alignment Study of Locally Gate-Controlled Graphene/Carbon Nanotube Junctions**

Mao Shiomi, Takayuki Arie, Seiji Akita and Kuni Takei; Osaka Prefecture University, Sakai, Japan.

Heterojunctions of nanomaterials have attractive attention due to interesting electrical and optical characteristics. One of the interesting materials is graphene, which has Dirac-cone band structure. Utilizing this band structure and other contacting semiconductor nanomaterials, diode and transistor behaviors can be controlled by applying a global back gate voltage. However, due to vertical integration of this heterojunction, each band structure cannot be separately controlled to observe different functions. Furthermore, although the barrier height as a function of gate voltage has been studied, detailed band alignment has yet to be studied due to difficulties of gate voltage separation between graphene and other nanomaterial. To address these challenges, we demonstrate a graphene-carbon nanotube (CNT) junction device laterally integrated with local gate electrodes for graphene and CNT. Furthermore, barrier height dependence is also investigated as a function of local gate voltages. CVD-grown monolayer graphene was transferred onto a Si/SiO2 substrate with Au source and drain electrodes. After graphene was patterned by an oxygen plasma, semiconductor-enriched CNT networks were deposited by modifying the surface of graphene and SiO2 surfaces with poly-L-lysine. SiO2/Al2O3/SiO2/dielectric layers were deposited over the substrate, followed by Al gate electrode deposition. To apply the gate bias at graphene, CNT, and junction of them, multi-gate stack structure was fabricated by repeating the gate dielectric and electrode deposition. Uniform formation of graphene, CNT, and junctions were confirmed using Raman spectroscopy and AFM. Dirac point of graphene was about -3 V, and ambipolar behavior of CNT/graphene transistor was observed. When graphene voltage from -6 V to 3 V was applied, threshold voltage is modulated from 0 V to 0.28 V. These mobilities are 7.0±1.6 cm²/Vs and 1.1±0.2 cm²/Vs for p-type and n-type behaviors, respectively. After analyzing the device as a function of temperature, thermal and tunnel emission probabilities were calculated. At the transition between thermal and tunnel emission, barrier heights were extracted at different local gate bias of graphene. Based on the results, barrier heights were linearly changed by changing the gate voltage, which is in good agreement with our expectation due to the Fermi level movement. The barrier heights are varied from ~84.5 meV to ~69 meV for n-type and ~85.5 meV to ~71.5 meV for p-type depending on the graphene gate voltage. The values are slightly lower than that of vertically integrated graphene/TMD materials. This may be caused by the multiple junctions with defects to the Fermi level of graphene due to solution process of CNT network formation. In summary, we could successfully fabricate the locally gate controllable graphene/CNT junction transistor and analyzed the barrier height at different local gate voltage corresponding to the Fermi level movement.

**NM01.07.14**

**Local Structures of Polycyclic Aromatic Hydrocarbon Molecules Encapsulated in Single-Walled Carbon Nanotubes Studied by Molecular Dynamics Simulations**

Ryo Nagai, Hironori Ogata and Yosuke Karaoke; Hosei University, Tokyo, Japan.

Carbon nanotubes (CNTs) is one of the most promising material because of their superior electronic, thermal and mechanical properties. Single-walled carbon nanotube(SWNTs) have a hollow space of about several nm in diameter. It is possible to encapsulate various functional molecules in hollow space and expected new functions by encapsulation. One of the polycyclic aromatic hydrocarbon (PAH) molecules, coronene has been reported to exhibit interesting fluorescent properties depending on the local structure. The unique luminescence properties of columnar stacked coronene encapsulated in SWNTs have been also reported.In this study, molecular dynamics simulation was performed to clarify the local structure and properties of various kinds of PAH molecules encapsulated in SWNTs systematically. We will report the detailed results of SWNT chirality dependence of encapsulated structures of PAH molecules.
Effect of Carbonyl and Hydroxyl Groups on the Performance of ITO-Decorated MWCNT Based Electrochemical Capacitors Neftali L. Carreno1,
Matheus Krelow1,2, Guillerme Maron1, Bruno Norenberg1, Lucas Rodrigues1 and Jose H. Alano1; 1University Federal-Pelotas, Pelotas - RS, Brazil; 2Instituto Federal Sul-rio-grandense Caupolica-CAVG, Pelotas, Brazil.

Owing to the energy needs of the modern world, numerous studies have been performed in order to develop new materials with advanced electrical properties to be applied in energy storage devices, especially capacitors and supercapacitors. Accordingly, carbon-based materials such as carbon nanotubes (CNT) and reduced graphene oxide (rGO) are regarded as great alternatives to be used in the clean energy industry. Also, the possibility of the development of nanocomposites with carbon-based materials, metallic nanoparticles and metal oxides becomes interesting for electrochemical applications, such as energy storage devices, capacitors, gas sensors and others, and is the main focus of many researches in the last few years. A potential candidate to be used in the surface modification of CNT’s is the indium tin oxide (ITO), since it presents very interesting electrical properties and is studied for several applications. In the present work, nanocomposites of CNT/ITO have been prepared using a microwave-assisted hydrothermal synthesis (MHS), with posterior annealing of 400 °C and 600 °C, in inert atmosphere, to obtain crystalline ITO. Hydroxylated (CNTOH) and carboxylated (CNTCOOH) multiwalled carbon nanotubes-MWCNT (30% w/w), indium nitrate and tin chloride were used as precursors. The obtained powder was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties were evaluated by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge, using a two electrode cell with current collectors made of 304 stainless steel, KOH 6 mol L-1 as electrolyte and filter paper as separator. The measurements were performed in a source meter Keithley model 2651A and a potentiostat IVIUM - Compactstat.e. XRD results showed that the sample annealed at 400 °C; the phase obtained was rhombohedral, while at 600 °C formed the cubic phase. Charge-discharge results showed values of 3.2 F/g and 1.4 F/g for CNTOH/ITO-400 and CNTOH/ITO-600, respectively, and 5.1 F/g and 0.3 F/g for CNTCOOH/ITO-400 and CNTCOOH/ITO-600, respectively. It is possible to observe that the specific capacitance of the samples with rhombohedral ITO was higher than for cubic, which can be explained by a degradation of nanotubes structure when submitted to higher temperatures. However, these findings require further characterization, such as Raman spectroscopy and FEG-SEM images, for example.

NM01.07.16
Fabrication of Gate Tunable Graphene Lateral Tunnel Diodes Takashi Uchino1, Kanako Shiga1, Kenta Sugawara1, Hirokazu Fukidome1, Akira Satou2 and Taichi Otsuiji2; 1Tohoku Institute of Technology, Sendai, Japan; 2Tohoku University, Sendai, Japan.

Two-dimensional materials have attracted attention in recent years because of their excellent electrical properties and can develop innovative devices [1-3]. In particular, single-layer graphene with the higher mobility and saturation velocity could push the limit of high-frequency devices [4]. In this work, we focus on fabrication and electrical characterization of gate tunable graphene lateral tunnel diodes to realize optical rectennas which receive and convert optical frequency electromagnetic radiation into DC output with high-efficiency and low-cost [5].

The gate tunable graphene lateral tunnel diodes were fabricated using monolayer graphene grown by chemical vapor deposition (CVD) on Cu foil and later transferred to 83-nm-thick SiO2 on Si substrates. Tunnel regions were formed by using electron beam lithography, and the tunnel length ranged from 60 to 150 nm. Tunnel dielectric consists of Si3N4 and Al2O3. The Al2O3 layer was formed by atomic layer deposition on the negative oxide of Al thin film. Metal electrodes (anode and cathode) were formed by electron beam evaporation of Ti/Pd/Au (0.5/20/100 nm) right after an oxygen plasma treatment to reduce contact resistance between graphene and electrodes. Top and back gate electrodes were formed by Ti/Au (20/80 nm) and Al (100 nm), respectively. Typical current-voltage (I-V) characteristics of the fabricated devices showed rectifying characteristics at a low voltage below 1 V. The on-state current of the lateral diodes increased with reducing the tunnel length. The lateral diodes have p-type rectifying characteristics for positive gate voltages and n-type rectifying characteristics for negative gate voltages. This result indicated that the tunnel barrier height could be controlled by applying gate voltage. We also measure the rectifying characteristics as a function of the back gate voltage to confirm the tunneling transport. The devices exhibited steep subthreshold slope (SS) of 40 mV/decade, which was lower than the theoretical limit of MOSFETs at room temperature indicating the devices were tunnel diodes.

References

NM01.07.17
Importance of Electrical Current in Post-Synthetic Graphitization Process for Property Improvements of Single Walled Carbon Nanotubes and Graphene Sheet Naoyuki Matsumoto, Azusa Oshima, Kenji Hata and Don Futaba, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Many papers have clarified that the healing of crystalline defects in materials improves various properties. In this study, we demonstrate a new approach for healing crystalline in single wall carbon nanotubes (SWCNTs) based on simultaneously applying electrical current and heat. In this way, we succeeded in improving the graphitization without inducing other changes to the structure, in particular diameter and wall number. To achieve this we designed and constructed a specialized treatment device capable independently applying current (~240 A cm-2) and heating (room temperature to 2000 °C). Our examination found that at 800 °C, 150 A cm-2 for 1 min, we could achieve a 3.2-times increase in crystallinity as indicated by an increase in Raman G- to D-band ratio, a 3.1-times increase in electrical conductivity (from 25.2 to 78.1 S cm-1), and a 3.7-times increase in thermal conductivity (from 3.5 to 12.8 W m-1 K-1). The simultaneous increase in electrical and thermal conductivities stems directly from defect healing, and importantly we observed no additional change in diameter or wall number. The simultaneous application of current is essential in maintaining the initial CNT structure (diameter and wall number) as demonstrated in a reference test where CNTs were treated without an applied current. Further studies have demonstrated the scalability of this process in achieving similar improvement (~3-fold) in both thermal and electrical conductivities, which results indicate the fundamentally scalable towards larger scale (i.e. gram-level or more) amounts of SWCNT. In addition to fundamental improvement in composition and structure, we applied this re-graphitization process to few-layer, free-standing exfoliated graphene. We achieved this by applying the electrical current (current density: ~900 A cm-2) in conjunction with heating (~900 °C) in-plane of an “exfoliated graphene sheet” with the original sample holder in an argon ambient. After treatment at 900 °C and 545 A cm-2 for 1 min, we observed a significant increase in graphitization as exhibited by a ~10-times increase in the Raman G- to D-band ratio (2.84 to 36.7) and no observed change in interlayer separation, i.e. (002) reflection by x-ray diffraction. Furthermore, we observed a ~2.0-times increase in electrical conductivity (from 1088 to 2275 S cm-1). These results demonstrate the use of a post-synthesis process to nanocarbon materials to improve crystallinity and the difference between its application towards SWCNTs and graphene. Therefore, we believe strongly that this process overcomes one of the major limitations of SWCNT and
graphene (other 2D-materials) toward real applications.

NM01.07.18

Damage Formation Due to Low-Energy He and Ne Ion Irradiation in MWCNTs
Sathana Eswara, Jean-Nicolas Audinot, Tom Wirtz and Patrick Philipp; Advanced Instrumentation for Ion Nano-Analytics (AINIA), MRT Department, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg.

Targeted tuning of the structure and properties of carbon nanotubes (CNT) using ion irradiation is very attractive for technological applications. To understand the damage formation and evolution due to ion irradiation in multiwalled (MW) CNT, we used 25 keV Ne⁺ and He⁺ ion irradiation with controlled fluences in the range of 10¹⁴ to 10¹⁸ ions/cm² and subsequently investigated the irradiated areas by TEM imaging and Raman spectroscopy. A new methodology involving Au TEM grids was developed to ensure compatibility across the different techniques and to preclude the Raman contribution coming from the amorphous carbon support of typical TEM grids. The experimental results indicate a significant difference in the damage evolution between He⁺ and Ne⁺ irradiation. Furthermore, the sample thickness was found to play an important role in determining the extent of damage. TEM imaging suggests that the thicker areas are significantly amorphized, while thin areas (t < 10 nm) were found to be relatively undamaged with only very minor changes in comparison to pristine samples. For He⁺ and Ne⁺ irradiation, damage formation evolves differently, with a change in the trend of the ratio of D to G peak in the Raman spectra being observed for He⁺ but not for Ne⁺. The experimental results were then compared with the Monte-Carlo (MC) simulations of ion-solid interaction by approximating the sample to a thin carbon membrane. Due to the small thickness of the MWCNTs, sputtering has been observed for the top and bottom side of the samples. Depending on thickness and ion species, the sputter yield is significantly higher for the bottom than the top side.

In this presentation, we will describe the new methodology that was developed for this study and discuss the experimental results from correlative TEM-Raman analysis of MWCNT under He⁺ and Ne⁺ irradiation together with insights drawn from MC simulations using SDTRIMSP.

NM01.07.19

Organic Solvent-Induced Spectral Shifts of Near Infrared Photoluminescence of Locally Functionalized Single-Walled Carbon Nanotubes
Yoshiaki Niidome, Tomohiro Shiraki, and Tsuyohiko Fujigaya; Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan; International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan; JST-PRESTO, Kawaguchi, Saitama, Japan.

Semiconducting single-walled carbon nanotubes (SWNTs), which have one-dimensional cylindrical structures with a graphene wall, show near infrared (NIR) photoluminescence (PL). As an interesting feature of SWNTs, the PL properties are sensitively changed by effects of microenvironments that are composed of surfactants and solvent molecules. Therein, physical properties of microenvironments such as polarity and polarizability could affect coulumb interactions between electron - electron or electron - hole in the tubes [1]. In recent studies, local chemical functionalization of SWNTs is reported to produce novel PL properties [2][3]. The locally functionalized SWNTs (lf-SWNTs) emit new PL (E₁₁*) whose wavelength are red-shifted over 100 meV from the original PL (E₁) of the pristine SWNTs and their quantum yields increase largely. These properties arise from electronic structure variation introduced by the functionalization and exciton trapping at the functionalized sites, respectively. Actually, we experimentally revealed that energy levels of the HOMO and LUMO shifted at the local functionalized sites with dependence on the chemical structures of the functionalized groups [4].

In this study, we examine microenvironment effects on the E₁₁* PL of lf-SWNTs in order to compare excitonic properties at the local functionalized sites and the pristine sites. Herein, we synthesized nitroaryl-functionalized SWNTs (lf-SWNTs-NO₂) that were solubilized in D₂O containing sodium dodecylbenzenesulfonate (SDBS). For microenvironment creation of an organic solvent [5], o-dichlorobenzene (oDCB), which was immiscible in water, was poured into the lf-SWNTs-NO₂ solution and vigorously shaken, then the separated aqueous layer was collected for measurements. After the experimental process, PL peaks of E₁₁* and E₁ were red-shifted, indicating that oDCB permeated into the hydrophobic regions between the nanotubes and the coating SDBS micelles. Interestingly, the shifted energy value of E₁₁* was larger than that of E₁; the result indicates that interactions of oDCB on the nanotubes might be varied at the local functionalized sites and the pristine sites. Details including the effects of other solvents will be discussed in this presentation.

References

NM01.07.20

Preparation of Size-Controlled Carbon Nanomaterials via Morphological Transcription from β-lactoglobulin Aggregates
Yoshifumi Orimoto, M Nuruzzaman Khan, Yutaka Kuwahara, Makoto Takafuli and Hirotaka Ibara; Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan.

Herein, we report a diverse and simple method that enables stabilization and transcription of protein - derived nano - sized superstructure. It is known that β-lactoglobulin used to forms aggregates by controlling specific protein concentrations and solution pH, ionic concentration and heating temperature, so it was thought that we succeeded in morphological transcription. Furthermore, CPNS after high temperature carbonization also maintained spherical shape with nano-sized carbon-shell. It was also possible to confirm the morphological stabilization of the superstructure before and after polymer coating under alkaline conditions. Prepared CPNS is expected to be used in fields such as nanosensor, drug delivery, and adsorbent. In addition, this method is expected to be used as a method for preparing and functionalizing carbon nanostructures, which is convenient and versatile than ever before.

NM01.07.21
Mechanism Study of Chemical-Vapor-Deposition Graphene Adlayers Pei Zhao, Xuewei Zhang and Hongtao Wang; Zhejiang University, Hangzhou, China.

In the past few years there have been many exciting achievements in the synthesis of large-size and high-quality monolayer graphene (MLG) using the chemical vapor deposition (CVD) method on Cu substrates. During the MLG growth, accompanying adlayers occur and remain a broad interest to researchers for a deep understanding of the graphene mechanism. When methane is used as the precursors, it is believed that the adlayers are grown underneath the previous layer, whereas when ethanol or other precursors with stronger reactivity is used, adlayer growth follows a layer-by-layer regime. In this work, we studied the growth mechanism of graphene adlayers using carbon isotope labelling of the precursors and Raman spectroscopy. Results show that when methane is used, the growth of the adlayers exhibits several different modes. For most of the adlayers, they maintain their AB-stacked or twist structures with the upper layer during the growth since their nucleation, but for some of them these stacking structures can suddenly change during the growth. Moreover, we also observed that the adlayers can nucleate tens of minutes later during the growth (not together with the first layer), with an AB-stacking with the upper layer. We also compared the results with previously reported work using ethanol, whose epitaxial nucleation of the second layer is mainly due to the active CH3 radicals with the presence of a monolayer-graphene-covered Cu surface. We believe that this study will help clarify more growth mechanism of graphene by CVD process, and lead to many new strategies for scalable synthesis of graphene with more controllable structures and numbers of layers.

References

NM01.07.22
Extraordinary Lithium Storage Property Form Transition Metal Oxide Electrodes by Introducing Porous CNT Sponges and Massive Oxygen Vacancies Mingchi Zou; College of Engineering, Peking University, Beijing, China.

Transition metal oxides (TMOs) are regarded as alternative anode materials due to their high theoretical capacity, nontoxic and low cost. However, it is unable to take into account of high capacity and stable cycling performance which hinder their practical applications. Here, we improve both specific capacity and stability of transition metal oxides by following two aspects: 1) composing with CNTs through a hierarchical coaxial nanostructure, and 2) introducing with massive oxygen vacancies. The synergistic reaction between TMOs (shell) and CNTs (core) through a hierarchical coaxial nanostructure can effectively enhance conductivity and reduce the Li+ diffusion distance, and consequently improve the rate performance, cycling stability and specific capacity. We develop an unique three-dimensional sponge-like CNT bulk material with excellent conductivity, high porosity and stable compressibility, which can be used as an ideal current-collector. Titanium dioxide (TiO2) is directly deposited onto the CNT sponge as a coaxial structure, forming a highly porous composite sponge electrode without any redundant additives (such as conducting agent and binder). As an anode for LIBs, TiO2@CNT sponge exhibit stable charging/discharging plateau voltages, higher capacity, better stability and rate performance comparing with pure TiO2 electrodes.

Moreover, due to the TMOs are directly deposited onto the CNT sponge, the morphology of electrodes are determined by the CNT sponge. We fabricate a 1D porous electrode by depositing CNT sponges on a single carbon fiber (CF) and then deposit manganese dioxide (MnO2) onto the CNT sponge and obtain a MnO2@CNT@CF fiber-shaped electrode for LIBs. Massive oxygen vacancies are introduced into TMOs to further improve the performance of LIBs. An unique electric field assistant annealing method is developed to treat TiO2@CNT sponges. Under the combined function of the temperature and electric field, oxygen vacancies are rapidly formed and migrated through TiO2, forming an amorphous TiO2@CNT sponge with a large number of oxygen vacancies (~45%) uniformly distributed in the hole TiO2@CNT exhibits a capacity as 604 mAh/g which is much higher than theoretical capacity of TiO2 (335 mAh/g). Even under high rate condition (10000 mAh/g), the capacity is stable as 110 mAh/g. This extraordinary performance is originated from the massive uniformly distributed oxygen vacancies which significantly enhance the conductivity and Li+ diffusion ability of TiO2. Using this electric field assistant annealing method, massive oxygen vacancies can be introduced into many other TMOs (such as MnO2 and SnO2).

In conclusion, we efficiently improve the lithium storage performances of TMO electrodes by composing CNT sponge with a coaxial structure and introducing massive oxygen vacancies uniformly. Our work has a prospect in achieving advanced LIB anodes with stable and high rate capacities for many practical applications.

NM01.07.24
New Carbon Allotropes—Novamene and Protomene as Future Advanced Carbon-Based Nanomaterials Daniel Choi1, Mohamed Alfahim2, Larry Burchfield2, Rashid Alfahim2, Kin Liao1, Abdel F. Isakovici1, Bao Huan An1, Tamador Elshohra1 and Nicola Manini2,3; Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Alfields, Inc, Abu Dhabi, United Arab Emirates; 3Universita degli Studi di Milano, Milano, Italy.

A new classification of carbon allotropes, called, Novamene is the first release in a series which fall into an entirely new class of carbon in 2016. As for the comparison with diamond and other carbon allotropes, thermal properties of Protomene can be differentiated. Since thermal expansion behaviors of Protomene are associated with interplane bonding, Protomene may experience structural phase change which can lead to a more rapid change in energy band gap and thermal expansion compared with diamond and silicon.

We will present our efforts of on-going development of fabrication techniques for new carbon allotropes including Novamene and Protomene based on both top-down and bottom-up approaches and modeling activities by means of Density Functional Theory (DFT) simulations.

References
Electronic properties including work function, carrier type, and conductivity were measured and correlated with their ORR catalytic activity for post-doping process and high-temperature annealing treatment, and evaluated their ORR catalytic activities in an acid electrolyte. In addition, their temperatures (> 1000 K). The obtained ultimate strength and ultimate stress show an anisotropic material; the highest ultimate strength was obtained for x simulations. We used the ReaxFF force field as available in the LAMMPS code. Our results [2] show that the protomene are very stable, up to very high temperatures (> 1000 K). The obtained ultimate strength and ultimate stress show an anisotropic material; the highest ultimate strength was obtained for x directions, with a value of ~102 GPa. As for the ultimate strain, the highest one was for z direction (27% of strain) before protomene mechanical failure (fracture).

Acknowledgments:
We would like to thank the Brazilian agency FAPESP (Grants 2013/08293-7 and 2016/18499-0) for financial support.

References:
onset potential, oxygen reduction current density at half-wave potential, and numbers of electrons transferred per oxygen molecule in the ORR, the AN-SWCNTs exhibited superior ORR catalytic activity to the N-SWCNTs. The work function of the AN-SWCNTs was lower than that of the N-SWCNTs, and the carrier type of the AN-SWCNT film was obviously n-type even in air. The conductivity of the AN-SWCNT film was higher than that of the N-SWCNT film. These results suggest that the low work function and high conductivity observed in the AN-SWCNTs can promote the ORR catalytic activity.

NM01.07.28
Towards Single Crystal Monolayer Films—Catalyst Engineering for High Quality CVD Graphene Oliver Burton and Stephan Hofmann; University of Cambridge, Cambridge, United Kingdom.

Chemical Vapour Deposition (CVD) has become the dominant technique for the growth of graphene and related 2D materials, driven by the emerging industrial demand for ‘electronic-grade’ materials that are consistent over large areas. Significant progress has been made using heterogeneous catalysis,[1] and using the most widely used substrates is polycrystalline copper foil. A fundamental challenge in devising a CVD process that consistently results in homogeneous single crystal graphene is the initial substrate: which has varying concentrations of different trace impurities that can affect the growth process. It has been shown that a simple oxidative pre-treatment of the Cu catalyst to remove residual carbon results in a significant reduction in nucleation density, allowing for a much larger graphene domain size to be achieved.[2] There is still a compromise between fast growth rates and reducing sources of defects such as grain boundaries. Further to this, adequate characterisation of large area monolayer graphene films has become a significant challenge on its own.

Here we report how these compromises in controlled graphene growth can be addressed by systematically studying modifications of the Cu catalyst. The effects of adding oxygen to the Cu bulk on graphene nucleation density, morphology, growth rate and quality are closely examined. The epitaxial relationship of graphene on different Cu textures is quantitatively analysed and the capability to significantly enlarge Cu grains and recrystallize the foil is demonstrated. By leveraging the epitaxial alignment seen on specific Cu facets, single crystal graphene films can be rapidly grown, paving the way for films with improved homogeneity. In addition, a novel method to characterise graphene quality on a larger scale is introduced based on a modification of established Raman characterisation strategies.


NM01.07.29
High-Performance Magnetorheological Suspensions of Fe3O4-Deposited Carbon Nanotubes with Enhanced Stability Hoyeon Kim, Junseok Choi and Yongseok Seo; Seoul National University, Seoul, Korea (the Republic of).

The magnetorheological (MR) performance of suspensions based on the Fe3O4-deposited carbon nanotubes (CNTs) was investigated by using a vibrating sample magnetometer (VSM) and a rotational rheometer. The Fe3O4-deposited CNTs were synthesized by the reduction process in which nano-Fe3O4 nanoparticles were generated and adsorbed on the surface of CNTs. All tested suspensions displayed excellent MR behaviors with high yield stress. The important parameter which determined the MR performance was the surface density of Fe3O4 on the CNT surface. The morphology was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). Most Fe3O4 particles adsorbed on the surface of PS/Fe3O4 particles to make the surface topology bumpy and rough which decreased the particle sedimentation velocity. Finally, Turbiscan apparatus was used to examine the sedimentation properties of Fe3O4-deposited CNTs suspensions. The suspensions showed excellent stability against sedimentation, much better than bare Fe3O4 particle suspension due to the inherent low density of CNT and its inside pore which can reduce the density mismatch between the nanoparticles and the carrier medium as well as the surface topology change due to the adsorption of Fe3O4.

NM01.07.30
Fabrication of Nanoporous Ultrathin Membranes by Cluster Ion Irradiation Ar dak Ain abay ev1, Aid yn Shaik ho v3, Ab at Zhuld ass ov1, Sean Kirkpatrick1, Michael Walsh3, Mititaka Terasawa4 and Zin et u la Z. Insepov1,2,3; 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan; 4Laboratory of Advanced Science and Technology for Industry, Kouto, Japan; 5Exogenesis Corp., Billerica, Massachusetts, United States.

Gas Cluster Ion Beams (GCIB) is a powerful tool for surface modification of various materials and theoretically and experimentally demonstrated the ability to create defects in ultrathin graphene-like films. In this study GCIB of Ar with acceleration energy  E = 30 kV (Exogenesis, MA, USA) and total fluences ranged from 1x1019 to 1x1021 ions/cm² is used to produce defects in ultrathin films such as graphene, graphene oxide, MoS2 and Si, HOPG as a reference. GCIB irradiated ultrathin films were characterized by NEXAFS and Raman spectroscopy, scanning electron and atomic force microscopy. The Raman spectroscopy (Horiba) study of the irradiated samples was conducted by a 632 nm laser wavelengths and 100x objective with a laser spot size of ~1 μm, 2 mW power and atomic force microscopy (AIST NT) measurements were carried out in a tapping mode by SUPERSHARP SILICON™ AFM probes for high resolution. NEXAFS spectroscopy measurements were carried out at the NewSUBARU BL09A beamline of the NewSUBARU SR LATTI facility at the University of Hyogo, using total-electron yield (TEY) method and without uncompleted correction of energy. Density functional theory (DFT) calculations have been performed to study the Raman spectra of pristine and graphene with vacancy defects. Large-scale parallel molecular dynamics (MD) simulations (LAMMPS) were employed for studying interactions of accelerated cluster ions with ultrathin films, such as graphene, MoS2, HOPG, and BN. The MD results showed formation of uniform holes, with the diameters of 10-20 nm, in the ultrathin films, and were used for optimization of the experimental fabrication of holes in 2D-films.

The DFT and MD simulations provides fundamental understanding of the argon bombardment of ultrathin films and its influence on Raman spectra of graphene.

NM01.07.31
Study of the Interfacial Interaction Between Carbon Nanotubes and Catalyst—The Effects on the Tube Diameter Mauricio Carvajal Diaz and Perla B. Balbuena; Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas, United States.

Single-walled carbon nanotubes (SWCNTs) are seamless cylinders of graphene that have been at the forefront of nanotechnology research for the past two decades. While mass-produced SWCNT powders are adequate for some applications, many emerging applications require stricter control over SWCNT properties and architectures, necessitating targeted growth, i.e. tailoring the physical properties of the SWCNTs (diameter, orientation/architecture, etc.). This work attempts to prove the key role of the graphene properties and the metal - catalyst interaction in the relation between catalyst size and nanotube diameter. We work on the assumption that the curvature energy is one of the most influential factors in the graphene film formation and a crucial constraint...
to determine the stable diameter of the nanotube during the growth. The calculation of interlayer binding energies using density functional theory (DFT) and pseudopotential functions has been valuable to find the transition diameter between fullerene and tube. Additionally, we propose a new model that links statistical mechanics theory with the possible strain energy states and allows the calculation of the expected or most probable diameter. This is just the first step to bring light to the yet undiscovered reigning principle for the nanotube’s diameter stability during nucleation.

NM01.07.32
Segregated rGO/P(MMA/PA) Bilayer Composite Systems with Improved Electrical Features Tajamal Hussain, Sidrah Ishaq, Adnan Mujahid and Azeem Intissar; University of the Punjab, Lahore, Pakistan.

Poly(methylmethacrylate) (PMMA) based reduced graphene oxide (rGO) and reduced polyaniline (rPA) segregated bilayer composites (rGO/PMMA/rPAI) with different compositions have been designed as high performance nanocomposites. Synthesis process of the rGO incorporated PMMA (rGO/PMMA) and rPAI incorporated PMMA (PMMA/rPAI) and rGO/PMMA/rPAI composites have been monitored by UV-visible and FTIR spectroscopy. Performance of the synthesized segregated bilayer composites has been studied by analyzing the electrical features measured at wide range of frequencies starting from few Hz to 1MHz. Substantial enhancement in the electrical properties was observed at relatively lower filler contents. Almost 15 times increase in value of dielectric constant was observed at just 0.7 wt% of rGO. Impressive increase in the electrical conductivity was achieved and percolation threshold value was observed as low as 0.06 wt%. Electrical features determined for these segregated bilayer composites are more outstanding than those of simple tri components PMMA based composites.

NM01.07.33
Organic Field Effect Transistors Incorporating Ultrapure Semiconducting Single-Walled Carbon Nanotubes Nicole Rice1, William Bodnaryk2, Brendan Mirka, Owen Melville1, Alex Adronov2 and Benoit Lessard3; 1University of Ottawa, Ottawa, Ontario, Canada; 2Chemistry, McMaster University, Hamilton, Ontario, Canada.

Printed electronics is a burgeoning field that has received intense research interest and is beginning to experience commercial successes. Single-walled carbon nanotubes (SWNTs) are a unique and promising building block for incorporation into next generation superfast electronic devices. SWNTs have very high carrier mobilities, with band gaps compatible for integration into logic circuits. Their excellent mechanical flexibility allows for potential incorporation into flexible printed electronics, enabling fully-printed transistors and circuits with performances that support low cost, large area fabrication. Progress in incorporating SWNTs into commercial devices has been hindered by the presence of metallic SWNTs, which are produced alongside semiconducting SWNTs during synthesis, and negatively impact device performance. Fabrication of ambipolar SWNT organic thin film transistors (OTFTs) with high carrier mobilities and high on/off ratios remains particularly challenging; many examples in the literature required high temperature, expensive and energy-demanding processes.

Since the initial discovery of conjugated polymer-assisted dispersion and purification of SWNTs in 2008, several polymer families have been successfully shown to selectively disperse semiconducting SWNTs. However, only a relatively small number of these supramolecular complexes have been incorporated into OTFTs. We used a novel conjugated polymer to exclusively disperse semiconducting SWNTs. The dispersion procedure requires a simple sonication and centrifugation, during which the metallic SWNTs sediment out. Solution purity was evaluated using UV-Vis-NIR and Raman spectroscopies. The resulting dispersions are amenable to solution processing techniques such as spin coating and drop casting, allowing for the potential for large area device fabrication at room temperature. Ambipolar OTFTs were fabricated under ambient conditions using this solution and tested in both air and under inert atmosphere. The presence of excess conjugated polymer, solution deposition techniques, SWNT density, surface treatment, and post-fabrication treatment were all investigated to determine which parameters facilitated the production of OTFTs with high mobilities (>20 cm2V-1s-1), high on/off ratios (106-108), negligible hysteresis, controlled threshold voltages, and high bias stability.

NM01.07.34
Bubble Tunable Novel Vibration Damping PDMS-Graphene Soft Nanocomposites Tong Zuo1, Kuangyu Shen1, Xiaoliang Li1, Isaac Macwan1, Prabir Patra1, Chandra S. Tiwari2, Peter S. Owuor2 and P. M. Ajayan2; 1Biomedical Engineering, University of Bridgeport, Bridgeport, Connecticut, United States; 2Materials Science and Nanoengineering, Rice University, Houston, Texas, United States.

Constrictions inclusions or other accidental cases occur very regularly. Often times constrictions leads to chronic traumatic encaphalopathy (CTE) and eventual death. Polydimethylsiloxane(PDMS)-based nanomaterial are gaining widespread attention in this regard. Here we report a unique bubble tunable graphene reinforced PDMS nanocomposites as a vibration dampening and possibly concussion resistant material. PDMS based nanocomposite was prepared by solvent swelling of the PDMS (Sylgard 184 from Dow Crowing Company) in chloroform/TEOS (4:1 ratio) mixture followed by ultrasonication of the graphene nanoplatelets in the solvent that swells the polymer. Various nanocomposite structures with and without bubbles were prepared. We studied the mechanical properties of PDMS-graphene nanocomposite as a function of temperature, pressure, nanoparticle size, solvent percentage, curing agent and filler concentration. The effect of different concentrations of graphene in the nanocomposite with and without bubble formation were measured and analyzed using dynamic mechanical analyzer (DMA) and impact testing. Physical interaction of PDMS adsorptions on the graphene were computed using molecular dynamic (MD) simulation. The influence of a well controlled bubble structure on the energy absorption behavior of the nanocomposite was explored. Stiffness of the nanocomposites increased with the loading of graphene. The role of bubble and bubble-graded nanocomposites is underway.

NM01.07.35
Intrinsic Wettability of Graphitic Carbons and Its Implication on Double Layer Capacitance Lei Li and Haitao Liu; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Graphitic carbons have been considered as hydrophobic for nearly eighty years. However, recent works in our lab1,2 showed that graphitic surfaces are much more hydrophilic than previously thought. Since the water-graphitic interface is critical to many important applications including electrodes, adsorbents, catalyst support, and solid lubricants, this unexpected finding could completely change the way graphitic materials are made, modeled and modified.

In this presentation, we will discuss on the intrinsic water wettability of graphitic carbons and its implication on double layer capacitance. First, our recent experimental results, e.g., contact angle, XPS, ATR-FTIR and ellipsometry, will be presented showing that pristine graphene and graphite are mildly hydrophilic and airborne hydrocarbons make the surfaces appear to be hydrophobic. Second. The implication of contamination will be illustrated through comparing the electrochemical activity and double layer capacitance of pristine and contaminated graphite. Lastly, future research directions to address a few important unanswered questions will be presented.

Reference:

**NM01.07.36**

**Intercalation of Fullerenes Between Graphene/Cu Interfaces**

Alexandre F. Fonseca1, Socrates O. Dantas2, Douglas S. Galvao2, Difan Zhang3 and Susan B. Sinnott4; 1State University of Campinas, Campinas SP, Brazil; 2Universidade Federal de Juiz de Fora, Juiz de Fora, Brazil; 3University of Florida, Gainesville, Florida, United States; 4The Pennsylvania State University, State College, Pennsylvania, United States.

Investigation of the structure and properties of the intercalated molecules between interfaces of two-dimensional layers or of a layered material and a substrate is a subject of great interest. Formation of crystalline patterns as well as induction of chemical reactions under two-dimensional covers are two of the main drivers behind this interest. One recent study by Reineke and collaborators [Nano Letters 15, 7421–7430 (2015)], showed the formation of amorphous and crystalline structures of C60 intercalated between graphene and a copper substrate. They further reported the existence of more or less strained graphene wrinkles, as well as detached graphene from substrate depending on the concentration or distance between the intercalated C60 molecules. Motivated by this work, we investigated the formation and thermal stability of graphene wrinkles as well as graphene attachment and detachment from substrate on previously distributed C60 and carbon nanotube molecules on copper substrate. We performed fully atomistic reactive molecular dynamics (MD) simulations using the third generation of the charge optimized many-body potential as available in the LAMMPS computational package. As the timeframe of spontaneous intercalation of C60 molecules between graphene and the substrate is too high to be feasibly simulated by MD methods, we simulated the “blanketing” of graphene on different concentrations of C60 and carbon nanotubes previously laid on the substrate. We tested both fixed and non-fixed structures, i.e., we predicted the change in the height of graphene, fullerene, and substrate when the fullerenes are not fixed. We then verified that graphene attaches to the substrate when the distance between the fullerenes is at least 6 nm. Below that distance, graphene becomes locally suspended and low strain is verified. While such studies of intercalation of molecules on interfaces formed by graphene-substrate are motivated by finding out ways to control wrinkling and strain in graphene, this work reveals the role of stability and wrinkling as well as the shape and structure of intercalated molecules under the action of graphene on the final structure and properties.

**NM01.07.37**

**Double Charge Neutrality Point Induced by H2 Exposure in Graphene Devices**

Cintia L. Pereira, Alisson R. Cadore, Natália P. Rezende, Leonardo C. Campos and Rodrigo G. Lacerda; Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil.

In this work, we present a study regarding the interaction between molecular hydrogen (H2) and graphene field effect transistor with different metals and contact geometries. We demonstrate that this interaction is strongly dependent on the characteristics of the graphene-metal contact interface. Three different contacts were probed: pure Au, Au/ Cr and Au/ CrO2 contacts. Interestingly, we observed that only for Au/CrO2 contact devices the emergence of a second charge neutrality point (CNP) in the resistance as function of gate voltage curves (“M-shape”) due the H2 exposure. This is the first time that such behavior (“M-shape”) is found due to a gas interaction with graphene devices. This effect was observed for different conditions of temperatures (25°C-200°C) and H2 concentrations (0.5%-50%) and it is totally reversible. Previous works about graphene-contact interaction, demonstrated that the difference of the work function between both materials generates a local p-type or n-type doping [1]. Added to the electrostatic doping generated by the back gate voltage, a pn junction is formed. Also, Cadore et al. verified that the H2 can modulate these pn junctions in graphene devices with Au/ Cr or Au contacts [2]. Thus, the formation of the two CNP that appear on devices with Au/CrO2 contacts can be explained by the fact that the charge density of the graphene under the electrodes and in the channel can be modulated by back gate voltage application. This, in two CNP appear without pinning the work function, and the difference between the Fermi level in both regions generates the two CNP [3]. Also, we believe that the thin layer of oxide formed (Cr2O3) may be responsible for a catalytic process and facilites the hydrogen flow inside the interface contact-graphene, hence increasing the influence from such regions of the electrical measurements. In other words, our findings suggest a way of inducing the decoupling of the work function between the metallic electrodes and graphene by the use of contacts Au/CrO2 and hydrogen gas exposure. Additionally, we demonstrate that the high variation of the resistance generated by the emergence of the second peak and the low time of response to hydrogen provides a system that is very promising for H2 sensor applications. This work was supported by CAPES, Fapemig (Rede 2D), CNPq and INCT/Nanomaterias de Carbono. References:


**NM01.07.38**

**Flexible CNT-Decorated PDMS Foams Enable Unprecedented Detection of Ultralow Strain and Pressure Coupled with Large Working Range**

Rossella Iglio1, Stefano Mariani2, Valentina Robbiano2, Luccano M. Strambini2 and Giuseppe Barillaro3; 1University of Pisa, Pisa, Italy; 2National Research Council, Pisa, Italy.

Low-cost piezoresistive strain/pressure sensors with large working range, at the same time able to reliably detect ultralow strain (≤0.1%) and pressure (≤1 Pa), are one of the challenges that have still to be overcome for flexible piezoresistive materials towards personalized health-monitoring applications. Here, we report on unprecedented, simultaneous detection of ultrasmall strain (0.1%, i.e. 10 µm displacement over 10 mm) and subtle pressure (20 Pa, i.e. a force of only 2 mN over an area of 1cm2) in compression-mode, coupled with a large working range (i.e., up to 60% for strain – 6 mm in displacement - and 50 kPa for pressure) using piezoresistive, flexible three-dimensional (3D) macroporous PDMS (pPDMS) foams decorated with pristine multi-walledCNTs1. pPDMS/CNTs foams with pore size up to 500 µm (i.e. twice the size of those of commonly used foams, at least) and porosity of 77%, decorated with a nanostructured surface-network of CNTs at densities ranging from 7.5 to 37 mg/cm2 are prepared using a low-cost and up-scalable process, through replica molding of sacrificial sugar templates and subsequent drop-casting of CNT ink. A thorough characterization shows that piezoresistive properties of the foams can be finely tuned by controlling the CNT density, and reach an optimum at a CNT density of 25 mg/cm2, for which a maximum change of the material resistivity (e.g., ρ2/ρ0=4 at 50% strain) is achieved under compression. Further static and dynamic characterization of the pPDMS/CNTs foams with 25 mg/cm2 of CNTs highlights a detection limit for strain and pressure of 0.03% (3 µm displacement over 10 mm) and 6 Pa (0.6 mN over an area of 1 cm2), respectively; moreover, good stability and limited hysteresis are apparent by cycling the foams with 255 compression-release cycles over the strain range 0-60%, at different strain rates up to 10 mm/min. Our results on piezoresistive, flexible pPDMS/CNT foams pave the way towards breakthrough applications for personalized health care, though not limited to, which were not fully addressable to date with flexible strain/stress sensors.

Photoluminescence Modulation of Single-Walled Carbon Nanotubes by Meta-Linked Bis-Aryldiazonium Modifiers

Boda Yu, Tomohiro Shiraki, and Tsuyoshi Fujigaya

1Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan; 2International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Nishi-ku, Fukuoka, Japan; 3JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, Japan.

A small amount of chemical modification of single-wall carbon nanotubes (SWNTs) has been reported to create modified sites with narrower band gaps on the tubes. The resultant locally functionalized SWNTs (IF-SWNTs) show new photoluminescence (PL) with red-shifted wavelengths and high quantum yields. The used SWNTs were (6,5) chirality-rich tubes (CoMoCAT) and they were solubilized in D2O containing sodium dodecylsulfate through sonication followed by ultracentrifugation. Chemical modification of SWNTs was conducted by mixing the solubilized SWNTs and synthesized meta-linked bis-aryldiazonium salts. When the meta-linked bis-aryldiazonium salt having the spacer of five methylene units (mC5-Dz) was reacted with SWNTs (mC5-IF-SWNTs), very slight changes were observed in the UV/vis/NIR absorption spectrum in comparison to that of pristine SWNTs, indicating that local chemical functionalization occurred. In sharp contrast, in the PL spectrum of mC5-IF-SWNTs, a new PL peak appeared at 1246 nm that was largely red-shifted from typical E1* and was the different wavelength value from the E2* of the previously reported IF-SWNTs using the para-linked bis-aryldiazonium salts. These results indicate that the structural difference between meta- and para-linked bis-aryldiazonium salts may induce unique spectral changes of E1, E2* for the IF-SWNTs. Other structural factors will be discussed in the meeting.

References


Experimental and Theoretical Study of Aqueous Dispersions of Graphene-Based Materials

Shan Jiang and Karl Coleman; Department of Chemistry, Durham University, Durham, United Kingdom.

Since the first reports of its isolation in 2004, graphene has received unprecedented interest from the scientific community. This is due to its remarkable properties such as high electron mobility, thermal conductivity and mechanical strength. However, in spite of this huge potential, a number of hurdles have existed which hinder graphene’s wholesale uptake by commercial applications. One of these is the need to improve the processability of graphene materials by improving their dispersibility in a range of aqueous and non-aqueous solvents. A wide range of approaches have been employed to try to improve the dispersibility of graphene in many solvents such as covalent functionalization of graphene sheet, aiming to enhance dispersibility by improving interaction with the solvent. The downside to all covalent modification techniques is that the presence of additional chemical functionalities disrupts the sp² matrix of the graphene sheets by introducing defect sites which can have a significant negative effect on the properties of the material. Surfactants have been used which adsorb non-covalently to the surface of the graphene sheets improving their dispersibility. However, residual surfactant molecules can have a negative impact on the properties of the graphene prepared and can be difficult to remove.

Herein, we have developed a method for improving the dispersibility of graphene and its related materials in commonly used, and low boiling solvents by making use of prior dispersion in good solvents (such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF)). This method allows reduced graphene oxide (rGO) to be dispersed in water at concentrations of up to 20 μg ml⁻¹ which is over a six-fold improvement compared to dispersion of untreated rGO prepared under the same conditions. Predispersion of rGO in NMP can produce NMPrGO which forms a stable dispersion in water, with less than 0.3% residual NMP, confirmed by the experimental characterizations. Furthermore, molecular dynamics (MD) simulations have been used to exploit how the dispersion process is facilitated by the organic solvent treatment (NMP and DMF in this study), and investigate graphene and solvents interactions, and solvent geometry and orientation with respect to the graphene sheet. Additionally, DFT calculations have been used to study the electrical properties and charge distribution upon organic solvent adsorption on the graphene surface, in order to rationalize the improved dispersibility in water and ethanol.

(4) Pigler, S. et al., Carbon 2012, 50 (10), 3666-3673.
from the channel as long as the electrode is bridged with the channel through the electrolyte—which we refer to as the remote gating. For effective remote gating, the distance between the gate and channel must be less than 200 μm. As the distance increases, the remote gating effect becomes weaker. The results demonstrate that the dynamic characteristics of the remote-gated graphene transistors can be maintained even if the gate electrode is located 1700 μm apart from the channel, which is comparable to the dynamic characteristics of a device using a direct-gated graphene transistor. Overall, the present results demonstrate the potential of Joule-heating-driven CVD towards fabricating remote-gated graphene transistors that can operate promptly even when they are gated from a distance. We confirmed that the effective current modulation of graphene transistor can be achieved at 1 kHz, even when the gate electrode is located 1700 μm apart from the channel, which were comparable to the dynamic characteristics of a device using a directly contacted gate electrode. The results indicate that the distance-dependence degradation on the dynamic characteristics of the remote-gated graphene transistors can be eliminated. The new device architecture provided here shows new opportunities to exploit graphene transistors for applications requiring long-range control.

**NM01.07.42**

Quantum Confinement Effect in the Absorption Spectra of Graphene Quantum Dots

Leon Yang and Kofi Addu-1, 2


Graphene quantum dots have emerged as functional material for myriad applications due to their unique properties such as deep ultraviolet and blue to green luminescence, two-photon induced fluorescence, minimal to no toxicity, chemical- photo-stability, and biocompatibility. These attractive properties of graphene quantum dots are mainly due to the bandgap opening of two-dimensional graphene quantum confinement effects, edge effects, surface functionalization, and doping. We present our results on the effect of both p- and n-doping on the absorption properties and correlate the results with the diameters to explore electronic and phonon confinement effects.

**NM01.07.43**

Antifouling and High-Permeation Mechanisms in Reverse Osmosis Nanocomposite Membranes made of Carbon Nanotubes and Aromatic Polyamide

Rodolfo Cruz-Silva1, 2, Aaron Morelos-Gomez1, 3, Josue Ortz-Medina1, 2, Yoshishiro Takizawa1, Ayaka Yamanaka1, 3, Michio Katouda1, 3, Syogo Tejima1, 3, Kenji Takeuchi1, 2, Takuya Hayashi1, 3, Mauricio Terrones1, 2 and Morinobu Endo1, 2, 3

1. Institute of Carbon Science and Technology, Shinshu University, Nagano, Japan; 2. Research Organization for Information Science & Technology, Tokyo, Japan; 3. Department of Physics, Department of Materials Science and Engineering, and Department of Chemistry, The Pennsylvania State University, State College, Pennsylvania, United States.

Nanocomposite membranes made with multiwalled carbon nanotubes (MWCNTs) and aromatic polyamide (PA) have been studied to improve their superfiltration performance, that combines high permeation, high salt rejection, good chlorine resistance, and low-fouling behavior. We have used a combination of experimental techniques, such as cross-flow filtration, microscopy and spectroscopy, whereas molecular dynamics studies were carried out to understand the membrane at the atomic level. The MWCNT-PA nanocomposite membranes were prepared by interfacial polymerization using an aqueous phase containing MWCNTs and an organic phase. Membranes were then evaluated under cross-flow and studied by x-ray photoelectron spectroscopy, Fourier transformed infrared spectroscopy, and electron microscopy. Organic fouling was studied using a protein (bovine serum albumin) solution, whereas scaling was produced using a mixture of calcium chloride and sodium bicarbonate that precipitates calcium carbonate. During these studies, the fouling of the membrane was followed in situ using fluorescence optical microscopy using an acrylic-made transparent cross-flow cell. The protein was labeled with fluorescein while calcite was added in the scaling study to render the calcium scales fluorescent. MWCNT-PA nanocomposite membranes showed considerably lower organic fouling and less scaling. Our findings show that the observed antiscaling and antifouling nature of the MWCNT-PA membranes is the result of several factors, among them: a smooth membrane surface morphology, a lower surface charge, an interfacial layer of water, and lower mobility of the membrane molecules. These results are important for the design and development of promising low-fouling RO membranes for water treatment. Regarding the water diffusion across the membrane, our studies show that instead of flowing inside the MWCNTs, an oriented diffusion mechanism explains the high water permeation of these membranes. MWCNTs reduce the diffusion path of water molecules across the membranes by providing a lower energy path. The proposed water diffusion mechanism offers an alternative and most likely explanation for the high permeation phenomena observed in CNTs and PA nanocomposite membranes, and its understanding is key to improve the performance of the nanocomposite reverse osmosis desalination membranes.

**NM01.07.44**

Coplanar Floating Gates Connected with Ionic Bridges for Remote Gating Graphene Transistors

Hyunwoo Jo1, Jong Ik Lee1, Hyeunseung Jung1, Wonwoo Lee2, Hojin Lee2 and Moon Sung Kang1

1. Department of Chemical Engineering, Soongsil University, Seoul, Korea (the Republic of); 2. School of Electronic Engineering, Soongsil University, Seoul, Korea (the Republic of).

Exploiting an electrolyte-based gate dielectric that relies on direct migration of ions allows design of unconventional transistor architecture. For example, the current density of a transistor channel can be modulated using a gate electrode that is not located directly on top/below the channel but placed apart from the channel as long as the electrode is bridged with the channel through the electrolyte—which we refer to as the remote gating. For effective remote gating, the electric double layer at both the electrode/channel and the electrolyte/gate interfaces has to be formed promptly. However, the promptness of the electric double layer formation relies on the distance between the channel and the gate. This indicates that the dynamic characteristics of a remote-gated transistors degrades with this distance. Here we present new device architecture to maintain the dynamic characteristics of a graphene transistor, even if its channel is gated remotely. The new structure employs multiple coplanar floating gates bridged through short ionic dielectric layers. Unlike the dynamic characteristics of a remote-gated graphene transistor employing a single, extended electrolyte layer, the devices with multiple, short electrolyte layers could operate promptly even when they are gated from a distance. We confirmed that the effective current modulation of graphene transistor can be achieved at 1 kHz, even when the gate electrode is located 1700 μm apart from the channel, which were comparable to the dynamic characteristics of a device using a gate located 200 μm apart. The results indicate that the distance-dependence degradation on the dynamic characteristics of the remote-gated graphene transistors can be eliminated. The new device architecture provided here shows new opportunities to exploit graphene transistors.

Reference


**NM01.07.45**

Hierarchically Structured Large Area Carbon-Nanosheets for Shape Deformable Electrochemical Capacitors

Jong Han Jun1, Hyeonjun Song2, Changsoo Kim3, In-suk Choi1, Youjin Jeong4 and Ji-Hoon Lee5

1. Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); 2. Department of Information Communication, Materials, and Chemistry Convergence Technology, Soongsil University.
The energy storage systems applied on wearable electronic devices should exhibit mechanical robustness, high cost efficiency, and high electrochemical activity in various human body motion. To solve these requirements, we introduce all-carbon-based large-area nanocomposites for freely-deformable electrochemical capacitors. Three-dimensionally incorporated all-carbon-based self-supported nanocomposites are composed of activated carbons (ACs) dispersed in carbon nanotube (CNT) sheets by direct spinning method without additives such as conductive agents and polymeric binders. On account of the synergetic effects from immensely porous AC particles providing large number of active sites, high electrical conductivity of CNTs, and facile ion accessibility in aqueous electrolyte solution utilized by the acid treatment, the nanocomposites show a greatly improved specific capacitance compared to that of conventional electrodes used metallic current collectors in terms of total mass of the electrodes. We also fabricated the deformable all-carbon-based electrochemical capacitors that showed excellent durability and electrochemical performances under extreme mechanical deformations of bending, folding, twisting, and stretching.

**NM01.07.46**

Fast Solution-Based Catalyst Preparation for Fluidized-Bed Synthesis of Submillimeter-Long Carbon Nanotubes

Risa Maeda¹, Toshio Osawa¹, Hisashi Sugime¹ and Suguru Noda¹; ¹Waseda University, Department of Applied Chemistry, Tokyo, Japan; ²Waseda Institute for Advanced Study, Waseda University, Tokyo, Japan.

Carbon nanotubes (CNTs) have attracted great interest for many potential applications. To realize such applications, low-cost production of high quality CNTs is highly demanded. Fluidized-bed chemical vapor deposition (CVD) is one of the candidates for the realization of mass production [1]. We previously reported fluidized-bed CVD synthesis and easy separation of submillimeter-long CNTs on/from ceramic beads with smooth surface [2]. Our previous reports revealed that the preparation of catalyst is important for CNT growth. Two methods have been examined for the preparation: ex situ sputtering and in situ CVD methods. Fe/Al₂O₃ catalyst by ex situ sputtering yields single-wall CNTs [3]. On the other hand, in situ CVD method enables the fast catalyst deposition in a few minutes [2,4]. Other methods including impregnation have been introduced for the catalyst preparation [5]. However, all these methods still have limitations. For the ease of sputtering and impregnation, they take long time. In situ CVD is quick but uneasy to make fine control of catalyst for single-wall CNTs. Therefore, in order to increase the productivity, it is required to find a method which realizes both the easy control of the catalyst and the short preparation time.

Here we report a fast solution-based catalyst preparation on ceramic beads for CNTs. We coated catalyst on beads by gas-pressurized filtration of ethanol solution of Fe(CH₃COO)₂ and Al(OC₃H₇)₃ in a vertical tube for a few minutes. We then synthesized CNTs on the beads. The beads yielded CNTs with submillimeter length but on a part of the bead surface due to the non-uniform catalyst deposition. After the separation of CNTs from the beads, the beads were reused to reduce the cost. The beads with re-coated catalyst yielded CNTs with higher coverage with increasing number of reuse, resulting in improved yield of CNTs. We will discuss the catalyst condition on the structure of the resulting CNTs.

**References:**


**SESSION NM01.08: Structure and Properties IV**

Session Chairs: Jeffrey Fagan, Ranjit Pati and Maruyama Shigeo

Wednesday Morning, November 28, 2018

Sheraton, 2nd Floor, Republic AB

**8:30 AM **NM01.08.01

In Situ TEM Studies on Phase Transition Mechanism of TMDs by Alkali Metal Intercalation

Xuedong Bai; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

In-situ transmission electron microscopy (TEM) method is powerful in a way that it can directly correlate the atomic structure with physical and chemical properties. By using the homemade in-situ TEM holders, the properties at nanoscale under various physical stimuli have been studied, including mechanical, electrical, and optical properties. For example, the physical properties of individual carbon nanotubes with known chirality have been reported previously. For this work, the real-time imaging of solid state electrochemical processes at atomic scale has been carried out by in-situ TEM. In this presentation, we will review our progress on the studies of phase transition mechanism of the two-dimensional layered transition metal dichalcogenides (TMDs) by alkali metal intercalation.

**9:00 AM **NM01.08.02

Controlling the Inner Dielectric Environment of Carbon Nanotubes to Tune Their Optical Properties

Sofie Cambré¹, Jochen Campo¹,², Bea Botka¹, Wouter van Werveke¹, Jan Obrazt², Wim Wenseleers¹ and Jeffrey Fagan³; ¹University of Antwerp, Antwerp, Belgium; ²Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The optical properties of single-wall carbon nanotubes (SWCNTs) are extremely sensitive to their external and internal environment. For example, filling the endohedral cavity with water molecules results in characteristic shifts and broadening of both the SWCNTs' radial breathing mode vibrational frequency and their optical (electronic) transitions, as well as a quenching of their emission.[1] Although mostly ignored in literature, solvent ingestion effects are substantial, and can also be used to passivate the nanotube interior, by controlled manipulation of the endohedral environment prior to dispersion.[2]
In this work, specific and tunable modification of the optical properties of SWCNTs is demonstrated through the direct encapsulation of guest molecules with widely varying dielectric constants. Over 30 different compounds with static dielectric constant varying from 1.8 to 109 have been encapsulated inside the SWCNTs and their spectroscopic analysis, in comparison to unfilled (empty) SWCNTs, demonstrates for the first time experimentally that the general effect of filler static dielectric on the nanotube optical properties corresponds to a monotonic energy reduction (red-shifting) of the optical transitions with increased magnitude for higher dielectric constants.

Systematic two-dimensional fitting of the fluorescence-excitation spectra enables the direct comparison of this red shifting as a function of nanotube diameter, modulus and chirality. In addition to these spectral shifts, the filling with dielectric molecules also reveals a general increase of fluorescence intensity with lower dielectric constants, with some fillers approaching the emission efficiencies of empty SWCNTs.

Our investigation hence demonstrates a new degree of modulation of the SWCNTs’ optical properties by simple endohedral ingestion of various guest molecules.

High-quality channel layer is required for next-generation flexible electronic devices. Graphene is a good candidate due to its high carrier mobility and unique ambipolar transport characteristics but typically shows a low on/off ratio caused by gapless band structure. Here we propose a graphene/MoSe₂ channel layer with high-k ion-gel gate dielectric. The graphene/MoSe₂ device shows both high on/off ratio and carrier mobility. Most importantly, it reveals ambipolar behaviors which are controlled by external bias, although such ambipolarity has never been previously reported in graphene/semiconductor barristor structures. Therefore, our graphene/MoSe₂ barristor with ion-gel gate dielectric can offer various high performances. Here we make a contact of graphene and MoSe₂. The graphene/MoSe₂ barristor exhibits high on/off ratio of 10⁶ and high mobility. The modulation of graphene’s Fermi level (E_F) by applying gate voltage (V_g) is confirmed by the change in Schottky barrier height at the graphene/MoSe₂ junction. Such field effects including ambipolar behaviors are locally investigated by using scanning photocurrent microscopy (SPCM).

In this work, a low temperature sol-gel technique was used to prepare graphene aerogels from graphene oxide (GO) nanosheets. Through this method, GO nanosheets simultaneously undergo reduction and crosslinking in presence of ammonia to form a hydrogel. The Critical point drying was performed on the hydrogels, and they were annealed at higher temperatures to produce graphene aerogels. Our studies indicated that the GO/ammonia ratio affects the reduction and crosslinking of the nanosheets, which in turn determine the packing density and pore size distribution in the final aerogels. The nature of the covalent bonds and the inter-sheet “bridges” observed in the SEM images were investigated using various spectroscopic techniques. These aerogels possessed considerably high surface areas in the range of 900-1500 m²/g and electrical conductivities comparable to those of copper and silver.

Nanosheets morphology and aspect ratio is another factor that determines the morphology and properties of GO aerogels. To study the effect of theses parameters, we have used semi-spherical crumpled graphene oxide (cGO) particles as the precursor for aerogel preparation. cGO particles were produced by spray drying aqueous GO dispersions. During this process, the 2D nanosheets are crumpled into 3D semispherical particles. Usage of these cGO particles instead of flat GO nanosheets led to a higher degree of crosslinking and packing density in a 100% cGO aerogel. A slight increase in the surface area (~1600 m²/g) was also observed in this sample. The synergistic effects of mixed GO/cGO precursors on the structure and properties of aerogels were also explored and characterized.

Establishing a 3D electrically percolating network in an insulating matrix is key to numerous engineering and functional applications including energy storage and conversion, sensing devices, and telecommunication. To this end, using hydrophobic carbon nanofillers like graphene or carbon nanotubes is tempting, but still results in suboptimal performance due to processing challenges including colloidal instabilities in aqueous media. Here, we demonstrate how natural cellulose nanofibers (1) can be in situ transformed into graphene-like sheets connected to a 3D network enhancing both electrical and mechanical properties, depending on their preparation method, chemical composition, and morphology. We envisage that our results can advance the processing science and technology to provide the improved hierarchical graphene composite materials needed for advanced applications in fields like energy and telecommunications.

References

11:30 AM NM01.09.06
Thermal and Electrical Conductivity of High Volume Fraction Aligned CNT/Polymer Composites Yoko Inoue, Kenta Ishigami, Motoyuki Karita and Takayuki Nakano; Shizuoka University, Hamamatsu, Japan.

Most of good material properties of carbon nanotube (CNT), including thermal and electrical conductivities, and tensile strength and modulus, appear in the direction of long axis of CNT. Therefore, to derive CNT properties into applications, alignment degree is one of the important structural parameters. In this study, aligned CNT sheet preforms were prepared by dry spinning from CNT forests. The aligned CNTs were mixed with epoxy or polyamide resin. A hot-melt method of the CNT sheet with the resin film enabled high CNT volume fraction up to 49 %. We investigated thermal and electrical conductivity of the high CNT content composites. Spin-capable CNT array was synthesized by chloride mediated thermal chemical vapor deposition (CM-CVD). Dimensions of CNT are 30 nm in diameter and > 1mm in length. By stacking the CNT webs, a CNT sheet was formed. Then, aligned CNT/polymer composite films were prepared by hot-pressing the CNT sheet and a polymer sheet simultaneously. We used a thermosetting polymer of B-stage epoxy and ZrO₂ (YSZ) matrices, respectively. The microstructure of the resulting materials was characterized by electron microscopy and spectroscopy (STEM/EELS), while the electrical and dielectrical properties were analyzed by impedance spectroscopy. The materials showed high electrical conductivity at only 2 % initial CNT content, while the FLG-YSZ nanocomposites exhibited mixed ionic-electronic conduction at ≤1% CNF, which is interesting for electrode materials in solid-oxide fuel cells. Besides the transport properties, the incorporated cellulose nanofibers largely improve the mechanical properties and also enable the use of technologically important machining methods for electro-conductive ceramics.

We envisage that our results can advance the processing science and technology to provide the improved hierarchical graphene composite materials needed for advanced applications in fields like energy and telecommunications.
**11:45 AM NM01.09.07**

Conformal Printing of Graphene Inks and Multilayered Devices onto Arbitrarily Shaped 3D Objects  
Leonard Ng, Xiaoxi Zhu, Guohua Hu and Tawfique Hasan; University of Cambridge, Cambridge, United Kingdom.

Printing has drawn a lot of attention as a means of low per-unit cost, high throughput and additive patterning of graphene inks for scaled-up functional thin-film factor device manufacturing. However, the traditional printing processes typically require a flat surface and hence the current graphene printing methods are incapable of achieving patterning onto arbitrarily-shaped objects such as 3D printed parts and even on human skin.

Here, we present a conformal printing method to deliver conductive graphene patterns on to arbitrarily-shaped 3D objects using a sacrificial layer. We first formulate a water-insoluble conductive graphene ink and print it on to an ultrathin polyvinyl alcohol (PVA) film using conventional printing processes. The printed graphene patterns are then floated onto water, allowing the dissolution of PVA, while retaining the graphene patterns. This allows transfer of the conductive graphene patterns directly onto arbitrarily-shaped 3D objects with high resolution. I will present the formulation process and the parameters vital to achieving this and demonstrate this process onto a variety of irregularly-shaped 3D objects. Using this approach, I will also demonstrate multilayered device fabrication/transfer, including simple 2D material based electric circuits and components as well as resistive and capacitive strain sensors, without requiring post deposition processing.

---

**SESSION NM01.10: Hybrid Structure and Properties II**  
Session Chairs: Jeffrey Fagan, Ranjit Pati and Maruyama Shigeo  
Wednesday Afternoon, November 28, 2018  
Sheraton, 2nd Floor, Republic AB

**1:30 PM **NM01.10.01  
Structure-Defined DNA-Carbon Nanotube Hybrids and Their Applications  
Ming Zheng; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

In this talk, I will present first our current understanding of structure-defined DNA-carbon nanotube hybrids, then a description of the DNA sequence selection problem, and finally utility of DNA-carbon nanotube hybrids in molecular sensing. An artificial perception system, *i.e.* molecular perceptron, is proposed to take full advantage of the structure diversity of DNA-carbon nanotube hybrids.

**2:00 PM NM01.10.02**  
Perylene-Based Functionalization of Carbon Nanotubes  
Antonio Setaro, Mareen Glaeske, Katharina Huth, Mohsen Adeli, Rainer Haag and Stephanie Reich; Freie Universität Berlin, Berlin, Germany.

Functionalization aims at granting compounds with additional features. This is achieved by typically attaching novel groups to the original systems. The aftermath of such process yields complexes whose characteristics often result in more than just the mere sum of the initial products. The specific character of the functionalized structure, moreover, depends upon the way the functionalization strategy has been pursued.

We will focus on the carbon nanotubes functionalization through perylene, an aromatic molecule emitting in the excitation window of most single-walled nanotubes commercially available. We have previously shown that the perylene core of custom surfactants was able to attach through pi-pi stacking interactions onto the sidewall of CNTs while ensuring efficient excitation transfer to the tubes. Here we will show how starting from the same elements (perylene and nanotubes) and pursuing different functionalization routines, we achieve systems with different features and functions. In particular, we will compare the characteristics of perylene-comprising polymers wrapped around the tubes with the peculiarities of perylene covalently attached to the nanotubes following a novel conjugation-preserving routine we recently developed. We will highlight the difference among the properties of the final products as well as the applications they would be suitable for.

---

**2:15 PM NM01.10.03**  
Molecular Recognition of Carbohydrates using Alternating Phenyl Boronic Acid Co-Polymers as Carbon Nanotube Corona Phases  
Minkyung Park, Jiyoung Ahn, Pingwei Liu, Daichi Kozawa, Volodymyr Koman, Song Wang, Gili Bisker, Seomyeong Kwak, Naveed A. Bakh, Michael A. Lee and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The molecular recognition of carbohydrates remains a major challenge due to their inherent structural complexity and low affinity for most substrates despite its importance in biological systems. Natural and synthetic lectins have been broadly studied and comprised the majority of molecular recognition strategies to date. However, in this work, we explore a class of specific polymers that adopt a unique 3D configuration and exhibit highly specific carbohydrate binding when adsorbed at the surface of a carbon nanotube. A compositionally diverse polymer library based on reversible addition-fragmentation chain-transfer (RAFT) polymerization of *ortho*, *meta*, and *para*-phenyl boronic acids (PBA) with acrylic, methyl acrylic, vinyl benzoic, and maleimidopropionic monomers, forming alternating, random, and block co-polymer variations is evaluated for the ability to selectively bind various monosaccharides and sugar alcohols. When adsorbed as a solubilizing corona phase onto single walled carbon nanotubes (SWNT), we demonstrate several examples, including a *meta*-PBA maleic anhydride) co-polymer that enables dulcitol over mannitol and sorbitol recognition despite differing by only one or two cis/trans hydroxyls. We also identify a *meta*-PBA 3-maleimido-propanic acid) co-polymer selective for D-(-)-arabinose over all other aldopentoses including L-arabinose. This corona phase molecular recognition represents the first synthetic systems capable of specific, chiral saccharide recognition, which satisfies the demand for high precision assays, chemical sensors, catalysts, and biological probes for difficult to detect carbohydrates.

---

**2:30 PM BREAK**
We propose a conceptually new structure, in which mono- or few-layer hexagonal BN seamlessly wrap around a single-walled carbon nanotube (SWCNT), and result in an atomically smooth coaxial tube consisting two different materials, SWCNT@BNNT. The structure is synthesized by chemical vapor deposition (CVD), and the length of the coaxial tubes can reach up to micrometers. As the reaction occurs on outer surface of the existing SWCNTs, we name this process conformal CVD. Various SWCNTs, e.g. vertically aligned array, horizontally aligned arrays, suspended SWCNTs, random networks and films, are employed as the starting material, and successful coating are achieved on all of them. TEM-EELS clearly demonstrated the BN-SWCNT coaxial structure in individual tube scale, while Raman, optical absorption, and cathode luminescence spectra clearly confirm the existence of this structure in large scale. After coating, the SWCNTs can be fully coated and thermal stability significantly increases. Our characterizations confirm that the outside BN coating started locally on the wall of a SWCNT and then merged into a BN nanotube on the curved surface of the SWCNT which served as a template. The thinnest inner SWCNT that can support the BN layer growth is found to be 0.6-0.7 nm. The number of walls can be tuned from 1 to few by controlling the CVD condition. The structure of inside SWCNTs are almost not effected by the conformal CVD, as evidenced by Raman and many other characterizations. The crystallization and cleanness of the starting SWCNT template are believed to be critical for the successful fabrication of outside walls. This structure is expected to have a broad interest and impact in many fields, which include but not limited in investigating the intrinsic optical properties of environment-isolated SWCNTs, fabricating BN-protected or gated SWCNT devices, and building more sophisticated 1D material systems.

Part of this work was supported by JSPS KAKENHI Grant Numbers JP25107002 and JP15H05760.

4:00 PM NM01.10.05 Thermal Conductivity Measurement of Single-Walled Carbon Nanotubes by Photoluminescence Imaging Spectroscopy Kazuki Yoshino1, Kazuma Nagano1, Makoto Horiguchi1, Yuichiro Tanaka1, Shohei Chiashi2 and Yoshiyuki Homma2; 1Tokyo University of Science, Tokyo, Japan; 2The University of Tokyo, Tokyo, Japan.

Single-walled carbon nanotubes (SWCNTs) are expected to have high thermal conductivity along the tube axis. However, experimentally obtained values of the thermal conductivity vary widely because of the difficulties in the thermal conductivity measurements as well as the characterization of SWCNTs. We have recently developed a novel method for measuring thermal conductivity using photoluminescence (PL) imaging spectroscopy [1]. We use a long SWCNT individually suspended between quartz pillars, and evaluate the chirality of SWCNT by PL and crystallinity by Raman spectroscopy. Because the measurements are done for chirality-assigned and isolated (not bundled) SWCNTs, the obtained conductivities are highly reliable. For (9,8) SWCNTs with 10–12 μm in length, the thermal conductivity was 1166 ± 243 Wm-1K-1 at 400 K. We can also obtain the temperature dependence of thermal conductivity from the temperature distribution along the tube axis. We will discuss the accuracy of the measurement based on the data for multiple chiralities.

This work was partially supported by a MEXT Grant-in-Aid for Scientific Research on Innovative Areas “Science of hybrid quantum systems” (grant no. 15H05869).


4:15 PM NM01.10.06 Scalable Fabrication and Characterization of Vertically Aligned Carbon-Nanotube/Polymer Membranes Richard J. Castellano1, Eric R. Meshot2, Francesco Fornasiero3, Robert Praino3 and Jerry Shan1; 1Rutgers University, Piscataway, New Jersey, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States; 3Chasm Technologies, Canton, Massachusetts, United States.

Membranes incorporating vertically aligned carbon nanotubes (CNTs) as through-pores have been shown to transport fluids at rates orders-of-magnitude faster than predicted by theory, offering promise as highly permeable membranes for applications as diverse as breathable yet protective garments, desalination membranes, and highly efficient filters. However, there is a need for cost-effective and scalable solutions for fabricating large-area vertically aligned nanotube membranes, ideally starting from bulk nanotubes. Here, we describe a new, solution-based fabrication technique for creating polymer composite membranes using electric-field alignment and electrophoretic concentration of CNTs initially dispersed in a solvent. The solvent is then replaced with a UV-curable oligomer, which is cured to controlled thickness to form a membrane with vertically aligned carbon nanotubes. After etching to open CNT pores, the pore size and total open area are assessed with He-N2 flowrate ratios, size-exclusion tests and aqueous KCl conductance measurements. By comparing to theory, a pressure-driven gas flow-enhancement factor of 200 - 300 is found for flow through the small-diameter nanotube pores, which is consistent with reports in the literature for membranes fabricated from CVD-grown aligned nanotube forests. We conclude by describing recent progress in significantly increasing nanotube number density and membrane permeability, and the remaining challenges for ultimate roll-to-roll fabrication of vertically aligned nanotube membranes.

To evaluate the influence of the synthesis temperature and the flux of the carbon precursor gas, experiments were performed between 600 and 800 °C, with hetero-atoms, like the nitrogen, in the electrical conductivity of the NC-CNTs-N is shown. Non-crystalline carbon nanotubes (NC-CNTs) were synthesized by chemical decomposition in vapor phase using nanoporous anodized aluminum oxide.

The proto-type graphene Hall sensor array shows the extremely high current-normalized sensitivity of ~ 2000 V/AT [1] by the employment of large-area hexagonal BN as a substrate for graphene. This sensitivity could be improved to almost 3000 V/AT [2] by the replacement of large-area synthesized graphene with exfoliated MoS2 flake, but the level of applied current for such a high sensitivity regime is too small. Therefore, we further examine the possibility of electrolyte gating in the graphene Hall sensor configurations with the usage of commercially available chemical-vapor-deposition grown graphene layer without hexagonal BN. Due to the suppressed charge-impurity scattering in the electrolyte, the current-normalized sensitivity can reach to the value of > 3000 V/AT with moderate current levels and noises. In addition, the choice of operating conditions for the source-drain and gate voltage biases is to be systematically discussed, while the way of predicting it without a real test under the magnetic field is introduced from the analytical model. Low voltage operation (~ 0.5V) of the electrolyte-gating graphene Hall sensor is the additional advantage for the applications in the mobile devices.

Carbon nanomaterials have been promising elements for a variety of future applications in electronics. Since the contact interfaces between carbon nanomaterials and metal electrodes influence the properties of assembled structures, the extensive studies on the interfaces have been conducted. The atomic configuration and electrical properties of the interfaces have been investigated to elucidate the conduction mechanism [1]. In situ transmission electron microscopy (TEM) using nanotip operation techniques allows the simultaneous observation of the structures and electrical properties of the junction of a carbon nanocapsule (CNC) and metal electrodes [2]. In this study, we applied in situ TEM to investigate the relationship of the structure and electrical resistivity of the interfaces between a CNC and metal electrodes. CNCs were dispersed in ethanol and were dropped on the edge surfaces of a gold (Au) nanotip. This nanotip and another bare nanotip were inserted in a transmission electron microscope. Single nanoparticle junctions (SNPJs) were assembled using the CNCs and the two Au nanotips (electrodes) by piezomaneupulation inside the microscope. After the preparation of SNPJs, their configuration was controlled by using piezomaneupulation and was observed in situ at an atomic scale. Simultaneously, the conductance of SNPJs was measured by a two-terminal method while applying bias voltages. These process of observations and electrical measurements were performed at room temperature in a vacuum of $1 \times 10^{-5}$ Pa. The observed high-resolution TEM images and currents were analyzed. We could observe several interfaces and measure their contact resistivity. Consequently, it was found that the contact resistivity depended on the orientational relationships of the interfaces.


**NM01.11.06**

**Structure and Electrical Properties of Interfaces Between a Carbon Nanocapsule and Metal Electrodes Studied by In Situ Transmission Electron Microscopy**

Manabu Tezura and Tokushi Kizuka; Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

Carbon nanomaterials have been promising elements for a variety of future applications in electronics. Since the contact interfaces between carbon nanomaterials and metal electrodes influence the properties of assembled structures, the extensive studies on the interfaces have been conducted. The atomic configuration and electrical properties of the interfaces have been investigated to elucidate the conduction mechanism [1]. In situ transmission electron microscopy (TEM) using nanotip operation techniques allows the simultaneous observation of the structures and electrical properties of the junction of a carbon nanocapsule (CNC) and metal electrodes [2]. In this study, we applied in situ TEM to investigate the relationship of the structure and electrical resistivity of the interfaces between a CNC and metal electrodes. CNCs were dispersed in ethanol and were dropped on the edge surfaces of a gold (Au) nanotip. This nanotip and another bare nanotip were inserted in a transmission electron microscope. Single nanoparticle junctions (SNPJs) were assembled using the CNCs and the two Au nanotips (electrodes) by piezomaneupulation inside the microscope. After the preparation of SNPJs, their configuration was controlled by using piezomaneupulation and was observed in situ at an atomic scale. Simultaneously, the conductance of SNPJs was measured by a two-terminal method while applying bias voltages. These process of observations and electrical measurements were performed at room temperature in a vacuum of $1 \times 10^{-5}$ Pa. The observed high-resolution TEM images and currents were analyzed. We could observe several interfaces and measure their contact resistivity. Consequently, it was found that the contact resistivity depended on the orientational relationships of the interfaces.


**NM01.11.07**

**Fabrication of Polyamide/Polyethersulfone Reverse Osmosis Membranes Containing Functionalized Carbon Nano-Onions Having Antibacterial Activity**

Somin Lee, Eun Yeob Choi, Jeongung Nam and Chang Keun Kim; Chung-Ang University, Seoul, Korea (the Republic of).

Polyamide/polyethersulfone (PA/PES) membranes containing carbon nano-onions (NOs) were fabricated for the application in reverse osmosis (RO) membrane with enhanced antibacterial properties. The PA/PES membranes were prepared by interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on the surface of PES as support membrane. Then, the resulting PA/PES membranes were incorporated with the NOs to give antibacterial activities and use as RO membrane. The PA/PES membranes containing NOs were prepared in two variants; one contains aminated NO (NO-NH2) and another contains acyl chloride-terminated NO (NO-COCl). Each functional group in both NOs was reacted with MPD or TMC in the PA membranes, resulting in grafting NO with PA membrane. The formation of PA membranes containing NOs was confirmed by some analyses including FT-IR, XPS, FE-SEM and TGA. The PA/PES/NO-NH2 membrane exhibited better antibacterial properties compared with the PA/PES/NO-COCl composite membrane. In addition, the PA/PES/NO-NH2 membrane showed high water flux without a loss in salt rejection. Thus, the excellent performances of PA/PES/NO-NH2 membrane make its potential applications as an effective RO membrane.

**NM01.11.08**

**Fabrication of Polyketone/Polyketone Grafted Multi-Walled Carbon Nanotube Composites Using a Grignard Reagent Containing Pyrene Derivative**

Jeongung Nam, Eun Yeob Choi, Somin Lee and Chang Keun Kim; Chung-Ang Univ., Seoul, Korea (the Republic of).

Aliphatic polyketone (PK) composites containing PK grafted multi-walled carbon nanotubes (PK-g-MWCNTs) were prepared and their physical properties containing interfacial adhesion between PK and multi-walled carbon nanotubes (MWCNTs) and mechanical strength of the composite were examined. To fabricate PK-g-MWCNTs, 1-pyrenylmethylmagnesium bromide (PMgBr) was absorbed on the MWCNTs surface by physisorption and then reacted with PK. During this procedure, Grignard reagent in the PMgBr reacted with ketone groups in the repeat unit of PK, resulting in grafting PK with MWCNTs. The formation of PK-g-MWCNT was explored by spectroscopy, electron microscopy, and thermal analysis. The interfacial adhesion energy between PK and PK-g-MWCNT was the highest value that can be achieved with PK and modified MWCNTs. The PK/PK-g-MWCNT composite exhibited better performances of PK/PK-g-MWCNT membrane make its potential applications as an effective RO membrane.

**NM01.11.09**

**Covalently Connected Graphene/Carbon Nanotube Hybrid Structure and Their Application**

Nam Dong Kim1, Yilun Li2, Yingchao Yang2, Caitian Gao1 and James M. Tour1; 1Korea Institute of Science and Technology, Bodong-eup, Korea (the Republic of); 2Mechanical Engineering, University of Maine, Orono, Maine, United States; Chemistry, Rice University, Houston, Texas, United States.

Carbon materials have great potential for advanced nanotechnology. They exist in various allotropes in several dimensions, such as 0D of C60 family and graphene quantum dots, 1D of carbon nanotube (CNT), graphene nanoribbon (GNR) and carbon fiber (CF), and 2D of graphene relate materials. Each of these allotropes shows unique and interesting properties making them representative nano-materials. Recently, hybrid system of those different carbon allotropes has great attentions to achieve an improved and synergetic properties. Making 3D hybrid structure gives many enhanced properties, such as high integrity, interconnectivity, porosity, conductivity and mechanical strength. New strategy to connect different carbon allotropes with covalent bonding allows us to fabricate more advanced structure which was not possible previously and to understand novel properties of materials. After first research about seamlessly connected graphene and carbon nanotube hybrid structure (G/CNT) has been reported, it has attracted great attentions due to its high surface area, excellent electrical and mechanical properties. In this presentation, several researches derived from G/CNT structure will be introduced. such as patterning, mechanical strength at the junction and energy storage application, and its powerful possibility will be discussed.
Use of environmentally friendly solid polymer electrolytes is important for battery technology. This work aims at investigating effect of lithium in chitosan-graphene films which can be useful for energy storage applications. Lithium ions are small in size. Lithium salts conduct electricity under electric field due to the mobile lithium ions which can easily migrate. Chitosan is an abundantly available biopolymer. It has good film forming ability. However chitosan films do not have good conductivity. Graphene-based functional materials have caused great interest in electronic, medical, environmental applications due to its large surface area, high electrical conductivity and high mechanical strength. H5 Graphene was purchased from XG Sciences, USA. The graphene platelets have approximate thickness of 15 nm and length of 5 micro meter. Chitosan solution was prepared by adding 1% (w/v) of chitosan powder, 1.5% (w/v) of acetic acid and 100ml of double distilled water. The solution was stirred for 30-40 minutes to form a transparent thick solution. A part of this solution was transferred to a plastic dish to form a film at room temperature. To proportionate amount of chitosan solution 33, 66 and 100% (weight with respect to chitosan) of lithium perchlorate (LiClO4) was added. To a part of the chitosan lithium solution 5% of graphene (weight with respect to chitosan) was added. The solution was stirred and heated for 30 min. This solution was poured on a plastic dish and dried at room temperature in order to obtain chitosan–graphene-lithium nanocomposites. The thickness of the nanocomposite films varied between 50-200 micro meter. Dielectric studies such as conductivity, dielectric constant, dissipation factor and impedance were measured using impedance spectrometer. The conductivity ranges from 10^-8 to 10^-4 S/cm for graphene-chitosan lithium system. The conductivity of chitosan was lowest. In the absence of graphene the conductivity increases with increasing LiClO4 concentration. Conductivity (at 100 Hz) for Chitosan, Chitosan 33% LiClO4, Chitosan 66% LiClO4, Chitosan 100% LiClO4 films are 6x10^-7, 2x10^-6, 2x10^-7 and 3.5x10^-7 S/Cm respectively. Conductivity (at 100 Hz) for Chitosan 5%LiClO4, Chitosan 5%LiClO4, Chitosan 5%LiClO4, Chitosan 5%LiClO4, Chitosan 5%LiClO4, Chitosan 5%LiClO4 are 3.5x10^-7, 5x10^-7, 1.5x10^-6 and 3.5x10^-7 S/Cm respectively. The conductivity measurements show that incorporation of graphene decreases the conductivity for films with 66 and 100% LiClO4. This indicates that graphene induces crystallization of Lithium salts thereby reducing the conductivity. SEM image shows that graphene affects the crystallization of LiClO4. Both LiClO4 and graphene increased the dielectric constant of the nanocomposites. Dissipation factor analysis showed that the relaxation behavior is affected due to incorporation of graphene. The dissipation was also relatively low (similar to chitosan), indicating that the nanocomposites do not have much heat loss.

Graphene, a one-atomic-thick material with honeycomb structure built from carbon atoms, which can be considered as a monolayer of graphite, is the most representative two-dimensional material. It has drawn tremendous attention due to fascinating electronic and mechanical properties. Graphene with no defect is believed to be the strongest material. Through all synthesis methods, chemical vapor deposition (CVD) is a facile approach to grow large-scale monolayer graphene, which is polycrystalline with inevitable defects and boundaries. Thus, the study on mechanics of graphene, particularly fracture behavior, is essential from both fundamental interest and technological importance. Numerous studies on fracture mechanics of graphene are emerging. The fracture toughness and crack propagation of graphene have been investigated by means of in situ methods and simulations. In these studies, fragmentation of graphene tends to initiate randomly at pre-existing defect locations, resulting in irregular morphology and is considered as a limitation in applications.

However, ordered fragmentation can be utilized in nanstructuring. Here, our works propose and demonstrate a facile method on controlling the fragmentation of graphene to fabricate ordered graphene nanoribbon arrays with sharp edges by taking advantage of the strong localized strain existing at the neck front during polymer cold-drawing process. For the thermoplastic polymer, a neck will form locally during a stretch. This necking phenomenon results from the mechanical instabilities of the polymer and will propagate along the entire length of polymer, which is called cold-drawing. The neck front moves uniaxially with strong localized strain while the deformation of after-necking areas ceases. We harness this strong localized yet moving strain to fragment graphene and show the fabrication of finely ordered graphene nanoribbons. The CVD grown monolayer graphene is transferred to polycarbonate substrate and then mounted on a linear travel stage. After the following cold-drawing process of the polycarbonate substrate, monolayer graphene nanoribbon arrays are fabricated. The structure and morphology of obtained monolayer graphene nanoribbons are systematically investigated using various microscopic and spectroscopic measurements. The potential applications for both chemical and physical sensing are explored. Future work will be conducted to investigate the fragmentation via polymer cold-drawing on multilayer graphene.
demonstrated to show its practical application in identifying the position of various objects. This study reveals its application prospect in areas such as motion tracking and small force application.

NM01.11.14
Malic Acid Carbon Dots—From Super-Resolution Live-Cell Imaging to Highly Efficient Separation Bo Zhu1, Yi Cui2, Shengyang Wang3, Ben P. Frank1, Denise Williams4, Richard P. Brown5, Eric S. Melby6, Robert J. Hames6, Zeev Rosenzweig1, D. H. Fairbrother1, Galya Orr1 and Christy L. Haynes6; 1Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States; 2Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, United States; 3Chemistry, The Johns Hopkins University, Baltimore, Maryland, United States; 4Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore County, Maryland, United States; 5Columbia Basin College, Pasco, Washington, United States; 6Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

As-synthesized malic acid carbon dots are found to possess advanced photobleaching properties compared to conventional dyes. Considering their excellent biocompatibility, malic acid carbon dots are suitable for super-resolution fluorescence localization microscopy under a variety of conditions, as we demonstrated in fixed and live tritium epithelial cells. In addition, during imaging experiments, the so-called “excitation wavelength-dependent” emission was not observed for individual as-made malic acid carbon dots, which motivated us to develop a time-saving and high-throughput separation technique to isolate malic acid carbon dots into fractions of different particle size distributions using C18-reversed phase silica gel column chromatography. This post synthesis separation allowed us to determine how particle size distribution influences the optical properties of malic acid carbon dot fractions, i.e., optical band gap energies and photoluminescence behaviors.

NM01.11.15
Electrically Probing and Tuning of Physisorption for Both Polar and Non-Polar Molecules on Graphene Wenzhe Zang1, Girish S. Kulkarni2, Karthik Reddy3, Hongbo Zhu4, Kyoungmoon Lee5, Xuadong Fan2 and Zhaozhong Zhong1; 1Department of Electrical Engineering and Computer Science, University of Michigan--Ann Arbor, Ann Arbor, Michigan, United States; 2Department of Biomedical Engineering, University of Michigan--Ann Arbor, Ann Arbor, Michigan, United States.

Nanoelectronic systems are perfect testbeds to study and mimic the physicochemical nature of noncovalent interactions which, though weak in nature (~100s of meV), form the bedrock of most biological and cellular processes. Furthermore, the ability to electrically tune the charge density (hence the chemical potential) in nanomaterials via electrostatic gating provides another knob to control such interaction. Unfortunately, nearly all existing electronic sensing methodologies are based on charge transfer (covalent interactions) which does not fully represent the interaction between the adsorbed vapor molecules and a pristine nanosurface. Here we present results of electrical probing and tuning of the noncovalent physisorption of both polar and nonpolar molecules on graphene surface by using two different sensing techniques — heterodyne sensing and µCmbFET sensing. Temperature-dependent molecular desorptions for six different polar molecules and five non-polar species were measured in real-time to study the desorption kinetics and extract the binding affinities. Furthermore, we demonstrate electrical tuning of molecule-graphene binding kinetics via electrostatic gating of graphene. Our results not only provide insight into the non-covalent interaction dynamics between both graphene and both polar and non-polar molecules, but also pave the way to electrically tailor physisorption dynamics at nanoscale interfaces.

NM01.11.16
Non-Linear Current-Voltage Behavior of Epoxy-CNT Composites Toshiyuki Sato1, Yoshitaka Kamata1, Hui Li2, Jian Song2, Howard E. Katz2 and Pawel Czubarow3; 1NTC, NAMICS, Niigata-City, Japan; 2Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 3EM-TECH, Southborough, Massachusetts, United States.

The electronics industry is always looking for new ways of protecting devices from over-voltage, or over-current scenarios. In the present work we will introduce novel low-voltage epoxy-carbon nanotube composites with high non-linearities in resistive devices. Plots of current versus voltage can be fit to powers of voltage > 2. Devices of different dimensions were made on single substrates by photolithographic patterning of interdigitated electrode pairs. These devices were tested at different speeds over different voltage ranges, and I-V relationships are compared. From the resulting data, the limiting resistances can be apportioned between injection barriers and bulk nanotube connectivity.

NM01.11.17
Effects of Graphene Oxide-Carbon Nanotube Hybrids as Nanofiller on the Interfacial Interaction in Nylon 6,6 Prepared by In Situ Interfacial Polymerization Beom-Gon Cho1, Seonghwan Lee1, Sang-Ha Hwang2, Jong Hun Han3, Han Gi Chae2 and Young-Bin Park4; 1Department of Mechanical and Aerospace Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 3School of Chemical Engineering, Chonnam National University, Gwangju, Korea (the Republic of).

Nylon 6,6 nanocomposites including well-dispersed graphene oxide (GO) and carbon nanotubes (CNTs) were successfully fabricated via in situ interfacial polymerization between two immiscible phases: organic phase assisted by poly(vinylpyrrolidone, PVP) surfactant containing adipoyl chloride with dispersion of GO and CNTs; aqueous phase containing hexamethylenediamine. Prior to the polymerization, GO was functionalized with thionyl chloride, resulting in acyl chloride-functionalized GO (AGO). The effects of incorporation of AGO and PVP on the state of dispersion were investigated. It was observed that the addition of AGO and PVP reduced particle flocculation, leading to a well-dispersed suspension as verified through dispersion stability analysis and UV–Vis spectroscopy. The interfacial interaction between the carbon nanofillers (AGO, CNTs) and nylon 6,6 chain can be induced via electrostatic interactions. These devices were tested at different speeds over different voltage ranges, and I-V relationships are compared. From the resulting data, the limiting resistances can be apportioned between injection barriers and bulk nanotube connectivity.

Acknowledgments
This research was supported by the Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning, Korea (Grant No. 2016M3A7B4027697), and the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea Government Ministry of Trade Industry and Energy (MOTIE) (No. 20174030201430).

References
Nonuniform strain fields in graphene have received much attention due to the tight relation between its morphological and electronic properties. In addition to the well-known pseudomagnetic field, another recognized effect induced by a nonuniform strain is the position-dependent Fermi velocity (PDFV) [1]. Pioneering experiments [2], through scanning tunneling spectroscopy (STS), have revealed the existence of a PDFV, but its effects on the graphene physics have been scarcely explored [3].

In this work, we present analytical and numerical studies of the local density of states (LDOS) measured by STS for graphene under a nonuniform strain, either in the absence or in the presence of a uniform magnetic field [4]. The analytical expressions of the LDOS, derived from an effective Dirac model in term of a PDFV, were verified by tight-binding numerical calculations. In consequence, such expressions can be useful to quantify appropriately nonuniform strain effects on STS experiments of strained graphene, including those of Landau level spectroscopy. Finally, our results demonstrate that PDFV effects should be considered in a full description of transport signatures of strain-induced pseudomagnetic fields in graphene.

This work has been partially supported by UNAM-IN106317 and CONACYT-252943. Computations were performed at Mizzti of DGTIC, UNAM. M.O.L. acknowledges the postdoctoral fellowship from DGAPA-UNAM.

References


NM01.11.19
Structural and Electronic Characterization of the Ripples in Single-Layer Graphene on Ge by STM/STS

Cesar A. Diaz Mendoza, Marcelo Eduardo Huguenin Maia da Costa and Fernando Lazaro Freire Jr; Physics, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil.

The graphene’s growth directly on germanium surface can be a good route to integrate graphene into nanoelectronic-devices. Several works deal with the syntheses and characterization of the graphene on Ge [1-3]. Graphene/Ge interface interaction is not fully understood. A remarkable aspect that we found was the presence of ripples. The ripples and their characteristics can modify the electronic structure, electron/hole puddle formation and carrier transport in graphene. The objective of this work is to identify and study how these ripples can modify the local density of states (LDOS) of the graphene growth by CVD on two different germanium crystalline orientations. The samples were characterized by the Raman Spectroscopy and Scanning tunneling microscopy and spectroscopy (STM/STS). Our experimental data shows that the graphene on Ge is strained of compressive biaxial type and such strain is related to the graphene’s growth directly on germanium surface. Nonuniform strain fields in graphene have received much attention due to the tight relation between its morphological and electronic properties. In addition to the well-known pseudomagnetic field, another recognized effect induced by a nonuniform strain is the position-dependent Fermi velocity (PDFV) [1]. Pioneering experiments [2], through scanning tunneling spectroscopy (STS), have revealed the existence of a PDFV, but its effects on the graphene physics have been scarcely explored [3].

In this work, we present analytical and numerical studies of the local density of states (LDOS) measured by STS for graphene under a nonuniform strain, either in the absence or in the presence of a uniform magnetic field [4]. The analytical expressions of the LDOS, derived from an effective Dirac model in term of a PDFV, were verified by tight-binding numerical calculations. In consequence, such expressions can be useful to quantify appropriately nonuniform strain effects on STS experiments of strained graphene, including those of Landau level spectroscopy. Finally, our results demonstrate that PDFV effects should be considered in a full description of transport signatures of strain-induced pseudomagnetic fields in graphene.

This work has been partially supported by UNAM-IN106317 and CONACYT-252943. Computations were performed at Mizzti of DGTIC, UNAM. M.O.L. acknowledges the postdoctoral fellowship from DGAPA-UNAM.

References


NM01.11.20
Structural Changes in Carbon Nanotube Yarn Exposed to Actual Space Environment

Motovuki Kariya1, Takayuki Nakano1, Yoku Inoue1, Yasuhiro Fuchita2, Takashi Hitomi2, Yoji Ishikawa2 and Naoko Baba2; 1Department of Electronics and Materials Science, Shizuoka University, Hamamatsu, Japan; 2Obayashi Corporation, Tokyo, Japan; 3Japan Manned Space Systems Corporation, Tsukuba, Japan.

Carbon nanotubes (CNTs), which have excellent thermal and mechanical properties, are promising materials as ground or space structures. Although there have been many ground-based characterizations of the influence of radiation on CNT, no work has been performed on effect of space radiation. In this study, multi-walled CNT (MWCNT) yarns fabricated by dry spinning method were exposed to the actual space environment on the international space station (ISS) for one or two years. During the flight, ground-based comparison tests, including irradiation of atomic oxygen (AO), electron beam and ultraviolet individually, were performed. For the ground-based comparison tests, significant deterioration in tensile strength was found for AO irradiated MWCNT yarns. Transmission electron microscopy and Raman spectroscopy observations revealed that crystal structure of MWCNT was damaged with showing sharp open edges of graphene. For the actual space test, quite similar damages and decrease of tensile strength were observed. This study was carried collaborative research project with Obayashi Corp. and Japan Manned Space Systems Corp., which is adopted by project using Exposed Experiment Handrail Attachment Mechanism of Japan Aerospace Exploration Agency.

NM01.11.21
Gilding with Graphene—Rapid Chemical Vapor Deposition Synthesis of Graphene on Thin Metal Leaves

Kaihao Zhang, Charalampos Androulidakis, Mingze Chen and Sameh Tawfick; Mechanical Science and Engineering, University of Illinois-Urbana Champaign, Urbana, Illinois, United States.

Gilding is the ancient process of coating intricate geometries with precious thin metal films. Fascinating Egyptian and Chinese sculptures, coated with <
200 nm thin metal leaves by this process, have resisted corrosion and other environmental degradations for thousands of years. Similarly, palladium (Pd) is used as gilding material for its excellent corrosion properties, mechanical performance and of course its silver color. This is the reason that the 150 nm thick Pd leaves by doping with a single layer of graphene via low pressure chemical vapor deposition (CVD) processes. Pd leaves are made by hammer forgem of micrometer thick foils. During this process, their thickness is reduced to 150 nm while the average grain size exceeds 20 μm. The Pd leaves made by high strain beating are stable at high synthesis temperature, resisting solid state dewetting owing to their extremely low grain triple junctions.

Using nanoindentation, we demonstrate the graphene’s ability to significantly strengthen Pd leaves by constraining dislocation motion and bridging grain boundaries and cracks in Pd leaves. The as-grown Pd-Gr composite leaves are indented by a diamond-coated atomic force microscope (AFM) probe with diameter of 100 nm. We found that the effective surface modulus of the Pd-Gr composite leaves is 223 ± 23.4 GPa, which is over 2.5-fold of that of the pristine Pd leaves (83.7 ± 14.2 GPa) by coating less than 0.05 wt. % Gr. Moreover, indentation on edge-notched doubly-clamped nanostrip enables the measurement of the critical stress intensity factor in mode I fracture of ultra-thin film materials. We will describe the several systematic experiments on Pd leaves and Pd-Gr composites to reveal the strengthening and toughening mechanisms operating in this new materials. This new nanocomposite material could open exciting opportunities in utilizing high quality 2D materials to coat large structures.

NM01.11.22
Size-Controlled Single Crystalline Graphene Quantum Dots—Synthesis, Luminescence Properties and Application in Electroluminescence Seek Hwan Lee and O Ok Park; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Graphene Quantum Dots (GQDs) is one kind of graphene nanostructure, and it has enormous attention because of their excellent properties originated from the existence of energy bandgap. For synthesizing GQDs, the bottom-up method is required over the top-down approach on synthesis step because it has more potential to control the size and edge status, which is directly related to their optical properties. However, preparation of GQDs using the bottom-up method requires very stringent conditions with specific organic materials after complicated reaction steps. Until now, generating uniform lateral sized GQDs at the synthesis step has not been much successful, although separation of GQDs according to the diameter size have shown marginal success such as stepwise dialysis.

Synthesis of high-quality GQDs with well-controlled size, shape and surface functionalization needs to be further explored. It is still challenging to synthesize the GQDs with clear hexagonal shaped graphic structure via solution chemistry because the conventional bottom-up processes exhibit low crystallinity and they exhibit broad photoluminescent (PL) spectrum and low quantum yield compare with the top-down method. Here, we report a novel bottom-up approach not just for the synthesizing single-crystalline graphene quantum dots (GQDs) with hexagonal shape but also discover a new phenomenon that constructing graphic carbon structure from an understanding of nitrogen site role on graphitization and inducing the catalytic reaction intermediate. In details on selected analysis data, 5 nm lateral sized sample has ~350 pm thickness, and 70 nm lateral sized sample has ~700 pm from atomic force microscopic data and both samples consist of more than 90% carbon species from x-ray photoelectron spectroscopic data. Furthermore, we investigated the origin of luminescence via exciton decay profile through femto-second pulsed laser excitation on various size-controlled GQDs. We discuss the size effect on decay profile to elucidate the origin of luminescence on GQDs by difference core and edge-generated exciton behavior. As the application, we fabricated deep-blue emissive GQDs-light emitting diodes. It shows 2.5 V as turn-on voltage, ~450 cd/m² as max brightness and (0.16, 0.06) as CIE 1931 coordinates.

NM01.11.23
Spatial and Energetic Correlations of Workfunction for Doping Level and Hysteresis in Gate-Tunable Reduced Graphene Oxide Hwiji Woo and Young Jae Song; SAINT, Suwon, Korea (the Republic of).

The graphene grown by chemical vapor deposition method (CVD) has been widely studied for device applications due to scalable growth of CVD. The reduced graphene oxide (rGO) also has attracted huge scientific and industrial interests since it can be easily synthesized in massive quantities. Even CVD-grown graphene as well as rGO show clear hysteresis in IV curves of the devices, mostly due to the inherent or inevitable defects of graphene, which originate from the CVD synthesis itself or the wet process of graphene transfer from the metal substrate to a dielectric substrate. In this work, we have measured workfunction of the graphene and rGO on SiO2 with varying the gate voltage and the distance of the probe from the source electrode. A spatial dependence mapping of workfunction in graphene and rGO layers from the source electrode (ground) showed different carrier injection with showing the hysteresis similar with that of graphene-based device. The energy shift of Dirac point and the amount of hysteresis in the graphene or rGO devices can be correlated with a crossing point (a neutral point) and the width in spatial and electric mapping of workfunction. Further details will be discussed in the presentation.

NM01.11.24
Coulomb Drag Effect in Graphene/MoS2 Heterostructures Youngjo Kim1, Min-Kyu Joo2, Byoung Hee Moon1, Hyun Kim1, Sanghyub Lee1, Hye Yun Jeong1 and Young Hee Lee2; 1Center for Integrated Nanostructure Physics, Suwon, Korea (the Republic of); 2Sookmyung Women's University, Seoul, Korea (the Republic of).

Two-dimensional heterointerfaces often provide extraordinary carrier transport as exemplified by superconductivity or excitonic superfluidity. Recently, double-layer graphene separated by few-layered boron nitride demonstrated the Coulomb drag phenomenon: carriers in the active layer drag the carriers in the passive layer. Here, we propose a new switching device operating via Coulomb drag interaction at a graphene (Gr)/MoS2 heterointerface. The ideal van der Waals distance allows strong coupling of the interlayer electron-hole pairs, whose recombination is largely suppressed by the vertical energy barrier at µ-Gr/n-MoS2 interface via dual-gate, whereas the lateral carrier transport is constructed via Coulomb drag. This device exhibits a high mobility (up to ~3,700 cm²V⁻¹s⁻¹) even at room temperature, while maintaining a high on-off current ratio (~10⁶), outperforming those of individual layers. In the electron-electron drag regime, graphene-like Shubnikov-de Haas oscillations are observed at low temperatures. Our Coulomb drag transistor could provide a shortcut for the practical application of quantum-mechanical 2D heterostructures at room temperature.

NM01.11.25
Catalytic Degradation of 4-Nitrophenol by Three-Dimensional Au/rGO Microspheres Hua Wang and Shifeng Hou; National Engineering and Technology Research Center for Colloidal Materials, Shandong University, Jinan, China.

Microspheres as catalysts or catalyst supports have attracted a great deal of attention over the last two decades. Here, gold nanoparticles (Au-NPs) encapsulated within the reduced graphene Oxide microspheres (rGO microsphere) were prepared by using a spray-drying method. The mass content of
Au-NPs in the rGO microsphere composite reached 46.5%, and the average size of the Au-NPs was (10±2.5) nm, which was distributed evenly through the rGO microsphere composite. The morphologies and structural characteristics of the materials were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) patterns. The as-prepared composite was used to catalyze the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess sodium borohydride and exhibited high catalytic activity. The catalysis process was monitored by UV spectroscopy, and the first rate constant of the catalytic reaction \( k \) was 3.05 × 10^{-3} s^{-1}, and the activation energy \( E_a \) was found to be 2.1710 J/mol.

NM01.11.26
Soft Aerogels Supported by ~1 wt% Carbon Nanotubes for Thermal Interface Materials
Satoru Kawakami, Shunji Kobayashi, Hisashi Sugime, Junichiro Shiomi and Suguru Noda; Applied Chemistry, Waseda University, Tokyo, Japan; The University of Tokyo, Tokyo, Japan; Waseda Institute for Advanced Study, Waseda University, Tokyo, Japan; Advanced Science and Engineering, Waseda University, Tokyo, Japan.

Thermal interface materials (TIMs) are used for enhancing heat transfer between solid surfaces by creating thermal paths. Their important characteristics are high thermal conductivity and softness for filling the air gaps. Many conventional TIMs consist of the thermal conductive fillers dispersed in polymer matrix, which has disadvantages of low thermal conductivity and poor thermal stability.

Here we propose aerogel TIM replacing polymer matrix with air matrix. Air matrix is released upon pressing and conductive fillers are in direct contact with each other. A soft sponge like self-supporting film can be fabricated using carbon nanotubes (CNTs), and this structure is able to support fillers 100 times larger in weight compared with their own weight [1]. In the case of hybridization with graphite particles, the porosity of the aerogel can be controlled in the range from 20 % to 70 % by changing the amount of CNTs [1]. Moreover, the CNTs do not disturb heat conduction between fillers because CNTs have high thermal conductivity, and the CNT has high thermal stability (500 °C in air). We selected silver having the highest thermal conductivity among metals as conductive filler. The aerogel TIM was fabricated by hybridizing Ag particles with CNTs. The TIM was self-supporting even when the amount of fillers were 200 times larger than that of CNTs. From the result of steady-state thermal resistance measurement, the thermal resistance of 99.5 wt% Ag-0.5 wt% CNT-TIM between two Cu rods was 60 mm² K/W under 0.8 MPa. Too thick TIM had high bulk thermal conductivity and a too thin one had high contact resistance. In addition, TIM showed lower thermal resistance with lower CNT content. Optimization of the structure is now underway, and the latest results will be reported.


NM01.11.27
Capitalizing on the Molybdenum Disulfide/Graphene Synergy to Produce Mechanical Enhanced Flame Retardant Ethylene-Vinyl Acetate Composites with Low Aluminum Hydroxide Loading
Yuan Xue, Xianghao Zuo, Yichen Guo and Miriam Rafailovich; Stony Brook University, Stony Brook, New York, United States; Pall Corporation, Port Washington, New York, United States.

We have engineered a flame retardant ethylene-vinyl acetate (EVA) composite which has the similar mechanical properties as polyvinyl chloride (PVC) and therefore may prove to be an alternative material for cable sheathing. Four composites were studied, EVA with aluminum hydroxide (ATH), EVA with ATH and molybdenum disulfide (MoS2), EVA with ATH and graphene nanoplatelets (GNPs), and EVA with all three components. Tensile testing showed nearly identical results for the EVA/ATH and EVA/ATH/MoS2 compounds, while the EVA/ATH/GNPs compound had higher mechanical properties. The compound containing all three components showed further enhanced mechanical properties, indicating that a synergy was established. This was further confirmed using Scanning Electron Microscopy (SEM) where GNPs were seen to increase the dispersion of the MoS2 and ATH components within the polymer matrix. Cone calorimetry test clearly showed a large decrease in heat release rate when GNPs were added, which was further enhanced by adding GNPs and MoS2 together. Application of the UL-94 test showed that only the compound containing 36 wt% of ATH and 2 wt% each of MoS2 and GNPs can achieve the UL-94 V0 rating.

NM01.11.28
Direct Ink Writing of Multi-Walled CNT Reinforced Alumina Matrix Composites for Conductive Ceramics
Chao Liu and Junjun Ding; New York State College of Ceramics at Alfred University, Alfred, New York, United States.

Alumina is a widely used ceramic material in due to its good chemical and thermal stability, light-weight and wear resistance [1-3]. However, the low fracture toughness and conductivity of alumina limit its broader application to build various devices [2]. Carbon nanotubes (CNTs) obtain good mechanical strength and electrical conductivity to reinforce ceramics [4]. Direct ink writing (DIW) is an ideal additive manufacturing method to build ceramics green bodies with the advantages of low cost and free design [5, 6]. In this work, we fabricate CNT-alumina composites to improve the mechanical strength and electrical conductivity. Multi-walled CNT (MWCNT) (6 and 10 wt %), alumina powder (90 and 86 wt %) and Ferro 3134 (4 wt%) were mixed together. 3.7 wt% ammonium polyacrylate (NH₄-PAA) of whole slurry was used as a dispersant and 3.3 wt% polyvinylpyrrolidone (PVP) was used as a binder. 25.9 wt% of deionized (DI) water was used to modify the viscosity of slurry. After 12 hours of ball milling, the well-dispersed slurry ink was used to build the CNT-alumina composites using a modified DIW 3D printer. After drying out for 24 hours, samples were sintered at 1400 °C for 3 hours in a high vacuum. Scanning electron microscope (SEM) was used to observe the microstructure of the cross section in both green bodies and sintered samples. SEM images showed the dispersibility of CNT in sintered samples was better than that in green bodies, indicating the effect of sintering to microstructure of ceramics. The density of sintered samples was measured using Archimedes' Method. The density of the composite containing 6 wt% MWCNT was 3.065 g/cm³ (80.29% of theoretical density); the density of composite containing 10 wt% MWCNT was 2.875 g/cm³ (77.10% of theoretical density), confirming that the density decreased with an increasing amount of CNT [7]. Further study will be focused on the measurement of fracture toughness, compression strength and electric conductivity. We will study the percolation theory for electrical conductivity of composites with different fractions of MWCNT. We will also study various sintering methods, such as spark plasma sintering and hot isostatic pressing.

Reference:

NM01.11.29
Growth Temperature Dependence of Low-Pressure CVD Graphene Directly Grown on R-Plane Sapphire
Yuki Ueda, Junpei Yamada, Taishi Ono,
Graphene has attracted much attention as a next-generation electronic material for its excellent properties such as ultra-high mobility. Large-size single-crystalline graphene is usually obtained on copper based catalyst with chemical vapor deposition (CVD). However, the property of the graphene is largely deteriorated by the transfer process for device fabrication. Therefore, the direct growth of graphene on the dielectric substrate is studied to overcome the problem. C-plane sapphire is conventionally used as a substrate for the direct growth of graphene [1]. There are very few studies about the optimization of crystalllographic plane of sapphire for the direct growth. In this study, we focus on the use of c-plane sapphire as a substrate, which is sometimes used for the growth of horizontally-aligned carbon nanotubes [2].

Graphene was directly grown on r-plane sapphire using low pressure CVD without metal catalyst. C-plane sapphire was also used for the comparison. Mixture gas of nitrogen (N$_2$), hydrogen (H$_2$), and diethylacetylene (C$_6$H$_{10}$: 3-Hexyne) was flown to a reactor for the growth of graphene. Growth temperature was systematically changed between 1090 °C and 1210 °C. In the case of c-plane sapphire, graphene was found to grow only in the pits of sapphire, which was formed during CVD. This is very similar to the result that Saito et al. reported [3]. They reported Al-rich surface appeared inside the pits and had a catalytic effect. In our experiment, the size of pits enlarged with increasing growth temperature. Also, the growth rate of graphene increased with growth temperature and, then, decreased over 1170 °C. On the contrary, in the case of r-plane sapphire, the surface was fully covered with single-layer graphene in all samples. D/G peak intensity ratio and wrinkle density of graphene decreased with increasing growth temperature. On r-plane sapphire, the graphene was found to grow simply in 2D nucleation mode. This is probably because the surface of c-plane sapphire has catalytic effect and enhances the decomposition of growth species. Therefore, the use of r-plane sapphire brings a faster growth rate and smoother surface than those on c-plane sapphire.

Acknowledgement: This work was supported in part by JSPS KAKENHI Grant Numbers 15H03558, 26105002.

References

NM01.11.30 Reinforcement of CNT Yarn by Graphitization and Cross-Linking CNTs Taichi Kita, Motoyuki Karita, Takayuki Nakano and Yoku Inoue; Shizuoka University, Hamamatsu City, Japan.

Carbon nanotube (CNT) has been reported to have high tensile strength of 150 GPa [1]. Since the discovery of dry spinning phenomenon from a CNT forest [2], a dry-spun CNT yarn has been an attractive material as the structural material. One of good things of the dry-spinning is that large-scale and highly aligned CNT structures are uniformly formed. However, since the CNTs are connected by van der Waals force, the spun yarn fails by relative sliding of CNTs, and its mechanical properties are far inferior to those of individual CNT. Moreover, even the relative sliding is suppressed by cross-linking CNTs in the yarn, tensile strength of individual CNT is not so high as expected because of crystal defects, resulting in moderate improvement of strength in the yarn. In this work, in order to reinforce the CNT yarn, CNTs were graphitized at high temperatures. Then CNTs were cross-linked by binder materials. Dry-spin capable MWCNT forests were grown by chlorine mediated CVD using FeCl$_3$ as catalyst [3]. The yarns were prepared by twisting drawn CNT webs [4]. The yarns were annealed at higher than 2500 °C in inert ambient. The highly graphitized CNT yarns were further reinforced by introducing azide-group cross-linker agent that makes covalent bonding in between CNTs. Mechanical and electrical properties of the reinforced CNT yarns will be reported.

References

NM01.11.31 The Mechanics of Reinforcement in Graphene-Based Nanocomposites Robert Young, Dimitrios Papageorgiou and Ian A. Kinloch; University of Manchester, Manchester, United Kingdom.

Although there has been a rapid growth of interest in polymer-based nanocomposites, the mechanics of reinforcement in such materials is still not yet fully understood. It has been established by the authors that stress transfer from the matrix to the reinforcement in nanocomposites reinforced by graphene nanoplatelets (GNPs) can be followed from stress-induced Raman band shifts. A detailed study has been undertaken of the mechanisms of stress transfer in a polymer of polymeric matrices with very different levels of Young’s modulus, $E_m$, reinforced by graphene nanoplatelets. The matrix materials studies have been natural rubber ($E_m$ ≈ 1 MPa), thermoplastic elastomers ($E_m$ ≈ 10-100 MPa) and polypropylene ($E_m$ ≈ 1000 MPa). The microstructure of the nanocomposites has been fully characterised using a range of different advanced analytical techniques that include, Raman imaging, x-ray computer tomography (CT) scans and polarized Raman spectroscopy that give an unprecedented level of information upon their microstructures. It is found that the addition of the GNPs leads to significant increases in stiffness in each polymer showing high levels of reinforcement are obtained. For each material the effective Young’s modulus of the graphene, $E_{eff}$, has been determined using the rule of mixtures and it has been found that this scales with the value of $E_m$. Additionally the stress-induced Raman bands shifts show different levels of stress transfer from the polymer matrix to the GNPs which again scale with the Young modulus of the matrix. For example, shifts of the order of 1 cm$^{-1}$/100% strain are found in the natural rubber matrix nanocomposites compared with ~10 cm$^{-1}$/1% strain for the polypropylene matrix nanocomposites with a value of $E_m$ three orders of magnitude higher. Studies of the mechanics of stress transfer in model composites consisting of single graphene flakes in polymeric matrices have also been undertaken by using Raman spectroscopy to map the strain distribution in the individual flakes. A unifying theory has been developed to predict the stiffness of the bulk nanocomposites from the mechanics of stress transfer from the matrix to the GNP reinforcement based upon these studies of deformation of the individual flakes. Excellent agreement has been found between the measured and predicted values of $E_{eff}$ and hence composite Young’s modulus for the bulk nanocomposites. It will be shown that the theory also enables factors such as interfacial bonding, reinforcement geometry and orientation to be taken into account.

Overall it is found that it is only possible to realise the theoretical Young’s modulus of graphene of 1050 GPa for discontinuous flakes as $E_m$ approaches 1 TPa; the effective modulus of the reinforcement will always be less for lower values of $E_m$. In general it is found that the highest levels of reinforcement will be obtained in nanocomposites with strong graphene-polymer interfaces and optimised reinforcement geometries and orientation.

NM01.11.32
Carbon based nanomaterials are currently in the limelight for their potential to replace expensive noble metal based electrocatalysts. Noble metal electrocatalysts (Pt, Pd, Au, Ru) suffer from monofunctionality (hydrogen evolution reaction (HER)/oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) favoured). As such, their use in electrocatalytic devices i.e. fuel cells, Zn-air batteries etc. is limited. Carbon based materials with controlled level of defects and high specific active surface area, can be tuned to serve as multifunctional materials. The overall oxygen electrochemistry towards ORR and OER is significantly lower than the noble metal group based electrocatalysts. Doping of nitrogen (or other heteroatoms) in the carbon structure also significantly improves their activity. In this context, a simple one-step pyrolysis route is used to synthesize exotic carbon based materials, especially core-shell nanostructures and nanotubes, using various transition metal precursors. It is observed that transition metal based alloy nanoparticles, in the vicinity of the carbon matrix significantly increases the cyclic stability and effective electrochemical window required for total water splitting or metal-air battery systems. Furthermore, the involvement of metal centres and their interaction with carbon and nitrogen in the generated carbon materials is investigated, which provides useful insights into the tunability and progress in such systems.

**NM01.11.33**

**Graphene Oxide-Templated Synthesis of Crumpled Holey Metal Oxide Nanosheets via Spray Pyrolysis for Enhanced Gas Sensor**

Rheehyun Kim, Ji-Su Jung, Dong-Ha Kim, Won-Tae Koo and Il Doo Kim; Material Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Two-dimensional (2D) metal oxides have widely been studied in various applications due to their intriguing properties, such as super high surface-to-volume ratio, ultra-thin thickness, high meso-porosity and small grain size. However, 2D nanostructures have the tendency to restack, so they can induce the decrease of surface area and amounts of accessible mesopores. In this work, crumpled SnO₂ nanosheets (NSs), crumpled ZrO₂ NSs, and crumpled SnO₂-ZrO₂ composite NSs (C_MO NSs, MO = SnO₂, ZrO₂ or SnO₂-ZrO₂) were successfully synthesized by using graphene oxide (GO) sheets as a sacrificial template and used as highly effective 2D oxide gas sensing layers. In detail, GO/metal ion composites were synthesized by dissolving metal precursor and GO in absolute ethanol to allow bonding between 2D GO and the metal oxide (GO in absolute ethanol to allow bonding between 2D GO and the metal oxide). Then, by conducting spray pyrolysis of the solution which is composed of dispersed GO/metal ion composites in DI water at 400 °C, the crumpled GO/metal oxide composites were fabricated. After calcination of them at 500 °C for 1 h, GO were thermally decomposed to form C_MO NSs. Crumpled metal oxide NSs have high surface-to-volume ratio and high distribution of macropores as well as mesopores, which are essential for efficient surface reaction and high gas permeability. Also, ultra-small grain size affects to form complete electron depletion layer for effective modulation of resistance. Additionally, n-n heterojunction from C_SnO₂/ZrO₂ NSs can induce the energy band bending to enhance the gas sensing capability. The gas sensing properties were proceeded to VOCs (volatile organic compounds) gas species, e.g., CH₃COOH, NO, C_H₄, C_H₃O, HCHO, H₂S and NO₂. The sensing test results demonstrated that C_MO NSs exhibited enhanced gas sensing performance toward formaldehyde (2.5 times higher response (R_p/R_u) than that of 2D metal oxide NSs) with high selectivity and fast response/recovery speed. Also, C_SnO₂/ZrO₂ NSs induced the improvement of gas sensing properties due to the creation of heterojunction (3 times higher response (R_p/R_u) than that of C_MO NSs). This work suggests the facile and effective synthesis method of C_MO NSs templated by the GO for enhanced gas sensor.

**NM01.11.34**

**High Electrical Conductivity of Carbon Nanotube/Poly(Acrylonitrile) Composite Fibers Fabricated via Current-Assisted Wet Spinning**

Yong-min Kim, Ho-Sung Yang and Woong-Ryol Yu; Seoul National University, Seoul, Korea (the Republic of).

Wet spinning process is one of the most common methods of producing polymer microfibers. Wet process has been used in particular for the polymers which can decompose near their melting temperature and thus defy melt spinning process. Poly(acrylonitrile) (PAN), a representative precursor of carbon fibers, belong to this kind of polymers. On the other hand, due to high thermal conductivity and electrical conductivity, carbon nanotubes (CNTs) have been used in PAN fibers to improve the conductivity of carbon fibers. Well-aligned CNTs are known to contribute high electrical conductivity. In this study, we developed high conductive CNT/PAN composite microfibers using a new process, so called current-assisted wet spinning. The current-assisted wet spinning is different from electrosprinning which utilizes the electric field to fabricate nanofibers from a charged solution. For the current-assisted wet spinning, the electrical current is applied to the spinning nozzle of wet spinning system, inducing the interaction of PAN and functional group of CNT and also more packing and alignment of PAN molecules via controlled diffusion between CNT/PAN and coagulation solutions. The electrical and mechanical properties of CNT/PAN fibers fabricated using current-assisted wet spinning were measured by the two-probe method and single fiber tensile test. 2D wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to characterize the microstructures of CNT/PAN fibers. Nuclear magnetic resonance spectroscopy (NMR) and X-ray photoelectron spectroscopy (XPS) analysis were performed to characterize the chemical bonding of CNT/PAN solutions and fibers. Finally, a mechanism behind high conductivity of CNT/PAN composite microfibers via current-assisted wet spinning was investigated and will be presented in detail at the Conference.

**NM01.11.35**

**Quasi-Freestanding Graphene on SiC by Argon Mediated Intercalation of Antimony**

Susanne Wolff¹, Florian Speck¹, Martina Wanke¹, Felix Timmermann², Manfred Albrecht³ and Thomas Seyller¹; ¹Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany; ²Institut für Physik, Universität Augsburg, Augsburg, Germany.

The intercalation of various elements under the buffer layer is an elegant method to produce so-called quasi-freestanding graphene (QFMLG) on SiC substrates. The modification of the graphene/SiC interface changes the electronic properties of QFMLG depending on the choice of the intercalant. Hence, intercalation represents a promising technique to tune graphene’s properties according to the specific application. So far, three methods for intercalation have been successfully demonstrated to work for different elements. Gaseous species like, e.g., hydrogen [1] or oxygen [2] can be intercalated by annealing in the respective atmosphere. Solids with low vapor pressure such as gold [3] or germanium [4] were intercalated by first depositing the material on top of the buffer layer followed by annealing at a certain temperature in ultra-high vacuum (UHV). On the other hand, solids with high vapor pressure require a different method. Recently it was shown that implantation [5] allows the intercalation of bismuth. In this presentation, using the example of antimony (Sb), we introduce another method to intercalate solid elements with high vapor pressure. The method is based on a reduced rate of sublimation of Sb from the surface when the sample is annealed in argon (Ar) atmosphere rather than in UHV.

To that end, Sb with a thickness of approx. 50 nm was deposited by molecular beam epitaxy on top of the buffer layer and the samples were annealed in 1 bar Ar at an optimized temperature of 550°C. X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) confirmed the intercalation and formation of quasi-freestanding graphene. Both, elemental Sb as well as oxidized Sb were observed at the interface. The latter is caused by the transport of the Sb-covered samples in air which leads to a thin oxide layer on top of the Sb. A two-step annealing process in 1 bar Ar where (i) the oxide is removed by annealing at 400°C and (ii) the intercalation is performed at 550°C leads to the intercalation of purely elemental Sb. Angle-resolved photoelectron spectroscopy (ARPEMS) reveals a moderate n-type doping of the samples which were intercalated with pure metallic Sb.
The aim of this study is to promote the ultra-fast, sensitive and real-time monitoring of different clinical cardiac Biomarkers (Myoglobin and Cardiac Troponins) for the diagnosis of the cardiac diseases like Acute Myocardial Infarction (AMI) using the 3D network of 2-ABA functionalized carbon nanotubes in a the Lab-on-a-chip configuration. The development of a rapid and practical immunosensor for detecting Cardiac markers in serum samples (standard as well as spiked) is desirable due to its roles in cardiacspecific diagnosis, risk stratification, and assessment. The main objective is to develop a biosensor exploiting microfluidics allowing in-situ self-functionalization. The sensitivity can be adjustable and the device can be used for detection of different cardiac biomarkers. The functionalization takes place in situ and selectively, just before the sensing, keeping the sensing area dry and inactive until the test starts, and conserving the functionality of the device. Also, the reagents and chips are stored separately and may be used before testing, without the need of overnight functionalization process or complex fabrication methods. The monitoring of the signal is performed in real-time and changes in impedance modulus (label-free electrochemical changes) are equivalently recorded by using an alternative and simpler voltage measurement. The label-free electrochemical biosensors are an attractive choice for fast, early diagnostics and monitoring of biological markers due to the direct conversion of a biological event into an electronic read-out signal.

Since the discovery of single-walled carbon nanotube (SWNT), SWNT has attracted with great interest because of their outstanding mechanical and electrical properties. For these reasons, researches for implementation of their electronic applications such as field-effect transistors (FETs), thermoelectric devices and biological imaging have been substantially promoted. However, the co-existence of metallic (m-) and semiconducting (sc-) SWNT have disturbed the effective use for electronic applications. In the recent, conjugated polymer wrapping of SWNT has specially aroused great attraction as a method for separation of SWNTs due to their advantages of high selectivity toward sc-SWNT and simple polymer sorting process. Although the π-π interaction between conjugated polymer and wall of SWNTs is related with the selective dispersion of SWNTs, the mechanism how to separate the sc-SWNTs remains as issues. In this research, we introduce the pyrene moiety as main chain of conjugated polymer to increase the π-π interaction with sc-SWNTs. New pyrene-based conjugated polymers were carefully designed and synthesized via suzuki polymerization. Their dispersion selectivity and diameter of sc-SWNTs enriched by pyrene-based conjugated polymers were characterized by various measurements such as UV-vis absorption spectra, Raman spectroscopy and Photoluminescence excitation/emission analysis. Finally, the sc-SWNTs were employed into FETs as an active layer.

Single-wall carbon nanotube(SWNT) is excellent material for many applications. Especially, SWCNTs with small diameter and high crystallinity are expected to have better property, however they are more difficult to synthesize which results in high cost (2-100 USD/g). One of the best synthesis methods for high quality CNT is floating catalyst chemical vapor deposition (FCCVD) [1-4]. However, the yield of CNT is still low which stems from the low efficiency of the formation of active catalyst nanoparticles. In the conventional CVD, because the gas which contain the catalyst source is heated gradually by the furnace, most of the catalyst nanoparticles aggregate and deactivate before the nucleation of the CNTs.

In this report, to generate more active catalysts, we designed a new process to control the gas temperature. The catalyst sources (ferroocene and sulfur) are rapidly (i.e., ~5 ms) heated to 1300 °C in the narrow flow path (Φ4 mm) to pyrolyze and vaporize efficiently. Then, the iron vapor is mixed with carbon sources (e.g., CH4, C6H6, etc.) and cooled down rapidly to 1150 °C in wide flow path (Φ40 mm), which enables the formation of the catalyst nanoparticles followed by the immediate nucleation and synthesis of the CNTs. The CNT yield was 2.5 mg/mm. The TEM observation showed 90% SWCNTs with 10% efficiency of the formation of active catalyst nanoparticles. In the conventional CVD, because the gas which contain the catalyst source is heated gradually by the furnace, most of the catalyst nanoparticles aggregate and deactivate before the nucleation of the CNTs.

References:

Modified Tour Method for Synthesis of Graphene for Solar Cell Applications Dulce K. Becerra Paniagua1, Merida Sotelo Lerma2 and Hailin Zhao Hu1; 1Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Temixco, Mexico; 2Universidad de Sonora, Hermosillo, Mexico.

Graphene products are obtained by reduction of graphene oxide (GO). A recently chemical procedure for GO synthesis is the Tour method [1]. In this method the GO was synthesized by the oxidation of graphite powder, using KMnO4 and a 9:1 mixture of H2SO4/H3PO4, the latter as a protective agent. In this paper a modified Tour method is designed to looking for a simple, easily controlled and an alternative approach for large scale production of GO for solar cell applications. We find that if a mixture of H2SO4/H2O2 is used instead of H2PO4, then the oxidation time of graphite can be reduced under the same reaction conditions: two hours of oxidation is enough for produce the equal amount of hydrophilic oxidized graphene material as compared to Tour method that requires about seven hours. The reduced graphene oxide (rGO) was prepared by the thermal and chemistry reduction of GO by employing ascorbic acid and ammonia solution at high temperature [2]. The GO and rGO samples were characterized by UV-Visible spectroscopy, FTIR spectroscopy, Raman spectroscopy, SEM, TEM and EDS. It is found that the GO prepared by modified Tour method yields a higher fraction of well-oxidized carbon material and could have the same advantageous in quality for achieving few-layers of graphene sheets for large-scale production than the
original Tour method. On the other hands, the results of XRD, EDS and UV-Vis of GO products reveal that the oxygenated groups that were present in GO products have been widely removed, this can be seen reflected in the atomic ratio C/O of rGO (3.7), it increase close to 70% with respect to the GO (1.3), so that almost 50% of the oxygenated groups were removed. Finally, thin films of GO and rGO were prepared by spin coating method with GO and rGO solutions. Optical and electrical properties of the films are analysed and their potential use as electron or hole transporting layers in perovskite solar cells are discussed. In particular, the presence of the remaining oxygenated groups in rGO reduces the electrical conductivity of the GO films, and, consequently, the power conversion efficiency of the solar cells. The removal of a higher percentage of oxygenated groups remains as a challenge in the synthesis of graphene products.

NM01.11.40
Electrical Performances of Carbon Nanotube Webs and Yarns Yoann Dini1,2, Jean Dijon1,2 and Jérôme Faure-Vincent1,3; 1Commissariat à l’energie atomique, Grenoble, France; 2Isère, Université Grenoble Alpes, Grenoble, France; 3Centre National de la Recherche Scientifique, Grenoble, France.

In electrical wiring, metal substitution by high conductivity materials like carbon nanotubes (CNT) is a near future challenge for high-end aeronautic and aerospace applications1,2. Several techniques exist to make CNT yarns. The most suitable, eco-friendly process for large-scale production is to directly dry spin CNTs grown by fixed- or floating-catalyst Chemical Vapor Deposition (CVD). For the last ten years, all published works on CNT yarns from CNT arrays made by fixed-catalyst CVD have faced the same resistivity limitation of around 1 mΩ.cm3. The basic reasons for this limitation are unclear. Is it the intrinsic CVD carbon nanotube quality or the disorganization of the CNTs inside the yarn induced by the CNT array? We recently developed a new carbon nanotube yarn production process based on a low temperature (630°C) and low pressure (1.2 mbar) hot filament CVD system. It allows us to produce small carbon nanotubes (7 nm average diameter) and yarns from our CNT arrays with state of the art resistivity (1.07 mΩ.cm). Our work answers the previous questions through extensive electrical transport studies of CNT webs and CNT yarns. Resistivity measurements from 3 K to 350 K are analyzed within the frame of known electronic transport models. The effects of the densification, the CNT lengths and the dopants on the yarn will be presented. Contrary to the typical explanation, we will show that the electrical contacts between carbon nanotubes in the yarn are good and do not limit the electrical transport at room temperature. Those contacts only hinder the yarn’s electrical transport at temperature below 70 K. We performed unique carbon nanotube web resistence measurements at room temperature. A careful scanning electron microscope image analysis of the CNT web reveals the fractal arrangement of the CNTs (fractal dimension of 1.75). Hence, we found that the average resistivity is 0.7 mΩ.cm for the CNT bundle and 0.5 mΩ.cm for the individual CNT. The CNT yarn resistivity is therefore similar to that of the CNT bundle. It appears that the 1 mΩ.cm resistivity limitation faced by yarns made from CNT arrays is mainly due to the individual CNT resistivity. Our work emphasizes that drastic enhancement of CNT yarn electrical resistivity can only be achieved by doping or by increasing the CNT quality.


NM01.11.41
Preparation of Carbon-Black/Polymer Composite Fibers Sang Young Yeo; Korea Institute of Industrial Technology, Ansan, Korea (the Republic of).

With the development of the wearable device industry, there is an increasing interest in conductive textiles, and research on conductive fiber manufacturing is actively being reported. Because carbon black has a high specific surface area, a composite is prepared by mixing with a polymer then a conductive network is formed in a small amount to improve electrical conductivity. In this study, carbon-black/polymer composites composed of polypropylene, polyester, and nylon matrix were prepared and their electrical properties were analyzed. The carbon-black/polyester composite film with good dispersibility showed the highest electrical conductivity and the lowest threshold value among 3 types polymer composites. The nylon composites with high polarity had dependent CL and compared to that diamond and ZnO [6]. The luminescence of hBN is confirmed to be unusually high and is found to remain constant from 10 to 300K. Enlightening analysis of this behaviour is provided by ab initio calculations of the excition dispersion in bulk hBN. First, the lowest-energy excition (X) is found at 5.97eV and to be indirect, as expected for an indirect band gap, with a binding energy equal to 300 meV. This dispersion behavior accounts for an assignation of the luminescence to phonon assisted recombinations of the indirect excition as proposed in [7] and for the assignation of the

SESSION NM01.12: Non-Carbon Structure and Properties
Session Chairs: Ranjit Pati and Yoke Khin Yap
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Republic AB

8:45 AM *NM01.12.01
Understanding Optical Absorption and Luminescence in hBN—From Bulk to the Monolayer Annick Loiseau; LEM, CNRS-ONERA, Chatillon, France.

hBN layers meet a growing interest for deep UV LED [1], and have become a strategic material for the fabrication of van der Waals heterostructures. Stacked with any other 2D material it can reveal the best of their physical properties [2]. However, hBN optoelectronic properties remain much less characterized and understood than other 2D materials.

In this talk, we review recent advances made thanks to the development of appropriate spectroscopies in the UV range - cathodoluminescence (CL) at 4K and Raman [3,4], combined with ab initio simulations [5]. Thanks to these tools, a h-BN characterization metrics has been developed on the basis of their original optical properties, governed, in the energy range 5.5 – 6 eV, by strong excitonic effects easily trapped at structural or chemical defects [3]. We shall discuss the interplay between structure, defects and spectroscopic properties and how these properties can be further exploited for sample benchmarking [3].

Beyond this effort, the talk will also address the recent advances made for the understanding of the high luminescence observed although bulk hBN is an indirect band gap material [1,6]. To that aim, the efficiency of radiative recombinations has been measured on a reference single crystal using temperature dependent CL and compared to that diamond and ZnO [6]. The luminescence of hBN is confirmed to be unusually high and is found to remain constant from 10 to 300K. Enlightening analysis of this behaviour is provided by ab initio calculations of the excition dispersion in bulk hBN. First, the lowest-energy excition (X) is found at 5.97eV and to be indirect, as expected for an indirect band gap, with a binding energy equal to 300 meV. This dispersion behavior accounts for an assignation of the luminescence to phonon assisted recombinations of the indirect excition as proposed in [7] and for the assignation of the
tiny peak observed in CL spectra at 5.956 eV to the zero-phonon radiative recombination of IX [6]. Further IX high binding energy is consistent with the temperature behavior of the luminescence, the high yield being the signature of a strong exciton phonon coupling. Second, calculations also confirm the direct exciton (dX) with a binding energy of 670 meV [6], an energy which turns to be only 100 meV above the indirect one. It comes out that bulk hBN displays a peculiar behavior where luminescence and optical absorption are due to different excitons. This situation totally evolves in the layer, the gap being direct and we could identify the dX line in the CL spectra recorded on very thin hBN layers [6].


9:15 AM NM01.12.03

Despite their similar crystallographic structures, boron nitride nanotubes (BNNTs) exhibit a range of physical and chemical properties distinct from carbon nanotubes (CNTs), which are mainly attributed to the partial ionic bonding character of BN. Here we present two markedly different properties between BNNTs and CNTs: interlayer mechanics [1] and reduction chemistry [2]. Firstly, we show using van der Waals (vdW) parameterized density functional theory (DFT) that the strong mechanical coupling between the buckled lattices of small-diameter BNNTs greatly elevates the threshold forces and internal friction with respect to the relative motion of BNNT walls. Unlike for CNTs, large differences between relaxed and unrelaxed energy corrugations of BNNTs could yield energy dissipation via the strain-induced anelastic relaxation of interlayer locking, resulting in the experimentally observed ultrahigh interlayer friction of BNNTs. Secondly, through DFT calculations and experimental studies of the covalent alkylation of BNNTs using 1-bromohexane, we demonstrate that the chemical reactivity of BNNTs towards radical molecules can be significantly enhanced via reducing the nanotubes (i.e., negatively charging). Our study predicts that the localization characteristics of the BNNT π electron system lead the excess electrons to fill the empty p orbitals of boron sites, which promote covalent bond formation with an unpaired electron in radical molecules.

References:

9:30 AM BREAK

10:00 AM *NM01.12.04
Boron and Metal Boride 2D Sheets and Nanotubes Sohrab Ismail-Beigi; Yale University, New Haven, Connecticut, United States.

Compared to carbon, bulk and reduced dimensional forms of pure boron present more complex bonding patterns and atomic-scale geometries. An underlying reason is that boron has the same number of valence orbitals as carbon but has one fewer valence electron (i.e., is “electron deficient”). This means that standard two-center bonding motifs between neighboring atoms in familiar structures, such as hexagonal or triangular networks, are not energetically favorable. This leads to complexity and richness in the phase space of boron structures. This situation has attracted significant scientific attention over the last two decades. While the initial literature consisted of primarily of first principles theoretical studies and predictions, the last few years have witnessed experimental fabrication and characterization of 2D boron sheets which in turn has greatly enhanced interest in these materials.

This talk will provide a brief overview of the initial theoretical predictions in this field followed by a summary of some of the more salient experimental and theoretical performed recently, including some of our work on 2D and nanotubular boron and metal boride nanomaterials. In the process, we will discuss the challenges and opportunities this field may face when attempting to fabricate and use boron nanostructures.

10:30 AM *NM01.12.05
Carbon and Beyond: A Colorful Palatte of 2D Materials Boris I. I. Yakobson; Department of Materials Science and Nanoengineering, Department of Chemistry, and the Richard E. Smalley Institute, Rice University, Houston, Texas, United States.

From our theoretical insight into evolutionary selection in synthesis of monocrystal graphene [1], into the paths of back-diffusion in growth of its bilayers [2], and into their possible conversion to monocrystal diamond films like diamond [3,4], we envisage a platform to emerge for design of the point (0D) defects in 2D-media as effective single-photon emitters (SPE) [5]. More diverse basic optics of numerous 2D materials [6] further expands possibilities for SPE realization, where theoretical assessment can guide experimental choices and tests.


11:00 AM *NM01.12.06
Recent Advancement in Boron Nitride Nanotubes and Nanosheets Yoke Khin Yap; Michigan Technological University, Houghton, Michigan, United States.

Hexagonal boron nitride (h-BN) is structurally like graphite and has continued to gain research interest from synthesis, characterization, to application. Mono and few layered h-BN are now commonly known as boron nitride nanosheets (BNNSs), as one of the emerging two-dimensional (2D) materials. On the other hand, seamless rolls of BNNSs are known as boron nitride nanotubes (BNNTs). BNNTs are meaningful as a role model of materials by design, as they are first predicted by theory and then experimentally realized. Due to the difficulty on the synthesis of BNNTs and BNNSs, their research progress is far slower than the structurally similar carbon nanotubes (CNTs) and graphene. In this invited talk, recent advancement of BNNTs and BNNSs will be discussed, in particular for their application in advanced electronic and biomedical applications. These advancements suggest that BNNTs and BNNSs are important nanomaterials that complement the application of CNTs, graphene, and 2D materials.
Integration of atomic force microscopy and laser spectroscopy traditionally makes possible to obtain more complex information about the studied object: whether it is a living cell, a polymeric composite, or nanotubes. In the report are given various examples of combined AFM and Raman microscopy NTGERA Spectra (NT-MDT Spectrum Instruments Co) applications to study both physical properties of the surface (topography, surface potential, magnetic or piezoelectric properties, conductivity, local stiffness) and structural properties measured by Raman spectroscopy will be reported. Normally combined study is done by means of Si cantilevers of top-visual shape to provide optical access to the tip from above by high-resolution objective (100x, 0.7 NA). It is also possible to use metal needles for scanning tunneling microscopy or tuning fork-based feed-back. Measurements can be carried out in a controlled gas or liquid environment, which may be important to maintain the properties of the sample or to eliminate the background low-wavenumbers Raman peaks from the N\textsubscript{2} and O\textsubscript{2} molecules present in air. The design of the spectrometer allows to use either edge filters or notch filters to suppress laser radiation and provide both Stokes and anti-Stokes scattering, including the THz range down to 10 cm\(^{-1}\) from Rayleigh scattering.

The most intriguing possibility that appears when integrating atomic force microscopy and Raman spectroscopy is to overcome the diffraction limit due to local amplification of the field near the tip apex [1]. To achieve strong enhancement of Raman signal in the Tip Enhanced Raman Scattering (TERS) mode, it is necessary to keep the tip at the surface of the sample as close as possible. The mode of nonresonant intermittent-contact microscopy, also known as Hybrid mode [2] allows the probe to be held in contact with the surface up to 70\% of time, while eliminating lateral forces during scanning and minimizing the pressure force. In addition, this method is also applicable to keep feedback in the liquid and when the sample is heated, when a significant drift of the cantilever bending is observed.

The presented results, using the example of graphene oxide flakes, show that HybriD mode allows to effectively enhance Raman scattering and, at the same time, significantly reduces the mechanical probe-sample impact during scanning process.

Literature

11:45 AM AM01.12.08
Broad Spectra Absorption of Boron Nitride and Molybdenum Disulphide Quantum Dots for Photovoltaic Devices Amit Acharya, Dongyan Zhang and Yoke Khin Yap; Michigan Technological University, Houghton, Michigan, United States.

After the discovery of semi-metallic graphene, layered materials such as hexagonal Boron Nitride (h-BN) and molybdenum disulphide (MoS\textsubscript{2}) have attracted a lot of attention. For example, h-BN sheets have become the indispensable underlayers for two dimensional (2D) devices with high electron mobility despite being electrical insulating. On the other hand, the indirect to direct band gap conversion in MoS\textsubscript{2} is due to the quantum confinement effect along the thickness axis of the 2D materials. Here, we present the synthesis and properties of h-BN and MoS\textsubscript{2} quantum dots (QDs) by creating quantum confinement in axes perpendicular to the thickness axis. These QDs offer unique and broad spectra absorption bands for effective photoelectron generation for use in QD-sensitized photovoltaic devices.

A top-down approach was employed to convert h-BN and MoS\textsubscript{2} particles into QDs by using sonication, and solvo-thermal in Dimethylformamide (DMF). The MoS\textsubscript{2} are 2-40 nm in dimension, while the BN QDs are 2-8 nm in dimension. We show that the fluorescent emission from these polydisperse QDs are excitation wavelength dependent. These MoS\textsubscript{2} QDs could absorb a wide spectrum range of light from 320-520 nm to produce fluorescence emission from 385-569 nm. The h-BN QDs can absorb a broader spectra from 300-580 nm with fluorescence emission of 380-620 nm. The broad absorption wavelength range of these QDs would meet the peak of solar irradiation spectrum to enable effective production of photoelectrons from the sun for the applications of photovoltaic devices. Detailed of these results will be discussed in the meeting.

1:30 PM *NM01.13.01
Harnessing the Versatility of Carbon Nanotubes for Printed Electronics Aaron D. Franklin; Duke University, Durham, North Carolina, United States.

Single-walled carbon nanotubes (CNTs) are one of the most versatile electronic materials ever discovered. Electronically, they can be semiconducting or metallic; mechanically, they are flexible yet have a tensile strength greater than steel; and physically they can be centimeters long to just a few nanometers. For nearly two decades, these diverse properties have excited and motivated researchers pursuing CNTs for electronic applications. However, thus far the versatility of CNTs has also been their greatest obstacle in terms of purification, precise positioning, and so forth. In this talk, I will discuss how the inherent versatility of CNTs can be appropriately harnessed for enabling certain applications. The tremendous progress in solution-phase processing of nanotubes has opened a path for their most suitable, near-term use as printed thin films. Recent advances will be presented in using printed thin films of CNTs for print-in-place additive electronics, sensors for harsh environments, and highly sensitive biosensors. Each of these is made possible by drawing from distinct properties of thin-film CNTs; properties unavailable from any other printable material. Perspectives on stability, reproducibility, and yield will also be offered, with evidence of the impact that printed silver contact morphology has on printed CNT thin-film transistor performance. The unique and reproducible behavior of printed CNT thin films suggests they be given greater consideration from the printed electronics community. In the company of organic semiconducting inks, and even that of non-printed metal-oxide semiconductors, printed films of CNTs are a standout with significant advantages and opportunities.

2:00 PM NM01.13.02
Low-voltage Operable, Highly-stretchable Carbon Nanotube Thin-Film Transistors with Novel Local Strain Control Structure Yuya Nishio2, Jun Hirota1, Shigeru Kishimoto1 and Yutaka Ohno1; 1; Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan; 1; Department of Electronics, Nagoya University, Nagoya, Japan.
Stretchable devices have intensively been studied towards a realization of wearable electronics for continuous monitoring of human activity and health condition. Recent works have demonstrated that carbon nanotube thin-film transistors (CNT TFTs) have excellent mechanical flexibility and stretching ability. [1-3] However, they still exhibited a degradation of drain current with applied strain. Another issue to be addressed is high-voltage (a few ten V) operation due to the polymer-based gate dielectric which is flexible and/or stretchable, but of low-dielectric constant. [3] wrinkled Al2O3 gate insulator was proposed for realizing low-voltage and stretchable CNT TFTs, but the degree of tensile strain was limited up to 20%. [2] Here, we have realized low-voltage operable and highly-stretchable all-carbon CNT TFTs by introducing a novel local strain control structure.

We fabricated CNT TFTs composed of a channel of a semiconducting-CNT thin film, transparent electrodes of a CNT thin film, and a 50-nm-thick Al2O3 gate dielectric layer on a stretchable poly(dimethylsiloxane) (PDMS) film. The device may exhibit some degree of stretching ability, however, in order to fully suppress the influence of strain on the device characteristics, we formed a local strain control structure with a rather hard polymer material on top of the channel region of a CNT TFT. We also performed the numerical analysis based on the finite element method to design the strain control structure.

The fabricated devices exhibited typical p-type transistor characteristics with a carrier mobility of 7.2 cm2/Vs and on/off ratio of about 104, and was operable at gate voltage of less than 5 V. By introducing the local strain control structure, only 14% of externally applied tensile strain was introduced in the channel region, whereas the CNT electrodes and the other field of the PDMS film were directly stretched. No significant degradation of drain current was observed against tensile strain up to 35%.


2:15 PM NM01.13.03

Fully-Printed Flexible Dual-Gate Carbon Nanotube Thin-Film Transistors with Tunable Ambipolar Characteristics for Complementary Logic Circuits Haochuan Wang1, Min Yu2 and Chuan Wang3; 1Electrical and Systems Engineering, Washington University in St. Louis, St Louis, Missouri, United States; 2Institute of Microelectronics, Peking University, Beijing, China.

Semiconducting single-wall carbon nanotubes (sSWCNTs) have been widely used as the channel material for high-performance printed flexible thin-film transistors (TFTs). Due to the absorption of moisture and oxygen in air, the printed sSWCNT TFTs generally exhibit p-type characteristics only. In this paper, we report fully-printed dual-gate sSWCNT TFTs that exhibit almost symmetric ambipolar characteristics. With the applied control gate voltage varying from -60 V to 60 V, a threshold voltage tuning range of 27 V is achieved, allowing the device to be effectively tuned into either predominantly p-type or predominantly n-type. The tunable ambipolar characteristics are found to be very stable over long period of time (4 months). By integrating two printed dual-gate TFTs biased with different control gate voltages, a complementary metal oxide semiconductor (CMOS) inverter with close to rail-to-rail output voltage swing is demonstrated. The use of dual-gate structure for achieving n-type printed carbon nanotube TFTs is much more controllable and repeatable compared to other methods such as chemical doping. Our work shows the feasibility of implementing more sophisticated complementary logic circuits using printed flexible carbon nanotube transistors.

2:30 PM NM01.13.04

Spectrally-Resolved Photoresponse in a Graphene-Based Gate Tunable Phototransistor Dehui Zhang1, Gong Cheng1, Zhen Xu1, Che-Hung Liu1, Meisi Guo2, Thomas Beechem3, Michael Goldflam1, François Leonard2, Steve Young1, David Peters1, Zhe Liu1, Audrey Rose Gutierrez2, Wenzhe Zhang1, Theodore B. Norris3 and Zhaohui Zhong1; 1University of Michigan, Ann Arbor, Michigan, United States; 2Institute of Microelectronics, Peking University, Beijing, China; 3CentraleSupelec, Gif-sur-Yvette, France; 1Sandia National Laboratories, Albuquerque, New Mexico, United States.

Graphene has a unique broadband absorption from visible to microwave due to its gapless nature. Integrating graphene with microcavities, photonic crystal or surface plasmonic structures can not only increase the strength of light-matter interaction, but also achieve some degree of spectral selectivity for enhanced light absorption around the designed wavelengths. However, the above-mentioned spectral selectivity results from some forms of resonance structures; therefore once the device is fabricated, the spectral response is fixed at the resonance wavelength for such devices. In our work, we demonstrate an electrically tunable, spectrally distinguishable photoresponse in a graphene-based phototransistor. The device is composed of a 6-nm amorphous silicon tunneling barrier sandwiched by two layers of graphene, one used as the channel and the other as the gate. By applying a sweeping voltage on the graphene gate layer while recording channel layer current, we discover gate-dependent photoresponse curves for different excitation wavelengths. Importantly, this electrical tuning of photoresponse offers a new mechanism for spectrally resolved photodetection with graphene detectors. As a proof-of-concept, we build a responsivity matrix of gate voltage and excitation wavelength by measuring the gate-dependent photoresponse curves for a finite number of wavelengths. Photodetection and spectral reconstruction for mono-color lights were then successfully demonstrated. More detail will be presented at the conference. Our results open the door for on-chip spectrometers free from complex optical setups and may find its applications in technologies such as hyperspectral imaging.

2:45 PM NM01.13.05

Aligned Carbon Nanotube Sheets Integrated in Liquid Crystal Device Cells M. A. Rahman1, Hakam Agha1, Meenu Murali1, Ji Hyun Park1, Kieu Truong2, Dongseok Suh2 and Glusy Scalia1; 1University of Luxembourg, Luxembourg, Luxembourg; 2Sungkyunkwan University, Suwon, Korea (the Republic of).

Sheets of unidirectionally oriented carbon nanotubes (CNTs) [1-2], among the various attractive applications, can be employed as transparent and conductive layer for switching but also, interestingly, for aligning liquid crystals (LCs) [3]. Even a single layer, tens of nanometers thick, can be used for applying electric fields strong enough to reorient LC molecules and, at the same time, for serving as an alignment layer for LCs. The successful implementation of new materials in LC cell geometries is a pre-requisite for future applications in device technology. CNT sheets as aligning electrodes are a relatively new entry that are showing very good performances for LC switching but also, present challenges to face. CNT sheets do not completely adhere to the substrate surface and methods to promote the adhesion, such as chemical treatment of the surfaces or polymer coatings, are needed. As it will be presented, the adhesion of CNTs on different types of underlying polymer films is indeed improved by ethanol treatment but the orientational order parameter of CNT sheets is affected at different extends [4]. The evaluation of the CNT sheet characteristics such as the degree of orientational order of the strands, the film thickness and its uniformity in properties like the electrical conductivity are of importance for the LC passive and active behavior. However, there are other characteristics that we will discuss here, that influence the LC behaviour, connected to the peculiar nature of the CNT sheets being formed by discrete elements, the nanotubes, even if connected in anisotropic networks. To understand the different aspects we investigate the CNT sheets using different techniques. For evaluating the morphology and the uniformity in properties we use electron and atomic force microscopy, profilometry and optical absorption. The electrical characteristics are investigated with and without LCs using DC as well as AC electric fields while monitoring the samples under a polarized optical microscope.

References:
Energy Transport in Polymer-Free Semiconducting Single-Walled Carbon Nanotube Networks

Here we demonstrate an approach aimed at replacing the strongly-bound polymers with variants that can be removed using simple solution-based chemical strategies, resulting in networks with vastly improved energy transport properties. We show that removal of the polymer results in a significant enhancement of the charge carrier mobility and electrical conductivity. Finally, we extend the approach to samples strongly enriched in a single chiral SWCNT species, which allows us to employ transient spectroscopic techniques to probe energy transfer and exciton transport through the SWCNT network with high spectral fidelity. We show that the efficiency of exciton transport is subtly dependent on the complex interplay between polymer removal and carbon nanotube bundling. Our studies highlight a methodology by which high-performance SWCNT thin films can be prepared that could realize their potential for electronic and optoelectronic applications.

References


Atomistic Modeling of Nanostructured Printed Graphene Coating Srilok Srinivasan1, Ganesh Balasubramanian2 and Suprem Das3; 1Department of Mechanical Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; 2Department of Materials Engineering and Mechanics, Lehigh University, Bethlehem, Pennsylvania, United States; 3Department of Industrial and Manufacturing Systems Engineering, Kansas State University, Manhattan, Kansas, United States.

Functional coatings have numerous properties, including anticorrosion, anti-icing, and self-cleaning leading to number of applications in future electronics, sensing, and energy. Although graphene has shown extraordinary properties that are demonstrated in past decade, scalable manufacturing and control of graphene’s structure could potentially transform the coating technology. Key to its function is the ability to tune local structure and understand its surface

3:00 PM BREAK

SESSION NM01.14: Structure and Properties V
Session Chairs: Ranjit Pali and Yoke Khin Yap
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Republic AB

Electron Microscopy Studies on Single-Walled Carbon Nanotubes Hua Jiang1, Ying Tian1,2, Yongping Liao1, Qiang Zhang1, Nan Wei1 and Esko Kauppinen1; 1Department of Applied Physics, Aalto University School of Science, Espoo, Finland; 2Physics Department, Dalian Maritime University, Dalian, China.

With the aid of advanced electron microscopy, we have established an approach using ED as a means to evaluate the validity of Raman spectroscopy for quantification of concentrations of metallic SWNTs (M%) or of semi-conducting tubes (S-SWNT%) [1]. We have proved that the Raman RBM intensities depend largely on the resonant conditions at certain wavelengths, rather than simply on concentrations. Up to the resonance conditions, some majority nanotube species revealed by electron diffraction measurements induce relatively weak, or even missing RBMs, and vice versa. This certainly leads to an uncertainty over Raman spectroscopy for quantitative assessment of metallic tube concentrations calculating from the relative peak intensities.

Chirality distribution maps of SWNTs produced by CVD methods with Fe nanoparticles as catalysts at various synthesis conditions have been analyzed by electron diffraction technique. As a recent advance [2], we have successfully achieved direct synthesis of single-walled carbon nanotube thin films with various colors using a novel floating-catalyst-CVD process with ferrocene-based iron catalyst particles and CO as the carbon source. The color is tunable by adjusting the reactor conditions, i.e. the temperature and especially the addition of CO2. Based on unique electron diffraction analysis of individual SWCNTs in our colorful SWCNT thin films, we were able to attribute the colors of the SWCNT thin films to their narrow diameter in certain ranges which give rise to absorption peaks in the visible region. It is demonstrated that the narrow (n, m) chirality distribution also accounts for the display of certain color of a SWCNT thin film.

References


Energy Transport in Polymer-Free Semiconducting Single-Walled Carbon Nanotube Networks Andrew J. Ferguson and Jeffrey Blackburn; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

The chemical structure of semiconducting single-walled carbon nanotubes (SWCNTs) results in optical and electronic properties of promise for a wide variety of applications. Until quite recently the presence of metallic SWCNT impurities has hampered efforts to gain a deeper understanding of their true potential, with the additional complication that most commercially available materials contain tens of different chiral species. Significant effort has been devoted to elegant enrichment strategies aimed at extracting tailored semiconducting SWCNT species from the raw soot, from the use of subtly tunable surfactant interactions to the exploitation of specific DNA sequences. However, conjugated polymers, typically based on the fluorene moiety, appear to show the greatest promise with regards to their high selectivity and viability for scalable manufacturing approaches.

Unfortunately, the van de Waals forces between the pi-electron systems of the polymer and SWCNT that enable the selective extraction of semiconducting SWCNTs with high purity also make removal of the polymer difficult. Since these polymers typically have a wide bandgap they act as an insulating coating on the surface of the individual SWCNTs within polymer networks, inhibiting the transport of energy in the form of excitons and/or charge carriers.

Here we demonstrate an approach aimed at replacing the strongly-bound polymers with variants that can be removed using simple solution-based chemical strategies, resulting in networks with vastly improved energy transport properties. We show that removal of the polymer results in a significant enhancement of the charge carrier mobility and electrical conductivity. Finally, we extend the approach to samples strongly enriched in a single chiral SWCNT species, which allows us to employ transient spectroscopic techniques to probe energy transfer and exciton transport through the SWCNT network with high spectral fidelity. We show that the efficiency of exciton transport is subtly dependent on the complex interplay between polymer removal and carbon nanotube bundling. Our studies highlight a methodology by which high-performance SWCNT thin films can be prepared that could realize their potential for electronic and optoelectronic applications.

4:15 PM NM01.14.03

Atomistic Modeling of Nanostructured Printed Graphene Coating Srilok Srinivasan1, Ganesh Balasubramanian2 and Suprem Das3; 1Department of Mechanical Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; 2Department of Mechanical Engineering and Mechanics, Lehigh University, Bethlehem, Pennsylvania, United States; 3Department of Industrial and Manufacturing Systems Engineering, Kansas State University, Manhattan, Kansas, United States.

Functional coatings have numerous properties, including anticorrosion, anti-icing, and self-cleaning leading to number of applications in future electronics, sensing, and energy. Although graphene has shown extraordinary properties that are demonstrated in past decade, scalable manufacturing and control of graphene’s structure could potentially transform the coating technology. Key to its function is the ability to tune local structure and understand its surface
energy evolution. Direct pulsed laser writing (DPLW) has been shown recently an efficient technique to surface nanostructure graphene coating to tune the contact angle of graphene from hydrophilic to superhydrophobic, leading to manufacturing of multifunctional graphene surface. In this work, using molecular dynamic (MD) simulations we show that the physical orientation of graphene flakes as well as its surface chemistry in a coating influence its wettability. We show that using DPLW the contact angle of graphene coating can be tuned significantly, starting from a hydrophilic (contact angle (CA) ~47.7°) to superhydrophobic (CA ~157.2°) nature. Since the cohesive interactions between water molecules remain invariant for degree of graphene orientation on a surface, the wettability of the surface is driven by the net attractive energies ($U_{h2o,c}$) between water molecule and carbon atoms in graphene due to the adhesive forces that changes with the petal orientation. Furthermore, the dangling bonds on the edges of the graphene ‘petal-like’ structures affect the wettability of the sample. Molecular dynamics (MD) simulations show that the –H termination induces hydrophobicity due to hydrogen repulsion whereas –CO termination makes the substrate hydrophilic due to the polar nature of the bonds. Additionally, we model the evaporation process of water droplets on these coatings that show delays in the water evaporation. Non-equilibrium molecular dynamics (NEMD) simulations reveal that the changes in Kapitza resistance and contact area with increasing contact angle results in a slower evaporation rates in the case of superhydrophobic graphene surface.

4:30 PM NM01.14.04
Probing on the Molecular Bonding of DMSO-DiI-MWCNT—A Route to Biological MWCNT Surface Modification Examined Through Synchrotron Spectroscopies—Theory and Experiment Wudmir Y. Rojas¹, Allen D. Winter¹, Torsten Bossing², Daniel Fischer², Sarbajit Banerjee³, David Prendergast⁴ and Eva M. Campo⁵; ¹Bangor University, Bangor, United Kingdom; ²Institute of Translational & Stratified Medicine, Plymouth, United Kingdom; ³National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ⁴Department of Chemistry, Texas A&M University, College Station, Texas, United States; ⁵Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ⁶National Science Foundation—Division of Materials Research, Alexandria, Virginia, United States.

Supramolecular chemistry of carbon nanotubes (CNTs) investigates the non-covalent functionalization of CNTs to preserve their pristine physical properties typically by p-pstacking with aromatic compounds, dispersion of CNTs with surfactants and polymer wrapping surrounding the CNTs for applications such as identification coating for biological sensing based on fluorescence and the use of CNTs for drug delivery. In this context, feasibility to use polymeric spacers as dispersant agents to reduce intratubular van der Walls forces requires adequate comprehension of nature and dynamics of the CNT-polymer interaction that will pave the way to inform on pharmacological carrier ability and biocompatibility linked with specific CNTs functionalization procedures.

In this work, a physico-chemical description of non-covalently functionalized multi wall carbon nanotube (MWCNT) with DiI and dimethyl sulfoxide through high-resolution electron microscopy, Raman and Near Edge X Ray Absorption Fine Structure (NEXAFS) spectroscopy has been employed. NEXAFS is a synchrotron tool capable to reveal molecular sensitivity description at interfaces, therefore, suitable to study non-covalent interactions. Furthermore, combination of experimental and constrained density functional theory simulations of NEXAFS spectra to propose a molecular model to analyze charge exchange at CNTs-dispersants (or loaded biomolecules) interfaces has been also applied.

Our findings suggest that incorporation of fluorescent markers does not change the morphological structure on MWCNTs. CH-p bonding with nearby molecules and Hydrogen bonding with external defects and graphitic lattice has been identified as well. Theoretical modelling suggests non-covalent interaction between dimethyl sulfoxide and CNTs.

4:45 PM NM01.14.05
Microfluidic Pathways Made from Alumina Nanotubes within Hydrophobic Carbon Nanotube (CNT) Barriers Cemile Aksu; North Carolina State University, Raleigh, North Carolina, United States.

An understanding of fluid transport within porous micro-and nanostructured materials is important for their use in microfluidic devices. In this paper we investigate the microfluidic behavior of alumina nanotube-based pathways within hydrophobic CNT barriers. These hybrid systems provide unique benefits toward the potential liquid transport control in porous structures with real-time sensing of those fluids. Specifically, we examine how the alignment of the alumina nanostructures with high internal porosity enables increasing the capillary action. Based on the Lucas and Washburn model (LW) and modified LW models, the microfluidic behavior of these systems is discussed. The predictions from the models for the time exponent for capillary transport in porous media are ≤ 0.5. The experimental results show that the average capillary rise in nanostructured media driven by capillary force followed the L(t)$^0.7$ law. Integration of electronic and microfluidic functions is also presented, taking advantage of the periodic hydrophobic/electrically insulating (pure alumina part) and hydrophobic/electrically conductive (CNT part) microlayers of the structure.
characterization of a hybrid aerogel based on reduced rGO decorated with silver nanoparticles (AgNPs) exploitable for the SERS detection of biomolecules at low concentration. Several synthesis conditions were approached by exploiting a one-pot hydrothermal process, starting from commercial GO and adding either AgNO₃ as silver precursor with different additives (such as trisodium citrate) or directly a pre-synthesized Ag colloid. The resulting 3-D porous sponge-like nanoarchitecture provides both a high surface area and a homogeneous spatial distribution of AgNPs arranged in order to maximize the Raman hot spots density and thus allowing to concentrate and adsorb biomolecules from highly diluted solutions. By decorating GO with AgNPs, the synergy of the EM field and CT enhancements can be exploited. The synthesized AgNPs/rGO aerogels were characterized by means of ARD, BET, XPS, FESEM, and TEM in order to single out the best performing aerogels to be processed for biosensing applications. Promising results were obtained in terms of SERS efficiency by using, as probe molecules, Rhodamine 6G in the 10⁻⁶ M - 10⁻⁵ M concentrations range, and 4-Mercaptobenzonic acid, in the 10⁻⁶ M - 10⁻⁵ M concentration range. Optofluidic chip were fabricated by coupling the optimized AgNPs/rGO aerogels to Polydimethylsiloxane (PDMS). Then the devices have been successfully functionalized both by thiol-ended oligos and porphyrin-ended biomolecules. These bioreceptor immobilization routes permit the application of the substrates as versatile SERS biorecognition bioships.

NM01.15.02
Functionaized Nano-Graphene Oxide as Multi-Modal Clinic for Effective Drug Delivery Manisha Chatterjee¹, Somensh Mahapatra² and Soumitra Satapathi²; ¹Lala Lajpat Rai Memorial Medical College, Meerut, India; ²Indian Institute of Technology Roorkee, Roorkee, India.

Nano-materials based drug delivery modalities to specific organs and tissue have become one of the critical endeavors in pharmaceutical research. Recently, two dimensional graphene has elicited considerable research interest because of its potential application in drug delivery systems. Here we report, the drug delivery applications of PEGylated nano-graphene oxide (nGO-PEG), complexed with a multiphoton active and anti-cancerous diarylheptanoid drug curcumin. Specifically, graphene derivatives were used as nano vectors for the delivery of the hydrophobic anticancer drug curcumin due to its high surface area and easy surface functionalization. nGO was synthesized by modified Hummer’s method and confirmed by XRD analysis. The formation of nGO, nGO-PEG and nGO-PEG-Curcumin complex were monitored through UVvis, IR spectroscopy. MTT assay and AO/EB staining found that nGO-PEG-Curcumin complex afforded highly potent cancer cell killing in vitro with a human breast cancer line mCF7.

NM01.15.03
Stable, Temperature Dependent Gas Mixture Permeation and Separation Through Suspended Nanoporous Single-Layer Graphene Membranes Zhe Yuan, Jesse D. Benck, Yannick Eatmon, Daniel Blankschtein and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Graphene membranes with nanometer-scale pores could exhibit extremely high permeance and selectivity for the separation of gas mixtures. However, to date, no experimental measurements of gas mixture separation through nanoporous single-layer graphene (SLG) membranes have been reported. Herein, we report the first measurements of the temperature-dependent permeance of gas mixtures in an equimolar mixture feed containing H₂, He, CH₄, CO₂, and SF₆ from 22 to 208 °C through SLG membranes containing nanopores formed spontaneously during graphene synthesis. Five membranes were fabricated by transfer of CVD graphene from catalytic Cu film onto channels framed in impermeable Ni. Two membranes exhibited gas permeances on the order of 10⁴ to 10⁵ mol m⁻² s⁻¹ Pa⁻¹, as well as gas mixture selectivities higher than the Knudsen effusion selectivities predicted by the gas effusion mechanism. We show that a new steric selectivity mechanism explains the permeance data and selectivities. This mechanism predicts a mean pore diameter of 3.0 nm and an areal pore density of 5.5×10¹³ m⁻², which is validated by experimental observations. A third membrane exhibited selectivities lower than the Knudsen effusion selectivities, suggesting a combination of effusion and viscous flow. A fourth membrane exhibited increasing permeance values as functions of temperature from 27 to 200 °C, and a CO₂/SF₆ selectivity of > 20 at 200 °C, suggestive of activated translocation through molecular-sized nanopores. A fifth membrane exhibited no measurable permeance of any gas above the detection limit of our technique, 2×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, indicating essentially a molecularly impermeable barrier. Overall, these data demonstrate that SLG membranes can potentially provide high mixture separation selectivity for gases, with CVD synthesis alone resulting in nanometer-scale pores useful for gas separation. This work also shows that temperature-dependent permeance measurements on SLG can be used to reveal underlying permeation mechanisms.

NM01.15.04
Encapsulation of Metallic Nanoparticles Near the Surface of Graphite Ann Li-Riosales and Patricia A. Thiel; Iowa State University and Ames Laboratory, Ames, Iowa, United States.

Graphite, in the bulk, is known to form graphite intercalation compounds (GICs) with certain elemental metals, for example, rare earth and alkali metals. These metals can insert between graphene sheets and alter the magnetic or transport properties of graphite. While intercalation in the bulk of graphite has received much attention, considerably less has been paid to intercalation near the surface of graphite, underneath only one (or a few) graphene layers. First of all, can one embed metals just beneath the graphite surface? Do the surface-intercalated metals adopt different structures compared to their bulk counterparts? What is the driving force for such surface intercalation? These are questions we seek to address.

The presentation will encompass strategies for achieving surface intercalation of metals in graphite. In short, embedding metal atoms just beneath the graphite surface requires two specific conditions: (1) ion-induced defects on the graphite surface, and (2) deposition of metals while holding the graphite substrate at elevated temperature. We find that this synthetic route works for a variety of metals, and the growth temperature is metal-specific. Results on dysprosium, copper and ruthenium will be presented. We use scanning tunneling microscopy to probe and characterize the surface intercalation. Based on experimental results and density functional theory, we find that the intercalated metal atoms at the graphite surface adopt very different structures compared to those in bulk GICs. Furthermore, metals that are not known to form bulk GICs can be encapsulated at the graphite surface. Finally, we find that some of the metals are well protected from atmospheric oxidation by the graphene overlayer. Our synthetic strategy opens up a new avenue for metals to interact with the graphite surface, and to create novel graphene-based nanomaterials.

NM01.15.05
Highly Conductive Copper Coated Reduced Graphene Oxide Fibers for Electromagnetic Shielding Fabrics Mingxin Li and Jie Lian; Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Despite no apparent evidence that the electromagnetic exposure to household mobile communication and other emitting devices poses harm to the general public, excessive electromagnetic radiation is of genuine concern for roentgenologists, radar engineers and pacemaker implanted patients. To alleviate such a concern, electromagnetic shielding clothing for these personnel made with thin steel wires are densely woven into cotton fibers. Here, we report a new method of producing copper-reduced graphene oxide core-shell fibers for the fabrication of lightweight electromagnetic shielding fabrics. Based on a simple electroplating process, a thin layer of copper oxide is coated onto the grooved surface of reduced graphene oxide fibers. After subsequent reduction, copper-coated reduced graphene oxide fibers with high electrical conductivity and high flexibility are obtained. A fabric woven with such fibers can provide comparable electromagnetic shielding to fabrics woven with metal wires, yet is appreciably lower in density.
The liquid phase exfoliated graphene nanoflakes are a high-yield and low-cost synthetic method, but the quality of the graphene nanoflakes is not high due to the presence of functional groups and structural defects. Therefore, the ability to improve the crystal structure of the graphene nanoflakes with excellent electrical properties is desirable for its applications in the field of flexible and printed electronics.[1]

In this talk, I will introduce an approach to structure repairing in electrochemically-exfoliated graphene flakes based on annealing with Ni thin film, accompanied by the laterally stitching of the isolated parts to form a continuous and monolithic film.[2,3] After annealing with Ni film, the graphene flakes-derived film has lower defect density, demonstrating that such a process for the crystal structure improvement is extremely effective. At the same time, the newborn-graphene in the space of the isolated flakes would stitch to form a continuous and monolithic film. After the structural repair, the electrical properties of graphene have been greatly improved, and the carrier mobility of graphene is more than 1000 cm² V⁻¹ S⁻¹, nearly 10 times higher than that of the process with Cu or 100 times higher than that of graphene via mere annealing. First-principles calculations on the adsorption of Ni and C atoms on different kinds of H-saturated graphene edges reveal that the binding energy depends upon the adsorption site, and the Ni case always gives a value 1.5 eV larger than that for the Cu case which is thus beneficial to the removing of edge saturates and allowing for a faster re-growth process. This approach for the graphene with structural design is promising for electronic and flexible applications. [4]

(Thanks to the support of the JSPS KAKENHI Grant Number JP 17F17337.)

References

NM01.15.06 High-Quality Monolithic Graphene Films via Solid-Phase Coalescence and Structural Repair of Exfoliated Flakes Xinning Li1,2, Cheng-Te Lin2, Ying Fang3, Renzhi Ma4 and Takayoshi Sasaki3; 1International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan; 2Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China; 3National Center for Nanoscience and Technology, Beijing, China.

Since its discovery in 2004, graphene has received enormous scientific interest due to the remarkable two-dimensional structure, making it highly promising for numerous applications. Electrodes in lithium-ion-batteries (LIBs) are one of these applications that could benefit from mechanical strength, high surface area and electrical conductivity of graphene. For the integration in commercial LIBs, it is important to develop simple, cost effective and scalable methods for the production of graphene-like structures. Due to the good dispersibility in water and other polar solvents, graphene oxide (GO) easily forms multi- and monolayers and therefore offers advantageous properties for a green and simple wet-chemical synthesis.

In this study, GO was synthesized and further processed by liquid and gas phase approaches to obtain GO films via pressure filtration with superior mechanical properties and adjustable thicknesses. These paper-like structures of regularly arranged GO flakes were mechanically stable, scalable to mass production and could be used as flexible ultrathin separators in LIBs given their high electronic insulation. Additionally, the sheet-like structure of GO is expected to suppress the polysulfide shuttle effect in lithium sulfide batteries. Moreover, films of its reduced form (rGO) could additionally be incorporated as cathode or anode material, providing several advantages over traditionally used materials. For instance, if used as anodes, these films facilitated an increased volumetric energy density due to a reduction in weight, as additional battery paste components such as current collector, carbon black and binding agent, were no longer necessary. This was supported by the low preparative effort of the freestanding electrode design. Moreover, nitrogen doping of these graphene-like structures via different approaches has been proven successful to increase the electrical conductivity and storage capacity of anodes. Further investigations focused on the influence of nitrogen-integration in the carbon structure on electrical and electrochemical properties. In terms of the electrical properties of graphene have been greatly improved, and the carrier mobility of graphene is more than 1000 cm² V⁻¹ S⁻¹, nearly 10 times higher than that of the process with Cu or 100 times higher than that of graphene via mere annealing. First-principles calculations on the adsorption of Ni and C atoms on different kinds of H-saturated graphene edges reveal that the binding energy depends upon the adsorption site, and the Ni case always gives a value 1.5 eV larger than that for the Cu case which is thus beneficial to the removing of edge saturates and allowing for a faster re-growth process. This approach for the graphene with structural design is promising for electronic and flexible applications. [4]
cathodes, rGO films served as a highly conductive backbone for lithium sulfide/rGO-composites, in which the active material was well-distributed within the carbon matrix. This prevents the agglomeration of lithium sulfide, buffers the volume change during cycling and offers a good accessibility for charge carriers. In this work, the integration of GO and rGO films into LIB half-cells thus demonstrated their exceptional versatility and high application potential.

NM01.15.10

Investigating the Frictional Behavior of Copper-Graphene-Copper Laminates Shruti Rastogi, Amirali Zangibadi, Katayun Barmak and Jeffrey W. Kysar; Columbia University, New York, New York, United States.

Reducing energy and material losses in moving mechanical systems due to friction and wear still remain a significant challenge. A monatomically thin layer of graphene deposited onto a surface is known to reduce friction significantly, but graphene is a brittle material so its wear properties are limited. This study investigates the friction and wear of a lamellar metal-graphene-metal composite. We demonstrate a transfer-free material design comprising of monolayer CVD graphene sandwiched between a Cu substrate and a thin Cu film deposited via physical vapor deposition (Cu-Gr-Cu). A series of scratch tests performed on the free surface of the Cu film shows a considerable decrease in coefficient of friction from 0.4 to ~0.12 and an improved wear resistance for the Cu-Gr-Cu laminate. The reduction in coefficient of friction is proposed to be associated with a lower degree of plastic deformation in the Cu-Gr-Cu laminate suggestive of graphene’s ability to impede the propagation of the plastic zone from the copper film to the underlying copper substrate. Weak Beam Dark field Imaging technique (in TEM) confirm lower density of dislocations present in Cu-Gr-Cu laminate when compared to the Cu-Cu laminate thus indicating the effectiveness of graphene in blocking the propagation of the plastic zone.

NM01.15.11


The mechanical properties of graphene oxide/poly(lactic acid) (GO/PLA) composites were studied to analyze the effect of GO sheet addition on PLA. GO was synthesized through chemical exfoliation and characterized by using FTIR, Raman spectroscopy and SEM. GO/PLA filaments with various compositions were formed using extruder and the mechanical test specimens were prepared from these filaments by two different methods: injection molding and 3D printing. The mechanical properties of polymer/GO composites which were formed through different techniques and with different compositions were compared.

NM01.15.12

Graphene Production by Mechanical Milling Testing Different Solvents Sergio E. Mancillas and Eddie Lopez Honorato; CINVESTAV Unidad Saltillo, Ramos Arizpe, Mexico.

One of the main challenges in the exploitation of nanomaterials is their production in large volumes. One possibility in the production of graphene is the use of attrition. This work presents the effect of different solvents on the production of graphene by mechanical milling of graphite flakes. Methanol, ethanol, acetone, hexane, toluene and xylene were used in the milling process without the use of any other additive. Our results indicate that the solvent used is important in the particle size distribution, the final microstructure and the graphene produced. The solvent used was also important during ultrasound separation as it affected the number of graphene layers obtained.

NM01.15.13

Electrical Properties of N-Doped Graphene Cu(In,Ga)Se2 Schottky Junctions Jesse Claypoole and Harry Efthathiadis; SUNY Polytechnic Institute, Albany, New York, United States.

While doping graphene P type is relatively easy, the typical methods of N doping graphene including electrostatic or chemical methods do not achieve high or persistent N doping of graphene when exposed to air. Diffusion of alkali from a semiconductor onto graphene offers a scalable and low cost way of tunably doping graphene N type and has the potential to improve the electrical properties a large range of devices including solar cells, photodetectors, and supercapacitors. The amount and type of alkali diffused from the semiconductor can be varied which can then tune the Fermi level of graphene which alters the graphene semiconductor junction's electrical properties. In this study, we investigate the effect of the diffusion of alkali from the semiconductor Cu(In,Ga)Se2 onto graphene on the electrical properties of a graphene Cu(In,Ga)Se2 schottky junction.

NM01.15.14

Computing Modeling of the Graphene-Water Interaction and Its Applications Jatin Kashyap1, Priyanka Solanki2 and Dibakar Datta1; ‘New Jersey Institute of Technology, Newark, New Jersey, United States; 2Montville Township High School, Montville, New Jersey, United States.

Ever since its discovery in 2004, graphene has been extensively investigated for various applications such as energy storage, environmental barrier, biomedical, electronics, etc. The planar graphene sheet is hydrophobic. However, with the change in topology, i.e., defects, wrinkling, etc., we can tune its interaction with water. By performing Molecular Dynamics (MD) simulation, we discovered that water microdroplets containing graphene nanosheet spontaneously segregate into sack-cargo nanostructures upon drying. These cargo-filled nanosacks are promising for many potential applications where nanoscale materials should be isolated from the environment or biological tissue. Besides this, we considered another situation where water diffuses in between graphene and the underlying substrate during its growth process. The diffused water tends to occupy the empty space of the pre-existing wrinkling of small height and keeps pushing the wrinkling to make it bigger. Upon drying, the wrinkling becomes sharper. Our results show that we can tune the density of diffused water and the magnitude of the initial wrinkles to obtain various wrinkled structures after graphene growth. Our simulation results provide guidelines for the experimentalists for efficient design of the graphene-water systems.

NM01.15.15

Energetic Stability and Electronic Properties of Graphene Bilayer over GaN Maria G. Moreno-Armenta1 and Jairo A. Rodriguez-Martinez2; ‘CNyN, Univ Nacional Autonoma de Mexico, Ensenada, Mexico; 2Fisica, Universidad Nacional de Colombia, Bogota, Colombia.

In previous work1 we have calculated the growth of a graphene monolayer, two models emerged as the most favored: for Ga poor conditions a 3sqg3x3sqg3 graphene structure on top of a 4x4(0001) GaN surface and for Ga rich condition a sqg21xsqg21 graphene structure on top of a 2sqg3x2sqg3 GaN(0001). Gallium double bilayer2 with a -1.10% and -0.72% mismatch respectively. The gallium rich model exhibit a magnetic moment of 0.19 Bohr magnetons/cell whereas the stable structure for Ga poor conditions does not presents magnetic behavior. Later we added a second graphene layer with the goal to find defects free epitaxial growth, which could serve as a basis to introduce defects or doping it with the best suited elements in such a way that we will be able
to fine tuning a band gap. We also made simulations of scanning tunneling microscope (STM) that revealed a long distance buckling interaction between both layers. Our calculations were based on the plane wave density functional theory and the Born-Hamann formalism for simulating STM images. In this work we are analyzing what is happening when a graphene monolayer approach to the GaN surface and then when a second graphene layer comes closer to the first one, we plot the energy as a function of the interlayer separation distance and the kind of GaN surface. In this fashion we get potential energy surfaces (PES), which allow us to simulate how the graphene monolayer behaves when it is growth in a less than ideal substrate and what happens to the graphene buckling in the grain frontier. The electronic properties of these systems are studied by calculating the band structure and the density of states. The calculations are performed by Density Functional Theory as implemented in the PWscf code of the Quantum ESPRESSO package. The data are not fully analyzed yet as the work is still in progress. Acknowledgments: DGAPA project IN114817. The authors are grateful to A. Rodríguez for his technical assistance. Calculations were performed at the DGCTIC-UNAM under project LANCAD-UNAM-DGTIC-150.

References

NM01.15.16
Continuous Langmuir-Blodgett Deposition and Transfer by Controlled Edge-to-Edge Aggregation of Floating 1D and 2D Nanomaterials Luzhu Xu, Hadi K. Khaligh, Adam Tetreault, Irene Goldthorpe, Shawn Wettig and Michael A. Pope, University of Waterloo, Waterloo, Ontario, Canada.

The Langmuir-Blodgett technique is one of the most controlled methods to deposit monomolecular layers of floating or surface active materials but has lacked the ability to coat truly large area substrates. In our work, by manipulating single layer dispersions of graphene oxide (GO) and other 1D or 2D materials (ex. molybdenum disulfide, reduced graphene oxide, CNTs etc.) into water-immiscible spreading solvents, unlike traditional Langmuir-Blodgett deposition which requires densification achieved by compressing barriers, we demonstrate the ability to control the 2D aggregation and densification behavior of these floating materials without the use of moveable barriers. This is done by controlling the edge-to-edge interactions through modified sub-phase conditions and by utilizing the distance-dependent spreading pressure of the deposition solvent. These phenomena allow substrates to be coated by continuous deposition and substrate withdrawal - enabling roll-to-roll deposition and patterning of large area substrates such as flexible polyethylene terephthalate. The aggregation of GO sheets into 2D domains under various sub-phase conditions were examined by in situ Brewster angle video microscopy. Moreover, by measuring the local spreading pressure using a Langmuir-Adam balance we conclude that the densification phenomenon of deposited sheets is induced by the spreading solvent acting on the floating materials. This allows us to engineer the film density by easily changing the spreading solvent. As an example, the performance of films deposited in this way are assessed as passivation layers for Ag nanowire-based transparent conductors.

NM01.15.17
Gas-Phase Synthesis of Substrate-Free Graphene—A Comparison of Different Hydrocarbon Precursors Adrian D. Munoz,1 Hartmut Wiggers2 and Christof Schulz2;1 Institute for Combustion and Gas Dynamics - Reactive Fluids, University of Duisburg-Essen, Duisburg, Germany; 2CENIDE, University of Duisburg-Essen, Duisburg, Germany.

Graphene is regarded as a potential material for many application fields due to its unique electrical, mechanical, and thermal properties. Since its first isolation in 2004, growing interest has evolved in the development of facile and scalable synthesis routes. So far, some groups already investigated synthesis techniques towards environmentally-friendly and catalyst-free graphene production from methane or ethanol based on plasma technology, however, the variation carbon precursors is only rudimentarily investigated so far.

In this paper, we present a facile synthesis method for preparing free-standing few-layer-graphene (FLG) by gas-phase pyrolysis carried out in a microwave plasma reactor. This scalable synthesis route can produce highly pure carbonaceous nanostructures with production rates up to several g/h, depending on the precursor used. However, it is still unclear which precursor requirements have to be fulfilled for the formation of high-purity graphene avoiding the formation of byproducts.

Five gaseous and eleven liquid hydrocarbons have been tested in order to identify prerequisites for graphene formation. The materials have also been processed to investigate the growth process and the microstructure of the respective products. The samples have been characterized by X-ray diffraction, Raman-, four-point conductivity measurements, XPS, TEM and BET. The results indicate that the gas-phase generated samples show either FLG, or graphitic particles or soot-like particles or composites containing two or all of them following no straight dependency. However, it was observed that only precursors with certain C:H:O-ratios like ethanol, acetone and isopropanol can deliver graphene in a good quality while oxygen-free precursors with a relatively high C:H-ratio like toluene and acetylene lead primarily to soot-like particles.

All other used precursors with different or same C:H-O- and C:H-ratios tend to produce composites containing besides graphitic particles, FLG and soot-like particles at the same time. The best samples made from ethanol show highly pure surfaces and highly ordered FLG with superior electrical conductivity of more than 4000 S/m.

NM01.15.18
Liquid Phase Exfoliation of Nanoscale Organic/WS2 Heterojunctions for Organic Electronics Abdus S. Sarkar1,2,3 and Suman K. Pal1,2,3;1 School of Basic Sciences, Indian Institute of Technology, Mandi, India; 2Advanced Materials Research Center, Indian Institute of Technology Mandi, Mandi, India; 3Energy Center, Indian Institute of Technology Mandi, Mandi, India.

Since, the discovery of single layer graphene in 2004, great attention has been paid to other two dimensional (2D) layered materials from the academic to industrial research. Recently, beyond graphene, the emerging 2D transition metal dichalcogenides (TMDs), such as semiconducting (2H-phase) tungsten sulfide (WS2) have drawn most vibrant areas of nanoscience research because of direct energy gap and fascinating optical and electrical properties in their low dimensional structure. However, most of the preparation (chemical) methods do not preserve the semiconductive properties of WS2. Here, we have prepared a novel two-dimensional semiconductor heterojunction of few layer WS2, which is exfoliated in the presence of an organic semiconductor (OS) in a chloroform solvent and characterized by various experimental techniques. Our AFM, SEM, TEM and Raman spectroscopy results suggested that the few hundred nanometer size, few layer (4-5 layers) thick WS2 sheets were exfoliated in chloroform solvent and grafted with the OS. Hexagonal pattern in HR-TEM image intimates the presence of 2H-phase WS2. Significant changed in the electrical behavior in the heterojunctions are presented. Insight spectroscopic analysis indicate the possible hybrid optoelectronic applications. Highly dispersed WS2 sheet with prior little aggregation after 180 days.

NM01.15.19
Synthesis of Ramified Porous Graphite Foams with Diverging Microtubes with Enhanced Electrical Properties and Surface Areas Weigu Li, Jianhe Guo and Donglei (Emma) Fan; The University of Texas at Austin, Austin, Texas, United States.

3-D graphene or graphite foams (GFs) have received immense research attention owing to their superior electrical, mechanical, and thermal properties. Extensive applications of such 3-D GFs have been demonstrated in energy, environment, health, and biomedical research. This work presents an innovative
mechanism, the Kirkendall effect, in creating 3-D microporous catalysts with tunable pore sizes for the growth of multilevel porous graphite foams (MPGFs) that offer higher stability, electric conductivity, larger surface area as well as electrocatalytic performance. In addition to conventional GFs. Based on MPGFs, another new type of ramified porous graphite foams (RPGFs) made of strategically created superstructures with covalently-attached diverging microtubes have also been synthesized. Such RPGFs exhibit even higher surface areas than MPGFs, which allows for efficient loading of active pseudocapacitive materials when applied as supercapacitor electrodes. We also integrate the RPGF-based flexible supercapacitors with a nanomotor manipulation system into a portable and self-powered device, which readily compels Au nanomotors to transport along arbitrary trajectories, e.g., tracing letters of “U” and “T”.

NM01.15.20
Gas Selective Permeability of Graphenelyne Membranes
Jesse Paulino, Daiane Damasceno Borges and Douglas S. Galvão; State University of Campinas, Campinas-SP, Brazil.

Biphenylene carbon (BPC), also called graphenelyne, is a hypothetical porous two-dimensional (planar) allotrope carbon [1] that can be obtained from selective dehydrogenation of porous graphene [2]. The BPC molecular geometry consists of an one-atom thickness sheet with regular dodecagonal pores of diameters of 3.2 Å. Its pores resemble typical sieve cavities and/or some kind of zeolites. An open question is if the BPC natural porosity gives a selective permeability property that can lead to promising technological applications, such as gas separation. In this work, we have investigated the permeability and selectivity of natural gases such as CO2, H2, N2, CH4, and CO though BPC membrane. Fully atomistic Molecular Dynamics simulations were performed to predict the gas adsorption and the gas permeability of single components, and separation mechanism of binary gas mixtures. The simulation system is composed of single BPC sheet into contact with a gas reservoir under different thermodynamics conditions (e. g. T, P). We have systematically analyzed the permeability of each gas and the molecular layers on the adsorbed layers after the flux is stabilized. The selectivity is also quantified for CO2/H2 (50:50), CO2/N2(15:85), CO2/CH4 (50:50), and CO2/CO (50:50) mixtures and the mechanism of gas diffusion is also discussed. The BPC porosity can be exploited to pressure tune gas selectivity. Our results show that BPC exhibits high H2 selectivity, ideally for hydrogen purification.


Multiplexed Superbioelectronic Nose Using Olfactory Receptors Conjugated-Graphene Field-Effect Transistor for Mimicking the Human Sense of Smell
So Jung Lee and Oh Seek Kwon; KRIBB, Daejeon, Korea (the Republic of)

Human sensory-mimicking systems, such as electronic brains, tongues, skin, and ears, have been promoted for use in improving social welfare. However, no significant achievements have been made in mimicking the human nose due to the complexity of olfactory sensory neurons. Combinational coding of human olfactory receptors (hORs) is essential for odorant discrimination in mixtures, and the development of hOR-combined multiplexed systems has progressed slowly. Here, we report the first demonstration of an artificial multiplexed superbioelectronic nose (MSB-nose) that mimics the human olfactory sensory system, leading to high-performance odorant discriminatory ability in mixtures. Specifically, portable MSBnoses were constructed using highly uniform graphene micropatterns (GMs) that were conjugated with two different hORs, which were employed as transducers in a liquid-ion gated field-effect transistor (FET). Field-induced signals from the MSB-nose were monitored and provided high sensitivity and selectivity toward target odorants.

Broadband Optical Properties of Self-Assembled 3D Graphene Structures
Krity Agarwal, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota, Minneapolis, Minnesota, United States.

Recent progress in nanoscale self-assembly has led to the realization of 3D nanostructures with unique optoelectronic properties through a surface tension driven self-folding of diverse 2D graphene patterns. The self-assembly of 2D patterned graphene can yield 3D micro/nanoscale polyhedrons such as closed and open cubic structures with free-standing 2D materials (graphene or graphite oxide) acting as faces of the cube. Self-assembly is a versatile technique that can realize 3D graphene cube of dimensions ranging from 100 nm to 200 µm. Here, we present simulation and measurement results to study of the optical properties of nanocubes at their plasmon resonance as well as the off-resonance broadband properties of the micro and nanoscale graphene cubes. At a nanoscale, the uniform plasmon coupling in 3D graphene nanocubes gives rise to hybridized modes with strong enhancement of the incident electric (E)-field. The hybrid modes demonstrate large area hotspots of constant field enhancement with a much slower decay of the field away from the surface, giving rise to a volumetric field that is 2 orders of magnitude stronger than that in 2D ribbons. Moreover, in the absence of plasmon resonance such as in 200 µm sized 3D graphene cubes, the rippled geometry induces a strong absorbance of 2-40% over the entire measured wavelength of 1-10 µm. Fourier transform infrared (FTIR) spectroscopy of the 3D graphene microcubes and Cavcell Multiphysics simulations reveal that the angle of incidence, number of graphene layers, and the ripple geometry can be modified to tune the absorbance in 3D graphene over a wider range than in 2D graphene. Thus, the 3D free-standing graphene cubes offer an opportunity to overcome the weak ~3% broadband absorption in 2D planar graphene. The highly confined volumetric field within the nanocubes and strong tunable absorption in graphene microcubes provide an opportunity for the development of non-contact ultrasensitive 3D plasmonic sensors and devices with a larger active area and higher efficiency.

Geometrical Modification of Hybridized Plasmon Modes in 3D Graphene Nanostructures
Krity Agarwal, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota, Minneapolis, Minnesota, United States.

A surface-tension driven self-folding mechanism has led to the realization of diverse self-assembled 3D architectures from patterned 2D ribbons, such as graphene-based pyramids, tubes, and cubes. The 3D graphene geometries exhibit distinct plasmon hybridization that cannot be excited in 2D graphene ribbons as a result of plasmon coupling over an extra spatial degree of freedom. However, a detailed systemic study of the plasmon coupling in 3D graphene geometries needs to be performed in order to efficiently utilize the hybrid plasmon modes for desired optoelectronic applications. We have investigated the plasmon coupling and found that the coupled plasmonic field enhancement in these 3D geometries is strongly dependent on the 3D shape, number of 3D edges, and surface angle of inclination. The uniform coupling in graphene nanocubes gives rise to large circular areas of constant field enhancement. Moreover, if the edges of the nanocubes are spatially separated by nanometer distances, circular field interference patterns are obtained with alternate rings for constructive and destructive coupling. The circular surface enhancement modes in 3D graphene nanocubes can be leveraged for novel optoelectronic applications. In contrast, the square graphene pyramids undergo a strong point enhancement at the apex of the pyramid arising from the inclined tapering faces meeting at the apex. The strong point enhancement propagates throughout the nanopyramid resulting in a volumetric field that is several orders of magnitude higher than in 2D graphene ribbons. Furthermore, as the number of faces and edges is increased to form pentagonal to octagonal pyramids, the point based enhancement can be transformed to uniform surface enhancement at the base of the pyramids. Thus, allowing geometrical parameters in the nanopyramids to be utilized for designing high-sensitivity plasmonic sensors that can assess low concentration analytes in the
bulk volume of targeted solution or the molecular surface binding properties at higher analyte concentrations. The graphene tube consisting of only 2 edges exists at the openings of the tube, a virtual hot-spot area of extremely high near-field enhancement is created due to radial plasmonic coupling at the small opening of the tube. The completely sealed tube demonstrates a strong hotspot, but, the hotspot covers only 13% of the volume of the tube. However, if the nanotubes are fabricated with small slits, the strongly coupled field exists throughout the tube structure giving rise to strong volumetric field. The volumetric field in nanotubes is especially desirable due to their open-ended geometry that can be leveraged for assessing targets flowing through the 3D tube. The self-assembled 3D graphene structures can be varied geometrically to achieve diverse point, edge, surface, and volumetric enhancement modes for achieving plasmonic devices exhibiting increased sensitivity and efficiency, and a high packing density.

**NM01.15.24**

**Carbon Nanoscrolls Formation from Bi-Layer Graphene Nanoribbons—A Reactive Molecular Dynamics Study**

Jose M. de Sousa, Vitor R. Coluci, Nicola M. Pugno and Douglas S. Galvao; 1State University of Campinas, Campinas-SP, Brazil; 2Instituto Federal do Piauí, Jose Raimundo Nonato, Brazil; 3University of Trento, Trento, Italy.

Carbon nanoscrolls (CNSs) are families of carbon-based nanomaterials, where unlike the closed carbon nanotubes, their geometrical aspect is like graphene layers rolling up into a spiral (papyrus-like) form. They have been extensively (theory and experiments) studied [1,2,3]. Due to its open-end topology, where the diameter can be easily varied make them ideal for applications such as hydrogen storage, actuators, tunable water channel, etc. Most of the theoretical works have considered single layer structures; there are only few works on multi-layered scrolls [4]. In this work we have investigated, through fully atomistic reactive (ReaxFF) molecular dynamics simulations, the dynamics formation and structural stability of scrolled structures formed from bilayer graphene nanoribbons. We have also considered these structures interacting with carbon nanotubes, which has been used as a ‘trigger’ to start the scrolling process [5]. Our results show that stable (up to high temperatures ~1000 K) structures can be obtained. We did not observe the formation of covalent bonds between layers and/or carbon nanotubes for the temperature range investigated.


**NM01.15.25**

**Properties of Bio-Inspired Low-Dimension Carbon Fiber and It’s Applications**

Seongwoo Ryu, 1,2 The University of Suwon, Hwaseong-si, Korea (the Republic of); 2Advanced Material Analysis Center, Hwaseong-si, Korea (the Republic of).

Over the past few decades, the fiber-based industry has achieved great progress in aerospace, military and many other industrial applications that require lightweight materials with high mechanical strength. As the demand for electronic devices has exponentially risen in recent years, the preparation of highly conductive fibers has become an important subject in the fiber industry. Low dimension carbon fibers such as carbon nanotube and graphene fibers may be an important material in advancing next-generation high-tech applications if their intrinsic mechanical, electrical and thermal properties can be maintained. By strategy of dopamine infiltration, oxidative polymerization and pyrolysis, we successfully fabricate low-dimension carbon composite fibers with remaining their intrinsic properties. The approach described herein presents a novel fabrication process that can enhance both the mechanical and electrical properties of low-dimension carbon based fibers.

**NM01.15.26**

**Dielectrophoresis-Based Fabrication of Carbon Nanotube-Based Electronic Devices**

Joevonte Kimbrough, Kenneth Davis, Sam Chance, Brandon Whitaker, John Elike, Roshawn Treadwell, JaTavia Cooper, Kayleb Hartage, Abram Jones, Alandria Henderson, Qunying Yuan and Zhigang Xiao; 1Department of Biological and Environmental Science, Alabama A&M University, Normal, Alabama, United States; 2Department of Electrical Engineering and Computer Science, Alabama A&M University, Normal, Alabama, United States.

We report the dielectrophoresis (DEP)-based deposition and alignment of semiconducting carbon nanotubes and the fabrication of carbon nanotube-based electronic devices. Semiconducting carbon nanotubes, which were dispersed ultrasonically in solutions, were deposited and aligned onto a pair of gold electrodes using the electric-field-directed dielectrophoresis method. The DEP-aligned tubes were further fabricated into carbon nanotube field-transistors (CNTFETs) and CNTFET-based electronic devices such as CNT-based inverters and ring oscillators using the microfabrication techniques. The aligned carbon nanotubes and fabricated devices were imaged using the scanning electron microscope (SEM), and the electrical properties were measured from the fabricated devices using the semiconductor analyzer. The semiconducting CNTs achieved higher yield in the device fabrication, and the fabricated electronic devices demonstrated excellent electrical properties.

**NM01.15.27**

**Multicolumn Gel Chromatography for Scalable Separation of Nanosheets Based on Size and Surface Chemistry**

Dorsa Parviz and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Liquid-phase exfoliation of two-dimensional nanomaterials yields nanosheet dispersions with broad size distribution and varying surface chemistry. This polydispersity in size and surface chemistry of nanosheets becomes less desirable when their properties are to be precisely controlled for different applications. Hence, scalable separation methods are highly demanded to make this class of materials industrially relevant. Here, we use multicolumn gel chromatography to separate nanosheets of graphene family based on their size (later size and thickness) and surface chemistry (density of functional groups or defects). We demonstrate that various parameters such as stabilizer type, pH, and ionic strength of the solvent alter the binding affinity of nanosheets on the gel and tune the elution time of nanosheets of different size and surface chemistry. Single particle tracking analysis was used as a powerful tool for quick and precise evaluation of nanosheets size distribution in bulk. Other spectroscopic techniques such as fluorescence and Raman spectroscopy were applied to investigate the surface of the separated nanosheets.

**NM01.15.28**

**Graphene Oxide Polydispersity**

Harish V. Kumar, Chinthani D. Liyanage and Douglas Adamson; University of Connecticut, Storrs, Connecticut, United States.

Graphene oxide (GO) finds applications in variety of areas including, but not limited to, electronics, energy, biomedicine, and optics. Variations in oxidation of GO and its impact on various applications have not been much investigated even though these variations tend to effect the properties of GO. In order to universally understand this variation in oxidation, we have defined an oxidation dispersity number (OD) for GO samples. We divide a given GO sample in a number of different oxidized parts. The characterization of these differently oxidized GO samples enable us quantifying the OD for a given
batch and can be used to tune the density of oxygen functionalities in a GO sample. This emulsion based method is pH dependent and can also be used to isolate a reduced graphene oxide (rGO) like material with a reduced value of Raman defect density. This rGO like material has the capability of replacing the more expensive and topological defects inducing methods presently available. Further, we investigate the properties of different GO samples on the basis of their OD numbers. This number shows that the dispersity of oxidation in a given sample does have an impact on its properties and thereby performance of corresponding applications.

NM01.15.29 Wax-Enabled Graphene Transfer Wei Sun Leong, Jin-Yong Hong, Haozhe Wang and Jing Kong; Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Charge carriers in freely suspended graphene can travel very fast (mobility ~200 000 cm²/V-s at 5K), but the reported values for large-area CVD graphene transferred on arbitrary substrate is several orders of magnitude lower, which has been attributed to the polycrystalline nature, surrounding medium, polymer residues, and wrinkles in graphene. The latter two factors were engendered by the polymer-assisted graphene transfer process. Here, we report a new wax-enabled graphene transfer technique that concurrently addresses the polymer residues and graphene wrinkles issues. Compared to poly (methyl methacrylate) (PMMA), the chemical structure of wax is much simpler and does not contain carbonyl (C=O) group, which is reactive to electrophiles or nucleophiles. Our density functional theory calculations further indicate that the adsorption energy of wax is 1.56 kcal/mol times lower than PMMA and wax radicals are not stable while PMMA radicals are stable enough to form covalent bonding with graphene. Remarkably, for graphene transferred with wax support layer, we observe not only much lesser polymer residues, but also a substantial wrinkle reduction in graphene surface, compared to that of PMMA, through atomic force microscopy studies. Field-effect transistors fabricated on wax-assisted transferred graphene shows the Dirac voltage is closer to zero and 2-fold higher electron mobility compared to that of PMMA. In short, wax-assisted transfer process opens a new avenue for the development of graphene-based electronics by minimizing charge carrier scattering centres in graphene (i.e. polymer residues and wrinkles in graphene).

NM01.15.30 Protection of Molecular Microcrystals by Encapsulation Under Single Layer Graphene Chris Bardeen, Elena Bekyarova, Wangxiang Li and Nathan Tierce; University of California-Riverside, Riverside, California, United States.

Microcrystals composed of the conjugated organic molecule perylene can be encapsulated beneath single layer graphene under mild conditions. Scanning electron and atomic force microscopy images show that the graphene exists as a conformal coating on top of the crystal. Raman spectroscopy indicates that the graphene is only slightly perturbed by the underlying crystal, probably due to strain. The graphene layer provides complete protection from a variety of solvents and prevents sublimation of the crystal at elevated temperatures. Time-resolved photoluminescence measurements do not detect any quenching of the perylene emission by the graphene layer, although nonradiative energy transfer within a few nanometers of the crystal-graphene interface cannot be ruled out. The ability to encapsulate samples on a glass surface under a graphene monolayer may provide a new way to access and interact with the organic crystal under ambient conditions.

NM01.15.31 First-Principles Investigation of a H₂O Molecule in a Heterogeneous Carbon/Boron Nitride (7,7) Nanotube Gwanwoo Kim and Gunn Kim; Department of Physics and Astronomy, Sejong University, Seoul, Korea (the Republic of).

We report behavior of a H₂O molecule inside a heterogeneous carbon nanotube/boron nitride nanotube (CNT/BNNT) structure. We have investigated energetic and electronic properties of our model system using density functional theory calculations. Considering the van der Waals interaction, we used Grimme’s DFT-D2 method implemented in the VASP package. For the model structure, the (7, 7) CNT and BNNT were chosen. The equilibrium distance between a water molecule and the CNT (BNNT) wall was calculated to be 3.3 Å (3.1 Å). In the CNT (BNNT), the energy of the water molecule was 103 meV lower (122 meV lower) at the center of the tube, and was 226 meV lower (257 meV lower) at the equilibrium position in the tube than in vacuum. The potential profile along the tube axis shows a dramatic change around the heterojunction. We plotted the projected density of states (PDOS) of hydrogen and oxygen atoms in the water molecule in the tube to check whether the orbital hybridization changes between the tube wall and the H₂O molecule, depending on the location of H₂O. The PDOS shows ~1 eV downshift in the DOS peaks of O and H atoms to the deeper valence bands when the H₂O molecule is in the (7, 7) BNNT than in the (7, 7) CNT.

NM01.15.32 Synthesis and Magnetic Properties of Metal-Free Nitrogen-Doped Graphene Quantum Dots Muhammad Sajjad1, Muhammad Shehzad Sultan1, Vladimir I. Makarov1, Frank Mendoza1, Wojciech M. Jadwisienczak1, Brad R. Weiner2 and Gerardo Morell1; 1Department of Physics, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States; 2Department of Physics and Astronomy, Western Kentucky University, Bowling Green, Kentucky, United States; 3School of Electrical Engineering and Computer Science, Ohio University, Athens, Ohio, United States; 4Department of Chemistry, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States.

Metal-free nitrogen doped graphene quantum dots (N-QGD) were synthesized and, for the first time to our knowledge, their magnetic properties were investigated. The results indicate that N-QGDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-QGDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-QGD material magnetic permeability for different ambient temperatures. From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements, carried out at 50 Oe magnetic field strength, we estimated the blocking temperature ƬB to be around 300 K. Based on the experimental data analysis, the magnetic permeability, number of correlated spins per single N-QGD, and number density of superparamagnetic N-QGD per gram of material were estimated. The excellent superparamagnetic properties together with optical properties manifested by N-QGDs have the potential to lead to high performance biomedical applications.

NM01.15.33 Effect of Non-Covalent Compatibilizers Agents in Mechanical and Thermal Properties of h-BN Nanosheets/Polymer Composites Sofia Vazquez-Rodriguez1, Eder I. Santos-Alvarado1, Luis E. Roman-Quirino1, Jose L. Aceval-Davila1, Angel A. Aguilar-Moriones2, Selene Sepulveda-Guzman2, Eduardo Arias2, Nora A. Garcia-Gomez2, Fernando A. Blanco-Flores3 and Rodolfo Cruz-Silva3; 1Universidad Autónoma de Nuevo Leon, San Nicolas de los Garza, N.L., Mexico; 2Centro de Investigación en Química Aplicada, Saltillo, Mexico; 3Shinshu University, Nagano, Japan.

Two-dimensional (2D) nanosheets such as those of transition metal dichalcogenides (TMDs) have become attractive due to the unusual properties associated with their ultrathin structure. Development of applications for these materials have been limited by the lack of a simple method to exfoliate them in single or few-layer flakes in large quantities. In this work, an exfoliation route of 2D materials such as graphene like boron nitride (hBN) using mechanical milling in solid state (cryomilling) and sonication was performed. Materials were cryomilled during 30 min and liquid sonicated. A reduction in particle
size of the powders materials after cryomilling was observed and a possible disorder of layers was evident because of the decrease in the intensity of the characteristic peak of the plane (002) in DRX patterns. After sonication process, the incorporation of 2D nanosheets in previously modified polymers by pyrolysis group, promoted changes in the optical, thermal and mechanical properties of i.e., polypropylene. The thermal diffusivity of thecomposite increased when the non-covalent compatibilizer was incorporated into the polymer even at low level of hBN concentration.

NM01.15.34 Structural Evaluation of Spin-Valves Comprising B-Doped Carbon Interlayers Hiroki Ishimoto1, Satoshi Takeichi2, Kazuki Kudo1, Ken-ichiro Sakai2 and Tsuyoshi Yoshitake1; 1 Applied Science for Electronics and Materials, Kyushu University, Kasuga-shi, Japan; 2 Control and Information Systems Engineering, Kurume College, Kurume-shi, Japan.

Spintronics is the fusion field of electronics and magnetics, and have attracted much attention from physical and practical viewpoints, because both electric charge and spin of electrons are utilized simultaneously. giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) effects have been the main principles of spintronics devices such as magnetic heads and magnetic random access memories (MRAM), which use changes in the electrical resistance accompanied by switching between parallel and antiparallel magnetization alignments. These phenomenon are occurred in trilayered spin-valve junctions composed of top and bottom ferromagnetic layers and a nonmagnetic interlayer. Therefore, spin-valves are suitable for investigating the spin-transport potential of interlayer materials due to the simple structure. It is expected that materials composed of light elements possess long spin-transport lengths due to weak spin-orbit interactions. Thus far, we have investigated structurally and electrically investigated ultrananocrystalline diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films. They comprise a large number of nano-sized diamond grains embedded in an a-C:H matrix, and have the following merits: (i) the production of p- and n-type conduction accompanied by enhanced electrical conductivities is possible by boron and nitrogen doping, respectively; (ii) they can be grown on foreign solid substrate; (iii) they can be grown at low temperature even on unheated substrates. Therefore, UNCD/a-C:H prepared by CAPD can be expected as a new candidate for a spin-transport material. Thus far, we have studied artificial lattices and spin-valve junctions comprising ferromagnetic Fe3Si and semiconducting FeSi2. In this study, based on experimental techniques in the previous studies, spin-valve junctions comprising B-doped UNCD/a-C:H interlayers and ferromagnetic FeSi and Fe layers were fabricated by a mask method, and they were structurally studied. Fe/B-doped UNCD/FeSi trilayered films were deposited on a p-type Si (111) substrate. The bottom FeSi layer and the top Fe layer were deposited by facing target direct sputtering (FTDCS) apparatus and B-doped UNCD/a-C:H was deposited by coaxial arc plasma deposition (CAPD) equipped with a 10 at. % B-blended graphite target. The microstructure was investigated by scanning transmittance electron microscopy (STEM). The magnetization curves of the junction measured at room temperature using a vibration sample magnetometer (VSM). From STEM image of the spin-valve junctions, it is confirmed that the UNCD/a-C:H interlayer exists in layer between the Fe and FeSi layers. From magnetization curves, it was observed the shape of the magnetization curve has clear two steps, which implies UNCD/a-C:H layers effectively act as interlayers between the Fe and FeSi layers without interdiffusion. The electrical properties of the spin-valve will be reported at the conference.

NM01.15.35 Optical, Electronic and Thermodynamic Properties of BN-Diamondoids Isomers—A DFT Study Marco d. Tavares1, Samir S. Coutinho1, Edvan Moreira1 and David L. Azvedo1,2; 1 Physics, Instituto de Física, Universidade de Brasília - UnB, Brasília, DF, Brazil; 2 Physics, Faculdade UnB Planaltina - FUP, Universidade de Brasilia, UnB, Área Universitária, Planaltina, DF, Brazil, Brasilia, Brazil; 3 Physics, Universidade Estadual do Maranhão-UEMA, São Luis, Brazil. 

We have systematically investigated the lowest-energy structures of boron nitride (BN) diamondoids, BnXn-based nanostructures (X = 4, 5 or 6), using the Density Functional Theory (DFT) and the Time-Dependent Density Functional Theory (TD-DFT) methods within the local density and generalized gradient approximations, LDA and GGA, respectively, were carried out to investigate the structural, electronic, thermodynamic properties and optical absorption of BN-diamondoids comparing to previous results for the adamantane (adc) and the sila-adamantane (sil) molecules, and even BN-adamantane proposed by Fyta [1]. The carbon atoms of the adamantane molecule have been substituted with Boron and Nitrogen atoms respecting the octet rule and considering homonuclear N-N or B-B bonds. Geometrical optimization of the nanostructures indicated that the BN-diamondoids exhibit good stability. The binding energy, HOMO-LUMO gaps and DOS were calculated to compare with the adamantane and sila-adamantane molecules. In addition, thermodynamical properties whose dependence with the temperature are discussed and indicating that all BN-isomers studied here could be synthesized, and its reaction should occur spontaneously in about 750 K. Finally, these BN-isomers have promising electronic and optical properties; in particular, the BnXn isomers (X = 4, 5 or 6) have an excellent optical absorption spectra in the range of ultraviolet radiation (UVA and UVB), and in particular, the 4BN-(196) isomer absorbs in the UV-Vis.
Advanced nanoengineered composites are a promising approach towards improving the mechanical performance of filamentary composites and adding multifunctionality to lightweight structures and vehicles. In particular, the integration of carbon nanotubes into composites through the circumferential growth of radially aligned carbon nanotubes (a-CNTs) onto microfibers has already demonstrated improvements in interlaminar fracture toughness, interlaminar shear strength, and electrical/thermal conductivities of alumina fiber composites. However, the implementation of this "fuzzy fiber" reinforced plastic (FFRP) architecture onto high performance carbon fibers (CFs) desired for demanding applications, has met with microfiber strength loss and effectively trades off in-plane strengths for through-thickness property improvements. This work presents an approach to growing high yields of CNTs on carbon fabrics to improve interlaminar properties while preserving the carbon fiber properties. Using a low temperature chemical vapor deposition (CVD) approach and a scalable method of catalyst deposition onto filaments, CNTs were directly grown on unidirectional (UD) carbon fabrics to form UD fuzzy CFs plies. Building on previous developments of woven fuzzy carbon fiber rein. The efficiency of the nanopumping effect triggered by Rayleigh travelling waves was predicted by FEMLAB and confirmed by experimental results. In present work, a large scale MD simulation package (LAMMPS) was used to verify that the nanopumping effect also exists in liquid water placed in pristine CNTs. Results of our simulations demonstrated that water molecules passed through CNTs and exited from the other CNT side. The efficiency of the nanopumping effect triggered by Rayleigh travelling waves was predicted by FEMLAB and confirmed by experimental results. Nevertheless, the implementation of this "fuzzy fiber" reinforced plastic (FFRP) architecture onto high performance carbon fibers (CFs) desired for demanding applications, has met with microfiber strength loss and effectively trades off in-plane strengths for through-thickness property improvements. This work presents an approach to growing high yields of CNTs on carbon fabrics to improve interlaminar properties while preserving the carbon fiber properties. Using a low temperature chemical vapor deposition (CVD) approach and a scalable method of catalyst deposition onto filaments, CNTs were directly grown on unidirectional (UD) carbon fabrics to form UD fuzzy CFs plies. Building on previous developments of woven fuzzy carbon fiber reinforced plastic (CFRP) laminates, vacuum assisted resin infusion was used to manufacture UD fuzzy CFRP laminates that have low interlaminar spacings (<15 μm) to increase the CNT fill fraction in the weak interlaminar region, and isolate CNT reinforcement effects. Both UD baseline CFRP and UD fuzzy CFRP were manufactured using a vacuum assisted resin infusion system with interlaminar spacings and laminate quality assessed through X-ray microcomputed tomography. Transmission and scanning electron microscopies reveal conformal CNT growth around carbon filaments prior to matrix introduction. Thermogravimetric data also shows the removal of the polymeric sizing layer on carbon fibers and the thermoplastic wet (that holds the CF tows together) through CVD processing and consequently informs matrix interface changes as well as process bounds for ensuring ply handleability. Further, short-beam shear testing data of UD fuzzy CFRP is presented, showing a 4% improvement in interlaminar shear strength. Thus, this work is an important step towards realizing hierarchical carbon fiber composites with improved interlaminar properties without compromising in-plane strengths, and provides a platform for future CNT growth optimization that may result in even larger property enhancements.
Applications of electromechanical probing for wafer testing progressively require smaller pitches, reliable and reproducible manufacturing and lower electrical contact resistances. Current electromechanical testing probes, for instance MEMS based vertical cantilever probes, have fundamental limitations in terms of the shortest pitch that can be achieved, cost and efficiency. The exceptional mechanical and electronic properties of carbon nanotubes (CNTs) make CNTs a promising candidate material for electromechanical probing applications. We synthesise vertically-aligned CNT structures by combining photo-thermal chemical vapour deposition (PTCVD) and photolithography and assemble them into a new type of metal-CNT-Polydimethylsiloxane (PDMS) composite structure for possible probing applications at both wafer-level chip-scale packaging (WL CSP) and wafer-level packaging (WLP) testing. Up to 600 μm tall, CNT-based vertical micro-spring type probes are demonstrated. We propose a design and architecture with a scalable approach, allowing for the assembly of thousands of probes in short manufacturing times, with easy pitch control that can facilitate testing at WL CSP and WLP packaging. Extra-long (~600 μm), vertically-aligned CNT probes are grown at high process temperatures and pressures, at rates up to 50 μm/min. The CNTs are metallic, multi-wall carbon nanotubes (MWCNTs) and are of good quality (I_d/I_g ~ 0.3). As-grown CNT probes are transferred to PDMS and metallised with Au, Pd and Cu to form a composite-like probe structure; with CNTs, acting as current carrying channels as well as micro-springs, providing good elasticity without compromising from the electrical conductance and a metal scaffold that stiffens the structure, whilst decreasing the overall contact resistance. Cyclic electromechanical characterisation of CNT-based probes showed reproducible contacts for up to 10,000 cycles, with a 50 μm compliance. For a 200 μm x 200 μm probe cross-sectional area, an average of 0.7 Ω contact resistance is achieved. Low contact resistance is realised by vertically-aligning CNTs, differing the combination of metallisation layers to obtain a good work function matching and wetting at the metal-nanotube interface. In addition, up to 16% compliance is observed and the mechanical failure mechanism is identified as micro-crack induced buckling in the plastic region. Overall, we demonstrate a scalable CNT-based micro-spring probe design as an alternative candidate to complex MEMS-based vertical cantilever probes for wafer probing applications at wafer level. Fabrication process can easily allow small pitch probes with minimal layout restrictions without compromising from electrical and mechanical properties. In addition, properties such as: stiffness, probe length and probe resistance are tunable via PTCVD deposition and metallisation processes allowing a wider range of probing applications.

NM01.15.41
Dynamic Mechanical Property of Multilayer Graphene Subjected to Supersonic Impact
Wanting Xie1,2 and Jae-Hwang Lee1; 1Department of Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Department of Physics, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Graphene is considered as one of the most promising anti-ballistic materials due to its high strength, stiffness, and low density. While its low-rate behavior has been studied for years, there are few experimental investigations at the high-strain-rate regime. By the observation of micro-spheres penetrating through free-standing graphene membranes in air, Lee and his colleagues (Science 346, 1092 (2014)) directly characterized mechanical properties of multilayer graphene at very high strain rates (~10³ /s). Their microscopic ballistic study demonstrated that the specific penetration energy of multilayer graphene was more than 10 times larger than that of steel for 600 m/s impact in the air. Independent numerical studies, however, predicted one order higher specific penetration energy than the experimentally measured value. A thickness effect was brought up to explain this discrepancy, as in modeling, a series of monolayer graphene was more efficient in energy dissipation than multilayer graphene with a same total mass. Moreover, aerodynamic effects of air were also suggested since the numerical simulations were carried out without introducing gases. For more precise quantification of the high-strain-rate properties of graphene, we have performed the micro-ballistic characterization in vacuum. Since the vacuum level is approximately 1/3,000 of the atmospheric pressure, undesired effects from air, including aerodynamic friction of a projectile and a membrane specimen, become negligible. As a projectile, 3.7 μm diameter silica sphere is accelerated and a suspended graphene membrane is subjected to projectile’s impact. With an ultrafast microscopic imaging system (up to 40 million frame per second), accurate velocities of the projectile before and after penetration are obtained. The specific penetration energy are directly calculated by the ratio of kinetic energy loss of the projectile and the mass of the membrane within the direct impact area of the projectile for different projectile’s velocities (100 – 1,000 m/s) and specimen’s thicknesses (10 – 100 nm). Post-mortem optical micrographs and electron micrographs are taken to measure the total crack length, crack number, and penetration area to explore their relationship with the penetration energy. The fine penetration features near the impact region are mainly examined by scanning electron microscopy.

NM01.15.42
Optical Visualization and Spectral Amplification of Single-Walled Carbon Nanotubes Through the Hygrosopic Salt Micro/Nanolenses
Yun-tae Kim and Chang Young Lee; Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea (the Republic of).

Micro/nanolenses of alkali metal halides are unique optical components that partially overcome the limitations of existing ones because of their hygroscopicity, solubility in water, tuneable refractive indices, excellent transmittance from UV to infrared, and high mobility of the constituent ions under an electric field. Forming such lenses and arranging them in a well-defined manner, however, remains a challenge. Here we demonstrate selective decoration of array of micro/nanolens along single-walled carbon nanotubes (SWNTs) using various salt species, which can be migrated along exterior of SWNT under an electric field. The lenses are promising for use in both the optical visualization and spectral amplification of underlying individual nanotubes. The lenses help detect molecular species located onto sidewall of a nanotube, such as amorphous carbon and diazonium that are not easily detectable using existing approaches. In addition, molecules dissolved in the solution can be captured within the lenses via exterior transport and then detected by Raman spectroscopy. Such lenses can be easily removed by a simple water rinse without degrading the properties of SWNTs. Thus, our approach will serve as a useful tool for the non-invasive visualization of nanostructures and spectral amplification of various molecular species.

NM01.15.43
The Exterior of Single-Walled Carbon Nanotubes as a Millimeter-Long Cation-Preference Nanochannel
Yun-tae Kim and Chang Young Lee; Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea (the Republic of).

In this study, the exterior of single-walled carbon nanotubes is shown to preferentially migrate cations over a millimeter length scale. Applying an electric field to drops of NaCl placed at both ends of the nanotubes causes transport of a cation-enriched solution counter-migrates along the adjacent substrate. This phenomenon is confirmed by Kelvin probe force microscopy and mass spectrometry imaging of individual nanotubes, as well as formation of bright and dark lines along the nanotubes in scanning electron microscopy (SEM). Blocking the exterior of the nanotubes prevents both the bright/dark lines in SEM and flow of current through the nanotubes, confirming the insignificance of interior ion transport and electron current. The cation-prefering transport results in the formation of positively charged salt crystals along the nanotubes (with a cation-to-anion ratio of 0.59:0.41 for KCl) followed by the subsequent shrinkage and growth of crystals in the direction of cation flux. Molecular dynamics simulations shows that cation–π interaction is responsible for such cation-preference observed during
transport. The loss of cation-preference upon covalent functionalization of the nanotubes further supports this mechanism. Utilizing the short-range cation-π interaction as a transport mechanism suggests broader applications in areas where charge-specific transport is desired.

NM01.15.44
Modeling the Bipolar Switching Effect in Graphene Oxide-Based Memristors
Andres Vercík and Luci C. Vercík; University of Sao Paulo, Pirassununga, Brazil.

The memory resistor, or memristor, was theoretically predicted by Chua in 1971 as the forth fundamental circuit element needed to complete the set of six mathematical equations relating four basic electrical variables: charge, current, voltage and magnetic flux. This idea remained as a missing element until its experimental realization in 2008 as TiO2-based memories. Since then, many researchers have directed their attention and efforts not only to the fabrication of memristors, using different materials, but also to understand the physics behind the switching mechanism, in order to control the processing and structural parameters that allow overcoming some drawbacks to obtain reliable and reproducible memory devices. Two-terminal devices, with the switching material sandwiched between two electrodes, are promising structures for the next generation of non-volatile resistive random access memory devices, with high speed, low-power consumption and excellent scalability. The two-dimensionality of the insulating graphene oxide sheets makes this material ideal for use in low-dimensional structures in nanoscale devices.

In this work, the transport properties of graphene oxide-based Metal-Insulator-Metal (MIM) structures are addressed. The graphene oxide (GO) was synthesized using an eco-friendly modified Hummers method. The obtained GO sheets were placed between gold electrodes, and the cycling current-voltage curves were measured by applying successive forward and reverse voltage sweeps in a range between -3 and 3V. When the absolute value of the measured current is plotted, in logarithmic scale, versus the applied voltage the typical butterfly-shaped curves are observed, which are better interpreted in terms of their first derivative, or differential conductivity, in order to understand the transport mechanism. A simple model is proposed, whose voltage dependence helps identifying the underlying physics responsible for the bipolar switching mechanism, such as bulk or electrode effects, conducting filament formation or tunneling. The analytical expressions used for the differential conductance for the low resistance state and the high resistance state (LRS and HRS respectively) leads to simple expressions for the I-V curves. The symmetry of the curves after several cycles is lost when compared to those measured on pristine devices, which might indicate the occurrence of filament forming effect, affecting the bipolar switching.

NM01.15.45
Rheological Characteristics of Chitosan - Gold - Graphene Gels
Radha Perumal Ramasamy; Department of Applied Science and Technology, ACT campus, Anna University, Chennai, India.

Gels are important class of materials and have wide applications. Gel polymer electrolytes is an interesting field and has gained much scientific attention in recent years. Controlling the rheological properties of gels can benefit its applications in fields such as batteries. In this research the effect of incorporation of graphene upon the rheological properties of chitosan-gold gels is explored. The chitosan solution was prepared by adding 1% (w/v) of chitosan powder of 1.5% (w/v) of acetic acid to double distilled water. The solution was stirred and heated at 60°C until a semitransparent thick chitosan solution was obtained. The solution was cooled to room temperature. To this solution, appropriate amounts of 1 M HAc/CH3OH were added to have 5 mM Au. Also graphene (grade H5 – XG Sciences) was incorporated in the gels to have 0, 10 and 20% of graphene (by weight compared to that of chitosan). The rheological and SEM measurements were made on these gels. The rheological measurements were made one day after the formation of the gels. The complex modulus for chitosan-5mM gold gels showed an increase from 100 Pa to 620 Pa as temperature increased from 25°C to 85°C. It then rapidly decreased to 36 Pa as temperature increased to 100°C. Chitosan-5Mm Au-20% graphene had a peak at 95°C. Hence the viscosity has maximum values at 85, 90 and 95°C for graphene concentrations of 0, 10 and 20% in chitosan-5Mm Au gels. Between 25 to 70°C the viscosity of chitosan-5Mm Au-10% graphene > chitosan-5mM Au > chitosan-5mM Au-20% graphene. Between 70 to 85°C the viscosity of chitosan-5mM Au > chitosan-5mM Au-10% graphene > chitosan-5mM Au-20% graphene. Phase angle measurements showed that chitosan-5Mm Au, chitosan-5Mm Au-10% graphene and chitosan-5Mm Au-20% graphene gels had lowest values at 80, 85 and 95°C respectively. These results indicate that the rheological properties are influence by the graphene incorporated in it. Interestingly, as graphene concentration increases to 20%, chitosan-5mM Au-20% graphene remains as a gel even at 100°C (as it has high viscosity) though chitosan-5Mm Au and chitosan-5Mm Au-10% graphene gels collapse at 100°C (as they have low viscosity). This indicates that graphene can be incorporated in gels to increase the temperature at which it can be operated. TEM images for graphene added to 5Mm Au solution (in room temperature) showed very less presence of gold nanoparticles. TEM images for chitosan-5Mm Au-10% graphene in room temperature (incubated for 10 days) showed presence of several sub-micron sized gold particles. Spherical, triangular and hexagonal shaped particles were observed. Some particles were as large as 500 nm. The particles were heterogeneous in sizes. TEM images for chitosan-5Mm Au-10% graphene heated to 30°C for 60 min (until the solution turned red in color) showed that uniform gold nanoparticles formed. Also gold nanoparticles attached to graphene indicating that graphene acts as nucleation site.

NM01.15.46
Interactions of Carbon Nanotubes with Magnetospirillum Magneticum via Carbon Nanotube/Polypyrrole Nanocomposite
Jake Dengelegi, Prabir Patra and Isaac Macwan; University of Bridgeport, Bridgeport, Connecticut, United States.

Being able to easily manufacture uniform chirality carbon nanotubes (CNT) is a difficult problem that we face today. There are many different ways that the carbon nanotubes orient themselves in making them either more metallic or semi-conducting in nature. Being able to separate these two types is very important to the semiconductor industry because semi-conducting carbon nanotubes are better suited for electronic devices such as transistors. Magnetospirillum magneticum (AMB-1) is a bacteria that can be used through magnetotaxis for controlled assembly tasks and it has also been shown that there are favorable interactions between the surface proteins, MSP-1 and flagellin of AMB-1 with glycine along with its flanking residues interacting only with metallic but not semi-conducting CNT. It has also been shown before that graphene, pyrrole, and carbon nanotubes can form a free standing film using cyclic voltammetry (CV) owing to the fact that the process of making the films containing only CNTs is extremely challenging because they are non-polar and cannot be polymerized independently. CV electro-polymerizes the pyrrole monomer into polypyrrole (Ppy) through a series of oxidation and reduction reactions along with CNT to be deposited on an electrode. In order to better study the interactions between CNT and AMB-1, this work is on the fabrication of a free standing nanocomposite CNT/Ppy film using CV with a specific aim to quantify such interactions using scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), electro-chemical impedance spectroscopy (EIS), and Fourier transform infrared spectroscopy (FTIR). In order to have large number of such interactions between AMB-1 and CNT only, we are working to find an optimum amount of pyrrole needed to make the film containing the most amounts of CNTs. We have been able to show that when 0.57mL of Ppy per 25mL of deionized water is polymerized, a free standing film (10 X 10 nm) with a greater percentage of CNT can be obtained. CV was used with a scan rate of 10mv/s, a low voltage of 800mV, a high voltage of 900mV, and 100 cycles. Based on the morphological characterization of the CNT/Ppy substrate along with AMB-1 using SEM and HRTEM as well as the data from FTIR and EIS, it is anticipated that AMB-1 does interact well with the CNT. The changes in the impedance in case of EIS with and without AMB-1 agree well with the AFM probing experiments and force distance data.

NM01.15.47
Enhancing Performance of Photovoltaic Solar Cell by P3HT:PCBM Doped Graphene Flakes as Photoactive Layer
Adnan Ali and Braham Alssaa;
Photoactive materials based on conjugated polymers are very promising candidates for Hybrid organic photovoltaic (OPV) cells. Conjugated polymers are inexpensive materials and therefore, their processing is very cost-effective and the ease of fabrication by solution processing make them more attractive. So far, OPV with modest efficiency are obtained. The low power conversion efficiency (PCE) of OPV is one of the main reason which has impeded large scale deployment. The low PCE of OPV solar cells is attributed to the low carrier mobility, which is closely correlated to the transport diffusion length of the charge carriers within the photoactive layers. 2D material like graphene which has huge carrier mobility, thermal and chemical stability and its compatibility of fabrication by solution processing techniques making it an excellent candidate for assisting charge transport improvement in the active layer of OPV cells. In this work, we report on the improvement of the optoelectronic properties and photovoltaic performance of photoactive blended layers i.e. P3HT:PCBM doped graphene flakes which was then integrated into a bulk heterojunction (BHJ) organic-photovoltaic-based device, using PEDOT:PSS on an ITO/glass substrate. Firstly, effect of graphene flakes content was studied in terms of the light absorption capacity which has shown increase with increasing concentration of graphene flakes. Besides this, quenching was observed through photoluminescence which is a clear indication of electron transfer between the graphene flakes and the polymeric matrix. P3HT:PCBM doped graphene flakes layer is incorporated into the BHJ as active layer. An increase in PV performance with respect to the reference cell was observed. The best PV performance was obtained for 3 wt.% loading of graphene flakes. The solar cell showed an open-circuit voltage (Voc) of 1.24 V, a short-circuit current density (Jsc) value of 6.18 mA cm⁻², a fill factor of 47.12%, and a power conversion efficiency of about 3.61%. It is obvious from the organic photovoltaic solar cell efficiency that sp² bonded carbon doping of photoactive conjugated polymer has strong role in its enhanced performance.

**NM01.15.48**
Mechanism Study of Graphene Adlayers in Chemical Vapor Deposition by Isotope Labeling

Xuewei Zhang, Zhenxing Zou, Yang Wang, Yunlu Wang, Le Mei, Zilong Zhang, Zehao Wu, Pei Zhao and Hongtao Wang; Zhejiang University, Hangzhou, China.

Bilayer graphene (BLG) has attracted enormous interest due to its outstanding mechanical, chemical, electrical and thermal properties with various potential applications. By applying a high ratio of H₂ to CH₄ in chemical vapor deposition (CVD) system, BLG can be synthesized with inverted-cake structures on polycrystalline Cu foils. Bilayer regions show distinct Raman spectra by carbon isotope labeling due to the different compositions of the graphene.

In this work, we studied the growth mechanism of BLG using carbon isotope labeling and Raman spectroscopy. Results show that the growth of BLG reveals several different modes. A new mode of “secondary” nucleation is firstly proposed in the growth of BLG, which means that graphene can be nucleated under the first layer tens of minutes later than the first layer. Moreover, during the BLG growth, the stacking structures of the two layers can suddenly change from AB-stacking to non-AB-stacking, while most of the BLG can still maintain their stacking structures during the whole CVD process. This work enables us to have a deep understanding of graphene growth mechanism as well as the layer control for large scale BLG using CVD.

**NM01.15.49**
LEEM Investigations of Polymer-Assisted Sublimation Grown Graphene on SiC

Philip Schädlich1, Florian Speck1, Georg Traeger2, Anna Sinterhauf3, Davood M. Pakdehi1, Klaus Pierz2, Martin Wenderoth2 and Thomas Seyller1; 1Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany; 2IV. Physikalisches Institut, Georg-August-Universität Göttingen, Göttingen, Germany; 3Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

Although much research has been conducted in the field of epitaxial graphene growth on silicon carbide (SiC), still new phenomena are discovered and need to be investigated in order to fully understand and control graphene synthesis and properties. Usually, during sublimation growth in argon at atmospheric pressure the substrate undergoes strong step bunching [1], which leads to relatively large step heights of multiple SiC unit cells. In contrast, the polymer-assisted sublimation growth (PASG) leads to flat and homogeneous graphene sheets on top of an SiC surface with step heights of mainly one or two SiC-bilayers [2]. This gives rise to a well-developed sequence of alternating SiC surface terminations underneath the graphene, which originate from different crystal truncations within the SiC unit cell at the surface [3].

Recently, scanning tunneling potentiometry measurements on graphene obtained by PASG revealed different values for the sheet resistance for graphene on different SiC terraces. Here, we present our results on PASG graphene investigated by low-energy electron microscopy (LEEM). The termination of the underlying SiC substrate is studied by LEEM bright field and dark field measurements as well as selected area low-energy electron diffraction (s-LEED) and atomic force microscopy. In addition low-energy electron reflectivity (LEER) spectra reveal slightly different electronic properties of the graphene on different SiC terminations. The relationship between the termination of the SiC substrate and the electronic properties of the PASG graphene as indicated by the LEER spectra is shown. Possible explanations for the local change in sheet resistance and the influence of the substrate are discussed.


**NM01.15.50**
Exceptional Multifunctional Properties of Non-Oxidized Graphene Aerogel/Epoxy Nanocomposite

Jin Kim1, Ne Myo Han2, Jungmo Kim1, Hyewon Yoon1, Minso Park1, Travis G. Novak1, AshrafalAzam1, Jinho Lee1, Kang-Kyo Kim1 and Seokwoo Jeon1; 1KAIST, Daejeon, Korea (the Republic of); 2MAE, HKUST, Hong Kong, Hong Kong.

Graphene aerogel, a three dimensionally interconnected porous structure, has gained significant attention due to its fascinating properties, such as high mechanical strength, electrical conductivity, thermal resistance, and ultra-light weight. Incorporation of graphene aerogel into a polymer composite is a promising route for fabrication of ultra-light multifunctional material, which is heavily demanded in various industries.

Recent studies have focused on optimization and alignment of graphene aerogel’s structure, in order to further improve the quality of the aerogel and the corresponding composite. Various methods have been developed for controlling the aerogel structure such as self-assembly, direct printing, and ice templating of graphene flakes. Initially, graphene oxide (GO) flakes was used for fabricating graphene aerogel with aligned structure, due to its abundant surface functional groups, which facilitate both aqueous dispersion and assembly of graphene aerogel. However, those functional groups also act as defects, which severely deteriorate the property of both GO flakes and its aerogel. Therefore, it is highly desired to fabricate graphene aerogel composed of graphene flakes with minimum damage.

Here we report a fabrication method to fabricate graphene aerogel composed only with highly crystalline non-oxidized graphene flakes (NOGFs). Bi-direction freeze casting technique was utilized in order to align the pore walls in two orthogonal directions, vertically and laterally. The graphene aerogel showed low defect concentration and oxygen content of 1.4 % according to Raman and XPS analysis. Due to the synergistic effect of both high quality of
Methods into Nano-Carbons and Fuels
A Comprehensive Study on Optimizing Conversion of Waste Plastics Using Diverse Catalysts, Carrier Gases, Flow-Rates and Pre-Treatment

Water splitting is one of the carbon-free hydrogen production methods. Electric power consumption of the hydrogen evolution reaction (HER) depends on the cathode materials. Although Pt is known as the most suitable cathode for HER under acidic conditions, identified resources of platinum are limited in the world. Hence, the development of alternative HER catalysts is required. Currently, MoS2 presents a promising alternative to Pt due to its low cost and high HER activity. The active sites of MoS2 are located at the edges, thus it is important to develop a simple synthesis process to obtain edge-rich MoS2. In previous research, edge-rich MoS2 of high crystallinity was synthesized under hydrothermal conditions, but the main problem of the process was the long reaction time (24-48 h). MoS2 synthesis via cathodic electrodeposition is one of the fast and facile processes because the deposited MoS2 can be applied directly for application. However so far, electrochemically deposited MoS2 showed low crystallinity and low purity with an amorphous structure. In order to realize high crystallinity MoS2 and short processing times, we propose a hydrothermal electrodeposition method to fabricate MoS2 electrodes. This method enables to synthesize crystalline thin films and to control the composition and morphology of the products by adjusting the operating temperature, pressure, and electrochemical conditions. In this research, we attempted to electrochemically deposit MoS2 on glassy carbon (GC) under hydrothermal conditions (200 °C, 10 MPa), and the MoS2/GC electrodes were then applied as HER cathodes. For the hydrothermal electrodeposition, a high-pressure vessel made of Hastelloy equipped with electrodes was used as a synthesis cell, and potentiostatic measurements were carried out at voltages of −1.5 V for 1-30 min. SEM and TEM images of samples synthesized by 1 min electrolysis revealed the formation of edge-rich MoS2 deposited on GC, while it seemed that the number of exposed edges of the products decreased with increasing reaction times. XRD patterns of working electrodes realized by electrodeposition for 1 min showed that crystalline MoS2 was deposited on the GC. From TOF-SIMS measurements, the product was mainly identified as MoS2, while compounds of molybdenum sulfides and oxides were observed in the case of the electrodes treated at ambient condition. HER catalytic activity measurements showed that products synthesized at hydrothermal condition exhibited higher HER performance than the samples synthesized at ambient conditions. Moreover, edge-rich MoS2 obtained for an electrolysis time of 1 min had higher activity compared to samples realized by longer electrolysis times, the higher HER activity being attributed to the edge-rich morphology of MoS2.

A Comprehensive Study on Optimizing Conversion of Waste Plastics Using Diverse Catalysts, Carrier Gases, Flow-Rates and Pre-Treatment

Fabrication of Edge-Rich MoS2 Cathodes for Water Splitting via Hydrothermal Electrodeposition

Water splitting is one of the carbon-free hydrogen production methods. Electric power consumption of the hydrogen evolution reaction (HER) depends on the cathode materials. Although Pt is known as the most suitable cathode for HER under acidic conditions, identified resources of platinum are limited in the world. Hence, the development of alternative HER catalysts is required. Currently, MoS2 presents a promising alternative to Pt due to its low cost and high HER activity. The active sites of MoS2 are located at the edges, thus it is important to develop a simple synthesis process to obtain edge-rich MoS2. In previous research, edge-rich MoS2 of high crystallinity was synthesized under hydrothermal conditions, but the main problem of the process was the long reaction time (24-48 h). MoS2 synthesis via cathodic electrodeposition is one of the fast and facile processes because the deposited MoS2 can be applied directly for application. However so far, electrochemically deposited MoS2 showed low crystallinity and low purity with an amorphous structure. In order to realize high crystallinity MoS2 and short processing times, we propose a hydrothermal electrodeposition method to fabricate MoS2 electrodes. This method enables to synthesize crystalline thin films and to control the composition and morphology of the products by adjusting the operating temperature, pressure, and electrochemical conditions. In this research, we attempted to electrochemically deposit MoS2 on glassy carbon (GC) under hydrothermal conditions (200 °C, 10 MPa), and the MoS2/GC electrodes were then applied as HER cathodes. For the hydrothermal electrodeposition, a high-pressure vessel made of Hastelloy equipped with electrodes was used as a synthesis cell, and potentiostatic measurements were carried out at voltages of −1.5 V for 1-30 min. SEM and TEM images of samples synthesized by 1 min electrolysis revealed the formation of edge-rich MoS2 deposited on GC, while it seemed that the number of exposed edges of the products decreased with increasing reaction times. XRD patterns of working electrodes realized by electrodeposition for 1 min showed that crystalline MoS2 was deposited on the GC. From TOF-SIMS measurements, the product was mainly identified as MoS2, while compounds of molybdenum sulfides and oxides were observed in the case of the electrodes treated at ambient condition. HER catalytic activity measurements showed that products synthesized at hydrothermal condition exhibited higher HER performance than the samples synthesized at ambient conditions. Moreover, edge-rich MoS2 obtained for an electrolysis time of 1 min had higher activity compared to samples realized by longer electrolysis times, the higher HER activity being attributed to the edge-rich morphology of MoS2.

A Comprehensive Study on Optimizing Conversion of Waste Plastics Using Diverse Catalysts, Carrier Gases, Flow-Rates and Pre-Treatment

Methods into Nano-Carbons and Fuels

As a result of China’s recent ban on the import of most plastic waste, the US and other industrialized countries that have been exporting their plastic waste to China for recycling will need to find new ways to handle the disposal of their wastes as much of it is already starting to pile up in landfills. In research conducted at Northeastern University, plastic wastes have been thermally recycled by pyrolytic gasification to nano-carbons and gaseous fuel. To achieve this conversion, a laboratory-scale pyrolytic gasifier was fed with waste plastics including (polyethylene, polypropylene, polyethylene terephthalate, polystyrene, etc., and combinations of the same) in inert (N2 or He or Ar or CO2) atmospheres with different flow rates (0.1-2 l/min). The plastic wastes were gasified in an electrically heated reactor at 600-800 C. Under these conditions, the pyrolyzate was pyrolyzed into a gaseous mixture of hydrocarbons and hydrogen. The pyrolyzate mixture was then conducted into a separate reactor where it was used as a carbon precursor for chemical vapor deposition process to synthesize carbon nanoparticles. The second reactor was set at 900-1000 C. Different grades of stainless steel wire cloths (SS-304, SS-316 and SS-316L) were used as catalytic substrates for the nanoparticle growth. The wire cloths were used either as-received or upon chemical etching by acid wash and/or heat-treatment in air, nitrogen or helium at 800 C, followed by rapid air quenching. In those cases, the yields were determined, by mass relative to the mass of carbon in the feedstock and ranged from 1% to 30%. With the purpose of purification and sorting, the catalysts and the produced Nano-materials were investigated for synthesis, structure and property characterization by SEM, TEM, AFM, TEM+EDX, HAADF and TGA. Results showed that the catalyst type, composition, and pre-treatment, as well as the type of waste plastic, are all influential on the yields and physical characteristics of the synthesized CNTs.

Keywords: Carbon Nanotube, Waste Plastics, Synthesis, Pyrolysis, Purification and Sorting

Investigation of Photocatalyzed Reduction of Technetium-99 Utilizing Titanium Dioxide, Graphene Oxide and Nanocomposites Thereof

Water contaminated with highly toxic long-lived radionuclides is a growing concern in the U.S. These contaminants are introduced into water sources from the legacy wastes of nuclear sites, and from nuclear reactors. Technetium-99 (99Tc) is one of the major nuclear waste contributors (~6% yield) generated from thermal neutron fission of uranium-235. It is considered a long-lived radioisotope with a half-life of 2.1x106 years and emits a weak beta with a max energy of 0.29 MeV. 99Tc is most prevalent in its oxidized form which predominantly exists as pertechnetate (Tc(VII)O4−). This contaminant is of concern in aqueous streams because of its inert nature that allows it to spread at nearly the same rate of water flow. To remediate 99Tc, reduction of pertechnetate has been the common approach because 99Tc is more reactive and less mobile when in a reduced state. The foundation of this work involved utilizing different functionalized nanomaterials as platforms to investigate the reduction and uptake of 99Tc. Titanium dioxide is a promising candidate as it has already shown to be a good material for removing toxic materials from the environment. Furthermore, it has a strong reducing potential and is found to be chemically inert in a variety of environments. Graphene oxide (GO) is an eco-friendly platform with a large surface area that provides tunability due to its chemically inert nature in a variety of environments. Graphene oxide (GO) is an eco-friendly platform with a large surface area that provides tunability due to its electrical conductivity of 122.6 S/m at 0.27 vol%. Both results are superior to those of epoxy composites based on GO aerogels, which demonstrate that incorporation of NOGFs is a promising approach for fabricating high quality graphene aerogel.

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films

Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films
Graphene and their derivatives graphene oxide (GO) and reduced graphene oxides (rGO) have been of great interest in technological device applications in nanoelectronics and bio-sensors. The great flexibility of GO based thin films and its compatibility with existing technologies help in understanding the device physics and engineering of GO based thin film devices for their practical applications. The simplest structure for studying electronic properties includes sandwiching the thin film between two metal electrodes and study behaviour of charge flow. Motivated with the initial observation of bistable resistive switching behaviour in Al(200°C)/GO(T)/ITO structure, this work is extended to demonstrate the influence of various metal contacts in GO thin film is interpreted using X-ray photoelectron spectroscopy and the role of these electrode materials in the electrical resistance in metal(M1)/GO(T)/metal(M2) device structures [with M1 = indium tin oxide (ITO); gold (Au), or aluminium (Al), and M2 = Al or Au] have been analysed. GO is synthesised by modified Hummers method. Thin films of GO are prepared by spin coating the dispersed solution of GO (1mg/ml) on metal substrate (M1= ITO, Al, or Au) followed by annealing at different temperatures, T= 100, 200, 300, and 400 °C. The materials, optical, and electrical properties are characterized for the GO powders and GO(T)/M1 thin films [3]. The top metal electrode (M1 = Al or Au) is formed by thermal deposition technique through shadow masking. Temperature dependent current-voltage (I-V) characteristics of resulting devices M2/GO(T)/M1 are measured using Keithley-4200 Semiconductor Analyser system. The temperature dependent resistance coefficients (α) estimate values of 4.2 x 10^{-3} and 5 X 10^{-3} in Al(200°C)/GO(T)/ITO device structures, respectively. The presence of Au and Al contents in depth profile XPS spectra of GO(T)/Al or Au films and metallic behaviour in the temperature-dependent electrical resistance through M2/GO(T)/Al or Au structures with the R0 equivalent to the corresponding submetal, indicate migration of atoms from Al or Au electrodes through the defect sites of GO till the other electrode and connects both the top and bottom electrodes the with formation of metal filament. The electrical resistance values indicates R_{Al/GO(200°C)/ITO} < R_{Au/GO(200°C)/ITO} < R_{Al/GO(T)/Al} < R_{Au/GO(T)/Au}. In Al/GOT(A)/Au and Al/GO(T)/Al devices show more conducting compared to R_{Al/GO(T)/ITO} due to presence of more metal contents forming the filament within the GO layer between the top and bottom contacts. The Al/GO(T)/ITO device assists only the elemental metal atoms of Al to migrate through the GO and favors the provides uniform parameter during growth process, leading to growth of near identical filament structures between the electrodes and formation of contact interfaces at Al(200°C)/T and GO(T)/ITO with identical thermal and electrical behaviours for all the interconnecting filaments.

NM01.15.55
Mechanical Assembling and Structuring Graphene Oxide Based Materials Jing Zhong; Harbin Institute of Technology, Harbin, China.

Mechanical Assembling and Structuring Graphene Oxide Based Materials
Jing Zhong*,†
†School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, Peoples’ Republic of China
‡Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150080, China

As a building block, graphene possesses intriguing mechanical, electrical, thermal property and chemical stability. Assembling graphene into macrostructures is very appealing, if those unprecedented properties can be inherited. However, it is the physical interaction between graphene nanosheets mainly control the performance of the assembled materials. On the other hand, it should be noted that graphene is probably the most anisotropic material that has ever been discovered, as manifested by the prominent contrast of bending modulus (in the order of ~2kT) and tensile modulus (~1 TPa), as well as the ballistic electron transport in-plane and tunneling between-planes. Therefore, it is extremely important to improve the alignment of graphene nanosheets in the same direction and reinforce the interaction between them. Keeping this in mind, we propose to employ mechanical strategies, namely dead-end filtration and centrifugal casting, with the advantages of high efficiency, high yield and universal, to super-align and condense-compact graphene nanosheets, both of which result to materials with outstanding performance [1-3]. Finally, we will also illustrate that the combination of proper rheology properties of graphene oxide based ink and 3D printing technique, materials beyond 2D film with much more complex structures can be obtained.

Reference:

NM01.15.56
Functionalization of Graphene Thin-Film Surface by Using 2- (dimethylamino) ethyl methacrylate by Plasma Enhanced Chemical Vapor Deposition Method Furkan Turgut and Mustafa Karaman; Chemical Engineering, Konya Technical University, Konya, Turkey.

The chemical reduction of graphene oxide is a promising route towards the large-scale production of graphene for commercial applications. Graphene is an atomic-scale honeycomb lattice made of carbon atoms. Due to its extraordinary mechanical, electrical, and thermal properties, graphene has potential applications in many fields. The reason of functionalize graphene with DEAEMA by using PECVD method is to enable the matrix to be form of composite with other chemicals. In this work, graphene oxide(GO) was synthesized from graphite by using modified Hummer’s method. Modified Hummer’s method according to other methods known in the literature; it is simpler and less costly in terms of processing steps. The synthesized graphene oxide(GO) was reduced with hydrazine hydrate to obtain a graphene. The obtained graphene was functionalized with amine group 2- (dimethylamino) ethyl methacrylate (DEAEMA) monomer by using plasma enhanced chemical vapor deposition (PECVD). Unlike other chemical vapor deposition methods, the PECVD method only polymerizes with the plasma that generated on the monomer surface without using an initiator in the system. To determine coating conditions; different reactor pressures, monomer flow rates, plasma powers and coating times were tested using PECVD method. Thickness of coating on surface was found by using profilometry, to characterize compounds FTIR and to determine GO surface morphology AFM analyses were used. As a result, the most efficient coating speed was determined as 69 nm/ min. Functionalization of graphene studies were carried out under the determined optimum coating speed condition. SEM, TEM and Raman analyses of the coated graphene oxides were carried out to investigate the morphological and chemical structure.

NM01.15.57
Elastic Properties of Bulk and Low-Dimensional Materials Using van der Waals Density Functional Kamal Choudhary; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

In this work we present a high-throughput first-principles study of elastic properties of bulk and monolayer materials mainly using the vdW-DF-optB88 functional. We discuss the trends on the elastic response with respect to changes in dimensionality. We identify a relation between exfoliation energy and elastic constants for layered materials that can help to guide the search for vdW bonding in materials. We also predicted a few novel materials with auxetic behavior. The uncertainty in structural and elastic properties due to the inclusion of vdW interactions is discussed. We investigated 11 067 bulk and 257
monolayer materials. Lastly, we found that the trends in elastic constants for bulk and monolayer counterparts can be very different. All the computational results are made publicly available at easy-to-use websites: https://www.ctcms.nist.gov/~knx6/VASP.html and https://jarvis.nist.gov/. Our dataset can be used to identify stiff and flexible materials for industrial applications.

NM01.15.58 Hydrogen Storage in Ti Atoms Decorated Boron-Nitrogen Doped Graphene—Effects of Electric Field on Hydrogen Adsorption and Desorption Santhanamoorthi Nachimuthu and Jyh-Chiang Jiang; National Taiwan University of Science & Technology, Taipei, Taiwan.

In the last two decades, the significant efforts have been made to develop alternative energy sources instead of fossil fuels because of increasing CO2 emissions and the environmental impacts. Besides, hydrogen has been concerned to be an ideal clean energy carrier among the other renewable energy sources because of its environmental friendliness. However, some challenges have to be addressed before hydrogen will become a conventional and commonly available energy carrier. Carbon-based materials such as graphene and carbon nanotubes have been designed for hydrogen storage due to their large surface area, lightweight, and tunable properties. Recently, we proposed a new strategy in which we considered three pure transition metal (TM) atoms or/and a combination of two TM atoms and one alkali earth metal atom (AEM) with high, medium and low hydrogen adsorption energies. These different metal atoms are used to decorate the Boron doped graphene sheet (BDG) and investigated their performance towards hydrogen storage capacity through spillover mechanism using first-principles calculations. Our results indicate that the activation energies for H atom diffusion are much smaller, indicating that a fast H diffusion on this proposed surface can be achieved. These TM and AEM atoms decorated BDG surface can have the maximum hydrogen gravimetric capacity of 6.4% for double-sided adsorptions. To further achieve higher gravimetric density, in this study, we have considered Ti atoms decorated on the Boron and Nitrogen co-doped graphene surface (BNDG) because B–N pair is iso-electronic to the C–C pair. However, controlling the binding strength of metal atoms with that of the BNDG surface is an important issue in the application of hydrogen storage. The recent studies have shown that the binding strength between the metal atom and the substrate can be controlled by means of applying an external electric field. Thus, the effects of the external electric field, as well as the effects of applying point charges on the designed medium towards its hydrogen storage capacity, will be discussed. We have also explored the stability of the decoration of metal atoms on BNDG sheet at higher temperatures using molecular dynamics simulations.

NM01.15.59 Multifunctional Laser Induced Graphene Composite Surface Phu X. Luong, Kaichun Yang and James M. Tour; Rice University, Houston, Texas, United States.

Fabrication simplification and multi-functionalization are keys for universalization/popularization of current nanomaterials in many fields. Laser Induced Graphene (LIG) is one of the promising candidates in this topic by its one step production with laser ablation of commercial Polyimide (PI) Kapton film under ambient environment and many of its exploring applications.[1] However, LIG potential for realistic applications is limited by the PI substrate it attaches on and its weak robustness. Here, we present two facile methods to fabricate LIG composite (LIGC) compatible with diverse materials that are “Swiss army knife” for multi-purpose applications.

The first method is the materials infiltration. Herein, we are able to engineer the morphology of several LIGCS to superhydrophobic with contact angle > 160 degree. The LIGCS retain the conductivity of the LIG and is suitable for many Joule heating applications, including de-icing and thermal therapy. Stretchable and highly conductive LIGCS is used for resistive memory device substrate and strain sensor. Additionally, LIGCS in constructional materials also show anti-biofouling property.

The second method is mechanically pressing the LIG onto the material surface by sanding. The combination roughness induced by both sand paper and LIG result in a stable superhydrophobic composite surface. By this simple method, we have been able to produce a number of superhydrophobic surface on commercial polymer with roll-off contact angle down to less than 1 degree.

Keywords: laser induced graphene, nanocomposite, superhydrophobic, Joule heating, de-icing, thermal therapy, memory device, anti-biofouling.


NM01.15.60 Molecularly-Linked Gold Nanoparticle Films Across the Insulator-to-Metal Transition—From Hopping to Strong Electron Correlations Monique Teg and Al-Amin Dhirani; Univ of Toronto, Toronto, Ontario, Canada.

Strong electron-electron interactions are widely believed to play a key role in a range of remarkable phenomena such as high Tc superconductivity among others. Strongly correlated electrons are often described by the Hubbard model, which captures important gross features of phase diagrams of strongly correlated materials. However, open challenges include experimentally mapping correlated electron phenomena beyond those captured by the Hubbard model.

We use both film thickness and electrolyte gating to study a metal-insulator transition in a new class of strongly correlated material, namely, nanostructured materials, using 1,4-butanedithiol-linked Au nanoparticle films as an example. On the insulating side of the transition, we observe Efros-Shklovskii variable range hopping and a soft Coulomb gap, evidencing the importance of Coulomb barriers. On the metallic side of the transition, we observe signatures of strong disorder mediated electron-electron correlations. Films near the metal-insulator transition also reveal a zero-bias conductance peak, which we attribute to a resonance at the Fermi level predicted by the Hubbard and Anderson impurity models when electrons delocalize and experience strong Coulomb electron-electron interactions.

NM01.15.61 Biogas-Slurry Derived Mesoporous Carbon for Supercapacitor Applications—Harnessing Microorganisms to Circumvent Hydrothermal Treatment for Highly Porous Electrode Materials Ceril Kingondo1, Enock T. Kibona2 and Cecil King’ond1; 1Botswana International University of Science and Technology, Palapye, Botswana; 2Department of Physics, Mkwawa University College of Education, University of Dar es Salaam, Iringa, Tanzania, United Republic of.

Surface area, pore texture and pore distribution have been shown to have a strong influence on capacitance. Therefore, hydrothermal treatment (HT) of the most common carbon source, biomass, prior to carbonization and activation has recently received heightened interest owing to its ability to deliver high surface area carbon nanomaterials with remarkable pore texture via deconstruction of cellulose polymeric network in biomass. Nevertheless, hydrothermal strategies involve high pressure and temperature and thus expensive. This study reports on circumventing HT in preparation of the carbon materials with outstanding mesoporosity for supercapacitor electrodes by use of biogas slurry. The deconstruction of cellulose polymeric network in this case is achieved by bacteria while the carbon source is still in the biodigester for biogas generation. In the study, pore structure and surface chemistry have been modified by altering activation time, temperature and KOH/carbon mass ratio. Mesoporous carbon materials are successively developed as evidenced by type IV isotherms obtained in nitrogen sorption studies. The materials afford BET, micropore and mesopore surface area of 515, 350, and 165 m² g⁻¹, respectively as well as a narrow pore width distribution of 3-4.5 nm. X-ray photoelectron results confirms the presence of functional groups of oxygen and nitrogen in
the samples which facilitates the pseudocapacitance. The materials activated at 700 °C, 3:1 KOH to carbon mass ratio, and for 120 min exhibit high specific capacitance of 289 F g⁻¹ at a scan rate of 5 mV s⁻¹. Shortening activation time to 30 and 60 min increases specific capacitance to 163 and 182 F g⁻¹, in that order. Additionally, at 3:1 KOH to carbon mass ratio and 60 min activation time, specific capacitances of 170 and 210 F g⁻¹ at 600 and 800 °C, respectively are obtained. Moreover, specific capacitance increases with increasing the KOH to carbon mass ratio from 148 F g⁻¹ for 1:1 to 163 F g⁻¹ for 3:1 at 700 °C. Electrochemical impedance spectroscopy studies demonstrate that the materials have high conductivity. In addition; capacity retention of 96% after 20,000 cycles is attained at a scan rate of 30 mV s⁻¹. The study shows that high performance electrodes can be designed from biogas slurry thereby eliminating the need for HT to get electrode materials with high surface area and porosities from biomass.

NM01.15.62 Hierarchical Carbon Nanostructures for Energy-Efficient Water Purification Yuchen Liu, Shiren Wang and Zimeng Zhang; Texas A&M University, College Station, Texas, United States.

In this presentation, we demonstrate a hierarchical carbon nanostructures for energy-efficient water purification. Specifically, 2D graphene nanosheets were intercalated with zero-dimensional fullerenene nanocrystals, and a fixed interlayer spacing of ~1nm was achieved for tuning water passage. The resultant hybrids were stacked via epoxy adhesive and then the cross-sectional filtration of slaty water was investigated. The as-prepared GO/C60 membrane obtains a high water flux up to 10.85 L h⁻¹ m⁻² bar⁻¹ with a salty rejection of 89.66%, which is sufficient to purify brackish water into drinkable water. The energy consumption is as low as 0.775 KWh/L, more than 20-fold less than commercial desalination process. Such hierarchical GO/C60 membrane exhibits long-term stability, and thus provides a great potential for energy-efficient water desalination.

NM01.15.63 Molecular Detection at Ultra-Low Concentration Using Potential Gradient Traps and Interlayer Coupling of Few-Layers MoS2: Pavel San1, Dianjun Nandi2, Hiofan Hoi1 and Manisha Gupta2; 1Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada; 2Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Single molecule detection has played an important role in monitoring of health and environmental conditions. Health monitoring efficiency depends upon detection of an immune response to pathogen, cell mutation, etc. at its early stages or low concentration. Traditionally, solid state nanopores are fabricated using silicon nitride (Si3N4) membranes. But 20-50nm thick Si3N4 membranes makes fabrication and reproduction of 2-5nm pores difficult, hampering detection sensitivity and accuracy. 2D materials with interlayer van der Waals forces, are a good choice for fabricating monolayer thin membranes. Molybdenum disulphide (MoS2) with surface charge (0.024 C/m²) similar to Si3N4 (-0.02C/m²) slows translocation without pore blockage, and also improves resolution. In this work, the advantage of using few layers MoS2 over monolayer MoS2 for low-concentration label-free detection has been demonstrated. The strong interlayers coupling creates a potential gradient along the van der Waals separated MoS2 layers, since the different layers feel different electric potentials. This causes trapping and detraping of the phosphate groups of DNA with the Molybdenum atoms at the nanopore. The increased negative-positive charge interaction pull providing platform for effective capture and detection at very low molecular concentrations, without the usage of any external trapping mechanism.

Here, we have conducted simulation and experiments to compare the detection efficiency of Si3N4 and MoS2 nanopores for dilute samples. We simulated translocation of nucleotide homopolymers in COMSOL Multiphysics. Our simulations show a 30-fold conductance improvement and three times lowering of translocation speed for a 5nm diameter pore on 4 layers (2.6nm) MoS2 compared to 50nm thick Si3N4, indicating a clear sensitivity improvement. Translocation experiments were conducted using 4E-4% IDT-ACTB1 and 60 mM KCl with Si3N4 and MoS2 pores, fabricated by photolithography, etching and TEM drilling. Here the concentration used for detection (4E-4%) implies a 10-fold sensitivity improvement when compared with detection demonstrated in literature (0.1-1%). MoS2 is seen to detect 102 molecules per minute whereas Si3N4 detected 20 molecules per minute at the ultra-low concentration without any external trapping mechanism. Moreover, the greatest dwell times obtained in literature for DNA sequencing using 100 mM KCl concentration is as low as 0.1-1 ms whereas our dwell times as large as 1100 ms were obtained in our study. MoS2 (0.3-1.4nA) demonstrates a significantly higher average blockade current as compared to Si3N4 (0.08-0.8nA). Simulation and experimental data for all nucleotides will be presented to show inherent capacity of few-layers MoS2 in improving molecular detection efficiency.

References

NM01.15.64 Complementary Dual Channel Gas Sensor Devices Based on Role-Allocated Heterostructure Garam Bae1,2, Woosook Song1, Sang Myung1, Jongsun Lim1, Sun Sook Lee1, Chong-yun Park1 and Ki-Seok An1; 1Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of).

Intriguing electronic properties of graphene related with massless Dirac Fermions have enabled the applications in highly sensitive gas sensors. However, it is widely recognized that the poor gas desorption behavior because gas adsorption occurs defective sites of graphene only. To overcome this insurmountable hurdle, we rationally designed hybrid films including ZnO thin films and CVD-grown graphene in order to combine advantages of ZnO thin films with reliable gas adsorption/desorption related with their gas reaction mechanism and graphene with extremely high gas sensitivity originated from its exceptional electronic structure. The complementary dual channel gas sensor based on roll-allocated graphene-ZnO heterostructures, in which ZnO acts as a gas adsorption channel and graphene plays a role as carrier conducting path, was fabricated by combining atomic layer deposition, chemical vapor deposition, and polymer-assisted wet transfer techniques. The effects of ZnO top-layer thickness on the gas sensing properties of the hybrid films were explored. As a result, NO2 sensitivity improvement of the optimized hybrid film-based gas sensor was achieved unambiguously as ~40 times higher than that of graphene-based gas sensors. Additionally, we systematically explored the electrical interaction between thickness-controlled ZnO thin films and graphene before and after gas adsorption to explain the correlation between charge transfer and gas sensing properties.

NM01.15.65 Dispersion Control of Reduced Graphene Oxide and Application to Inverted Organic Solar Cells as a Hole Transport Layer Jong-Jin Park1,2, Jin-Mun Yoon1,2, Kyoungine Hwang1, Yeon-Ju Kim1, YeonSu Choi1 and Dong-Yu Kim1; 1Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); 2Korea Atomic Energy Research Institute, Jeongeup, Korea (the Republic of).

Graphene-based materials have received tremendous attention due to their excellent mechanical and electrical properties. Among them, graphene oxide (GO), which chemically exfoliated from graphite, is possible to solution process in aqueous solutions owing to having oxygen-containing functional groups on its basal plane and edges. Moreover, they have active sites for reduction of GO and covalent functionalization of GO with small organic molecules or inorganic nanomaterials. For these reasons, GO have been researched in many applications such as polymer composites, biomedical, and energy-related
materials. In particular, reduced graphene oxide (rGO) reduced by functionalized hydrazine from GO is promising alternative material to poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) as hole transport layer (HTL) in organic solar cells because it allowed the controllability of electronic properties through versatile functionalization and can improve the long-term stability of solar cells. However, rGO is difficult to apply in inverted organic solar cells because of limited dispersity in alcohol based solvent such as 2-propanol (IPA). The rGO is usually dispersed in dimethylformamide (DMF), which melt the organic active layer. Therefore, more research is required about controlling the dispersibility of rGO while maintaining their electrical properties in order that rGO apply to inverted organic solar cells as a HTL via solution process. In this study, we introduced trifluoromethoxy group on the rGO surface (FMrGO) for controlling the dispersibility of rGO while maintaining their electrical properties. FMrGO is well dispersed in IPA and 2-ethoxyethanol due to the flexible methoxy groups. The structural, optical, and thermal properties of FMrGO was characterized by Infrared spectroscopy, EA, XPS, UV-vis spectroscopy and TGA and their work function was estimated by UPS. Finally, we introduced the FMrGO film as a HTL on the active film through solution process and investigated the effect of FMrGO on device performance and long-term stability of inverted organic solar cells.

NM01.15.66
Self-Powered Motion Sensor Using Flow-Less CNT Sheet Nanogenerator Hyelynn Song, Usang Jeong and Yonghyup Kim; Seoul National University, Seoul, Korea (the Republic of).

Carbon nanotube (CNT), which has one-dimensional atomic structure, is highly accessible to external stimuli because of its high surface area to volume ratio. Thus, electronic configuration of CNT can be strongly influenced by tiny perturbations. The unique interaction between CNT and its surrounding stimuli has been of particular interest over the past decade. A thorough understanding of the interaction enables to develop a wide range of applications, such electrical bio/chemical sensors and actuators with unrivaled performance. Previous researches proved that CNT can generate electrical energy by converting mechanical energy of fluid into electrical energy. The transfer of momentum from the molecules in flowing fluid to the acoustic phonons in the CNT is induced, which in turn drag free charge carriers in the CNT. The driving of free carriers generates a potential difference along the CNT length, but this phenomenon is only realized in low dimensional nano carbon structures. The ability of generating electrical power can be enhanced in highly aligned structures of nanomaterial along the flow direction because this structural characteristic can decrease scattering of dragged charge carriers.

In this work, we investigated the effect of charge carrier drag in CNT by using more intuitive way of electrostatic induction. A highly aligned, free-standing structure of CNT sheet is used to enhance the charge dragging effect as well as to minimize peripheral influences from a substrate. Up to hundreds of microvolt can be generated, it is affected by sweeping speed, inter-distance between charged object and nanotube sheet, surface charge and number of nanotube sheet layers. Simple fabrication method of series connection is the most powerful aspect of continuously drawable nanotube sheet, which is simply completed by one-step winding of CNT sheet on the polyethylene terephthalate (PET)/copper foil/PET laminated substrate. As a practical demonstration of the CNT device, simple fabrication method of series connection is the most powerful aspect of continuously drawable nanotube sheet, which is simply completed by one-step winding of CNT sheet on the polyethylene terephthalate (PET)/copper foil/PET laminated substrate. As a practical demonstration of the CNT device, we have demonstrated CNT sheet based self-powered motion sensor for tracing finger movements. Coulombic interaction between finger and free charge carriers in CNT sheet induces efficient charge carrier transfer via electrostatic attractive force. Effective motion sensing for moving direction and speed is possible by detecting its electrical output. Motion sensing and energy harvesting are simultaneously available, thus external power source is not needed because of its ability to provide electrical power by itself. This fundamental studies has great significance in dry-state energy harvesting using nano carbon material which is quietly distinct from previously reported liquid-based energy harvesting studies. Furthermore, suggested self-powered motion sensor can read finger movements (just like a finger commend in a smart phone), requiring no need of touch panels.

NM01.15.67
Enhancement of Electrical Conductivity of Carbon Nanotube Fibers by Nitrogen Doping with Plasma Treatment Seunghi Hong1, Bon-Cheol Ku1, Yoong Ahn Kim2 and Jun Yeon Hwang1; 1Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Wanju, Korea (the Republic of); 2Department of Polymer Engineering, Graduate School, Chonnam National University, Gwangju, Korea (the Republic of).

Carbon nanotube(CNT) fiber has been substantially realizing the outstanding property of the individual CNT (high strength, light weight, electrical conductivity...) in bulk materials. Due to superb intrinsic properties, CNT fibers are promising for alternative of metal wire. However, there is still challenging for commercialization of CNT fibers. One of major difficulties is CNT-CNT contact resistance, which decreases the electrical conductivity of CNT fibers. To overcome this drawback, nitrogen doping is an effective way to enhance the intrinsic conductivity of CNT fibers by increasing electron carrier density. As for typical doping process, not only quaternary N(NQ) electron donor but also pyridinic(Npy) and pyrrolic(NPyrr) nitrogen types are achievable. Since NQ and Npy, localize electrons resulting in increasing the electrical resistance, controlling the doping site of nitrogen is critical issue. In this study, NQ and Npy types were selectively removed by acidic reduction process without oxidation. The acid treated CNTs showed liquid crystalline behaviors, which can be directly spinning of CNT fibers without complex process. We have verified the improved electrical properties of CNT fiber related with bonding types of nitrogen in CNT fibers.

NM01.15.68

Perfect absorbers have many application in different fields including photovoltaic, antireflective rular absorption coatings for defence, energy harvesting and emissivity control. Here, we design and fabricate a near perfect optical broadband absorber, having absorption capacity of 99.4% from 300 to 2000 nm wavelength range. Etched Silicon wafer is used as base layer to fabricate multilayered optically graded assembly, while carbon nano tubes layer used as a top layer for impedance matching. Subsequent layers are selected as per increasing refractive index and varying micro/nano features for efficient light trapping. Less than 1% of reflectivity in entire range up to 50° beam angle has been observed. Moreover multilayered assembly shows contact angle of more than 160° with roll-off angle of less than 5° which showed that it is not only a near perfect absorber but also a self-cleaning superhydrophobic surface. Conclusionly, the properties of multilayered optically graded assembly impacts attractive applications of this superabsorber in the field of photovoltaic.

NM01.15.69
Spatially Resolved Solid-State Reduction of Graphene Oxide Thin Films for Anti-Fuses Maica Morant-Miñana1, Klaus Mullen1, Dago De Leuven2 and Karmel Asadi1; 1Max-Planck Institute for Polymer Research, Mainz, Germany; 2CIC energiGUNE, Miñano, Spain; 3Delft University of Technology, Delft, Netherlands.

The current paradigms at both the industrial and research level produce reduced graphene oxide (rGO), an imperfect form of graphene, only in the bulk form. For a wide range of applications, from microelectronics to water permeation, spatially resolved and controlled reduction of GO in (thin-) film is needed. Such applications require a paradigm shift in the reduction process, which should be free from intentionally used auxiliaries such as electrolytes and high temperatures.
Reestablishment of electrical conductivity in GO, is (partially) obtained by reduction through high temperature treatment in a reducing atmosphere, or using strongly reducing chemicals or electrolytic processes. The reduction methods are suited for bulk graphene oxide. Spatially resolved reduction of thin films of graphene oxide is important for wide range of applications such as in microelectronics, where an electrolyte-free, room temperature reduction process is needed. We present spatially resolved solid-state reduction of graphene oxide thin films. We show that the reduction mechanism is based on electrolysis of water that is adsorbed on the graphene oxide thin film. The RGO is obtained at room temperature with spatial resolution simply by application of voltage. The reduced graphene oxide thin-films show sheet resistance of only several kOhm, with weak temperature dependence. Graphene oxide can be produced on a large scale and processed using low-cost solution coating techniques. Spatially resolved reestablishment of conductivity in GO can be used in electrically controlled water permatation or in micro- and nanoelectronic applications for instance as an anti-fuses.

NM01.15.70
Study of the Vibrational Properties of Linear Carbon Chains Encapsulated by CNTs at Low Temperature Nathalia L. Coim1, Wellington Q. Neves2, Paulo T. Araujo2, Alexandre R. Paschoal2 and Antonio G. Souza Filho1; 1Physical, Univeersidade federal do Ceará, Fortaleza, Brazil; 2Instituto Federal de Educação, Ciência e Tecnologia do Ceará - IFECE, FORTALEZA, Brazil; 3Physics, The University of Alabama, Tuscaloosa, Alabama, United States.

Linear carbon chains, also known as carbones, are essentially one-dimensional (1D) systems that present carbon sp hybridization. The research involving linear carbon chains has been a hot topic in recent years mostly due to their unique properties and potential for technological applications. These chains are highly unstable under ambient conditions, but the internal volume of the nanotubes offers ideal conditions for stabilizing such systems. Techniques of encapsulation by DCWNTs and MWNTs have been successful to produce long linear carbon chains with lengths reaching several hundreds of nanometers. In this work, a systematic investigation has been conducted on linear chains of carbon encapsulated by double- (Cn@DWCNT) and multi-walled carbon nanotubes (Cn@MWCNT). Temperature studies in such materials are important for considering possible applications under extreme conditions (e.g. space and nuclear reactors). Our preliminary studies using low temperature Raman spectroscopy investigations of Cn@MWCNT-Bulk (300K at 20K) showed that the band frequency of the chains (~1,800 cm⁻¹) increased when the temperature was reduced. However the results seem to indicate an anomaly in the frequency behavior for temperatures below 60K, in which a decrease of the Raman frequency takes place with decreasing the temperature. We also observed that the frequency variations are reversible in the range of temperatures from 4K to 300K. To investigate this effect in detail, these studies will be conducted at the individual level. In other words, both Cn@DWCNTs and Cn@MWCNTs will be isolated and then investigated under low temperature. Dispersion of these materials has been successfully attained and isolated species have been confirmed by Atomic Force microscopy (AFM) measurements and Raman spectral features.

References

NM01.15.72

Graphene, a one-atom-thick sheet of carbon atoms arranged in a honeycomb-like pattern lattice, has attracted much attention owing to its potential applications in the fields of electricity, conductivity, energy generation, batteries. Intensive recent studies report the wetting transparency of graphene, suggesting that the wettability of graphene is partially governed by the underlying substrate and is more hydrophobic with increasing the number of graphene layers. This infers that its surface energy is decreased with increasing the number of graphene layers. Amongst those studies, the static contact angle measurement is a highly employed method for characterizing the graphene surface wettability; however, this technique requires large scale surface coverage of graphene to contact the milliliter size of water droplet at the solid-liquid interface. This is rather challenging since one cannot precisely control the number of graphene layers at the contact line. This challenge is often ignored despite being the origin of the uncertainty in the measurements that have led to contradictory interpretations. In order to shade light to this controversy, we combine bimodal atomic force microscopy [1] and micro-Raman spectroscopy to measure the surface energy of the graphene surface on different substrates. It is well-known that the number of graphene layers can be determined by the ratio of 2D to G peak in the Raman spectra. Therefore, the graphene sample is fabricated by using a designed two-step chemical vapor deposition method, which has large enough area of monolayer, bilayer and multilayer of graphene on the substrate, respectively. This deposition enables us to precisely measure the same area of graphene sample by using AFM and micro-Raman spectroscopy. Our experimental results show that in contradiction with graphene wettability transparency theory, the derived graphene surface energy increases with increasing the number of graphene layers. We also use density functional theory to directly predict the surface wettability of graphene on different substrate based on [2] and obtain results that qualitatively agree with our AFM experimental characterization.


NM01.15.71
Enhancing Thermal Conductivity and Mechanical Performance of PLA/PBAT Blends with Boron Nitride and Graphene Xianghao Zuo1, Yuan Xue1, Frederick Nitta2, Jinghan Tang3, Vicki Xu4 and Miriam Rafailovich1; 1Stony Brook University, Stony Brook, New York, United States; 2Henry M. Gunn High School, Palo Alto, California, United States; 3Mater Dei High School, Santa Ana, California, United States; 4Mission San Jose High School, Fremont, California, United States.

Thermal management is critical to the continually growing electronics industry to prevent devices from overheating and losing their functionality. As low-cost, lightweight, and highly versatile materials, polymers exhibit great potential for heat exchange applications, but their low thermal conductivity is a barrier to their effectiveness. Additive fillers are usually added into polymers to help enhancing the thermal conductivity.

In this study, we investigated the thermal conductivity of blends of PLA (polylactic acid) and PBAT (polybutylene adipate terephthalate) with graphene nanoplatelets (GNPs) and hexagonal boron nitride (hBN). It is hypothesized that the thermal conductivity of the PLA/PBAT nanocomposite would be elevated when adding the fillers compared to neat polymer blends. Contact angle measurements between polymer droplets on hBN and GNP layers deposited on a silicon wafers were used to determine the polymers’ relative affinities for the fillers. The calculation of the word of adhesion between fillers and polymers indicates that both hBN and GNP exhibited more affinity for the PBAT phase than the PLA phase, which means the fillers would be interspersed in the PBAT phase. PLA/PBAT blends with various concentrations of hBN powder and GNP were blended at 180 using a twin-screw mixer at 150 rpm. The thermal conductivity of PLA/PBAT and PBAT blends with hBN alone was tested at the beginning. Slow increase in thermal conductivity with increasing weight fraction of hBN was obtained. To better enhance the thermal conductivity, considering that we have demonstrated that with the larger size of the fillers which meet the size of the domain in the
polymer matrix, they will have a better arrangement, we decided to apply Graphene H-1-5 in the blends to make some new attempts. The results show that as the GNP content of the nanocomposite increased relative to the hBN content, the thermal conductivity increased significantly. Then, the samples were molded into different sizes to test the impact and tensile properties. The mechanical data indicates that although the combination of hBN and Graphene can help increasing the thermal conductivity significantly, it is difficult to maintain the mechanical properties. Therefore, to enhance the thermal conductivity of the polymer blends with relatively high mechanical performance is a new challenge. We did mechanical tests separately with PBAT/PLA/hBN and PBAT/PLA/GNPs and found that hBN can better maintain the mechanical properties. Thus, we tried different ratios of hBN and graphene and kept the total amount of the filler at 30 wt%. The results show that even 3% of hBN can help maintaining the impact toughness at 85.62 J/m, which is pretty high value that meets the demand for most of the applications.

SESSION NM01.15.73
A Novel Non-Enzymatic PEDOT:PSS/GO/MnO2 Based Biosensor for Hydrogen Peroxide Detection in Biological Samples Vedashree Sirdeshmukh1, Shreshita Mishra1, Indrayani Kadam1 and Amap A. Kale1; 1College of Engineering Pune, Pune, India; 2Applied Sciences, College of Engineering Pune (T.OEP), Pune, India.

Hydrogen Peroxide (H2O2) is a well-known reactive oxygen species produced in various biological phenomena. In various pathological and physiological conditions, higher concentrations of H2O2 can cause lipid peroxidation, DNA base modification, protein degradation etc. H2O2 present in quantities of about 20-50 µM or more can have deleterious effects as it can easily dissolve in aqueous solutions and penetrate biological membranes easily. Hence, sensitive and selective detection of H2O2 is important under physiological conditions.

In this work, we report on a non-enzymatic electrochemical method for the facile and sensitive detection of H2O2. We explored the approach of conducting polymer-nanocomposite as efficient transducer platform. We synthesized three-phase composite polymer system of PEDOT:PSS/GO/MnO2, comprising poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS), graphene oxide (GO) and manganese dioxide (MnO2). On being exposed to H2O2, MnO2 undergoes a redox reaction which is responsible for the sensing ability of this material. The composite was prepared using the conventional solution mixing method and then used to modify screen printed electrodes. The physicochemical characterization was carried out using Scanning Electron Microscopy, UV-Visible Spectroscopy, Raman Spectroscopy and Fourier Transform Infrared Spectroscopy. Cyclic Voltammetry results showed that the nanocomposite showed high electrochemical activity for the detection of hydrogen peroxide (H2O2) in alkaline medium. The PEDOT/GO/ MnO2 based electrode exhibits high sensitivity and selectivity for electrochemical detection of H2O2 with a sensitivity of 0.5µM. The present study demonstrates that such a novel nanocomposite is promising for fabrication of non-enzymatic H2O2 biosensors. This method can further be explored for Point-Of-Care detection.

SESSION NM01.16.01
From Energy Harvesting to Living Plants—Concepts in Biosensing and Energy Conversion Using Carbon Nanomaterials Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Our lab at MIT has been interested in how the 1D and 2D electronic structures of carbon nanotubes and graphene respectively can be utilized to advance new concepts in molecular detection, as well as energy generation. By taking advantage of the exceptional electronic properties of these nano-structures, we continue to discover potential application spaces where carbon can play an important role. For example, we have pioneered a novel technique called Corona Phase Molecular Recognition, or CoPhMoRe, for discovering synthetic, heteropolymer corona phases that form molecular recognition sites at the nanoparticle interface. By screening libraries of synthetic heteropolymers chemically adsorbed onto single-walled carbon nanotubes (SWNT), we have engineered new optical biosensors that exhibit high selective recognition for bio molecules, such as riboflavin, L-thyroxine, dopamine, nitric oxide, sugar alcohols, estradiol, and fibrinogen. These results have significant potential for using SWNT-based sensors to interface to biological systems, allowing monitoring pathways at the sub-cellular, cellular, tissue, and whole-animal scale. I will also highlight our recent efforts in initiating an endeavor we call “Plant Nanobionics”. We use these techniques to deliver and transport functional nanoparticles into living plants to grant them non-native functions. Our goal is to engineer plants to take over many of the functions now performed by electrical devices. I will introduce the nanoparticle co-localization mechanism in a plant, and highlight some of our recent nanobiotic plant prototypes including a light-emitting plant. Lastly, I will briefly describe several applications of carbon nanomaterials in the energy space that have come out of our lab. There is a pressing need to find alternatives to conventional energy generation techniques, specifically those that rely on elements in finite global supply. We introduce Asymmetric Doping Cells (ADC), which convert chemical potential to electrical energy by means of spatially selective doping along a nanostructured conduit or particle. These ADCs have applications to energy harvesting from aqueous and organic solvents, as well as electro-catalysis for chemical synthesis. An inverse length-scaling of the maximum power as L−1.03 that creates specific powers as large as 30.0 kW kg−1 highlights the potential for microscale energy generation. We also introduce carbon materials for what we call thermal resonators that make use of thermal storage elements with high effusivity – the product of the thermal conductivity and heat capacity to the one half power. Thermal resonators base on carbon can harvest energy indefinitely from ambient thermal fluctuations of various frequencies, opening new possibilities for remote applications.

SESSION NM01.16.02
Overcoming Efficiency Limits of Carbon Nanotube-Laminated Metal-Free Perovskite Solar Cells Using 3D/2D FAPbI3 Will Jones1, Jin-Wook Lee2, Esko Kauppinen3, Yang Yang2, Yutaka Matsuo1, 4 and Maruyama Shigeo1; 1The University of Tokyo, Minato-ku, Japan; 2University of California, Los Angeles, Los Angeles, California, United States; 3Aalto University, Aalto, Finland; 4USTC, Hefei, China.

Perovskite solar cells (PSCs) have progressed remarkably through a heated power conversion efficiency (PCE) race. With a surge of research efforts, the certified PCE of the lab scale PSCs increased to 22.7% for last 5 years. Now the research efforts are being focused on enhancing the durability of the devices and reducing the production cost. PSCs typically require a metal electrode is thermally evaporated on top to serve as a counter electrode. These top metal electrodes, however, are known to substantially increase the process and material cost as expensive gold or silver layers are deposited under high vacuum. Furthermore, the metal electrodes are found to be not robust enough to render long-term stability of the PSCs as the metal ions migrate into the bulk of the device under an operational condition to react with the active materials, thus degrading the device.

As an alternative to the metal electrodes, researchers have incorporated single-walled carbon nanotubes (CNTs) into the PSC system. The CNT is a
favorable electrode material, owing to its hydrophobic nature, earth-abundance, and mechanical robustness. The application of CNT realizes CNT-based PSCs with good stability and versatility. Among the reported CNT-used PSC devices, aerosol-synthesized CNT top electrode (or back electrode) replacing metals in PSCs has shown the most promising potential. The application of CNT as the top electrode substantially enhances the stability of PSCs by removing the ion migration, and drastically reduces the fabrication cost as it can be easily deposited onto devices by a simple mechanical transfer. Despite such advantages, there are three factors limiting the PCE of the CNT top electrode-based PSCs that need to be addressed: 1) the work function of the CNT does not align with the perovskite, leading to loss in potential 2) CNT top electrode is less conductive than the metal counterparts, limiting the fill factor of the devices 3) the CNT back electrode is not reflective that the devices cannot maximize the light harvesting efficiency. In this work, we addressed those three issues by engineering CNT electrode and photo-active layer. We tuned the work function of CNT electrodes and increased their conductivity by using a vapor-assisted doping of trifluoromethanesulfonic acid (TFMS). Furthermore, by incorporation of Cs-based 2D perovskite-added low bandgap formamidinium perovskite, we enabled the harvesting of long-wavelength light, enhancing the photocurrent of the devices. By combining those technologies all into one device system, CNT electrode-based PSCs produced a PCE of 17.6% with a $J_{SC}$ of 24.21 mA cm$^{-2}$, $V_{OC}$ of 1.005 V, and FF of 0.72. The obtained PCE is the highest among the values reported from CNT top electrode-based PSCs. Moreover, the resulting CNT-PSCs exhibited higher high-temperature operational stability than those of the devices based on metal electrodes as well as conventional CNT electrodes.

9:15 AM NM01.16.03
Electricity Generation from Interface Between Flowing Water and Graphene 
Takeru Okada1, Golap Kalita2, Masaki Tanemura2, Ichiro Yamashita2, M Meyyappan1 and Seiji Samukawa1; 1Tohoku University, Sendai, Japan; 2Nagoya Institute of Technology, Nagoya, Japan; 3Osaka University, Osaka, Japan; 4NASA Ames Research Center, Moffett Field, California, United States.

Since the global energy demands are rapidly increasing, energy harvesting from the environment has received much attention. Environmental energy sources such as sunlight, wind, vibration, heat, and flow have been exploited to various extents for electricity generation. Among them, water flow exists in various forms and has potential for developing electricity generators. The interface between flowing water and graphene also shows potential of electricity generation. The energy harvesting by flowing water along the interface of graphene has been studied. The mechanisms proposed to date are still not deterministic, however, surface conditions are key factors for the understanding of the physical mechanism and maximizing the performance. The surface conditions include electric potential at the phase interface and wettability of graphene, both of which can be tuned by heteroatom doping. In this paper, the role of the surface condition of graphene on flow-induced electricity generation is investigated by heteroatom doping.

Nitrogen-doped graphene was used to investigate the role of surface condition on electricity generation. Characterization of the nitrogen doped graphene was carried out by x-ray photoelectron spectroscopy and Raman spectroscopy. In our typical experiment condition, at least 70 % of the doped nitrogen was graphic nitrogen. Atomic concentration of nitrogen was approximately 1 %. The electricity was studied with transferred graphene and deionized (DI) water droplets by manually dropping the droplets (0.1 ml). Pristine graphene shows approximately 80 mV and the highest voltage from nitrogen-doped graphene was approximately 380 mV, thus more than 3 times higher voltage generation was observed.

The enhancement of voltage generation by nitrogen doping is explained as follows. The electronic state of the nitrogen-doped sites is considered to have an important role. Nitrogen doping of carbon in various applications acts as an electron donor by providing the unshared electron pair of nitrogen in graphene. The local charge of graphic nitrogen is positive and that of the surrounding carbon atoms is negative. This is explained by the electron transfer from nitrogen atom. The inside of the droplet sitting on top of graphene is affected by the negative charge on the graphene surface, leading to potential formation at the interface. The induced negative charge reduces electric double layer at the interface, resulting in the formation of steep potential [1].

We have investigated the effect of graphene doping on flow-induced power generation between graphene and water interface and found that the nitrogen-doped graphene shows enhancement of power generation. The surface charge of the nitrogen-doped graphene reduces the electric double layer thickness, resulting in the formation of a steep potential, which contributes to higher power generation.


9:30 AM NN01.16.04
Advancement of High Conductivity Carbon Conductors Brian Landi; Rochester Institute of Technology, Rochester, New York, United States.

Macroscopic assemblies of carbon nanotubes (CNTs) in wire format have been proposed for a variety of applications including power and data transmission for both aerospace and terrestrial scenarios. Wires fabricated from CNTs have demonstrated superior flexure tolerance, weight savings, and corrosion resistance over their traditionally used metal counterparts. Current research is focused on translating the exceptional electrical properties of individual CNTs to bulk CNT wires through fabrication technologies like extrusion and densification, chemical doping, and metal-incorporated hybrids. In this talk, a summary of CNT conductors being advanced from high-purity laser-vaporized single wall carbon nanotubes (SCWNTs) as well as commercial CNT materials will be provided. Acid dispersion and extrusion of SCWNTs into a coagulant bath has been used to fabricate wires, with the coagulation dynamics shown to govern the resulting wire structure leading to electrical conductivities of 5-11 MS/m. Alternative approaches to enhance CNT electrical conductivity have been demonstrated using IBR chemical doping whereby low-dipole moment solvent systems favor the IBR-CNT interaction over the IBr-solvent and the solvent-CNT interactions. Recent work has also utilized densification and chemical doping with KAuBr4 to improve the conductivity of commercially scaled CNT yarns by 6x, while increasing the current density at failure by 67% to 35 MA/m2 in air. The thermal stability of KAuBr4 is proposed to provide the greater electrical stability at elevated current levels. Lastly, site-selective copper nanometal seeding through chemical vapor deposition (CVD) is demonstrated as a viable method in concert with solution electodeposition of bulk Cu to enhance the electrical conductivity of a low-density CNT rope. A Cu-CNT hybrid conductor has achieved a specific conductivity of 5632 Sm2/kg and electrical conductivity of 28.1 MS/m. A summary of high-current behavior and limitations to the current carrying capacity of these wires in air due to oxidative failure will be presented. Maximum current densities for SWCNT wires in a helium environment exceed fuse-law behavior for aluminum wires of equivalent diameter. The progress and opportunities for continued advancement of carbon conductors will be highlighted.

10:30 AM NN01.16.05
Tailoring Electronic Structure of SWCNTs for Transparent and Conductive Film Applications Alexey Tsapenko1, Daria Kopylova1, Alena Alekseeva2, Fedor Fedorov1, Evgenia Gilshetyn1, Vsevolod Iakovlev1, Pramod Rajanna1 and Albert Nasibulin1, 2; 1Skolkovo Institute of Science and Technology, Moscow, Russian Federation; 2Aalto University, Espoo, Finland.

Single-walled carbon nanotubes (SWCNTs) are among the strongest candidates for the replacement of commonly used transparent and conductive films (TCFs) based on doped metal oxides, such as indium tin oxide (ITO). SWCNTs possess unique multifunctional nature, which is based on their outstanding combination of mechanical strength and flexibility, chemical stability, exceptional electrical conductivity and optical properties [1]. However, to fully utilize these properties in modern transparent electrode applications, SWCNT-based TCFs have to demonstrate the optoelectronic performance at the level of high-end ITO-based TCFs. This has not been achieved for SWCNT films yet and as a result limit their practical usage. Using gold chloride as the most effective dopant for the SWCNTs, we improve their optoelectrical characteristics by optimizing the doping solvent and
Carbon nanotubes are widely regarded as very promising heat conductors. Although that is certainly true for individual carbon nanotubes [1-3], the situation is not that simple for carbon nanotube networks [4,5]. The way the heat is transported through the material is highly dependent on the carbon nanotube alignment, length, purity and other parameters. In fact, the influence is so strong that the spectrum of reported thermal conductivities for carbon nanotube networks ranges from thousands or hundreds of W/mK down to values lower than unity. In this contribution, we would like to show how careful surface modification enabled us to tune the thermal conductivity of the material. Free-standing carbon nanotube films of different composition and microstructure were manufactured and their thermal properties were measured by the previously reported method [6]. The results show a big potential of carbon nanostructures for a wide range of thermal management applications.

References:
We also realized differential amplifiers on a flexible plastic film. Bottom-gate CNT TFTs with purified semiconducting CNTs were used as the active
of capacitance-voltage characteristic was also built by considering the non-quasi-static effect in the Mayer model. CNT-based analog or analog/digital
charge equation in weak inversion characteristics was modified. The proposed model well expresses the output characteristics. The frequency dependence
water sensory and easy to be knitted into textiles. The water-polar-electrode-bridged mechanism, light-emitting performance and water sensory properties
Here, we describe and demonstrate light-emitting fibers based on carbon nanotube yarns with a unique planar device concept. The light-emitting fibers are
improvements in light-emitting elements, like fibers and textiles that function as information displays or provide fashionable effects in clothing, sensors
applications, including wearable electronics, implantable devices and sensory skins. Various applications in soft electronics could benefit from
transport properties of the DEP assembled devices will also be discussed.

Device modelling is indispensable for circuit design. We built the RC-ladder device model based on the charge based model for CNT TFTs, where a
correction of pinch off condition was taken into account, considering the contact resistances between CNTTs. In order to fit the subthreshold current, the
charge equation in weak inversion characteristics was modified. The proposed model well expresses the output characteristics. The frequency dependence
Wearable sensor devices have the potential to revolutionize preventive medical care and health promotion technologies. Carbon nanotube (CNT) thin films
are promising electronic materials for transistors and integrated circuits [1-3], biosensors [4,5], and other passive components to build flexible and
stretchable devices with excellent wearability and performance. Recently, high-yield and reproducible fabrication of CNT TFTs have become possible by
using purified semiconducting CNTs, leading extensive study on circuit applications. An integration of analog circuits with a sensor is essential for
wearable sensor devices to amplify the sensing signal as preventing external noise. A differential amplifier is a fundamental analog amplification circuit
used for various sensor devices. In this work, we are focusing on the analog circuit application of CNT TFTs. To design CNT-based analog circuits, circuit
simulation tools have been developed with a precise device model which has been built on the basis of electrical characterizations of CNT TFTs. We have
realized differential amplifiers on a flexible and transparent plastic film.
Device modelling is indispensable for circuit design. We built the RC-ladder device model based on the charge based model for CNT TFTs, where a
correction of pinch off condition was taken into account, considering the contact resistances between CNTTs. In order to fit the subthreshold current, the
cut-off frequency was 210 kHz.

Acknowledgments: The semiconducting CNTs were provided by TASC. This work was partially supported by JST/CREST.

References
Conventional protective garments are passive protection systems that sacrifice breathability (i.e. inhibit water vapor transport) to prevent exposure to hazardous agents. This trade-off leads to overheating in extended wear of protective clothing and severely limits the duration of their active use. For in-the-field personnel protection from chemical and biological (CB) agents, smart dynamic materials are highly desirable that exhibit a reversible, CB-triggered, rapid transition from a breathable state to a protective state. Materials of this type are expected to be particularly effective in mitigating physiological burden because a less breathable but protective state can be actuated locally and only when needed.

To achieve adaptive protection and simultaneous thermal comfort, we have developed a chemical threat responsive material based on a surface-functionalized carbon-nanotube (CNT)-membrane, in which vertically-aligned CNTs function as the only pores in a polymeric barrier film. Upon exposure to a chemical warfare agent (CWA), responsive polymers grafted at the membrane surface collapse and close the CNT pore entrance to CWA permeation, thus enabling the membrane to switch from a highly breathable state to a protective state.

To demonstrate this concept, we first fabricated membranes with sub 5-nm CNT pores and quantified their breathability and rejection properties before functionalization with CWA-responsive polymers. Our results show that these membranes provide MVTR up to 11,000 gr/m²/day, thus exceeding state-of-art breathable fabrics (eVent, GoreTex, etc.) even if the moisture conductive pores are only a few nm wide. Measured water-vapor permeability in 1.9-nm CNT channels under a relative humidity gradient is ~100 times larger than Knudsen diffusion prediction, and this flow enhancement decreases for larger diameter tubes. Complete rejection of 3-nm charged dyes, 5-nm uncharged gold nanoparticles, and ~40-60-nm Dengue virus from aqueous solutions during filtration tests demonstrate that our CNT membranes provide a high degree of protection from bio-threats by size exclusion.

Then, we covalently grafted actuating polymers responsive to G-agent simulants to the surface of these CNT membranes. Upon exposure to simulants, these membranes switch from a breathable state with MVTR>4,000 gr/m²/day to a protective state with MVTR>1,000 gr/m²/day. Permeation tests reveal that simulant transport is reduced by 1-2 orders of magnitude in the protective state. Finally, we demonstrated that a simple base treatment reopens the CNT pores effectively and that regenerated membranes can be re-used for multiple cycles without performance loss.
Plasma Functionalized Defected Single-Walled Carbon Nanotubes as Promising Material for Gas Sensing Application

Alena A. Alekseeva¹, Fedor S. Fedorov¹, Daria S. Kopylova¹, Stanislav Evlashin¹, Anton Anisimov² and Albert Nasibulin¹; ¹Skolkovo Institute of Science and Technology, Moscow, Russian Federation; ²Canatu, Moscow, Finland.

Mobile gas sensors operating at room temperature with low power consumption, high sensitivity and selectivity are required in many industries as well as in everyday life namely for detecting explosive, combustible and toxic gases, food and air quality monitoring. The main element of the gas sensor is its’ sensitive material which determines sensors’ sensitivity, selectivity, response time and signal recovery, operation temperature and stability. Single-walled carbon nanotubes (SWCNTs) is a unique material for gas sensors application. Coupled with chemical, thermal and mechanical stability, SWCNTs have large specific surface area with all carbon atoms located on their surface making them exceptionally sensitive for adsorption of gases at room temperatures. In this work we propose a simple approach of SWCNTs low frequency plasma treatment, which on the one hand introduce defects into the structure of nanotubes, which increases gas adsorption and thus increase sensitivity. On the other hand, it allows to obtain different functional groups on SWCNTs surface depending on the plasma atmosphere to increase selectivity of the material. In this study we investigate SWCNTs conductivity upon adsorption of inorganic gases such like carbon monoxide, nitrogen dioxide and ammonia, and assess the optimal operation temperature and gas concentration detection limits. Particularly, we present the study of oxygen plasma treated SWCNTs with induced defects and oxygen containing groups on its surface which increase SWCNTs sensitivity to such gases as carbon monoxide (respond is 0,5%), nitrogen dioxide (respond is 15%), ammonia (respond is 1.5%), hydrogen disulfide (respond is 0.8%) at room temperature.

The authors acknowledge the Russian Science Foundation (project No. 17-19-01787).

All Solution-Processed p-n Junction Diodes

Daisuke Yamamoto¹, Takayuki Arie¹, Seiji Akita¹ and Kuni Takei¹, ²; ¹Osaka Prefecture University, Sakai, Japan; ²JST PRESTO, Chiyoda, Japan.

Solution-based device fabrications are now of great interests due to attractive applications of printed flexible and stretchable electronics, which are required to form active components on an amorphous film using deposition and/or printing methods. However, due to difficulties of both p-type and n-type semiconductor formations on a film, most of the studies reported previously are based on Schottky diodes and transistors. To address this bottleneck and challenge, we here propose a solution-based p-n junction diode using developed IZO film and CNT network film formation and integration techniques as n-type and p-type semiconductor materials, respectively. Furthermore, barrier height between IZO and CNT films are also discussed based on the experimental results.

p-n junctions were formed by all solution process on Si/SiO₂ substrates. First, an IZO precursor was spin-coated on the SiO₂ surface with oxygen plasma treatment. After spin coating, it was cured at 300 °C in air ambient. After patterning the IZO film, semiconductor-enriched CNT solution was deposited by using van-der Waals interaction between the chemical-treated SiO₂/IZO surfaces and CNTs. After cleaning the substrate, Ag electrodes were painted on IZO and CNT films. Finally, the samples were annealed at 150 °C in N₂.

Transistor behaviors of IDS-VGS using Ag source-drain electrodes and a global back gate were measured. IZO and CNT transistors shows relatively good n-type and p-type behaviors, respectively, with high ON/OFF current ratio of >10⁴. Next, CNT/IZO p-n junction diode was characterized. Based on the results, good rectified behaviors with >10⁴ forward/backward current ratio were observed. After confirming the diode behaviors, barrier height of IZO and CNT was determined by measuring the diode characteristics as a function of temperature. From the experimental results and calculations, the barrier height of them was ~200 meV, which is in good agreement with the theoretical band alignment of CNT and IZO.

In conclusion, we developed p-n junction diode and analyzed the barrier height of CNT and IZO junctions. These material systems will be applied for the flexible devices in near future.
Nanoparticles play a central role in the rapidly growing nanoscience and nanotechnology fields. Atomic level tailoring of nanoparticles is of great importance in order to map out the structure-property relationships. Recent success in the synthesis of atomically well-defined nanoparticles has offered exciting opportunities to pursue many fundamental issues that were difficult to tackle with polydisperse nanoparticles. This talk will present several cases of single-atom, single-electron level manipulations of metal nanoparticles, such as doping a single Ag or Cu atom into a gold nanoparticle and site-specific “surgery” of surface motifs of a nanoparticle with controlled charge state. Such atomic-level manipulations provide unique opportunities for investigating how the structure and composition precisely impact the particle’s properties and functionality at the single-atom, single-electron level. New strategies for achieving such goals have been devised. Overall, the pursuit of single-atom level tailoring opens up new opportunities for controlling nanoparticles on an atom-by-atom basis.

Total synthesis, where desired organic- and/or bio-molecules could be produced from simple precursors at atomic precision and with known step-by-step reactions, has prompted centuries-lasting bloom of organic chemistry since its conceptualization in 1828 (Wöhler synthesis of urea). Such expressive science is also highly desirable in nanoscience, since it represents a decisive step towards atom-by-atom customization of nanomaterials for basic and applied research. Although total synthesis chemistry is less established in nanoscience, recent years have witnessed seminal advances and increasing research efforts devoted into this field. In this talk, I will discuss our recent work on introducing and developing total synthesis routes and mechanisms for atomically precise metal nanoclusters (NCs). Due to their molecular like formula and properties (e.g., HOMO-LUMO transition, strong luminescence and stereochemical activity), atomically precise metal NCs could be regarded as “molecular metals” (or metallic molecules / molecular-like metals), holding potential applications in various practical sectors such as biomedicine, energy, catalysis and many others. More importantly, the molecular-like properties of metal NCs are sensitively dictated by their size and composition, suggesting total synthesis of them as an indispensable basis for reliably realizing their practical applications.

In recent years, it has become possible to synthesize gold clusters, silver clusters, and alloy clusters with atomic precision using thiolate or phosphine (PR3) as a ligand. The electronic/geometric structures and size-specific physical/chemical properties of these metal clusters have also been investigated extensively. Similar to these metal clusters, platinum (Pt) clusters have also attracted much interest. An attractive feature of Pt clusters is their high catalytic activity in a variety of reactions. In the precise synthesis of these Pt clusters, carbon monoxide (CO) or PR3 is used as the main ligand. However, little information has been obtained on the electronic structure and physical/chemical properties of Ptn(CO)m(PR3) clusters to date. In this research, the final objective is to obtain experimental information about the largely unknown electronic structure of Ptn(CO)m(PR3) clusters. To this end, we precisely synthesized a Pt17 cluster ([Pt17(CO)12(PPh3)8]+; n = 1, 2) protected by CO and triphenylphosphine (PPh3) by a simple method and studied its geometric and electronic structure. Mass spectrometry, elemental analysis, and single-crystal X-ray structural analysis of the product revealed that the obtained Pt17(CO)12(PPh3)8 comprises positively charged [Pt17(CO)12(PPh3)8]+ and [Pt17(CO)12(PPh3)8]+; having a geometric structure similar to that of neutral Pt17(CO)12(PPh3). The optical absorption spectroscopy and electrochemical measurements of [Pt17(CO)12(PPh3)8][SbF6] (n = 1, 2) demonstrated that [Pt17(CO)12(PPh3)8][SbF6] (n = 1, 2) has a discrete electronic structure. Furthermore, the emission spectroscopy revealed that [Pt17(CO)12(PPh3)8][SbF6] (n = 1, 2) exhibits photoluminescence in the near-infrared region. In this presentation, I also talk about our recent results on the precise synthesis and one-dimensional structures of alloy clusters including Pt element.
space is further broadened, new cluster compositions, structures and interfaces can be discovered. We will provide an atomic-level view of alkynyl-protected gold nanoclusters. The syntheses of a series of gold nanoclusters with “direct reduction” method will be reported. The total structure determination of these clusters will be described. The stability and optical properties of these nanoclusters will be discussed based on electronic structural analysis. In addition, ligand effects on the catalytic performance of gold nanoclusters will be presented. We believe the success in these systems will stimulate more effort in discovering new aspects this class of gold nanoclusters with alkynyl groups in the protective layer.

11:15 AM NM02.01.06 Overview of the Ligand-Gold Interfaces and the Case of the N-Heterocyclic Carbenes De-en Jiang; University of California, Riverside, Riverside, California, United States.

Ligands play an important role in the stabilization and functionalization of Au nanostructures and in self-assembled monolayers. Despite the increasing number of organic groups capable of stabilizing gold in addition to the popular thiolate ligands and the emerging alkynyl groups, there has been no systematic comparison of organic ligands regarding their binding strength to gold. To facilitate the future experimental design of promising ligands for gold surfaces, nanostructures, and nanoclusters, we provide a comprehensive view of the ligand-gold interface for six types and 27 ligands from first principles dispersion-corrected density functional theory. We find a surprising contrast between simple and bulky N-heterocyclic carbenes (NHCs). The bulk NHCs benefit from greater van der Waals contributions and additional Au—H-R hydrogen bonds. In fact, we find that alkynyl groups and bulky NHCs demonstrate the strongest binding with the gold surfaces. We further explore the computational design and show the viability of NHC-protected gold nanoclusters of magic stability. The overall trend from the present work not only confirms the emerging role of alkynyl ligands but also predicts the very promising direction of using bulky NHCs to achieve stable gold nanoclusters and interfaces.

11:30 AM NM02.01.07 Structural Control of Quaternary Ammonium Cationic Gold Nanoclusters Tetsu Yonezawa, Yohei Ishida, Mai Thanh Nguyen, Kunihiro Narita and Ryan D. Corpuz; Hokkaido Univ, Sapporo, Japan.

Quaternary ammonium is a cationic group which is always show positive change at any pH conditions. Many reports have been published on thiolate-gold nanoclusters but almost all of them were covered by non-ionic or anionic thiol compounds. Only a few reports of amino-thiol-stabilized gold nanoclusters can be found but no report of quaternary ammonium thiolate-stabilized ones. For the first time, we prepared quaternary ammonium-stabilized fluorescent gold nanoclusters by sputtering processes. Furthermore, we have successfully prepared Au25 clusters stabilized by quaternary ammonium thiol. In this case, counter anion plays an important key. Bromides cannot well stabilize Au25 clusters and they decomposed rapidly. But after changing this counter anion to PF6- or other soft anions, very stable fully cationic Au25 nanoclusters could be obtained.

11:45 AM NM02.01.08 Tailoring the Atomic Structure of Gold Nanoclusters by Doping—Using an 23-Gold-Atom Nanocluster as an Example Qi Li and Rongchao Jin; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

In this work, we demonstrate three different doping modes when an atomically-precise nanocluster: \([Au_{23}(SR)_{16}]^-\) is doped with different metals (Cd, Cu, Ag), including (i) simple substitution, (ii) surface reconstruction and (iii) total structure transformation. Both experimental and theoretical results demonstrate that the dopant concentration is critical: the original structure of \([Au_{23}(SR)_{16}]^-\) is retained under slight doping, but it starts to change under high concentrations of Cd and Ag dopants. Our results suggest that doping in nanoclusters is not just a simple substitution of original atoms or filling a vacant site; instead, it can be explored as a useful method to tailor the structure of nanoclusters partially (e.g., Cd doping of Au23) or totally (e.g., Ag doping of Au23). Overall, this work greatly expands doping chemistry for tailoring the structures of nanoclusters and is expected to open new avenues for designing nanoclusters with novel structures using different dopants.
Ultrasmall nanoparticles with a diameter below 2 nm are promising as specialized carriers for targeted drug delivery. Functionalized with specific binding motifs, they open up innovative opportunities in a wide range of applications, e.g., nanomedicine. A possible application is the specific targeting of protein-epitopes. A versatile approach to the functionalization with specific epitope-binding motifs, i.e., peptides and proteins, is covalent binding of the gold-surface with sulfur-containing molecules. NMR spectroscopy gives valuable insights into the characteristics of the binding situation on the surface.

L-cysteine as a typical sulfur-containing biomolecule was chosen to elucidate the binding of ligands to ultrasmall gold nanoparticles (d < 2 nm). Cysteine is the only thiol-containing amino acid and therefore an ideal model compound for the binding to gold nanoparticles. The nanoparticle preparation was carried out by reduction of HAuCl with NaBH₄. L-cysteine was directly attached to the gold nanoparticles via gold-sulfur binding. The purification of the cysteine-capped nanoparticles was performed by multiple centrifugation and washing steps.

To investigate the binding of L-cysteine to the gold nanoparticle surface, isotopically labeled L-cysteine (¹³C and ¹⁵N) was used. 2D ¹H-DOSY, ¹³C-DOSY and 3D ¹H-¹³C-HSQC-DOSY NMR spectroscopy of the gold nanoparticles enabled the determination of the hydrodynamic particle diameter in excellent agreement with the metallic core diameter by high-resolution transmission electron microscopy.

The binding of L-cysteine to the gold nanoparticles via the thiol group was confirmed by ¹H and ¹³C NMR spectroscopy and 2D-NMR spectroscopy (²H, ¹H-COSY, ¹³C-HSQC and ¹³C,¹³C-INADEQUATE). To exclude the binding of L-cysteine to the gold nanoparticles via the amino group, ¹⁵N NMR spectroscopy was carried out. Quantitative ¹³C NMR spectroscopy and atomic absorption spectroscopy enabled the calculation of a loading of approximately 100 L-cysteine molecules on each gold nanoparticle. By X-ray photoelectron spectroscopy, 95% elemental gold was identified whereas about 5% was oxidized. This confirms the existence of metallic gold nanoparticles, functionalized with L-cysteine as model compound.

We show that NMR spectroscopy is especially well suited to analyze ultrasmall gold nanoparticles due to their small particle size, leading to excellent spectra of dispersed nanoparticles that elucidate the binding situation of L-cysteine on the gold surface.

Polydopamine (PDA) is a nature inspired biopolymer that can be synthesized through self-assembly under mild controlled environment. Due to the catechol functional groups, PDA can form coordination bonding with various metallic ions. In our work, we utilized the strong affinity between PDA and various metal cations, including Cu²⁺, Ni²⁺, and Co²⁺, to obtain metal ion doped PDA (mPDA). The mPDA powders were irradiated under electron beam using a transmission electron microscope. As the electron beam intensity increased, nucleation and growth of nanoscale precipitates were observed.

Electron diffraction and EDX analysis indicated these precipitations were metal nanocrystals. The morphology of the metal nanoparticles varied depending on the metal specie. This discovery indicates electron and perhaps other irradiation sources can be used to induce nanoparticle in metal-doped PDA, which may be useful to modify the properties of PDA-based thin film materials. On the other hand, our study implies PDA can be used as a platform for growth of nanoparticles, which may have potentials in various engineering applications.
etching of gold nanocrystals in the graphene liquid cell was induced through a combination of pre-loaded iron chloride and oxidative species generated by electrodeposition. Control over the chemistry in the graphene liquid cell pockets allowed the nanocrystal dynamics and mechanisms to be related back traditional synthetic techniques. The electron beam dose rate controlled the rate of atom removal, and the initial concentration of iron chloride established the potential of the oxidative etching.

Pre-synthesized gold nanocubes and nano-rhombic dodecahedra (RDD), with \{100\} and \{110\} surface facets respectively, were oxidatively etched while monitoring the effect of chemical potential on the facet trajectories. Both the cubes and RDD transformed to intermediate tetrahexahedra (THH) shapes with \{hk0\} surface facets. When etching the cubes in this non-equilibrium regime, lower initial concentrations of iron chloride led to intermediate \{hk0\} facets with lower h/k values. However, etching the RDD at differing initial iron chloride concentrations led to same intermediate THH with \{hk0\} facets of h/k = 2.5. Monte Carlo simulations corroborated the role of chemical potential in controlling the facets for the cubes but not the RDD. Zero temperature kinetic models show that removing a 6-coordinated edge atom on the nanocrystals reveals 7-coordinate inner atoms for cubes but 6-coordinate inner atoms for RDD. Therefore, chemical potential controls the facets for cubes by modulating the probability ratio of removing inner versus edge atoms. This fundamental understanding of kinetically-driven shape transformations will aid efforts to make nanocrystals with high-energy facets.

These through in situ TEM studies, the formation of non-equilibrium nanocrystal structures were watched at the single particle level in solution, and the mechanisms of etching were elucidated. This mechanistic understanding of nanocrystal etching will hopefully inform future synthetic efforts to control facets and structures for energetically unfavorable shapes.

3:00 PM *NM02.02.06

Hydrogen-Doped Gold-Based Superatom—Synthesis, Structure and Transformation Tatsuya Tsukuda1, 2; 1University of Tokyo, Tokyo, Japan; 2Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto, Japan.

Gold clusters protected by ligands or stabilized by polymers are viewed as superatoms from the analogy of the electronic structures with those of the conventional atoms. It has been demonstrated that H atom mimics Au atoms in bare Au clusters: the electronic and geometric structures of Au clusters are retained after replacement of the Au atom with H atom \[1\]. A recent theoretical study proposed that an H atom behaves as an Au atom in the Au cluster Au2(3SR)6 (SR = thiolate) and contributes its 1s electron to the superatomic electron count \[2\]. Small nonplasmonic Au clusters stabilized by polymer exhibit localized surface plasmon resonance in the presence of NaBH4 due to electron donation from the adsorbed H atoms \[3, 4\]. These results suggest that structures and properties of gold superatoms can be tuned through doping H atoms. However, a molecular-level understanding has not been attained about the interaction between H and Au superatoms.

The present work focuses on the interaction of H with phosphine-protected Au-based clusters \[Au(AuPH)3]+ and \[PdAu(AuPH)3]+ which can be viewed as oblate gold superatoms with 6 electrons. We observed by mass spectrometry and NMR spectroscopy that a hydride (H−) was doped into these gold-based oblate superatoms upon the reaction with NaBH4. Density functional theory calculations of the products \[AuH(AuPH)3]+ and \[PdH(AuH)(PPh3)8]+ demonstrated that hydride is bonded to a coordinatively unsaturated site at the center and that the \[AuH2]+ and \[PdH2]+ core can be viewed as nearly spherical superatom with closed electronic shells. The hydride-doped superatoms \[AuH2]+ remained during the growth to \[PdH2]+. These hydride-mediated growth processes will provide a new atomically precise synthesis of Au clusters via bottom-up approach.


4:00 PM *NM02.02.07

Stronger-Than-Pt Hydrogen Adsorption in a Au25 Nanocluster for the Hydrogen Evolution Reaction Guoxian Hu1, Zi Li Wu2 and De-en Jiang1; 1University of California, Riverside, Riverside, California, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Atomically precise metal nanoclusters have recently emerged as a novel class of catalysts for the hydrogen evolution reaction. From first-principles density functional theory, we show that the eight coordinatively unsaturated (cus) Au atoms in the Au25(L3)8 cluster \[L3 = 1,8-bis(diphenylphosphino)octane\] can adsorb H stronger than Pt, thereby being a potentially promising catalyst for the hydrogen evolution reaction (HER). We find that up to six H atoms can adsorb onto the Au25(L3)8 cluster and they have close-to-zero Gibbs free adsorption energies \(\Delta G_{H}\). From the HOMO–LUMO gaps, frontier orbitals, and Bader charge analysis, we conclude that H behaves as a hydride or electron-withdrawing ligand in the Au25(L3)8 clusters, in contrast to the metallic H in thiolate-protected Au nanoclusters. Our study demonstrates that ligand-protected Au clusters with cus Au sites will be the most promising candidates for realizing Au–H nanoclusters and can act as excellent electrocatalysts for the HER.

4:15 PM *NM02.02.08


Monolayer-protected clusters (MPCs) represent a class of nanomaterials that can be synthesized and isolated with structural (both compositional and geometric) specificity. Hence, MPCs provide model systems for understanding the nanoscale structure-function interplay. We have recently shown that femtosecond time-resolved two-dimensional electronic spectroscopy (2DES) can be used to isolate carrier dynamics of specific MPC electronic states.Here, 2DES studies of a family of MPCs in the 1-2 nm size range will be presented. These results show that the optical, electronic, and spin-state properties of MPCs are extremely sensitive to the electronic configuration of nanometal orbitals. For example, the magnetic properties of Au25(SR)18, where SR represents an alkanethiol, can be switched reversibly by oxidative opening of the eight-electron Superatom P orbital. Electronic interactions between assembled MPCs also exhibit spin-dependent magnetic phenomena not present in the isolated building blocks. Ultrafast spectroscopy on dimerized 20-atom MPCs reveal inter-partner spin-dependent dynamics not observed for the monomer. In contrast to the discrete carrier dynamics typical for MPCs, larger nanoparticles exhibit collective electronic behavior. I will provide a comprehensive description of how 2DES can be employed to describe the dynamics of metals spanning the non-metallic cluster and metallic particle domains.
Gold Treatment of Silver Nanoparticles and Their Enhanced Antimicrobial Activity

It has been known that silver ions released by silver nanoparticles have bactericidal effect against a wide spectrum of bacteria. Silver ions can induce redox reactions on the membrane transport proteins of bacteria thereby deactivating them. Silver ions are also capable of impairing the energy transfer mechanism of bacteria during respiration process. However, the nanoparticles are unstable and easily form aggregates, which decreases their antibacterial activity.

To improve the dispersion stability of silver nanoparticles in aqueous media, and to increase their effectiveness as antibacterial agents, we coated triangular plate-like silver nanoparticles (silver nanoplates, Ag NPLs) with one or two layers of gold atoms (Ag@Au1L NPLs and Ag@Au2L NPLs, respectively). These gold coatings improved the dispersion stability in aqueous media with high salt concentrations. Ag@Au1L NPLs showed stronger antibacterial activity on pathogenic bacteria than Ag NPLs and Ag@Au2L NPLs. Furthermore, the Ag@Au1L NPLs decreased the number of bacteria living in RAW 264.7 cells. The Ag@Au1L NPLs displayed no cytotoxicity towards RAW 264.7 cells, and the Ag@Au1L NPLs could be used as an antibacterial agent for intracellular bacterial infections.

Next, we prepared hollow-shaped alloy nanoparticles made of silver and gold atoms (Ag/Au NPs) by treating silver nanoparticles with gold ions, not core-shell type gold-coated silver nanoparticles as described in the previous section. The antibacterial activity of the hollowed Ag/Au alloy nanoparticles was stronger than the original silver nanoparticles. Additionally, the release of silver ions from the hollowed Ag/Au nanoparticles was higher than the original silver nanoparticles.

The gold atoms on the surface of silver nanoparticles or in the alloy nanoparticles made of silver and gold atoms affected the oxidation of the silver atoms in the nanoparticles. Since chloride ions can affect the migration of gold atoms on silver, in turn, the migration of gold atoms might affect the exposure of silver metals to the culture medium and the subsequent release of silver ions. These gold treatments are effective methods to improve the antimicrobial activity of silver nanoparticles.

Surface Architecting in Palladium Nanoparticle Synthesis

Morphology dependent properties of nanoparticles have been utilized in various applications and especially nanoparticles composed of high-index facets have attracted significant attention in catalysis with its high density of atomic steps serving as active sites for reactions. However, despite vigorous efforts for delicate control of nanoparticle morphology, controlled fabrication of specific surface structures within a few nanometer scale still remains as a big challenge due to instability of high-index facets. Previously, we demonstrated aqueous based seed-mediated two step growth method to synthesize high-indexed gold nanoparticles with morphological variations by control of reaction parameter and introduction of organo-thiol shape controlling additives. Strong interactions between the organo-thiol based additives and the metal surface induces directional growth depending on the shape-modifier structures.

Herein, based on this established system, we demonstrate precise surface structure control with organo-thiol additive during palladium nanoparticle synthesis. Resulting nanoparticles show multi-stepped surface structures which varies from cubic based planar step patterns to spiral step patterns composed of multiple high-index facets. We demonstrate superior catalytic activity of “multi-stepped” nanoparticles. Morphology variation is originated from collaborative interactions between kinetic modifiers and shape modifying additives during the growth step. Reduction kinetic was controlled by growth solution pH, where various types of acids were introduced to the growth solution. Higher proton concentration in the synthesis environment induced slower electron withdrawing of reducing agent to affect geometrical shape and uniformity. Additionally, dramatic change in nanoparticle morphology was observed respect to the acid type when shape modifying organo-thiol group was introduced to the reaction solution. These anion dependent morphology change is related to specific interactions between organo-thiol molecule and anions to modify growth directionally. Our study provides crucial design constraints for fine morphology tuning during nanoparticle synthesis which allows systematical control of nanoparticle surface structures for potential catalysis application.

Correlation Between Positive Surface Charge Density on Silver Nanoparticles and Separation Performances in Facilitated Olefin Transport Membranes

It has been accepted that the separation performance for olefin/paraffin mixtures has been improved through composite membranes containing silver nanoparticles (Ag NPs) dispersed in a common polymeric matrix when their surface is positively charged by electron acceptor. Here, a correlation between the surface positive charge density, represented by the binding energy, on Ag NPs and the separation performance was also obtained: the remarkably high mixed-gas selectivity above 150 for a 50/50 (v/v) propylene/propane mixture and the propylene permeance about 0.9 GPU. The correlation between the surface positive charge density and the gas separation performance was observed to be linear regardless of the electron acceptor used. This correlation thus suggests that the major determinant of the olefin/paraffin gas separation performance is not the chemical characteristics of electron accepting compounds, but the induced surface positive charge density on Ag NPs. Therefore, it is concluded that surface charge density of Ag NPs is a key factor in determining the separation performance of facilitated olefin transport membranes.

Micro/Nanostructured Lamella Phases Make 2205 Stainless Steel Have Superior Strength and Ductility

Strength and ductility are mutually trade off usually in steels and alloys. Grain refinement to nanoscale can make the conventional steels several times stronger, but invariably leads to poor ductility. Here we demonstrate a micro/nanostructured lamellar phases in 2205 stainless steel prepared by aluminothermic reaction and followed hot rolling that produced a superior yield strength of 780MPa, ultimate tensile strength of 979 MPa and elongation of 54%. The elongation is the highest in the reported steels with that level of strength. The product of tensile strength and elongation exceeds 50 GPa% and is the highest value that was reported in the literatures. The steel consists of micro/nanostructured lamellar ferrite phase and micro/nanostructured lamellar austenitic phase in which the dislocation free hard nano grains dispersed in soft coarse grains. The high strength is attributed to strengthening of dislocation...
free nano grains and interface between the two phases. The unusual high ductility originates from cracks propagation resistance by the nano grains and the two phase interfaces.

**NM02.03.05**

Highly Efficient Ni-B Amorphous Alloyed Catalysts on Ni Foam for Nitrobenzene Hydrogenation

Gang Chen,1,2 Xin Zhu,1,2 Rong Chen,1,2 Qiang Liao,1,2 Dengding Ye,1,2 and Biao Zhang1,2. Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Chongqing, China;¹ Institute of Engineering Thermophysics, Chongqing University, Chongqing, China.

In this work, Ni-B amorphous alloyed catalysts used for a gas-liquid-solid three phase reaction were synthesized on Ni foam by electroless plating method, which was evaluated by the reference reaction of nitrobenzene hydrogenation. Such design offered several advantages. First of all, the low-cost Ni-B amorphous alloyed catalysts showed superior catalytic activity and selectivity towards the hydrogenation reaction. Besides, the use of Ni foam as the support materials could increase the surface area for loading the Ni-B amorphous alloyed catalysts. Moreover, its interconnected macropore structure was beneficial for the transport of the gas/liquid reactants to the active sites. The morphologies and size distributions and the chemical composition of the prepared Ni-B amorphous alloyed catalysts were characterized by SEM, XRD and XPS, respectively. The actual loading of the Ni-B amorphous alloyed catalysts was analyzed using ICP-MS technology. The hydrogen chemisorption on the Ni-B amorphous alloyed catalysts was characterized by temperature programmed desorption of H₂ (H₂-TPD) analyses. Finally, the catalytic performance was evaluated by nitrobenzene hydrogenation in a continuous flow monolithic microreactor under various parameters. The experimental results indicated that the developed Ni-B amorphous alloyed catalysts deposited on the Ni foam was able to improve the catalytic performance.

**NM02.03.06**

Effect of Nanoparticles on Liquid State Dewetting of Bismuth Thin Films

Krishna Kumar, Mrudula Kavuri and Parasuraman Swaminathan; Indian Institute of Technology Madras, Chennai, India.

Metallic thin films are unstable in as deposited state. These films tend to break up and agglomerates when annealed. This is known as dewetting and driven by surface energy minimization of the film – substrate interface. Dewetting occurs in both solid and liquid state and while it can be detrimental, where high temperature performance is required, it can also be used to fabricate nanoparticles arrays on substrate for different applications [1].

Enhancing the thermal stability of metallic thin films is of importance, especially for high temperature applications. Recently, we reported that addition of silver nanoparticles on copper thin films suppresses the solid state dewetting of copper thin film [2]. In this work, we explore the effect of added nanoparticles on the liquid state dewetting behaviour of bismuth thin films. We study three system, copper, silver and gold nanoparticles deposited on bismuth thin films on amorphous carbon TEM grids. Transmission electron microscopy results shows that gold and silver nanoparticles accelerate bismuth dewetting, while copper nanoparticles suppress the process. A model is presented to explain these differences.

**References**


**NM02.03.07**

Inkjet Printed Encapsulation of Gold Nanoparticles inside Cell-Adhesive Chitosan Hydrogels

Álvaro Artiga1,2, Sonia García-Embid1,2, Inés Serrano-Sevillal, Gabriel Alfranca, Laura De Matteis1,2, Scott G. Mitchell1,2, Carlos Sánchez-Somolinos1,2 and Jesús M. de la Fuente1,2. 1Instituto de Ciencia de Materiales de Aragon (ICMA), CSIC/University of Zaragoza, Zaragoza, Spain; 2CIBER-BBN, Instituto de Salud Carlos III, Madrid, Spain; 3Instituto de Nanociencia de Aragon (INA), University of Zaragoza, Zaragoza, Spain.

The unique physicochemical properties of gold nanoparticles (AuNPs) make them highly applicable for drug release, optoacoustic imaging, biosensing and photothermal therapy, among others. This work highlights unique methodologies for the encapsulation of AuNPs in chitosan hydrogels to increase their applicability and efficacy in health-related applications, in particular for photothermal therapy (PTT).

In PTT, AuNPs are employed to convert light energy into heat for the selective ablation of target cells. Anisotropic AuNPs such as nanoprisms, rods and stars, are frequently employed because they absorb near-infrared light that is harmless for surrounding cells. In previous work, we have compared the heating capability, cellular internalization, toxicity and thermoablation capacity of two different types of anisotropic AuNPs: gold nanorods (AuNRs) and nanoprisms (AuNPs) [1]. Although both AuNRs were highly efficient photothermal converters, AuNRs possessed a more efficient heating capability. However, the in vitro thermoablation studies clearly demonstrated that AuNPs were more effective at inducing cell death by PTT due to their greater cellular internalization, while AuNRs could not be employed for this purpose due to their extremely low cellular internalization.

We succeeded in improving the PTT application of AuNRs by entrapping them inside a cell-adhesive chitosan hydrogel using anionic polyethelmetals (POMs) as gelling agents [2]. These functional nanocontainers remained non-cytotoxic and presented the ability to adhere to the cytoplasmic membranes of cells avoiding any need for cellular internalization, thus rendering them as highly efficient PTT agents. However, one key disadvantage of this entrapment methodology is the lack of control of the size and size-dispersion of the nanocontainers.

In order to improve these drawbacks, we have developed a novel strategy for AuNP microencapsulation in chitosan hydrogel by inkjet printing [3]. Inkjet printing, as a high-throughput, continuous and automatic technology poses relevant industrial potential for microencapsulation. In particular, our approach has showed a high degree of production, excellent control of the microcapsules size, high encapsulation efficiency and ease of scale-up, obtaining almost monodisperse chitosan microcapsules containing AuNPs. We are currently studying the use of these chitosan hydrogels for oral administration of gold nanoparticles in vitro and in vivo.

**References**


**NM02.03.08**

Fabrication and Morphological Control of Palladium Film with Three-Dimensional Nano-Network Structure as a Hydrogen Gas Sensing Material by Organic Acid Chelation

Takui Ube, Akizumi Kawamoto, Tomoya Nishi and Takashi Ishiguro; Department of Material Sciences, Tokyo University of Science, Tokyo, Japan.

The large specific surface area of nano-porous materials realizes both high catalytic activity and resource savings. Thin film materials have homogeneity in large areas and can be applied to sensor devices or electrode materials for batteries. The traditional and general method of fabricating a nano-porous noble
metallic thin film is the dealloying method, i.e., the selective corrosion of an alloy of a noble metal and a base metal by a strong acid, such as hydrochloric acid or sulfuric acid. In this study, we fabricated a palladium (Pd) thin film with three-dimensional (3D) nano-network structure (3DPdNNF) by the dealloying method without discharging any material with possibly high environmental impact, such as waste solution containing heavy metals or strong acids. The dealloying was conducted in aqueous solutions of organic chelating agents of citric acid and ethylene-diamine-tetraacetic acid (EDTA) and sodium carbonate. All agents are used as a food additive and have environmentally friendly characteristics. Furthermore, the base metal used was aluminum (Al). However, Pd has a hydrogen-storage property with hydrogen gas selective permeation, and it is expected to be useful for developing sensor devices to detect only hydrogen gas. However, pure Pd metal has low repetitive durability for hydrogen gas exposure due to irreversible deformation and destruction caused by its hydrogen-storage property. In this study, we aimed to fabricate a 3DPdNNF by the above method and utilize its stress relaxing action due to the nano-network structure to apply it to a hydrogen gas sensor with repetitive durability.

The thin film preparation was performed using the RF-sputtering method, and AI–Pd alloy (82at% Al–18 at% Pd) films were deposited on substrate (glass, Si wafer, and elastic carbon film) to a thickness of 70 nm. The dealloying process was conducted in mixed aqueous solution of organic chelating acid (100 μmol/L) and sodium carbonate for pH adjustment. The optimized pH value and temperature were 10.0 and 368 K, respectively.

The Al–Pd film was reformed to uniform 3DPdNNF with high Pd purity (> 99 at% Pd). The pore size of the network could be controlled to within the range of 2.90–12.5 nm by three parameters of the gas conditions during the sputtering deposition and the pH values and chelating agents in the dealloying processes. We evaluated the hydrogen gas sensing performance as a 3DPdNNF utilization of a high Pd purity and large specific surface area film. The fabricated 3DPdNNF showed a response to hydrogen gas by changing the electrical resistance in the kΩcm range with repetitive durability for hydrogen gas exposure.

NM02.03.09
Sputter Deposition onto Liquid to Prepare Pt and Pt Alloy Nanoparticles
Lianlian Deng1, Mai Thanh Nguyen1, Tomoharu Tokunaga2, Syo Matsumura1 and Tetsu Yonezawa1; 1Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan; 2Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan; 1Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka, Japan.

Platinum (Pt) and Pt-based (e.g., Pt/Cu, Pt/Au, Pt/Ag) alloy nanoparticles (NPs) have been demonstrated as high performance catalysts. Usually Pt and Pt-based alloy NPs have been synthesized via chemical reduction methods. However, impurity and incomplete removal of byproducts and toxic reductants can hinder catalytic properties. On the other hand, due to the difference in reduction potential of metal salts and/or difference in decomposition temperature of metal complexes, core-shell structure or phase segregation were observed in the formed bimetallic NPs. This is often seen in bimetallic NPs of immiscible elemental components in the bulk state such as Pt/Al. In our research, we have proposed to prepare highly uniform Pt and Pt alloy NPs, such as Pt/Cu and Pt/Au alloy NPs, by sputtering at room temperature onto a low vapor pressure liquid, polyethylene glycol (PEG, Mw 600). The method combines the advantages of sputtering to produce atoms and clusters for any metal from the bulk counterparts and the suppression and control of particle growth by the liquid medium in vacuum sputtering chamber. Thus varying the sputtering parameters allows for particle size control and tunable alloy NPs' composition. Sputtering was performed onto PEG and TEM grid. Sputtering current applied to each magnetron was separately controlled and varied in order to tune the composition in the resulting bimetallic NPs. Various characterization methods such as UV-Vis, XRD, XPS, TEM, HRTEM and STEM-HAADF and STEM-EDX mapping have been used to analyze the obtained NPs. TEM, HRTEM and STEM showed that Pt NPs with tunable sizes from 0.9 nm to 1.4 nm and narrow size distribution were produced. In addition, we found that negligible particle aggregation happened in PEG and Pt NPs were stable even after keeping in the dark at room temperature for several months. The slight growth of Pt NPs in PEG during storage was found accompanied with the consumption of free Pt atoms in PEG. The method was applied for a Pt/Cu alloy target and the effect of sputtering parameters such as sputtering time, the rotation speed of PEG on particle size has been studied. Pt/Cu alloy NPs have been synthesized by sputter deposition for the first time. Furthermore, we showed that we were able to produce Pt/Au alloy NPs using a double-target sputtering. The target design allowed us to finely control Pt/Au alloy NPs' composition via simultaneous sputter deposition onto PEG. The results showed that particle size and composition are strongly correlated and can be tailored by varying the sputtering current. Increasing Pt content resulted in smaller particle size and particles with same composition had similar sizes. Moreover, the agglomeration of NPs is dependent on the Pt content. Our findings in the relation among particle size, particle composition, and aggregation state of the formed NPs with respect to its composition can shed light into the formation mechanism of Pt-based alloy NPs.

NM02.03.10
The Role of Silver Nano-Particles/Colloids on Conduction Mechanisms of Current Through Ag Gridlines of Si Solar Cell
Kening Ren, Veyssel Unsur, Ahrar A. Chowdhury, Yang Ye and Abasifreke Ebong; Chemistry, University North Carolina at Charlotte, Charlotte, North Carolina, United States.

Fire through dielectric (FTD) contact is the dominant technology for contacting a commercial silicon solar cell because of its low-cost and high throughput attributes. During the FTD process, the glass frits in the Ag paste melt and etch the dielectric (anti-reflecting layer) first, to have Ag metal contact directly to the bulk Si. The redox reaction between the glass frits melting and dielectric etching leads to the formation of a recrystallized glass layer, which distributes within the Ag gridlines and bulk Si emitter surface, and silver nano-particles, which are mainly silver alloys (Ag2Te and PtTe) encapsulated in the glass layer. When without the Ag2Te and PtTe nano-particles/colloids, due to the existence of glass layer, silver gridlines rarely directly contact with the bulk silicon and electrons have to tunnel through the glass layer. However, in this work, Ag2Te and PtTe are semimetals which have very narrow bandgaps. The existence of Ag2Te and PtTe nano-particles/colloids in the glass layer can change the electrical property of the glass layer. Thus, the specific contact resistance of silver gridlines cannot be calculated based on simplified metal-semiconductor contacts. The possible electron transport on the silver/silicon interface includes: 1. through silver gridline contact directly with bulk silicon; 2. tunneling through an ultrathin glass layer; 3. through Ag2Te and PtTe nano-particles/colloids assisted tunneling; 4. through multistep tunneling. This suggests that the contact resistivity in the presence of Ag2Te and PtTe nano-particles/colloids is independent of the inverse square root of emitter peak surface concentration. Lower contact resistances were measured in the presence of Ag2Te and PtTe nano-particles/colloids with relatively low peak surface concentration.

NM02.03.11
Kinetics of Detwinning in Chemical Vapor Deposited Nickel—Critical Structures Determining the Stability of Nano-Twin Lamellas
Hao Sun; Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada.

Nickel carbonyl vapor deposition (CVD) is a novel metal-forming process used to produce thin-shell molds with a higher level of efficiency and a lower cost than traditional mold making techniques. Not only is the production process highly effective, but the deposited CVD Nickel shell is also both harder (a tensile yield strength of ~584MPa) than nanocrystalline electroformed Nickel (~4-7%) with a grain size of 21-30nm. The combination of high strength and high ductility of the CVD Nickel shell is attributed to its unique bi-modal grain structure with large columnar grains embedded in a nanocrystalline matrix. A high density of nano-twins in large columnar grains significantly improve the working hardening capacity and ductility of CVD Nickel, but they are thermodynamically unstable. Most coherent twin boundaries (CTBs) transform into dislocation cells during annealing at temperature higher than 400 degree centigrade. While the driving force for detwinning is well-known, the mechanism by which CTBs disappear is still puzzling. Based on both experimental observation and simulation analysis, we found that although the driving force for detwinning is determined by the density of nano-twins, the thermal stability of each CTB...
in CVD Nickel is only determined by incoherent twin boundaries (ITBs) and its intrinsic grain boundary dislocations (IGBDs). Driven by the tensile strain originated from grain growth in the nanocrystalline matrix of CVD Nickel, IGBDs detach from CTB planes during detwinning. The emerging dislocations rearrange into sub-grain boundaries which then remove some CTBs during their migration. Twin lamellas terminated by ITBs transform back to the matrix stacking by the migrating ITBs which can also release sessile grain boundary dislocations into the crystal. Our results suggest that replacement of the nanocrystalline matrix in CVD Nickel with nano-twin structure can eliminate the tensile strain originated from grain growth, so nano-twins in CVD Nickel without nanocrystalline matrix might have a much higher level of thermal stability than that in CVD Nickel with bi-model grain size distribution.

NM02.03.12
Electrochemical Synthesis of Ag-Cu Bimetallic Nanostructure for Oxygen Reduction Reaction (ORR) Junian Chen and Shien Ping Feng; The University of Hong Kong, Hong Kong, Hong Kong.

Highly active and economic catalysts for oxygen reduction reaction (ORR) are always important for renewable energy technique. Since more than half of the voltage loss in fuel cell comes from the cathodic ORR process, and most of the commercial available catalysts for ORR is Pt-based. Herein, a new Ag-Cu bimetallic nanostructure was developed by electrochemical method, the fabricated Pt-free material shows a great performance towards ORR, which is comparable to the Pt/C commercial catalyst. The selectivity of the catalyst was carefully studied by scanning electrochemical microscope (SECM). Result shows the ORR by Ag-Cu bimetallic nanostructure prefer a four-electron reduction process, with H2O as the main product and trace amount of H2O2 can be detected. However, similar pure Ag nanostructure presents a much lower selectivity, which indicates the introduction of Cu is essential. Possible model was established to explain the enhancement as well. This Ag-Cu bimetallic nanostructure suggests a potential to be developed as cathodes in fuel cell, with a highly active and relative low cost.

NM02.03.13
In Vitro and In Vivo Toxicity of Metal-Doped Titanium Oxide Nanoparticles Su-Eon Jin1, Seok Won Hong2 and Hyo-Eon Jin2; 1Inha University, Incheon, Korea (the Republic of); 2Ajou University, Suseon, Gyeonggi-do, Korea (the Republic of); 3Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

Metal-doped titanium oxide (TiO2) nanoparticles were developed as enhanced photocatalysts with disinfection and purification potential. However, they can be hazardous to both the environment and human health. In this study, the toxicity of nickel (Ni) and platinum (Pt)-doped TiO2 nanoparticles (Ni-TiO2 and Pt-TiO2 nanoparticles) to skin and eye cells and a mouse skin model was evaluated. Physicochemical properties of nanoparticles were characterized using field emission-scanning electron microscopy, field emission-transmission electron microscopy, and X-ray photoelectron spectroscopy. Cytotoxicity was also evaluated at concentrations of 0.0001 to 10 mg/mL in HaCaT and ARPE-19. To investigate in vivo acute toxicity, 1 to 123 mg nanoparticles/1.5 cm² were applied to hair-removed dorsal skin in a mouse model, and skin tissues and body condition were monitored. Metal-doped TiO2 nanoparticles had a spherical crystalline shape with nanoscale sizes less than 100 nm. In nanoparticles, 1.0% Ni2p and 0.26% Pt4f were detected at 871.2 eV and 74.4 eV for Ni-TiO2 and Pt-TiO2 nanoparticles, respectively. Cell viability in HaCaT was higher than that in ARPE-19 at a range of 0.1 - 10 mg/mL nanoparticles. In ARPE-19, superior cell viability was observed at 1.0 mg/mL and more than 1.0 mg/mL Ni-TiO2 nanoparticles compared with Pt-TiO2 nanoparticles. In vivo, body weight and ALT/AST levels were not significantly altered by Ni-TiO2 nanoparticle exposure. Histology, skin thickness, and inflammation grade were also comparable to control mice. Thus, metal-doped TiO2 nanoparticles show minimal toxicity in skin cells and a mouse skin model, indicating their potential for various applications.

NM02.03.14
Morphological and Microstructural Evolution of Polycrystalline Thin Films Resego Phiri; Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Palapye, Botswana.

Modern thin film industries require precise tailoring of thin films properties to have excellent performance at specific applications intended. Atomic scale understanding of the microstructure of polycrystalline thin films is necessary for the control and manipulation of the film properties for a wide range of industrial applications. Thin film growth of thin films influence grain shapes, distribution of grains and the crystallographic orientation of the grains thereby affecting their reliability and performance. This article reviews the present understanding of the mechanism(s) determining the microstructural evolution of polycrystalline films and the related structure zone models. General trends in microstructural evolution, grain morphology and texture formation mechanisms are discussed in terms of their fundamental kinetic processes. The temperature dependency of the film microstructure is described using Thornton structure zone models.

NM02.03.15
Synthesis and Characterization of Redox-Sensitive Mixed Metal Complexes Joseph T. Race, Lauren Knappenberger and Scott Williams; Rochester Institute of Technology, Rochester, New York, United States.

A mixed metal inorganic complex which resembles redox sensitivity will be presented. Molecular switches experience a reversible physical change due to various external stimuli such as: high energy radiation, electrical current, heat, magnetic fields, and ultraviolet or visible light. We have synthesized a series of Group IVB and VB complexed to VIIIB metals that undergo intermolecular electron transfer upon high energy exposure resulting in a state change. In addition, we have found that substituting a Group IVB with selected Lanthanide metals results in fluorescently active compounds. We will present how the additional mechanism was enabled that resulted in the growth of highly crystalline Ni, Co and Ni-Co nanowires in addition to the nanostructured film. Excellent quality nanowires for high melting point metals are difficult to grow using the standard electrodeposition into nanoporous anodized aluminium templates method [2,3]. The new template-less growth conditions reported here indicate that an alternative method to produce highly crystalline nanowires...
for high melting point metals has been identified. Novel roles for oxygen, carbon and chlorine chemistries in the nanocrystallite and nanowire growth processes are identified. We identify specific growth models for both nanocrystal and nanowire from quantitative TEM, SEM, SAED, EDS and AFM results.


NM02.03.17 Fabrication of a Transparent Conducting Electrode Based on Silver Nanowires for Organic Photovoltaic Devices Heejeong Shin and Hyeosung Cho; Chemistry, Hanyang University, Seoul, Korea (the Republic of).

A solution-processed transparent conducting electrode was fabricated via layer-by-layer (LBL) deposition of graphene oxide (GO) and silver nanowires (Ag NWs). First, graphite was oxidized with a modified Hummer’s method to obtain negatively-charged GO sheets, and Ag NWs were functionalized with cysteamine hydrochloride to acquire positively-charged silver nanowires. Oppositely-charged GO and Ag NWs were then sequentially coated on a 3-aminopropyltriethoxysilane modified glass substrate via LBL deposition, which provided highly controllable thin films in terms of optical transmittance and sheet resistance. Next, the reduction of GO sheets was performed to improve the electrical conductivity of the multilayer films. The resulting GO/Ag NWs multilayer was characterized by a UV-Vis spectrometer, field emission scanning electron microscope, optical microscope and sheet resistance using a four-point probe method. The best result was achieved with a 2-bilayer film, resulting in a sheet resistance of 6.5 Ω sq−1 with an optical transmittance of 78.5% at 550 nm, which values are comparable to those of commercial ITO electrodes. The device based on a 2-bilayer hybrid film exhibited the highest device efficiency of 1.30% among the devices with different number of graphene/Ag NW LBL depositions.

NM02.03.18 Highly Sensitive Temperature Sensors with Ag Nanocrystal Thin Films Bang JunSung, Oh Soong Ju, Junhyuk Ahn and Ho Kun Woo; Nanocrystal Electronics Laboratory, Korea University, Seoul, Korea (the Republic of).

We introduce a strategy to design a highly sensitive temperature sensors using Silver (Ag) nanocrystal (NC) thin films. Resistive temperature sensors were fabricated on using poly(dimethylsiloxane) (PDMS) substrate through ligand exchange process [1] and interfacial engineering process. We take advantages of high thermal expansion coefficient of PDMS to control the interparticle distances of Ag NCs, and eventually to improve the sensitivity. We achieved a very sensitivity with temperature coefficient of resistance of 0.1/K. We discussed the origin of the high sensitivity by investigating structural, chemical, electrical, and electromechanical properties as well as the charge transport mechanisms. We also examine the stability, reliability, and sensitivity of our sensors. This work offers and effective way to design low-cost and high-performance sensors.

NM02.03.19 Designing Wearable Strain Sensors with Ag Nanocrystall Thin Film Through Halide Ligand Exchange Strategies Junhyuk Ahn, Soongju Oh, Bang JunSung and Ho Kun Woo; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

Through all solution-processed methods, wearable strain sensors with high gauge factor are demonstrated using thin film of Ag nanocrystals (Ag NCs). Controlling of interval between Ag NCs enables to control a flow of electrons through hopping mechanism and/or tunneling effect, which can enhance gauge factor. In this study, halides ligand treatment is proposed to design interval between nanoparticles to obtain high performances at solid state. Higher sensitivity of ligand treatment with I- is demonstrated by comparisons of experimental results of halides: Br-, Cl-, I-. The origin of the higher performance is discussed with various characterization methods. Careful studies to further enhance the sensitivity is conducted by controlling various conditions in ligand exchange process. These high sensitivity thin film Ag NCs strain gauge sensors allow to measure a delicate movement or signal from various objects. This work provides a low cost and simple method to design high sensitivity wearable sensors for various field such as robotics, or healthcare systems.

NM02.03.20 Encoded Silver Nanoshells as Surface-Enhanced Raman Spectroscopic Nanoprobes for Diagnosis of Alzheimer’s Disease In-Jun Hwang, Jin-Kyung Yang, Sin Lee and Jong-Ho Kim; Hanyang University, Ansan, Korea (the Republic of).

Recently, early diagnosis of Alzheimer’s disease (AD) has attracted considerable attention in the field of nanomedicine and biosensing. In particular, detection of plasma biomarkers specific for AD, including amyloid beta (Aβ40 and Aβ42), is considered a promising, cost-effective, and non-invasive method for diagnosis of AD. Herein, we present a facile approach for designing a nanoprobe based on surface-enhanced Raman scattering (SERS) for the sensitive and selective detection of Aβ40 and Aβ42 in blood. To this end, Ag nanoshells (AgNSs) bearing Raman labels were synthesized in a single step under very mild conditions (25 °C and 60 min). As-prepared AgNSs had a uniform shell thickness and nanogaps of 2 nm, resulting in significant electromagnetic field enhancement. In addition, each AgNS exhibited a unique and intense SERS signal without overlapping, allowing the multiplex and sensitive detection of Aβ40 and Aβ42. The AgNSs conjugated with a specific antibody for Aβ40 or Aβ42 was able to detect each target protein at concentration as low as 100 fg/ml in a fast and simple manner.

NM02.03.21 Evaluation of Thin-Film Interfacial Properties Using Single Nanoindentation Test Jinwo Lee, Woojoo Kim, Ohmin Kwon and Dongil Kwon; Seoul National University, Seoul, Korea (the Republic of).
Nano technology is developed consistently in all kinds of industry like chemical, Bio, Energy. Especially thin-film process improvement and material changes is researching actively. Through variety material and processing, High quality thin film element must have clearly purpose for electric and optical ability and also request a reliable device which is over standard mechanical properties. A thin film’s reliable question is depend on interfacial characterization, so evaluating interfacial characterization is the most important things in this test. So far, Peel off test, 4 point bending test and scratch test are usually used among lots of test in order to evaluate a thin film’s feature. But those test is inconvenience to make sample, and hard to check a characteristic evaluation of characteristic interface because of mechanical properties. So, this research is introduced how to test a thin-film by indentation test, and confirmed availability of interfacial properties by nanoindentation test. Determination of the mechanical properties of thin films on substrates by nanoindentation has always been difficult because of the influence of the substrate and interface on the measured properties. In order to measure film-only properties, a commonly used rule of thumb is to limit the indentation depth to less than 10% of the film thickness. As the film gets harder, the substrates and interfacial effects appear at lower indentation depth. Many researchers derived the conclusion from the theoretical and experimental methods. In the case of thin films which have thickness under than from nanometers to micrometers, it has no choice but must include the substrates and interfacial effects. Owing to the quantitative consideration about interfacial effects was hard, modeling equations with no interfacial effects is used.

NM02.03.22
Stress-Induced Chemical Reaction of Ti/Si Multilayered Nano-Films
Hiroyuki Hirakata, Takashi Kawai, Yoshiyuki Kondo and Kohji Minoshima; 1Department of Mechanical Engineering and Science, Kyoto University, Kyoto, Japan; 2Department of Mechanical Engineering, Osaka University, Osaka, Japan.

When a sufficient energy is applied at a local point in multilayered nano-films composed of alternating layers with a thickness of 10 nm order, an exothermic reaction occurs and a compound is generated at the local region. The generated heat then spreads into an adjacent unreacted region. If the temperature in the neighboring region becomes high sufficient to cause additional mixing, a self-sustained propagating reaction (SPR) occurs. SPR is induced by not only by electrostatic discharge, electrical heating, and laser irradiation, but also by mechanical impact. SPR by mechanical impact can be divided into two phenomena: i.e., (i) initial reaction by mechanical loading and (ii) ignition and propagation of reaction wave. Many studies have been conducted on (ii) SPR properties such as the ignition threshold and the speed of propagation. On the other hand, for (i), the detailed mechanisms of the initial chemical reaction due to mechanical loading has been unclear. This chemical reaction occurs at well below melting points and eutectic temperature, implying that the chemical reaction can occur by solid-state reaction. The atomic mixing in the solid-state can be brought about by diffusion or plastic deformation. Since the reaction occurs in very short time, we focus the role of plastic deformation.

The purpose of the study is to clarify the mechanisms of initial chemical reaction of Ti/Si multilayered nano-films by mechanical loading. Since the multilayered nano-films have structural anisotropy, the deformation mechanism depends on the loading mode with respect to the stacking direction. In this study, we focus the deformation and chemical reaction under compression loading in the stacking direction as a basic mode. We fabricated truncated cone-shaped specimens by focused ion beam from a polycrystalline-Ti/1-2 nm thick amorphous-Si multilayered nano-films (biayer thickness: ~30 nm) deposited by electron beam evaporation, and then conducted compression experiments under in situ observation by field emission scanning electron microscopy. We evaluated the chemical reaction or change in crystal structure through transmission electron microscopy (TEM) observation and selected-area electron diffraction to the deformed specimens.

The specimens yielded at a true stress of ~3 GPa under compression, and showed gradual hardening behavior. TEM observation confirmed that each layer was plastically deformed or thinned, and then the mixing of Ti and Si occurred. The selected-area electron diffraction revealed that a new crystal structure, estimated to be Ti₅Si₄ or TiSi₂, was generated on the Ti/Si interface and in the Ti layer. These results indicated that the mixing of each layer was induced by plastic deformation due to compressive stress and the compound of Ti and Si was generated. The exothermic reaction can be controlled or generated at a desired site by the local mechanical loading, and so it can be used for various applications such as local heating in large-scale devices.

SESSION NM02.04: Growth and Interface of Nanostructures
Session Chairs: De-en Jiang and Mika Pettersson
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Commonwealth

8:30 AM *NM02.04.01
Confined Growth of Metal Nanostructures
Yadong Yin; University of California, Riverside, Riverside, California, United States.

Metal nanostructures have been studied quite extensively in the research area of heterogeneous catalysis long before the introduction of the concept of nanoscience and nanotechnology. The significant progress achieved in the past twenty years in chemical synthesis has enabled precise control over not only the size but also the shape of the metal nanostructures, and therefore attracted intense interest not only in catalysis but also optoelectronics due to the well-known effect of localized surface plasmon resonance. In this presentation, I will introduce our recent progress in the synthesis of colloidal metal nanostructures in confined spaces using various templating methods, and further manipulation of their secondary structures. By combining the confinement of templates with the seed-mediated growth strategy, we demonstrate the significant advantages of this general method over the conventional ones in creating a large variety of nanoplastics with novel plasmonic properties.

9:00 AM NM02.04.02
Near Surface Nucleation and Particle Mediated Growth of Colloidal Au Nanocrystals
Maria Sushko, Yingwen Cheng, Jinhui Tao, Guomin Zhu, Jennifer Soh, Elias Nakouzi, James J. De Yoreo and Jun Liu; Pacific Northwest National Laboratory, Richland, Washington, United States.

During non-classical growth of nanostructures via assembly of primary nuclei, nucleation and assembly are assumed to be distinct processes: nanoparticles nucleate randomly aggregate to form extended structures through Brownian motion in the presence of long-range attractive interactions. Here we investigate the relationship between these two processes by using in situ AFM, in situ, ex situ and cryo TEM and UV-Vis spectroscopy to observe growth of colloidal gold and simulations to develop a mechanistic model of the process. Our results reveal an inexorable link between nucleation and assembly with nuclei forming almost exclusively within a ~1 nm interfacial region of existing particles. The new particles immediately close the gap either through a diffusive jump or via growth of a neck between the seed and new particle, generating aggregates exhibiting features commonly attributed to oriented attachment of independently nucleated particles. In addition, pH was identified as a control parameter for manipulating crystallization pathway through shifting the balance of chemical potentials of solution species. The results demonstrate that creation of initial particle interfaces leads to local environments
that redirect growth towards non-classical processes.

9:15 AM *NM02.04.03
Controlling Absolute Dimensions of Gold Nanorods Catherine J. Murphy; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Gold nanoparticles of controlled size and shape display brilliant optical properties throughout the visible and near-infrared portions of the electromagnetic spectrum. Gold nanorods, usually 15-20 nm in diameter with tunable lengths of 20, 30, 40, 50, 60 nm, show two plasmon bands corresponding to transverse and longitudinal excitations. The length/width ratio (aspect ratio) of gold nanorods is well-known to dictate the relative positions of the two plasmon bands. Recently in my laboratory we have developed a synthesis of "mini gold nanorods" in which the particle diameters are 5-8 nm, and lengths are 10, 20, 30 etc. nm. These absolutely smaller nanorods display similar plasmon bands to their larger counterparts, but the relative proportion of light scattering compared to light absorption differs. This talk will describe the synthetic procedures to create mini-rods as well as comparisons of properties between mini-rods and "regular" rods.

9:45 AM NM02.04.04
Symmetry Breaking and Shape Control in Gold Nanorod Growth—From Conception to Old Age Joanne Etheridge, Wenming Tong, Michael Walsh, Hadas Katz-Boon and Alison Funston; Monash University, Monash University, Victoria, Australia.

Symmetry-breaking is the essential step required for an isotropic seed particle to grow into an anisotropic shape. Using specially designed electron microscopy methods and strategically-chosen synthetic routes, we investigate the mechanisms behind symmetry breaking and shape control in gold nanorod growth, from conception to old age [1-4]. We observe the symmetry-breaking event that triggers the formation of the embryonic nanorod; an asynchronous formation of new surface structures in the cuboctahedral gold seed particles [1,3]. We show that the size at which the seed particle breaks symmetry depends sensitively on the Au/Ag ion ratio and describe a mechanism as to how this, in turn, controls the initial nanorod aspect ratio [2,3]. After observing the initial symmetry breaking event, we investigate the evolution of the nanorod morphology over an extended timeframe, for periods up to 3 orders of magnitude longer than the conventional 1 - 2 hours [4]. Following initial rapid anisotropic growth, the nanorods grow isotropically, and over longer times (weeks), tend ultimately towards the same reduced aspect ratio, irrespective of the AgNO3 concentrations. Furthermore, we measure the orientation and stability of different facets [5,6] and show how the nanorod transitions from faceted to curved when allowed to grow for extended periods [4]. Collectively, these observations suggest that the ultimate final aspect ratio is dictated by the surface energetics of the cylindrical sides compared to the hemispherical tips, with little dependence on the initial AgNO3 concentration. In other words, the AgNO3 concentration mainly asserts control over aspect ratio at the symmetry breaking point, rather than during later growth. Altogether, these observations provide a rational framework for controlling width, aspect ratio and facet orientation in the growth of single crystal gold nanorods.

References:

10:00 AM BREAK

10:30 AM NM02.04.05
Quantitative Chemical Mapping of Soft-Hard Interfaces on Gold Nanorods Ilanka Janicek1, Joshua G. Hinman2, Jordan Himman2, Huei-Huei Chang2, Kenneth Suslick1, Catherine J. Murphy2 and Pinshane Huang1; 1Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Soft-hard interfaces at the surface of nanoparticles (NPs) determine interaction potentials, including the mechanisms of growth, spatial reactivity, colloidal stability, and nanoparticle functionality [1]. For example, molecular ligands are thought to guide growth and symmetry breaking in anisotropic NPs. These ligands can also act as soft templates for site-selective deposition of functional coatings [2, 3]. Thus, quantitative details of the local attachment, distribution, and structure of soft-hard interfaces would enable the development of methods for high-yield, monodisperse NP synthesis.

Conventional techniques to characterize soft-hard NP surfaces—such as nuclear magnetic resonance, small angle x-ray scattering, and other bulk methods—lack the spatial resolution necessary to probe key details, including how the surface structure and chemistry varies within and between individual particles [1]. Yet in NPs, polydispersity is a defining characteristic, and surface energies and interactions vary widely based on local facet, curvature, and composition. While electron microscopy can address this challenge, an ideal approach requires a combination of: low-background substrates, the ability to quantify elemental distributions of small molecules, and the efficiency necessary to probe multiple NPs. Here we report a particle-by-particle analysis of soft-hard interfaces on gold nanorods (AuNRs) using aberration-corrected scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) spectrum imaging on graphene substrates.

In order to demonstrate the ability of electron microscopy methods to probe soft-hard interfaces, we investigate anisotropic mesoporous silica functionalization of AuNRs. Mesoporous silica can be deposited with site selectivity to either the ends or the sides of AuNRs. Such growth is thought to be templated by the anisotropic distribution of capping ligand cetyl trimethylammonium bromide (CTAB) [2, 3]. We deposit AuNRs onto suspended graphene substrates and use EELS spectrum imaging to map the presence of carbon, silicon, and oxygen. We directly observe a mesoporous silica frame with carbon content indicating the presence of a residual CTAB shell surrounding the particle. Using graphene as a reference, we quantify the CTAB present before and after silica deposition. These results indicate that before deposition, AuNRs are coated with a few-nm thick CTAB layer corresponding to ~5,000 ligands/particle. This density is small when compared to the ~60,000 ligands/particle on silica-coated AuNRs. Our methods thus represent the first direct, quantitative chemical analysis of soft-hard interfaces of metal nanoparticles.

References:
A key way to impart specific function to metallic nanoparticles is to functionalize their surface with ligands, allowing a range of applications including chemical and biological sensing; theranostics; and catalysis. For gold nanoparticles, this typically involves incubating nanoparticles in solutions containing thiol-terminated ligands and allowing the ligands to self-assemble on the surface of the gold through the formation of gold-thiol bonds. However, the structure and organization of the resulting ligand shell at the metal-organic interface is difficult to visualize. This talk will describe how single molecule fluorescence and super-resolution microscopy provide insight into surface organization of DNA-functionalized gold nanorods as a function of different preparation strategies. In cases when the DNA binds in a collapsed, disordered configuration, plasmon heating facilitates dynamic surface reorganization to a more ordered, upright geometry. By understanding how changes in surface preparation protocols impact the resulting ligand shell, we will be able to synthesize more reproducible functionalized nanostuctures.

Amplification of Chirality Transfer to Nematic Liquid Crystals by an Enhancement of the Anisotropy Factor in Chiral Ligand-Capped Gold Nanorods

A new way to impart chiral function from metallic nanoparticles is to functionalize their surface with chiral ligands. The present approach significantly increases the chirality transfer efficiency from the chiral ligand to the nematic liquid crystal. This result is coherent with other data on the anisometric shape of GNRs with enhanced anisotropy or Kuhn’s dissymmetry factors.

A key way to impart specific function to metallic nanoparticles is to functionalize their surface with ligands, allowing a range of applications including chemical and biological sensing; theranostics; and catalysis. For gold nanoparticles, this typically involves incubating nanoparticles in solutions containing thiol-terminated ligands and allowing the ligands to self-assemble on the surface of the gold through the formation of gold-thiol bonds. However, the structure and organization of the resulting ligand shell at the metal-organic interface is difficult to visualize. This talk will describe how single molecule fluorescence and super-resolution microscopy provide insight into surface organization of DNA-functionalized gold nanorods as a function of different preparation strategies. In cases when the DNA binds in a collapsed, disordered configuration, plasmon heating facilitates dynamic surface reorganization to a more ordered, upright geometry. By understanding how changes in surface preparation protocols impact the resulting ligand shell, we will be able to synthesize more reproducible functionalized nanostuctures.

References:


* Author for Correspondence: thegmann@kent.edu

In Situ X-Ray Scattering Guides the Synthesis of Functional Nanocrystals

Synthesizing nanocrystals with precisely controlled size, shape, and structure is of great importance for understanding their properties. Although significant developments have been achieved in colloidal synthesis, it remains challenging to synthesize nanocrystals in a predictive way due to a lack of mechanistic understanding of the synthesis. In this talk, I will discuss my recent research efforts on precise syntheses of nanocrystals guided by *in situ* synchrotron X-ray scattering.

The first part of this talk describes using *in situ* small angle X-ray scattering (SAXS) under "realistic" synthetic conditions to elucidate the formation kinetics of monometallic Pd nanocrystals in the presence of different ligands, which enables precise synthesis of a broad library of monodisperse Pd nanocrystals with 1 nm size control. The real-time SAXS also allows us to observe an unprecedented rapid crystallization of nanocrystals into three-dimensional superlattices at high temperatures and their continuous growth within the superlattices, which provides new insights on interparticle interactions during colloidal synthesis. In the second part of the talk, I will demonstrate a mechanistic understanding of the formation of bimetallic PtSn nanocrystals at the atomic scale using simultaneous SAXS and wide angle X-ray scattering (WAXS). This type of *in situ* characterization can be readily extended to other nanocrystal systems to advance their rational synthesis.

References:


Measuring the Facet-Selective Electrochemistry that Drives Anisotropic Growth of Metal Nanostructures

The number of applications for anisotropic metal nanocrystals in biomedicine, catalysis, and electronics has grown rapidly over the last decade. However,
the origins of anisotropic growth of metal nanocrystals in solution remain unclear due to the lack of experimental methods that can test previously proposed hypotheses. For pentagonally-twinned nanowires of Cu, Ag, and Au, researchers have hypothesized that organic capping agents selectively inhibit atomic addition to the \{100\} facets on the sides of nanowires, and thereby induce anisotropic nanowire growth through atomic addition to \{111\} facets on the ends of nanowires. However, there is little experimental evidence to support this hypothesis, and it does not explain why most syntheses require halide ions to grow Cu, Ag, and Au nanowires.

This presentation will show how electrochemical measurements on single crystals can be used to test hypotheses for how anisotropic growth of a metal nanocrystal occurs. In one study with Cu(100) and Cu(111), rather than acting as a capping agent, ethylenediamine (EDA) increased the rate of atomic addition to nanowire ends by keeping the Cu(111) surface relatively free of surface oxidation in the highly basic growth solution (>12 M NaOH). In another synthesis of Cu nanowires that involves the reduction of CuCl\(_2\) in the presence of hexadecylamine (HDA), we show that this capping agent passivates both Cu(100) and Cu(111) surfaces equally. However, the introduction of chloride ions in a narrow range of concentrations disrupts the alkylamine monolayer on Cu(111) but not Cu(100), causing Cu to preferentially deposit onto \{111\} facets on the ends of the nanowires. As in experiments, DFT calculations reveal there is an intermediate Cl coverage window in which HDA chemisorbs to Cu(111) but physisorbs to Cu(111), enabling the selective addition of Cu atoms to the less-protected \{111\} facets on the nanowire ends. This study shows single-crystal electrochemistry, in combination with DFT, can reveal unexpected mechanisms for how anisotropic growth occurs.

SESSION NM02.05: Plasmonic Structures
Session Chairs: Grant Johnson and Jianping Xie
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Commonwealth

1:30 PM *NM02.05.01
Plasmonic Nanocrystals with High Refractive Index Sensitivity and Thermal Stability Sara E. Skrabalak; Indiana University, Bloomington, Bloomington, Indiana, United States.

Seed-mediated co-reduction is a versatile route to multimetallic nanocrystals with shape definition. This method has been used to achieve stellated Au-Pd nanocrystals with high symmetry, which is guided by the shape of the seeds used for bimetallic deposition. This presentation will highlight recent studies into the tunable optical properties of these nanocrystals for use as LSPR sensors and photothermal agents. As will be shown, compared to all-Au nanocrystals, the Au-Pd nanocrystals display higher sensitivity to changes in local refractive index as well as greater shape stability when heated. This presentation will be coupled with a detailed discussion of multimetallic nanocrystal synthesis by seeded methods and a broader discussion of the challenges associated with characterizing and modeling the composition of multimetallic nanostructures.

2:00 PM NM02.05.02
Peptide-Directed Synthesis of Chiral Plasmonic Gold Nanoparticles Hyo-Yong Ahn, Hye-Eun Lee and Ki Tae Nam; Material Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

The integration of chirality with plasmonic materials offers a new possibility for nanophotonics including polarization control, enantioselective sensing, and negative refractive index in the visible range. Since the light manipulation of chiral plasmonics relies on delicate nanomaterials, a majority of chiral nanostructure was created by precise lithographic techniques and molecular self-assembled template. Although remarkable chiral structures have been made by these techniques, spontaneous formation of three-dimensional inorganic nanostructure without mirror symmetry is an important challenge and still has not been achieved on a single nanoparticle.

In this study, we developed a peptide-directed strategy for synthesizing chiral plasmonic nanoparticle that allows for the precise control over handedness and chiroptical responses.[1-3] We demonstrated that interactions between peptides and gold surface enable “chirality transfer” to drive the spontaneous development of chirality during the nanoparticle growth. The intrinsic chirality of kink of inorganic high-Miller-index \{h\ k\ l\} planes (h ≠ k ≠ l ≠ 0) served a critical role to provide an enantioselective binding site for peptide on crystalline facets of gold nanoparticles. These unique peptide-gold interactions led to the evolution of asymmetric structure in an individual nanoparticle and consequently created a novel helicoid morphology with a 100-nm size. The highly twisted feature of chiral components in the helicoid gold nanoparticles gave rise to remarkably strong plasmonic optical activity; dissymmetry factor of the randomly dispersed nanoparticle solution reached 0.2 at visible wavelengths and can be further controlled by sequence, handedness, and an enantiomeric ratio of peptides. Theoretical calculation clarified that this optical activity is associated with the formation of strong chiral nearfield at high-order plasmonic mode. Surprisingly, based on the wavelength-dependent polarization rotation ability, a solution of the helicoid gold nanoparticle can modulate the color of transmitted light in a wide range of visible wavelengths. This color transformation operates in real-time by rotating a polarizer and can be observed in naked-eye. In this regard, we expect that our peptide-directed approach will promote the rational design and fabrication of three-dimensional chiral plasmonic metamaterial, as well as improve an understanding of the enantioselective interaction of peptide and inorganic material.


2:15 PM *NM02.05.03
New Earth-Abundant Metallic Nanoparticles for Plasmonics John S. Biggins1, Josee Richard-Daniel4, Sadegh Yazdi1 and Emilie Ringe1, 2, 6, 8
1Department of Chemistry, Rice University, Houston, Texas, United States; 2Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 3Department of Engineering, University of Cambridge, Cambridge, United Kingdom; 4COPL, Université Laval, Quebec, Quebec, Canada; 5Renewable and Sustainable Energy Institute (RASEI), Joint Institute with NREL, University of Colorado Boulder, Boulder, Colorado, United States.

Nanoparticles (NPs) of some metals (commonly Cu, Ag, and Au) sustain oscillations of their electron cloud called localized surface plasmon resonances (LSPRs). These resonances can occur at optical frequencies and be driven by light, generating enhanced electric fields and spectacular photon scattering, opening applications including photocatalysis, photothermal therapy, and enhanced spectroscopies, to name a few. However, current plasmonic metals, in particular Ag and Au, are rare, expensive, and have a limited resonant frequency range. Recently, much attention has been focused on earth-abundant Al, but Al NPs have interband transitions that damp LSPRs in the IR. Here we report earth-abundant Mg NPs that may surmount this limitation. Our colloidal synthesis forms 100-300 nm diameter, 30-50 nm thick hexagonal nanoparticles, reflecting Mg’s simple hexagonal lattice, as shown by SEM and HRSTEM (Figure 1). STEM-EDS and STEM-EELS mapping reveals a self-limiting layer of oxide analogous to that observed in Al NPs, passivating both Cu(100) and Cu(111) surfaces equally. However, the introduction of chloride ions in a narrow range of concentrations disrupts the alkylamine monolayer on Cu(111) but not Cu(100), causing Cu to preferentially deposit onto \{111\} facets on the ends of the nanowires. As in experiments, DFT calculations reveal there is an intermediate Cl coverage window in which HDA chemisorbs to Cu(111) but physisorbs to Cu(111), enabling the selective addition of Cu atoms to the less-protected \{111\} facets on the nanowire ends. This study shows single-crystal electrochemistry, in combination with DFT, can reveal unexpected mechanisms for how anisotropic growth occurs.
The growth of metal nanoparticles on a solid substrate with precise control over their positions is one of the main challenges of plasmonics. Here, we introduce a facile approach based on photoinduced deposition of metal nanoparticles from the liquid phase on a solid substrate, driven and controlled by plasmons. The solid substrate consists of nano gaps in a silver stripe covered by a flat polystyrene film. Surface plasmons excited at the nano gaps initiate and control the growth of silver nanoparticles. We demonstrated that by confinement of light in this way highly ordered lines of silver nanoparticles can be grown with a width of 200nm over the whole laser spot area. Moreover, the near-field intensity pattern formed by the incoming laser light and the light scattered at the surface plasmons (SPs) is able to form much smaller (70nm in width) silver nanoparticle lines experimentally observed in our work. This facile approach opens a new path towards photochemical and plasmon-mediated fabrication of different sophisticated nanostructures. It does not require the usage of an expensive light source, materials or vacuum condition. Only photosensitive chemicals and a suitable light confining structure are needed.
new insights for the understanding of plasmon-mediated spin dynamics.


4:30 PM NM02.05.08
Near-IR Photothermal Ag Nanoparticles-Polymer Nanocomposite Layers with Controlled Plasmonic Coupling for Biofilm Eradication Shuzhi Zhou, Padyrk Merkl and Georgios A. Sotiriou; Karolinska Institute, Solna, Sweden.

With the ever-growing threat of catheter-associated infections, the development of highly effective treatments against bacterial biofilms is crucial while at the same time challenging. For this reason, physical ways to eradicate biofilms are sought, with a popular one the local temperature increase by plasmonic metals and near-IR laser light that is typically induced by expensive gold (nanoshells, nanorods) and complex silver (nanotriangles) nanostructures. Here, a stimuli-responsive polymer nanocomposite simulating the surface of polymer catheters incorporating plasmonic photothermal nanoparticles was designed aiming to destroy biofilms by heat and/or heat-triggered antibiotic drug release. The agglomeration degree during flame nanoparticle synthesis and, thus, controlled plasmonic coupling of inexpensive spherical silver (Ag) plasmonic nanoparticles supported on inert amorphous SiO2 was optimized by adjusting the deposition time on substrates and SiO2 content in the particle films. This enhanced the localized surface plasmon resonance and light absorption in the near-IR region and facilitated efficient heat conversion upon irradiation with an 808 nm laser. Heat generated from the PDMS-Ag nanoparticle-layer-PDMS nanocomposite under near-IR irradiation inhibited the viability of clinically-relevant biofilms. Additionally, laser-induced heat was able to trigger drug release from poly(2-hydroxyethyl methacrylate) hydrogels that were coated on the polymer nanocomposites surface, enabling these nanocomposites to achieve on-demand, heat-triggered antibiotic release against biofilms. The facile, scalable and inexpensive fabrication method of the developed anti-biofilm polymer surfaces based on plasmonic photothermal layers liberates the field from the use of expensive materials and processes facilitating their broad employment and clinical translation.

4:45 PM NM02.05.09
Solution-Derived Plasmonic Metal Surfaces for Optical and Thermal Applications Jyotirmoy Mandal and Yuan Yang; Columbia University, New York, New York, United States.

Solution-based processes, such as galvanic displacement reactions, are a simple method for creating plasmonic metal nano- and micro-structures. However, despite their simplicity, their potential to fabricate metasurfaces tailored for thermal and optical applications remains to be explored in detail. In this talk, we present galvanic displacement reactions as a facile pathway to make plasmonically active metasurfaces tailored to function as, among other examples, selective solar absorbers, super-broadband absorbers/emitters, and stray light absorbers for astronomical and imaging applications. For instance, galvanic displacement reactions are known to yield solar absorbers with solar absorbance > 0.95 and hemispherical thermal emittance <0.1 [1]. Similar reactions can yield super-broadband absorbers with excellent, wide-angle absorbance (e.g. ~0.95 at incidence angles > 60°) from the visible to infrared wavelengths of light. Additional functionalities arising from the optical selectivity of the surfaces and combination with other materials will also be discussed.

With regard to synthesis, galvanic displacement reactions are attractive, as they can be conveniently tuned to yield specifically tailored plasmonic surfaces for different optical and thermal applications. Furthermore, they are simpler, less expensive and greener than currently used fabrication techniques (e.g. vacuum deposition). Lastly, they are compatible with unexotic metals or alloys such as steel, which broadens their applicability. Considering the above uses, these aspects make galvanic displacement-based reaction pathways viable and highly attractive for making plasmonic metasurfaces.

media. The silver-cobalt oxide core-shell nanocrystals (Ag@Co3O4) were synthesized using bi-polar pulsed plasma discharge in water for catalytic oxygen reduction in alkaline solutions. Microstructural and compositional analysis using HRTEM equipped with high resolution EDX elemental mapping verified that the reactive oxygen species generated from plasma-assisted decomposition of water molecules played important role in controlling the phase structure of the nanoparticles. In the presence of abundant oxygenated species, the Ag@Co3O4 core-shell was formed by the preferential oxidation of Co at the surface. The electrochemical measurements for oxygen reduction reaction revealed that the electrocatalytic activity of the Ag@Co3O4 core-shell nanocrystals were higher than that of pure Ag and Co3O4 nanoparticles. This enhanced catalytic activity could be attributed to the electronic effects induced by an upshift in the d-band center via charge transfer between Ag and Co. For the Ag@Co3O4 core-shell architecture, the active Ag interacted more extensively with the Co3O4 monolayer shell at the surface. Owing to this favorable structure, the ORR activity was higher on the core-shell surface than for the subcluster-segregated nanoalloys. This was unlike uniform contacts, and it led to weakened electronic effects. Thus, it was concluded that Ag@Co3O4 core-shell electrocatalysts will be promising candidates for potential applications in catalysis.

Acknowledgement
This work was supported by the National Research Foundation of Korea (NRF) grants funded by the Korea Government (NRF-2016R1D1A1A09918072)

NM02.06.03
Mechanical and Electrical Properties of Nanowire-Based Flexible Galvanic Skin Response Sensor Sun Hwa Park, Ji Hye Park and Jae Yong Song; KRISS, Daejeon, Korea (the Republic of).

Monitoring systems to read human bio-signal have been developed with increasing healthcare applications. Among them, galvanic skin response (GSR) sensor has been used to measure skin conductance, defined as electrical conductance between two regions of skin. GSR sensor can help to evaluate a stress and a lie detection because skin conductance is changed by the sweat gland activity indicating a psychological or physiological arousal. Recently, GSR sensors have been fabricated in the forms of fingerband, armband, hairband and patch. However, these sensors have some limitation due to low sensitivity and difficulty for wearable devices.

In this study, we introduce a low-cost and facile fabrication of highly flexible GSR nanosensor (less than 5 mm in size and 6 um in thickness) which is composed of vertically aligned Ag/Au core-shell nanowires (200 to 300 nm in diameter) embedded in a polyeimide matrix. Vertical configuration of the nanowires within GSR nanosensor enables the sensor to measure skin conductance through thickness direction while the nanosensor is insulating in the in-plane direction. The nanowire based GSR sensor is flexible enough to be easily adapted to the curved skin. Experimental results show that the nanowire based GSR sensors have more excellent sensitivity than commercial GSR sensor. The bending and cycling tests showed that the sensitivities of the GSR sensors are reliably maintained for three months.

NM02.06.04
Regulation of EGFR Signal Transduction by Dynamic Receptor Clustering Qianyun Zhang; Chemistry, Boston University, Boston, Massachusetts, United States.

Epidermal growth factor receptor (EGFR) is a transmembrane receptor tyrosine kinase, whose dysregulation and abnormality have been associated with oncogenesis. Current EGFR targeted therapeutic approaches have failed to meet expectations due to the mutation of EGFR or the resistances of tumor to the treatment. So the development of an efficient receptor targeted drug would be successful only if the molecular mechanism underlying the EGFR signaling pathway are fully understood. It has been known that clustering of receptors play important roles in cell signaling. Thus, we will study the distribution of the epidermal growth factor receptors on the cellular membrane as well as in early endosome in the response to the ligand binding.

Noble gold nanoparticles (NPs) has been used as tool in biosensing and tracking due to their unique optical properties. The most useful property of NPs is that they can induce plasmon coupling, then leads to a spectral shift in the scattering spectrum of the coupled NPs labels. This shift can be conveniently detected by conventional far-field light microscopy, so called Plasmon Coupling Microscopy (PCM). Heterogeneous EGFR distribution will be optically indicated by EGF conjugated gold NPs clusters with different size and colors. Thus, we will develop a gold palisom ruler that can characterize the compartmentalization of growth factor in cancerous cell lines. The first aim is to investigate the regulation of surface receptor clustering to signaling strength. To do that, it is necessary to correlate the spatial organization of EGFR clustering, as measured by PCM, with the receptor activation. The triggered EGFR signaling can be quantified by detecting its phosphorylation levels by specific antibodies.

The next question is how receptor tyrosine kinases determine different cell-fate decisions despite sharing the same signaling cascades. One hypothesis is the tight control of the endosomal distribution of EGF could serve to regulate signal transmission. The cell respond to higher EGF concentration by increasing the number of endosomes, and the average number of phosphorylated EGF receptors in each endosome remains almost constant. If we expose cell to gold NPs with different EGF ligand density, the endosome contained NPs cluster would be different. Thus, we could test hypothesis by quantitatively analyzing the endosomal distribution of EGFR and downstream signaling outcome.

The correlation of EGFR clustering and signaling activation will explicit explain how growth factor activation of this process depend on receptor clustering. Furthermore, we will address the question that whether intercellular EGFR clustering facilitates the decisions of signaling outcome. Therefore, the study of the mechanism of tyrosine kinase receptor in signaling pathway could help to augments efficacy of EGFR targeted therapeutic treatments in the future.

NM02.06.05
Seed-Mediated Co-Reduction Synthesis of Intermetallic Au-Cu Nanocrystals—Insight into the Size-Dependent Disorder-Order Transformation Hannah M. Ashberry, Jocelyn T. Gamler and Sara E. Skrabalak; Indiana University, Bloomington, Indiana, United States.

Intermetallic nanoparticles often show increased catalytic efficiencies and durability towards electrocatalytic processes, such as the oxygen reduction reaction and reduction of carbon dioxide. Typical syntheses of intermetallic materials include thermal annealing of the alloyed counterpart and colloidal chemical syntheses. While both methods can produce intermetallic nanoparticles, little is known about the transformation from the random alloy to intermetallic phase. Previously demonstrated in the Skrabalak group was a size-dependent disorder-to-order transformation from random alloy to intermetallic Au-Cu nanoparticles. Such a size dependent transformation has also been observed in semiconductor systems. Here, this size-dependent transformation is explored with Au-Cu nanoparticles. Specifically, monodisperse Au50Cu50 and Au60Cu40 intermetallic nanoparticles were synthesized by seed-mediated co-reduction using Au-Cu random alloys as seeds. The study of the growth mechanism by analyzing reaction aliquots by TEM and XRD supports that such a disorder-to-order transformation is a general feature that can be exploited with seed-mediated co-reduction to achieve high quality intermetallic samples. This demonstration advances understanding of intermetallic nanoparticle formation in colloidal synthesis, which can expedite the development of electrocatalysts.
Selective Heterogeneous Growth of Polyhedral Cu Nanoshell for Plasmonic Light Scattering Enhancement and Quantitative Naked-Eye Bio-Detection
Jae-Ho M. Kim, Jeong-Fun Park, Mouhong Lin, Sungi Kim, Gyeong-Hwan Kim and Jwa-Min Nam; Chemistry, Seoul National University, Seoul, Korea (the Republic of).

Nanoparticles (NPs) such as AuNPs have wide applications in molecular detection, labelling, and imaging due to their compatible size, large surface area, availability of various conjugation methods, richness in core-shell chemistry, as well as geometry-dominant optical properties such as localized surface plasmon resonance and plasmonic coupling properties. The magnitude of the intrinsic optical properties of individual NP probes are, however, insufficient to detect targets at trace levels. Further, the simplicity, assay speed, and portability are critical elements, especially in developing fast but reliable naked-eye-based bioassays. To address these issues, Ag-based enhancement, known as silver staining, has been extensively studied so far to amplify Rayleigh scattering, surface-enhanced Raman scattering, colorimetric signals and electrical signals. However, the lack of specificity on detection label and low controllability of Ag shell formation limited its practical applications.

Here, we introduce a selective heterogeneous growth of polyhedral Cu nanoshell on Au nanoparticle. This is based on highly controllable polyethyleneimine(PEI)-mediated Cu polyhedral nanoshell (CuP) formation chemistry, specifically formed on AuNP probes, and used this CuP formation method for straightforward, intensive and quantifiable optical signal enhancement. The optical signals from one-to-one overgrown metallic polyhedral nanoshells are amplified about two orders of magnitude, and readily detectable with naked-eyes or an ordinary smartphone camera. In the case of DNA assay (anthrax sequence), we detected 8 fM DNA on an archetypal DNA microarray chip with a dynamic range from 8 fM to 800 pM in this manner. Also for virus detection (norovirus target in this case), clinical stool samples were used, and as low as 2,700 virus copies were detected with >2-orders of dynamic range. The high sensitivity and quantification capability of this CuP enhancement were superior to any other previously reported bio-detection methods detectable with naked eyes. The Cu nanoshell formation chemistry provides a new paradigm in controlling optical properties from selectively overgrown Cu shell nanostructures and their use in bio-detections.

Enhanced Radiation Shielding with Conformal Light-Weight Nanoparticle-Polymer Composite
Qingxuan Li, Qilin Wei and Ming Su; Northeastern University, Boston, Massachusetts, United States.

This abstract reports a new property enabled by nanoparticles, where bismuth nanoparticles added in a polymer matrix can block X-ray radiation several times more efficient than microparticles at the same mass ratio. Bismuth nanoparticles are made with cellulose nanofibers and dispersed evenly into a polymer. A four time reduction in the mass of bismuth material is identified at 2% mass ratio when nanoparticles (3 nm diameter) are used in composite to shield a given flux and energy of radiation, in relative to those of microparticles (5 µm diameter). The enhancement in radiation shielding is primarily attributed to close packing of nanoparticles along projection direction of incoming X-ray, which is enabled by strong affinity of nanoparticles to interstitial space of cellulose nanofibers and even distribution of nanoparticles in polymer. Given its low cost, light weight and structure conformability, bismuth nanoparticle-polymer composite will find its use in a wide range of fields related to personal radiation protection.

A Quantitative Electron Microscopy Study of the Bending of Seed-Mediated Grown Gold Nanorods
Xin Wen1, 2, Torben N. Pingel2, Kasper Moth-Poulsen1 and Eva Olsson2; 1Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden; 2Department of Physics, Chalmers University of Technology, Gothenburg, Sweden.

Gold nanorods are promising candidates for applications in medicine, optics, electronics and chemistry since they have attractive optical and physical properties, especially strong absorption of localized surface plasmon resonance. In order to manipulate absorption of light in unprecedented ways, researchers have studied how to bend gold nanorods using lasers. However, we have observed gold nanorods synthesized by a binary-surfactant seed-mediated growth method exhibiting high resolution transmission electron microscopy (TEM) and found that they were bending a few degrees spontaneously. The study on formation of bending structure and the deformation in the rods also benefits understanding the dynamic process of gold nanorods' growth. Further researches on TEM have shown that the gold crystal lattice is tilting a small angle (less than 10 degree) around [010] zone axis continuously, which is also transversal axis of the rod. Besides, there is no lattice defects observed on the bending gold nanorod in high resolution images. In order to understand bending mechanism, the distribution of silver element added in growth solution was studied by Energy-dispersive X-ray spectra. We found very little amount of silver concentrated on the outer layer of a gold nanorod, which is the possible reason that causes the bending structure.

Selective Heterogeneous Growth of Polyhedral Cu Nanoshell for Plasmonic Light Scattering Enhancement and Quantitative Naked-Eye Bio-Detection
Qingxuan Li, Qilin Wei and Ming Su; Northeastern University, Boston, Massachusetts, United States.


Mitsuhiro Iwasaki1, Yukatsu Shichibu1, 2 and Katsuaki Konishi1, 2; 1Graduate School of Environmental Science, Hokkaido University, Sapporo, Japan; 2Faculty of Environmental Earth Science, Hokkaido University, Sapporo, Japan.

Recent progress in the crystal structure determination of ligand-stabilized gold clusters has revealed that not only nuclearity but also geometrical structures of inorganic units affect their electronic structures and optical properties. The perturbation effect of the ligand environment is an important feature for developing designer clusters with specific functions, but the role of the organic units is still elusive. In this work, we placed focus on the effect of proximal π-system of organic unit on the optical properties of the gold cluster. A series of core + exo type Au5 clusters decorated by diphenylethene (dppp = Ph2P(=CH2)PPh3) and aryloleolate ligands were synthesized, and their optical properties were studied to obtain insights into the perturbation effect of the organic ligands. Various thiolate and acetylide ligand were induced on the Au5 framework via the reaction of divalent Au5 cluster ([Au5(dppp)3]2+) with the corresponding alkyne and thiol. The produced clusters were characterized by electrospray ionization mass spectrometry and elemental analysis. Pyridinium-substituted Au5 clusters ([Au5(dppp)(SPy)]2+) exhibited absorption and photoluminescence responses to protonation events of pyridyl moieties. Upon protonation, 2- and 4-pyridinemethylate clusters showed larger red shifts of absorption and photoluminescence bands than 3-pyridinemethylate, suggesting that the observed band shifts are associated with the resonance structure of the pyridiniumylates. On the other hand, emission intensities of all regioisomers increased largely. X-ray crystallographic and NMR analyses revealed the electron-deficient pyridinium rings form π-stacks with proximal phenyl groups of dppp in the protonated form. Thus, it was suggested that the rigidity of the ligand environment induced by π-π interactions leads to the enhancement of emission efficiency. These results indicate that optical properties of small gold clusters can be modulated through the electronic and steric perturbations by surrounding organic units.
Simulations that closely mimic the experimental conditions, including the degree of particle roundness, the softening of the particle contacts with the substrate/indenter, and the testing temperature.

We demonstrate that faceted single-crystalline Nickel and Ni-Fe alloy nanoparticles exhibit an ultrahigh compressive strength unprecedented for crystalline metals. Most of the particles yielded with a large strain burst, and their strength exhibited a strong dependence of on the particle size. The strength of colloidal gold nanoparticles with different shapes (rod, star, and sphere) can be quickly assembled by resonance matching with light. One assembly with a diameter of tens of micrometers can be completed within a minute, and patterned arrays of this assembly can also be prepared rapidly. We believe that our proposed method will have a huge impact on the future development of optical and electronic systems, as well as the building-up of plasmonic nanomaterials.

Small scale testing of single crystalline metallic particles offers a unique opportunity to understand the nucleation-mediated plasticity mechanisms. Single crystalline Nickel-Iron (Ni-Fe) particles with different iron content were prepared by solid state dewetting of Ni-Fe bilayers on sapphire substrate. The capillary interaction with pre-patterned solid substrate has been utilized. However, the direct assembly of colloidal nanoparticles without chemical linkers and pre-patterned substrates remains challenging. Here, we propose a novel approaches for rapid and direct positioning of colloidal plasmonic nanoparticles onto diverse solid substrates via photothermal convection lithography. It is based on the photothermal conversion effect of plasmonic nanoparticles by resonant light focusing, which induces convective flow. The convective flow further forces the colloidal nanoparticles to assemble at the illumination point of light. The size of the assembly is increased by either increasing the light intensity or illumination time. Also, we accelerate the assembly by modulating of experimentally controllable variables such as light intensity and solvent viscosity. We show that three types of colloidal gold nanoparticles with different shapes (rod, star, and sphere) can be quickly assembled by resonance matching with light. One assembly with a diameter of tens of micrometers can be completed within a minute, and patterned arrays of this assembly can also be prepared rapidly. We believe that our proposed method will have a huge impact on the future development of optical and electronic systems, as well as the building-up of plasmonic nanomaterials.

Rapid and Direct Assembly of Colloidal Plasmonic Nanoparticles via Photothermal Convection Lithography

Convenient and Inexpensive Highly-Efficient Nickel Nanowire Catalysts

References:

Size and Composition Effects in Compression of Ni-Fe Particle Prepared by Solid State Dewetting of Bilayers

Self-Organized Formation of Multilayer Structure in a High Nitrogen Stainless Steel During Solution Treatment

Compared with traditional stainless steels, high nitrogen stainless (HNS) steels have been widely used due to their high strength, toughness along with excellent corrosion resistance and low cost, by partial replacement of Ni (austenite-forming element) by N element. The evolution of the microstructure of a Cr13Mn9Mo4N0.4 stainless steel is investigated by solution treatments at 1010, 1060, 1200 and 1250 degree Celsius for 30min, respectively. A complex multilayer structure has been found. A ferritic layer with nano-scaled particles precipitated along ferrite boundaries, at the surface, is formed. The precipitation of nano-scaled particles in the ferritic surface layer indicates possible diffusion barriers for nitrogen from subsurface to surface. This self-organized formation of multilayer structure can broaden the application of HNS steel to magnetic functional areas.

NM02.06.11

NM02.06.10

NM02.06.12

NM02.06.13

NM02.06.14
Surfactant-Free Synthesis of Cu₂O Yolk-Shell Cubes Decorated with Pt Nanoparticles for Enhanced H₂O₂ Detection Jian Lyu1,2, Chuncai Kong1, Sen Yang1 and Zhimao Yang1; 1Department of Materials Physics, Xi’an Jiaotong University, Xi’an, China; 2Department of Nanoeengineering, University of California, San Diego, San Diego, California, United States.

Cu₂O yolk-shell cubes decorated with Pt nanoparticles were synthesised by a liquid-phase, surfactant-free and multi-step route (Figure 1a). ZnCl₂ ions and O₂ dissolved in solution lead to the formation of the yolk-shell Cu₂O cubes. The as-prepared yolk-shell Cu₂O cubes were used as the substrate to hold the growth of Pt nanoparticles though a commonly used photo-reduction reaction without damages of the yolk-shell structures. Then, the as-prepared Pt-Cu₂O composites were used as the active materials for the fabrication of the nonenzymatic sensor for H₂O₂. Decorating Pt nanoparticles hugely increased the electrochemical sensing performance of Cu₂O, compared with the bare yolk-shell Cu₂O cubes. Meanwhile, the Pt-Cu₂O based H₂O₂ sensors show good electrochemical selectivity to the reduction of the H₂O₂, indicating its great promise to serve as the electrocatalytic materials for the sensing of the H₂O₂.

NM02.06.15 Retention of Anti-Cancer Activity of Curcumin after Conjugation with Gold Quantum Clusters—An In Vitro and In Vivo Xenograft Study Puneet Khandelwal1, Aftab Alam1, ArpanKumar Choksi1, Samit Chattopadhyay2 and Pankaj Poddar2; 1Indian Institute of Technology Kanpur, Kanpur, India; 2CSR-National Chemical Laboratory, Pune, India; 3NCCS, Pune, India; 4ICICB, Kolkata, India.

Cancer is a leading cause of death worldwide. However, a significant progress has happened in the cancer theranostics, a huge scope of the development is still exist. Chemotherapy is the most commonly used modality for cancer treatment. Curcumin is one of the very important therapeutically important drug molecules which has applications in wide range of diseases but could not be used clinically much because of its poor water solubility. The nanoparticles based platforms are used to enhance the solubility of curcumin. Since last two decades, metal nanoclusters are becoming increasingly popular for biomedical applications because of their very small size around 1-2 nm, biological inertness, a wide range of luminescence from UV to NIR. Therefore, in the present work, gold quantum clusters (Au QCs) are used to increase the curcumin water solubility by using it as both reducing and capping agent for the synthesis of Au QCs. These curcumin conjugated Au QCs (C-Au QCs) were studied for their cytotoxicity to normal (NIH3T3) as well as cancer cells (MCF7). The curcumin conjugated gold nanoparticles (C-Au NPs) and GSH conjugated Au QCs were also synthesized to evaluate the effect of size and capping agent on the anticancer property. The cytotoxicity mechanism of Au QCs was studied in detail using FACS and western blot analysis. Further, the antitumor activity of C-Au QCs was studied in xenograft mice model and found that C-Au QCs were able to effectively inhibit the tumor growth. The major organ section analysis showed that the C-Au QCs did not exhibit cytotoxicity to the organs. Based on the results, the C-Au QCs are believed to be a promising candidate to treat cancer effectively in near future.

NM02.06.17 Visible Migration of Gold Based on Localized Plasmon Effect on a Paper Substrate Nobuko Fukuda1, Sakae Manaka1 and Toshiharu Enomae1; 1National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 2University of Tsukuba, Tsukuba, Japan.

We visually observed color changes of a paper substrate on which gold particles were deposited during a period since deposition. The isolated gold particles are formed on the coated paper by thermal vapor deposition with 0.01 nm/s of the deposition rate for 500 s. The size of each gold particle is about a few 10s nm just after deposition, according to the surface image of the paper collected with a scanning electron microscope (SEM) and an atomic force microscope (AFM). The reflection spectrum for the surface measured with an integrating sphere spectrophotometer shows a high reflection from 400 to 510 nm and the surface color is bluish. The color is derived from localized surface plasmon resonance of the gold particles. After it was placed in air at room temperature for 6 months, the color changed from bluish to reddish. The spectrum shows a high reflection at more than 600 nm. The size of the gold particles after 6 months widely varies from a few 10s nm to 100s nm. Some particles seem to coalesce and the space between grains obviously has widen according to SEM observation. These results suggest that migration of the gold particles on the coated paper occurs at room temperature. In the case that the thermal vapor deposition with 0.01 nm/s was carried out for 1000 s, an incomplete gold sheet with gaps is formed on the paper substrate. The sheet thickness is about 10 nm. The reflection spectrum shows a high reflection at more than 500 nm and the surface color is yellowish and slightly metallic. After it was placed in air at room temperature for 6 months, the color changed from yellowish to reddish. The SEM and AFM images of the surface after 6 months showed isolated gold particles with more than 100 nm in diameter and more than 100 nm in height. It seems that dewetting, isolating, and coalescence of the gold have sequentially occurred on the coated paper. In addition, we expect that the rate of the color changes based on the migration of gold depends on the surface conditions such as roughness, surface free energy, adhesive force, and so on.

NM02.06.18 Preparation and Characterization of NiMnOx Particles Toward Supercapacitor Application Hikaru Ishitsuka and Yoshikazu Suzuki; Graduate School of Pure and Applied Science, University of Tsukuba, Tsukuba, Japan.

Recently, with the increase in worldwide energy demand, rechargeable energy devices and materials are actively studied. Especially, supercapacitor is a promising application in energy storage devices due to its high power density, good reversibility and cycle characteristics. Manganese oxide-based transition metal compounds are candidates for supercapacitor materials. NiMnO₂ has excellent conductivity, stability and electrostatic capacity and does not contain noble metal. NiOCl₂·2Ni(OH)₂·4H₂O (1 mmol), MnO₂ (3 mmol) and urea (15 mmol) were dissolved in 30 mL distilled water to obtain homogeneous solutions. The solutions were hydrothermally treated at 120-160 °C for 6 h, and Ni-Mn precursors were obtained. The as-prepared precursors were calcined at 350 °C for 3 h. The obtained powder samples were characterized by XRD, and the microstructure was investigated by SEM and TEM. The specific surface area was evaluated by N2 adsorption method.

NM02.06.19 Nano-Phase Separation Sintering in Titanium-Magnesium Alloys Kathrin Graetz1, Jonathan Paras1 and Christopher A. Schuh1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Mubea Performance Wheels, Gurten, Austria.

While mechanical milling reliably produces nano-sized grains in metal alloy powders, consolidating as-milled powders into bulk parts—while still retaining the desirable nanocrystalline structure—remains a challenge. This work seeks to use alloying to lower the free energy of grain boundaries and decrease the driving force for coarsening in nanocrystalline Ti alloys, permitting solid-state sintering to high density. Mg is identified as a nano-grain stabilizer for Ti, and the effects of Mg composition on powder consolidation by pressureless sintering are explored. The mechanical milling of Ti-Mg alloys produces grain sizes on the order of 20 nm along with a supersaturation of Mg solute in Ti. Accelerated sintering occurs upon heating, triggered by nano-phase separation of Mg out of solution, in some cases leading to relative densities >95% at low processing temperatures, while maintaining ultrafine grain sizes. The thermal stability of the grain structure is also characterized over a range of temperatures and a kinetic relationship for the coarsening behavior of Ti-Mg alloys is determined.
Surface Versus Incorporated Pd on SnO$_2$—Influence on Gas Sensing

Sebastian Keller, Nicolay J. Pineau, Andreas T. G"{u}ntner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Size, shape and location of catalytic active Pd on SnO$_2$ has a strong impact on gas sensing properties. In specific, it greatly enhances the sensitivity of gas sensors and reduces response and recovery times and is therefore often applied. However, the exact role of Pd size, location and amount is rarely investigated and remains a trial and error approach. Here, the location (i.e. surface or incorporated) and size of Pd on SnO$_2$, and its role on gas sensing are systematically investigated and optimized at the nanoscale. In a first step, SnO$_2$ nanoparticles with different amounts and locations of Pd were prepared by flame aerosol and wet chemical synthesis. The amount of incorporated and surface Pd was investigated by X-ray diffraction, tunnelling electron microscopy and Pd-leaching. Sensing films of these particles were obtained by doctor blading them onto substrates with interdigitated electrodes. The optimized gas sensors exhibit superior sensitivity to trace analytes even at relevant low ppb levels and could therefore readily be used to detect environmental pollutants, monitoring food quality, detect entrapped humans after a calamity, as well as in medical breath analysis.


Design of Localized Surface Plasmon Absorption in Square-Shaped Silver Nanoparticles

Abhikesh Ramachandran, Anmol Walia and Madhusudan Singh; Indian Institute of Technology Delhi, New Delhi, India.

Shaped nanoparticles are known to enhance absorption in a tailored manner due to the enhancement of electric field modes in incident light. Various fabrication techniques have made it possible to produce nanoparticles with accurate sizes and in a variety of external media resulting in a controlled red shift in the absorption spectrum. This control is valuable in the design of absorbers for potential detector and photovoltaic applications, besides optical coatings. In this work, the dependence of the absorption spectrum on various parameters such as square nanoparticle edge length, height, aspect ratio, wavelength and polarization of incident light, external medium as well as the effect of a proximal conductive substrate was investigated using finite difference time domain numerical techniques, and enhancement factors derived. Absorption peaks were found to redshift from ~625 nm to ~890 nm upon an increase of the edge length from 150 nm to 250 nm (height constant), but blue shift upon increasing height of the nanoparticles (edge length constant). The peak location is found to be strongly dependent on the aspect ratio, but not the volume of the nanoparticles. Higher refractive indices resulted in redshift of the absorption (fixed distance to the conductive substrate). Resonant energy transfer is seen to happen through enhanced absorption for in-plane polarization of light. These results are expected to provide a better path to the rational design of optical absorption through localized surface plasmon resonance of square nanoparticles produced through techniques such as chemical synthesis and e-beam lithography.

Correlating Interfacial Solvent Structures with Catalytic Behavior by Total Scattering

Mirco Eckardt and Miriam Zobel; University of Bayreuth, Bayreuth, Germany.

Noble metal nanoparticles (NP) play a major role in modern heterogeneous catalysis. Reaction conditions like temperature and pressure impact the catalytic activity and selectivity. [1] Although a solvent effect is commonly accepted as a decisive parameter in liquid-phase catalysis, its fundamental understanding on a molecular level is still missing. Pair distribution functions (PDF) analysis based on high-energy X-ray scattering experiments can access the size of and the molecular ordering within solution shells around colloidal NPs. [2] To correlate solvent-dependent catalytic activity with the interfacial solvent structure, we performed the selective hydrogenation of styrene to ethylbenzene under atmospheric hydrogen pressure in various organic solvents like tetrahydrofuran (THF) and toluene. Dodecanethiol stabilized palladium (Pd) NPs with an average diameter of 3 nm acted as catalyst. The difference-PDF signal of the THF dispersions reveals four restructured layers of THF molecules stretching 2 nm away from the NP surface. Corresponding catalytic studies (gas chromatography) allow a structure-activity correlation. Finally, GC-MS can be coupled to in-operando PDF measurements (1 min time resolution) to track structural changes of both NP and interfacial solvent layers in liquid-phase catalysis.


Control of Nanoporous Pd-Al Film Structure by Dealloying Reaction of Al-Pd Alloy Film Using Organic Acids as Chelating Agents

Takashi Ishiguro, Akizumi Kawamoto and Takaji Ube; TUS, Tokyo, Japan.

Nanoporous materials are applied to sensors, catalysts, etc. because of their large specific surface area. For example, since palladium (Pd) selectively reacts with hydrogen gas, application as a sensor is expected. One of the most usual methods to form the nanoporous materials is dealloying, which is chemical or electrochemical dissolution process of the base metal from the precursor alloy with target material. In this case, strong acids such as hydrochloric acid and sulfuric acid or strong alkali are usually used. In contrast to this, we have proposed a dealloying process using environmentally friendly chemicals. Ultrasensitive nanoporous Pd-Al film had been successfully formed by citric acid-assisted hot-water-treatment of Al-Pd alloy film. (T. Harumoto, Y. Tamura, et al., AIP Advances 5, 017146 (2015)). Here the citric acid played a role as a chelating agent for forming the complex with Al$_3^+$ ions. On the other hand, there was a disadvantage that the reaction rate was slow, e.g. it took 30 minutes for dealloying reaction of 70-nm-thick Al-Pd alloy films to be saturated. Therefore, in this study, in order to accelerate the dealloying reaction rate, pH value of the reaction solution was controlled from 4 to the alkaline side. In addition to the citric acid, as the reaction solution, ethylenediaminetetraacetic acid (EDTA) having high chelating ability was also examined. 70-nm-thick Al-Pd (82at%Al) alloy films were prepared by rf sputtering method using Al target with Pd sectors. pH value was controlled by adding NaHCO$_3$ to citric acid solution or Na$_2$CO$_3$ to EDTA solution. Time variation of the visible light transmittance (VLT) during dealloying processing at 370 K was measured by using a digital high-vision video camera. Structure of the film on elastic carbon film were observed by using scanning transmission electron microscope.

Saturation time of VLT in the pure citric acid solution at pH=4.0 was 30 min. By adding NaHCO$_3$ to this citric acid solution, pH value changed to 9.0 and then saturation time of VLT was shortened to 9 min. Furthermore, when reacting with EDTA at pH=10.0, the saturation time was reduced to 90 sec. By changing chelating agent from the citric acid to EDTA, the film morphology also changed from high-density nanopore (diameter of about 10 nm) structure to nanopore network structure. In addition, the film composition after the dealloying treatment increased up to 92at%Pd in the case of EDTA (pH=10.0) from 85 at%Pd in the case of citric acid (pH=4.0).

It was considered that dissociation of citric acid and EDTA was promoted under the pH conditions on the alkaline side and the chelating ability was activated. As a result, it was found that by controlling the pH value according to the type of chelate, the dealloying reaction rate was accelerated to 20
Fullerene Nanopottery—Design, Shaping and Interconnecting Hollow Nanostructures Fei Han and Hongyu Chen; Nanyang Technological University, Singapore, Singapore.

Hollow nanostructures have been widely applied in nanoscience, but their fabrication remains at a primitive level. Most hollow nanostructures are enclosed spheres. Even creating a bottle in nanoscale is extremely difficult, not to mention creating more complex shapes and assembling interconnected systems. Interconnected hollow system is one of the most fundamental structures both in living system and in human industry, e.g., blood vessel system and nerve system in livings, various tube systems in city, and modern buildings consisted by corridors and rooms. However, the concept of interconnecting hollow spaces still remains blank in nanoscale, which is critical to the synthesis of such structures.

We bring pottery, the oldest and simplest method to create and assemble hollow structures, into nanoscale, to realize the systematical design, synthesis, assembly, and interconnection of hollow nanostructures. Individual fullerene hollow structures of tailored shapes, such as bowls, bottles, and cucurbits, are synthesized through a bottom-up process within one-step. Most importantly, the method allows modularized interconnection of hollow units into interconnected hollow systems. The synthesized structures have a hydrophobic interior and a hydrophilic outer surface. As a proof-of-concept, we create multi-compartment nano-containers, with different hydrophobic nanoparticles isolated in the separate pockets. Hopefully, these findings could expand the synthetic freedom for hollow nanostructures, building a bridge from isolated hollow units to interconnected hollow systems, and hence, have the potential to broaden their applications in a wide range of fields.

In Situ Analysis of Conductive Films Formation Using Cu Nanocrystals Arnau Oliva Puigdomenech 1, Filip Geenen 2, Christophe Detavernier 2 and Zeger Hens 1; 1Chemistry, Ghent University, Ghent, Belgium; 2Solid State, Ghent University, Ghent, Belgium.

Introduction
The constantly growing market of printed electronics requires the development of new materials that can be turned into conductive inks and allow for economic device fabrication. Hereof, due to its top-of-the-line conductivity and affordable cost, conductive inks based on copper nanocrystals have been extensively studied in the recent years. A particular focus of this work has been the prevention of copper oxidation, which can compromise the conductivity of the eventually printed copper. Typically, oxidation has been suppressed by the incorporation of antioxidants or the formation of a shell around the Cu nanocrystals. While effectively slowing down oxidation, such approaches come at the expense of costlier synthesis reagents and conditions. Instead of preventing oxidation at all costs, we propose a flexible and economical synthesis route of Cu nanocrystals, demonstrate by in-situ x-ray diffraction that surface oxidation can be reversed upon sintering, and how the sintering conditions vary depending on the copper nanocrystal size and surface termination.

Results and Discussion
Copper nanocrystals were synthesized by thermal decomposition of copper formate in oleylamine. SEM and TEM imaging presented quasi-spherical nanoparticles resistant as 20 µΩ●cm, which confirms the potential of nanocrystals for printed electronics.

Conclusions
We propose a flexible and efficient synthesis method that yields Cu nanocrystals. We use them as models to study the reduction of copper oxide in Cu nanocrystal films. We find that the unavoidable oxidation of the surfaces can be reversed via sintering. We prove that the temperature at which conversion to copper occurs markedly depends on the size and the surface termination of the nanocrystals. We demonstrate that sintered films attain a resistivity as low as 20 µΩ●cm, which confirms the potential of nanocrystals for printed electronics.

References

Synthesis and Characterization of Biogenic Selenium Nanoparticles with Antimicrobial Properties Made by Staphylococcus aureus, Methicillin-Resistant Staphylococcus aureus(MRSA), Escherichia coli and Pseudomonas aeruginosa David Medina, Gujie Mi and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Antimicrobial resistance is a global concern that affects more than 2 million of people each year. Therefore, new approaches to kill bacteria are needed. Nanotechnology is one of the most promising approaches. While metallic nanoparticle synthesis methods are well studied, they are often accompanied by significant drawbacks such as cost, extreme processing conditions, and toxic waste production. In this work, we explored the environmentally safe synthesis selenium nanoparticles, which have shown promise in killing bacteria

Using Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus subsp. aureus Rosenbach and Methicillin-resistant Staphylococcus aureus(MRSA) were used to synthesize biogenic selenium nanoparticles, 90-150 nm selenium nanoparticles were synthesized under standard conditions using an environmentally-safe approach. Bacterial cultures, prepared in Luria-Bertani (LB) media, were inoculated with 2 mM sodium selenite (Na2SeO3) solution to activate the detoxification process that leads to the synthesis of nanoparticles. The nanostructures were characterized using Transmission Electron Microscopy, Energy Dispersive X-Ray (EDX) to determine the chemical compositions and Inductively coupled plasma mass spectrometry (ICP-MS) to validate the chemistry within the samples. Nanoparticles were also characterized and tested for their ability to inhibit the bacterial growth through optical density measurements in a SpectraMax M3 spectrophotometer, and colony forming unit assays. Besides, biocompatibility tests of the nanoparticles with human tissue were accomplished, growing human dermal fibroblast (HDF) cells in media in the presence of biogenic selenium nanoparticles. After an incubation time of 24 hours, the cell growth was analyzed using MTS assay.
It is demonstrated that the bacterial strains used can generate biogenic selenium nanoparticles. The antimicrobial activity of these biogenic selenium nanoparticles was tested against Escherichia coli and Staphylococcus aureus to discover their antibacterial ability. Nanoparticles can produce a decay in the standard bacterial growth. Besides, the growth of Staphylococcus aureus was significantly inhibited for those nanoparticles synthesized by Staphylococcus aureus. In vitro cytotoxicity assays were performed with human dermal fibroblasts (HDF) cells. The experiments showed that all nanoparticle concentrations tested did not inhibit the growth of cells while also confirming a high percentage of cell viability.

As a conclusion, selenium nanoparticles with small and uniformly shape were synthesized with a relatively homogeneous size distribution. Decay in the bacterial growth was achieved against both Gram-positive and Gram-negative bacteria, showing no significant cytotoxicity effect when they were cultured with human dermal fibroblasts (HDF) cells.

NM02.06.28
Nanoshaping of Metallic Liquid by Stretching—Evading Lithography Zhonglue Hu and Golden Kumar, Texas Tech University, Lubbock, Texas, United States.

Metal nanostructures are integral parts of nanoscale devices and fundamental studies on characterization of size-effects. However, these technological and scientific advancements are hampered by the complex and expensive lithography-based fabrication techniques. Here, we present a novel lithography-free nanomanufacturing by elongation and rupture of glass forming metallic liquid. This approach allows facile fabrication of various structures such as nano-tips, nano-wires, and dog-bone-shaped nano-structures without lithography or expensive templates. The flow behavior of metallic liquids is tuned through temperature and strain-rate to control the shape of resulting structures upon elongation and rupture. Quantitative studies on individual structures are performed to understand the correlation between the initial size/shape, temperature (viscosity), elongation speed (strain-rate), and final shape/size.

NM02.06.29

The study of metal chalcogenide molecular clusters as functional units in macromolecular systems has rapidly expanded in recent years. Their tunable properties allow them to be used in a variety of applications, including energy storage, lighting, magnets and catalysis. While the self-assembly of metal chalcogenide clusters in the solid-state is well studied, their incorporation into polymer systems has been limited. We report a new block copolymer containing a site-differentiated Co6Se8 molecular cluster capable of multi-electron redox processes. The block copolymer system self-assembles in solution to form vesicle structures at the mesoscale whose walls can be further crosslinked after assembly. Moreover, the vesicles can be loaded with molecular cargo such as with a methylene blue dye. This talk will describe the synthesis, self-assembly and characterization of the novel cluster-containing diblock copolymer. The integration of a transition metal-containing molecular cluster into well-defined block copolymers offers exciting possibilities to develop multifunctional assemblies for further applications in catalysis, electrochemistry, and biomedicine. This cluster-containing polymer could also be used to direct hierarchical assembly of novel metal chalcogenide mesostructures.

NM02.06.30
Investigation of the Effect of Gold Nanoparticle on Alkaline Phosphatase Enzyme Activity for Using Influenza A Diagnosis Studies Yasemin Badam Kılıç, Günsen O. Eren and Rabia Caikır Koc, Bioengineering Department, Yildiz Technical University, Istanbul, Turkey.

In our present study it is focused on examining of effect of colloidal gold nanoparticles which have 40 nm in diameter to ALP-IgY conjugate in order to use in Influenza A diagnosis applications. Influenza A affects all age groups worldwide, and causes significant loss of workdays, human suffering, and mortality every year. Matrix protein 2 (M2) is a structural protein of influenza A viruses and plays an important role in the virus life cycle. M2e is the high sequence conservation of extracellular domain among all known human influenza A viruses. Therefore, M2e peptide specific IgY antibodies were chosen in this study for development of ELISA methods based on gold nanoparticles conjugation.

Transmission Electron Microscopy (TEM-EDX) demonstrated that particles have 40 nm in diameter it is confirmed that IgY-ALP conjugate was successfully bound to gold nanoparticle. Nano-ELISA results demonstrated that after one hour incubation at 37°C absorbance values of IgY-ALP conjugate was higher than IgY-ALP-Au conjugate in every concentrations. In addition kinetic rate was measured by UV-vis analysis and these results indicated that reaction rate of IgY-ALP-AuNPs was slower than IgY-ALP while absorbance values are higher when gold nanoparticle was bound to IgY-ALP conjugate. Fourier Transmission Infrared Spectroscopy (FTIR) results indicated that gold nanoparticle has effect on ALP enzyme structure. The transmittance peaks of amide I and amide II bonds of IgY-ALP-Au conjugate changed due to presence of gold nanoparticle when compared to IgY-ALP conjugate alone.

In result it can be said that gold nanoparticles have a negative effect on ALP enzyme kinetic rate when it used for enzyme-linked immunosorbent assays. Au-NPs increases the activation energy of ALP-substrate interaction due to conformational change and therefore absorbance values of IgY-ALP-Au complex are much lower than IgY-ALP conjugate in ELISA procedure.

Funding and Acknowledgement
This study was supported by the Scientific and Technological Research Council of Turkey with the project titled “The development of a rapid diagnostic kit using the immunochromatographic method of depending on an M2e peptide-specific IgY antibody for the diagnosis of influenza A infection” (Project No: 115S132).

Authors would like to thank the Scientific and Technological Research Council of Turkey.

NM02.06.31
The Core-Shell Engineering on Energy Product of Magnetic Nanometals Shonqiang Ren and Jingming Zhang; University at Buffalo, The State University of New York, Buffalo, New York, United States.

The exchange coupling between magnetically hard and soft materials possesses many desirable magnetic characteristics and thus is extensively explored for high energy product magnets. Here we demonstrate a solution-based growth of magnetically hard and soft FePt-FeCo (Core-shell) nanoparticles with the controllable shell thickness. The transition from spin canting to exchange coupling of FePt-FeCo core-shell nanostructures leads to a 28% increase in the coercivity (12.8 K0e) and a greater than two-fold enhancement in the energy product (9.11 MGOe), as compared to the FePt nanoparticles. Besides the traditional solution method, a eutectic molten salts method has been developed to synthesis L1s hard magnetic phase in one step. The benefit of this method is the ease of removal chemical residual after reaction, and reduce the total preparation time of the L1s phase of FePt. The as-synthesized FePt powder has a coercivity of 15 K0e while no further treatment was needed. The results shown here imply that the eutectic method and core-shell engineering have the potential to enhance the energy product of next-generation nano-magnets.

NM02.06.32
The Role of Aminosilane Loading Density on the Formation of Gold-Coated Superparamagnetic Core/Shells with Enhanced Dual Surface Heating to Combat Tumor

Manal Almasmari,1,2,3 Roa Fardous,2,3 Edreese H. Alsharab,3,4 Abdalaziz Almalik,3,4 and Ali H. Alhasan1,3,4
1 College of Science and General Studies, Alfaisal University, Riyadh, Saudi Arabia; 2 KACST-BWH/Harvard Centre of Excellence for Biomedicine, Joint Centers of Excellence Program, King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia; 3National Center for Pharmaceutical Technology, Life Science and Environmental Research Institute, King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia.

Despite significant development in the therapeutic strategies for breast cancer, some challenges remain. Conventional treatments such as chemotherapy and surgery cause serious side effects. Among the various approaches to enhance the efficacy of breast cancer therapies, is the use of gold-coated magnetic nanoparticles, which have dual functionality acting as both magneto- and photo-thermal agents. Such nanoparticles may prove valuable in enhancing the therapeutic efficacy if synthesized as quantum-sized nanoparticle, which is still challenging. In this study, we tackle the synthesis of quantum-sized superparamagnetic (Fe3O4) nanoparticles (~10 nm as an inner core) coated with a thin shell of gold (~14 nm) and explore their efficiency to generate heat as a result of their superparamagnetic properties and strong NIR absorption. Our findings show that gold shell formation around a core of quantum-sized nanoparticles is troublesome unless the loading density of 3-aminopropyltriethoxysilane (APTES) onto Fe3O4 nanoparticles is maximized in order to increase the number of gold nanoparticles per Fe3O4 nanoparticle. Exposing Fe3O4/Au core/shell nanoparticles to an external magnetic field and NIR irradiation (~808 nm) results in complete apoptosis–mediated breast cancer death at 45°C, significantly reducing tumor growth in comparison to single mode treatments (magnetic or laser hyperthermia). Apparently, our quantum-sized core-shell nanoparticles afford greater heat efficiency when successfully applied as a dual magneto- photo-thermal therapy for breast cancer.

NM02.06.33

PH-Controlled Dealloying Route to Hierarchical Bulk Nanoporous Zn Derived from Metastable Alloy for Hydrogen Generation by Hydrolysis of Zn in Neutral Water

Jintao Fu,4 Ziling Deng,1 Timothy Lee,6 John S. Corsi, Zeyu Wang,3 Dongyang Zhang,1 and Eric Detsi;6 University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Dealloyed nanoporous metals made of very reactive elements have rarely been reported. Instead, reactive materials are used as sacrificial components in dealloying. The high chemical reactivity of non-precious nanostructured metals makes them suitable for a broad range of applications such as splitting water into H2 gas and metal hydroxide. On the other hand, the same high chemical reactivity hinders the synthesis of nanostructured metals. In this talk, I will present a nanofabrication route to hierarchical bulk nanoporous Zn and demonstrate its potential to produce hydrogen from neutral water. Typically, we used a pH-controlled dealloying strategy to fabricate bulk nanoporous Zn with bulk dimensions in the centimeter range via the selective removal of Al from metastable face-centered cubic bulk ZnAl at 96% parent alloys. The corresponding bulk nanoporous Zn exhibits a hierarchical ligament/pore architecture characterized by primary ligaments and pores with average feature size in the sub-micrometer range. These hierarchical structures are made of ultrafine secondary ligaments and pores with characteristic feature size in the range of 10-20 nm.

I will show that the bulk nanoporous Zn can spontaneously split water into H2 and Zn(OH)2 at ambient temperature and pressure, and continuously produce H2 at a constant rate of 0.08 mL/min per gram of Zn over several hours. It is anticipated that in this hierarchical bulk architecture, the macropores facilitate the flow of water in the bulk of the material, while the mesopores and ultrafine ligaments provide a high surface area for the reaction of water with Zn. The bulk nanoporous Zn/water system can be used for on-board or on-demand H2 applications during which H2 is produced when needed, without prior storage of this gas compressed in cylinders as it is currently the case. [1]

References

8:30 AM *NM02.07.01

Synthesizing Cooperative Metal-Support Interfaces for Catalysis

Sheng Dai1,2; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2 Department of Chemistry, The University of Tennessee, Knoxville, Knoxvillle, Tennessee, United States.

Understanding the cooperative interactions of metals with active supports is essential to tailoring their catalytic activities and/or control of reaction pathways. These interfacial interactions can be achieved through two mechanisms: interfacial charge redistribution (electronic interaction) and interfacial atom transport (chemical interaction). In the last two years, a number of new advances have been made by our BES team toward tuning the metal-support interactions. The success of our approach capitalizes on nanoconfined spaces (e.g., confined interface restructuring), complex oxide supports (e.g., perovskite oxides), and 2D material edge sites (e.g., boron nitride), demonstrating that uniquely strong interfacial interactions and cooperativities between nanoparticles and supports can emerge through judicious structural choices of metals and supports. This presentation will be focused on the following three synergistically linked research activities: (1) sacrificial strong metal-support interactions, (2) “intelligent” metal-support interactions, and (3) charge-flow metal-support interactions. The interconnections among the above three metal-support interactions will be also discussed.

9:00 AM NM02.07.02

Understanding and Controlling Nanoparticle Entrenchment in Oxide Supports

Abha A. Gosavi, Justin Notestein and Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

On rapid heating to high temperatures and under inert conditions, metal nanoparticles exhibit entrenchment in the SiO2 layer on a silicon wafer to create nanoparticles. This phenomenon occurs above a critical temperature of around 1000°C, at ramp-rates above 3.3°C/sec, resulting in nanoparticles as deep as 250 nm or more, depending on the thickness of the SiO2 layer. We have studied and characterized this entrenching behavior and subsequent nanopore formation for a wide variety of metal nanoparticles, including Au, Ag, Pt, Pd and Cu. Using Pd on SiO2 as our model system for studying the behavior of nanoparticle entrenchment, we have established the critical conditions (temperature, times and ramp-rates of heating) required to observe entrenchment. The subsequent trends in this behavior with changing particle size and spacing have also been identified. We have thus tried to establish a mechanism by which nanoparticle entrenchment occurs and competes with other surface phenomenon (sintering, evaporation and diffusion) that occur for silicon dioxide supported metal nanoparticles at high temperatures.
The behavior of metal nanoparticles under entrenchment conditions was also studied for various different oxide supports (TiO$_2$, HfO$_2$, and Al$_2$O$_3$) and compared to the nanopore formation on SiO$_2$. We observed that while nanoparticles supported on TiO$_2$ and HfO$_2$ undergo surface coarsening under high temperature treatment, Al$_2$O$_3$ acts a barrier to nanoparticle entrenchment and subsequent pore formation. This behavior inspired a novel tri-layer approach for immobilizing Au nanoparticles in SiO$_2$ supports. By creating a tri-layer architecture consisting of SiO$_2$ on Al$_2$O$_3$ on silicon wafers, we could control the depth to which nanoparticles entrenched between 3-5 nm. This small range enabled us to sufficiently entrench particles for the purpose of immobilization but still maintain access to the nanoparticle surface for catalytic activity studies. The two advances of moving into the sub-15 nm nanoparticle size regime and of controlled particle immobilization through entrenchment have important implications in studying site-isolated and stabilized metal nanoparticles for applications in sensing, separations, and catalysis. As proof-of-concept, we evaluated the reduction of 4-nitrophenol by NaBH$_4$ catalyzed by Au nanoparticles buried 3 nm into the trilayer substrate.

While the nanoparticles immobilized in the tri-layer supports can be used for catalysis, the nanopores formed in the course of the entrenchment could have a wide range of applications on their own. These linear, high-aspect ratio nanopores have diameters comparable to those of the starting nanoparticles (~15 nm) and can be hundreds of nanometers long. The size and surface density of the nanopores can be tuned by changing the particle sizes and distribution of the nanoparticles being heated. The resulting porous, planar materials could have applications in sensing and separation of large molecules.

9:15 AM NM02.07.03
Size-Controlled Synthesis of CuNi Nano-Octahedra and Their Catalytic Performance Towards 4-Nitrophenol Reduction Reaction
Can Li$^1$, Yiliang Luan$^1$, Bo Zhao$^2$, Amar Kumbhar$^3$ and Jiye Fang$^4$; $^1$SUNY Binghamton, Binghamton, New York, United States; $^2$Texas Tech University, Lubbock, Texas, United States; $^3$University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Compared with noble metal catalysts, non-noble metallic nanocrystals (NCs) as a new class of catalysts have attracted increasing attention due to their low cost, abundant content in the Earth’s crust, and outstanding catalytic performance in some reaction such as oxidation, hydrogenation, and electrocatalysis. It is well-known that some specific crystal facets on the catalysts can promote the catalytic activity. However, most reported NCs with some exclusive facets are noble metal or metal oxide based catalysts. There are limited studies on the synthesis of facet- (or shape-) controlled non-noble metallic NCs. As standard reduction potentials of the non-noble metals are much lower than those of the noble metals, the relatively high sensitivity and instability of the non-noble metal NCs, especially when they expose to air or aqueous solution, make it hard to harvest non-noble metal NCs in controlled shape and size.

Herein, we demonstrate a size-controlled synthesis of CuNi nano-octahedra using a hot colloidal solution approach. Boron morphology was used as a reducing agent to promote a rapid nuclei formation. The as-synthesized CuNi NCs could be stably dispersed into an organic solvent such as hexane with capping ligands anchored on their surface. Two different sizes of CuNi nano-octahedra were chosen and investigated in this report. A number of synthetic factors such as the ratio of oleic acid and oleylamine were identified and optimized in order to efficiently control the size and shape. It was further determined that the concentration remarkably played a key role in the size-control of the CuNi nano-octahedra. In terms of the catalytic evaluation, the size effect of CuNi nanocatalysts on 4-nitrophenol reduction activity was carried out. Our study indicates that the obtained CuNi nano-octahedra exhibited higher catalytic activity compared with those CuNi NCs reported previously, and their performance was strongly size- and shape- dependent due to the surface area and the specific atomic arrangement of the {111} surfaces.

9:30 AM NM02.07.04
Room Temperature Electrodeposition of Palladium Based Intermetallic Electrocatalyst
Yunfei Wang, Du Sun, Justine Wagner, Tomojit Chowdhury, Thomas J. Kempa and Shoji Hall; The Johns Hopkins University, Baltimore, Maryland, United States.

Recently, ordered intermetallic compounds have become emerging materials for catalysis. The synthesis of ordered intermetallic compounds usually requires annealing at temperatures > 700 C. Here we present a method of preparing ordered intermetallic Pd31Bi12 at room temperature via electrochemical deposition. According to the phase diagram, this system is thermodynamically stable at temperatures between 550 C to 605 C, indicating that the deposited material is metastable. The Pd31Bi12 morphology consists of a compact nanoparticulate film, the particles sizes range from 30nm to 100nm. We assessed the catalytic activity of this material for the oxygen reduction reaction, Pd31Bi12 exhibits 60 times higher specific activity than Pd and Pt at 0.85V. The half wave potential of Pd31Bi12 is 0.93V, 43mV higher than Pd and 69mV higher than Pt. Pd31Bi12 also displays high stability under accelerated durability cycling, after 10K cycles a 4 mV shift of its half wave potential, and 40% decay in specific activity is observed. Ultraviolet photoelectron spectroscopy is applied to compare the valence band of Pd31Bi12. The results show that alloying Bi with Pd drastically lower the center of valence band compared with Pd, thus reduce adsorption energy of intermediate in oxygen reduction reaction. In conclusion, we have demonstrated that electrodeposition can be used to prepare thin films of ordered intermetallic Pd31Bi12 on glassy carbon electrodes. Pd31Bi12 is a highly active and stable material for performing the reduction of O2 to H2O.

9:45 AM NM02.07.05
A General Route to Synthesize Core@Shell ORR Nanocatalysts
Joceelyn T. Gamler, Hannah M. Ashberry and Sara E. Skrabalak; Indiana University, Bloomington, Indiana, United States.

The need for sustainable energy platforms drives catalyst design and synthesis. In the case of organic liquid fuel cells, improvements in terms of activity, durability, and cost are needed for oxygen reduction reaction (ORR) catalysts, which are largely Pt-based. Typical routes to overcome the high cost and unfavorable surface-adsorbate interactions are to incorporate a secondary transition metal, either through a core@shell architecture or alloy formation; this addition decreases expensive metal loadings and tunes the surface-adsorbate interaction in accordance with the Sabatier principle. The present work demonstrates the versatility of seed-mediated co-reduction (SMCR) to deposit PtM (M = Ni, Co, Cu, Fe) random alloyed shells on PdCu B2 intermetallic seeds, integrating the concepts of a core@shell architecture and alloyed surfaces into one nanostructure. Control of both shell thickness and Pt:M ratio are also demonstrated. The catalytic activity as a function of shell thickness for a model system, B2@PdNi, was evaluated for the ORR. The series of B2@PtM catalysts are also evaluated for the ORR to determine the role surface composition plays in activity and durability. Collectively, this work aims to develop synthetic techniques to achieve complex nanocatalyst compositions.

10:00 AM BREAK
removed from the products. The strong oxidizing power of the traditional oxidants easily leads to overoxidation of alcohols to ketones, lowering the selectivity and yield of aldehydes. In contrast, using ambient oxygen as oxidant is proposed to develop an environmentally friendly synthesis strategy that does not require additional separation. However, ambient oxygen is lack of the power to oxidize alcohols at mild temperatures. Therefore, precisely controlling the oxidizing power of the oxidants becomes crucial to promote the selective oxidation of alcohols to aldehydes. We focus on the use of appropriate metal catalysts (i.e., quantum-sized metal nanoparticles) to improve the selective oxidation with ambient oxygen by converting the molecular oxygen adsorbed on the catalyst to more active species. The change of adsorption states of oxygen relies on the efficient generation of hot electrons in the quantum-sized metal nanoparticle catalysts that are under illumination of visible light. Selective aerobic oxidation of benzyl alcohol to benzaldehyde represents an example to demonstrate the feasibility of enhancing reaction kinetics on quantum-sized platinum group metal (PGM) nanoparticle catalysts with the assistance of simulated solar irradiation.

11:00 AM NM02.07.07
Synthesis of New Nanoparticle Catalysts for Application in Direct Methanol Fuel Cells Jil Rüter, Hauke Heller and Horst Weller; University Hamburg, Hamburg, Germany.

Direct methanol fuel cells (DMFCs) show great potential for applications in portable power sources or hybrid vehicles.[1] One key challenge for the commercialization is to reduce the high costs of fuel cells due to expensive catalyst materials. The electrocatalysts, mostly based on platinum, are dispersed on a high surface area supporting material. Therefore, a reduced and effective use of the costly platinum is essential. In this context, multimetallic nanoparticles with controllable size and composition are interesting materials to reduce the amount of utilized catalyst material and simultaneously enrich the accessible catalytic metals on the surface. The size, composition and structure of the nanoparticles have a high influence on the efficiency. An increase of the catalytic activity has been proved by combining platinum with various transition metals (e.g. nickel, cobalt, ruthenium)[2] as alloy or core-shell structure, while reducing the cost at the same time. The combination of specific transition metals with platinum increases the activity of oxygen reduction reaction (ORR) due to ligand and strain effects.[3] Moreover, it is advantageous to use core-shell-nanoparticle (CSN) systems, as the platinum amount can be further reduced by using it only on the outer shell. The investigated Ni@Au@NiP[4] and NiPd@NiPt[5] CSNs exhibit a great potential for application as DMFC catalysts due to their high catalytic activity, low platinum amount, high surface area and stability. Here, we demonstrate nanoparticles with an average diameter of 5 nm and a narrow standard deviation. The gold interlayer enhances the durability of platinum due to the prevention of oxidation and dissolution of platinum during the cycling process. Besides platinum, palladium is an attractive material as it has a positive effect on the stability and activation and a lot of different combinations of platinum and palladium or a substitution of platinum may be possible as well. Furthermore, the carbon source for supporting the catalyst material is of great interest. Carbon nanotubes (CNTs) may be an alternative to conventional carbon materials due to their high surface area as well as remarkable mechanical and electric properties.[5] CNTs consist of (multiple) graphene layers in cylindrical form with a closed fullerene end cap. We show that nanoparticles and CSNs were successfully supported on hierarchically ordered CNTs, which are synthesized by chemical vapor deposition and grown on steel meshes. Combining the multimetallic CSNs with CNTs could induce an enhanced catalytic activity. In future, further combinations of palladium and platinum will be investigated.

11:15 AM NM02.07.08
Development of New Solid-Solution Alloy Nanoparticles for Catalytic Applications on the Basis of Density-of-States Engineering Kohei Kusada1, Dongshuang Wu1, Tomokazu Yamamoto2, Syo Matsumura2, Wei Xie2, Michihsia Koyama2, Katsutoshi Sato2, Katsutoshi NagaoKA3 and Hiroshi Kitagawa3; 1Kyoto University, Kyoto, Japan; 2Kyushu University, Fukuoka, Japan; 3National Institute for Materials Science, Tsukuba, Japan; 4Oita University, Oita, Japan.

The properties of elements are correlated directly with their electronic states. If we can realize a concept of “density-of-states (DOS) engineering”[1] for the design of materials having the most suitable electronic structure for the targeted properties, we will be able to make full use of available elements and relieve the resource problems. To freely control an electronic state of a material, the solid-solution alloy is advantageous because its electronic state can be continuously controlled by tuning the compositions and/or combinations of the constituent elements. However, the majority of bulk alloy systems are the phase-separated type under ambient conditions. Recently, we demonstrated that the nanosize effect offers a chance to find a way out of this metallurgical difficulty; that is, we can obtain metal nanoparticles (NPs) having new phases that do not exist in bulk states.[2] In general, a nanoparticle with the same crystal structure as the corresponding bulk material can be obtained. However, if we find appropriate synthetic conditions, it allows us to develop novel NPs adopting new phases including solid-solution alloy NPs consisting of immiscible combinations.

In this work, we discuss the structural and chemical properties of PdRu2 and AuIr2 alloy NPs as the examples of DOS engineering. Both of binary alloy systems are immiscible and solid-solution alloys of these systems have not been obtained so far. We first succeeded in synthesizing the solid-solution alloy NPs and characterized the alloy structures by synchrotron X-ray powder diffraction technique and scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy. It is noted that obtained PdRu and AuIr solid-solution alloy NPs showed very enhanced catalytic properties for three-way catalysis and oxygen reduction reactions, which are comparable to Rh and Pt, respectively.[3] The calculation results indicated that the formation of solid-solution alloy realized new electronic states and provided enhanced properties.


11:30 AM NM02.07.09
Investigating Subnanometer Transition Metal Catalysts for Methane Activation from First Principles Victor Fung1, Zili Wu2 and De-en Jiang1; 1University of California, Riverside, Riverside, California, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Subnanometer transition metal clusters have received significant attention as promising materials for catalysis, particularly over their bulk counterparts. The electronic structure of the exposed metal sites can vary significantly with atomic size and geometry, which presents the opportunity to design metal clusters of a specific atomic size and composition for the desired catalytic application. One such application is towards methane conversion, which requires
suitable catalysts to promote the activation of its strong C-H bond. Using density functional theory, we investigate a selection of promising transition metal clusters and identify promising candidates based on strong methane adsorption and low C-H activation barriers. Our results conclude that facile C-H activation is closely related to the ability of the metal sites to complex with the methane molecule. We further show that these methane activation properties are extremely size, geometry and composition dependent, with significant implications for eventual experimental applications. These studies provide the first step in designing realistic metal cluster catalysts for methane conversion.

11:45 AM NM02.07.10
Determining Metallic Nanoparticle Core Structures from Atomic Pair Distribution Function (PDF) Data
Soham Banerjee1, Chia-Hao Liu1, Jennifer Lee2, Anton Kovyakh3, Viktoria Grasmik3, Oleg Prymak4, Christopher Koenigsman5,6, Haiqing Liu1, Lei Wang5,6, Milinde Abeyskoon6, Stanislaus S. Wong3, Matthias Epple5, Christopher B. Murray5,6 and Simon J. Billinge1,7, 1Department of Applied Physics and Mathematics, Columbia University, New York, New York, United States; 2Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark; 4Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany; 5Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York, United States; 6Department of Chemistry, Fordham University, Bronx, New York, United States; 7Department of Materials Science and Chemical Engineering, State University of New York at Stony Brook, Stony Brook, New York, United States; 8Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York, United States; 9Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Accurate determination of the structure of noble metallic nanomaterials is a key step towards understanding and controlling their properties. This is especially challenging for small particles, below 10 nm, where x-ray diffraction data is often broad and diffuse and not amenable to quantitative crystallographic analysis. In these cases a better approach is the use of atomic pair distribution function (PDF) analysis of synchrotron x-ray total scattering data. Even in this case, extracting detailed models of nanoparticle cores is notoriously difficult.

Nanoparticle models based on close packed crystallographic cores, often simple but at times elaborate, lead to characteristically poor or unreliable fits. We data. Even in this case, extracting detailed models of nanoparticle cores is notoriously difficult.

In these cases a better approach is the use of atomic pair distribution function (PDF) analysis of synchrotron x-ray total scattering data. Even in this case, extracting detailed models of nanoparticle cores is notoriously difficult.

Multinary transition metal nanoparticles (NPs) are of interest for energy applications, e.g. as catalysts in fuel cells. As an immense composition space exists for multinary NPs, efficient experimental strategies are necessary to identify which particular compositions have new or highly-optimized properties. Here, combinatorial co-sputtering (1) from up to five elemental targets (e.g. Cr-Mn-Fe-Co-Ni) was used to synthesize multinary NP libraries into ionic liquids.

Multinary transition metal nanoparticles (NPs) are of interest for energy applications, e.g. as catalysts in fuel cells. As an immense composition space exists for multinary NPs, efficient experimental strategies are necessary to identify which particular compositions have new or highly-optimized properties. Here, combinatorial co-sputtering (1) from up to five elemental targets (e.g. Cr-Mn-Fe-Co-Ni) was used to synthesize multinary NP libraries into ionic liquids.
Due to their low vapor pressure, ionic liquids can be used as substrates that are able to stabilize NP dispersions. The suitability of different ionic liquids for different metal combinations can be tested with high-throughput by using arrays of ionic liquids which are sputtered with one material system (2). The multinary NPs were characterized using atomic-scale characterization methods such as Cs-corrected high-resolution transmission electron microscopy, (scanning) transmission electron microscopy and energy dispersive X-ray spectroscopy. With these techniques the chemical composition as well as size, shape, crystallinity and defects of the NPs are obtained. Effects on the resulting crystallinity of the NPs were found by using either direct current or high-power impulse magnetron sputtering. Furthermore, catalytic properties of the NPs were measured by potential-assisted immobilization of the NPs at a microelectrode which allows the evaluation of their intrinsic electrocatalytic activity in alkaline media. The obtained results indicate that the multinary nature of the NPs affects their catalytic activity: e.g. quinary NPs were found to be more active than all of the respective quaternary subsystems. (1) König, D., Richter, K., Siegel, A., Mudring, A. V. & Ludwig, A. High-throughput fabrication of Au-Cu nanoparticle libraries by combinatorial sputtering in ionic liquids. Adv. Funct. Mater. 24, 2049–2056 (2014).


SESSION NM02.09: Biological Applications
Session Chairs: De-en Jiang and Grant Johnson
Wednesday Afternoon, November 28, 2018
Sheraton, 3rd Floor, Commonwealth

3:00 PM NM02.09.01
Antimicrobial Peptide-Based Platform with Fluorescent Gold Nanoclusters for Selective Detection of Listeria monocytogenes
Kamaljit Kaur; Chapman University, Irvine, California, United States.

Listeria monocytogenes is a Gram-positive foodborne pathogen that causes infections such as listeriosis and meningitis. The mortality rate from such infections exceeds 20 percent, which designates this microbe as a high threat to humans (1). Highly sensitive and selective detection of pathogenic bacteria from various samples ranging from human specimens to food samples is a major challenge in industry and medical fields (2, 3). Here we have developed a novel peptide-based biosensor platform utilizing fluorescent gold nanoclusters for quick and easy detection of L. monocytogenes species from different samples. Leucocin A, a potent antimicrobial peptide from class IIa bacteriocins, is used to selectively bind specific receptor present on Listeria monocytogenes, namely, mannose phosphotransferase system permease. A self-assembled monolayer (SAM) of peptide on glass surface is exposed to contaminated sample allowing target bacteria to bind to the immobilized peptide on the surface. The peptide-bound bacteria are then labeled with highly fluorescent gold nanoclusters directly on the glass surface allowing quick detection of bacteria with a limit of detection (LOD) of 2000 cfu in each 10 microliter sample (4). The gold nanoclusters are made by mixing and spotting aqueous tetrachloroauric acid and 3-mercaptopropionic acid (MPA) on top of bacteria on the glass slide. The gold nanoclusters thus formed label the bacteria, and absorb in the UV range and emit fluorescence in the visible to near infrared region (~612 nm) where other biomolecules do not fluoresce and interfere. The biosensor assay developed here is unique as it allows detection of L. monocytogenes in <1 hour and does not require trained personnel. Compared to other techniques for the detection of L. monocytogenes, this method is simple, fast, and requires no sample preparation.


3:45 PM NM02.09.02
Renal Clearable Catalytic Gold Nanoclusters for In Vivo Disease Monitoring
Colleen Loynachan1, Ava Soleimany2, Sangeeta Bhatia2 and Molly Stevens1; 1Imperial College London, London, United Kingdom; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent advances in the synthesis and characterization of ultra-small gold nanoclusters (AuNCs) have enabled their use as sensitive probes for fluorescence and x-ray contrast bioimaging applications.1 However, their intrinsic catalytic activity has yet to be explored for biosensing in vivo. Employing peroxidase-mimicking catalytic AuNCs as reporter probes in sensing applications may enable rapid and facile disease diagnosis at the point-of-care.2 We propose to address this need by leveraging both the catalytic activity of AuNCs and the precise size filtration of the kidney to develop a nanocatalyst amplification platform that produces a direct colorimetric urinary readout of disease state. Here we have engineered AuNC-functionalized protease nanosensors that are disassembled in response to dysregulated protease activity at the disease site. Liberated AuNCs are then efficiently filtered into the urine, where a colorimetric urinary assay enables rapid disease detection in mouse models of cancer and pulmonary embolism.

Renal clearable AuNCs were synthesized via a versatile bio-templated process which introduces protease cleavable peptide sequences on the particle surface with orthogonal functional handles for further site selective modification. The resulting ca. 1.5 nm noble metal nanoclusters exhibited both luminescence and robust catalytic activity. Renal clearance studies in vivo showed that ca. 60% of the injected dose of functionalized AuNCs leave the body via this route and retain their catalytic activity in urine. Peptide functionalized AuNCs were tethered to a protein carrier to form nanosensor complexes, and specific proteolytic cleavage of AuNC complexes was demonstrated in vivo by gel filtration chromatography. Finally, disease detection was demonstrated in vivo in a mouse model of colorectal cancer by monitoring catalytic activity of cleared AuNCs in collected urine. After injection with tumor-specific AuNC nanosensors, urine from tumor-bearing mice showed a 20-fold increase in colorimetric signal compared to healthy mice in our assay.

We developed a library of catalytic AuNC probe complexes which can be efficiently excreted into urine in response to specific enzymatic levels in vivo. This simple and sensitive colorimetric urinary assay can be read by the naked eye in <1 h and has enabled non-invasive disease detection in mouse models of cancer and pulmonary embolism. We envision that this approach will be applicable for rapid detection of a diverse range of disease-associated proteases.

Furthermore, constant potential electrolysis on electrodes modified with these clusters exhibits drastically different product selectivity. That is, whereas CO is predominantly produced on Au25(SR)18 with a selectivity higher than 90%, nearly 75% H2 is produced on PtAu24(SR)18. Density functional theory calculations show that the product selectivity appears to be closely related with the adsorption energies of the reactants, i.e., CO2 and proton on the electrode surface. This understanding is critical for the design of efficient electrocatalysts for CO2 conversion.

Angiogenic tumor vessels are hallmarks of cancer and critical sites for drug delivery, angiogenic therapy, chemotherapy, and immunotherapy. Better characterization of tumor microvasculatures in vivo could lead to better understanding of the tumor microenvironment, improved monitoring of tumor progression and therapeutic responses, and more accurate patient prognosis. Optical coherence tomography angiography (OCTA) provides three-dimensional microvasculature image of the tissue by detecting the dynamic scattering produced by flowing red blood cells (RBC's), and becomes an emerging tool for in vivo microvascular imaging due to its micrometer spatial resolution and millimeter tissue penetration depth. However, due to the abnormal blood flow in the angiogenic tumor vessels and strong light attenuation by the tumor tissue, it is challenging to image the complete tumor microvasculature with traditional OCTA. In this work, we demonstrate that gold nanoprism (GNPRs) can be used as intravascular OCT contrast agents for significantly improved imaging of tumor microvasculatures in the second near infrared window (1100–1400 nm). With the injection of incremental concentrations of PEGylated GNPRs in the mouse blood, higher density of microvasculature can be observed in the tumor tissue of melanoma mice models on the OCT angiograms. After the GNPR concentration reached 2 nM in the bloodstream, OCTA showed an increase of tumor vascular density by 136% compared to the baseline angiogram image. Longitudinal OCTA study shows that the highest vascular density was achieved at 5 min post-injection. Two photon microscopic imaging validated that there is no extravasation of GNPRs within 5 min of injection.

DNA Modified Gold Nanoparticles for Drug Delivery in Cells

DNA modified gold nanoparticles have been extensively studied as a versatile platform for drug delivery due to their ability to recognize and bind to specific messenger RNA signatures and selectively kill model cancerous cells as opposed to healthy cells. New classes of nanoparticle dimers that can accommodate multiplexed synergistic actions of sensing and drug delivery in cells. These multitasking particle assemblies are able to selectively release anticancer drugs in response to specific messenger RNA signatures and selectively kill model cancerous cells as opposed to healthy cells.

References:
Mechanical behaviors of nanomaterials, such as metallic nanowires and nanoparticles, are usually controlled by dislocation nucleation due to the absence of pre-existing glide dislocations in such a small volume. Dislocation theory suggests that a significantly high stress needs to be applied to nucleate a dislocation, leading to an ultrahigh strength of nanomaterials. Thus, nanomaterials has drawn a great attention as the candidate of advanced structural materials. In order to understand the mechanical behavior of nanomaterials, thus, it is critical to understand the dislocation nucleation behavior in detail. Spherical nanoindentsation has been widely used to study the dislocation nucleation phenomena. Upon loading on the flat surface of low dislocation density material, the Hertzian contact of tip can induce the maximum load at the inside of material, leading to the dislocation nucleation. This nano-scale volume plasticity is nearly identical to the plasticity of nanomaterials. So, spherical nanoindentsation is a great method to study the plasticity at small length scales. Tungsten is an excellent model system to investigate dislocation nucleation. Its strong hardness allows the low dislocation density at the underneath of the free surface after the fabrication of flat surface. In this study, therefore, we studied the dislocation nucleation behavior of [0 0 1] tungsten single crystal under spherical nanoindentsation with different indenter tip radii. The surface of tungsten single crystal was chemo-mechanically polished. The spherical nanoindentsation was performed with the tip radii, 0.2, 2, 4, and 20 micrometers, and the critical stress of dislocation nucleation were measured using the Hertzian contact mechanics. Our results show that the critical stress of dislocation nucleation is a strong function of the tip radius. The dislocation theory suggests that the critical stress of dislocation nucleation must be constant regardless of loading condition, but this is inconsistent with our results. We found that stress gradient on the potential site of dislocation nucleation could be different according to the tip curvature, leading to the different critical stress of dislocation nucleation. Therefore, the combined stress gradient theory with the Herzan contact mechanics and confirmed that our model explains the dependence of the tip radius on the critical stress of dislocation nucleation very well. Our new model can be applied in any general cases when the inhomogeneous stress field is available in the nanoscale volume of metals such as the bending of nanowires or the compression/tension on nanoparticles. We confirmed that the same phenomenon is observed in uni-axial compression of dislocation-free gold nanoparticles, and the size effect of its yield strength can be understood by our stress gradient model. In sum, our spherical indentation study can shed a light into a fundamental understanding on the plasticity of nanomaterials.

NM02.10.03

Effect of Synthetic Parameter on the Cytotoxicity of CdTe/CdSe Nanoparticles Against Osteosarcoma Cell Line 

Vuyelwa Ncapayi1, 2, 3, Sandile P. Songca4 and Samuel O. Oluwafemi1, 2; 1Applied Chemistry, University of Johannesburg, Johannesburg, South Africa; 2Centre for Nanomaterials Science and Technology, University of Johannesburg, Johannesburg, South Africa; 3Centre for Nanomaterials Science and Technology, University of Johannesburg, Johannesburg, South Africa; 4Chemistry, Walter Sisulu University, East-London, South Africa.

LM-8 is a murine osteosarcoma cell line associated with bone tumor and is commonly found in young adult and children. The LM-8 cell line has Nuclear factor (NF)-κB which make them high resistance to irradiation thus limiting their treatment only to chemotherapy and surgery and this has become a source of concern for cancer therapy. In addressing this problem, quantum dots (QDs), which has high potential application in cancer treatment not only as imaging tool but also as a drug transport agent have been proposed as a possible agent to address this problem. Thus, in this study, we herein report the synthesis of CdTe/CdSe QDs core/shell NPs via a simple, economical and green method in the absence of inert atmosphere. The temporal evolution of the CdTe/CdSe QDs cytotoxicity against osteosarcoma cell line was investigated by varying the pH and reaction time. The optical properties of the as-synthesised quantum dots were monitored by UV-Vis and photoluminescence spectrophotometer, while electron microscope was used for structural properties. Prolonging the reaction time and increasing the pH resulted in highly monodispersed CdTe/CdSe core-shell NPs with good optical properties in the near infrared region and high cell viability. The high fluorescence intensity and improved cell viability against the osteosarcoma cell line confirm QDs great potential for imaging and drug delivery applications.

NM02.10.04

Synthesis and Processing of Polymer-Nanoparticle Hybrid Materials for H2 Sensing

Alicja Stolak, Ida Holm, Iwan Darmadi, Christoph Langhammer, Christian Muller and Kasper Moth-Poulsen; Chalmers University of Technology, Göteborg, Sweden.

Nanoparticles bearing Surface Plasmon ( SPR) and Localized Surface Plasmon Resonance ( LSPR) phenomena are excellent tools for novel concepts and technologies such as the creation of bio- and chemosensors7–9, plasmonic lasers, optical metamaterials, photovoltaic devices and metal photocatalysts. However, there is a number of challenges related to the use of nanoplasmic systems related to stability, composition and the large-scale incorporation in real devices. To address the above, we have used wet-chemical synthesis of palladium based plasmonic nanoparticles with tunable optical properties, and implemented these into suitable polymer matrixes, in order to invent cheap, easy and robust nanocomposites. Subsequently the nanocomposites will be applied to realize the creation of an optical hydrogen sensor.

In this project Pd NPs for H2 sensing have been synthesized and successfully implemented into a PMMA matrix resulting in a H2 active nanocomposite. The synthesis of nanoparticles is mainly surfactant based which has series of disadvantages that need to be mitigated such as the disruption of inhomogeneous stress field is available in the nanoscale volume of metals such as the bending of nanowires or the compression/tension on nanoparticles. Our new model can be applied in any general cases when the dependence of the tip radius on the critical stress of dislocation nucleation must be constant regardless of loading condition, but this is inconsistent with our results. We found that stress gradient on the potential site of dislocation nucleation could be different according to the tip curvature, leading to the different critical stress of dislocation nucleation. Therefore, the combined stress gradient theory with the Hertzian contact mechanics and confirmed that our model explains the dependence of the tip radius on the critical stress of dislocation nucleation very well. Our new model can be applied in any general cases when the inhomogeneous stress field is available in the nanoscale volume of metals such as the bending of nanowires or the compression/tension on nanoparticles. We confirmed that the same phenomenon is observed in uni-axial compression of dislocation-free gold nanoparticles, and the size effect of its yield strength can be understood by our stress gradient model. In sum, our spherical indentation study can shed a light into a fundamental understanding on the plasticity of nanomaterials.

NM02.10.05

Magneto-Optically Active Mn-Doped 2D Quantum Structures

Chi Li1, Sheng-Chih Hsu1, Tom Lin2 and Yihsin Liu2; 1National Taiwan Normal University, Taipei City, Taiwan; 2Chemistry, Washington University, St. Louis, Missouri, United States.

Mn-doped 2D quantum structures are potential diluted magnetic semiconductors (DMS) for spintronic applications, showing strong coupling of spin states with electronic states. The 2D CdSe(ethylenediamine)0.5 containing Mn2+ of various concentrations (0.5-7.7%) were successively introduced to explore optical, magnetic and spin interactive properties within single atomic layers. Giant magneto-optical effects and exciton dynamics are revealed by multiple internal transitions (e.g. 4T1 to 4A1) phosphorescence between 580-660 nm and magneto-optic Kerr effect (MOKE). Strong sp-d exchange interaction of nearly isolated Mn2+ in 2D regimes suggests giant Zeeman effect in magnetic circular dichroism (MCD). Additionally, three anisotropic g-values are characterized in orientation-dependent external paramagnetic resonance (EPR) experiments. Magnetic properties (C=2.62x10^5 emu K/G, μFe = 1.32 μB) from superconducting quantum interference devices (SQUID) with the magneto-optical studies above suggest effective chemical doping of magnetic ions and possibilities of spintronic applications for 2D semiconductors.
Through High-Resolution Transmission Electron Microscopy (HRTEM), we acquired the crystals sizes between 10–30 nm and the diverse morphologies of silver nanocluster.

By Powder X-Ray Diffraction (XRD), we acquired the crystal structure. As for the acetone solution via a magnetic stirrer, we obtained a silver nanocluster.

The most unexpected result we obtained, seen via an optical microscopy, was the detection of a circular morphology depending on employed solutions and the two wet nanomaterials techniques (by either a magnetic stirrer or an ultrasound equipment). All the samples were under the same room conditions of temperature (20–24°C) and humidity (40–60%).

NM02.10.09 Silver Nanoparticles and Ion Silver in the Antimicrobial Activity
Luiz F. Gorup, Francisco N. Souza Neto, Andressa M. Kubo and Emerson R. Camargo, Federal University of Sao Carlos, Sao Carlos, Brazil.
Plasmonically Enhanced Virus Inactivation in a Flow Cell Geometry

Mina Nazari1, Min Xi2, Rahm Gummulura1, Mi Hong4, Björn Reinhard1,5 and Emerson R. Camargo1

Magnetic Resonance Imaging (MRI) allows for early detection of diseases that normally present once treatment is futile (e.g. cancer, cardiovascular dysfunction, or neuropathology). With such an important role, any increase to its functionality will have a great impact in medicine. The MRI can be improved – MRI contrast agents (CAs) can increase signal intensity, enhancing the contrast between healthy and abnormal tissues to allow for clearer diagnosis. MRI CAs provide an opportunity to target specific cells, leading to novel detection methods.

The principle underlying MRI is Nuclear Magnetic Resonance (NMR). NMR is observed as an absorption and emission of electromagnetic radiation by spinning nuclei in an external magnetic field. CAs enhance the MRI quality by affecting the amount of time it takes for the nuclei to relax after excitation.

There are two relaxation times, $T_1$ and $T_2$, that affect the quality of the image. Gadolinium (Gd) chelates, a commonly used CA, offer increased $T_1$ relaxation.
metals of group IB as Au, Ag and Cu. In this work a procedure to control the surface morphological of Ga2O3 nanometric films using Au, Ag and Cu. The

Different Power

Structural and Magnetic Properties of TM Doped ZnO Films Produced by Growing ZnO/MT/ZnO Arrays by RF-Magnetron Sputtering at

characterized by XRD and SEM.

nanostructured films. Both types of ions have partially filled d and f shells, respectively, causing unpaired electrons of the TM ions into the ZnO

nanomaterials, the thermal decomposition method and hot injection utilizing oleylamine as capping agent. The prepared copper nanoparticles were

particularities on the film magnetic behavior, as the increase on the Curie temperature or the magnetoresistive behavior. With the aim to analyze the

influence of the TM dopant and the nanostructure issues on the magnetic characteristics, this study was directed to clarify the origin of the

magnetoresistance on TM doped ZnO nanostructured films (ZnO:TM) grown by the non-equilibrium RF-sputtering method at distinct RF-power regimes.

The nanoscale alternative is the gadolinium oxide (Gd2O3) nanoplate (NP) system. Using these NPs will evade the toxic and tumbling faults of the Gd

chatelates while maintaining the T1 CA properties of Gd. Gd in NPs is thermodynamically stable, preventing any metal deposition or adverse renal effects. This allows NP CAs to be used on the 14% of the total population that has preexisting kidney disease. The larger size of the NPs reduces tumbling in the bloodstream. NPs have a larger Gd to volume ratio which concentrates the part of the system that directly affects T1 relaxation. Encapsulation of the oleic acid coated Gd2O3 NPs with an amphiphilic sulfonic acid copolymer allows for successful phase transfer. Functionalized polyethylene glycol (PEG) derivatives added to this system can enhance its biocompatibility and its targeting properties.

Gd2O3 NPs offer a novel method for detecting non-alcoholic fatty liver disease (NAFLD). Kupffer cells in the liver are found at elevated concentrations with NAFLD. These cells uptake NPs at a high rate in the body. Gd2O3 NPs will accumulate in these cells when NAFLD is present, appearing bright white on MRI. Currently, there doesn’t exist a method to detect NAFLD early enough to treat it but the Gd2O3 nanometal system offers a promising approach.

The Synthesis of Copper Nanoparticles from Thermal Decomposition of Amino Carboxylate Copper Complexes

This paper reports the synthesis of copper complexes with four different ligands; glycine (gly) alanine (ala) valine (val) and picolinic acid (pic). The products were characterized by Fourier Transform Infrared (FT-IR) Spectroscopy, Thermogravimetric analysis (TGA) and Elemental Analysis (EA). The potential use of these complexes as precursor to prepare nanoparticles has been investigated. Two different methods have been applied to produce nanomaterials, the thermal decomposition method and hot injection utilizing oleyamine as capping agent. The prepared copper nanoparticles were characterized by XRD and SEM.

Structural and Magnetic Properties of TM Doped ZnO Films Produced by Growing ZnO/MT/ZnO Arrays by RF-Magnetron Sputtering at Different Power

The optical, Structural and morphological properties of the Ga2O3: M arrays were evaluated using transmittance, X-ray diffraction, scanning electron microscopy and Raman spectroscopy. A relationship between the growth procedure and the resultant microstructure and optical properties is proposed. The nanoparticles were characterized by XRD and SEM.

Effect of the Surface in the Amorphous Ga2O3 Thin Films by Metals of Group IB

Gallium oxide (Ga2O3) is a metal oxide material with a, \( \gamma \), \( \delta \), \( \epsilon \) and \( \beta \) polymorphs; among these polymorphs, the compound \( \beta-\text{Ga}_2\text{O}_3 \) with monoclinic structure is the only thermodynamically stable. There are many reports on the effect on the surface modification caused by doping of \( \beta-\text{Ga}_2\text{O}_3 \) doping with metals of group IB as Au, Ag and Cu. In this work a procedure to control the surface morphological of Ga2O3 nanometric films using Au, Ag and Cu. The procedure is based in the growth of nanometric multilayers Ga2O3/metal/Ga2O3 by RF sputtering and DC-sputtering at room temperature conditions. To study of surface morphology and structural characteristics the amorphous-Ga2O3: M arrays were annealed in dry N2 atmosphere at 600 °C by 30, 60 and 120 min. The morphological results can be related to the evolution of the amorphous character of the films towards the nanocrystalline phase driven by the nature of the intermediate Metal. The optical, Structural and morphological properties of the Ga2O3: M arrays were evaluated using transmittance, X-ray diffraction, scanning electron microscopy and Raman spectroscopy. A relationship between the growth procedure and the resultant microstructure and optical properties is proposed.
1064 nm and a receptivity of 20 kHz was used for the ablation. From the results of SEM image and XRD measurements, the average particle diameter of the AlNP was 19 nm. The magnetic properties of the AlNP powder were measured by SQUID. The M-H curve showed superparamagnetism. But Pauli paramagnetic component was not found from M-T curve.

In order to apply this AlNP powder as a solid material, it was mixed with silver paste and solidified by heat treatment. Note that it was confirmed that the AgNP obtained by drying the silver paste was weakly diamagnetic. The magnetic properties of the composite of AlNP and AgNP ((AlNP)/(AgNP)) showed interesting properties. Here, the number ratio of AlNPs and AgNPs in the composite material is expressed as (AlNP)/(AgNP). Basically, the magnetic properties of the composite material were superparamagnetic. Although the magnitude of its saturation magnetization increased with the value of x, it did not increase monotonically but reached a maximum when x = 0.8. In the M-T curves of the composites, there was a paramagnetic component independent of the temperature. The value of this paramagnetic component was also not proportional to the value of x, and it was the maximum when x = 0.4. This result suggests that the paramagnetic component is not due to defects but Pauli paramagnetism. Even more surprisingly, hysteresis was observed in the M-H curve for the samples with x = 0.6 and 0.8, indicating that the samples are ferromagnetic material. Although the origin and mechanisms of the magnetic properties of these composite materials are under investigation, the experimental results show that the unique magnetic moment is induced in the composites and the existence of the magnetic exchange interaction inside the composites.

NM02.10.17
Bulk Nanoporous Aluminum for On-Board Hydrogen Generation by Metal Hydrolysis John Corsi and Eric Detsi; Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Hydrogen gas technology is a promising replacement for fossil fuels as a next generation mobile energy solution because of its high gravimetric energy density and minimal environmental impact. However, there are still many scientific and engineering challenges that must be addressed before a true “hydrogen economy” can be realized. Although hydrogen gas has a very high gravimetric energy density, it has a low volumetric energy density. One solution that avoids the safety concerns of transporting and storing pressurized flammable gases is the on-demand production of hydrogen from water-reactive nanostructured materials. This has been demonstrated for materials such as silicon nanoparticles. It is difficult to produce reactive nanomaterials that are oxide free, high yield and allow for morphological tuning. One technique for producing metallic nanostructures is dealloying, a process in which the less noble component of an alloy is selectively chemically removed, leaving behind a bicontinuous structure of nanoscale metal ligaments and voids. Two types of dealloying include chemical dealloying, in which an acid is used as an etchant, and electrochemical dealloying, in which an external voltage or current is used to etch the material. In this work, we propose a scalable fabrication method of nanostructured aluminum through electrochemical dealloying and demonstrate the ability to use this material for hydrogen production through water splitting [1,2].

References:

NM02.10.18
Metallic AsSb Nanoinsclusions Strongly Enriched by Sb in AlGaAsSb Metamaterials Vladimir V. Chaldyshev1, Nikolay Bert1, Vladimir Nevedomski1, Vitalii Ushanov1, Maria Yagovkina1, Nikolay Cherkashin2, Valeri Preobrazhenski2, Mikhail Putyato3 and Boris Semyagin3; 1Ioffe Institute, Saint Petersburg, Russian Federation; 2CEMES-CNRS, Toulouse, France; 3Institute of Semiconductor Physics, Novosibirsk, Russian Federation.

Motivated by the recent experimental discovery of plasmon resonance in the infrared optical spectra of AlGaAsSb metamaterials, we have studied the microstructure of AsSb nanoinsclusions embedded in the AlGaAsSb matrix by low-temperature molecular-beam epitaxy followed by high-temperature annealing. Measurements of the interplanar spacings in the nanoinsclusion lattice by transmission electron microscopy in both diffraction and high-resolution (HRTEM) modes as well as high-resolution x-ray diffraction showed that the AsSb nanoinclusions possess the rhombohedral A7 structure characteristic of bulk As and Sb. The nanoinsclusions appeared to be strongly enriched by antimony (over atomic 90%) even when the Sb content in the matrix is as small as 2.8 atomic %. Our analysis of the Al-Ga-As-Sb phase diagram showed that the observed strong enrichment should happen just above the AsSb alloy melting point as prescribed by the local thermodynamic equilibrium in the system. The determined composition of the AsSb nanoinsclusion case a substantial lattice mismatch with the AlGaAsSb matrix. By comprehensive structural investigations we determined the orientation relationships between the atomic lattices. The c-axes of the nanoinsclusion lattice, which can be described as hexagonal, is oriented along one of the <111> directions of the matrix, which possesses the zinc-blende structure. The [-2110] direction in the inclusion is parallel to one of the corresponding <110> directions in the matrix. As a result of the lattice mismatch, large AsSb nanoinclusions are accompanied by satellite dislocation loops. In order to determine strain components inside and outside the nanoinclusions we performed geometric phase analysis (GPA) of a HRTEM image with the reference to a known undistorted and quasi-similar lattice. By GPA we also determined the Burgers vector of the dislocation loops, which appeared to be perfect prismatic with b = a[001]. We considered the corresponding problem of elasticity and show that the dislocation loop formation reduces the total elastic energy in the system. The established composition and microstructure of AsSb inclusions in AlGaAsSb laid a solid basis for deeper insight into plasmonic properties of the metal-semiconductor metamaterial.

NM02.10.19
Monodisperse Dual Plasmonic Au@Cu2-xE (E=S, Se) core@shell Supraparticles—Aqueous Fabrication, Multimodal Imaging and Tumor Therapy at In Vivo Level Yunsheng Xia; Anhui Normal University, Wuhu, China.

We herein report aqueous fabrication of well-defined Au@Cu2-xE (E=S, Se) core@shell dual plasmonic supraparticles (SPs) for multimodal imaging and tumor therapy at the in vivo level. By means of a modified self-limiting self-assembly based strategy, monodisperse core@shell dual plasmonic SPs, including spherical Au@Cu2-xS SPs, Au@Cu2-xSe SPs, and rod-like Au@Cu2-xS SPs, are reliably and eco-friendly fabricated in aqueous solution. Due to plasmonic coupling from the core and shell materials, the as-prepared hybrid products possess an extremely large extinction coefficient (9.32 L g-1 cm-1 for spherical Au@Cu2-xS SPs) at 808 nm, which endows their excellent photothermal effect. Furthermore, the hybrid core@shell SPs possess the properties of good biocompatibility, low nonspecific interactions, and high photothermal stability. So, they show favorable performances for photoacoustic imaging and X-ray computed tomography imaging as well as photothermal therapy of tumors, indicating their application potentials in biological field.

NM02.10.20
High Activity Heterogeneous Catalysts by Plasma-Enhanced Chemical Vapor Deposition of Volatile Palladium Complexes on Biomorphic Carbon Lasse Jürgensen, Michael Frank, Lisa Czypmiel and Sanjay Mathur; Inorganic Chemistry, University of Cologne, Cologne, Germany.

New palladium complexes based on alky and alkenolate ligands were synthesized and structurally characterized. Combination of delocalized allylic sp2-
hybridized carbon centers and a strongly binding N=O chelating unit (e.g. 3,3,3-trifluoro(pyridin-2-yl)propen-2-ol) offered a promising combination of high volatility and thermal lability not commonly observed in noble metal precursors. Application of the new Pd compounds in thermal metal organic and plasma-enhanced chemical vapor deposition demonstrated their clean and efficient decomposition pathways, which in conjunction with their intriguing air stability made them efficient precursors for Pd films and clusters. Plasma-enhanced chemical vapor deposition of the palladium compounds on biomorphic carbon used as a porous substrate with high surface area and interconnected channels delivered recyclable carbon-supported Pd catalysts (Pd@BioC), which showed excellent selectivity, stability, and recyclability in C–C coupling reactions.

NM02.10.21

Directed and Self-Assembly of Elemental and Bimetallic Thin Films in the Au-Ag-Ni System via Pulsed Laser Dewetting

David A. Garfinkel1, Philip D. Rack1,2, Ryan Allaire1, Jason Fowlkes1,2, Lou kondic1, Miguel Fuentes-Cabreram and Rezee Emery1; 1University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2CNMS, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3New Jersey Institute of Technology, Newark, New Jersey, United States.

Both directed and self-assembly of metallic thin films via pulsed laser induced dewetting have been demonstrated as viable techniques for generating ordered arrays of metallic nanoparticles. The liquid phase dewetting of single component materials has been the subject of much study, and thus the relevant instabilities in 2D films and 1D filaments, and competing fluid forces of surface energy, viscosity, and inertia, are relatively well understood. The addition of a second component, however, creates intriguing and complementary chemical instabilities and free energy landscapes that can facilitate or compete with the hydrodynamics. For instance, phase instabilities at high temperatures can compete with the dewetting dynamics, and provide an avenue to create unique particle morphologies. Here we will examine both patterned and continuous thin film dewetting of elemental and bimetallic films in the Au-Ag-Ni system. Beyond promising bifunctional magneto-plasmonic properties and applications, the chosen material system also features three unique bimetallic phase behaviors: near complete immiscibility in the solid and liquid phase (Ag-Ni), complete miscibility (Au-Ag), and liquid miscibility with a miscibility gap in the solid phase (Au-Ni). The primary focus is devoted to Au-Ni and Ag-Ni due to the presence of immiscibility in both systems. In this presentation we will briefly overview some of the previous work on single component pulsed laser dewetting, and in particular on the 1D breakup of lithographically patterned thin film strips. We will then compare the Rayleigh Plateau instability and hydrodynamic transport in Ag-Ni and Au-Ni, and illustrate how phase separation affects the dewetting dynamics. We will show complementary molecular dynamics simulations as well as continuum simulations, which will demonstrate how the relevant timescales of the hydrodynamic/chemical instabilities and transport affect the resultant nanoparticle morphology.

NM02.10.22

Nanoporous Metallic Aluminum-Covered Polyimide Nanopaper as Carbon-Free Cathode for Lithium-Air Batteries

Jiwon Jung1, Su-Ho Jung2, Tae Gwan Yoon3, Ki Ro Yoon1, Changhun Kim1, Jun-Young Cheong1, Su-Ho Cho1, Hye Moon Lee4 and Il Doo Kim1; 1KAIST, Yuseong-gu, Korea (the Republic of); 2Korea Institute of Materials Science, Chunchon, Korea (the Republic of).

Although conductive and cheap aluminum (Al), common cathode current collector in Li-ion batteries, is well known to be stable at high voltage, its active use in Li-air batteries has been limited because of a lack of synthetic method for porous, metallic Al layer with high surface area. Herein, we first developed nanoporous metallic aluminum (Al)-coated polyimide nanopaper (PI@nAl Np) as carbon-free air cathode for flexible Li-air batteries: First, self-standing PI Np was synthesized via electrosprinning of PAA solution (pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) in N,N-dimethylformamide (DMF)) followed by imidization. Then, using our own Al ink developed by our group (patented in USA), the nAl overlayers were conformally coated on entire surfaces of the PI Np; thickness of Al coating layer was precisely optimized in terms of electronic conductivity (<1 ohms/square), flexibility and pore blockage in controllable manner. The finely designed PI@nAl Np showed greatly important features as porous cathode: (1) Mechanically durable PI Np without reactive carbon in electrolyte provides flexible, porous and light-weight matrix for diffusing O2 and accommodating Li2O2 in large void reservoirs. (2) nanoporous metallic Al coating layers serve as sufficient reaction sites and facile pathway for electron transport. The PI@nAl Np exhibits a highly stable capacity at a fixed capacity of 1000 mAh g−1 for over 300 cycles at a current density of 400 mA g−1. We conducted close-investigation of reaction products in light of morphology, parasitic side reactions in carbon-free air cathode. Flexible pouch- and cable-type Li-air battery cells with the PI@nAl Np were successfully fabricated and applied as power sources for flexible electronics (5.0 V LED and 6.0 V ‘Otto Bot’ operating). Our synthetic strategy will open new opportunities to invent nanostructured Al materials for diverse applications.

NM02.10.23

Silver Core/Silicon Nanocrystal Shell Hybrid Nanoparticle as Antimicrobial Agent

Asuka Inoue1, Hiroshi Sugimoto1, Byungji Kim2, Michael J. Sailor3 and Minoru Fujii1; 1Department of Electrical and Electronic Engineering, Kobe University, Kobe, Japan; 2Materials Science and Engineering Program, University of California, San Diego, San Diego, California, United States; 3Department of Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States.

Silver nanoparticles (AgNPs) are often used for antimicrobial applications, especially against Gram-negative bacteria, such as E. coli. Upon dissolution, AgNPs release Ag ions that bind to nucleic acids and thiol-containing compounds (i.e. amino acids in enzymes and proteins) to inhibit bacterial growth. However, AgNPs suffer from agglomeration and oxidation, which both degrade antimicrobial activity. To overcome this challenge, AgNPs are often coated with polymers. Recently, we developed a hybrid nanoparticle that is composed of an Ag core and a monolayer shell made of silicon (Si) nanocrystals. [1] With a hydrophobic shell formed by Si nanocrystals, the hybrid nanoparticle is able to disperse in water without agglomeration. Moreover, the size of AgNPs and the thickness of their shells can be tuned by adjusting concentration of Ag ions and Si nanocrystals. A major advantage of the hybrid nanoparticle is that it can be formed into a smooth and flexible film of antimicrobial nanoparticles by simply drop-casting the solution onto a substrate. Herein, we present the potential of the hybrid nanoparticle as an antimicrobial agent against E. coli, as a model Gram negative bacterium. The antimicrobial action of the hybrid nanoparticle is similar to bare AgNPs, in that Ag ions are released from the hybrid nanoparticle core through the Si nanocrystal shell to inhibit bacterial growth. Furthermore, use of the drop-cast films as antimicrobial coatings were studied as a function of structural parameters (i.e., diameter of the Ag core, diameter of Si nanocrystals forming the shell), and antimicrobial efficacy was tested in an agar diffusion assay. The results demonstrate a strong antimicrobial activity by the hybrid nanoparticle film, compared to the bare AgNp film. Moreover, the extent of bacterial growth inhibition depended strongly on the structure of the hybrid nanoparticle. Quantitative analyses reveal that hybrid nanoparticles diffuse on agar by releasing Ag ions, and that the area of the growth inhibition is determined by the diffusion rate which is in turn determined by the structural parameters of the hybrid nanoparticle. The hybrid nanoparticle remains effective when stored in aqueous solution or in air.


NM02.10.24

2D Single-Crystalline Copper Nanoplates as a Conductive Filler for Electronic Applications

Tae-Wook Kim; Korea Institute of Science and Technology, Wanju, Korea (the Republic of).

Metal nanoparticles have received much attention due to their versatile use in catalysis, optoelectronics, magnetics, biotechnology and microelectronics
applications. Because the nanoparticle size is known to be an important factor to enhance the activity or functionality for practical applications, various synthetic methods have been introduced, and a potential growth mechanism has been proposed to explain the relationship between the crystal structure and the optical, physical and electrical functionalities. In this study, we synthesize copper nanowires (Cu NWs) and copper nanoparticles (Cu NPLs) using a hydrothermal process. The combination of a mild reductant, stabilizer, and shape modifier allow the dimensional control of the Cu nanocrystals from one-dimensional (1D) nanowires to two-dimensional (2D) nanoparticles. HR-TEM reveals that the prepared Cu NPLs had a single-crystalline structure. From the XPS analysis, we found that iodine plays an important role in the modification of the copper nanocrystals through the formation of an adlayer on the basal plane of the nanoplates. We successfully synthesized Cu NPLs with an average edge length of 10 μm, and these Cu NPLs are the largest copper 2D crystals synthesized by a solution-based process so far. The application of the metallic 2D crystals as a semi-transparent electrode proves their feasibility as a conductive filler, exhibiting very low sheet resistance (0.4 Ω/sq). The efficient charge transport is due to the increased contact area between each Cu NPL, i.e., so-called plane contact (2D electrical contact).

NM02.10.25

Synthesis and Size Analysis of DNA Conjugated Bio-Hybrid Nanostructures Soubantika Palchoudhury¹, Abdullah Arabshahi², Yasmin Foster¹, Uday Ghar‡¹ and Armel Boutchuen²; ¹Civil and Chemical Engineering, University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States; ²SimCenter, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

The remarkable advances in synthesis techniques has led to a wide variety of complex nanostructures in recent years. The hybrid nanostructures essentially integrate multiple nanoparticles into one unit to facilitate tailored material properties. Synthesis of bio-hybrid nanostructures integrating biological moieties with inorganic nanoparticles has been of particular interest due to their novel material properties and applications in bio-imaging and drug delivery, but these structures are synthetically challenging to achieve. These hybrid nanostructures are also increasingly complex in terms of metrology. We report the synthesis of a novel hybrid nanostructure containing shape-controlled iron oxide nanoparticles conjugated to metal nanoparticles (e.g., Au) via DNA linkers. The synthesized bio-hybrid nanoparticles are stable in the aqueous phase and are characterized via a transmission electron microscope. The size and surface charge of a nanoparticle is an important metric for several biomedical applications such as targeted drug delivery as it affects the nanoparticle's circulation in vivo. However, it is challenging to establish a metric to accurately assess the size of these bio-hybrid nanoparticles due to their complex structure and morphology. In this study, size and zeta potential of the different bio-hybrid nanostructures synthesized have been investigated in detail on a Litesizer particle analyzer to develop a reliable material characterization method to assess the size of complex nanostructures. The study will be highly useful for biomedical applications like imaging and drug delivery.

NM02.10.26

Facile Signal Amplification of Colorimetric DNA Detection Using “Nano-to-Ion” Processes for High Sensitivity Hye In Cho and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

A number of signal amplification methods have been investigated to achieve high sensitivity of DNA detection schemes. In general, the signal amplification of DNA detection can be classified largely into two categories, depending on the type of the amplification target: DNA targets themselves, and artificially designed surrogate targets. These approaches have been widely taken advantage of in industry and academia owing to the high selectivity and sensitivity of the detection results. However, the amplification of target DNA, such as the polymerase chain reaction (PCR) and the rolling circle amplification (RCA), are limited with their cumbersome, time-consuming enzymatic reactions. To overcome such obstacles, the surrogate target amplification has been developed and employed in various DNA detection schemes, such as bio-barcode assays, with advantages including short detection time, no need for enzymatic reactions, and high sensitivity. Unfortunately, however, the design and incorporation of surrogate targets are accompanied with undesired expenses and labor.

In this work, we developed a DNA detection assay based on the conventional sandwich schemes using magnetic microparticles (MMPs) and silver nanoprobes, each functionalized with probe DNA strands, but with highly reliable and facile amplification technology. Importantly, we took advantage of the presence of nanoparticle probes without amplifying any targets or surrogate targets. Instead, a single nanoparticle probe can be transformed into numerous ions via a “nano-to-ion” process. This numeric enhancement can be directly correlated with the signal enhancement and eventually the improved limit of detection (LOD). To obtain the colorimetric signals, the tremendous number of silver ions is quantitatively analyzed using the C–Ag–C coordination chemistry in assistance with DNA-modified gold nanoparticles. Furthermore, for the better sensitivity of DNA detection, we obtained the photoluminescence of semiconductor quantum dots, which was another quantitative correlation parameter as a function of the silver ion concentration.

NM02.10.27

Investigation of (WO₃), Cluster and Tungsten Oxide Nanoparticle Formation Using Time-of-Flight Mass Spectrometry Stefan Kunis¹, Christof Schulz¹, ² and Hartmut Wiggers¹, ²; ¹IVG, Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Duisburg, Germany; ²CENIDE, Center for Nanointegration Duisburg-Essen, Duisburg, Germany.

Tungsten oxide (WO₃) is an important gas sensing material due to its sensitivity to, e.g., acetone, toluene, and hydrogen sulfide. The detectability of these gases and the insensitivity to high humidity makes WO₃ interesting for non-invasive breath diagnostics [1]. The acetone concentration in the breath is an indication of diabetes, the concentration of toluene can indicate lung cancer. All these applications require high surface area and thus small particles. Time-of-flight mass spectrometry (TOF-MS) in combination with molecular-beam sampling enables the inline investigation of nanoparticle formation in the gas phase. Molecular-beam sampling instantaneously interrupts all reactive gas-phase processes and thus allows a spatially resolved measurement of gas-phase and particle-phase. TOF-MS can be used to identify the composition as well as intermediate species (clusters) at various locations in a reactor. To gain insight in the tungsten oxide nanoparticle formation process, respective measurements were performed in low-pressure flat-flame.

WO₃ nanoparticles are synthesized by the decomposition of tungsten hexafluoride (WF₆) in a premixed hydrogen/oxygen flame. Due to low pressure (20–30 mbar), an almost one-dimensional, spatially extended flat flame is formed enabling spatially-resolved measurements. A small sample of the aerosol is expanded through a nozzle and a skimmer into high vacuum to form a particle-laden molecular beam. The progress from the initial decomposition of the gaseous precursor to the formation and growth of (WO₃) clusters and nanoparticles can be studied by varying the distance between the burner head and the nozzle position. The distance between the sampling nozzle and the burner (height above burner, HAB), represents the residence time within the reactor. As previous investigations indicate fragmentation of tungsten oxide clusters [2] during TOF-MS measurements, electron ionization was substituted with soft ionization with a vacuum UV (VUV) lamp avoiding fragmentation.

The results show a sequential cluster formation and particle nucleation. The number concentrations of differently sized clusters strongly vary indicating “magic” cluster sizes during the nucleation process. The fuel-to-oxygen ratio affects cluster growth and phase composition and low oxygen concentrations cause the formation of sub-stoichiometric clusters. Substituting a small part of hydrogen with methane changes the flame chemistry due to additional charges resulting in a significant decrease of smaller cluster sizes and a shift to larger cluster sizes.

NM02.10.28

Universal Template-Synthesis Method for Three-Component Nanostructures Han-Jung Ryu, Jang Ho Joo and Jae-Seung Lee; Materials Science and
Trimetallic nanoparticles have attracted growing interest recently because of their superior chemical and physical properties. They show excellent catalytic properties which belongs to their synergistic effects based on electronic charge transfers between multiple metal atoms. Despite of these unique properties, however, trimetallic nanoparticles have to suffer from high reaction temperatures, harsh reductants and multistep procedures during their synthesis. To overcome these obstacles, nanosized templates can be used as one of promising solutions. Template methods are widely used for nanomaterial synthesis, because they can provide nucleation sites to facilitate the reduction process of metal precursors. After the removal of the templates, the resultant hollow nanoparticles can obtain high surface area, which is one of the most important virtues for catalyst. In this work, we demonstrate a universal template-assisted room-temperature synthetic method for trimetallic noble metal nanoparticles which were replications of silver halide nanotemplates. As a proof of concept, we demonstrate two types of trimetallic nanoparticles, each composed of Pd-Au-Ag and Pt-Au-Ag, which were synthesized using the universal synthetic method. Importantly, the shape of the trimetallic nanoparticles was able to be controlled by adjusting the shape of the templates. The structural properties and composition of the trimetallic nanoparticles were thoroughly analyzed by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), elemental mapping, and X-ray diffraction (XRD). Finally, the outstanding catalytic performance of the trimetallic nanoparticles for reduction of harmful toxic Cr (VI) ions were monitored by UV-vis spectrophotometry. They exhibited great catalytic performances for the reduction process because of their synergistic effects owing to multiple types of metals and high surface area derived from hollow structures.

NM02.10.29
Fabrication of Transparent Nanostructural Iridium/Iridium Oxide Film for Biomedical and Electrochemical Applications Ming-Ting Hsieh and Pochun Chen; National Taipei University of Technology, Taipei, Taiwan.

Ir and iridium oxide are attractive materials for biomedical and electrochemical applications due to their desirable stability, electrochemical performance, and biocompatibility. Nanostructured iridium/iridium oxide possesses several advantageous properties including large surface-to-volume ratio, light weight, optical transmittance, and desirable electrical and electrochemical capability. However, controlling film morphology and inter-connectivity of nanostructural iridium/iridium oxide is very difficult. Nanoporous iridium/iridium oxide has excellent properties, and it can also provide extremely high surface area in applications for catalysis, sensors, and bioelectrodes. In addition, the transparency of the nanoporous iridium/iridium oxide can provide a great benefit for biomedical devices such as electronic skin and implantable optogenetic probes.

In this study, we employed a facile process to fabricate a transparent and uniform iridium/iridium oxide film by chemical bath deposition with proper heat and electrochemical treatments. Besides, the formation mechanism of the nanoporous iridium/iridium oxide film was illustrated by a detailed thermodynamic calculation. In addition, we carried out a transfer printing process to attach the nanostructural iridium/iridium oxide film on transparent substrates including ITO and polyimide. We characterized and evaluated the deposited films. The surface morphology, roughness, hydrophilicity, crystallinity, oxidation state, and electrochemical performances of the iridium/iridium oxide film were analyzed.

NM02.10.30
Metal-Curcumin Nanoparticles—Synthesis, Characterization and Therapeutic Potential Apoorva Singh1, Pooya Ghosh2, Suranjana Mukherjee2, Sunita Sharma3, Swagata Dasgupta2, Gayatri Mukherjee2 and Koel Chaudhury1; 1School of Medical Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, India; 2Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, India; 3Institute of Reproductive Medicine, Kolkata, India.

In recent years, highly promising and innovative approaches involving complex formation of the curcumin molecule with transition metals has proven effective in overcoming the limitations associated with clinical translation of curcumin, i.e. low systemic bioavailability and hydrolytic instability. Owing to the significant role played by transition metals in pathological processes, these metal-curcumin complexes can act as a double-edged sword due to increased specificity and cytotoxicity. Though the complexes exhibit enhanced therapeutic potential, the low aqueous solubility still remains a challenge in achieving targeted drug delivery. Herein, we propose that nanof ormulation of metal-curcumin complexes may pave a new way towards drug delivery and therapeutics due to high stability, bioavailability that may result in longer circulation time.

The objective of the present study is to synthesize metal-curcumin nanoparticles (NPs) with high stability, solubility and long-term sustained drug delivery. For this purpose, the biocompatible and degradable FDA approved poly (lactic-co-glycolic) acid polymer was used as the vehicle along with poloxamer-407 to increase the stability of NPs. Two transition metals, Copper (Cu), and Zinc (Zn) were respectively complexed with curcumin in the ratio 1:1 and characterized using spectroscopic techniques. A nanoprecipitation technique was used to prepare NPs and the formulations evaluated in terms of particle size, zeta potential, surface morphology, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), entrapment efficiency (EE) and in vitro release kinetics. In addition to chemical characterization, the therapeutic potential of the NPs was investigated in different cancer cell lines and primary endometrial stromal cells isolated from endometriotic lesions.

It was found that the prepared NPs were in the size range of 180-220 nm with EE of 77±2.43 to 82±4.43%. The low polydispersity index and high negative zeta potential indicated monodispersiv and stable nature of NPs. FTIR and XRD confirmed the entrapment of respective compounds within NPs without any major structural alterations, while release kinetics indicated a sustained release pattern exhibited by Cu- and Zn-Cur NPs as compared to Cur NPs over a period of time. The enhanced anti-proliferative activity of metal-Curcumin NPs was evident in all the cancer cells lines and primary endometriotic cells as compared to Cur NPs. In conclusion, for the first time metal-Cur NPs with high aqueous solubility, bioavailability and diverse potential benefits were successfully prepared and characterized.

NM02.10.31
Masking Strategies for DNA Detection—What can Mask Catalytic Nanoparticle Surfaces for DNA Targets? Won Kyu Lee, Yoon Hyuck Kim and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

DNA-functionalized gold nanoparticles (DNA-AuNPs) have been widely used for sensitive and selective colorimetric detection of nucleic acids, because they exhibit excellent chemical and physical properties such as sharp melting profiles, cooperative binding properties, reversible assembly properties, and intense optical properties based upon the surface plasmon resonance (SPR). In particular, the conventional nanoparticle-based “luminescent” test schemes proved the DNA-AuNPs to be powerful and efficient diagnostic tools in various diagnostic applications for DNA targets. The color changes were determined by the [target] and the presence of mismatches, which were correlated with the interparticle distance of the DNA-AuNPs. While simple and rapid, however, this detection scheme had to suffer from low sensitivity, and often low signal intensity, especially at lower [DNA-AuNPs]. As a result, this assembly-based colorimetric detection scheme is practically of little interest in the community. Considering its fundamental reliability and simplicity, however, it would be a significant advance if a modification could improve its sensitivity and signal intensity.

We previously demonstrated a conceptually advanced detection scheme, where the protein target binding leads to the masking of catalytic nanoparticle surfaces. Eventually, the catalytic activity of the particles can be systemically controlled, which can be quantitatively correlated with the color signals. In case of DNA targets, however, they are not sufficiently large enough to “mask” the nanoparticle surfaces. Instead, the DNA targets can “assemble” the DNA-AuNP probes as described in the conventional assembly-based schemes, which ultimately results in masking DNA-AuNP surfaces using other DNA-AuNPs. Taking advantage of this masking strategy, where the concentration of the target DNA controls the exposed surface area of AuNPs, the detection
scheme in this work could be highly sensitive and selective for the colorimetric detection of DNA targets. In order to characterize and elucidate the processes controlling the exposed surface area of DNA-AuNPs, we analyzed the laboratory samples using an ICP-OES spectrometer (Inductively Coupled Plasma Optical Emission Spectroscopy), scanning electron microscopy (SEM) and dynamic light scattering (DLS). Melting transitions were also obtained as a function of temperature by monitoring the extinction change at 525 nm using UV-visible spectroscopy. Furthermore, we investigated the catalytic properties of the assembled DNA-AuNPs for the oxidation of α-phenylenediamine (OPD) and the reduction of 4-nitrophenol (4-NP). Our masking strategy studies of the DNA-AuNP assembly process will play a significant role in demonstrating colorimetric detection of the target DNA based on the self-assembly of gold nanoparticles.

NM02.10.32  
Effect of Hydrogen on the Mechanical Properties of Nanocrystalline α-iron Using Atomistic Simulations  
Mohamed A. Hendy1, Tarek Hatem1 and Jaafar A. El-Awady2; 1The British University in Egypt, Cairo, Egypt; 2Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Hydrogen embrittlement is a persistent problem causing premature failure for steels. Nanocrystalline metals have unique mechanical properties compared to coarse grain counterpart which makes them suitable for future structural applications. In order to assess the effect of hydrogen on nanocrystalline α-iron, 3D Molecular dynamics (MD) simulations have been performed for bulk random-oriented nanocrystalline α-iron. The simulation cells are of size 76nm × 76nm × 76nm composed of 40 grains of different size with periodic boundary conditions. The simulation cells are deformed by applying strain along the x-axis with strain rate of. The effect of hydrogen on the deformation mechanism and fracture have been investigated through simulating a hydrogen-free nanocrystalline iron cell and hydrogen charged one with hydrogen concentration of 100 appm. In both cases, intergranular failure has occurred, however, the results showed a significant reduction in fracture strain for hydrogen-charged simulation cell compared to the hydrogen-free one. Moreover, hydrogen accelerated intergranular crack propagation. The hydrogen charged simulation cell experienced different deformation activities compared to hydrogen free one. For both cases, many deformation modes interact and co-exist (twinning, partial dislocation emission and grain boundary sliding).

NM02.10.33  
Flame Inspired Nanostructuring—Flexible Ceramic Hybrids for Advanced 3D Nanotechnologies  
Yogendra K. Mishra; University of Kiel, Kiel, Germany.

Recently introduced flame based approach offers unique opportunities for advanced metal oxide nanostructuring, ranging from quasi 1D nanowires to microscopic 3D porous interconnected tetrapodal networks.[1] The present strategy offers direct integration of ZnO nano- and microstructures and their networks on the desired substrates for various applications, e.g., whispering gallery modes, photocatalysis or nanosensing (UV/gases) applications.[1,2] The flame grown ZnO tetrapods ZnO nano- and microstructures exhibit very low cytotoxicity and they have shown strong potentials against antiviral applications.[3] The unique 3D shape of the ZnO tetrapods facilitates them to be used as efficient fillers for fabricating advanced composites, e.g., self-reporting composites[4] and many others. The 3D porous, flexible and conducting network from ceramic materials are now-a-days very important because of their technological relevance and the developed flame method offers desired synthesis of various ZnO and SnO2 nanomaterials.[1] These 3D porous networks can be decorated with other nanostructures for designing hybrid multifunctional materials[7] and can also be used as sacrificial templates to grow new nanomaterials.[8,9] Additionally, polymers can also infiltrated within the network to make different polymer based composites and template can be removed later on, if needed, to develop porous polymers.[10] An overview about the possible nanostructuring opportunities by the flame method will be presented and few application examples will be discussed.

References:
[1] Particle & Particle Systems Characterization 30, 2013, 775-783
[10] Nature Communications 8, 2017, 1215

NM02.10.34  
Reversible Magnetic Agglomeration—A Mechanism for Thermodynamic Control Over Nanoparticle Size  
Dale L. Huber1, Grant Bleier1, John Watt1, Simocko K. Chester2 and Judith Lavin1; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2San Jose State University, San Jose, California, United States.

We present a method for the synthesis and precise size control of magnetic nanoparticles in a reversible magnetic agglomeration mechanism. In this approach, nanoparticles nucleate and grow until a critical susceptibility is reached, in which magnetic attraction overcomes dispersive forces, leading to agglomeration and precipitation. This phase change in the system arrests nanoparticle growth and gives true thermodynamic control over the size of nanoparticles. We then show that increasing the alkyl chain length of the surfactant, and hence increasing steric stabilization, allows nanoparticles to grow to larger sizes before agglomeration occurs. Therefore, simply by choosing the correct surfactant, the size and magnetic properties of iron nanoparticles can be tailored for a particular application. With the continuous addition of the precursor solution, we can repeat the steps of nucleation, growth, and magnetic agglomeration indefinitely, making the approach suitable for large scale syntheses.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE’s National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

NM02.10.35  
Engineering Nanoscale Selenium Surface Functionalization for Clinical Antibacterial Applications  
James W. Maxley, Paria Ghannadian and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Antibiotic resistance (ABR) is rapidly gaining attention within the scientific community as an escalating threat to the global health care infrastructure. The increasing frequency of occurrence of resistant bacterial strains, specifically multidrug resistant (MDR), extensively drug resistant (XDR), and totally drug resistant (TDR) phenotypes, would seemingly necessitate demand for a new generation of small-molecule drugs for clinical implementation. Fortunately;
the compounded effects of administrative barriers, technical complications, and selective economic pressures has significantly reduced the rate of discovery for new antibiotic species. Novel approaches for the management of bacterial growth in clinical settings are clearly desirable. One such approach is the development of nanoscale selenium surface functionalization for medical materials and instrumentation.

Selenium nanoparticle functionalization was achieved by heterogeneous nucleation along a range of solid supports provided by academic and federal collaborators. These materials were coated in small-batch processes, in which the supports (2 mm x 2 mm x 0.5 mm) were immersed in a reaction solution (100 μM glutathione, 25 μM sodium selenite, and 80 μM sodium hydroxide) for 60 seconds, followed by several washing stages with deionized water. Nanoparticle coatings were characterized with atomic force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and contact angle measurement. Functionalized surfaces were assessed for antibacterial properties by means of colony forming unit (CFU) assay with gram-positive (Staphylococcus aureus, ATCC 25923) and gram-negative (Escherichia coli, ATCC 25922) bacterial strains.

Physical characterization demonstrated that treatment yielded homogeneous surface coverage, with average particle interspacing smaller than the dimensions of both S. aureus and E. coli. Chemical characterization verified that observed nanoparticles were composed of elemental selenium. CFU assay demonstrated a statistically significant reduction in S. aureus bacteria over a 12 hour interval for the two current test materials, carbon-microfiber sheets and basalt-epoxy blocks. For carbon-microfiber sheets, treatment resulted in a 32% and 63% reduction in CFU at the targeted operational temperatures of 50 °C and 40 °C, respectively. For basalt-epoxy blocks, treatment resulted in a 77% and 82% reduction in CFU at the targeted operational temperatures of 60 °C and 50 °C, respectively. A trend of reduced bacterial colonization has also been observed for E. coli in preliminary studies.

Nanoscale selenium surface functionalization has demonstrated antibacterial efficacy along clinical surfaces in vitro. Future studies will focus on elucidating the mechanism of antibacterial activity, assessing mammalian cell biocompatibility, and determining antibacterial efficacy under biofouling conditions.

NM02.10.36
Colloidal ReO₃ Nanocrystals—Extra Rhenium d-electron Instigating a Metallic Optical Behavior Sandeep Ghosh; The University of Texas at Austin, Austin, Texas, United States.

Plasmonics exhibited by nanocrystalline metals has been an active area of research, mostly due to interest in exploring their unique optical response. Although elemental metals like gold and silver have been the major focus in these studies, other materials have also been shown to exhibit a metallic optical response. In this presentation, we will describe a solution based synthesis of nanocrystals (NCs) of rhenium (VI) oxide (ReO₃) which exhibit localized surface plasmon resonance (LSPR) specific to the metal's unique electronic band structure. The presence of an extra d-electron in the outer electron shell of the rhenium (VI) ion leads to partial filling of the conduction band and manifests in its characteristic metallic conductivity and optical properties. The colloidal synthesis of these NCs follow a simple wet-chemistry method, based on the reduction of Re(VII) precursor to the Re(VI) oxidation state. This is different from the usual chemical mechanism that a majority of the metal oxide NCs of interest, coupled with unavailability of suitable Re(VI) precursors. In this presentation, these synthesis challenges and strategies employed to overcome them and design a successful chemical route will be described. The as-obtained NCs exhibit an LSPR optical response in the visible-near-infrared region, and are stabilized in solution by L-type ligand coordination. The advantage of such ligand coordination is demonstrated by the ease of switching between solvents of choice without having to go through the cumbersome ligand exchange procedure, most prevalent otherwise in case of X-type ligation in colloidal NCs. These NC solutions were then spin-coated on appropriate substrates and further characterized by means of electrical transport and spectroelectrochemical measurements.

NM02.10.37
Polyelemental Nanopatterns via Low-Energy Plasma Bombardment for High Performance Gas Sensor Woo-Bin Jung and Hee-Tae Jung; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Three-dimensional nanopatterns that consist of polyelemental components are promising platform for potential applications, whereas there are no effective strategies for fabrication of polyelemental nanopatterns, in which three-dimensional architectures can be explored in a systematic and site-specific manner. Generation of high resolution (<30 nm) nanoscale pattern with multi-components regardless types of elements is one of the biggest challenge in nanotechnology because of difficulties of nanoscale mixing and 3D nanopatterning at the same time. Recently, a few study based on precursor such as diphenylphosphine and block copolymer template have been reported, but previous approaches are limited to shape and combination depending on compatibility of elements.

In this study, we accomplished significant progress toward developing general method for fabricating complex nanostructures with a mixture of two or more types of elements. By simply using low-energy plasma bombardment process, followed by secondary sputtering on the sidewall surfaces of the pre-pattern, the polyelemental components with diverse shapes and high resolution were generated. Unlike previous approaches, this discovery is significant in terms of the fabrication of a wide range of polyelemental complex nanostructures. Firstly, this method is not restricted to the selection of elements and their combination, and a wide range of combination of metals and semiconductors can be generated by the simple deposition of metals or semiconductors on a substrate. Secondly, nanostructures with several components of greater than three can be fabricated by simply plasma bombardment process on multi-layered films. Thirdly, the complex shapes and array of multi-component nanostructures with high resolution (~10 nm) and tunable inner structures can be achieved. Finally, this approach can be applied to hydrogen gas sensing, with the highest sensing speed observed using Pd–Au bimetallic nanopatterns. Notably, only one Pd-based bimetallic line-shaped nanostructure was examined in this study; this may not even be the best one, but its performance exceeds that of conventional materials. This study is expected to open the door for a large family of multi-component metals for use in a wide range of applications.

NM02.10.38
Intermetallic L1₀-MP (M=Fe, Co) Nanoparticles Advance Pt Catalysis in Fuel Cells Junru Li and Shouheng Sun; Brown Univ, Providence, Rhode Island, United States.

Stabilizing transition metals (M) in Pt alloy under acidic conditions is challenging, yet crucial to boost Pt catalysis towards oxygen reduction reaction (ORR) in fuel cells. ~9 nm tetragonal core/shell L₁₀-MP/Co nanoparticles with 2-3 atomic layers of strained Pt shell were synthesized for ORR. At 60°C in acid, the tetragonal L₁₀-MP better stabilizes M than its cubic A1-MP counterpart. L₁₀-FePt/Co showed superior activity to commercial Pt/C catalyst in the membrane electrode assembly (MEA) and almost no activity drop after 30,000 voltage cycles at 80°C. L₁₀-CoPt achieved mass
activities (MA) of 0.56 A/mgPt before durability test and 0.45 A/mgPt after 30,000 voltage cycles in the MEA at 80°C, exceeding the DOE 2020 targets on Pt activity and durability (0.44 A/mgPt in MA and ~40% loss in MA after 30,000 cycling). Density functional theory study suggests that the ligand effect of Co and the more compressive strain brought by Co compared to Fe better tunes the binding of oxygenated species to the 2–3 Pt shell, thus leading to enhanced ORR performance in fuel cells.

NM02.10.39
Hot Carrier Generation via Surface Plasmons Polaritons for Enhanced Glycerol Electro-Oxidation Reaction

Kyoungwha Chung1,2; Yu Jin Jang1,2; Akira Baba3; Jianfang Wang4; and Dong Ha Kim1; 1Ewha Womans University, Seoul, Korea (the Republic of); 2Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); 3Chinese University of Hong Kong, Hong Kong, Hong Kong; 4University of Niigata, Niigata, Japan.

Surface plasmon polaritons (SPPs), which can be observed from the metal films or the metal gratings, dissipate only through non-radiative decay, whereas localized surface plasmons (LSPs) in metal nanocages decays either via radiative or non-radiative relaxation processes. The non-radiative decay of plasmonic energy can generate hot electrons, which possess higher energy than Fermi level. Plasmonic hot carriers are promising for applications in optoelectronics, plasmonics and energy conversion. However, plasmonic hot carrier generation was mostly carried out in metal nanostructures supporting LSPR modes, while very few works were reported with SPPs. In this work, surface plasmon resonance (SPR)-enhanced hot-carrier generation was demonstrated for a model electrocatalytic reaction in Kretschmann configuration. SPR coupling was employed to overcome the low efficiency of thin film-based photon-to-carrier conversion. Arrays of Au nanobipyramids decorated with Pt nanoparticles (AuNBPs@AgPt) were introduced on Au film surfaces to form the nanoparticle-on-mirror (NPoM) geometry and the performance for the glycerol electro-oxidation reaction exhibited ~2.5 times improved photocurrent evolution under illumination of p-polarized light compared with the activity based on the neat Au film with the photon-to-hot carrier conversion efficiency of 2.4 × 10−4. The results obtained in this study may pave a way to provide new opportunities for the SPP-driven energy conversion applications for electro-/photocatalysis and redox species-mediated optical sensing.

NM02.10.41
Dehydration Sensing of a Polymer Film via Plasmonic Nanoparticles
Miliana Lisinova1,2; Ralph E. Martin Department of Chemical Engineering, UARK, Fayetteville, Arkansas, United States; 2School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.

It is well known that plasmonic nanoparticle's possess a high sensitivity to the refractive index sensitivity of the surrounding medium. Such capabilities already widely explored in bio-plasmonic detectors to sense adsorption events. The high refractive index sensitivity allows to utilize plasmonic nanoparticles to distinguish hazardous solvents vapor from the water vapor.

However, the dehydration/dehydration sensing by plasmonic nanoparticle's which detect water molecules absorption/desorption by soft matter has not been introduced yet. The dehydration sensing of the soft matter is of a particular interest due to the difficulties of the utilization standard techniques in characterization dehydration process of the ultra-thin films or their complexity and extremely high cost. Therefore the development novel approach to control water molecules desorption seems a great challenge. Moreover, the non-traditional method of the water molecules absorption/desorption studies in soft matter to simulate tissue are required. Among prospective candidates for the refractive index sensitivity by plasmonic nanoparticle's are relatively new type materials such as plasmonic nanocages (NCs) which possess the ultra-high refractive index sensitivity of ~1000 nm/RIU. Such high refractive index sensitivity by NCs allows to distinguish a minor changes in refractive index of about 0.01 RIU to 0.001 RIU.

The aim of the research is on the elucidation of the applicability of the refractive index sensitivity of the plasmonic NCs in evaluation dehydration of the ultrathin transparent polymer films, such as poly(vinyl alcohol) (PVA). The PVA has been chosen because of the wide applicability in biomedical field due to the non-toxicity and biocompatibility, better film and fiber forming, excellent chemical resistance and water solubility.

The study is the first to examine the dehydration kinetic of the free standing films based on PVA via refractive index sensitivity of the NCs. Unlike well-studied plasmonic substrates which allows to research adsorption molecules on the surface, the incorporation plasmonic nanoparticles between the polymer layers, polymer/NCs/polymer, allows to research water molecules absorption which involves whole volume of the film. The utilizing nanoparticles allows to estimate rate of polymer film hydration/dehydration. For instance, the NCs introduced to polymer with 2 μm thickness of each layer possess the dehydration time of about 180 (s), dehydration rate ~0.22 (vol% per s) and dehydration rate constant ~ 50X10−4 (s−1).

The work was supported by the University of Arkansas Foundation. I thank Jingyi Chen and Samir V. Jenkins for synthesis of the plasmonic bimetallic nanocages and Nano Bio Photonics group (npbphotons.uark.edu). The initial research was performed under supervision of Prof. Mostafa El'Sayed and Dr. Mahmoud Mahmoud at GATECH supported by U.S. Department of Energy, Office of Basic Energy Sciences under award # DE-FG02-09ER46604.

NM02.10.42
DNA-Coated Gold Nanoparticles for the Detection of mRNA In Vivo Within Hydra Vulgaris Animals

Maria Elena Kyriazis1; Maria Moros4; Araf El-Sagheer2; Tom Brown1; Claudia Tortiglione1 and Antonios Kanaras1; 1University of Southampton, Southampton, United Kingdom; 2Istituto di Cibernetica “E Caiamiello”, Pozzuoli, Italy; 3University of Oxford, Oxford, United Kingdom; 4University of Zaragoza, Zaragoza, Spain.

The ability to detect and monitor biomolecules such as mRNA in live cells has been shown to be of great importance. For example, changes in mRNA expression levels in individual cells have been associated with the development of diseases such as cancer. Common detection strategies are often based on real-time polymerase chain reaction, microarray analysis or in situ hybridisation. However, promising developments have been made by associating nucleic acids with gold nanoparticles (AuNPs) creating a so-called spherical nucleic acid (SNA). These systems have been shown to successfully penetrate the cell membrane without the aid of transfection agents and resist nuclease degradation. When hybridised to fluorophore complements, DNA-coated AuNPs have shown great promise at visualising mRNA in living cells as they exhibit high signalling and have low background fluorescence. Nevertheless, there is less work associated with the use of such systems in a more complex in vivo environment.

In this study we demonstrate the targeted detection of mRNA using DNA-coated AuNPs in the freshwater polyp Hydra vulgaris. Hydra, an invertebrate model that has been thoroughly used in nanomedicine is found at the base of metazoan evolution and presents an intermediate complexity between cell cultures and vertebrates. We show the biocompatibility of DNA-coated AuNPs upon incubation with live animals and specifically focus on selectively imaging Hymyc1 mRNA, whose downregulation is found to be associated with the progression of common cancers. We demonstrate how a precise and recognisable fluorescent pattern can be observed, which mirrors the expected Hymyc1 expression pattern thus indicating high levels of specificity. However, target specificity is also demonstrated via the use of DNA-coated AuNPs for the detection of mRNA that is not expressed within Hydra where a fluorescent signal is significantly absent. Ultimately this research aims to expand our knowledge on the behaviour of the aforementioned systems within live animals in order to further optimise and develop it into a system that could successfully combine efficient mRNA sensing and targeted drug delivery within an in vivo environment.
NM02.10.43
Revisiting Design of Upconverting Nanoparticles for Efficiency and Lasing
Bruce E. Cohen; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Multiphoton imaging techniques that convert low energy excitation to higher energy emission are widely used to improve signal over background, reduce scatter in subsurface imaging, and limit sample photodamage. Multiphoton imaging relies on luminescent probes able to efficiently sum the energies of 2 or more incident photons, as well as lasers powerful enough for multiphoton excitation. Lanthanide-doped upconverting nanoparticles have proven to be among the most efficient multiphoton probes, but even UCNPs with optimized lanthanide dopant levels require laser intensities that may be problematic for living systems. Here, we develop protein-sized, alloyed UCNPs (aUCNPs) that can be imaged at the single particle level at laser intensities below 300 W/cm², over 300-fold lower than needed for comparably-sized doped UCNPs. Using single UCNP characterization and kinetic models of lanthanide energy transfer, we find that addition of inert epilayer shells radically changes optimal lanthanide content from Yb³⁺, Er³⁺-doped NaYF₄ nanocrystals to fully alloyed compositions. At high levels of the emitter Er³⁺, these ions can adopt a second role to enhance the effective aUCNP absorption cross-section by desaturating sensitizer Yb³⁺ or by absorbing photons directly. Core/shell aUCNPs are brighter than comparably sized doped UCNPs at all laser intensities tested, over 4 orders of magnitude. Core/shell aUCNPs 12 nm in total diameter can be imaged with strong contrast (signal:background >25) through several millimeters of tissue in live mice using a laser intensity of just 0.1 W/cm². aUCNPs open up the possibility of using both low irradiance and low-energy excitation wavelengths for non-destructive bioimaging experiments. Additional recent work about dye-sensitized UCNP emission and UCNP-based micron-sized lasers will also be discussed.

New work from:


NM02.10.44
Highly Porous Black Metals Formed by High-Pressure Thermal Evaporation
Jun Gi Min and Sangwoo Ryu; Kyunggi University, Suwon, Korea (the Republic of).

Vacuum thermal evaporation is one of the well-known deposition processes to form dense films of metals. In conventional thermal evaporation process, heterogeneous nucleation and growth of the evaporated metal species on the substrates are key mechanisms of the dense films. The evaporation method introduced in this presentation utilizes high pressure inside the vacuum chamber during the evaporation so that it causes repeated collisions of evaporated metal atoms with each other, which is led to homogeneous nucleation and growth before arriving at the substrates. This process results in the formation of nanoporous structures composed of nanoparticle aggregates of the parent metals. The porosity and the color of the porous metals varies depending on the working pressure of the background inert gas. The porosity estimated by the dimensions determined by the electron microscopy exceeds 95% and the obtained nanoporous structures absorb almost all visible light showing black color. Herein, we present the details of this high-pressure thermal evaporation, examples of Au, Cu, Sn, and applications to chemical sensors or Li-ion batteries.

NM02.11.01
Fabrication of Hollow Metal Nanoshapes by Solid State Dewetting and Oxidation of Al on Sapphire Substrate
Nimrod Gazit¹, Gunther Richter², Amit Sharma¹, Leonid Klinger¹ and Eugene Rabkin¹; ¹Technion-Israel Institute of Technology, Haifa, Israel; ²Max Planck Institute for Intelligent Systems, Stuttgart, Germany.

The Al-Al couple is a classic example of a system in which the Kirkendall effect and Kirkendall porosity represent a major reason for failure in microelectronic devices. In this work we demonstrated that the Kirkendall effect during controlled oxidation of Al in the Al-Au core-shell nanoparticles can be utilized for the synthesis of hollow particles of the intermetallic phase.

We produced metallic nanoshapes by performing a solid state dewetting treatment of Al thin film deposited on sapphire substrate, followed by the deposition of thin Au layer on the top of dewetted sample. Annealing of the core-shell nanoparticles in air resulted in outdiffusion of Al from the particles, formation of pores, and growth of the Au₈Al₇ intermetallic phase in the particles. We demonstrated that the driving force for hollowing is the oxidation reaction of the Al atoms at the Au-sapphire interface, leading to the homoepitaxial growth of newly formed alumina at the interface. We developed a kinetic model of hollowing controlled by diffusion of oxygen through the Au thin film, and estimated the solubility of oxygen in solid Au.

NM02.11.02
Nanoparticle Megalibraries—Expanding the Materials Genome Through Size
Edward J. Kluender¹, James L. Hedrick¹, Rahul Rao², Benji Maruyama² and Chad A. Mirkin²; ¹Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; ²Air Force Research Laboratory, WPAFB, Ohio, United States; ³Chemical Engineering, Northwestern University, Evanston, Illinois, United States; ⁴Chemistry, Northwestern University, Evanston, Illinois, United States.

The nanomaterial landscape is so vast that a combinatorial approach, with complex parameter inputs, is required to fully understand the underlying structure-function relationships. To address this challenge, a new approach for the synthesis and screening of megalibraries of unique nanoscale features (>10 million features) with tailorable size, shape, and composition has been developed. Polymer pen lithography, a massively parallel scanning probe lithographic technique, is combined with a novel method for spray-coating the pen array with gradients of inks such that each pen in the array has a different, but deliberately chosen, quantity and composition of ink. With this technique, gradients of Au-Cu bimetallic nanoparticles have been synthesized on SiO₂ micropillars, and then screened for activity by in situ Raman spectroscopy with respect to single-walled carbon nanotube growth (SWNT) via chemical vapor deposition. Through this methodology, Au-Cu, a structure not previously known to catalyze SWNT growth, has been identified as the most...
active composition.

9:00 AM NM02.11.03
High Density Ag Nanoparticle Clusters for High Sensitive SERS Substrate Han Lu and Mingliang Jin; South China Academy of Advanced Optoelectronics, South China Normal University, GuangZhou, China.

Surface-enhanced Raman scattering (SERS) is a powerful analytical tool for sensitive detection of chemical[1] and biological molecules[2] even allowing the single-molecule detection[3]. The nanoparticle clusters (paired, trimers, tetramers and linear chains) has emerged as one of the most efficient and widely used configurations in studies involving surface-enhanced phenomena, producing intense electromagnetic fields in the interstices of a reasonably simple structure. Numerous methods have been developed to fabricate nanoparticle clusters in the past few decades, including evaporative self-assembly[4], surface modification[5], template-guided assembly[6] and light-directed assembly[7]. However, these methods are time-consuming and expensive. Thus, it is a challenge to fabricate a simple and cheap nanoparticle clusters for a surface enhance Raman spectroscopy (SERS) substrate with high sensitivity to detect single-molecules and excellent reproducibility and stability of signal. In this work, we introduce a simple method that generates Ag nanoparticle clusters for SERS substrate with high sensitivity and excellent reproducibility based on galvanic reaction in one step without any additional assembly steps. We systematically investigated the effect of the concentration of cetyltrimethylammonium bromide (CTAB), reaction time and temperature on the morphologies of Ag nanostucture. Fig.1a shows the SEM images of Ag nanoparticle clusters. Fig.1b-c shows the SERS spectra of 1 × 10^13 M R6G aqueous solution and 1 × 10^10 M L-Phenylalanine solution respectively, in which the main vibrational features of R6G molecules and L-Phenylalanine molecules are clearly observed, which reveals excellent Raman sensitivity in the Ag nanoclusters SERS substrate. The Ag nanocluster clusters may serve as high sensitivity SERS substrate for wide-ranging applications in single-molecule detection and molecule diagnostics.

9:15 AM NM02.11.04
Holistic Structural Hierarchy in Metal Nanoparticle Composite Superlattices Robert J. Macfarlane; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural hierarchy is a powerful design concept where specific geometric motifs are used to influence material structure across multiple size regimes. These complex levels of organization are typically achieved in the laboratory by conceptually breaking a material down into the smallest components that can be manipulated (e.g. individual molecules, macromolecules, or nanoparticles), and using the geometric information in those components to control how they build up into larger length scale patterns. Conversely, complex assemblies in natural systems are commonly achieved through a more holistic approach where assembly behaviors at the molecular, nano, and macroscopic scales are interlinked. This means that not only does structural information contained in molecular building blocks filter upwards to dictate material form at the nano to macroscopic levels, but also that the environment created by the larger length scale features can affect the behavior of individual components. Despite the potential of such a method of materials design, our ability to mimic these natural processes and holistically program structural hierarchy in artificial materials is still severely underdeveloped. Here, we demonstrate a metal nanoparticle-based building block that enables nanoscale geometry to function as a design handle to directly modulate the assembly behavior of a collection of supramolecular binding groups. The ability to use nanoscale geometry to modify molecular behavior allows a single set of nanoparticles to access different nanoscale bonding valencies, resulting in different mesoscale particle arrangements and different supramolecular bond strengths. The formation of distinct hierarchical structures at the nano and mesoscale is therefore both a consequence of and a direct influence on the molecular binding events that drive assembly. The use of nanoscale geometry to dictate supramolecular binding provides a major step forward in understanding how the assembly of hierarchically ordered artificial materials can be done in a holistic manner across multiple size regimes.

9:30 AM NM02.11.05
Nanostructured Hybrid Metal-Polymer Nanoparticle Systems and Continuous Flow Chemistry Synthesis Riggberto C. Advincula; Case Western Reserve University, Cleveland, Ohio, United States.

The synthesis of various hybrid metal-polymer nanomaterials pre-supposes the ability to utilize various synthetic approaches based on topologically exact dendrimers (and star polymers) and their ability to surround the metal as stabilizing ligands. For the polymer component, the use of macromonomers is known to synthesize the various block copolymer and miktoarm systems that can surround the metal nanoparticles core. In dendrimers, this can be based on convergent and divergent approaches of carefully designed AB2 monomers to dendrons that can be linked. In this work, we outline and demonstrate the use of various dendrimer and polymer synths to form hybrid nanoparticle systems. We also describe the use of continuous flow chemistry fabrication methods at the benchtop level to make metal nanoparticles and atomic clusters resulting in higher throughput synthesis and better distribution. We describe control of the metal nanoparticle synthesis parameters based on pressure, temperature, flow rate and mixing ratios. The grafting on surfaces and electropolymerization methods enable us to apply these nanomaterials hybrid into electron and charge transfer properties. These materials have the potential for use in catalysis. Also, a key to the analysis of such materials is the use of surface sensitive analytical methods as well as microscopy imaging methods.

9:45 AM NM02.11.06
Fabricating Ultra-Low-Density Nanoporous Metals by Freeze-Casting Nanowire Suspensions Alyssa L. Trokes, Tyler M. Fears, Fang Qian, Tom Braun, Anna Ringuette, Joshua A. Hammons, Michael Nielsen, Jean-Baptiste Forien, Theodore Baumann, T. Yong Han, Sergei Kucheyev and Michael Bagge-Hansen; Lawrence Livermore National Laboratory, Livermore, California, United States.

Ultra-low-density (1-30 mg/cm³) nanowire aerogels are a new class of monolithic nanoporous materials with potential applications in energy storage, generation, and utilization. These materials can be fabricated by freezing suspensions of metal nanowires and gently removing the solidified matrix, e.g., via freeze-drying, to prevent collapse of the porous nanowire network. As such, the macroscopic properties of the final aerogels are intrinsically linked to the composition of the feedstock suspensions, namely solvent composition, nanowire dimensions, and surface ligands. Herein will be discussed recent developments at Lawrence Livermore National Laboratory to produce high-quality ultra-low-density metal (Cu, Ag, Au) aerogels with ligaments of controlled diameter between 5 and 30 nm via a facile freeze-casting approach. We will demonstrate how the modification of suspension characteristics can be used to tune the final mechanical, electrical, and chemical properties of the aerogels. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

10:00 AM BREAK

10:30 AM NM02.11.07
Bias-Dependent Chemical Enhancement and Non-Classical Stark Effect in Tip-Enhanced Raman Spectromicroscopy of CO-Terminated Ag Tips Rebecca Gieseking1,2, Joonhee Lee3, Vartkess Apkarian4 and George Schatz2; 1Department of Chemistry, Brandeis University, Waltham, Massachusetts, United States; 2Department of Chemistry, Northwestern University, Evanston, Illinois, United States; 3University of California, Irvine,
Tip-enhanced Raman spectromicroscopy (TERS) with CO-terminated plasmonic tips can probe Ångstrom-scale features of molecules on surfaces. The development of this technique requires understanding of how chemical environments affect the CO vibrational frequency and TERS intensity. At the scanning tunneling microscope junction of a CO-terminated Ag tip, we show that rather than the classical vibrational Stark effect, the large bias dependence of the CO frequency shift is due to ground-state charge transfer from the Ag tip into the CO π* orbital softening the C-O bond at more positive biases. The associated increase in Raman intensity is attributed to a bias-dependent chemical enhancement effect, where a positive bias tunes a charge-transfer excited state close to resonance with the Ag plasmon. This change in Raman intensity is contrary to what would be expected based on changes in the tilt angle of the CO molecule with bias, demonstrating that the Raman intensity is dominated by electronic rather than geometric effects.

Metal Enhanced Fluorescence (MEF) has promising applications in the field of optical displays, bio-sensing and photodynamic therapy. In this work, we exploit the plasmons of embedded silver nanoparticles (Ag-NPs) fabricated by ion implantation to enhance the fluorescence of Coumarin 515 dye (C515) via MEF. Ion implantation of 70 keV Ag ions in quartz matrix at different fluences was carried out to synthesize Ag-NPs inside quartz matrix. The formation of Ag-NPs is characterized by the optical absorption measurements. Rutherford Backscattering Spectrometry (RBS) measurement was used to obtain the depth profile and concentration of silver within the substrate. From the RBS results, it was determined that front edge of the layer containing Ag was formed at an average depth of 16 nm below the surface, which closely agreed with Stopping and Range of Ions in Matter (SRIM) calculations. Increase in the size of the Ag-NPs is observed as the fluence of the silver within the substrate is increased. The MEF of drop casted C515 dye was studied using steady-state emission and excitation spectra measurements. Photoluminescence (PL) enhancement factor ranging from 1.2 to 2.1 with a maximum enhancement for the largest fluence was obtained. The observed MEF was ascribed to a combination of plasmon enhancement with larger nanoparticles due to increase in fluence and to increase plasmonic hot spots.

A theory has been established to describe the formation of facets on metal crystals grown from their melt. There exists a temperature for each crystallographic orientation below which it will form a facet, and above which the metal surface will be rounded and atomically rough. Here we have extended this theory to electrodeposition. We used potentiostatic electrochemical impedance spectroscopy to measure the approximate surface energy of Au at different applied potentials to determine the roughening temperature for each potential. From this, we grew different nanostructures with different proportions of facets and tested them as electrocatalysts for CO2 reduction.

With increasing worldwide demands for green energy, catalyst engineering has rapidly developed for several decades. Noble metals such as platinum (Pt) show outstanding catalytic activity and stability in various energy production/conversion techniques. However, high cost of the noble metal catalysts disturbs growth of energy industry. Bimetallic nanoparticles are emerging as low-cost but high-efficiency catalysts. Catalytic reactions only occur on the surface of nanoparticles, therefore, it is essential to understand surface morphology and atomic arrangements of alloy nanoparticles in order to improve their catalytic properties. In this study, we predicted energetically stable atomic arrangements on the surface and shape of different bimetallic nanoparticles such as Au-Pt, Cu-Pt, and Pd-Pt by Monte Carlo (MC) and molecular dynamics simulations. This works provide phase diagrams of the bimetallic nanoparticles in terms of size, shape, atomic composition and temperature of the system. Also, the trends in mixing alloy nanoparticles are discussed with regard to difference of binding energies between two elements.

Droplet-based reactors for nanoparticles are receiving attention due to their ability to maintain thermal and compositional equilibrium within and between droplets, enabling flow operations for inline analyses and the scale-up of nanomaterial syntheses. This presentation will show the versatility of these microreactors by synthesizing different dimension-controlled and shape-controlled nanostructures through manipulation of the relative flow rates of reagent stock solutions. Specifically, different Pd shell thicknesses can be grown on cubic or octahedral Au seeds. In addition, Au-Pd nanocrystal shapes ranging from sharp-branched octopods to core@shell octahedra can be controlled using seed-mediated co-reduction on Au octahedral seeds. This approach allows process conditions to be modified inline, rather than from batch to batch, to achieve particles with different shell thicknesses and shapes, and this procedure should be applicable to other multicomponent systems.

Selective Control of Crystal Structure in Solid-Solution Alloy—fcc and hcp Phases in Au–Ru Nanoparticles Quan Zhang, Kohei Kusada, Dongshuang Wu, Tomokazu Yamamoto, Syo Matsumura, Yoshiki Kubota and Hiroshi Kitagawa; ‘Chemistry, Kyoto University, Kyoto, Japan; 2Kyushu University, Fukuoka, Japan; 3Osaka Prefecture University, Osaka, Japan.
The crystal structure is one of the most dominant factors that strongly affect the properties of an alloy because its electronic and surface structures change drastically with the crystal structure. A solid-solution alloy, in which the constituent atoms are randomly and homogeneously mixed at the atomic scale, generally adopts one of three principal crystal lattice forms: body-centred cubic (bcc), hexagonal close-packed (hcp) and face-centred cubic (fcc) structures. However, once its constituent elements and composition are fixed, the crystal structure of the alloy is uniquely determined. Therefore, it is difficult to change the crystal structure of a solid-solution alloy at a certain composition. Here, we propose a new approach for selective control of the crystal structure in solid-solution alloys by using a chemical reduction method. By precisely tuning the reduction speed of the metal precursors, we demonstrated the first example of selective control by synthesizing fcc- and hcp-AuRu3 alloy nanoparticles (NPs). The alloy adopts an fcc structure when the Au precursor starts to be reduced slightly earlier, while it adopts an hcp structure when the reduction of Ru precursor begins slightly earlier. The structures of the obtained NPs were investigated using synchrotron powder X-ray diffraction analysis and atomic resolution scanning transmission electron microscopy (STEM). The mechanism of crystal structure control is discussed by using the results of UV-Vis spectral and electrochemical analyses. The influence of crystal structure on the catalytic performance for oxygen evolution reaction (OER) was also examined. 


2:00 PM NM02.12.03
*In Situ Nucleation Mechanism of the Nanometer-Sized Precipitates of the AA7050 Aluminium Alloy* Tsai-Fu Chang1, Yang Yo-Lun1, Hsiao-Chien-Nan2, Li Wei-Chih1 and Yang Jer-Ren1; 1National Taiwan University, Taipei, Taiwan; 2Department of Mechanical Engineering, Imperial College London, London, United Kingdom; 4E.A. Fischione Instruments, Inc., Pittsburgh, Pennsylvania, United States.

Cs-corrected high-angle-annular-field scanning-transmission-electron microscopy (Cs-corrected HAADF-STEM) with nanometer-scale energy-dispersive X-ray (EDX) was employed to investigate the transformation mechanisms of the η → η precipitation sequence of AA7050, an Al-Zn-Mg-Cu alloy. Evidence from Cs-corrected HAADF-STEM coupled with EDX showed that in-situ nucleation of a new η2 precipitate (one form of η) took place, wherein it gradually developed from the original η precipitate via a similar hexagonal structure with different compositions. The in-situ transition product was composed of two distinctive regions; one was identified as η', and the other, as η.

2:15 PM NM02.12.04
*Mono- and Bimetallic Nanoparticles of Noble Metals—The Influence of the Composition and Nanostructure on Biological Effects* Alexander Rustič1, Marina Breitsch1, Kateryna Loza3, Kevin Pappert1, Viktoria Grasnik1, Marc Heggen1, Manfred Köller1, Christina Sengstock2 and Matthias-Epple3; 1Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CeNIDE), University of Duisburg-Essen, Essen, Germany; 2Bergmannsheil University Hospital/Surgical Research, Ruhr-University Bochum, Bochum, Germany; 3Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Jülich, Germany.

Metallic nanoparticles represent a well-established field of nanoscience, medicine, catalysis, and industry. Due to the numerous applications, a contact with biological systems is unavoidable. Depending on the nanoparticles’ characteristics, the biological response can be rather different. Therefore, a detailed investigation of the structure and composition of monometallic, alloyed, and core-shell nanoparticles is a decisive factor for the assessment of biological effects. In addition to colloid-chemical and spectroscopic methods for the characterisation of nanoparticle dispersions, high-resolution (HRTEM) and scanning transmission electron microscopy (STEM) are advantageous to elucidate size, crystal structure (e.g. domains), and internal composition of mono- and bimetallic nanoparticles.

Spherical Rh, Pd, Pt, Ag, Au, and bimetallic (alloy, core-shell) nanoparticles (5-10 nm) were wet-chemically prepared, stabilised with poly(N-vinylpyrrolidone) and characterised by colloid-chemical and spectroscopic methods. Particle diameters as determined by analytical disc centrifugation and dynamic light scattering correspond very well to the results obtained by HRTEM. The overall elemental composition was determined by atomic absorption spectroscopy and X-ray powder diffraction. The nanostructure and elemental distribution was assessed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDX).

The biological studies comprised the analysis of the antimicrobial activity against gram-positive and gram-negative bacteria as well as the biocompatibility towards human mesenchymal stem cells (hMSC). Silver-containing nanoparticles with a high silver content showed a significant concentration- and time-dependent antimicrobial effect against *S. aureus* and *E. coli* as well as a toxicity towards hMSC. The other metals showed neither an antimicrobial effect nor a toxicity against hMSC. Interestingly, Rh, Pt and AgPt (≥50 % Pt) nanoparticles led to a nodule-like convergence of hMSC indicating a cell activation.

2:30 PM NM02.12.05
*Chiromagnetic Nanoparticles and Gels* Jiheon Yeom1, André F. de Moura2 and Nicholas A. Kotov1; 1University of Michigan, Ann Arbor, Michigan, United States; 2Federal University of São Carlos, São Carlos, Brazil; 3Massachusetts Institute of Technology, Boston, Massachusetts, United States.

The manipulation of chiroptical effects using a magnetic field is one of the ubiquitous interplays of chirality and magnetism. Ceramics such as transition metal oxides are intriguing in this regard, since many useful magnetoptical properties involve electric and magnetic transitions to amplify or modulate the chiroptical activities of the system. Here we synthesized chiral magnetic nanoparticles (NPs) using cobalt to investigate the enhancement of the rotatory optical activity and magnetic field modulations. The obtained NPs showed g-factors as high as 0.02 and strong optical rotation in the visible range that is at least 10 times higher than conventional chiral metal or semiconducting NPs. It was also possible to observe an increase of light transparency in the UV region with an external magnetic field. The chiral ceramic NPs prepared herein are versatile and fundamental experimental systems for potential application in chiroptical and magnetoelectrical effects, as well as for the investigation of (up to second-order) magneto-chiral and magneto-dielectric effects.

2:45 PM NM02.12.06
*Near-Infrared Fluorescent Metal Nanoclusters for the Gene Delivery and Bioimaging* Yuanqing Sun, Yiming Ouyang, Jiaqing Luo and Jian Liu; College of Science, China University of Petroleum, Beijing, Beijing, China.

We synthesized tunable near-infrared fluorescent gold nanoclusters (AuNCs) protected by branched polyethylenimine (PEI) modified by surface segmental attachment of sulphydryl groups (PEI-SH). The cationic polymer PEI-SH with positive charges enables AuNCs to perform gene delivery, and the gene transfection efficiency can reach 22.8%. Moreover, the fluorescence of AuNCs is tunable from visible red light (wavelength 609 nm) to NIR light (wavelength 811 nm) with high quantum yields, which is very suitable for bioimaging. To obtain nanomaterials with longer fluorescent wavelength in
near-infrared region (NIR), we introduced Cu element into system to prepare Au/Cu alloy nanoclusters, which possessed the second near-infrared region (NIR-II) fluorescence emission at 1080 nm. The Au/Cu alloy nanoclusters exhibit high quantum yields (~2%), which are 5 times higher than that of the commercial carbon nanotube. More interesting, Au/Cu alloy nanoclusters show tunable luminescence from NIR-I (811 nm) to NIR-II (1130 nm) corresponding to increasing the content Cu element in the nanoclusters. The Au/Cu alloy nanoclusters with high photoluminescence intensity, good fluorescence stability and low cytotoxicity can be used as an excellent NIR-II fluorescent probe for potential applications in the field of in vivo NIR-II fluorescent imaging.

3:00 PM BREAK

3:30 PM NM02.12.07
Thermomechanical Nanomolding of Crystalline Metals—The Smaller the Easier Jan Schroers1 and Ze Liu2; 1Yale University, New Haven, Connecticut, United States; 2Wuhan University of Technology, Wuhan, China.

Molding, associated with a materials flow-ability, becomes increasingly more difficult with decreasing mold size. The flow-ability of crystalline metals is usually much lower than that of thermoplastics, gels, and some glasses. As a consequence, attempts to mold on the nanoscale have been limited to thermoplastics, gels, and glasses, while crystalline metals have not been considered. Here, we report a thermomechanical nanomolding method for crystalline metals which becomes easier, quantified by the ratio of mold depth to mold diameter, with decreasing mold diameter. As the underlying diffusion mechanism is present in all metals and alloys, discovered nanomolding process provides a toolbox to shape essentially any metal and alloy into nanosize features. Technologically, this highly versatile and practical thermomechanical nanomolding technique offers a method to fabricate high-surface area metallic nanostructures which are impactful in diverse fields of applications including catalysts, sensors, photovoltaics, microelectronics, and plasmonics.

3:45 PM NM02.12.08
3D Nano-Printing Technique Based on Ion-Assisted Aerosol Lithography Woook Jung1,2, Yoon-ho Jung1,2, Petr Pikhitsa2 and Mansoo Choi1,2; 1Seoul National University, Seoul, Korea (the Republic of); 2A Global Frontier Center for Multiscale Energy Systems, Seoul, Korea (the Republic of).

On demand of miniaturization of 3D structure manufacturing following up the growth of nanodevice study, developing bottom-up based nanoparticle assembly technique has received attention. Establishing successful capability of 3D structure is closely related to precise positioning of nanoscale elements into 3D structures. We have developed Ion assisted aerosol lithography (IAAL) for charged metal nanoparticles assembly, making it possible to deposit nanoparticles to the desired location. IAAL utilizes the distorted local electric field induced by accumulated ions on a pre-patterned substrate to manipulate the trajectory of charged metal nanoparticles as they get attracted to the substrate by electrostatic attraction. The distorted electric field has brought the nanoparticles to the desired location. IAAL utilizes the distorted local electric field induced by accumulated ions on a pre-patterned substrate to manipulate the trajectory of charged metal nanoparticles as they get attracted to the substrate by electrostatic attraction. The distorted electric field has brought the nanoparticles to the desired location. IAAL utilizes the distorted local electric field induced by accumulated ions on a pre-patterned substrate to manipulate the trajectory of charged metal nanoparticles as they get attracted to the substrate by electrostatic attraction. The distorted electric field has brought the nanoparticles to the desired location.

This direct 3D nano-printing technique, which utilizes the charged metal nanoparticles as building blocks, has an ability to depositing various materials. Manufacturing various shapes of multicomponent 3D metal nanostructures is relative ease for demanding applications.

This work was supported by Global Frontier R&D Program on Center for Multiscale Energy System by National Research Foundation (NRF) under the Ministry of Science, ICT and Future Planning, Korea (Grant no.2012M3A6A7054855).


4:00 PM NM02.12.09
Covalent Surface Functionalization of Ultrasmall Gold Nanoparticles (2 nm) by Click Chemistry for Protein Targeting Selina B. van der Meer1, Kateryna Loza2, Christine Beuck2, Peter Bayer2 and Matthias Epple1; 1Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CeNIDE), University of Duisburg-Essen, Essen, Germany; 2Department of Structural and Medicinal Biochemistry, University of Duisburg-Essen, Essen, Germany.

Ultrasmall gold nanoparticles of 2 nm diameter are smaller than most proteins and therefore should allow a specific epitope targeting on a protein surface. Thereby, the conformation and the function of a protein can be manipulated.1 A surface functionalization of the gold nanoparticle with azide groups and a subsequent click reaction, i.e. a copper-catalyzed azide-alkyne (CuAAC) cycloaddition, permits an orthogonal covalent conjugation under mild conditions.2 Azide-terminated ultrasmall gold nanoparticles were prepared by reducing tetrachloroauric acid in the presence of an azide-carrying cysteine-containing tripeptide.1 Functional molecules with an alkyn function were covalently attached to the particles by CuAAC click chemistry. The hydrodynamic diameter of the functionalized gold nanoparticles was measured by diffusion ordered NMR spectroscopy (DOSY), also ensuring the absence of dissolved molecular impurities or reaction by-products.4 Disc centrifugal sedimentation (DCS) and transmission electron microscopy (TEM) showed the dispersion state of the nanoparticles and the diameter of the metallic core. Atomic absorption spectroscopy (AAS) gave the gold concentration and allowed us to compute the particle number concentration. 1H-1H-TOCSY NMR spectroscopy showed the binding between the gold surface and the cysteine of the tripeptide. The successful click reaction to the azide-functionalized gold nanoparticles was demonstrated by DOSY with propargylglycine as model compound clicked to the gold nanoparticle surface. This synthetic route offers a wide range for the synthesis of covalently functionalized ultrasmall gold nanoparticles for protein targeting.

REFERENCES
We thank the Deutsche Forschungsgemeinschaft (DFG) for funding within the framework of CRC 1093: Supramolecular Chemistry on Proteins and the Ernst Ruska Centre, Forschungszentrum Juelich, especially Dr Marc Heggen, for access to the transmission electron microscopes.

Whereas the equilibrium shape of a metallic nanocrystal can be predicted by the Wulff construction, it can hardly be anticipated when this nanocrystal is covered by a shell formed of another metal. Different parameters are well known for their influence on the geometry of core-shell nanocrystals; these are, for instance, the size of the nanocrystals or the core / shell volume ratio. However, the construction of a metal-metal internal interface during the growth process should also play a determining role.

In order to analyze this mechanism, we choose to combine experimental and modeling approaches. Nanoclusters are experimentally grown using a ultra-high vacuum (UHV) physical vapor deposition method, magnetron sputtering, in order to limit interaction with their environment (gas, liquid, ligands…) during the growth process. This process makes it possible to use high temperatures which promote atomic diffusion during deposition or annealing steps. In addition, it is possible to proceed sequentially, by growing the shell on the previously formed core, or to proceed by co-deposition of the core and shell metals. The modeling approach combines DFT calculations with large-scale (MD) or Monte Carlo (MC) molecular dynamics simulations to study systems with size comparable to the experimentally grown nanocrystals (5-15 nm).

After a presentation of the different parameters that should be taken into account during the formation of the crystalline interface, with a particular emphasis on the concept of nanoepitaxy, we will report the results obtained on the Fe-Au system. This system is indeed of particular interest as it is likely to adopt a core-shell geometry fully compatible with applications in the biomedical field.

Through our combined experimental and modeling results, we will then discuss the effects of size and composition on the equilibrium shape of the nanoclusters as well as the evolution of the iron core when coated by the gold shell.

References:
Surface analysis of nanowires is inherently difficult as most surface science techniques have been designed to address “infinite” flat 2D surfaces. However, with some clever sample design and dedicated measurement strategies it is possible to use most surface common analysis methods also on nanowires. As a result, it is possible to measure nanowire surface geometry, chemistry and electronic properties down to the atomic scale. As examples, I will show how scanning probe and photoelectron spectroscopies/microscopies can be used for detailed surface analysis of nanowires, even during device operation. An emphasis will be on explaining the strategies that enable you to use most surface science tools for studies of high aspect ratio nanostructures and devices at the highest possible performance levels.

2:30 PM BREAK

3:00 PM
Characterization of Surface and Interface States in Nanowires and Application to Electronic Devices Paul C. McIntyre; Stanford University

4:00 PM
Using Nanowires in Novel Device Concepts in Photovoltaics Esther Alarcon-Lladó; AMOLF

Semiconductor nanowires (NWs) are promising building blocks for next generation solar energy conversion at low cost. NW ensembles constitute a new class of metamaterial. While the photonic properties of small dielectric structures have been widely studied within the framework of Mie scattering, coupling to poorly confined waveguided modes drives the absorption spectrum in NWs. This tutorial session describes how vertical NWs interact with light. We will show the theoretical and experimental methods to investigate these properties. Based on the special light-matter interactions in NWs, we discuss completely new designs of solar cells that are not possible in the bulk form.

SYMPOSIUM NM03

Nanowires and Related 1D Nanostructures—New Opportunities and Grand Challenges
November 26 - November 30, 2018

Symposium Organizers
Jordi Arbiol, ICREA and Institut Català de Nanociència i Nanotecnologia
Kimberly Dick Thelander, Lund University
Michael A. Filler, Georgia Institute of Technology
Anna Fontcuberta i Morral, École Polytechnique Fédérale de Lausanne

Symposium Support
Applied Materials
INDEED Network

* Invited Paper

SESSION NM03.01: Nanowire Photonic Devices: Photodectors and Sensors
Session Chairs: Jordi Arbiol and Martin Eickhoff
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Back Bay D

8:30 AM *NM03.01.01
GaN/AlN Nanowire Photodetectors—From the UV to the IR Akhil Ajay1, Maria Spies2, Jonas Lähnemann1, Martien den Hertog2 and Eva Monroy1; 1INAC-PHELIQS, CEA-Grenoble, Grenoble, France; 2Institut Néel, Grenoble, France.

Nanowire photodetectors attract broad interest due to their low dimensionality, small electrical cross-section, and ultrahigh photocurrent gain. In the ultraviolet region, ZnO and GaN nanowires have been intensively studied as spectrally-selective photodetectors. For this application, III-nitride nanowires present advantages in terms of heterostructuring possibilities and stability against chemical, mechanical or electrical stress. In a single-GaN-nanowire UV photodetector, the efficiency can be enhanced by the insertion of a GaN-AlN heterostructure [1,2], which leads to an increase of the responsivity by about two orders of magnitude, improved linearity, and the possibility to select the detected wavelength, while maintaining a UV/visible contrast larger than six orders of magnitude. Furthermore, devices with a linear photoresponse to the optical power can be implemented by using nanowires with a thickness below a certain threshold [3]. On the other hand, the insertion of quantum dots in nanowires is also interesting for infrared photodetection using intraband transitions. Therefore, intraband transitions in GaN/AlN nanowire heterostructures have been investigated, varying the geometry and doping level of the GaN insertions [4]. Based on this research, we present the first single-nanowire quantum well infrared photodetector (NW-QWIP), operating at the 1.55 μm telecom band [5]. Finally, the study has been extended to cover the mid-infrared spectral range, up to around 6 μm, using intraband transitions in GaN/Al0.4Ga0.6N dots-in-a-wire.

Comparison of such materials showed the dependence of 1-D nanostructured device UV response properties on ZnO morphologies.

With d-spacing approximately 2.6 angstroms, while 1-D nanostructure-grown samples exhibited similar or slightly lower (002) preference, indicated by the reaction of chemisorbed oxygen and photo-generated charge carriers at grain boundaries. The demonstrated ultrathin nanowire arrays, the observed superlinear photoconductivity can be explained by a new type of photoelectrochemical thermionic charge emission mechanism involving the reaction of chemisorbed oxygen and photo-generated charge carriers at grain boundaries. The demonstrated ultrathin nanowire device and synthesis fabrication methods have potentials for fully CMOS-compatible integration of nanowire sensor devices and circuitries. The identified photoelectrochemical grain boundary thermionic emission mechanism provides an improved understanding on the superlinear photoconductivity observed in nanostructured materials.

9:15 AM NM03.01.03
Plasmonic Au/ZnO Nanowires for Room Temperature NO2 Detection
Bo Zhang, Jiyu Sun and Puxian Gao; University of Connecticut, Storrs, Connecticut, United States.

Plasmonic Au-ZnO nanostructures with a size less than the incident light wavelength have been found to exhibit a localized surface plasmon resonance (LSPR) that may lead to strong absorption, scattering, and local field enhancement. These resonances, associated with noble metal nanostructures create sharp spectral absorption and scattering peaks as well as strong electromagnetic near-field enhancements. However, operation of ZnO gas sensors is limited to elevated temperature, which leads to reduced energy consumption and large sensor size. Thus, reducing operating temperature or room temperature gas detection become significant in future sensor development. In this work, by utilizing the wavelength tunable photo-irradiation, selective gas detection has been demonstrated at room temperature based on Au/ZnO nanowire arrays. The Au/ZnO nanowires were synthesized by the microwaves-assisted hydrothermal deposition of ZnO nanowires followed by Au nanoparticle (NP) dip-coating process. Compared to pristine ZnO, the Au-ZnO nanowire sensor performance was enhanced in both UV and visible regions, especially with highly enhanced sensitivity observed at 550 nm. The sensitivity towards 20 ppm NO2 could reach as high as 250%, and the detection limit is determined to be around 1 ppm at 25 °C. The sensitivity enhancement resulted from UV is due to the migration of photo-generated electrons from Au NPs to ZnO. On the hand, the sensing mechanism in the visible region is primarily due to the LSPR effect of Au. The oscillated electrons become more sensitive to the charge density and dielectric environment of Au. Besides, a large selectivity was found for NO2 gas over CO, NH3 and O2 at 330 nm UV irradiation. The ratio of cross sensitivity towards target gas and interfering gases is larger than 300. It is clear that with tunable light irradiation, room temperature NO2 gas detection could be achieved using plasmonic Au/ZnO nanowires with high sensitivity and selectivity.

Reference

9:30 AM NM03.01.04
UV Sensitivities of Catalyst-Free Grown ZnO 1-D Nanostructures on High Crystallinity Atomic Layer Deposition Seeds
Yun-Yi Chu1, Shang You Tsai1, Chun-Chi Chen2 and Fu-Hsiang Ko1; 1Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 2Nano Device Laboratories, National Applied Research Laboratories, Hsinchu, Taiwan.

Zinc Oxide is a nontoxic material, with a wide direct band gap (3.4 eV), high exciton binding energy (60 meV) and good thermal stability, making it suitable for UV LEDs, photo catalysts, UV sensors and gas sensors. At the surface of zinc oxide, a layer of positive space charge is usually formed to cancel out the charge of surface oxygen species. Removal and addition of said surface oxygen species may affect the electrical properties at the surface. Utilizing this mechanism, applications such as sensor devices were studied by others. Here, we explored the various factors that may affect the UV absorbing and sensing properties of ZnO 1-D nanostructured devices, including crystallinity, contact junctions, and morphology. Regarding morphology, 1-D nanostructures have high surface area ratios and can exhibit surface properties in larger scales, as the structures can be viewed as wrapping surfaces around lines.

In this study, 1-D nanostructured ZnO UV sensors were developed on silicon dioxide using an atomic layer deposition (ALD) seed and chemical vapor deposition (CVD) nanostructure growth to investigate nanostructure properties. An ALD process was selected to deposit the seed layer due to the capability of uniform thickness growth and excellent crystallinity. The CVD process with vapor-solid (VS) growth provided a clean method to grow zinc oxide nanostructures without introducing unnecessary additives, by using a source of zinc metal powder and high purity oxygen. Compared to wet chemical methods and vapor-liquid-solid (VLS) growth of ZnO nanostructures, the VS processes would not have salts and metal particles, which may affect devices in undesired ways, such as salt interactions with humidity, Ohmic or Schottky contacts by metal particles with ZnO and stability issues of metal catalysts.

Different 1-D nanostructures such as nanowires and free-standing nanorods were deposited through the control of seed layer quality, zinc source temperature and substrate undercooling. Characterization of ZnO structures was done by SEM, X-ray reflection (XRR) and XRD techniques for morphology, thickness and crystallinity; UV-VIS, Photoluminescence spectroscopy and a Keithley 2400 instrument were used for the absorption, emission spectrums and UV irradiated conductivity change. The ALD seed ZnO layer showed highly preferred (002) plane crystal growth by a strong XRD peak with d-spacing approximately 2.6 angstroms, while 1-D nanostructure-grown samples exhibited similar or slightly lower (002) preference, indicated by XRD peaks. Structures with conductivity responses after 5 minutes of 3V UVA LED (345nm to 425nm, < 0.5 mWatts) irradiation from 3% to 22% were observed, with diagonally crossing nanowires showing lower responses, and vertical free-standing nanorods of higher responses. Comparison of such materials showed the dependence of 1-D nanostructured device UV response properties on ZnO morphologies.
Light Emitting Silicon Nanowires—From Photonics to Sensing Applications
Antonio A. Leonardi1,2,3, Maria José Lo Faro4,2, Dario Morganti1,2, Cristiano D'Andreà1, Barbara Fazio1, Paolo Musumeci1, Pietro Antoni1, Cirino S. Vasi2, Gerardo Palazzo1, Luisa Torsi2, Francesco Priolo1,4,6 and Alessia Irrera1;1 Dipartimento di Fisica ed Astronomia, Università degli Studi di Catania, Catania, Italy; 2Istituto per i Processi Chimico Fisici, Consiglio Nazionale delle Ricerche, Messina, Italy; 3Sezione di Catania, Istituto Nazionale di Fisica Nucleare, Catania, Italy; 4Matis-IMM, Consiglio Nazionale delle Ricerche, Catania, Italy; 5Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari, Italy; 6Scuola Superiore di Catania, Catania, Italy.

The scientific community has devoted an increasing interest to quantum confinement materials. In particular, silicon nanowires (Si NWs) are considered one of the most appealing resource to be employed in nanoscaled devices. Si NWs with an efficient room temperature (RT) light emission would represent a great industrial advancement, opening the route to a wide range of unexpected photonic applications. Nevertheless, to achieve a good control on quantum confined Si NWs fabrication is complex and challenging with the current technology. The most diffuses approaches such as lithography or Vapor-Liquid-Solid techniques suffer of different limits restraining the realization of quantum confined Si NWs. We demonstrated the realization of an ultradense array (10^12 NWs/cm^2) of light emitting Si NWs by using a modified metal assisted chemical etching without any type of mask or lithography. This method is fast, cheap and compatible with the standard Si technology. NWs achieved by this technique exhibited a very bright RT PL and EL tunable with NWs size in agreement with the occurrence of quantum confinement effect. With this method we demonstrated the realization of a 2D random fractal array of aligned Si NWs without any lithographic process or mask and by using a fractal gold layer realized by a Si technology compatible approach. We were able to control and tune the optical properties of the system by changing the fractal morphology of the Si NWs array [1]. In-plane multiple scattering and very strong light trapping with diffuse reflectance below 0.1% related to the fractal structure were observed overall the visible range [1-2]. An innovative generation of Si NW-based optical biosensor is realized, which exploits the PL properties for the ultrasensitive and selective detection of proteins [3] in a wide range of concentrations. The occurrence of non radiative phenomena introduced by the target analyte on the NWs surface determines the quenching of the PL signal. In particular, we realized a sensor for C-reactive protein (CRP), which is crucial for heart-failure pathology. Cardiovascular problems are some of the major cause of death for both men and women. The availability of high sensitivity, low cost and reliable CRP sensors is a priority demand in clinical diagnosis for cardiovascular diseases. Si NWs sensors are fast, highly selective and offer a broad concentration dynamic range. Moreover, these sensors reach a FM sensitivity permitting non-invasive analysis in saliva [3]. Si NWs open the route towards new optical label-free cheap sensors and a full compatible with the standard Si technology for primary health care diagnosis of biomarkers. Moreover, by changing the functionalization the use of Si NW sensors opens the route towards a new class of promising label free optical sensors for different application fields.

3. ACS Photonics 5 (2), 471–479, 2018

10:00 AM BREAK

SESSION NM03.02: Metal Halide Perovskite Nanowires
Session Chairs: Jordi Arbiol and Eva Monroy
Monday Morning, November 26, 2018
Sheraton, 2nd Floor, Back Bay D

10:30 AM NM03.02.01
Probing Fundamental Charge Carrier Dynamics in Metal-Halide Perovskite Microwires
Eva L. Unger1,2 and Aboma Merdasa3; 1Chemical Physics and NanoLund, Lund University, Lund, Sweden; 2Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

Metal halide perovskites exhibit favorable properties for optoelectronic devices. This talk will summarize results on metal halide perovskite wires illuminating fundamental properties of metal-halide perovskites. Intermittency effects in the photoluminescence suggest the existence of photo-induced dynamic state in metal-halide wires that lead to non-radiative recombination.[1] For wires longer than 10 µm, photoluminescence quenching at defined positions along the wire suggest localized states that periodically become activated, leading to efficient charge carrier quenching. The gradient in photoluminescence, the charge carrier diffusion length can be estimated from this one-dimensional model system.

Structural defects also play a role in the observed phase coexistence and hysteresis during the tetragonal to orthorhombic phase transition in methylammonium lead iodide wires.[2] The phase transition temperature appears to be dependent on the local defect concentration with more defective domains more readily transforming from the tetragonal to orthorhombic domain. This leads to charge carriers being funneled to lower energy tetragonal sites during the phase transition shown by photoluminescence microscopy and super-resolution imaging.


11:00 AM NM03.02.02
Orientation-Dependent Hybrid Perovskite Conversion of VLS-Grown Lead Halide Nanowires
Hyewon Shim and Naechul Shin; Chemical Engineering, Inha University, Incheon, Korea (the Republic of).

Organic-inorganic hybrid perovskites, such as methylammonium lead iodide (CH3NH3PbI3) have shown outstanding optoelectronic properties, promising extensive application in solar harvesting. Although most hybrid perovskite materials have been synthesized under solution process, recent demonstrations of the vapor phase synthesis of the hybrid perovskite nanostructures suggest there is an emerging interest in controlling their properties under highly-confined structures. In particular, single-crystalline 1D lead halide nanowires can be prepared via vapor-liquid-solid (VLS) growth mechanism through the self-catalyzed growth mechanism, which then converted to hybrid perovskite. Since the conversion occurs on the preformed nanowire, electronic properties 1D perovskite depend on the original nanowire structure. In this study, we report the VLS growth of lead iodide (PbI2) nanowires on a c-sapphire (0001) substrate followed by conversion to CH3NH3PbI3 using methylammonium iodide, and confirm that the degree of perovskite conversion depends on the growth orientations of PbI2 nanowires. We observe two different growth directions; vertically-oriented [0001] nanowires and kinked nanowires. Photoluminescence (PL) measurements on each growth direction suggest that the oriented nanowires exhibit a higher degree of conversion compared to the [0001] oriented nanowires. In addition, [0001] oriented nanowires exhibit the position-dependent degree of conversion, depending on the presence of the catalyst tip on top of the nanowire. In particular, the conversion is observed both on the catalyst tip and the base of nanowire, suggesting
methylammonium iodide incorporates into the nanowire either by vapor trasport and surface diffusion. Our observation indicates that the vapor phase conversion of PbI2 to CH3NH3PbI3 is a diffusion-limited process. This finding is an important step towards an structure engineering of perovskite nanowires.

11:15 AM NM03.02.03
First-Principles Insights of Electronic Structure in Quasi-One-Dimensional Van der Waals Materials Baiyu Zhang and Xiaofeng Qian; Texas A&M University, College Station, Texas, United States.

Low dimensional materials have been one of the focus areas in materials science for more than three decades. In particular, the low dimensionality and reduced dielectric screening lead to pronounced optoelectronic properties such as excitons and polaritons. Here we demonstrate that quasi-one dimensional (1D) materials exhibit unique electronic structure and optical properties promising for low-cost photovoltaics and novel optoelectronics. First, we will present our first-principles study of a few quasi-1D van der Waals crystals with non-toxic and earth-abundant elements, and will elaborate the role of 1D structure and defects on their highly anisotropic optical and electronic properties. Our results shed light on new thin-film photovoltaic systems with excellent defect tolerance. Second, we will show that quasi-1D van der Waals crystals exhibit exciting nonlinear optical effects, and a microscopic picture is provided based on first-principles theory. We believe the theoretical findings presented here will open up many exciting opportunities in quasi-1D materials and nanostructures.

11:30 AM *NM03.02.04
Growth and Optoelectronic Applications of Single-Crystal Nanowires of Metal Halide Perovskites Song Jin; Madison, University of Wisconsin, Madison, Wisconsin, United States.

The remarkable performance of lead halide perovskites in solar cells can be attributed to the excellent photophysical properties that are also ideal for lasers and light-emitting devices (LEDs). The chemical and structural characteristics of halide perovskites make their crystal growth behaviors very different from conventional inorganic semiconductor materials. Here we first report new insights on the crystal growth of halide perovskites and developed the solution growth of single crystal nanowires, nanorods, and nanoplates of methylammonium (MA), formamidinium (FA) and all-inorganic cesium (Cs) lead halides perovskites (APbX3) via a dissolution-recrystallization pathway. We also developed the vapor phase epitaxial growth of aligned CsPbX3 perovskite nanowires and single-crystal thin films. Moreover, nanostructures of metastable perovskite phases, such as FAPbI3 and CsPbI3, can be stabilized via new chemical strategies by using surface ligands. These single-crystal nanowires are excellent model systems to study the intrinsic properties of perovskite materials, such as carrier transport and ionic interdiffusion. We also demonstrated high performance room temperature lasing with broad tunability of emission color from 420 nm to 824 nm from single-crystal lead halide perovskite nanowires with estimated lasing quantum yields approaching 100%. LEDs can also be fabricated with nanoscale structures of 3D or 2D perovskites. The excellent properties of these single-crystal perovskite nanowires of diverse families of perovskite materials with different cations, anions, and dimensionality make them ideal for fundamental physical studies of carrier transport and decay mechanisms, and for enabling high performance semiconductor lasers, LEDs, and other optoelectronic applications.

SESSON NM03.03: Nanowire Quantum Devices
Session Chairs: Anna Fontcuberta i Morral and Eva Unger
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Back Bay D

1:30 PM *NM03.03.01
Epitaxy of Hybrid Bi- and Tri-Crystal Quantum Materials by Molecular Beam Epitaxy Peter Krogstrup1, 2; 1Niels Bohr Institute, Copenhagen, Denmark; 2University of Copenhagen, Microsoft Quantum Materials Lab, Copenhagen, Denmark.

Interfaces are key elements in nanostructured device architectures. The quality of interfaces is particularly important for quantum devices where the device performance depends on the order, uniformity and purity of the interfaces that takes part in the quantum device structure. Hybrid nanowire materials with semiconducting, superconducting and magnetic components properties constitute some of the most promising candidates in the search for materials suitable for topological quantum computing [i]. I will discuss the mechanisms of hybrid epitaxy by Molecular Beam Epitaxy [ii] that lead to well defined interfaces between crystals of different structural and electronic properties. I will present on new characterization schemes of how to extract information from the hybrid epitaxial materials and discuss the challenges and material requirements needed for realizing and eventually manipulating topological protected quantum states.


2:00 PM NM03.03.02
In Situ Patterned Superconductor/Semiconductor Nanowires Damon J. Carrad, Martin Bjergfelt, Martin Aagesen, Thomas N. Kanne, Filip Krizek, Peter Krogstrup, Thomas S. Jespersen and Jesper Nygård; Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark.

We present electrical and structural characterisation of superconductor/semiconductor hybrid nanowires consisting of previously unexplored materials combinations. Each superconductor was deposited in-situ after semiconductor growth, without breaking vacuum. This ensures a clean and transparent interface between the semiconductor and superconductor; a crucial requirement for inducing a ‘hard’ BCS superconducting gap in the nanowires. Additionally, we developed a shadow mask method for patterning the superconductor layer during deposition. This allowed us to fabricate functional devices without need to develop specific etches and/or lithography techniques for each material. The method thus streamlines growth and fabrication while minimizing the risk of materials degradation during post-processing. We have demonstrated several key architectures including tunnel probes, Josephson Junctions and Majorana islands. These devices facilitated characterization of induced superconductivity properties in InAs nanowires, and provided insights into the requirements for obtaining a hard gap. Also of interest were the nanoscale superconducting properties of each material since the critical temperatures and critical magnetic fields differ strongly from bulk values. In particular, the materials we studied show dramatically increased out-of-plane critical field compared to aluminium, which is highly desirable for many proposed applications in topological superconductivity. The ability to fabricate
devices based on a wide variety of interfaces broadens the scope for future applications of superconductor/semiconductor hybrid devices.

2:15 PM NM03.03.03
Spin-Orbital Kondo Effect in InAs Nanowire Crystal Phase Double Quantum Dots
Heidi Potts1, Malin Nilsson1, Sebastian Lehmann1, Adam Burke1, Kimberly A. Dick1,2 and Claes Thelander1; 1 Division of Solid State Physics and NanoLund, Lund University, Lund, Sweden; 2 Centre for Analysis and Synthesis, Lund University, Lund, Sweden.

Semiconducting nanowires offer a unique platform to study fundamental physical effects. Recent advances in crystal phase engineering enable switching between zinc-blende and wurtzite crystal phases in InAs nanowire growth. Using this knowledge, a quantum dot (QD) can be created consisting of a thin zinc-blende section between two wurtzite tunnel barriers [1]. Furthermore, the QD can be split into two parallel coupled QDs using two local sidegates and a global backgate [2]. This system can be considered an artificial molecule, for which the electron population on the two dots can be changed separately, and the tunnel coupling between the two dots can be tuned. This offers a great flexibility to study for example the interaction between electrons and spins located on the two dots [3].

In this work, we use the crystal phase InAs QD system to investigate Kondo transport. The Kondo effect is an extensively studied many-body phenomenon which can be observed in QDs with two degenerate levels containing only one particle. Experimentally, the spin-degeneracy is often used to study the Kondo-effect. Recently the degeneracy of two orbitals in parallel coupled QDs has also been used to explore the so-called orbital-Kondo effect [4-6]. Special interest has arisen in the condition where both the spin- and the orbital-Kondo effects are present, resulting in a SU(4) symmetry. The challenge in experimental studies is to distinguish between the spin- and orbital-Kondo effects.

The InAs parallel QD system allows us to study the crossing of two spin-degenerate orbitals, one from each QD. The large single QD orbital spacing results in even-odd level spacing, making it evident whether the electron population on the dot is even or odd. At zero magnetic field, we observe enhanced conductance at zero bias due to spin-Kondo transport when one (or both) of the QDs contains an odd number of electrons. We further observe a Kondo peak when two orbitals from the QDs are aligned and contain only one electron. The zero-bias peak due to the spin degeneracy splits in magnetic field (Zeeman effect). Similarly, we demonstrate that the zero-bias peak due to the orbital degeneracy splits when detuning the orbital energies. The large g-factor of InAs allows us to study the orbital-Kondo effect independently of the spin-Kondo effect, and to demonstrate that the zero-bias peak at the orbital degeneracy persists, even though the spin-degeneracy is lifted by applying a magnetic field.

In conclusion we demonstrate both spin- and orbital-Kondo effects in InAs nanowire QDs formed by crystal phase engineering, and clearly show how the system can be tuned to have either one or both effects present at zero bias.


2:30 PM *NM03.03.04
Selective Area Epitaxy of a Materials Platform for Scalable Quantum Computing
Philippe Caroff; Station Q Delft, Microsoft Quantum, Delft, Netherlands.

Nanofabricated III-V semiconductor superconductor heterostructures have demonstrated potential to advanced quantum transport physics, in particular to host the elusive Majorana quasiparticles. Virtually all progress on the materials side in the last 6 years has relied on high quality vapor liquid solid growth of III-V free-standing nanowires functionalized at a later stage by ex-situ deposited Al. Despite these early successes a more robust, scalable materials platform is still missing to enable the future topological quantum computer.

Here I will report on our progress in using molecular beam epitaxy (MBE) to grow both III-V semiconductor nanowire networks and a high quality epitaxial s-wave metal superconductor, using selective area epitaxy. I will first introduce the current state of the art, advantages and challenges of the selective area approach and MBE with respect to other growth techniques and geometries. Then a new method to successfully map the selective area epitaxy window in the ultra-high purity MBE environment will be detailed. Fundamental knowledge gained by growth studies will be applied to obtain reproducible, high yield advanced high spin-orbit III-V nanowire/superconductor networks. The materials properties and quality are assessed by a combination of morphological, compositional and structural analyses.

3:00 PM BREAK

SESSION NM03.04: Narrow Bandgap Nanowires
Session Chairs: Philippe Caroff and Michael A. Filler
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Back Bay D

3:30 PM *NM03.04.01
High-Quality Narrow-Band Gap III-V Semiconductor Nanostructures Grown by Molecular-Beam Epitaxy
Jianhua Zhao; Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China.

Among the III-V group semiconductors, InAs and InSb nanosheets have attracted much attention since they exhibit narrow-band gaps, high electron mobilities, strong spin-orbit couplings and giant g factors. These unique properties make them ideal materials for applications in high-speed and low-power electronics, infrared optoelectronics and especially topological quantum computing. All these applications need not only a high crystal quality but also a high degree control of the material morphology. In my talk, I will firstly give a brief introduction about our work on the successful growth of free-standing single-crystalline InSb nanosheets/nanowires on one-dimensional InAs nanowires stems on Si (111) substrates by molecular-beam epitaxy (MBE) [1,2]. Then I will present the growth of the wafer-scale free-standing high-quality two-dimensional InAs nanosheets also by MBE. These InAs nanosheets show the outstanding electrical and optical properties. Finally, I will forward to our recent progress on the heterostructures composed with the narrow-band gap
Semiconductor nanowires are often grown from metal nanoparticle seeds via the solution-liquid-solid (SLS) or the vapor-liquid-solid (VLS) mechanism. Germanium nanowires and nanorods have a broad spectrum of potential applications including electronic devices, lithium ion batteries, sensors etc. We present in this contribution the growth of highly crystalline Ge nanowires and nanorods at temperatures as low as 170 °C. [1] These structures grow either via the solution-liquid-solid (SLS) or the vapor-liquid-solid (VLS) mechanism depending on the growth conditions employed. The decomposition of the Ge precursor is catalyzed by the presence of Ga seeds as suggested by the growth temperatures below the onset of the thermal composition of the pure precursor. The compositional and structural characterization of the anisotropic Ge nanostructures has been carried out by different analytical methods including TEM, EDX as well as XRD. The analyses demonstrated the incorporation of unusually high Ga contents of up to 3-4 at% in the Ge. Unusually high metal incorporation in group IV nanowires has been observed for other semiconductor/metal combinations, but the effect on the electronic properties typically not very significant. [2] The electrical characterization at different temperatures of individual Ge nanowires demonstrates a very low resistivity and a quasi-metal like behavior. [3] Temperature treatment at slightly higher temperatures can be used to induce phase separation of this material with metastable composition leading to Ga segregation. We will also demonstrate how to switch between thermodynamically controlled Ge NW growth and the kinetically controlled formation of Ga-hyperdoped Ge.

References:


4:30 PM NM03.04.04

Selective Patterning of Si/Ge Surfaces and Nanowire Heterostructures via Surface Initiated Polymerization Amar Mohabir, Trent Weiss, Gozde Tutucucoglu, Eric M. Vogel and Michael A. Filler; Georgia Institute of Technology, Atlanta, Georgia, United States.

Functional devices (e.g., transistors) contain one or more features with nanoscale dimensions. When such devices are to be produced at very large manufacturing rates (e.g., for large-area integrated circuitry), an alternative to top-down patterning is necessary to define key features. In this study, we show how Si and Ge surfaces can be selectively masked using the surface-initiated growth of polymer films. Our approach is particularly useful for patterning axially-encoded Si/Ge nanowire heterostructures. Surface masking of Si, but not Ge, is accomplished in a two-step procedure. Atom transfer radical polymerization (ATRP) of polymethylmethacrylate (PMMA) first occurs from a surface-tethered initiator. The selectivity of initiator attachment leads to thick and thin PMMA layers on Si and Ge surfaces, respectively. Unwanted PMMA on the Ge surface is subsequently removed by a clean-up etch. We use this fashion opens up the possibility of nanoscale patterning in a truly scalable manner.

4:45 PM NM03.04.05

Seeded Nanowire Growth from Lithium Alloys Sang Yun Han, Matthew G. Boebinger, Neha Kondekar, Trevor Worthy and Matthew McDowell; Georgia Institute of Technology, Atlanta, Georgia, United States.

Semiconductor nanowires are often grown from metal nanoparticle seeds via the solution-liquid-solid (SLS) or the vapor-liquid-solid (VLS) mechanisms.
Although SLS or VLS growth of semiconductor nanowires is common, related wire growth in all metal systems is rare. Here, we report a new synthesis method that results in the spontaneous growth of nano- and microwires from Li-rich bulk alloys containing Au, Ag, or In at relatively low temperatures (\(-300^\circ C\)). Wire growth was induced by heating metal foil bilayers in an argon environment to cause alloying, followed by cooling. Optical microscopy of samples during this heating and cooling procedure showed that wires grew only during cooling. Scanning electron microscopy (SEM), cryo-transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS) showed that the wires consisted of Au-, Ag-, or In-rich metal tips and polycrystalline LiOH shafts. Based on these results and systematic experiments to determine growth parameters by varying heating temperature, metal molar ratio, and cooling time, we conclude that the wires grow from alloy seed particles as lithium metal and are converted to LiOH during and/or after growth due to exposure to H\(_2\)O and O\(_2\). The growth mechanism involves the traverse of the two-phase region containing Li metal and liquid alloy on the phase diagram, which causes Li growth from the Li-rich alloy particles. The Li needed for growth is supplied to the seed particles via surface diffusion of Li from the Li-rich alloy reservoir below. It is also thought that the growth of passivating LiOH plays a key role in determining the 1-D morphology. While there are a few important differences, such as the source of the growth species, this mechanism is similar to VLS or SLS growth of semiconductor nanowires. These experiments revealing wire growth from Li-rich alloys demonstrate a new, simple, low-temperature method for nanostructure synthesis, and the results indicate that nanowire growth in other all-metal systems is also possible.

**NM03.05.01**

On the Visible-Light Photoelectrochemical Activity of Double-Walled TiO\(_2\) Nanotubes Obtained by Anodization in Ionic Liquids

Herberto Wendel\(^1\), Renato V. Gonçalves\(^1\), Adriano F. Feit\(^1\), Pedro Migowski\(^2\), Jairton Dupont\(^2\) and Sérgio R. Teixeira\(^3\)

\(^1\)Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, Brazil; \(^2\)Centro Interdisciplinar de Nanociência e Micro-Nanotecnologia, Pontifícia Universidade Católica do Rio Grande do Sul, Porto Alegre, Brazil; \(^3\)Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.

In recent decades, a rapid development has been achieved in the development of semiconductors oxide photocatalysts for solar-to-hydrogen energy conversion through water splitting. Anodic TiO\(_2\) double-walled nanotubes (DWNTs) have been explored due to its stability and superior activity compared to single-wall nanotubes (SWNTs). In this work, DWNTs transformation of self-organized TiO\(_2\) SWNTs was studied and their photoelectrochemical properties investigated in detail. The as-formed TiO\(_2\) SWNTs morphological properties were considerably affected by the amount of 1-n-butyl-3-methyl-imidazolium tetrafluoroborate ionic liquid (IL) and NH\(_4\)F in the mixed or pure electrolytes. Besides several discussions in the literature, we show that the double-walls were formed after annealing at 400 °C because of decomposition of IL entrapped in the nanotubes, as evidenced by XPS and FESEM analysis. The TiO\(_2\) DWNTs exhibited a photocurrent density of 1.36 mA\(\text{cm}^{-2}\) at 1.23 V\(_\text{OHE}\), 1.8 times higher than TiO\(_2\) SWNTs (0.77 mA\(\text{cm}^{-2}\)) under one sun illumination. Similar behaviour was obtained when the samples were illuminated only with UV light (\(\lambda < 400\) nm). However, under visible light irradiation (\(\lambda > 400\) nm), TiO\(_2\) DWNTs presented 15.9 times more photocurrent compared with TiO\(_2\) SWNTs. IPCE experiments confirmed the superior activity of TiO\(_2\) DWNTs which extends to the visible range up to 480 nm.

**NM03.05.02**

Tuning Composition of PdPt NPs over TiO\(_2\) Nanowires for Optimized Catalytic Activities Towards the Oxygen Reduction Reaction

Anderson Gabriel Marques d. Silva and Susana I. Córdoba de Torres; Universidade de São Paulo, São Paulo, Brazil.

The synthesis of bimetallic nanoparticles at metal oxides surfaces represents an emerging strategy to maximize catalytic performances and increase stability of heterogenous catalysts. However, the controllable synthesis of these nanohybrids as well as the systematic role played by the addition of a second metal in their composition over catalytic performances remains unclear. Here, we present an approach based on the optimization of both the support material and active phase to achieve superior catalytic performance in the oxygen reduction reaction, consisting in small PdPt NPs deposited onto TiO\(_2\) nanowires. The composition could be systematically tuned by varying the molar ratios between Pd and Pt metal precursors. They displayed an uniform 1D morphology, monodisperse PdPt NPs sizes, no agglomeration, strong metal-support interactions, and high concentration of oxygen vacancies at their surface. These features led to improved activities and stabilities for the Pd\(_{25}\)Pt\(_{75}\)-TiO\(_2\) sample towards the oxygen reduction reaction (ORR) relative to the commercial Pd/C and Pt/C catalysts as well as other reported materials. Moreover, a volcano-type relationship between the activity and the PdPt loading was detected. We suggest that the optimized catalytic activities observed for the Pd\(_{25}\)Pt\(_{75}\)-TiO\(_2\) catalyst are a result of the higher concentrations of oxygen vacancies and Pd(0)/Pt(0) species investigated by XPS analysis. We believe that the catalytic activities and stabilities described herein for the ORR because of the optimization of both the support and active phase may inspire the development of novel catalytic systems towards a wealth of sustainable transformations.

**NM03.05.03**

Centimeter Long Nanowires Based on a Polymer Fiber Scaffold for Improved GHz Frequency Telecommunication Devices

Aykut Aydin\(^1\), Lu Sun\(^2\), Xian Gong\(^2\) and Roy G. Gordon\(^1, 2\)

\(^1\)Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; \(^2\)School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Bundles of twisted conductive wires are used as effective inductors in communication devices that operate in the lower MHz frequencies. To make such a bundle be useful in the GHz frequency range, the constituent wires need to be around a micron or less in diameter. They also need to be sufficiently long and strong for the twisting process, and each individual wire needs to be coated with an insulator. Nanowires prepared with most conventional methods do not meet these requirements.

We present a new method for the preparation of flexible and centimeter long nanowires using a polymer fiber scaffold. Poly(m-phenylene isophthalamide) fibers are electrospun onto a rotating collector such that single strands of centimeter long fibers with diameters in the range of 300 – 600 nm can be collected. These fibers are sufficiently strong when suspended on frame-shaped holders that they can be coated with various deposition methods. With physical vapor deposition methods, since the deposition follows line-of-sight coverage, the frames can be coated from two opposite sides to maximize the conformity of the layer. Highly conformal layers can be deposited onto the fibers with chemical vapor or atomic layer deposition, and the polymer fibers are thermally stable enough (\(\sim 350^\circ C\)) to survive most such methods.
NM03.05.04
Growth and Characterizations of Coherent Si$_{1-x}$Ge$_x$/Si$_{1-x}$Ge$_x$ Graded Multishell Nanowire Heterostructures 
Jinkyoung Yoo and Nan Li; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

High-mobility carrier transport channel at nanoscale is an important platform for electronic devices and quantum transport studies. Recent interest on implementation of topological quantum computation with semiconductor nanomaterials requires fabrication of high-mobility conduction channel in nanowires. Group-IV semiconductors (Si and Ge) have been considered candidates for nanowire-based topological quantum computers due to spin-orbit interaction, especially for Ge. However, Si/Ge-based heterostructures were not suitable materials for high-mobility conduction channel, such as III-V-based heterostructures. Recent advances in group-IV materials growth show that strained Ge quantum well embedded in graded Si$_{1-x}$Ge$_x$ heterostructures in thick film architecture can have high-mobility enough to observe quantum Hall effect. Here, we present the growth and transport characterization of Si$_{1-x}$Ge$_x$/Si$_{1-x}$Ge$_x$ (0<x<1) graded multishell nanowire heterostructures. The nanowire heterostructures show structural coherency. Moreover, the nanowire heterostructures can have several carrier transport paths: core Si wire, sandwiched strained shell, outmost shell by changes of experimental conditions. The coherent graded nanowire heterostructures were prepared by low-pressure chemical vapor deposition. The core Si$_{1-x}$Ge$_x$ nanowires were grown by Au-catalyzed vapor-liquid-solid process with silane and germane. Subsequently, Si and SiGe multishell layers were epitaxially grown by chemical vapor deposition. By controlling the ratio of silane and germane the composition of SiGe was controlled. The electrical conductivity type and doping concentration of core SiGe NWs and outmost SiGe shells were controlled by introducing diborane and phosphine. Top-gated single nanowire heterostructure devices with multi-terminals were fabricated by e-beam lithography and metallization processes. Transmission electron microscopy was employed to characterize the structural properties of the interfaces between adjacent layers. Fully single crystalline coherent graded multishell nanowire heterostructures were successfully prepared. The transport characteristics at various temperatures will be discussed in detail.

NM03.05.05
Influence of Growth Sequence on Single Axial Junction InP Nanowire Solar Cells 
Jungkil Kim et al. Photon-triggered nanowire transistors. We believe that our photon-triggered NW transistors using a more reliable and simple fabrication procedure. We employed the 100-nm-diameter bottom-up Si NWs that possess the n-type high doping level and extremely smooth surface. First, the Si NWs were dispersed on a Si$_3$N$_4$ substrate and PMMA was uniformly coated on the NWs. The PMMA with a length of 360 nm was opened on a NW by electron-beam lithography. Then, the exposed NW region became porous by metal-assisted chemical etching method in which Ag nanoparticles are used as catalyst. Next, the electrical contacts on both ends of the NWs were fabricated by first mechanical transfer to a thermally oxidized Si substrate followed by EBL patterning to define electrodes and wet etching to remove the surface native oxide. Finally, Ti/Au electrodes on nanowires were formed by electron beam evaporation and lift-off.

A series of nano-scale characterization techniques such as photoluminescence, cathodoluminescence, photocurrent mapping and electron beam induced current on the solar cells were employed to characterize the p-n junction configuration and understand the device behavior. It is found that due to the suppression of Zn-diffusion, an improved efficiency up to 7.73% has been achieved in nanowire solar cells with the n-p growth sequence compared with the efficiency up to 6.5% achieved in the axial p-n nanowire solar cells.

NM03.05.06
Photon-Triggered Transistor in Bottom-up Silicon Nanowire Ha-Reem Kim, Jungkil Kim, Hoo-Cheol Lee, Jae Hyuck Choi and Hong-Gyu Park; Korea University, Seoul, Korea (the Republic of).

Exposing a porous Si segment to light can trigger a current in a Si nanowire (NW) with a high on/off ratio. Using this unique property, photon-triggered NW transistors, photon-triggered NW logic gates, and a single NW photodetection system have been recently demonstrated. In this work, we develop photon-triggered NW transistors using a more reliable and simple fabrication procedure. We employed the 100-nm-diameter bottom-up Si NWs that possess the n-type high doping level and extremely smooth surface. First, the Si NWs were dispersed on a Si$_3$N$_4$ substrate and PMMA was uniformly coated on the NWs. The PMMA with a length of 360 nm was opened on a NW by electron-beam lithography. Then, the exposed NW region became porous by metal-assisted chemical etching method in which Ag nanoparticles are used as catalyst. Next, the electrical contacts on both ends of the NWs were fabricated by another electron-beam lithography and thermal evaporation. To characterize the device properties, the electrical current was measured while the laser was focused on the porous Si segment. The current level was controlled by the power of incident laser as well. The measured on/off ratio was ~10$^5$ at a forward bias of 5 V. In addition, we investigated the porous-segment-length-dependent responsivity of the NW device with the porous Si segment. When the porous segment length is shorter than 360 nm, the responsivity decreased because of the high dark current level. Furthermore, we demonstrated the NW transistor device with ten porous Si segments in a single Si NW, using our new fabrication procedure. We believe that our photon-triggered NW transistors offer a new venue towards programmable logic elements and ultrasensitive photodetectors.


NM03.05.09
AACVD Synthesis of p-n Metal Oxide Nanowires for Gas Sensing—From NP-Decorated to Core-Shell Prototypes 
Eric Navarrete$^1$, Carla Bittencourt$^2$, Polona Umek$^3$, Frank Guell$^4$ and Eduard Llobet$^1$; 1Universitat Rovira i Virgili, Tarragona, Spain; 2Research Institute for Materials Science and Engineering, Université de Mons, Mons, Belgium; 3Jozef Stefan Institute, Ljubljana, Slovenia; 4Electronics, Universitat de Barcelona, Barcelona, Spain.

We have demonstrated coated fibers with a conductive metal layer and an outer insulating layer to produce wires that can be twisted into a bundle to serve in telecommunication devices. We have also demonstrated adding multiple alternating layers of metal and insulator to make core-multishell structures that could have applications in photonics and related fields. Being compatible with a large range of deposition methods, this polymer fiber scaffold offers a new way making centimeter long nanowires with high materials generality.
Motivation:
Single crystalline, metal oxide semiconductor nanowires (NWs) loaded with metal oxide nanoparticles (NPs) are very promising for developing a new
generation of inexpensive, yet highly sensitive and more stable gas sensors.1 By supporting p-type metal oxide NPs on n-type metal oxide NWs, both
chemical and electronic sensitization effects can be obtained, which can dramatically tune the response to target gases of the resulting hybrid
nanomaterials, thus enabling the engineering of selectivity. Here we show that the aerosol-assisted chemical vapor deposition (AACVD) is a technique that
enables growing a wide range of nanostructures. In particular, the synthesis of single crystalline metal oxide NWs supporting homogeneously distributed,
mono-modal metal oxide NPs in a wide range of loading levels is studied (from few sparse NPs to a complete coverage leading to core-shell
nanostuctures). SEM, TEM, XRD, XPS, Raman and PL are used to analyze results. Gas sensing properties (response, selectivity and stability) are obtained
and sensing mechanisms are discussed in detail.

Results:
AACVD is run at moderate temperatures and atmospheric pressure, which enables the direct and fast (matter of minutes, rather than hours in high-vacuum)
growth of nanomaterials in a wide range of application substrates including MEMS, ceramic or flexible polymeric transducers for achieving
chemoresistors. We demonstrate the growth of single crystalline WO3 n-type NWs, loaded with metal oxide NPs of p-type late transition metals (Pt, Pd, Ni,
Co or Ir). Single-step or two-step AACVD methods are implemented to achieve a wide range of metal oxide loadings onto WO3 NWs (from under 1% at.
to higher than 15% at.), as confirmed by XPS. NWs are up to 20 microns in length and about 50 nm in diameter and NPs are 2 to 5 nm in diameter. While
in a single-step AACVD the precursors for NWs and NPs are mixed together, in the two-step AACVD two independent processes are conducted
(WO3 NWs are grown at first and then loaded with metal oxide NPs). A two-step process is needed for correctly achieving high loading levels and core-
shell nanowires. The selection of late transition metals and the loading levels has enabled us to design highly selective materials for H2, NO2 or H2S with
moderate humidity interference and low operating temperatures (from 250°C down to room temperature). The reasons for this superior performance are due
to chemical (catalytic) and electronic (modulation of potential barriers at the p-n heterojunction interfaces) sensitization effects that will be discussed in
detail.

AACVD is revealed as an excellent approach for growing high-quality 1-D nanomaterials in a flexible and scalable way. The technique allows for fine
tuning the gas-sensing properties of nanomaterials, particularly selectivity, paving the way for realizing inexpensive, highly performing devices.


NM03.05.10
Ag-Decorated ZnSe Nanowires—Charge Transfer and Luminescence Modifications
Aswathi Kanjamurapath Sirivan, Lorenzo Di Mario, Silvia Rubini and Faustino Martelli; Istituto Officina dei Materiali, CNR, Trieste, Italy; Istituto di Struttura della Materia, CNR, Rome, Italy; Istituto per la Microelettronica e i Microsistemi, CNR, Rome, Italy.

Because of their complementary optical properties, plasmonic nanoparticles (NPs) and semiconductor nanostructures when combined may enhance their
opto-electronic properties making them important heterostructures with high potentialities in photocatalytic and photovoltaic applications.1 When the two
materials are in close vicinity, indeed, many interactions between the electronic states of the semiconductor and the surface electrons within the metal NPs
occur, with interaction enhancement when the electronic states of the two materials are close in energy. Examples of materials with this property are silver
NPs and ZnSe, with the localized surface plasmon resonance (LSPR) of silver resonant with the ZnSe band-gap (2.7 eV at RT).2 In this work we investigate
how Ag NPs affect the optical properties of ZnSe nanowires (NWs) and give rise to charge carrier transfer from the NPs to the NWs, ZnSe NWs were
grown by molecular beam epitaxy at low temperatures (300-350°C) in order to assure a good optical quality.3 A thin Ag film (5 nm) is evaporated on the
NW sidewalls and the Ag NPs are obtained by thermal dewetting. Photoluminescence (PL) and fast transient absorption spectroscopy (FTAS) in pump-
probe mode with a temporal resolution of 50 fs were carried out on as-grown and Ag-decorated samples. The presence of Ag NPs drastically modifies the
temperature PL spectra of ZnSe NWs. The Near-Band-Edge (NBE) recombination is enhanced and the impurity-related recombination show a
shrinking of the relative emission with well-defined band of equally spaced peaks corresponding to the LO-phonon replica of ZnSe. The transient
absorption spectra showed an increase of the rise time and a decrease of the decay time of the ZnSe band-gap bleaching signal in the presence of the Ag
NPs indicating carrier transfer between the Ag plasmons and the ZnSe NWs, and increased phonon-carrier scattering, respectively. Finally, both the low
temperature PL and FTAS show a decrease in the relative intensities of the defect band, typical of ZnSe, in the presence of Ag NPs. The physical origin of these
effects will be discussed at the conference.4

1 S. Linic et al., Nat Materials 10, 911 (2011).
4 This work has received funding from the Horizon 2020 program of the European Union for research and innovation, under grant agreement no. 722176
(INDCEED).

NM03.05.11
Synthesis of Perylene Diimide, Carbon and Boron Nitride Nanofiber Aerogels from a Single Precursor
Sally DeMaio-Turner, Hu Long, Marcus A. Worsley and Alex Zettl; University of California, Berkeley, California, United States; Lawrence Livermore National Laboratory, Livermore, California, United States.

Aerogels are a fascinating class of materials that possess high surface areas and large porosities, while maintaining low densities. They have the ability to
incorporate macroscopic amounts of material into a single multifunctional structure without sacrificing the intriguing properties of the building block. For
these reasons, aerogels based on nanomaterials have been the subject of extensive research. One dimensional nanomaterials in particular have received
interest due to their large exposed surface areas and low densities, making them candidates for supercapacitor and battery electrodes, hydrogen storage,
water treatment, and chemical sensing, among others.

In this talk, I will show that using a single polycyclic aromatic hydrocarbon precursor, aerogels based on 1D semiconductor nanofibers, conductive
nanofibers, and insulating nanofibers can be synthesized. This route is both inexpensive and scalable. Perylene diimide hydroxide (PTCDI) is used as a
precursor and converted to the diimide form, which in situ self-assembles into nanofibers. At high concentrations of PTCDI, the nanofibers entangle to
form a self-supporting hydrogel and a strong forward solvent nanofibers. Through carefully selected carbonization temperatures and a subsequent ammonia/boric acid treatment, carbon nanofiber (CNF) and boron nitride nanofiber aerogels are synthesized, respectively. We present several
parameters which can be altered to produce a dynamic range of properties such as pore structure, density, as well as crystallinity of nanofibers. Extensive
characterization of the material with Raman and infrared spectroscopies, X-ray diffraction, as well as scanning and transmission electron microscopies is
completed to confirm the chemical composition, crystallinity, and morphology of the materials. These nanofiber aerogels are expected to be promising for
many prospective applications including electron transport layers and battery electrodes for organic semiconductor aerogels, supercapacitors and
electrolytes for conductive CNF aerogels, and as additives in the formation of nanocomposites for BN nanofiber aerogels.
Impurity Effects on GaP Nanowire Optical Properties

Bruno C. da Silva, Odilon D. Couto Jr., Fernando Ikawa and Monica A. Cotta; University of Campinas, Campinas, Brazil.

III-V semiconductor nanowires have been highlighted as promising structures for high efficiency optoelectronic devices and as an alternative to integration with Silicon technology. However, some challenges remain, as the limitation of gold as catalyst due to the deep levels in Silicon and, more specifically, questions about the optical properties of wurtzite (WZ) GaP nanowires, such as the exact band gap energy and the origin of deep level emissions. Here we present the optical analysis of hexagonal GaP nanowires grown by chemical beam epitaxy using gold catalysts; we have grown very large WZ GaP nanowires to enhance the very weak signals of the fundamental optical transitions of the hexagonal material. Thus we were able to carry out excitation photoluminescence spectroscopy (PLE), as well as Raman and photoluminescence spectroscopy. We speculate that the broad emission bands are associated to defects, such as gallium vacancies and complex involving phosphor vacancies. This is supported by the results of the optical emission spectra of doped samples, undoped and different growth conditions. We also noted an enhancement of the Donor-Acceptor Pair recombination, compared with other emission bands, with impurity doping which is consistent with the presence of the gallium vacancy attributed to the latter bands. In order to avoid impurity effects on the growth dynamics, we have explored aluminum catalyst particles. Since Aluminum does not originate deep levels in silicon, it also may pose as an alternative for III-V semiconductor nanowires integration into current silicon technology.

Self-Catalyzed Growth of GaAs$_{x}$Sb$_{1-x}$ Axial Nanowires on Mono-Layer Graphene by Molecular Beam Epitaxy

Surya Nalamati$^{1}$, Prithviraj Deshmukh$^{2}$, David Snyder$^{3}$, Jeffrey Kronz$^{1}$, Michael Zuger$^{3}$, Lewis Reynolds$^{3}$, Yang Liu$^{4}$ and Shanthi Iyer$^{1,2}$; $^{1}$Electrical and Computer Engineering, North Carolina A&T State University, Greensboro, North Carolina, United States; $^{2}$Nanoengineering, North Carolina A&T State University, Greensboro, North Carolina, United States; $^{3}$Penn State Applied Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania, United States; $^{4}$Materials and Science Engineering, North Carolina State University, Raleigh, North Carolina, United States.

GaAs$_{x}$Sb$_{1-x}$ semiconductor nanowire (NW) arrays are of great interest for the next generation infrared (IR) photodetectors due to the ability to tune the bandgap in this material system from 0.73 eV to 1.42 eV, encompassing the important communication wavelength range. Graphene as a substrate is very attractive due to its favorable material characteristics, namely, high electrical conductivity, optical transparency, mechanical flexibility along with it being cheaper for large area synthesis, making it a potential alternative to conventional III-V substrates. Hence, GaAs$_{x}$Sb$_{1-x}$ NWs on graphene provides a pathway for fabricating next-generation flexible and cheaper SWIR photodetectors. Presence of only weak van der Waals bonds between the layers and absence of dangling bonds in graphene pose a challenge to achieve NWs in an axial configuration. In this work, epitaxial growth of GaAs$_{x}$Sb$_{1-x}$ (x<0.1) NWs by using Ga-assisted molecular beam epitaxy on monolayer graphene/SiO$_2$/Si has been demonstrated. Growth optimization that leads to minimal 2D growth, vertical NWs with good spatial distribution across the sample will be presented. A systematic and detailed study on growth parameters, namely temperature, V/Ill flux ratio and initial Ga shutter opening time dependencies was carried out. Micro-photoluminescence (µ-PL) measurements on the NWs thus grown under optimized conditions exhibited an emission peak at 1.35 eV with full-width half maxima (FWHM) of 69 meV. Further, NWs grown on monolayer graphene substrate manifest higher intensity and lower FWHM compared to nanowires grown on Si/SiO$_2$ substrate with similar growth recipe, suggesting the superior optical quality of the nanowires. Raman Spectra of graphene exhibits the symmetric shape of GaAs$_{x}$Sb$_{1-x}$ LO and TO phonon modes at 260.7 cm$^{-1}$ and 282.2 cm$^{-1}$, respectively. These are redshifted with respect to the corresponding reference GaAs$_{x}$Sb$_{1-x}$ (x=0.075) NWs peaks grown on (111) Si substrate suggesting increased Sb incorporation in the NWs. Raman Spectra of graphene exhibits D, G and 2D peaks at 1350 cm$^{-1}$, 1581 cm$^{-1}$ and 2674 cm$^{-1}$, respectively in which a weak D mode is observed, attesting to minimal defects after growth of NWs.

Band Structure and Carrier Dynamics in Single InGaAs and InGaAs/InP Nanowires

Samuel M. Linser$^{1}$, Araj A. Shojaei$^{1}$, Giriraj Jnawali$^{1}$, Howard E. Jackson$^{1}$, Leigh M. Smith$^{1}$, Amira Ameruddin$^{2}$, Philippe Caroff$^{3}$, Hark Hoe Tan$^{2}$ and Chennupati Jagadish$^{2}$; $^{1}$Department of Physics, University of Cincinnati, Cincinnati, Ohio, United States; $^{2}$Dept of Electronic and Materials Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia.

We employ transient Rayleigh scattering (TRS) and photoluminescence (PL) to dynamically and statically characterize the band structure of single semiconducting nanowires. Our samples include Wurtzite InGaAs nanowires and InGaAs-InP core-shell nanowires. Employing ultrafast pump and probe pulses, our TRS measurements show a substantial increase in the carrier lifetime because of passivation of the InGaAs shell. Optical transitions in both the bare InGaAs core and the core-shell structure exhibit band-to-band transitions which are substantially above the expected Zincblende band edge. We anticipate development of PL measurements in these wires to help identify the fundamental band edge. Thermalization dynamics extracted from our TRS spectra suggest that the core-only wires cool rapidly via optical phonon emission, whereas the core-shell wires cool by a slower process with early optical and later acoustic phonon emission.

Exploring Alternative Catalysts for the Bottom-up Synthesis of Silicon Nanowires

Ashkan D. Dashtestani, Arezo Behroudj, Ardeeshir Moeinian, Waheed Ahmad and Steffen Strehle; ULM University, Ulm, Germany.

Silicon nanowires can be readily grown in a bottom-up manner by utilizing the well established metal-catalyzed vapor-liquid-solid (VLS) synthesis. Within the last decade, various silicon nanowire devices, such as label-free transducers, were demonstrated. However, the use of metal catalysts, such as gold, must be critically reviewed considering for instance device yields, nanowire conformity, metal incorporation as well as cross-contamination within the device fabrication process. In this regard, we widely explored alternative strategies in comparison to gold to facilitate reliable and controlled silicon nanowire synthesis and device fabrication. In particular, we studied various catalyst materials like silver, gold alloys, platinum silicides and even metal-free techniques. Here, we were able in all cases to growth silicon nanowires partly with significantly increased epitaxial growth yield. Also p- and n-type doping were realized. The implementation of ultra-thin platinum silicides allowed us for instance to grow silicon nanowires that lack the typical metal catalyst tip presumably based on so-called silicide mediated crystallization rather than VLS growth. In principle, all these alternative methods facilitate nanowire device assembly or growth-in-place strategies. Nevertheless, metal-induced electronic trap formation and surface degradation remain as critical challenges.
issues. Therefore, we studied further also metal-free synthesis protocols allowing already at the present stage to locally grow nanowires in high density presumably in a self-catalytic manner. Besides growth and morphological aspects, we discuss the nanowire purity, the surface Fermi-level pinning as well as the surface charge carrier concentration. For the nanowire synthesis itself, a home-built low-pressure chemical gas phase reaction system was utilized in the temperature range of 475°C to about 800°C using the precursors SiH4/H2 as well as B2H6 and PH3 for p- and n-type doping, respectively.

NM03.05.18
1D Nanowires of 2D Silicon-Based Chalcogenide Si2Te3 Keyue Wu1, Jiyanghang Cui1, Xiaoshou Chen1 and Jingbiao Cui1; 1Physics and Materials Science, University of Memphis, Memphis, Tennessee, United States; 2College of Electrical and Photoelectronic Engineering, West Anhui University, Lu’An, China.

Si2Te3 is a 2D material with a unique crystal structure where Si atoms form dumb-bells sandwiched between the Te layers, i.e. Si-Si dimers in the sites between the hexagonally close-packed Te atoms1. Covalent bonds are formed between the Te and Si within each layer while weak van der Waals bonding exists between the layers to form a layered crystal structure. A theoretical study showed that rotation of the Si dimer with four possible orientations within the Si2Te3 layer gives rise to a unique structural variability that could have potential new applications in electronic and optoelectronic devices2. Recently single-crystal Si2Te3 nanowires are synthesized by chemical vapor deposition (CVD) and thin layers of Si2Te3 were mechanically obtained by using scotch tape to peel the layers off from the CVD microplates3.

In this study, we have for the first time successfully synthesized 1D nanowires of 2D Si2Te3. It was found that the nanowires grow along c-axes, i.e., along the [0001] direction, and is the stack of layered nanosheets with van der Waals force to form the unique one-dimensional structures. Two-dimensional materials preferably grow into thin layers and the stack of the layers by van der Waals force to form a few layers or bulk materials. Though not common, it is possible for the 2D materials such as SnTe to form nanowires4. The one-dimensional nanowires of 2D materials offer a new horizon for fundamental study as well as new opportunities for applications. Future more, the 1D NWs of Si2Te3 material exhibit a unique resistance switching behavior under an applied potential, which is of great interest for both fundamental understanding and practical applications in ReRAM and memristors.


ACKNOWLEDGMENTS
This work was supported by National Science Foundation (DMR-1709528), Natural Science Foundation of Educational Commission of Anhui Province of China (KJ2015A150), and National Natural Science Foundation of China (21377099). Computational resources were provided by the NSF XSEDE under grants TG-DMR 170664 and 170076, and by the High-Performance Computing Facility at the University of Memphis.

NM03.05.19
Large Scale Uniformity in Electroluminescence Emission of Well-Oriented Nanofin LEDs Robin P. Hansen and Babak Nikoobakht; National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, United States.

One-dimensional (1D) nanostructures have been examined for their use in the semiconducting industry as well as numerous fields such as on-chip light sources, nanophotonics and optoelectronics. The ability to produce arrays of such devices on a large scale setting would advance their development and use bringing them to a mass manufacturing scale.

Presented here is a bottom up synthesis technique for the production of semiconducting nanofins on p-GaN (0001) substrate providing an ideal II-VI, II-V, heterojunctions for UV-visible LEDs. The initial growth is a vapor-liquid-solid (VLS) growth process which results in lateral ZnO nanofins that grow epitaxially across a GaN surface. Methods will be discussed on how to energize select nanodevices at the user’s discretion. We show a remarkable uniformity in electroluminescence of nanoscale light sources owed to the control we have created in organizing 1D-nanostructures in their place and direction such that electrical connections can be made to individual nanostructures. In this regard I present steps for the removal of defective nanostructures and the preparation of them for electrical connections. I also present evidence of high quality heterojunctions and their uniformity across a large area based on the sharp electroluminescence UV peaks observed among the fabricated nanoscale light sources. The developed process remains compatible with current semiconducting processes and can be extended for complex device schemes such as computer chips as well as large scale production of miniaturized light sources.

NM03.05.20
Electrospun Metal Nanofibers for Application in Flexible Transparent Electrodes Robert Frohnhoven, Tim Ludwig and Sanjay Mathur; University of Cologne, Cologne, Germany.

In the last decade, in order to replace the market-leading high-cost and brittle indium tin oxide (ITO) as a material for transparent conductive electrodes, all-solution-processed 1D metal nanofibers are very promising tools for biological applications5. Their small dimensions, which are on the same length scale as many cell
components, make them an ideal tool to probe and stimulate cells with minimal perturbation. However, it has been shown that accessing the cytosol with nanowires is challenging and either a centrifugation step, or the application of an electric field, is necessary in order to reach intracellular access.\(^2\)\(^3\) Here, we use alumina hollow tubes made from GaP nanowires to inject biomolecules into cells. We will present our progress towards accessing the cell interior, transfecting cells, as well as probing the cellular cell state.


NM03.05.22

Lattice Mismatch Strain and Confinement in Nanoscale Si/SiO₂ Structures Fabricated Using Thermal Oxidation Erin Vaughan, Danhong Huang, Clay Mayberry and Ashwani Sharma; Space Vehicles Directorate, Air Force Research Laboratory, Albuquerque, New Mexico, United States.

The transport behavior of semiconductor materials is influenced by lattice-mismatch-induced interfacial (Si/SiO₂) strain coupled with confinement in the nanoscale regime in such a way that the carrier transport properties are beneficially affected. These properties in semiconductors are thought to change gradually from bulk to nanoscale. In the transition region the governing physics changes from classical to quasi-quantum to quantum, and the electrons begin to exhibit more wave-like behavior than particles, and thus react to narrow-paths and interface effects. Additionally, the single discrete charge becomes a significant fraction of the total current. Further, the established macroscopic nature of resistance, capacitance, and inductance changes to a more exotic microscopic one in this regime. Although others have described anomalous effects in scaled versions of Si device structures on their electronic and optical properties as compared to bulk devices, a detailed experimental study describing the incremental transitioning effects of scaling that led to these anomalous effects has not yet been conducted. In this work, we report on the fabrication and characterization of nanoscale planar, wall-like, and wire-like Si/SiO₂ nanoscale structures. As the Si nanostructure dimensions were scaled down to the quantum regime by thermal oxidation of the Si, changes to the band structure and carrier effective mass were observed by both optical and electrical techniques. Thermal oxidation of the Si region is a method that is both highly controllable and effective for fabricating high-quality nanostructures. The oxidation process improves surface roughness at the interface, while also drawing impurities and contaminants away from the core and interface. Photoluminescence measurements showed changes in the peak energies, which illustrates changes in the band structure, as the Si/SiO₂ dimensions are scaled. Metal-semiconductor-metal devices containing these nanostructures were fabricated to further characterize the material properties as a function of scaling. Room temperature dark current measurements showed that conductivity increased as the Si dimensions were reduced. This result is indicative of decreased resistivity and increased mobility and carrier velocity. A decrease in photocconductivity response was observed in samples with Si regions smaller than about 30 nm, which can be attributed to confinement effects on the hole mobility. Transient-time response measurements were also performed to examine the carrier generation and recombination behavior as a function of scaling. Signal rise times decreased for both carrier types by an order of magnitude as Si dimensions were reduced from 200 to 20 nm, meaning that the carrier velocity is indeed increasing with smaller scale structures. This result is indicative of decreased Si band gap energy and carrier effect mass.

NM03.05.23

Engineering the Wetting Behaviour of Gallium Nanodroplets and Correlation with GaAs Nanowire Orientation Leo Ghisalberti, Rajrupa Paul, Akshay Balgarkashi, Lucas Gunia, Woonjong Kim, Martin Friedl, Craig Carter and Anna Fontcuberta i Morral; 1École Polytechnique Federale de Lausanne, Lausanne, Switzerland; 2Massachusetts Institute of Technology, Boston, Massachusetts, United States.

III-V nanowires (NWs) represent promising building blocks for new generation devices in fields such as electronics, optoelectronics, photovoltaics and quantum computation.\(^1\)\(^2\) Among the possible growth techniques available, the vapor-liquid-solid (VLS) approach provides the possibility to modify the crystal phase and growth directions by engineering the catalytic droplet.\(^4\)\(^5\)

So far most studies have focused on Au-catalyzed NWs growth. Here we focus on self-catalyzed Ga-assisted growth. We modify the contact angle of Ga by modifying the surface energy of the substrate. In a combined theoretical and experimental approach, we identify the range of possible shapes and contact angle of the droplets that can be obtained by modification of the underlying substrate. Among the surface coatings considered are SiO₂, TiO₂, TiO, MoO₃, SiN and graphene. We demonstrate what materials combinations reduce the wetting of the Ga nanodroplets. Finally we correlate the contact angle with the orientation and growth direction of the NWs. This work opens new avenues for a full control of the growth direction and orientation of nanowires and thus for an integration with a large variety of substrates.


NM03.05.24

GaAs-In(Al)GaAs Core-Shell Nanowire Lasers on Silicon Thomas Stuttner, Tobias Kostenbader, Andreas Thurn, Daniel Ruhstorfer, Jochen Bissinger, Hubert Riedel, Michael Kaniber, Gregor Koblmueller and Jonathan Finley; Walter Schottky Institut, Garching, Germany.

Semiconductor nanowire (NW) lasers are nanoscale coherent light sources that exhibit a small footprint, low-threshold lasing characteristics, and properties suitable for monolithic integration onto Si photonic circuits. An important milestone on the way towards novel on-chip photonic functionalities is the integration of individual, deterministically addressable NW lasers on Si waveguides with efficient coupling and mode propagation in the underlying photonic circuit. In this presentation, we demonstrate the monolithic integration of single GaAs-based NW lasers directly onto lithographically defined Si ridge waveguides (WG). When subjected to optical excitation, the observed lasing behavior shows clear “s-shape”-characteristics, linewidth narrowing and threshold values down to 19.8±1 µJ/cm², which is the lowest value reported to date for this kind of integrated lasing structure.\(^1\) The lasing mode of individual NW lasers is shown to couple efficiently into propagating modes of the underlying orthogonal Si WG, preserving the spectral characteristics during mode propagation in the WG in sound agreement with Finite-Difference Time-Domain (FDTD) simulations. Using a WG structure with a series of mask openings along the central mode propagation axis, we further illustrate the out-coupling properties of both spontaneous and stimulated emission and demonstrate propagation of the lasing mode over distances > 60 µm, despite absorption in the silicon dominating the propagation losses.\(^1\)

By replacing the bulk GaAs active gain medium in the NW-laser structure by multiple InₓGa₁₋ₓAs quantum wells (MQW), the emission wavelength can be shifted towards telecommunication bands in order to reduce the absorption losses in silicon. In total, seven 8 nm thick QWs are embedded in 10 nm thick (Al)GaAs barriers. Starting from an In-molar fraction of nominally 15%, lasing emission shows a distinct red shift (>80 meV) compared to NW-laser structures which host pure GaAs MQWs as gain medium.\(^2\) By successively increasing the nominal In-molar fraction up to ~40%, while controlling the incorporation of In by growth temperature, we demonstrate that lasing can be achieved close to 1.2 eV (~1050 nm).\(^3\) We further show that controlling
emission wavelength and lasing characteristics depends sensitively on a number of structural properties, which are evaluated by correlated scanning transmission electron microscopy (STEM) and atom probe tomography (APT) analysis of the coaxial NW-MQW laser structure.


NM03.05.25
Vapor-Solid Selective Area Molecular Beam Epitaxy and Doping of Catalyst-Free GaAs Nanowires on Silicon
Daniel Ruhstorfer, Simon Mejia, Hubert Riedl, Jonathan Finley and Gregor Koblmüller; Walter Schottky Institut, Technische Universität München, Garching, Germany.

III-V semiconductor nanowires (NWs) have gained significant interest due to their potential of monolithic integration on silicon to create various different nanoscale devices on-chip. For all the prospective devices utilizing NWs, control of the doping profiles is key and directly affects performance when designing the necessary pn-junctions. In common vapor-liquid-solid (VLS) grown NWs, doping has proven to be difficult due to non-uniform incorporation of dopants during growth [1] and the reservoir effect that is caused by the droplet catalyst. Particularly in GaAs, where in planar samples the growth of n-type material directly from the vapor phase using the amphoteric dopant silicon is well established, so far only p-type material could be realized for VLS-grown NWs. Literature from liquid phase epitaxy points out that the preferential incorporation of Si dopants on Ga lattice sites only occurs for temperatures beyond 860°C [2], which are inaccessible in VLS molecular beam epitaxy.

In this contribution, we present our recent advances in establishing the selective area molecular beam epitaxy of completely catalyst-free Si-doped GaAs NWs on silicon. We achieve this by applying a high temperature surface treatment to our SiO2-masks to mask the surface of non-masked segments before growth, which transforms the usual 7x7 surface of (111)-silicon to a 1x1-As terminated surface reconstruction. The GaAs NWs are then grown in a high arsenic pressure regime, in which we find the NW aspect ratio to increase with increasing V/III flux ratio and with decreasing mask opening diameters, achieving peak aspect ratios greater than 20. By varying the growth temperature, we manage to exceed a total NW length of 1µm for 1h of growth time. While the yield of undoped NWs decreases for smaller mask openings, adding a high doping flux of silicon increases the yield to over 95% and decreases fluctuations in length and diameter drastically [3].

In TEM, our NWs show a high density of twinned segments, indicating a twinning induced growth mechanism where the twin induced rotation of the crystal structure exchanges fast and slowly growing facets, leading to enhanced axial growth rates. We discuss how the influence of doping affects this mechanism so that the experimentally observed increase in yield and uniformity can be explained.

In addition, we investigate the Raman spectra of the Si-doped GaAs NWs with various doping levels for signatures of the site distribution of the amphoteric silicon dopants while material quality and carrier density is probed by photoluminescence spectroscopy and electrical properties are characterized by NW-FET measurements.


NM03.05.26
Ab Initio Studies of the Electronic and Optical Properties of Eu Doped GaN Nanowires
Assa Aravindh Sasikala Devi, Naresh Alaal and Iman S. Roqan; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

Nanostructures comprising of rare earth (RE) doped wide band gap nitrides are of interest for optoelectronic applications, such as in visible lasers [1]. One material of particular interest in this context is GaN doped with RE elements due to its exceptional electronic and optical properties. Here, we present the properties of Eu-doped GaN nanowires (NWs) grown along the wurzite [0001] orientation, calculated using density functional theory (DFT) based on the generalized gradient approximation (GGA), including the Hubbard (U) parameter. We used the plane wave code VASP to carry out the computations [2].

Energy formation calculations show that Eu atoms are the more stable on the NW surface, than native point defects. However, as the number of Eu atoms increases, an outward lattice relaxation occurs, to accommodate the increase in number of atoms, and reduces the formation energy of point defects. The Density of States (DOS) indicate that the Eu f-states are located in the band gap of GaN. DOS also show that valence band maximum (VBM) shifts towards/away from the Fermi level in presence of N and Ga vacancies (VN and VGa), which may give rise to intra-band f/f transitions that are related to optical centers. Optical calculations reveal that the prominent absorption peaks appear between 0 and 3 eV. Moreover, our analyses show that there is no significant change in the peak positions in the optical absorption spectra of Eu-doped NWs as Eu concentration increases. Thus, our theoretical predictions suggest that Eu-doped GaN NW is a favorable candidate for optoelectronic applications.

Reference

NM03.05.27
Detection of Cellular Traction Forces Using GaP-GaInP Nanowires
Zhen Li, Christelle Prinz, Karl Adolfsson and Magnus Borgstrom; Solid State Physics, Lund University, Lund, Sweden.

Cellular traction forces play a crucial role in many cellular processes, including deformation, division and differentiation. We have previously demonstrated that vertical nanowire arrays can be used for assessing cellular traction forces. Compared to other measurement methods, nanowires have an ultra-small (< 100 nm) diameter and can therefore improve the spatial resolution of force measurements. In our first attempt, we used GaP nanowires, functionalized with organic fluorescent dyes for measuring cellular forces during neuronal growth (1). However, the fast bleaching of the dyes limited the acquisition time of our experiments.

Here we use nanowires with a GaP base and a photoluminescent GaInP tip with negligible bleaching (2) to measure the traction forces of MCF-7 and
MCF-10A cells (i.e. cancer and normal-like epithelial breast cells). A high spatial resolution force map is created using automated image analysis based on the localization of the photoluminescent tips of the nanowires. We show that the force distribution and magnitude differ between MCF7 breast cancer cells and MCF10A normal-like breast epithelial cells, and that monitoring traction forces can be used to investigate the effects of anticancer drugs (3).

NM03.05.28
A Facile Route to Structural Design of Zinc Stannate (Zn2SnO4) Nanofibers and Functionalization with Co-Catalysts for High Performance Acetone Sensor เฮ็้ม จี จุ๊ง; ศาสตราจารย์จิน จี จุ๊ง; ฮี ซู จวอ; ฮี ดุ จี ควน; 1KAIST, จุน, ประเทศเกาหลี; 2Massachusetts Institute of Technology, บอสตัน, แมสซาชูเซตส์, สหรัฐอเมริกา.

The metal oxide based chemiresistive sensors are getting attention as emerging exhaled breath sensors due to their flexibility in production, low cost, and easily interpreted results. To enhance the sensing properties, nanostructures with large surface area and high porosity are highly desired since the gas reactions, which are transformed into an electrical signal such as resistance, occur on the surface of the metal oxide.

Zinc stannate (Zn2SnO4) possesses high electrical conductivity, high thermal stability, and high chemical sensitivity. Furthermore, Zn2SnO4 nanofibers can be easily synthesized using electrospinning method. During electrospinning, the morphology of the nanofibers can vary depending on which polymer is used.

In this work, the Zn2SnO4 nanofibers with high porosity were synthesized via in situ phase-separation between poly(vinyl acetate) polymer and inorganic metal precursors (zinc acetate and tin acetate), elongation of poly(vinyl acetate) polymer during the electrospinning step, and subsequent calcination. As a result, longitudinal pores were formed within Zn2SnO4 nanofibers, which offered large surface area and pore volume. In addition, Zn2SnO4 nanofibers were co-functionalized with graphene oxide and palladium to further increase the sensitivity and selectivity toward acetone molecules. The graphene oxide and palladium co-functionalized Zn2SnO4 nanofibers showed a dramatically enhanced response toward acetone (Racetone/Rair = 125 at 5 ppm), which was 3.78-fold higher than that of pristine porous Zn2SnO4 nanofibers (Racetone/Rair = 33.07 at 5 ppm). Furthermore, the graphene oxide and palladium co-functionalized Zn2SnO4 nanofibers exhibited superior selectivity toward acetone compared to interfering gases, namely, toluene, pentane, carbon monoxide, and hydrogen sulfide in a highly humid atmosphere (95% RH) (Racetone/Rair < 6.5). This work paves the way for a facile route to structural design of metal oxide nanofibers and co-functionalization with catalysts for high gas sensing performance, and also demonstrated the extremely sensitive acetone detection capability in highly humid condition such as exhaled breath.

NM03.05.29
Direct Synthesis of α-CsPbI3 Nanowires with a 1.73 eV Bandgap by Two-Injection Method จุว จูน, หลง จูน, จินฟง จัง แอนด์ เหา จ่วน; ฮูฮาวจิ้น จิวเวิ่น นาวิส แอนด์ เทคโนโลจี, หวูฮาน, จีน.

One-dimensional all-inorganic halide perovskites have emerged as one of the most prominent materials in the application of photoelectric devices due to remarkable properties such as low defects, morphological anisotropy, mechanical flexibility as well as fast charge transfer capability. Particularly, the one-dimensional cubic (α) phase CsPbI3 has the narrowest band gap of 1.73 eV among all-inorganic lead halide perovskites, suggesting the greatest potential in the solar cells application. However, the direct synthesis of α-CsPbI3 nanowires (NWs) is challenging and remains unfulfilled because the reaction usually involves a phase change process, resulting in an orthorhombic (δ) phase with the wider bandgap of 2.82 eV. Herein, we report a simply synthetic approach to directly grow α-CsPbI3 nanowires at low temperature using a two-injection method. The as-synthesized CsPbI3 nanowires can be up to 20 μm in length and have an average length of 14 μm. The XRD results verify that these cubic phase nanowires can be steady at room temperature for 90 days. The CsPbI3 nanowires show a photoluminescence (PL) peak located around at 685 nm and the UV-vis absorption spectrum further reveals that the band gap is about 1.73 eV. The excellent optical properties of the CsPbI3 nanowires offer great potential in the field of optoelectronic devices.

NM03.05.30
Chitosan-Templated Bimetal Catalysts Loading on Porous Metal Oxide Nanofibers—Exceptionally Improved Gas Sensing Performance พิยง จิน จ็อง แอนด์ ได จี ควน; มหาวิทยาลัยอินดัสทรีไอแอนซ์ แอนด์ เทคโนโลจี, จุน, ประเทศเกาหลี.

Metallic particles prepared from chitosan-metal complexes (CS-M) possess very small size (< 5 nm) and high dispersibility because they are encapsulated by chitosan molecules. Due to these advantageous properties, CS-M have been frequently applied in catalysis, e.g. for hydrogenation, air cathode, and removal of dyes. Similarly, semiconducting metal oxides (SMOs) based gas sensor also requires highly dispersed small-sized catalysts to significantly enhance sensing performance. Thus, CS-M can be regarded as highly useful templates for functionalization of catalysts on SMOs based gas-sensing materials. Moreover, since chitosan decomposes at high temperature, it can generate numerous mesopores on supporting SMOs, which facilitate surface gas reactions. In this work, for the first time, we demonstrate chitosan-templated catalysts on one-dimensional metal oxide scaffolds as superior chemiresistors, e.g. for human breath analyzer and indoor air monitoring system. First, as a breath analyzer, we synthesized chitosan-templated Pt nanocatalyst loaded mesoporous SnO2 nanofibers by combining chitosan-Pt complex with electrospinning route. Due to the well dispersed ultrasmall (~2.6 nm) Pt catalysts and enhanced mesoporosity by decomposition of chitosan template, Cs-Pt loaded SnO2 NFs showed outstanding response (Rgas/Rair = 141.92 at 5 ppm), excellent selectivity, long-term stability, and fast response (12 s/recovery (44 s) speed toward 1 ppm of acetone at 350 °C and human breath humidity condition (90% RH). Second, we extended catalysts from single metal (Pt) to heterogeneous metal oxides (NiO-Fe2O3) by using chitosan-Ni/Fe dual complexes. Moreover, by controlling ratio of Sn precursor to polymer in electrospinning solution, we developed SnO2 fiber-in-tube (FIT) structure, thus resulting in formation of NiO-Fe2O3 sensitized mesoporous SnO2 FITs. NiO-Fe2O3 loaded SnO2 FITs exhibited unparalleled response (Rgas/Rair = 7.44), superior cross-selectivity, and extremely fast response speed (12 s) toward 0.2 ppm of formaldehyde gas at 350 °C and indoor air humidity condition (30% RH). The strategy employed in this work can pave the way for highly reliable and simple sensitization of catalytic particles on sensing layers.

NM03.05.31
Effect of Annealing on the Microstructure and Properties of GaSb Nanofibers Induced by Ions Irradiation พิยง จิ้น, จุน จิ้น, จุน จิ้น, จุน จิ้น; มหาวิทยาลัยอินดัสทรีไอแอนซ์ แอนด์ เทคโนโลจี, จุน, ประเทศเกาหลี.

The binary compound semiconductor GaSb is one of candidate materials for manufacturing high-frequency, low-power electronic devices. At room temperature, Fe+ ion beam irradiation of GaSb bulk single-crystal wafer. The nanofibers possess special optoelectronic properties after recovering lattice damage by furnace annealing. It makes GaSb semiconductors gain highly potential applications in the field of optoelectronic device fabrication. At room temperature, Fe+ ion beam irradiation of GaSb at 400 keV with the fluences of 1×1016 Fe+/cm2. Amorphous GaSb nanofibers were induced by ion irradiation of bulk GaSb single-crystal wafer. The nanofibers possess special optoelectronic properties after recovering lattice damage by furnace annealing. It makes GaSb semiconductors gain highly potential applications in the field of optoelectronic device fabrication.
of the GaSb LO phonon absorption peaks decreased after ion beam irradiation. And two new modes are observed at ~150 cm⁻¹ and ~114 cm⁻¹, respectively.

NM03.05.32
Silver Nanowire Based Flexible Transparent Electrodes with Different Drying Conditions Seobum Chu, Dongwook Ko, Hyojin Song and Jongbok Kim; Kumoh National Institute of Technology, Gumi, Korea (the Republic of).

ITO (Indium Tin Oxide), which is the most typical transparent electrode, has excellent electrical conductivity and transmittance and is applied to various optoelectronic devices. However, it is inappropriate as next generation transparent electrode because it is not flexible. Ag nanowire (AgNW) based transparent electrode with excellent optical and electrical properties, great flexibility is a strong candidate to replace ITO. To construct AgNW based transparent electrode, people generally spin-coat AgNW solution on the substrate and then dry it at hotplate to evaporate the solvent. However, some substrates are weak to heat and requires different drying methods. Here, we investigate how drying methods affect surface structures and physical properties including the electrical and optical properties in AgNW based transparent and flexible electrodes. Specifically, we spin coated polymethyl methacrylate (PMMA) on the cleaned glass substrate to make easy separation of the AgNW from the glass. Then, the AgNW was spin-coated on the substrate at 1000 rpm for 1 minute. As drying methods for AgNW film, we adopted three different approaches: i) drying it on hotplate, ii) natural drying it in air and iii) drying it under vacuum. When drying it on hotplate, drying time was fixed at 1 min and temperature was from 50°C to 120°C. In case of natural drying and drying under vacuum, drying time was from 5 min to 30 min at room temperature, respectively. Then, NOA 63, a photocurable polymer, was spin-coated on it, followed by UV curing and peeling it to complete flexible electrode fabrication. The surface of AgNW based electrodes was observed by AFM and SEM, and their transmittance was analyzed using a UV-Visible-NIR spectrometer. In surface roughness, we found that room temperature-dried and vacuum-dried transparent electrodes are more rough than that of the heat-dried transparent electrode. In the transmission, the heat-dried and room temperature-dried and vacuum-dried transparent electrode has almost the same transmittance regardless of drying time. We also measured the conductivity of various AgNW based electrode using 4-point sheet resistance meter. The conductivity of the heat-dried transparent electrode tends to increase with increasing drying temperature. However, the conductivity of the transparent electrodes which were dried at room temperature and vacuum tended not to increase. Then, we measured contact angle on the electrodes. The contact angle of the transparent electrode dried at 120°C was considerably decreased compared to the other conditions. As a result, we prepared AgNW based electrodes under different drying condition and characterized their electrical, optical, surface properties and contact angle characteristics. Then we found that drying at room temperature can generate AgNW based electrodes with comparable conductivity and transmittance to vacuum drying and heat-drying.

NM03.05.33
Investigation of Magnetic Properties of Cobalt Ferrite Nanorods Formulated Through a Facile Templated Electrodeposition Method Brent Williams, Robert Croson and Carlos Castano; Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States.

Rare-earth based materials have been dominating the magnetic industry for centuries. Due to their nonquenched spins in the f block, materials such as NdFeB and Terfenol have the best magnetic properties for magnetostriiction which can be used for magnetic lensing and permanent magnets for electric motors and generators. However, due to the cost of rare-earth materials formulating magnetic materials from the 3d block elements have been investigated. Cobalt ferrite which contains both magnetostriactive and a high demagnetization field needed for a permanent magnet has been thoroughly studied. For many of these applications high thermal stability and magnetic anisotropy is needed to withstand thermal decomposition and loss of magnetization. Ferrites are known for their high thermal stability and cobalt ferrite in particular is known to have a high magnetocrystalline anisotropy in comparison to other magnetic oxides and a high ferro-paramagnetic transition temperature around 800 K. However, decreasing particle size to single domain structures also leads to a decrease in thermal stability as well as Curie temperature. In order to compensate for the size effects, routes for formulation of nanorods or nanowires are being established. Elongated particles form an easy axis for free electron spins which may enhance coercivity, thermal stability and Curie temperature through a phenomena called shape anisotropy. While routes for synthesizing cobalt ferrite are well established, many of the facile routes lead to agglomeration or wide size distribution, while control of particle size and shape normally depends on high boiling point solvents which accumulate waste and reproducibility in bulk is an issue. Within this work cobalt ferrite nanorods with control over rod diameter have been established through electrodeposition into an anodized alumina template. Unlike previous routes which, need nonenvironment friendly solvents, this method is done mainly at room temperature in an aqueous solution. The magnetic properties of the system were studied to observe the improved magnetic properties including coercivity and Curie temperature which is attributed to shape anisotropy. With this research facile routes for formulating magnetic materials with better control over particle dimensions were established for applications in magnetic sensing and permanent magnets.

NM03.05.34
Large-Scale Synthesis of Byproduct-Free Zn₃P₂ Nanowires Using Highly Porous Zn Pellets Yixi Chen¹, Rakesh Polinnaya¹ and Sreeram Vaddaraju¹, ²; ¹Chemical Engineering, Texas A&M University, College Station, Texas, United States; ²Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Nanowires have been shown to be promising materials as building blocks for the next-generation electronic and optical devices. Translating these successes in the laboratory to commercial applications, however, requires the capabilities of mass production of high-quality nanowires, which not only afford control over the dimensions of the obtained nanowires, but also ensure that the obtained nanowires are byproduct-free. Herein, a novel approach to synthesis of Zn₃P₂ nanowires in a gram scale is described, in which highly porous Zn pellets were directly converted to that composed of Zn₃P₂ nanowires by chemical vapor deposition (CVD). No unreacted reactants remain mixed with the nanowire product. This method is an improvement over previous works demonstrating the mass production of nanowires using phosphorus reaction with heated zinc foils, and it can be extended to synthesize other nanowires in a large quantity.

NM03.05.35
Fabrication of Epoxy-Based Shape Memory Polymer Composites Embedded with Highly Elastic Nanowires Yixi Chen¹, Nazanin A. Kazerooni², Arun Srinivasan¹ and Sreeram Vaddaraju¹, ²; ¹Chemical Engineering, Texas A&M University, College Station, Texas, United States; ²Mechanical Engineering, Texas A&M University, College Station, Texas, United States; ³Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Shape memory polymers (SMPs) have been shown to be promising materials for biomedical and aerospace applications. However, relative to shape memory alloys, they exhibit lower recovery stresses, lower recovery speeds, and lower cycle lives. With the intent of improving these properties,
Role of Wire-to-Wire Junction Resistance in Percolation Resistivity of Transparent, Conductive Metal Nanowire Networks

Junying Li, Jeremy Hicks, Tsung-Ying Tsai, Shreshtha Mishra and Ant Urail; Electrical and Computer Engineering, University of Florida, Gainesville, Florida, United States.

There has been significant research interest recently in random networks of one-dimensional (1D) elements, such as carbon nanotubes, graphene nanoribbons, and metal nanowires, for next-generation transparent conductors. In particular, silver and copper nanowire networks exhibit high transmittance, low sheet resistance, mechanical flexibility, and fast deposition. These unique properties make metal nanowire networks promising candidates to replace indium tin oxide (ITO), which suffers from brittleness, scarcity, high cost, and slow deposition.

Monte Carlo simulations are employed to calculate the resistivity of metal nanowire networks, which is governed by percolation transport. In most simulations, it is assumed that the resistance of the wire-to-wire junction is much larger than that of the nanowire itself, resulting in a junction resistance-dominated network. Although this is the case for carbon nanotube networks, recent experiments have shown that, for metal nanowire networks such as silver, the junction resistance can be significantly lowered by post-deposition treatments such as thermal annealing, plasmonic welding, joule heating, and mechanical pressing. In such cases, the nanowire resistance becomes comparable to the junction resistance and can no longer be ignored. When the junction resistance approaches zero, the network becomes nanowire resistance-dominated, which is the lowest resistance limit for a given set of nanowire and device parameters. Furthermore, by controlling the junction resistance, the resistivity of the network can be tuned, opening up further applications such as resistive switching.

In this work, we perform systematic Monte Carlo simulations to study the effect of the wire-to-wire junction resistance on the resistivity and percolation critical exponents of metal nanowire networks. In particular, we compute the network resistivity as a function of the wire-to-wire junction resistance over a span of six orders of magnitude, ranging all the way from a junction resistance-dominated to a nanowire resistance-dominated network. We study this effect when other nanowire/device parameters are also varied, namely nanowire density and length, device length and width, nanowire alignment, and nanowire curviness. We find, for example, that the effect of curviness on resistivity decreases for nanowire resistance-dominated networks. We also investigate the effect of the wire-to-wire junction resistance on the percolation critical exponents over a wide range of nanowire and device parameters. We find that the junction resistance plays a critical role in determining both the resistivity and the critical exponents of metal nanowire networks.

These studies illustrate how the junction resistance affects the macroscopic resistivity of the network. They also show that Monte Carlo simulations are an essential tool for providing insights into the percolation resistivity of transparent, conductive metal nanowire networks.
trifluoroethylenchlorofluoroethylene) [PVDF-TrFE-CFE] to form multilayer heterostructure nanocomposites. In addition to the interfaces between the polymer and nanowires, additional interfaces introduced between nanowires and nanowires give rise to the permittivity and displacement of the nanocomposites, which contributes to enhanced discharged energy density. Also, the effect of nanowires on the relaxation process of nanocomposites was studied by dielectric spectroscopy. The addition of nanowires could decrease the apparent activation energy for space charge relaxation and the constant in VFT equation related to activation energy for α relaxation, resulting from the existence of nanowires will shorten the distance for charge motion as well as segregate polymer chains and diminish the inter molecular cooperativity. What’s more, the introduce of nanowires with a large aspect ratio could influence much area of the polymer matrix and improve the local homogeneity, which results in a more concentrated relaxation time for α relaxation.

NM03.05.42

Using Ultrathin Parylene Films as an Organic Gate Insulator in Nanowire Field-Effect Transistors

Jan Gluschke¹, Jakob Seidl¹, Roman Lyttleton¹, Damon J. Carrad¹-², Jack Cochrane¹, Sebastian Lehmann¹, Lars Samuelson¹ and Adam P. Micolich¹; ¹UNSW Australia, Sydney, New South Wales, Australia; ²Center for Quantum Devices, University of Copenhagen, Copenhagen, Denmark; ³Solid State Physics/NanoLand, Lund University, Lund, Sweden.

We demonstrate the use of the organic polymer parylene (poly p-xylencylene) as an ultra-thin (~20 nm), lithographically-patterned gate insulator for use in nanoscale transistors. Parylene is well known for its biocompatibility and is FDA approved for human implantable devices, which sees it widely used for medical implant encapsulation. It is also common as an environmental protection coating for printed circuit boards and other industrial electronics. In these applications the parylene films are much thicker, typically 0.5 to 50 microns. Even where parylene has been used as a transistor gate insulator, for example in organic semiconductor transistors [1], the film thickness is ~200 nm to avoid pinholes adversely affecting the device. Indeed, ultra-thin parylene is often thought unsuitable due to pinhole issues, we show this issue can be surmounted for the tiny interfacial areas in nanoscale devices.

We used a custom-built parylene deposition system to put a ~20 nm thick conformal coating onto a 50 nm diameter InAs nanowire field-effect transistor [2]. This device relies on two key properties of parylene: the ability to deposit directly from the gas-phase and its high solvent resistance. The former enables conformal deposition like commonly used oxides, e.g., SiO₂, Al₂O₃ and HfO₂, deposited by atomic layer deposition. Notably, parylene deposition can be performed onto chemically-treated semiconductor surfaces without destroying the surface chemistry in contrast to ALD. The solvent resistance means parylene is amenable to resist-based lithographic patterning, enabling the fabrication of devices as simple as top-gate transistors and as complex as the gate-all-around (GAA) transistors. An added advantage is that parylene is readily etched by oxygen plasma, removing the need for the toxic hydrofluoric acid etches used with oxides. Our gate-all-around transistors give sub-threshold slopes as low as 140 mV/decade and on-off ratios exceeding 1000 at room temperature with low gate leakage (~20 pA) and high yield.

The material and fabrication processes should be transferable to a variety of other semiconductor materials, including graphene, transition metal dichalcogenides and topological insulator systems, as well as a variety of other nanoscale device designs. The ability to deposit ultra-thin parylene films and pattern them at the nanoscale with standard lithographic techniques opens the way to their more widespread use in nanoscale electronics. The intrinsic biocompatibility of parylene means this work is particularly relevant to bioelectronics applications from neural sensing to medical implants.


NM03.05.43

p-GaAs Nanowire Transistors with Near-Thermal Limit Gating

Rifat Ullah¹, Frank Meyer¹, Jan Gluschke¹, Shagufta Naureen², Philippe Caroff²-⁴, Peter Kroegsturp³, Jesper Ngyár³ and Adam P. Micolich¹; ¹UNSW Australia, Sydney, New South Wales, Australia; ²RSPE, The Australian National University, Canberra, Australian Capital Territory, Australia; ³Center for Quantum Devices, University of Copenhagen, Copenhagen, Denmark; ⁴Microsoft Station Q, Delft University of Technology, Delft, Netherlands.

Modern integrated circuits are heavily reliant on complementary architectures featuring both n- and p-type transistors to minimise power consumption. Continued miniaturisation spurred the development of nanowire CMOS, most recently focussing on III-V nanowire field-effect transistors (NWFETs) integrated on Si to obtain high performance at low cost. Progress has been better for n-type than for p-type. Near-thermal limit gating performance has been obtained for n-type NWFETs. Integration on Si and GHz operation have also been demonstrated. Challenges with growth, doping and fabrication of high-quality gates and ohmic contacts have impeded progress for p-type NWFETs.

Candidates for p-type III-V NWFETs include GaSb, GaAs, In(Ga)As, InP and InSb. In-based materials are hard to deploy because surface state effects make them naturally n-type. Thus the prevailing p-type material is GaSb. It can be challenging to grow, it is also natively p-type due to antisite defects, meaning it cannot also be used for n-type applications. GaAs is natively intrinsic and can be doped to make n- and p-type devices. However, reliable low resistance contacts have been a roadblock for p-GaAs NWFETs [1].

We have developed p-GaAs NWFETs with near-thermal limit gating, low contact resistance and competitive frequency response with strong potential for nanowire CMOS applications. The key to low resistance ohmic contact was adding a heavily Be-doped GaAs shell to the nanowire. We obtain contact resistance as low as 30 kΩ for a shell acceptor density NA = 1.5 x 10¹⁹ cm⁻³ using unannealed AuBe contacts [1]. This shell doping is so high that nanowire CMOS applications. The key to low resistance ohmic contact was adding a heavily Be-doped GaAs shell to the nanowire. We obtain contact resistance as low as 30 kΩ for a shell acceptor density NA = 1.5 x 10¹⁹ cm⁻³ using unannealed AuBe contacts [1]. This shell doping is so high that nanowire CMOS applications. The key to low resistance ohmic contact was adding a heavily Be-doped GaAs shell to the nanowire. We obtain contact resistance as low as 30 kΩ for a shell acceptor density NA = 1.5 x 10¹⁹ cm⁻³ using unannealed AuBe contacts [1]. This shell doping is so high that nanowire CMOS applications. The key to low resistance ohmic contact was adding a heavily Be-doped GaAs shell to the nanowire. We obtain contact resistance as low as 30 kΩ for a shell acceptor density NA = 1.5 x 10¹⁹ cm⁻³ using unannealed AuBe contacts [1]. This shell doping is so high that nanowire CMOS applications. The key to low resistance ohmic contact was adding a heavily Be-doped GaAs shell to the nanowire. We obtain contact resistance as low as 30 kΩ for a shell acceptor density NA = 1.5 x 10¹⁹ cm⁻³ using unannealed AuBe contacts [1].

The second involves carefully etching the shell at the gate location to make a p-GaAs nanowire MESFET [3]. The advantage is that the gate is self-insulating due to the GaAs Schottky barrier. Our device gives strong performance compared to single horizontal p-GaSb nanowire MOSFETs [4], with typical sub-threshold swing of 62 mV/dec, within 4% of the thermal limit, on-off ratio ~10⁵, contact resistance ~30 kΩ and high-fidelity ac operation up to 10 kHz, opening the path to all-GaAs nanowire complementary circuits with simplified fabrication and improved performance.

Inorganic Nanowire Enabled Next Generation High Performance Battery Separators

Novarials inorganic nanowire battery separators have superior performance: ultrahigh safety (nail penetration safe), ultralong cycle life (double cycle life), and high power density etc. Novarials has a technical leadership on preparation, processing and characterization of a variety of inorganic nanowires. Using these inorganic nanowires, we have developed several nanowire based technology platforms including bendable ceramic nanowire membranes, flexible ceramic hollow fiber membranes, and inorganic nanowire enabled battery separators. We will share these amazing industry achievements with energy community.

Band Structure of Wurtzite InAs Nanowires Measured by Polarized Photocurrent Spectroscopy

We use polarized photocurrent spectroscopy to measure the optical band gap and valence band structure of wurtzite InAs nanowires. The nanowire device was fabricated from 50nm diameter nanowires dispersed on a Si/SiO2 substrate, and two titanium/aluminum metal pads were deposited at either end of the nanowires using photolithography and liftoff. Using tunable excitation light polarized along the long axis of nanowire and perpendicular to that, the band structure of this hexagonal wurtzite material was revealed. According to theory, the transition from the first valence band to the conduction band in a wurtzite structure is only allowed for the light perpendicularly polarized to the c-axis (long axis) of the nanowire. In contrast, carriers can be optically excited from the second and third valance bands to the conduction band with either polarization. The data shows a 0.43eV fundamental band gap at room temperature, 70 meV greater than the zincblende structure, as expected. In addition, the splittings between the valence bands are measured and appear to be consistent with theory.

Highly Conductive Nanorods Underlayer Effect to the Hematite Nanorods with TiO2 Passivation Layers for Photoelectrochemical Water Splitting

Host-guest nanochannel system has proven to be a successful strategy in overcoming the poor majority (electron) collection of α-Fe2O3 electrode for photoelectrochemical (PEC) water splitting. Here we report a novel Sb-doped SnO2 nanorod underneath the α-Fe2O3 nanorod sheathed with TiO2 for PEC water splitting. The experimental results, corroborated with theoretical analysis demonstrate that the Sb-doped SnO2 nanorod underlayer effect to the α-Fe2O3 nanorod sheathed with TiO2 plays an important role in enhancing the PEC water splitting performance. We report the growth of well-defined Sb-doped SnO2 nanorods as a conductive scaffold to improve α-Fe2O3 PEC water oxidation performance. The α-Fe2O3 grown on Sb-doped SnO2 nanorods exhibits improved performance for PEC water oxidation compared to α-Fe2O3 grown on flat fluorine-doped tin oxide (FTO) glass. Furthermore, a simple and facile TiCl4 chemical treatment further introduces the TiO2 passivation layer forming onto the α-Fe2O3 to reduce recombination and eliminate adverse reactions on the surface.

Microbial-Nanowire Enabled Diffusive Memristor Working at Ultralow Cellular Voltages

A type of diffusive memristors has been constructed using microbial protein nanowire-based thin film. The operating voltage in the device was observed to be <80 mV, falling into the biological cellular voltage regime (e.g., cell membrane potential or action potential). The memristor can also mimic the synaptic Ca2+ dynamics with similar temporal response. The material composition (e.g., protein) and ultralow working voltage (e.g., cellular voltage) in the devices have led to both material and functional proximity/mimicry to biological synapse.
Guided Nanowire Optoelectronics Ernesto Joselevich; Weizmann Institute, Rehovot, Israel.

The large-scale assembly of NWs with controlled orientation on surfaces remains one challenge toward their integration into practical devices. During the last few years we reported the growth of perfectly aligned, millimeter-long, horizontal NWs of GaN [1], ZnO [2], ZnSe [3], ZnTe [4], CdSe [5], CdS [6], CsPbBr3 [7] and other materials, with controlled crystallographic orientations on different planes of sapphire [1-7], SiC [8], quartz [9], and spinel [10]. The growth directions and crystallographic orientation of the NWs are controlled by their epitaxial relationship with the substrate, as well as by a graphoepitaxial effect that guides their growth along surface steps and grooves. As a proof of concept for future applications, we demonstrated the massively parallel “self-integration” of NWs into circuits via guided growth [11]. Here we will show how guided nanowires with complex morphologies and heterostructures can be used for the bottom-up fabrication of nano-optoelectronic devices, including photodetectors, photodiodes and photovoltaic cells [12].

References

9:00 AM NM03.06.02 Crystallographic Mapping of Guided Nanowires by Second-Harmonic Generation Polarimetry Regev Ben-Zvi1, Lior Neeman1, Dan Oron2 and Ernesto Joselevich1, 3Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; 3Complex Systems, Weizmann Institute of Science, Rehovot, Israel.

The growth of horizontal nanowires (NWs) guided by epitaxial and graphoepitaxial relations with the substrate is becoming increasingly attractive owing to the possibility of controlling their position, direction and crystallographic orientation. In guided NWs, as opposed to the extensively characterized vertically grown NWs, there is an increasing need for understanding the relation between structure and properties, specifically the role of the epitaxial relation with the substrate. Furthermore, the uniformity of crystallographic orientation along guided NWs and over the substrate has yet to be checked. Here we perform highly sensitive second-harmonic generation (SHG) polarimetry of polar and nonpolar guided ZnO NWs. We optically map large areas on the substrate in a nondestructive way, and find that the crystallographic orientations of the guided NWs are highly selective and specific for each growth direction with respect to the substrate lattice. In addition, we perform SHG polarimetry along individual NWs and find that the crystallographic orientation is preserved along the NW in both polar and nonpolar NWs. However, while polar NWs show highly uniform SHG along their axis, nonpolar NWs show a significant change in the local nonlinear susceptibility along a few microns, reflected in a reduction of 40% in the ratio of the SHG along different crystal axes. We suggest that these differences may be related to strain accumulation along the nonpolar wires. We find that SHG polarimetry to be a powerful tool to study both selectivity and uniformity of crystallographic orientations of guided NWs with different epitaxial relations.

9:15 AM NM03.06.03 Direct Integration of Multifunctional Nanowire and Nanofiber Networks on a Single Chip for Selective Gas Detection David Graf, Ashish Lepcha, Aida Raauf, Albert Queraltó, Rishabh Garg, Matthias Grosch, Thomas Fischer and Sanjay Mathur; University of Cologne-Inorganic Chemistry, Cologne, Germany.

The high surface-to-volume ratio of nanowires as well as the typically high crystallinity and directional charge carrier transport of metal oxide NWs are beneficial for the use in chemo-resistive gas sensors. Semiconducting n-type SnO2 nanowire networks have been site-selectively deposited on gas sensor platforms by chemical vapor deposition (CVD) approach based on a catalyst-mediated vapor-liquid-solid (VLS) growth mechanism. Compared to classical screen-printed SnO2 sensors, the direct integrated nanowire network demonstrated superior sensing performance in terms of sensitivity and response time. To date, selective detection of target gas molecules in complex gaseous compositions or in presence of high humidity is quite challenging. We improved the lack of selectivity toward gaseous species through surface decoration with metal oxide (VO2, Nb2O5) or noble metal (Rh, Pd) nanoparticles by a second CVD step and investigated the sensing mechanism. For this approach, we developed tailored volatile molecular precursors based on bidentate heteroarylalkenolate and enaminonate ligands. To improve the sensing performance under high humidity, which is very important for clinical breath analyses, we electrospun a nanofiber mesh consists of zeolite microcrystals (Mordenite, ZSM-5 and BEA) embedded in thermal stable polymer on top of the sensor. The hydrophilic porous nanofiber mesh acts as water vapor adsorbing or selective filter material to improve the sensitivity and selectivity. Moreover, we fabricate ternary metal oxide (BiFeO3, LaFeO3, PrNbO4 and Sn2Nd2O7) nanofibers on top of the sensor platform, which exhibit excellent selective sensing characteristics. The selective synthesis of the perovskite and pyrochlore materials were achieved by deploying bimetallic alkoxide precursors. Gas sensing measurements demonstrated the highly sensitivity towards SO2 below 0.5 ppm of ferrite materials and the selective H2 detection of pyrochlore Sn2Nd2O7.

9:30 AM NM03.06.04 Controlling Morphology and Composition of Self-Assembled InAsP and InAlAs Nanowires on Monolayer Graphene Substrates Mohadesheh A. Baboli1, 2, Michael A. Slocum2, 3, Alessandro Giussani2, Hyun Kum2, 4, Thomas S. Wilhelm1, 2, Stephen J. Polly2, Seth Hubbard1, 2 and Parsian Mohseni1, 2; 1Microsystems Engineering, Rochester Institute of Technology, Rochester, New York, United States; 2NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York, United States; 3Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio, United States; 4Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Monolithic integration of high crystal quality III-V semiconductors with two-dimensional (2-D) monolayer nanosheets can be achieved via growth of high aspect ratio nanowire (NW) structures using the pseudo-van der Waals epitaxy (vdWE) approach. In this regime, growth of dislocation-free NWs is accommodated by weak vdW forces between a 2-D nanomaterial, with no surface dangling bonds, and the III-V epilayer. However, the monolayer substrate offers limited possibilities for arrangement of the overlaying crystal based on the lattice constant of the III-V compound, the finite number of atomic positions on the 2-D surface, and the limitations imposed by the binding energy of adatoms at available residence sites. Here, we present self-assembly of vertically-aligned, high aspect ratio InAsP1-x, InAlx,As, and core-shell InAsP-InP NW arrays on single layer graphene (SLG) via vdWE.
using metalorganic chemical vapor deposition (MOCVD). By altering growth temperature \( (T_G) \) and molar flow ratio of precursors \( (\rho) \), compositional and morphological tuning of hybrid ternary III-V on-2-D nanomaterials systems is realized. For InAsP \( \rho \) NWs, the hydride precursor molar flow ratio \( (\rho_{H_2}) \) is varied from 0 to 0.98 at growth temperatures of 650 °C and 700 °C. The morphology and number density of NWs, as well as parasitic island coverage, are observed to be independent of \( \rho_{H_2} \). Although growth at \( T_G = 700 ^\circ C \) enables higher solid-phase P-incorporation, increasing temperature also adversely affects NW number density. To overcome this challenge, heterostructured InAsP/InAs NWs are grown in a two-temperature growth regime with InAs bases formed at \( T_{G,base} = 650 ^\circ C \), followed by InAsP segments formed at elevated \( T_{G,shell} \geq 700 ^\circ C \). This approach permits growth of high number density NWs with InAsP \( \rho \) segments having composition \( y \approx 0.80 \). Higher P-content segments are grown as shell layers on existing InAsP core segments. Next, the dependences of InAl\(_x\)As NW morphology, verticality, and number density on growth temperature and composition are investigated. At constant \( T_G = 600 ^\circ C \), composition dependences are studied by varying the metalorganic precursor molar flow ratio \( (\rho_{H_2}) \) between 0 and 0.75. Similarly, at constant \( \rho_{H_2} = 0.50 ^\circ C \), temperature dependences are studied in the 600 °C ≤ \( T_G \) ≤ 700 °C range. Optimal conditions are presented for uniform-diameter and vertical InAlAs NWs at \( T_G = 650 ^\circ C \) and \( \rho_{H_2} = 0.50 \). A growth mechanism for vdWE of ternary InAsP and InAlAs NWs is proposed to relate the observed trends for NW number density and morphology to lattice coordination and binding energy of growth species on SLG. We anticipate the use of such hybrid III-V-on-2-D nanomaterials in low-cost and flexible optoelectronic device applications.

9:45 AM NM03.06.05
Surface-Guided Halide-Perovskite Nanowires—New Building Blocks with Unusual Properties for Optoelectronics

Ronit Popovitz-Biro, Lothar Houben and Ernesto Joselevich; Weizmann Institute of Science, Rehovot, Israel.

Metal-halide perovskites (MHPs) are remarkable optoelectronic materials due to a rare combination of low-cost fabrication and exceptional properties. Recently, nanowires of MHPs have emerged as promising building blocks for various optoelectronic application and as an intriguing one-dimensional system for investigating and modeling fundamental MHPs properties. Both for research and applications, controlled and well-defined nanowire systems are highly advantageous, and at times a real necessity. Here we employ a surface-guided approach to grow horizontally aligned arrays of single-crystal CsPbBr\(_3\) nanowires. The nanowires grow with well-defined facets and a uniform crystallographic orientation to form aligned arrays with 6-fold and 2-fold symmetries. We highlight the advantages of such arrays for fundamental research, as we investigate their optical properties, and present a unique perspective on photon-transport processes and anomalous diameter-dependent emission shift. In addition, we demonstrate the potential of planar MHPs nanowires as building blocks for functional devices by fabricating photodetectors that exhibit faster response times than any CsPbBr\(_3\)-based photodetectors reported so far. Arrays of horizontally aligned MHPs nanowires are a promising platform for investigating the intriguing properties and potential applications of these unique materials.

10:00 AM BREAK

SESSION NM03.07: Selected Area Growth and Nanowire Arrays

Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Back Bay D

10:30 AM *NM03.07.01
GaN Nanowire Devices Grown with Selective Area Epitaxy

Kris A. Bertness; National Institute of Standards and Technology, Boulder, Colorado, United States.

We have developed a highly flexible process for selective-area growth of GaN nanowires on silicon substrates with polarity-controlled buffer layers. With this process, fully selective nanowire growth can be obtained by molecular beam epitaxy in both dense arrays or for isolated nanowires, enabling a wide range of device architectures. Self-shadowing of growth fluxes can be eliminated in isolated nanowires, allowing for synthesis of junctions and heterostructures with radial geometries. In this talk, we examine first the optical and electrical characteristics of nanowire LEDs grown by this technique, which have an n-type core and a conformal p-type shell layer. Electrical contact is made to the core through the GaN nucleation layer and to the p-type shell via a top surface metallization layer, allowing for measurement of single nanowires or parallel measurement of multiple nanowires. Under forward bias, these nanowire LEDs produce electroluminescence at 380 nm, corresponding to donor-acceptor-pair recombination from electrons injected in the p-type shell. In this design, however, the shell thickness is comparable to the minority carrier diffusion length so that most electrons pass through the p-type shell to the contact without recombining with holes, and efficiencies are low. We have demonstrated dramatically improved light emission by introducing heterostructures such as replacing GaN with AlGaN in the p-type shell. We will also discuss using selective epitaxy to place these nanowire LEDs on AFM cantilever tips by growing and processing the LEDs on silicon-on-insulator substrates and then etching cantilevers out of the substrate. Finally, we will present data that suggests the array structure produces strong surface phonon-polariton interactions.

11:00 AM NM03.07.02
Selective Area Growth of In\(_{x}\)Ga\(_{1-x}\)As Nanowires on HfO\(_2\) Templates for Highly Scaled nMOS Devices

Paloma Tejedor; Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas, Madrid, Spain.

The replacement of the strained Si channel in n-metal-oxide-semiconductor-field-effect-transistors with III-V compound semiconductors, particularly In\(_{x}\)Ga\(_{1-x}\)As, is considered nowadays the best alternative to improve the drive current at low supply voltages in high-performance CMOS applications at sub-10 nm-technology nodes. As the device is scaled down, the reduction of the source/drain contact geometries results in current crowding and a significant increase in access resistance. Mitigating this effect is hence one of the most difficult challenges to fabricate highly scaled III-V devices. In this work, we present the development of a self-aligned process based on selective epitaxial growth of In\(_{x}\)Ga\(_{1-x}\)As \((x \approx 0.1)\) raised source and drain nanowire structures on etched recessed areas adjacent to a nanopatterned high-k dielectric, i.e. HfO\(_2\), using conventional and atomic H-assisted MBE as key process to integrate high mobility III-V materials in 3D device architectures.

In the first part of this work we studied the interaction of atomic H with the surface of HfO\(_2\) prior to the epitaxial process in ultra-high vacuum, by using AFM, ToF-SIMS, ARXPS and HR-TEM. The study showed that in the 350-400 °C temperature range in-situ cleaning with atomic H effectively reduces the concentration of the major impurities on the HfO\(_2\) surface, which occurs through a layer-by-layer etching reaction with activation energy of 23 Kcal/mol\(^1\). The second part of the work was devoted to the investigation of several fundamental aspects of the selective epitaxial growth of In\(_{x}\)Ga\(_{1-x}\)As nanowires on HfO\(_2\)/GaAs templates fabricated by interferometric lithography. Special emphasis has been placed on the impact of atomic H on the process window for III-V selective growth, the nucleation and growth dynamics, the relief of lattice mismatch in the open trenches and the structure and composition of the epi-layers grown on the prepatterned substrates. Selective growth has been observed for all values of \( x \) between 0 and 1. HRTEM images have revealed the
conformality of the growth and the absence of microtrench formation near the HfO2 mask edges. Our results have demonstrated that the use of atomic H lowers the temperature process window for selective growth down to 400 °C, due to the lower energy of nucleation required on the H-terminated III-V surface and the blocking of HfO2 active sites by H, which inhibits the nucleation of the III-V compound on the masked areas. HRXRD measurements have shown that the best crystal quality corresponds to InGaAs samples grown at 500 °C, with little differences between samples grown by H-assisted and conventional MBE. Finally, those InGaAs alloys grown on H-treated HfO2 patterned substrates exhibit a higher uniformity in chemical composition (absence of In segregation) and full strain relaxation for x≤0.5.

Financial support by the Spanish Government under grant MAT2016-78433 and by CSIC under grant 2018E058 is greatly acknowledged.

11:15 AM NM03.07.03
Ordered GaAs p-n Radial Junction Nanowire Arrays on Silicon Wonjong Kim, Léo Balembois, Jelena Vukajlovic-Plestina, Gozde Tutuncuoglu, Dmitry Mikulik, Pablo Romero, Lucas Guniat, Martin Friedel and Anna Fontcuberta i Morral; EPFL, Lausanne, Switzerland.

Semiconducting nanowires (NWs) are expected to play an important role on third-generation photovoltaics. The vertical configuration of the NW is shown to be promising for enhancing absorption cross-section due to resonances and light-concentrating effect1,2. In this work, we present in-depth studies on self-assisted GaAs NW arrays grown on silicon by molecular beam epitaxy. Reproducible high yield (> 85 %) of vertical NW arrays3 enables us systematic doping studies on our GaAs NW arrays. Although there are several groups reporting NW array based photovoltaic devices4,5, to date there have been very few reports on MBE grown ordered GaAs NW array on silicon6. We will present our latest results on our GaAs NW array-based devices and discuss the growth and doping mechanism, comparing our findings to previous results obtained for self-assembled GaAs NWs7,8. We demonstrate experimentally the effect of device performances on inter-wire spacing, doping concentration of the NW core and shell within the array system which can be of fundamental importance for the realization of NW based photovoltaic devices.


11:30 AM NM03.07.04
The Geode Process—A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanowires Martiza Mujica, Gozde Tutuncuoglu, Victor Breedveld, Sven H. Behrens and Michael A. Filler; Georgia Institute of Technology, Atlanta, Georgia, United States.

Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, unfortunately, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize functionally-encoded semiconductor nanowires at throughput orders of magnitude beyond the state-of-the art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica microcapsules, whose interior surface serves as a high-surface area growth substrate. Microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microparticle structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires with programmable dopant profiles on the microcapsule interior, which not only shows the versatility of the process, but also allows the impact of precursor gas transport limitations to be characterized.

11:45 AM NM03.07.05
In Situ Reflectometry Measurements and Simulations of Highly Oriented Vertical VLS Growth of Germanium Nanowire Assemblies Michael Braun1, Lucas Guniat1, Anna Fontcuberta i Morral1 and Paul C. McIntyre1; 1Laboratoire des matériaux Semiconducteurs, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland; 2Materials Science and Engineering, Stanford University, Stanford, California, United States.

Aligned arrays of semiconducting nanowires have drawn significant interest, in part because of their relevance for end-of-roadmap electronic and nanoscale optoelectronic devices. In all these applications, the in-situ analysis of nanowire growth is advantageous, both for understanding fundamental aspects of the growth kinetics and for process monitoring. While several methods have been commercialized for thin film growth monitoring, laser reflectometry analysis of nanowire growth is a more novel application. In this study, we report an in-situ method of monitoring the vapor-liquid-solid (VLS) growth of germanium nanowires via a simple laser and detector system, operating at an oblique angle. The monitoring system is mounted on a lamp-heated, cold-wall chemical vapor deposition (CVD) chamber. Previous studies have reported on either vertical reflection from nano-patterned nanowire arrays, or grazing reflection from highly non-vertical random nanowire arrays with a broad range of diameters. In contrast, we have grown highly vertical (≥ 99.9 %) randomly dispersed nanowire arrays with a range of controlled diameters and areal densities, and at a range of growth pressures. These conditions enable us to analyze the nucleation time, growth quality, and growth rate of the same samples for growth times beyond 30 minutes. Analysis was based on fitting the exponential decay of the signal and oscillation period of the successive constructive/destructive interference effects. The experimental measurements are compared to simulation via a novel evolution of numerical finite difference frequency domain (FDFD) simulations as a function of growth time. These simulations are performed in two and three dimensions as well as with supercells of nanowires of non-identical spacing. The supercells attempt to separate artifacts from photonic crystal effects of the periodic simulation compared to the random experimental arrays. Simulation results are compared to a simple thin film effective-index model as a gauge of the impact from resonant modes and enhanced scattering from nanoscale features.

1:30 PM *NM03.08.01
Thermal Phonon Engineering with Nanowires Martin Maldovan; Georgia Institute of Technology, Atlanta, Georgia, United States.

In recent decades, the improved ability to manipulate electrons and photons has made possible remarkable technological developments in electronic, optoelectronic, and energy applications. Contrarily to electrons and photons, a similar degree of control over thermal phonons (i.e., thermal lattice vibrations) has not yet been achieved. Considering the remarkable success on using electronic and photonic materials to manipulate electrons and light, it is certainly valuable to extend this knowledge to lattice thermal vibrations and create new approaches to manipulate heat flow.

In this talk, I discuss semiconductor nanowires (NWs) as a powerful material platform for manipulation of thermal phonons and control of heat flow. I will show how the rational design of structural and material properties of nanowires can be used to tailor the thermal phonon transport properties. Nanowire atomic structure and composition, surface characteristics, porosity, and morphology are among the physical variables that can be exploited to control thermal energy transfer. This “thermal phonon engineering” of nanowires can be leveraged to achieve unprecedented control over nanoscale heat conduction.

2:00 PM NM03.08.02
Thermal Transport in Si Nanowires with Axially Modulated Diameters Gozde Tutuncuoglu1, Abhinav Malhotra2, Sampath Kommandur2, Shannon Yee1, Martin Maldovan1,3 and Michael A. Filler1; 1Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2G. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 3School of Physics, Georgia Institute of Technology, Atlanta, Georgia, United States.

Semiconductor nanowires, because their nanoscale structure can be precisely engineered, offer exciting opportunities to control thermal transport. Despite initial demonstrations that morphology, diameter, and surface roughness can modify the thermal conductivity of Si nanowires, these effects remain poorly understood and difficult to rationally engineer. In this work, we combine state-of-the-art nanowire synthesis, thermal transport characterization, and modeling to understand, predict, and control heat transport in Si nanowires. The synthesis of nanowires with axially-modulated diameters is accomplished by combining the vapor-liquid-solid (VLS) mechanism with the post-growth selective etching of axially-encoded doped segments. A single nanowire, suspended four-bridge thermal transport method eliminates the impact of contact resistance on the measured thermal conductance. Simulations using the complete frequency- and temperature-dependent solution to the phonon-Boltzmann equation permit an accurate description of phonon-surface interactions. We find that thermal conductivity decreases as the modulated diameter decreases and it can be further engineered by the aspect ratio of the diameter-modulated section. We also determine the relative importance of backscattering and wave effects. By connecting local nanowire diameter and morphology to phonon transport and the resulting thermal properties, our work paves the way for the rational design of future thermal materials.

2:15 PM NM03.08.03
Understanding the Kink Effect on Thermal Transport Through Nanowires Yang Zhao, Lin Yang, Qian Zhang and Deyu Li; Vanderbilt University, Nashville, Tennessee, United States.

Transport mechanisms underlying heat transfer in micro/nanoscale structures are of fundamental interest and critical for a broad range of applications, including thermoelectrics, electronic device thermal management, and data storage. In the past two decades, the effects of the characteristic size, surface roughness and acoustic phonon softening on thermal transport through nanostructures have been studied, which provides powerful strategies to alter the thermal transport properties of nanomaterials. Here we show that kinked morphology could be a new degree of freedom to tune thermal conduction in nanowires and further disclose the phonon transport mechanisms in kinked nanowires.

From experimental studies, we found that the thermal conductivity of kinked boron carbide nanowires can be reduced by up to 36% as compared to corresponding straight nanowires of similar diameters and carbon concentrations. Analysis indicates that this level of reduction means that the kink structure poses ~30 times larger thermal resistance than the corresponding straight nanowire segment of an equivalent length. The pronounced kink resistance is attributed to the strong backscattering of highly focused phonons in the kink region, which is supported by the interesting discovery that defects in the kink region, instead of posing resistance, actually assist phonons passing through the kink by increasing phonon scattering rates at the kink.

To further explore the kink effect, we further conducted measurements on kinked silicon nanoribbons with multiple kink structures. Compared to boron carbide nanowires, a single kink in the silicon nanoribbon poses only ~1.2 times thermal resistance because of its significantly lower elastic anisotropy. However, a maximum thermal conductivity reduction of 21% can be achieved by having multiple kinks in the silicon nanoribbons.

To further disclose phonon transport mechanisms in kinked nanowires, we performed non-equilibrium molecular dynamics simulations to model thermal transport through straight and kinked silicon nanowires. Results clearly demonstrate that back scattering of phonons from the free surface of the kinked region is the underlying mechanism for the additional kink resistance. Furthermore, by adding heavy isotope atoms into the kink region, we verify the experimental observation that defects can indeed assist phonon transmission through the kink region via scattering phonons into the other branch of the kink.

2:30 PM NM03.08.04
Significant Effects of Electron-Phonon Interactions on the Lattice Thermal Conductivity of Quasi-1D NbSe2 Nanowires Lin Yang1, Yi Tao2, Jinyu Liu1, Chenhan Liu1, Qian Zhang1, Yang Zhao1, Qijiang Mao1, Yunfei Chen1 and Deyu Li1; 1School of Mechanical Engineering, Southeast University, Nanjing, China; 2Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana, United States.

The interaction between electrons and phonons is a fundamental process in solids and plays critical roles in various physical phenomena. While the effects of electron-phonon (e-ph) interactions on electronic properties of condensed matter have been extensively studied, its contribution to lattice thermal conductivity is still in debate and quantitative analyses have been largely lacking. Through systematic studies of the transport properties of niobium triselenide (NbSe2) nanowires, we show the significant influence of e-ph coupling on the lattice thermal conductivity ($\kappa_L$), which provides direct evidence on the importance of e-phonon coupling in $\kappa_L$.

NbSe2 belongs to a class of van der Waals (vdW) materials with quasi-one-dimensional (quasi-1D) crystal structures, where covalently-bonded molecular chains assemble together via vdW forces. Owing to the restricted dimensionality, the density of free electrons in NbSe2 spontaneously develops a wave-like variation due to a lattice distortion when temperature drops below a critical value ($T_{CDW}$), which is called charge density wave (CDW). The variation of charge carrier concentration upon the onset of CDW results in the spontaneous change of e-ph coupling strength, which is reflected as the abnormal peaks in the extracted lattice thermal conductivity.
To confirm that e-ph interactions cause the distinct signatures in $\kappa_e$, we combine first-principles calculations with a phenomenological model to extract the contribution of e-ph scattering. Extensive modeling efforts show that without considering e-ph scattering, $\kappa_e$ follows the typical shape for crystalline materials with a smooth profile in the whole temperature range. However, with the e-ph scattering term introduced, the modeled $\kappa_e$ can fit the experimental data remarkably well. The perfect match of the shape for the two abnormal peaks strongly indicate that it is indeed the e-ph scattering that leads to the distinct signature in $\kappa_e$. Moreover, for nanowires with smaller transverse dimensions, the peaks in $\kappa_e$ are less significant due to competing scattering mechanisms, which is also well captured by the theoretical model.

The observed abnormal peaks in $\kappa_e$ provide solid evidence to answer the long-standing, fundamental questions of whether and how e-ph interactions affect phonon transport. Given the ubiquitous nature of e-ph coupling in semiconductors and metals, this discovery will lead to new understanding of transport processes in microelectronic, photovoltaic and optoelectronic devices, which will enable further improved device design and performance.

SESSION NM03.09: Transport and Energy Conversion
Session Chairs: Michael A. Filler and Martin Maldovan
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Back Bay D

3:00 PM BREAK

3:30 PM *NM03.09.01

It has been predicted [1,2] that thermoelectric energy conversion based on ideal energy filters can, in principle, be performed near thermodynamically ideal efficiency limits, but this prediction has never been experimentally verified. Using a quantum dot (QD) embedded into a semiconductor nanowire, we directly measured the engine’s steady state electric power output. Taking into account also the calculated electronic heat flow, we find that at maximum power conditions the electronic efficiency is in agreement with the Curzon-Ahlborn efficiency, and that the overall maximum electronic efficiency is in excess of 70% of Carnot efficiency. [3] I will describe how these results may be used to enhance energy conversion efficiency also in solar cells, by harvesting non-equilibrium electronic energy based on photothermoelectric principles [4], and will show first results demonstrating a high open-circuit voltage [5].


4:00 PM NM03.09.02
Transport Phenomena and Thermoelectric Properties in Modulation-Doped GaAs/AlGaAs Core-Sphere Nanowires Sergei Past, Jonathan Becker, Damon J. Carrad, Dominik Ibler, Jakob Seidl, Anton Faustmann, Bernhard Lotisch, Gerhard Abstreiter, Jonathan Finley and Gregor Koblmueller; Walter Schottky Institut and Physik Department, Technische Universität München, Garching, Germany.

Generating electricity from waste heat has the potential to have a noticeable impact on our ecological footprint, provided the conversion efficiency is high enough. Semiconductor nanowires (NW) are central to this effort since electrical and thermal effects can theoretically be decoupled in 1D systems, which will enable further improved device design and performance.

A suitable platform for circumventing this problem is presented in this work, employing radial modulation-doped core-shell NWs. Our studies are based on Si-delta doped high-mobility GaAs/AlGaAs core-shell NW heterostructures, which hold the potential for both high-performance steep-slope NW-field...
effect transistors (NW-FETs) [1] and for in-depth investigations of low-temperature quantum transport [2]. Top-gated NW-FETs were used to study the quantum transport characteristics at low temperature (4–7 K) on a set of core-shell NWs with different GaAs core diameter. During pinch-off we observe clear plateau-like signatures, consistent with the depopulation of quasi-1D subbands as confirmed by correlated simulations for the range of core diameters investigated [2]. Subsequent Seebeck effect measurements show distinct spikes in the Seebeck voltage as a function of applied gate voltage and different heater powers which correspond to the 1D-like plateaus in conductivity [3]. Furthermore, thermal conductivity measurements were carried out on suspended NWs using Raman spectroscopy [4], to probe the effect of the surrounding AlGaAs barrier on phonon scattering and reductions in the thermal conductivity of GaAs NWs at room temperature. We found that Si-delta-doped GaAs/AlGaAs core-shell NWs exhibit reduced thermal conductivity with respect to their uncapped pure GaAs NW counterpart, being in the range between 7 and 12 W/(m K)[3]. Ongoing experiments aim to extract systematically the Seebeck coefficient to ultimately provide quantitative results for the figure of merit ZT.

References


4:15 PM NM03.09.03
Flexible Nanowire LED—Optimization of White Light Based on Phosphor Down Conversion
Nunoo Amador Méndez1, Nan Guan1, Dai Xing1, Hezhi Zhang1, Akamsha Kapoor2, Catherine Bougerol3, Lorenzo Manconi4, Martin Foldyna2, Subrata Das5, Sudipta Som,6 François Julien,7 Joel Eymery7, Christophe Durand6 and Maria Tchernycheva1; 1Center of Nanoscience and Nanotechnology, Orsay, France; 2Université Grenoble Alpes CEA, Grenoble, France; 3Université Grenoble Alpes CNRS, Grenoble, France; 4LIPCM-CNRS, Palaiseau, France; 5National Institute for Interdisciplinary Science and Technology, Kerala, India; 6National Taiwan University, Taipei, Taiwan.

Flexible light sources and displays are key emerging technologies highlighted in the Photonics 2020 roadmap. Today, this market is dominated by organic semiconductors. Despite their low cost, the organic devices cannot compete with inorganic devices in terms of lifetime and efficiency. Still the mechanical rigidity of the inorganic semiconductor thin films limits their application in the areas where bended surfaces or flexible devices are required. To make them flexible, the emitter size should be reduced.

Semiconductor nanowires attract a strong attention for fabricating LEDs with new functionalities. The high material quality of the nanowires results in advantageous optical and electrical properties. In addition, they have a small footprint and are mechanically flexible. Therefore, semiconductor nanowires are excellent candidates for optoelectronic applications requiring high efficiency and mechanical flexibility.

In this presentation, we report the fabrication and characterization of flexible white nanowire LEDs [1]. The devices rely on the blue electroluminescence from the InGaN/GaN nanowires, which is downconverted by micro-sized phosphors in a PDMS layer. The nanowires are grown by MOVPE technique without catalyst on c-sapphire substrates. Seven core/shell InGaN/GaN quantum wells are radially overgrown around the n-doped GaN stems and covered with a p-doped GaN shell. To process flexible LEDs, semiconductor nanowires are encapsulated into a PDMS, mechanically peeled-off from their growth substrate and the resulting membrane is contacted with a flexible transparent silver nanowire mesh. A PDMS cap doped with micro-phosphors is added on top of the nanowire LED. To optimize the quality of the white light (namely, the chromaticity coordinates, the CCT and CRI), different phosphors were investigated. Namely, orange-emitting Sr1.95Eu0.04Tb0.01Si5N8 (1 wt% Sr3N2) coated by 2.5 wt% Mg(OH)2 and yellow Y2.95Ce0.05Al5O12 (1 wt% BaF2) phosphors were used and different thicknesses of the capping layer were analyzed. The resulting electroluminescence of the flexible devices was recorded under different injection current. The pumping blue nanowire LED wavelengths was also changed from λ=430 to λ=460 nm by adjusting the In content in the quantum wells. The chromaticity coordinates of the white LED previously reported [1] were x=0.3011 and y=0.4688 with a CCT and CRI of 6306 K and 54, respectively. Increasing the mass aspect ratio of micro-phosphors/PDMS of the capping layer we reached a CRI value of 91. An overall improvement of the white light quality is achieved by optimizing the pump wavelength and the type of micro-phosphors. The best-achieved values were located in x=0.3028 and y=0.3577 with a CCT and CRI of 6629 K and 88, respectively.

4:30 PM NM03.09.04
Surface Passivation Study of Single p-i-n Doped InP Nanowire Solar Cells Using EBIC
Lucas Hrachowina and Magnus Borgstrom; Solid State Physics, Lund University, Lund, Sweden.

Photovoltaics enable the direct conversion of solar energy to electricity and thus play an important role in sustainable energy production. Nanowires have several superior properties compared to their bulk material and with a specific pattern of a nanowire array it is possible to reach similar efficiencies like thin films by using only a fraction of the material. In order to utilise the potential of nanowire solar cells, electron-beam-induced current (EBIC) has been used to characterise as-grown wires. However, it has been shown that due to the high surface-to-volume ratio the surface passivation of InP nanowires plays a crucial role, even though the surface recombination velocity of native InP is quite low.

In this study, as-grown p-i-n doped single InP nanowire solar cells are compared with nanowires passivated by a selection of atomic layer deposited oxides in a nanoprobe system inside a SEM. In this way, key parameters for solar cells can be measured without the need to process samples into functional solar cells. Furthermore, EBIC is used to optimise the junction in the nanowires for immediate feedback on the carrier generation. The gathered information will extend knowledge about InP surface passivation and help to manufacture InP nanowire solar cells with higher efficiencies.

4:45 PM NM03.09.05
Global Optimization of GaAs Nanowire Solar Cells on Silicon
Kyle W. Robertson1, Ray R. LaPierre2 and Jacob J. Krich2; 1Physics, University of Ottawa, Ottawa, Ontario, Canada; 2Engineering Physics, McMaster University, Hamilton, Ontario, Canada.

The efficiency of nanowire solar cells is particularly sensitive to device parameters including the nanowire height, diameter, doping levels, and passivation, requiring careful optimization to enable the highest efficiencies. We present a coupled opto-electronic model of an array of passivated axial-junction GaAs nanowire solar cells on silicon substrates. For the optical model we utilize a modified formulation of rigorous coupled wave analysis (RCWA), which we call the continuous variable formulation (CVF). The CVF is designed to reduce the Gibbs phenomenon and yield more accurate local fields relative to conventional RCWA implementations. From the results of the optical model, we extract carrier generation rates, which are fed into the industry-standard self-consistent coupled Poisson and drift-diffusion solver, Synopsys Sentaurus. We use this combined wave-optics and electrical model to perform fully automated, global optimization of device parameters. We show the efficiency gains that are possible by optimizing the nanowire diameter, array period,
Silicon nanowires and fibers are conventionally prepared through chemical vapor deposition growth off of a metal catalyst at elevated substrate temperature. Such structures are especially of interest for lithium ion battery anodes and may also be useful for chemical sensing, in both cases due to their very high surface area. In this report we present on the fabrication of nanoscale silicon fibers grown under highly unusual conditions. We find that, following nanosecond laser ablation of a silicon surface in SF6 gas, an extended soak in the chamber for several months at room temperature results in the formation of a dense “spaghetti”-like network of silicon nanofibers all over the exposed surface of the wafer, including outside of the laser-irradiated areas. These fibers contain oxygen and fluorine, and show evidence of aluminum-containing spherical particles at their tips. Removal of the wafer shortly after irradiation shows no evidence of fibers, indicating that the structures are not formed during the laser irradiation. Moreover, other specific conditions must be met: the experiment must be performed in an aluminum chamber, the specimen must sit in the same environment the entire time, and the total irradiation must be sufficiently long. We posit a mechanism whereby the laser ablation forms a long-lived radial containing silicon and fluorine, which etches aluminum from the chamber walls. This then deposits on the silicon surface and acts as a catalyst for nanowire growth. We report on experimental support for this model obtained from gas-phase measurements at several post-ablation intervals.

Highly Stable Copper Nanowire Network Transparent Electrodes Sevinç Polat Genlik1, Dogançan Tigan1, Sahin Coskun1, Kerem E. Ercan2, Yusuf Kocak3, Emrah Ozensoy4 and Huseu E. Unalan1; 1Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; 2Department of Chemistry, Bilkent University, Ankara, Turkey.

Silver nanowires (Cu NWs), on the other hand, are not far behind the silver nanowires and hold great promise due to their lower cost and comparable electrical conductivity in the network form. Oxidation is the biggest barrier in front of the large scale utilization of Cu NWs. Bulk copper itself is also susceptible to oxidation and several methods have been proposed for its protection. Inspired from bulk copper, in this work, we utilized benzotriazole (BTA) as an organic corrosion inhibitor to improve the stability of Cu NWs. High aspect ratio Cu NWs are synthesized by an environmentally benign hydrothermal method and highly transparent and conducting Cu NW networks (20 ohm/sq sheet resistance at a transmittance of 88%) are fabricated through spray deposition. Following the deposition of Cu NW networks, they are spin coated with a solution of BTA for passivation. Long term stability of the passivated electrodes under ambient and severe humidity conditions are systematically investigated and compared to that of bare control samples. It is found that BTA inhibits the formation of an oxide layer on Cu NWs for at least one year of storage under ambient conditions. In addition, no significant change in sheet resistance of passivated Cu NW networks is observed (R/R0 < 1.1). High humidity conditions accelerated the degradation of bare Cu NW network electrodes and they become insulating after 2 days under 70% RH condition, while they become insulating after a day under 90% RH. On the other hand, initial sheet resistance of BTA protected samples is maintained up to 10 days under 70% RH condition, while it is maintained for 7 days under 90% RH. Moreover, attenuated total reflectance infrared spectroscopy (ATR-IR) is used to monitor the thermal stability of BTA for the protection of Cu NW networks and BTA is found to be thermally stable up to 125 °C. All in all, this highly effective and simple strategy to improve the stability of Cu NW networks will certainly open new avenues for their large scale utilization in various optoelectronic devices.
To summarize, we successfully fabricated type-II p-GaAsSb/n-InAs NWs with high uniformity. These results are promising to develop high-performance NW devices. This work was supported by JST CREST Grant Number JPMJCR16Q3, Japan.

References

NM03.10.04

Ultralight Gold Nanowire Aerogels Fang Gai, Alyssa L. Troksa, Tyler M. Fears, Tom Braun, Michael Nielsen, Sergei Kucheyev, Theodore Baumann, T. Yong Han and Michael Bagge-Hansen; Lawrence Livermore National Laboratory, Livermore, California, United States.

We report the first ultralight gold aerogel monoliths with tunable densities down to single-digit mg/cc. Free-standing aerogels are fabricated by freeze-casting of gold nanowire suspensions to produce gold aerogels with densities between 6 to 40 mg/cc. Electron microscope studies revealed that the aerogels consist of interconnected, high-aspect ratio gold nanowires, with diameters of ~5 nm, forming a robust percolated network. Energy-dispersive X-ray spectroscopy together with X-ray photoelectron spectroscopy confirm that the aerogels are comprised of high-purity gold. We further investigated the effect of altering the initial solvent composition on the resulting pore structures of gold aerogels, as exemplified by aqueous and water/tert-butanol solutions. The results show an abrupt transition from hierarchical porosity across different length scales to a uniform, nanosized pore geometry. We also measured distinct mechanical properties between the two structures. Compared to previous methods of gold foam fabrication, our method does not involve the use of foreign organic scaffolds or metal alloys to achieve structural robustness, and therefore enables potential applications where high-purity, ultralight gold materials are required such as catalysis, electrode materials and sensors. This work was performed under the auspices of the U.S. Department of Energy Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NM03.10.05

The Effect of Misfit Strain on Phase Transition Behaviors and Electron Transport Properties in Vanadium Dioxide Low-Dimensional Structures Yangping Zhang1, 2, Weiming Xiong1, 2 and Yue Zheng1, 2; 1State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou, China; 2Micro and Nano Physics and Mechanics Research Laboratory, Sun Yat-sen University, Guangzhou, China.

Vanadium dioxide (VO₂), as a typical metal-insulator transition (MIT) material, exhibits a transition from insulating (M1, M2 and T) to metallic (R) phase. The transition accompanied by the great changes in conductance, optical transmittance and mechanical properties, which make it has potential applications in electrical and optical switches, etc. When the structure of VO₂ reduces into low dimension, (e.g., nanowire (NW), nanobelt (NB), nanodot (ND), etc.), some novel physical properties different from its bulk material could be observed because of the size and surface/interface effects. However, the MIT behavior and electron transport properties of VO₂ low-dimensional structures (LDSs), especially the LDSs grown on the substrate and affected by the mismatch strain, are still lack and should have further investigations. In this work, abundant VO₂ LDSs (i.e., zero-dimensional NDs, one-dimensional NWs, NBs and two-dimensional nanoplatelets (NPs)) were fabricated by pulsed laser deposition. The effects of each deposition factor, i.e., substrates, deposition temperature, oxygen pressure, pulse number and annealing process, on the growth of VO₂ LDSs were systematically investigated. The results demonstrate that the NWs and NBs favor to grow on <0001> Al₂O₃ and <0001> SiO₂ substrates, respectively. By adjusting the oxygen pressure, the length/diameter ratio of NW can be conveniently controlled. Interestingly, vertically-grown NWs and NPs were also fabricated by controlling the pulse number and annealing process. High resolution transmission electron microscopy images and selected area electron diffraction patterns confirm the high crystallinity of the NW, vertically-grown NW and NP. Importantly, the MIT behaviors and electron transport characteristics were studied by temperature-dependent X-ray diffraction and current-voltage measurement, respectively. The results clearly reveal that the properties of VO₂ LDSs are strongly correlated to the mismatch strain between LDSs and substrate lattice. Under the strong effect of substrate, LDS (i.e., NW) transforms from an insulating T phase to another insulating M2 phase without the coexistence of these two phases. Under the relative weaker effect of substrate, two insulating (i.e., M1 and M2) phases could coexist in LDSs (i.e., NB, vertically-grown NW and NP) during the phase transition process, and the transition temperature could also be affected. Intriguingly, the discrepant electron transport properties corresponded to the MIT behaviors were also observed in NW and NB. The results show that the M1 and M2 phases compete with each other in the NB during the phase transition owing to the interaction of VO₂ and substrate lattice. This work provides a simple and controllable technique for fabricating VO₂ LDSs, and an efficient method for controlling the transition temperature and electron transport properties through the morphology of VO₂ as well as the misfit strain from the substrate.

NM03.10.06

Understanding the Composition of Ternary III-V Nanowires Forming from Quaternary Au-Based Liquid Melts Egor Leshchenko1, Masoomeh Ghasemi1, 2, Vladimir Dubrovskii3 and Jonas Johansson1; 1Solid State Physics and NanoLund, Lund University, Lund, Sweden; 2Physics Department, Persian Gulf University, Booshehr, Iran (the Islamic Republic of); 3ITMO University, St. Petersburg, Russian Federation.

Semiconducting nanowires are a promising class of nanoscale objects whose properties are dramatically different from the bulk counterparts. Thanks to their unique properties, nanowires hold great promise for nanotechnology with many nanoelectronic, optoelectronic and energy harvesting applications. Such versatility is explained by the possibility of modulating nanowire physical properties by tuning their structure, size, morphology, and chemical composition [1]. The majority of research on nanowire growth technology is devoted to binary systems, especially to GaAs nanowires, while ternary nanowires are less studied. To fully realize the NW potential prospects and expand their functionality, the construction of more complex materials with precise composition control is required. So, the ability to control the composition of ternary nanowires enables almost unlimited bandgap engineering. However, it is near to impossible to control the composition of ternary nanowires without understanding of underlying growth mechanisms and modeling. In this perspective, we present an analytical approach for understanding and tuning the composition of a ternary solid material nucleating from a quaternary liquid melt. The calculations are based on the two-component nucleation theory with realistic descriptions of all the considered phases. We apply this theory to a nucleation-limited regime of the vapor-liquid-solid Au-catalyzed and self-catalyzed growth. Within the model, the solid composition is obtained as a function of the liquid composition for the In-Ga-As-Au, Al-Ga-As-Au, In-Ga-Sb-Au and In-Sb-As-Au systems. The results show that the ternary nanowire composition can be controlled over a wide range by modulating the composition of the catalyst droplet and temperature except for systems with high pseudobinary interaction parameters. For such systems (In, Ga, Sb and In, Ga, As), formation of ternary NWs is thermodynamically forbidden in a wide range of solid compositions at relevant temperatures due to the miscibility gaps. The current contribution presents an important step for the fundamental understanding of the ternary NW formation. However, a direct comparison between the obtained results and experimental data is seriously hampered because of unknown liquid composition during the growth. That is why we developed a simple kinetic model which gives a relationship between the vapor and liquid phases. Combination of this kinetic vapor-liquid model with the thermodynamic liquid-solid model allows us to skip the liquid phase and model growth of ternary nanowires using available experimental data such as the flux ratios and the nanowire composition.

References
References


Acknowledgements

EDL and JJ gratefully acknowledge financial support from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant 722176 (project acronym INDEED).

Acknowledgement

The project was supported by the European Union Horizon 2020 research and innovation program under the MSCA grant agreement No 722176, Microsoft Station Q, the European Research Council (ERC) under the grant agreement No 716655 (HEMs-DAM ), and the Microsoft Quantum project.

NM03.10.07

Platforms for Synthesizing Scalable Nanowire Networks by Molecular Beam Epitaxy Sabbir A. Khan, Joachim E. Sestoft, Filip Krizek, Yu Liu, Tomaš Stankevič and Peter Krogstrup; Center For Quantum Devices and Station Q Copenhagen, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark.

III-V semiconductor nanowire networks are promising candidates for high speed electronics and quantum applications. In this study, we investigate a suitable platform for epitaxial growth of scalable semiconductor nanowire networks. We consider two possible directions for nanowire networking, firstly, bottom up free-standing nanowire networks grown via the vapor-liquid-solid (VLS) method and secondly, selective area grown (SAG) nanowire networks from lithography defined patterns in dielectric masks. For InAs/InSb VLS nanowire networks, we engineer an InAs (100) substrate by making (111) B faceted trenches or (111) B faceted SAG and later use this (111) B faceted platform for growing VLS nanowire networks with high yield and scalability using molecular beam epitaxy (MBE). We also show SAG nanowire junctions with different directions and structures, in a lithography defined windows, which is certainly another promising route for scalability. Both directions are appropriate platforms for quantum transport measurements using in-situ epitaxial growth of superconductors (aluminum in our case) on the semiconductor nanowires.

Synthesis and Characterization of NiO/SnO2 Heterostructures María Taeho, David Maestre and Ana Cremades; Física de Materiales, Facultad de CC. Físicas, Universidad Complutense de Madrid, Madrid, Spain.

Combining nano- and microstructures of different semiconducting oxides in order to synergize their properties is gaining increasing attention in recent years [1-3]. In particular, fabrication of p-n heterojunctions in 1-dimensional structures has been attested as one of the most promising strategies to develop optoelectronic devices with enhanced applicability in photocatalysis and solar cells, the fabrication of which is still a challenging task in material science. Different approaches have been used in the fabrication of heterostructures, usually involving subsequent growth stages based in the bottom-up paradigm. In this work, NiO/SnO2 heterostructures have been fabricated in a single step following a catalysis free vapor-solid process which avoids the use of catalyst or external substrates. Individual SnO2 and NiO micro- and nanostructures have been also fabricated as a reference. SnO2 is a well-known n-type material with demonstrated applications in gas sensing, catalysis or optoelectronics. On the other hand, NiO is one of the very few p-type wide bandgap semiconducting oxides with potential applicability in electrochromic devices, sensors, magnetic devices, batteries, catalysis and supercapacitors. NiO/SnO2 heterostructures can overcome the limitations of the original binary oxides and broaden their applicability, which motivates this study. In the vapor-solid process used in this work, a controlled mix of metallic Sn and Ni pressed into a pellet is used as precursor, and thermal treatments were performed at 800°C during 10 hours under a controlled Ar flow. Following this method, a large concentration of nanowires, some microns length, grow on the surface of the treated pellet. X-ray diffraction (XRD) and Raman spectroscopy, in combination with energy dispersive x-ray spectroscopy (EDS) and scanning electron microscopy (SEM) confirm the presence of rutile SnO2 nanowires grown on NiO micrograins with cubic rock-salt structure. The luminescence of these heterostructures is dominated by the characteristic emission of SnO2, which consists of bands at 1.94 and 2.25 eV, related to the presence of oxygen vacancies, and a band at 2.58 eV associated with surface defects. NiO presents emissions at 1.45 eV and a complex emission at 2.45 eV due to Ni vacancies. Variation of the precursors, mixture ratio and parameters of the thermal treatment lead to changes in the growth of the heterostructures.


Acknowledgements

EDL and JJ gratefully acknowledge financial support from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant 722176 (project acronym INDEED).

NM03.10.08

Synthesis and Characterization of NiO/SnO2 Heterostructures María Taeho, David Maestre and Ana Cremades; Física de Materiales, Facultad de CC. Físicas, Universidad Complutense de Madrid, Madrid, Spain.

Combining nano- and microstructures of different semiconducting oxides in order to synergize their properties is gaining increasing attention in recent years [1-3]. In particular, fabrication of p-n heterojunctions in 1-dimensional structures has been attested as one of the most promising strategies to develop optoelectronic devices with enhanced applicability in photocatalysis and solar cells, the fabrication of which is still a challenging task in material science. Different approaches have been used in the fabrication of heterostructures, usually involving subsequent growth stages based in the bottom-up paradigm. In this work, NiO/SnO2 heterostructures have been fabricated in a single step following a catalysis free vapor-solid process which avoids the use of catalyst or external substrates. Individual SnO2 and NiO micro- and nanostructures have been also fabricated as a reference. SnO2 is a well-known n-type material with demonstrated applications in gas sensing, catalysis or optoelectronics. On the other hand, NiO is one of the very few p-type wide bandgap semiconducting oxides with potential applicability in electrochromic devices, sensors, magnetic devices, batteries, catalysis and supercapacitors. NiO/SnO2 heterostructures can overcome the limitations of the original binary oxides and broaden their applicability, which motivates this study. In the vapor-solid process used in this work, a controlled mix of metallic Sn and Ni pressed into a pellet is used as precursor, and thermal treatments were performed at 800°C during 10 hours under a controlled Ar flow. Following this method, a large concentration of nanowires, some microns length, grow on the surface of the treated pellet. X-ray diffraction (XRD) and Raman spectroscopy, in combination with energy dispersive x-ray spectroscopy (EDS) and scanning electron microscopy (SEM) confirm the presence of rutile SnO2 nanowires grown on NiO micrograins with cubic rock-salt structure. The luminescence of these heterostructures is dominated by the characteristic emission of SnO2, which consists of bands at 1.94 and 2.25 eV, related to the presence of oxygen vacancies, and a band at 2.58 eV associated with surface defects. NiO presents emissions at 1.45 eV and a complex emission at 2.45 eV due to Ni vacancies. Variation of the precursors, mixture ratio and parameters of the thermal treatment lead to changes in the growth of the heterostructures.


Acknowledgements

EDL and JJ gratefully acknowledge financial support from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant 722176 (project acronym INDEED).

NM03.10.09

Study of Medium Influence in Solvothermal Synthesis of BiSI Nanorods and the Challenges in Their Application in Ionising Radiation Detection María Membrí Frutu1, Ivana Aguiar2, Maria E. Perez Barthabaru2 and Laura Formaro2; Grupo de Desarrollo de Materiales y Estudios Ambientales, Area Radioquímica, Facultad de Química, Universidad de la Republica, Montevideo, Uruguay; 2Grupo de Desarrollo de Materiales y Estudios Ambientales, Departamento de Desarrollo Tecnológico, CURE, Universidad de la República, Rocha, Uruguay.

BiSI is a ternary semiconductor which can be employed in X and gamma ray detection at room temperature due to the following properties: band gap of 1.57 eV, density of 6.4g/cm³, and absorption coefficient for 60keV radiation of 5.6cm⁻¹g. This work deals with the synthesis mechanism of BiSI nanorods by the solvothermal method, followed by the study of the fabrication conditions to obtain BiSI pellets, and finally it determines the response to ionizing radiation of prototype detectors built with the pellets. The solvothermal synthesis uses Bi2S3 and I2 as precursors, 180°C temperature, and 20 h reaction time. The media used was either H2O or ethylene glycol (EG). The pellets were fabricated using the synthesized BiSI, varying the applied pressure and heat treatment (HT) conditions. Prototype detectors were built with the pellets by evaporating Au as contacts and attaching Pt wires with Aquadag and encapsulating them with acrylic. X-ray diffraction was used to identify the products phase and study the preferred orientation of the nanorods in the pellets. The morphology and size of the BiSI nanorods were studied under a transmission electron microscope, while the micro structural properties of the pellets were studied by scanning electron microscopy. For the detectors the dark current density (j0) and response to different doses of a 241Am source were studied with j-V curves with forward biasing. The electrical properties were related to the microstructure of the pellets. The solvothermal method yielded pure crystalline BiSI when EG was the medium, while with H2O remnant Bi2S3 was found. The decreasing of reaction times proved that Bi2S3 is not dissolved either in EG nor H2O, indicating that Bi2S3 works as a self-sacrificing template in the formation of BiSI. Furthermore, the Bi2S3 employed has a nanorod morphology, and in both cases BiSI grew in nanorod shape, although for BiSI with EG, amorphous carbon particles were also observed. The pressure seems to induce a preferred orientation of the nanorods within the pellet, but no difference was observed between the fabrication conditions. Alternatively,
HT of pellets produced a change in morphology only for BiSI with EG. The $j_{m}$ measured for BiSI with H$_2$O was in the order of mA, and no further characterizations were made, for these detectors were not suitable for room-temperature detection. For BiSI with EG, the $j_{m}$ of the HT pellet was one order of magnitude lower than for the pellets without it, and its response to the $^{241}$Am source, linear, with a signal to noise ratio of 7 for 20V. Finally, resistivities were calculated, and the best value obtained was in the order of 10$^9$$\Omega$-cm for HT sample. While carbon particles appeared to be a disadvantage for detector performance, they lowered $j_{m}$, allowing for ionizing radiation detection at room temperature. Further work is to be conducted to orient nanorods parallel to the electric field, which would improve charge carrier transport and hence detector performance.

NM03.10.10
Axially Modulation of Metal-Insulator Phase Transition of VO$_2$ Nanowires by Graded Doping Engineering for Optically Readable Thermometers
Pai Geng, Dejun Kong, Pengcheng Chen, Run Shi and Chun Cheng; Southern University of Science and Technology, Guangdong, China.

Temperature measurement is essential to a variety of scientific experiments and technological application. Quantities of thermometers which were used for thermal sensing at macroscopic length scales have been developed and produced. However, it's still challenging to do the in situ and quantitative temperature measurement of nanoscale objects with a convenient and simple approach. In this work, we demonstrate a new type of optically-readable VO$_2$ nanowire-based thermometer. By changing the conditions of reaction, the hydrothermal synthesis of intrinsic H-doping VO$_2$ (M) nanowires has been achieved. During the hydrothermal reactions, the concentration of hydrogen doping can be adjusted by changing the concentration of reductive agent and fusing ratio. After annealing treatment, the dopants or vacancies in as-grown hydric VO$_2$ nanowires can be redistributed or eliminated. Because of the hydrogen doping through hydrothermal fabrication and the hydrogen engineering via a post-annealing process, the single-domain VO$_2$ nanowires obtains a unique axially-gradient phase transition behavior, which makes the advanced thermometer possible. The optically-readable VO$_2$ nanowire-based thermometer is user-friendly and appropriate to microscopic size. What's more, it also has ultra-high relative sensitivity (>17.4% K) and temperature resolution(<0.026K) via optical microscope. It can even achieve an extremely high resolution of (>10-5K) when combining with transmission electron microscope (TEM). The advanced thermometer we demonstrated enables the sensitive monitoring of the thermal environment of small space or the temperature of even nanoscale structure which greatly facilitates the nanoscale scientific experiments and technological application.

References


NM03.10.11
Hydrothermal Synthesis of Highly Ordered Monoclinic Phase VO$_2$ Nanowire Array and Research of Microactuator Application
Pengcheng Chen, Pai Geng, Run Shi and Chun Cheng; Southern University of Science and Technology, Shenzhen, China.

Since 1975, the vanadium dioxide has gradually attracted intensive attention for its special metal-insulator transition (MIT), which is followed by amazing applications in electrical, optical and mechanical properties. Based on the change of volume along the structure, Armando Rua in 2010 used polycrystalline thin film of VO$_2$ and Si to produce the double-layer chip, which will occur significant bending when it reaches the phase transition temperature [1]. Besides, Wu also carried out outstanding works based on VO$_2$ bimorph micro-actuator in recent years, like micro-actuator with large amplitude and high power density [2]. These results show that the double-layer chip has a good prospect on the micro-actuator with large displacement, high speed, and large strength, revealing the potential applications on the micro flow valve, micromanipulator, and shape memory structure. However, the application and development of VO$_2$ micro-actuator encountered some obstacles. Polycrystalline films due to grain boundaries, strain-stress and composition ratio will lead to unstable performance of the micro-actuator and the difficulty to further improve it [3]. In comparison, super-aligned VO$_2$ nanowires can effectively improve that [4]. While the current high temperature thermal evaporation method has many disadvantages, such as high power consumption, low yield, and not easy transfer of products from the substrate. To overcome these problems, we propose an approach that using V$_2$O$_5$-H$_2$C$_2$O$_5$ aqueous system to produce the precursor solution under the hydrothermal reaction. Then a layer of antimony is deposited on the smooth surface of quartz substrate by PVD method, next the substrate is inverted into the precursor solution to make the nanowire array growing. In a conclusion, this method could make a large-scale preparation of super-aligned VO$_2$ nanowire arrays. The average length of the array is about 30 μm with 100 nm of diameter, and the density is very large with very high purity. It also solves the transfer problem due to the array growing on the smooth surface, then we use the special polymer to take off the array from the substrate to make films with consistent orientation. Thereby, we could assemble an actuator with the films to do further research.

Reference:

NM03.10.12
Small Channel-Length SiC Nanowire Field-Effect Transistors
Ali Uzun and Kasif Teker; Electrical and Electronics Engineering, Istanbul Sehir University, Istanbul, Turkey.

Low-dimensional semiconductor materials offer new ways to develop nanoscale electronic and optoelectronic devices and components. From the class of wide band gap semiconductor nanomaterials, SiC nanowires combine the unique properties of one-dimensional materials with that of superior intrinsic SiC characteristics and offer great opportunities for high power and high frequency electronic devices as well as in sensors capable of operating at high temperatures or hostile environments.

This study presents a systematic investigation of electronic transport properties of p-type SiC nanowire field effect transistors (SiC/NW-FET) with multiple channel lengths (smallest channel length SiC/NW-FET reported). The investigation has focused on the parameters including transconductance ($g_{m}$), carrier mobility ($\mu_{c}$), ON-OFF current ratio (gating effect - $I_{ON}/I_{OFF}$). Further, a comprehensive comparison of our experimental measurements with the previously reported theoretical and experimental studies is presented.

MOCVD-grown long SiC/NWs with diameters about 60 nm are placed on a highly doped SiO$_2$/Si substrate. The electrodes (Cr/Au: 3nm/100nm) are defined by the e-beam lithography (EBL) with varying channel lengths of 120 nm, 220 nm and 1.5 μm followed by metal deposition through e-beam evaporation. The initial electrical measurements from the fabricated p-type SiC NWs-FETs exhibited transconductance of 6.9x10$^{-9}$ A/V (@ $V_{ds}$ = 0.05V),
carrier mobility of $1.7 \text{ cm}^2/\text{V} \cdot \text{s}$, carrier concentration ($n_a$) of $3.72 \times 10^{20} \text{ cm}^{-3}$, and $f_{20}/f_{90}$ ratio more than $10^6$ for a device with 120nm channel length. The gate effect achieved in this study is the highest value reported in the literature for a SiCNW-FET, to the best of our knowledge. As a consequence, this study shows the great potential of SiCNW-FETs to be utilized in nanoelectronic and nanophotonic applications.

NM03.10.13

Fully Transparent and Printable Thin-Film Transistor Devices Based on Si Nanowires Chan Zhao1,2, Cezhou Zhao1,2 and Li Yang1,2; 1Xi’an Jiaotong-Liverpool University, Suzhou, China; 2University of Liverpool, Liverpool, United Kingdom.

Recently, 1-D nanomaterials, such as semiconductor nanowires (SiNWs), have emerged as interesting materials for the fabrication of high-performance transistors with electronic performance comparable to and in some cases exceeding that of the highest quality single-crystal materials. Preparation of crystalline SiNWs is the use of metal-assisted chemical etching, where solution-nucleated metal plays the important role of a nanoscale electrode in the electrochemical etching of a single-crystalline Si wafer. The metal nanoparticles, such as Ag, oxidize Si that is in contact with them by taking electrons from Si. The oxidized Si, or SiO2, is then etched away by HF in the etching solution, leaving a pit or hole on the Si surface. Finally, Si nanowires result from areas where no metal is present. This can be done even at room temperature without involving high temperature, low pressure, or costly equipment and hazardous materials, which makes metal-assisted chemical etching simple, easy, and economical. Here, we report on studies of transparent and printable thin-film transistor (TFT) devices based on SiNWs. The NW-based devices exhibit uniform characteristics with average field-effect mobilities exceeding 100 cm²/Vs. The nanowires can be aligned and selectively deposited via spray gun under air pressure as a result of evaporation-induced polar solvent flow. Prototype nanowire-based TFTs (NW-TFT) devices on glass substrates showed excellent optical transparency and transistor performance in terms of transconductance, threshold voltage range, and on/off ratio. High on-currents and field-effect mobilities were obtained from the NW-TFT devices even at low nanowire coverage. The SiNW-based TFT approach offers a number of desirable properties such as low growth temperature, high electron mobility, and optical transparency and low operation voltage, and may lead to large-scale applications of transparent electronics on diverse substrates.

NM03.10.14

Homoeptaxial Growth of GaN Nanorods via Irregular Masks Chang Hsun Huang, Wei I Lee and Yi-Chia Chou; Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan.

Gallium nitride (GaN) is widely explored for applications in optoelectronics and high-power electronic devices [1]. For GaN nanomaterials, the high-aspect ratio characteristic combined with quantum confinement reveal the feasibility for light-emitting diodes and lasers to control light extraction with tunable bandgap [2]. Among several nanomaterials of GaN, the rods of it grown without metal catalyst have shown strain relaxation and are more suitable for nanofabrication process without metal contamination. Moreover, GaN nanorods (NRs) with c-orientation provide non-polar and semi-polar facets for reducing the quantum-confined Stark effect (QCES) and thus increase the emission efficiency and intensity of optical devices [3].

In this work, we propose an uncomplex and low cost approach using an irregular mask for GaN NR fabrication on GaN substrate via hydride vapor phase epitaxy (HVPE). The grown GaN NRs are isolated by uncoalesced SiO2 islands, served as irregular mask, and they grew along c-orientation with high aspect ratio. The maximum growth rate of GaN NRs can be achieved of ~1 µm/min. Furthermore, we demonstrate the growth mechanism of GaN NRs under various growth parameters. In addition, in-situ etching effect during the growth of GaN NRs is also discovered. The structural and optical properties of the GaN NRs will be demonstrated in the paper.

References


NM03.10.15

Highly Luminescent Double-Heterojunction Nanorods Gryphon Drake and Moonsub Shim; University of Illinois Urbana-Champaign, Urbana, Illinois, United States.

Colloidal semiconductor double-heterojunction nanorods are promising materials for electroluminescent applications due to their favorable band structure and enhanced light coupling efficiency compared to core/shell quantum dots. However, their photoluminescence quantum yield is less than half of the best core/shell structures. However it has been shown previously that Zn-oleate used to grow the ZnSe shell on CdS-CdSe nanorod seed as well as the rate of ZnSe growth in competition with the etching process. We demonstrate significant improvements in ensemble emission linewidth and photoluminescence quantum yield while retaining the advantageous structure and functionality of double-heterojunction nanorods as emitting materials in light emitting diodes with low turn-on voltage and high brightness.

NM03.10.16

Tunable Morphology and Doping of ZnO Nanowires by Chemical Bath Deposition Using Metal Nitrate Pierre Gaffuri1,2; Estelle Appert1; Odette Chaix-Pluchery1, Laetitia Rapenne1, Mathieu Salaün2 and Vincent Consonni1; 1Univ Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble, France; 2Univ Grenoble Alpes, CNRS, Institut Néel, Grenoble, France.

Over the last decade, ZnO nanowires (NWs) have been used for a wide variety of optoelectronic devices, including UV photodetectors and solar cells. For all these applications, their electrical properties, such as their conductivity and mobility, should be controlled as much as possible. ZnO is intrinsically n-type owing to the high density of oxygen vacancies and hydrogen and can intentionally be n-doped, for example, by aluminium. The doping of ZnO NWs has however been mainly performed by vapor deposition techniques. In the present work, ZnO NWs are doped with different metals by using the low-cost, low-temperature, and easily implemented chemical bath deposition (CBD) technique. Metal nitrate is added in various concentrations to the standard precursors (i.e. zinc nitrate and HMTA [1]) in deionized water. It is shown by scanning and transmission electron microscopy (TEM) that this addition completely modifies the structural morphology of ZnO NWs. The formation mechanisms are thoroughly investigated and supported by thermodynamic simulations. The incorporation of metal dopants is further investigated by energy dispersive x-ray spectrometry using scanning TEM. In particular, temperature-dependent Raman spectroscopy measurements show the occurrence of additional modes, indicating the presence of the related dopants [2].

* Author for correspondence: estelle.appert@grenoble-inp.fr
Controlling the growth and properties of ZnO nanowires (NWs) is critical for their efficient integration into nanoscale engineering devices [1]. Owing to the nature of the wurtzite structure, ZnO exhibits a spontaneous polarization along the c-axis. The resulting polarity is known to affect the growth and properties of ZnO single crystals and epiplex films [2], but the polarity-induced effects are mostly unknown in NWs. While ZnO NWs grown by vapor phase techniques are Zn-polar, ZnO NWs grown by chemical bath deposition (CBD) can be of either O- or Zn-polarity [3], which opens the way for more deeply investigating these effects. In this context, we thoroughly address the issue of the polarity-dependent growth and properties of ZnO NWs by CBD following the selective area growth approach [4]. To leave polarity as the only varying parameter, ZnO NWs are grown under identical conditions, during the same run of experiment on O- and Zn-polar ZnO single crystals patterned by electron beam lithography with the same pattern consisting of fifteen different domains combining a wide range of hole diameters and periods. Well-ordered O- and Zn-polar ZnO NW arrays with high structural uniformity are grown on all the domains. The comparison of their typical dimensions unambiguously reveals that Zn-polar ZnO NWs have significantly higher growth rates than O-polar ZnO NWs for all the fifteen domains [4]. The origin of the difference is discussed in the light of surface configurations and interactions in aqueous solution at the top polar c-faces of the ZnO NWs. Additional electrical characterizations of the NWs using four-point probe resistivity measurements are performed on single O- and Zn-polar ZnO NWs [5]. These findings show the relevance of considering polarity as an important quantity to control the growth and physical properties of ZnO NWs by CBD.

We find that the rate of droplet consumption depends on the local environment of each nanowire. In the patterns with small pitch (< 500 nm), where each nanowire is surrounded by other nanowires, the rate of droplet consumption is higher than in patterns with larger pitch. This is due to the increased interfacial area between the nanowires and the droplet, which facilitates the consumption of the droplet. In contrast, in patterns with large pitch, the droplet consumption rate is lower due to the reduced interfacial area.

One way of obtaining a high yield of thin III-V nanowires is to interrupt and resume the growth during standard epitaxy process. This technique leads to a higher yield of thin III-V nanowires than continuous growth. In this study, we investigated the crystalization of Ga droplets on the top of self-catalyzed GaP nanowires. The nanowires were grown on patterned SiOx/Si(111) substrates. The substrates contain patterns with different pitches and hole size. After 2 minutes of Ga deposition without As flux and 20 minutes of nanowire growth at a nominal V/III ratio ~1.2 and temperature ~600°C, we have performed a crystalization step under various P and Ga fluxes. We find that the rate of droplet consumption depends on the local environment of each nanowire. In the patterns with small pitch (< 500 nm), where each nanowire is closely surrounded by other nanowires, the droplet is consumed faster than for patterns with bigger pitches (as well as droplet on nanowires at the border on the patterned area with small pitch).

We propose a simple model describing the evolution of droplet contact angle and radius during crystallization. This model can be used for predicting the geometry of the final crystallized droplet for given III-V fluxes and crystallization time. This data are important for developing the strategy for growing thin nanowires with controlled diameter and length on the top on a thicker stem. The understanding of the processes occurring during crystallization should also allow us to fabricate diameter-modulated nanowires and axial compositional and crystal-phase heterostructures within.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722176.

This paper discusses the interaction and effect of different atomic layer deposition (ALD) parameters on the properties of a seed layer used to grow zinc oxide (ZnO) nanowires (NWs) by chemical bath deposition (CBD). Independent ALD thin film deposition parameters and their effects on the growth of ZnO NWs are available in the literature. However, to the best of our knowledge, there is little known about the combined influence of these parameters on the NW growth.

ZnO is a direct wide bandgap semiconductor (3.37 eV) with a high exciton binding energy (60 meV). It can be synthesized in many different one-dimensional morphologies. ZnO NWs are one of the most attractive due to some of their intrinsic properties, e.g. their high surface area and aspect ratio. The combination of electrical properties and 1D morphology makes ZnO NWs a very promising material for a wide variety of applications such as field effect transistors, water treatment, sensors or solar cells.
ALD is a thin film deposition technique based on the stacking of deposited atomic or molecular layers from the precursors, which yields thin films (around 30 nm in this work) with conformal surface coverage and compositional control. In ALD, different precursors (diluted zinc and water in this case) are dosed alternately under a constant flow of nitrogen gas with a purge time when only nitrogen flows. Each precursor chemisorbs to the previous layer of the film, forming atomic layers. Thus, an ALD cycle consists of the sequence of pulses and purges of the precursors. It is essential to have control over the different properties of the film such as composition, crystallite size, roughness or thickness as they have a direct effect on the properties of the as-grown NWs (orientation, size and crystallography). These properties are controlled by tuning the deposition parameters, e.g. temperature, number of cycles or the pulse and purge times.

The CBD process involves two chemicals, the zinc source (Zn(NO3)2*6H2O) and the reducing agent, hexamethylenetetramine. These reagents are dissolved in DI water before the substrate with the seed layer is submerged in the solution. Various characterization techniques such as scanning and transmission electron microscopy (SEM & TEM), x-ray diffraction (XRD), x-ray photon spectroscopy (XPS) and photoluminescence (PL) were utilized to investigate the properties of the NWs and to study the changes resulting from the thin film deposition parameters. This investigation thus demonstrates the controlled growth of single crystal wurtzite phase ZnO NWs using this low-cost process.


NM03.10.20 Nanowire Network Based Multifunctional All-Optical Logic Gates Vladislav Khayrudinov1, He Yang1, Veer Dhaka1, Hui Jiang2, Anton Autere3, Harri Lipsanen1, Ziyou Sun1 and Henri Jussila1; 1Department of Electronics and Nanoeengineering, Aalto University, Espoo, Finland; 2Department of Applied Physics and Nanomicroscopy Center, Aalto University, Espoo, Finland; 3QTF Centre of Excellence, Department of Applied Physics, Aalto University, Espoo, Finland.

All-optical nanoscale logic components are highly desired for various applications because light may enable logic functions to be performed extremely quickly without the generation of heat and crosstalk. All-optical computing at nanoscale is therefore a promising alternative but yet requires the development of a complete toolbox capable of various logic functionalities. Herein, we demonstrate nanoscale all-optical switches by exploiting the polarization dependent light emission property of crossbar InP and AlGaAs nanowire networks. These networks can perform various logic operations, such as AND, OR, NAND, and NOR binary logic functions. Furthermore, based on these logic operations, our networks successfully enable all-optical arithmetic binary calculations, such as n-bit addition. Our results underscore the promise of assembled semiconductor nanowire networks as a building block of on-chip all-optical logic components for future nanophotonics.

NM03.10.21 Development of Hybrid Structures for the Electrodynamic Screen (EDS) Films to Mitigate Energy Yield Loss Incurred by Solar Collectors Due to Soiling Annie Rabi Bernard, Ryan Eriksen and Malay Mazumder; Boston University, Brookline, Massachusetts, United States.

Over the last few years, silver nanowire (AgNW) has gained prominence as the ideal material for transparent electrodes owing to its high conductivity, transmission efficiency and availability over other transparent conductive electrode materials. Enhancement of the stability of AgNW in an outdoor environment is currently widely researched, since the nanowires prove to be short-lived when exposed to harsh on-field conditions over an extended period of time. This study aims at establishing environmentally stable and viable AgNW electrodes of an Electrodynamic Screen (EDS) film, by the inclusion of one or more protective layers of zinc Oxide (ZnO) prepared in lab in a 1) stacked structure where the AgNW electrode has a layer of ZnO on top for protection or a 2) sandwiched structure wherein the AgNW electrode is covered by ZnO layers, protecting it from the top and bottom. A second experiment to include a protective polymer based overcoat layer atop the AgNW electrodes of the EDS film is also discussed here. The EDS film technology consists of an ultrathin glass layer on which rows of parallel electrodes are deposited. The EDS film, when retrofitted on solar collectors, has proved to be a viable solution to mitigate the energy yield loss caused by soiling. Concerns regarding the presence of electrodes that could block a section of the incoming light to the solar collector and thereby potentially decreasing the output of the solar cell are addressed by using AgNW as it is a transparent conducting ink material. When dust particles are in contact with the optical surface, the EDS film charges the dust particles electrostatically, applies an electrostatic repulsion force to levitate the dust layer and removes it with a sweeping action by an electromagnetic traveling wave. Measurements of the dust removal efficiency of the EDS film will be performed after extended/accelerated exposure to UV light, high humidity, and moisture. Testing procedures of the hybrid AgNW electrode structures consist of calculated UV exposure measurements in lab as well as field testing setup, while checking the conductivity and performance of the electrodes of the EDS in terms of its efficiency in removing dust. The electrodes will be activated by a three phase voltage ranging up to 1.2 kilo volts and tests will be done to ensure the viability of the electrodes when subjected to such high voltage. EDS film thus developed will also be subjected to high temperature and humidity conditions simulated in an environmental chamber installed in lab. A complete water immersion test will also be performed in order to ensure functionality and efficiency of the EDS film in the case of rain.

NM03.10.22 Electrodeposition of Nanowires into Silica and Alumina Templates with Pore Sizes Down to 2 nm Andrew L. Hector; University of Southampton, Southampton, United Kingdom.

Supercritical fluids have low surface tension and viscosity, so provide high mass transport rates in nanoporous structures. However, due to low dielectric constants and the need to work at elevated temperature and pressure there is little published work on electrodeposition from supercritical systems. The deposition of tin nanowires from supercritical difluoromethane into 13 and 55 nm anodic alumina templates will be described. The size limits of the technique have also been tested with tin deposition into ~2 nm pore mesoporous silica templates, and the evidence for deposition into these very small pore systems will also be described.

NM03.10.23 Synthesis of Folate Receptor Targeting Coaxial PDA-F-A/P(MAA-co-EGDMA) Nanotubes for Drug Delivery Sezin Sayin1, Ali Turfani1 and Gozde Ozaydin Inci2,3; 1Materials Science and Nano Engineering, Sabanci University, Istanbul, Turkey; 2Sabanci University Nanotechnology Research and Application Center (SUNUM), Istanbul, Turkey; 3Center of Excellence for Functional Surfaces and Interfaces (EFSUN), Istanbul, Turkey.

Nanotubes have an important role in drug delivery application. Biocompatible and biodegradable nature makes polymeric nanocarriers preferable. Functional and responsive polymers can be loaded without degradation of drug molecules. Polymeric nanotubes result in longer residence time and greater activity due to cylindrical shapes. The scope of this study is to synthesize pH responsive coaxial nanotubes with folate receptor targeting for cancer.
treatment applications. Coaxial nanotubes are fabricated with the outer side of polydopamine-folic acid and inner side of p(MAA-co-EGDMA). Initiated chemical vapor deposition (iCVD) technique involving free radical polymerization is used for H response, non-soluble poly(methacrylic acid-co-ethylene glycol dimethacrylate) p(MAA-co-EGDMA) nanotubes fabrication. Conformal deposition is achieved by anodized aluminum oxide (AAO) template. Due to vapor phase synthesis, disadvantages of solution-based fabrication methods as solvent toxicity can be prevented in iCVD fabrication. Structures and compositions of nanotubes are characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. Thickness measurements and swelling behavior are investigated by ellipsometry. Drug loading and release mechanisms are studied using model drug molecule.

NM03.10.24
Microstructural Properties of ZnO Nanowires Grown by Hydrothermal Synthesis on GAZO Thin Films Edigar Muchuwe1,1, , Thangiah S. Sathiraj2 and Huggins Nyakotyo1,1, 1Botswana International University of Science and Technology, Palapye, Botswana; 2Bindura University of Science Education, Bindura, Zimbabwe.

ZnO nanowires have gained significant research attention in recent years due to their novel properties which make them suitable for use as transparent electrodes in optoelectronic devices such as solar cells, touch screens and light emitting diodes. ZnO nanowires exhibit a single crystalline structure which has few grain boundaries and defects, leading to better optoelectronic properties than those of bulk and thin film forms of ZnO. In addition, ZnO nanowires have large surface-to-volume ratios and efficient charge transport along the wire axis which makes them more attractive for transparent electrode fabrication and light harvesting in solar cell structures. In the present work, we present the morphological characterization of ZnO nanowires grown by hydrothermal synthesis on glass substrates seeded with GAZO thin films.

The GAZO thin films were prepared by radio frequency magnetron sputtering using a 99.99% purity Ga/Al/ZnO (1.14:0.62/98.24 wt%) target (HHV, UK) of diameter, 76.2 mm and thickness, 3 mm. The sputtering conditions included, target to substrate distance of 130 mm, base pressure of 1.13 x 10^-5 mbar, working pressure of 1.20 x 10^-2 mbar, argon flow rate of 12 sccm, substrate temperature of 100 °C, rf power of 150 W and seed layer thickness of 385 nm. The ZnO nanowires were subsequently grown by suspending the GAZO thin film substrate upside-down in a mixture of equimolar 25 mM zinc nitrate hexahydrate (Zn(NO3)_2.6H2O, 99% purity, Sigma-Aldrich, USA) and hexamethylenetetramine (HMTA, C6H12N4, Sigma-Aldrich, 99% purity, USA) aqueous solutions at 90 °C for 2 h. After the growth process, the samples were rinsed thoroughly with deionized water to remove any residual zinc salts and dried in air at room temperature. Surface morphology of the GAZO seed layer and ZnO nanowires was characterized by atomic force microscopy (AFM) using a Bruker Dimension Edge AFM and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7100F, Japan), respectively. Elemental compositions were studied by energy dispersive spectroscopy (EDS) equipped in the FE-SEM.

AFM microscopy revealed that the GAZO seed layer had a root mean square surface roughness of 6.1 nm and was uniformly covered with particles of mean size 77.8 nm. These nanoparticles acted as nucleation centres for nanowire growth. The ZnO nanowires were well-aligned with hexagonal prism shapes and uniform diameters (100-200 nm) along their entire lengths. EDS spectrum confirmed that the ZnO nanowires were closer to stoichiometric ZnO (1:1).

NM03.10.25
Template-Free Synthesis of Highly Luminescent Organic Nanorods by Air Oxidation of para-Substituted Anilines Yoonsang Park1 and Woosung Kwon2; 1Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); 2Chemical and Biological Engineering, Sookmyung Women's University, Seoul, Korea (the Republic of).

Oxidation of aniline provides useful multi-dimensional organic nanostructures with a wide variety of morphologies and sizes ranging from the nanometer scale to the micrometer scale. In this study, novel one-dimensional luminescent organic nanorods (ONs) were synthesized through air oxidation of para-substituted anilines without any shape-guiding surfactants. These ONs show highly crystalline rod-like structures due to π-π interactions between the phenazine-like structures which are formed by air oxidation of para-substituted aniline. Also, ONs show bright, photostable, deep-red luminescence with high quantum efficiency (up to 46%). From photoluminescence spectroscopy, absorption spectroscopy, time-correlated single photon counting, and time-dependent density functional theory calculation, it is revealed that their luminescence are originated from the phenazine-like structures. Finally, we demonstrate the potential application of our ONs as a freestanding color filter for deep-red-light-emitting devices that could be applied for color pixels of future displays. Our study provide a new strategy for the synthesis of luminescent organic nanomaterials, and show their potential for optoelectronic applications.

NM03.10.26
Rational Design of Hierarchical Nanosheet-Based SnO2 Nanotubes Functionalized with Pt Catalyst for Application in Exhaled Breath Sensor Hee-Jin Cho, Ji-Soo Jang, Won-Tae Koo, Dong-Ha Kim and Il Doo Kim; KAIST, Daejeon, Korea (the Republic of).

Tailoring of semiconducting metal oxides (SMOs) with hierarchical nanostructures is of importance to accurately detect sub-ppm concentrations of biomarkers for easy diagnosis of specific diseases through exhaled breath analysis. Therefore, several researches have been reported to maximize the surface area and porosity of gas sensing layers since the pore size and pore distribution significantly affect the penetration of biomarker molecules into the sensing layers, whereas a large surface area provides more reactive sites, thereby enhancing the sensitivity. In this work, efforts were made to improve the sensitivity and the selectivity toward acetonol detection using one-dimensional (1-D) SnO2 nanotubes. First, we prepared hierarchical SnO2 nanostructures, which consisted of hollow nanotubes in the core and the two-dimensional (2-D) nanosheets on the shell. The nanosheet-based hollow SnO2 nanotubes were synthesized by a combination of electrospinning approach and hydrothermal method. The carbon nanofibers were fabricated as a scaffold for the 1-D structure. Then the growth of SnO2 nanosheets and the removal of core carbon nanofibers were achieved by the hydrothermal route followed by high temperature calcination. The nanosheet-based pure hollow SnO2 nanotubes exhibited highly sensitive acetonol sensing property (R_0/R_Acetone = 25 at 5 ppm). Secondly, to further improve the sensitivity and selectivity, the catalytic functionalization was performed. The Pt functionalized nanosheet-based SnO2 nanotubes exhibited superior acetonol detection capability under highly humid condition similar to that of exhaled breath (95% RH). The enhanced sensing characteristics suggested a significant potential for precise detection of acetonol in exhaled breath using the Pt functionalized nanosheet-based SnO2 nanotubes.

NM03.10.27
Surface-Engineering of Zinc Oxide Nanowires Encapsulated with Zeolitic Imidazolate Framework-8 for Gas Sensors Jin Su Jeon1,1, 1, Woosook Song1, Sung Myung1, Sun Sook Lee1, Jongsun Lim2, Jinha Hwang2 and Ki-Seok An1; 1Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Hongik University, Seoul, Korea (the Republic of).

Recently, hybridization of metal oxide nanostructures with functional materials has been gaining a lot of attention for enhancing gas sensing performance. Especially, zeolitic imidazolate framework-8 (ZIF-8), a subclass of metal organic frameworks (MOF), is an adoptable material for integrating ZnO-based gas sensors owing to its high internal surface area, subnanometer-sized cavities, thermal stability, and chemical controllability. It is well-established that
the hybridization of ZnO with ZIF-8 allows the improvement of gas selectivity owing to molecular sieving capability induced by well-defined porous structures. Core-shell size = 3.4 Å. Here, we focused on the effects of preconcentration of ZIF-8 hybridized with ZnO nanowires in terms of NO2, NH3, and H2 gas sensitivity as well as gas selectivity. Hydrothermally-grown ZnO NWs are employed as a support material for the nucleation and growth of ZIF-8 nanocrystals, in which their morphological features were optimized by adjusting growth conditions including solution concentration, reaction time, and temperature. The thickness of encapsulated ZIF-8 can be effectively manipulated by the concentration of HmIM, which strongly affects to gas sensitivity of ZIF-8/ZnO NWs-based gas sensors because of a variation in gas diffusion path. For ZIF-8/ZnO NWs synthesized using 8 mM HmIM solution, NO2, NH3, H2 gas sensitivity was improved significantly compared to that of pristine ZnO NWs. Based on these results, two effects are anticipated to improve both gas sensitivity and selectivity after the hybridization of ZnO NWs with ZIF-8 nanocrystals.

NM03.10.28

Perovskite Nanocatalysts Sensitized SnO2 Fiber-in-Tube Scaffold Toward Superior Formaldehyde Gas Sensors Joon-Young Kang, Ji-Su Jang, Won-Tae Koo, Dong-Ha Kim and Il Doo Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Sensitive and selective gas detection of low concentration (even at sub-ppm level) have been required in various fields for indoor air quality and accident prevention. Among various chemical gas sensing materials, electrospun one-dimensional semiconducting metal oxides (SMOs) are considered as ideal building blocks, due to their large surface area, high porosity, and facile synthesis process. To further enhance their sensing performances, catalytic functionalization is essential in SMOs-based gas sensors. Conventionally, noble metal catalysts, such as Pt, Pd, and Au, have been widely studied to promote the gas sensing properties of SMOs by means of electronic and/or chemical sensitization. However, nanoscale noble metals are readily agglomerated and degraded during long operation cycles at high sensing temperature. Therefore, a new catalytic material with high thermal stability and low cost is highly desired for SMOs-based chemiresistors.

In this work, highly porous SnO2 fiber-in-tubes (FITs), which are sensitized with perovskite oxides, i.e., La1.04Sn1.02Cu2.3Mn0.7O8.5 (LSCM) particles as chemical sensitizers, are used as a superior formaldehyde (CH2O) sensing layer. LSCM particles affected the morphologies of electrospun Sn precursor/polymer composite fibers during the calcination step, resulting in the fiber-in-tube (FIT) SnO2 structures with high surface area and porosity. Furthermore, LSCM particles with a high oxygen vacancies concentration and a large work function significantly provide surface oxygen species (O2-) that promote electron depletion on the surface of SnO2, leading to the dramatic resistance variation. As a result, LSCM-loaded SnO2 FITs (LSCM@SnO2; FITs) provide remarkably high response to formaldehyde (Rmax/Rmin = 26.50 to 5 ppm) and excellent selectivity against interfering gases (H2, CH4, NH3, C2H8O, C3H6, CO, and C2H2), even without using noble metal catalysts. Particularly, the role of complex composition of LSCM particles, played in the oxygen supply effect of LSCM particles, and the synergistic effect with FIT structures, were first described in this work. These observations demonstrate the potential use of LSCM@SnO2 FITs for real-time monitoring of indoor air quality, especially toward formaldehyde, which is not accurately detected by conventional metal oxide based sensors.

NM03.10.29

Templated Synthesis of Dy-BiFeO3 Nanotubes and Assessment of Its Photocatalytic Performance as Compared with Nanoparticulate Systems Carlos Ostos and Lima M. Castro, Antioquia, University of Antioquia, Medellin, Colombia.

In recent years semiconductor photocatalysis under visible light irradiation has become of great importance as an alternative technology for environmental remediation. Despite the intensive efforts on developing semiconductor materials for improving the efficiency on these tasks, there is still a shortage in the development of an efficient photocatalyst. At this point, nanostructured BiFeO3, a p-type semiconductor with a small band gap (2.2 eV) emerges as a promising material with multifunctional properties for harnessing in photocatalytic applications. Nevertheless, the good photocatalytic performance is strongly correlated with the design of the semiconductor at the nanoscale. Among various structures, one-dimensional (1D) nanostructured BiFeO3 photocatalysts are very interesting owing to their unique properties. To mention some, 1D geometry provides fast and long-distance electron transport. Furthermore, the high length-to-diameter ratio enhances the light absorption. And finally, 1D nanostructures have a larger specific surface area as compared with corresponding commonly used nanoparticulate material. The remarkable characteristics of the material make it of great significance to investigate into its potential photocatalytic activity.

For comparison purposes, in this work we present the synthesis of both 0D and 1D systems of Bi1-xDyxBiFeO3 (0 ≤ x ≤ 0.15), with structural configurations that offer important multifunctional characteristics. Moreover, the replacement of Dy3+ ions into the Bi3+ sites, has the purpose of optimizing the physical properties of the material and encouraging its performance in the degradation of organic compounds in diluted aqueous media. The synthesis of phase-pure Bi1-xDyxBiFeO3 0D systems was systematically monitored via sol-gel route and the dimensional parameters of 1D systems were regulated from their assembly in commercial and lab made anodized aluminium oxide (AAO) templates. The desired geometrical features of the lab made templates were selected by means of Box-Behnken experimental design. After selecting the best pore features, the templates were immersed into aqueous and non-aqueous precursors solutions, with the aim to assess the wettability of templates and its influence into 1D morphologies. The microstructural characterization of the as obtained Bi1-xDyxBiFeO3 (0 ≤ x ≤ 0.15) 0D and 1D systems was assessed by means of XRD, SEM, TEM and BET. Finally, the photocatalytic activity by the Rhodamine B degradation as a test molecule, demonstrates that tubular structures supported in commercial AAO with 15% of Dy substitution had the greater performance in comparison with one dimensional structures supported in lab made templates and the assessed 0D systems. The rates of degradation reported in this work are higher than the reported before for bismuth ferrite one-dimensional structures.

NM03.10.30

Coaxial Copper Nanowire Network Core—Polymer Shell Nanocomposites as Supercapacitor Electrodes Mete Batuhan Durukan1,2, Sevin Polat Genlik1, Dogancan Tigan1 and Husnu E. Ural1,2; 1Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; 2Energy Storage Materials and Devices Research Center (ENDAM), Middle East Technical University, Ankara, Turkey.

Metallic nanowires hold significant potential to be used in energy storage devices, such as batteries and supercapacitors due to their high surface area and electrical conductivity. Among metallic nanowires, silver nanowires so far dominated the literature due to their reproducible, controllable and large scale synthesis. Copper nanowires on the other hand are still at their infancy; but, hold strong promise to replace silver nanowires due to their comparable optoelectronic properties and low cost. In this work, hybrid nanocomposite electrodes with copper nanowire core and polypyrrole shell (Cu NW/PPy) were fabricated and electrochemically characterized. Hybrid nanocomposite electrodes were fabricated through spray deposition of Cu NW networks onto glass substrates, followed by electrochemical deposition of PPy onto Cu NW network. Electrodeposition was performed onto Cu NWs by applying a constant current in an electrolytic solution containing benzotriazole (BTA), oxalic acid and pyrrole monomer. Capacitive behavior of the hybrid coaxial nanocomposites was investigated through cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy. Cu NWs facilitated the charge transfer and PPy behaved both as a pseudocapacitive material and as a protective shell to improve the electrochemical stability of Cu NWs. Preliminary analysis shows a specific capacitance of 0.12 mF/cm2 at a scan rate of 100 mV/s in 1 M LiClO4 in PC. Thorough analysis on the electrochemical stability and capacitive behavior of the fabricated nanocomposite electrodes will be presented in conjunction with different electrochemical coating parameters and different electrolytes.
Electrochemical Phosphate Sensors Using Silver Nanowires Treated Screen Printed Electrodes

Md Tawabur Rahman, Md Faisal Kabir, Ashim Gurung and Qiuquan Qiao; Electrical Engineering & Computer Science, South Dakota State University, Brookings, South Dakota, United States.

Essential biomolecules of the human body and plant growth depend upon the proper amount of phosphate ions. Phosphorus has critical values in both agricultural and biomedical applications. There is a need for inexpensive, portable, repeatable, highly sensitive, and field deployable sensors with wide detection range to monitor the health of water system and field soil. This paper aims to develop an electrochemical phosphate sensor using novel ammonium molybdate tetrahydrate/silver nanowires (AMT/AgNWs) modified screen printed electrode (SPE) for phosphate detection to achieve simplicity, high sensitivity, wide detection range, and high repeatability and portability. The cyclic voltammetry measurements exhibited the sensitivities of AMT modified SPE without and with AgNWs are 0.1 μA/μM and 0.71 μA/μM, respectively. The use of highly conductive AgNWs significantly increased the sensitivities of the AMT/SPE. Besides, AgNWs and AMT modified SPE (AMT/AgNWs/SPE) showed a very wide detection range of 5 μM–1 mM. The maximum relative standard deviation of around 5% confirms the repeatability of the proposed sensor. This paper suggests that AMT/AgNWs/SPE is promising for simple, low-cost, and portable phosphate ion detection.

NM03.10.32
Control the One-Dimensional Growth of PbSe Nanorods Through Dipole-Dipole Interaction
Yiteng Tang1, Zhoufeng Jiang1, Paul J. Roland2, Randy Ellington2, Wenhui Wan3, Yuguang Yao4, Fan Zhang3 and Liangfeng Sun5; 1Bowling Green State University, Bowling Green, Ohio, United States; 2University of Toledo, Toledo, Ohio, United States; 3Beijing Institute of Technology, Beijing, China; 4The University of Texas at Dallas, Dallas, Texas, United States.

Lead selenide (PbSe) represents a promising thermoelectric material owing to its high thermolectric figure of merit. This property is expected to be further enhanced in anisotropic one-dimensional structures. A few research groups have synthesized colloidal PbSe nanowires/nanorods previously, where the one-dimensional oriented attachment was identified to be the primary growth mechanism. However, the microscopic mechanism of the growth is still poorly understood.

In our experiments, we demonstrated that long nanorods could only grow in reaction solution while the PbSe quantum dots were terminated by short ligands. If the quantum dots are terminated by long ligands, few nanorods are formed. This means that the attaching process can be turned on or off by tuning the length of surface ligands on the quantum dots, i.e. the dipole-dipole interaction between them. Using the amount of surface charge obtained experimentally by another research group, we calculated the dipole-dipole interaction energy between the quantum dots in the reaction solution and compared it with the thermal energy at the reaction temperature. We found that the calculated dipole-dipole interaction energy is above/below the thermal energy when the short/long ligands were used to terminate the PbSe quantum dots, which is consistent with the experimental results. Not only it reveals that the dominant growth mechanism is the one-dimensional oriented attachment of quantum dots, but also it proves that the length of the surface ligands on the quantum dot can control the process.

The reaction temperature also has a significant effect on the growth of nanorods. At higher reaction temperature, the dominant growth mechanism shifts from kinetics (oriented attachment) to thermodynamics. In the latter case, no nanorods but large quantum dots are formed.

The synthesized nanorods have a high photoluminescence quantum yield of more than 30% and photoluminescence lifetime near 1 microsecond. Both indicate that the nanorods have low defects and a high quality.

NM03.10.33
Cadmium Telluride Nanowires Growth for Photovoltaic Application
Manuel Apollo1, Wojciech Stepniowski2, Massimo Tormen3 and Kenneth Duruse4; 1University of Liverpool, Liverpool, United Kingdom; 2Lehigh University, Bethlehem, Pennsylvania, United States; 3ThunderNIL Srl, Trieste, Italy.

There is a global drive to increasing the efficiency, performance and cost effectiveness of renewable energy sources including the photovoltaic (PV) devices. Currently the PV market is dominated by silicon (Si) solar cells technology. Although their performances, they suffer technological limitations, such as an indirect bandgap and low absorption coefficient. An alternative material like cadmium telluride (CdTe), a II-VI semiconductor, exhibits a direct bandgap of approximately 1.45eV, which enables optimal absorption of the solar radiation. Therefore high efficiency CdTe solar cells are thinner and more economically convenient than Si solar cells[1].

In addition, it is possible that nanostructures may be used to create new kinds of devices with enhanced optical performance over existing structures. It is the aim of our project to explore these opportunities, in particular the possibility of growing nanowires (NWs) in the template assisted method, using aluminum oxide membranes or nanoimprints supplied by ThunderNIL Srl.

Once obtained the templates, different techniques relating the nanostructures growth (sublimation, VLS, CSS, spattering, spin coating) will be explored. The nanostructures so obtained will be characterized via XRD, SEM, UV-UVS-IR. It is the aim to then fabricate and test working solar cell devices from the nanowire materials via impedance analysis, current-voltage, capacitance voltage, PV performance (Air Mass 1.5).

Our goal is to demonstrate that is possible to manufacture high performant and cost effective CdTe nanostructured solar cells.

References:

NM03.10.34
Facile, Sing-Step Hydrothermally Synthesized Sb-Doped ZnO Nanorod Arrays with Highly Improved Efficient UV-Sensing Properties
Donghyung Kim, Hongsseon Song, Miniki Baek, Minseok Lee, Dokyung Kim and Kijung Yong; Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

The synthesis of electrical and optical property-modulated, low-dimensional metal oxide semiconductors has been adopted for the development of nanodevices. However, conventional modulation methods, such as doping and alloying, generally require complex and expensive processes, such as multi-step high-temperature reactions, gas-phase growth, high-vacuum processes, etc. Alternatively, in the current study, the facile and cost-effective synthesis of Sb-doped ZnO nanorod arrays (NRAs) is achieved using a simple hydrothermal growth process at 95 °C. Through a single-step reaction, Sb atoms are substitutionally doped at the Zn atom sites with control of the Sb concentration. Sb dopants and Sb-induced oxygen vacancies increase the electron concentration in the ZnO NRAs, enhancing the electrical conductivity of the ZnO NRAs and inducing the further adsorption of ambient oxygen molecules on the nanorod surface. Upon UV irradiation of the highly oxygen-adsorbed, Sb-doped ZnO NRAs, the desorption of oxygen induces greater conductivity changes compared to the undoped samples. Based on this enhanced resistivity change, UV sensor devices were fabricated, and an improved reversible UV sensing performance was observed, with a 9-fold enhancement in the photocurrent of the ZnO NRAs after Sb doping. Moreover, UV sensing is achieved...
even under an extremely low bias of 10⁻⁴ V, suggesting the promising application of this material in extremely low-power UV sensor devices.

**NM03.10.35**  
**Polarization-Sensitive Single-Crystal Sb2Se3 Nanowire Motor** Xiaojun Zhan; The University of Hong Kong, Hong Kong, Hong Kong.

Antimony selenide (Sb2Se3), a non-toxic earth-abundant promising absorber material for light harvesting, is inherently one dimensional crystal structure, covalent band within the chain and van der waals bond out of the chain. Such anisotropy has been studied for crystal oriented solar cell device and strong in-plane asymmetry of Sb2Se3 nanosheets. However, all of recently reported light-stimulated nano/micromotor systems haven’t utilized the polarized light, potential substitutional channel to wavelength or light intensity. Here an atomic smooth axis-oriented single-crystal Sb2Se3 nanowires are successfully prepared through vapor transport deposition method (VTD) possessing higher electrical conductivity than hydrothermal synthesized and bulk film counterparts and polarized response of incident light. Furthermore, coupled with a layer of conformal N type zinc oxide (ZnO), polarized light intrigued nano/micromotors’ motion is achieved for the first time. Besides the solar cell device behaviors of single-crystal Sb2Se3 nanowire and bulk Sb2Se3 film are compared and suggest the experimental limit for crystal oriented Sb2Se3 solar cells.

**NM03.10.36**  
**Influence of Gold Catalyst on the Growth of Titanium Nitride Nanowires** Panupong Jaipan¹, Chandra Shekar Reddy Nannuri¹, Nikhil R. Mucha¹, Adele Moatti², Jagdish Narayan², Svitlana Fialkova³ and Dhananjay Kumar³; ¹Mechanical Engineering, North Carolina Agricultural and Technical University, Greensboro, North Carolina, United States; ²Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States.

A systematic study was conducted to investigate the influence of Au catalyst thickness and Au nanodots size on the growth and morphological properties of Titanium Nitride (TiN) nanowires. The Au nanodot size has a significant influence on the diameter and length of the TiN nanowires. The fabrication of TiN nanowires induced by gold catalyst was successfully achieved at 800 °C. The nanowires were found to have their diameters in the range of 9 nm to 13 nm and their lengths from 96 nm to 430 nm. Our study has shown that Au nanodots with diameters in the range of 10-13 nm allows favorable conditions for TiN nanowire growth. On the other hand, the Au nanodots size with a diameter less than 10 nm are not able to induce the growth of TiN nanowires due to a high activation barrier to grow a nanowire with a small radius of curvature even in the presence of the catalyst. Furthermore, if the nanodot size is larger than 14 nm, the particle tends to behave as a bulk gold and loses its catalytic activity. The existence of a lower and upper threshold limit in the Au nanodots size is marked by the absence of TiN nanowire formation in both regions.

8:30 AM *NM03.11.01  
**Nano-Heterostructures Based on Oxide Nanowires—Synthesis and Characterization** Bianchi Mendez; University of Complutense, Madrid, Spain.

Oxide nanowires are an attractive family of functional materials that offer a lot of versatility in the applications: optical and mechanical resonators, lasing, sensors, photo-catalysis, solar cells, and biomedical and healthcare usages, to name a few. Besides, when it comes to the nanoscale, they can adopt a wide range of morphologies within the quasi-one dimension (nanowires, nanobelts, or nanorods). Some of the current challenges are focused on getting controllable doping, controllable luminescence or controllable architectures. In this last case, it would be worthy of attention to explore novel nano-heterostructures by making junctions of different oxides and/or even different dimensionality. We have experience on the study of physical properties of single oxides nanowires, and in particular their optical properties. Here, we report the synthesis and characterization of complex nanostructures of oxide nanowires in which Ga₂O₃ and Zn₂GeO₄ nanowires combine with SnO₂ particles, flakes or wires. The synthesis method is the thermal evaporation of the suitable chemical precursors on a catalyst-free basis via a vapor-solid mechanism. One of the key points to get the selected architectures is the presence of certain impurities, which influences the growth direction of the axis nanowire. This is important since the central oxide nanowire serves as substrate for the nano-oxides grown on it. The growth model of the nano-heterostructures will be discussed with the aid of high-resolution transmission electron microscopy.

9:00 AM NM03.11.02  
**Bottom-up Engineering of Hematite Nanowire Heterostructures for Photoelectrochemical Water Splitting** PengYi Tang¹,², HaiBing Xie¹, LiJuan Han¹, Carles Ros², Marti Biset Peiro³, José Ramón Galán-Mascarós¹,⁴, Teresa Andreu², Juan R. Morante² and Jordi Arbiol¹,⁴; ¹Institut Català de Nanociència i Nanotecnologia (ICN2), CSIC and BIST, Barcelona, Spain; ²Catalonia Institute for Energy Research (IREC), Barcelona, Spain; ³Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Tarragona, Spain; ⁴ICREA, Pg. Lluís Companys 23, Barcelona, Spain.

The development of technologies for H₂ production or CO₂ reduction strongly relies on an abundant supply of protons and electrons liberated by water oxidation. [1-2] Therefore, photoelectrochemical (PEC) water oxidation is an important anodic half-cell process in the development of a sustainable artificial solar fuel system. In the PEC devices design, coupling water oxidation catalysts with active photoanode materials has become the most promising methodology, since the attachment/integration of the catalyst on the semiconductor light absorbers could kinetically facilitate interfacial charge transfer reactions.

In this contribution, we have fabricated ITO/Fe₂O₃/Fe₂TiO₅/FeNooH multi-layers nanowire heterostructures via combination of sputtering, hydrothermal, ALD, photo-electrodeposition methods for photoelectrochemical (PEC) oxygen evolution application. Structural, spectroscopic and electrochemical investigations disclose that the origin of the superior catalytic performance is owing to the interfacial coupling effect of ITO underlayer (Sn doping and conductivity promoter), ultrathin Fe₂TiO₅ coating (Ti doping, energetics and surface state density modulation) and FeNooH eletrocatalyst (varying surface state energy level). [2]

Meanwhile, an alternative earth-abundant CoFe prussian blue analogues (CoFe PBA) is incorporated in core-shell Fe₂O₃/Fe₂TiO₅ type II heterojunction nanowires as photoanodes for PEC water oxidation. The observed photocurrent is improved from 0.12 mA cm⁻² to 1.25 mA cm⁻² at 1.23 V vs. RHE under illumination by involvement of ultrathin Fe₂TiO₅ layer and CoFe PBA WOCs coating. Further investigation of the PEC mechanisms via
photoelectrochemical impedance spectroscopy unveils that the enhanced PEC performance of hematite nanowires is attributed to the enhanced charge transfer efficiency owing to the tuned energy level and density of surface state. [3-4]

References

[4] Pengyi Tang, LiJuan Han, Paul Pacciok, Marti Biset Peiró, Hong-Chu Du, Xian-Kai Wei, Lei Jin, Hai-Bing Xie, Qin Shi, Teresa Andreu, Joan Ramon Morante, Mónica Lira-Cantú, Marc Heggen, Rafał E. Dunin-Borkowski, José Ramón Galán-Mascarós, Jordi Arbiol, to be submitted.

9:15 AM NM03.11.03
Surmounting the Carrier-Transport and Stability-Bottleneck of III-Nitride Nanowire Solar-Water-Splitting Device for Efficient and Sustainable Hydrogen Generation [4] Mohammad F. Chowdhury*, Hong Guo and Zetian MI, 1, 2; 1, 2-Electrical and Computer Engineering, McGill University, Montreal, Quebec, Canada; 1, 2-Electrical Engineering and Computer Science, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 1, 2-Department of Physics, McGill University, Montreal, Quebec, Canada.

Hydrogen generation from the two of the most abundant free resources available on earth, i.e. sunlight and water via photocatalytic water splitting, is a very appealing approach for the crucial societal transition to a clean and sustainable energy resource future. High-efficiency devices for photovoltaic-assisted photoelectrochemical (PEC) water splitting and electrolysers are reported in conductive electrolytes with selective pH adjustments. However, direct splitting of pure or sea water with significantly enhanced device-longevity at concentrated sunlight holds enormous promise for hydrogen generation at pH-neutral condition without any external bias, sacrificial reagent or conductive electrolytes. Progress in this field has been limited by the low photocatalytic efficiency of conventional metal-oxide materials. We have recently demonstrated that nearly defect-free GaN-based nanostructures can meet the thermodynamics for overall water splitting (OWS) [1]; and by tuning the surface Fermi-level through controlled Mg-dopant incorporation, the apparent quantum yield for solar-to-hydrogen conversion can be enhanced by nearly two orders of magnitude under UV [2] and visible light illumination [3-4]. In this work, we demonstrate multi-band InGaN nanosheet photochemical diode (PCD) structures, which can induce spontaneous charge carrier separation and steer them toward distinct redox sites for water oxidation and proton reduction reaction. During the synthesis of InGaN PCD nanosheets, p-type dopant (Mg) concentrations are rationally tailored, which induces a large built-in electric field between the two parallel surfaces. Due to the presence of a net built-in potential (~300 meV) along the lateral dimension, the two surfaces are enriched with photo-generated holes and electrons to perform water oxidation and proton reduction reactions, respectively [5]. With spatially separated catalytic sites and reduced carrier recombination, the nanoscale PCDs exhibit stoichiometric H2 and O2 evolution, with a production rate of ~1.62 mmol h⁻¹ cm⁻² and ~0.784 mmol h⁻¹ cm⁻², respectively, which is equivalent to a solar-to-hydrogen efficiency over ~3%. We are currently developing a novel III-Nitride nanostructured device on Si wafer which, when decorated with suitable co-catalyst nanoparticles on surfaces, can demonstrate unprecedented performance-stability in photochemical water splitting reaction - the longest ever measured for any semiconductor photocatalysts or photoelectrodes without protection/passivation layers in unassisted solar water splitting with an STH >1%. With further structural and surface engineering of the nanowires, we aim to enhance the solar-to-hydrogen efficiency in the range of 5-10%.


9:30 AM NM03.11.04
GaN Nanowire Arrays for Photocatalytic Applications [5] Julia Winne1, Sabrina Armeier, Richard Hudecek and Martin Stutzmann; Walter Schottky Institut, Technische Universität München, Munich, Germany.

In recent years, group III-nitride nanowires (NWs) have attracted increasing interest for device fabrication due to their high crystal quality, large surface-to-volume ratio and their waveguide character. The favorable energy position of their bands with respect to many oxidation and reduction reactions and their chemical stability under harsh environments make them interesting candidates for photocatalytic applications, e.g. water splitting or CO2 reduction. The integration of group III-nitride NW arrays on GaN-based light emitting diodes (LEDs), serving as a platform for electrically driven NW-based photocatalytic devices, enables an efficient coupling of the light from the planar LED to the GaN NWs. Here, we present a systematic numerical study of the influence of the NW geometry, i.e. diameter, period and length, and the illumination wavelength on the coupling of the light from the LED into the GaN NW arrays. We found that for large NW periods the interaction of light with the GaN NW arrays is to the waveguide modes, providing an enhanced evanescent field around the NWs, whereas for dense NW arrays, it is additionally affected by the inter-wire coupling and the excitation of in-plane waveguide modes. Transmission measurements of GaN NW arrays on transparent sapphire substrates confirmed the coupling of light into waveguide modes. Experimental measurements of GaN NW arrays on GaN-based LED substrates verified an efficient coupling of the light from the LED to the NWs. For NW-based photocatalytic applications, we found that GaN NW arrays with diameters for which the incident light is coupled weakly to the waveguide modes, providing an enhanced evanescent field around the NWs, have to be chosen for a maximum illumination of the NW surface and, thus, a maximum excitation of photocatalytic reactions. Fluorescence measurements are performed in order to investigate the optical coupling of the evanescent field and dye molecules immobilized on the NW surface. [1]


9:45 AM NM03.11.05
Seed-Layer Free Zinc Tin Oxide Tailored Nanostructures for Nanoelectronic Applications Produced by Low-Temperature Hydrothermal Synthesis [6] Ana Rivasco, Rita Brunquinho, Jorge Martins, Elvira Fortunato, Rodrigo Martins and Pedro Harquinhã; i3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology, Universidade NOVA de Lisboa and CEMOP/UNINOVA, Caparica, Portugal.

Looking at the actual technology development, we are facing an increasing demand for smart and multifunctional surfaces on all sorts of objects and shapes. With this, flexible and transparent electronics is being pushed to unprecedented performance and integration levels [1]. Thus appears the necessity for a new generation of materials combining sustainability, low dimensions and still a wide range of properties compatible with its application on transistors, memories, sensors or even energy-harvesting components. For this end, indium-free multicomponent oxide nanowires (NWs) such as zinc-tin...
oxide (ZTO) are some of the most promising material systems for an upcoming generation of sustainable yet high performing transparent nanoelectronics. Being a ternary oxide ZTO is a multifunctional material, with a wide applicability in for example photocatalysis, nanoelectronics, sensors and energy harvesting. ZTO can crystalize in Zn$_2$SnO$_4$ and ZnSnO$_3$ phase, with different types of structures possible for each phase. However its synthesis is hard to control, due to the presence of two cations. In this context, this work presents a detailed study on the influence of both chemical [2] and physical [3] parameters in the hydrothermal synthesis of seed-layer free ZTO nanostructures at temperatures of only 200 °C. The low-temperature hydrothermal methods explored here proved to be a low-cost, reproducible and highly flexible route to obtain multicomponent oxide nanostructures, namely Zn$_2$SnO$_4$ nanoparticles and ZnSnO$_3$ nanowires with length ∼ 600 nm. Optical and electrical properties close to the reported for nanostructures obtained by high temperature processes were achieved. Particularly, band gaps of 3.60 and 3.46 eV, for ZnSnO$_3$ and Zn$_2$SnO$_4$, respectively, and a resistivity of 1.42 kΩ.cm for single ZnSnO$_3$ nanowires were obtained. For electrical characterization, nanomanipulators inside SEM were used, after a localized deposition of Pt electrodes by e-beam assisted gas decomposition. The seed-layer-free nature of the developed synthesis allowed a facile application of the ZTO nanowires for photocatalytic applications and memresistive devices with very promising results being already obtained for both cases. These two illustrate how a wide array of applications can be successfully envisaged, given the flexible nature of a seed-layer free synthesis, and furthermore showing that good performance can still obtained even when considering low temperature hydrothermal methods.


10:00 AM BREAK

SESSION NM03.12: Nanowire Growth Mechanisms
Session Chairs: Kimberly Dick Thelander and Takeshi Yanagida
Wednesday Morning, November 28, 2018
Sheraton, 2nd Floor, Back Bay D

10:30 AM *NM03.12.01
In Situ TEM Imaging of Semiconductor Nanowire Growth by the Electrochemical Liquid-Liquid-Solid (ec-LLS) Method Stephen Maldonado; University of Michigan, Ann Arbor, Michigan, United States.

Presently, the majority of methods for bottom-up synthesis of crystalline nanowires follow a common set of themes. First, high temperatures and/or low pressures are used to drive the thermal decomposition of vapor phase precursors to their zero-valent forms. Second, the precursors/reactants are heavily refined and often difficult to handle, and store. Third, growth reactors involve some elements of heating and/or low pressures to effect nanowire growth. New synthetic strategies that avoid these aspects, without sacrificing material quality, could enable new applications and device manufacturing opportunities for semiconductor nanowire materials. Electrodeposition is one alternative methodology that can produce nanowires with simple infrastructure and at low temperatures. Our lab has pioneered the ec-LLS concept as a particular electrodeposition tactic that blends electrochemistry with melt crystal growths. For nanowires, ec-LLS draws strong parallels from vapor-liquid-solid (VLS) growth concepts, but can be conducted in air, on the benchtop, and with unrefined (oxide) precursors. Despite the similarities with VLS, ec-LLS also introduces factors of surface charge, electrostatic fields, and precisely tunable electrochemical driving forces that can affect the nucleation and crystal growth steps. Our ongoing work highlights how these different factors can be understood and ultimately leveraged for specific target material properties. This presentation highlights data that describe our latest insights on the controlling factors in electrochemical liquid-liquid-solid (ec-LLS) growth processes for semiconductor nanowire synthesis. The presented results will include in-situ videos of ec-LLS nanowire growths that describe the conditions necessary to nucleate and grow nanowires at ambient temperatures. Additional supporting ex-situ TEM, atom probe tomography, and electrical characterization data will be presented that speak to the purity and conductivity of as-prepared Ge nanowires.

11:00 AM NM03.12.02
Epitaxy of Semiconductors on 2D Materials via Solid Phase Catalytic Growth Frances M. Rossi1, Priyanka Periwal2, Joachim Dahl Thomsen3, Dmitri N. Zakharov4, Mark C. Reuter1, Lynne Gignac1, Timothy J. Booth5 and Stephan Hofmann2; 1IBM T. J. Watson Research Center, Yorktown Heights, New York, United States; 2Department of Electrical Engineering, University of Cambridge, Cambridge, United Kingdom; 3Department of Micro- and Nanotechnology, Technical University of Denmark, Kongens Lyngby, Denmark; 4Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

Control of crystal growth and the integration of heterogeneous materials are central to the semiconductor industry. A key challenge is therefore to create well-defined interfaces reproducibly between materials that are lattice mismatched. Several strategies have proven successful for materials integration: catalytic crystal growth is used to self-assemble nanostructures such as nanowires that integrate lattice mismatched crystals, while van der Waals epitaxy can unify lattice mismatched 2D materials. However, forming well defined interfaces between 2D materials and standard 3D materials, such as Si and Ge, remains a challenge. Here we show that the catalytic pathways for semiconductor deposition that have been developed for nanowire growth can be exploited to grow epitaxial Ge, Si and other semiconductor nanocrystals on 2D materials such as graphene and hexagonal boron nitride. By using solid metal nanoparticle catalysts that are themselves epitaxial on the 2D materials, we show that epitaxial Si and Ge nanocrystals can be formed by a vapor-solid-solid growth mechanism. In situ transmission electron microscopy is used to explore the reaction pathways for this process, which takes place at lower temperature and with an improved degree of epitaxy compared to direct chemical vapor deposition or deposition using liquid phase catalysts. We discuss the prospects for the formation of nanostructure arrays and single crystal thin films.

11:15 AM NM03.12.03
Morphology Dependent Strain Relaxation in Horizontally Grown ZnSe@ZnTe Core-Shell Nanowires and Its Effects on Electronic Band Alignment Sara Martí-Sánchez1, Eitan Oksenberg2, Marc Botifoll2, Christian Koch3, Quintin Ramasse3, Ernesto Joselevich3 and Jordi Artisal1, 4; 1Catalan Institute of Nanoscience and Nanotechnology (ICN2), Bellaterra, Spain; 2Department of Materials and Interfaces, Weizmann Institute of Science, Rejovot,
Core-shell Ge\(_{1-x}\)Sn\(_x\) nanowires synthesized via VLS one-dimensional crystal growth have been demonstrated to exhibit desirable optical properties. The core-shell strain plays an important role in the enhanced photon emission. We characterize the strain in these nanowires using strain mapping in scanning transmission electron microscopy in 4D-STEM diffraction, a spatially resolved technique. 4D-STEM is also sensitive to lattice defects such as Sn-rich lattice plane inclusions in the GeSn shell of core-shell Ge\(_{1-x}\)Sn\(_x\) nanowires. Coupled with defect imaging, we can better understand the formation and the origin of defects in GeSn. Although characterization of strain in core-shell nanowire cross-sections is complicated by sample mechanical relaxation, choice of thinning orientation allows accurate spatially localized strain measurements. Phase field simulations of the core-shell nanowire structures provide an estimate of the expected strain, which matches well with experimental measurements from 4D-STEM, and explains the formation of six-fold symmetric Sn-poor spikes in the Ge\(_{1-x}\)Sn\(_x\) shell.

Over the recent years III-V semiconductor NWs have become widely studied nanostructures for nanophotonics, optoelectronics and advanced nanoelectronics. The ability to control the NWs’ diameters and lengths give rise to tunable quantum confinement effects [1]. For InAs NWs very strong quantum confinement effects are expected to occur for diameters well below 30 nm [2] – a regime which has hitherto been difficult to reach by conventional bottom-up growth methods. Here, we develop such ultra-confined InAs NWs with size dimensions far below 30 nm and further aim to understand their optical properties and charge carrier dynamics set by the 1D electronic subband structure. The presented InAs NWs are grown along the [111] direction on SiO\(_2\)-masked Si (111) using a completely catalyst-free vapour-solid (VS) growth mechanism [3, 4] via selective-area molecular beam epitaxy (SA-MBE).

In a first approach we show how by direct bottom-up SA-MBE the NW dimensions can be controlled by tuning both growth parameters and substrate pattern design. After optimizing V/III ratio and temperature, we illustrate that the interwire separation (growth pitch) and the growth time are critical for reaching sub-30 nm InAs NWs. In contrast, the shape and diameter of the mask opening seem less influential as the NWs grow randomly from the edge of the mask opening. This way we obtained, InAs NWs with diameters as low as ~20-25 nm.

In a second approach, we explore a so-called reverse reaction growth (RRG) mechanism to intentionally thin as-grown InAs NWs by in situ thermal annealing [1, 5]. Starting from > 1 \(\mu\)m long NWs with diameters of > 60 nm we performed various different thermal annealing experiments by varying in situ vacuum conditions, As-overpressure, annealing temperature and time. Most interestingly, under controlled As-overpressure the InAs NW sidewalls start to thermally decompose from the top in distinct hierarchical sequences. Using sacrificial NWs and specific pitch-dependent kinetics, we thereby realized so far InAs NWs with diameters < 15 nm.

Ongoing experiments are also shown which (i) identify the influence of the RRG mechanism on the microstructure using TEM (transmission electron microscopy), and which (ii) explore the level of radial quantum confinement in the ultrathin InAs NWs by \(\mu\)-photoluminescence (PL) spectroscopy. First preliminary low-temperature PL spectra of a NW-array with sub-30 nm diameter show a substantial blue-shifted peak emission (> 0.48 eV) compared to conventional unconfined NWs [5]. The data are further correlated with simulations of the optical transition energies under the influence of strong radial quantum confinement.

1 B. Loitsch et al Advanced Materials, 27 (2015), 2195
3 J. Becker et al ACS Nano, 12 (2018), 1603
The photoluminescence (PL) emission properties of group III-nitride nanowires and nanowire heterostructures sensitively respond to changes in the chemical environment in gaseous and liquid atmospheres. At the same time, the presence of photogenerated charge carriers on their surface can trigger chemical processes by charge transfer into electronic levels/molecular orbitals of adsorbed gas molecules or surrounding electrolytes, as it is also employed in photo-electrochemical water splitting. Hence, monitoring of the PL and controlling the photocurrent allows for analyzing and initiating photoactivated chemical surface processes as well as establishing new principles for opto-chemical nanosensors or chemically sensitive nanophotonic probes. We demonstrate these strategies by discussing different examples such as detection and analysis of water adsorption, optical pH-sensing or dynamic imaging of biochemical cellular processes. When coated with ultrathin oxide coatings such as TiO$_2$ or CeO$_2$, InGaN/GaN nanowires can serve as nanophotonic probes to monitor ion transport and diffusion processes in the oxide film. As examples we discuss optical in-situ monitoring of oxygen self-diffusion in CeO$_2$-coatings as well as Li$^+$-intercalation in TiO$_2$.

The concern about the presence of toxic and potentially harmful gases in outdoor and indoor environments is continuously increasing. Numerous types of gas sensor devices and systems are used to monitor the presence of these gases in the atmosphere. Among the different possibilities, solid state gas sensors are an excellent choice due to their low cost and low power consumption thanks to MEMs technology, and remarkable performances obtained with metal oxide nanowire-based gas sensors in terms of sensitivity and response time. However, metal oxides usually lack in selectivity, being only able to distinguish among oxidizing or reducing gases. A solution to this problem is the called e-nose, where pattern recognition across sensor arrays with different sensing characteristics (using different materials or operation temperatures) is applied. The present work demonstrates for the first time that site-selective growth of different materials in the form of nanowires for sensing applications is possible on a single chip in a well-defined geometry. The growth of nanowires on top of micromembranes can be easily adjusted and represents a simple and suitable fabrication process for the direct integration of different nanowire-based resistive multifunctional devices. The use of chemical vapor deposition techniques is compatible as a CMOS post-processing and, therefore, the impact of preparing gas sensors on any kind of chips for multifunctional devices is unimaginable. This proof-of-concept is exemplified by the deposition of SnO$_2$, WO$_3$ and Ge nanowires on different membranes of one single chip and their gas sensing responses towards different concentrations of CO, NO$_2$ and humidity diluted in synthetic air are shown. The devices presented here have the same gas sensing behavior as devices made on separate chips and CVD chambers. The principal component analysis (PCA) of the collected data allows gas separation and identification and, thus, it is proved that the system is a well-operating nanoelectronic nose.

Metal-oxide semiconductor gas sensors are viable alternates for highly sensitive and selective detection of different gases and air pollutants, which provide various advantages such as miniaturization, low cost gas detection, and real-time monitoring. Various strategies have been used to increase the gas response and selectivity, including modulating the sensing temperature, [1] morphological control, [2] catalyst doping/loading, [3] and catalytic filtering of interference gases [4]. Constructing heterostructures between two different oxides is an effective method to enhance gas response, via controlling the conductivity at p-p, p-n, and n-n interfaces, as well as the selectivity, through synergistic catalytic effects between different materials. In particular, reports given by the group of Miura [5] and Noh [6] show that the gas sensing properties could be enhanced by adding WO$_3$ to NiO based sensors or NiO to the WO$_3$ based sensors. Inspired by this fact, it is very essential to design NiO/WO$_3$ heterostructures for studying their gas sensing properties. WO$_3$ is an n-type semiconductor, and has been intensively studied as a gas-sensing material [7]. On the other hand, NiO is a p-type semiconductor attaining considerable attention for gas-sensing applications in the past few years [8].

The main idea behind this work is to bring together the properties of two different nanostructure materials into a single sensing platform by using a simple, low cost and high yield method. In this way, one platform with different materials properties can be used detect the variety of gases. Herein, we report the novel preparation and characterization of NiO/WO$_3$ branched 1D-1D nano-heterostructures, consisting of inner NiO nanowires [8] and outer WO$_3$ nanowires obtained through vapor-phase method. The surface morphology of the nanowires was investigated by using scanning electron microscopy (SEM). For structural characterization, instead, GI-XRD, transmission electron microscopy (TEM) and Raman spectroscopy were performed. The structural characterizations shows the presence of nickel tungstate (NiWO$_4$) phase in the nanostructures. Finally, NiO nanowire and NiO/WO$_3$ heterostructure based conductometric gas sensing devices have been fabricated and tested towards different gases spcies such as (NO$_2$, H$_2$, CO, VOC’s) and their sensing performances have been compared. Interestingly, NiO/WO$_3$ NWs heterostructure based sensing devices shows superior performance compared to NiO sensors.

References:
Ultrafast Lights up the Nanoscale—Pushing the Limits of THz Spectroscopy to Reveal Novel Nanowire Optoelectronic Properties with fs-Temporal and nm-Spatial Resolution

By Jessica L. Boland
University of Oxford, Oxford, United Kingdom; University of Regensburg, Regensburg, Germany.

Between the microwave and infrared regions of the electromagnetic spectrum lies the so-called "terahertz gap," a band of terahertz (THz) frequencies which are difficult to access by conventional photonic or electronic technologies. Due to their high charge carrier mobilities and tunable charge carrier lifetimes, III-V semiconductor nanowires exhibit great potential for optoelectronic devices operating at these THz frequencies. For example, high performance nanowire-based photoconductive THz detectors [1] and ultrafast switchable THz polarisation modulators [2] have been recently demonstrated.

Just as III-V nanowires show great promise for THz devices, the THz spectral region is greatly promising for the development and optimisation of III-V nanowire materials. Specifically, transient THz spectroscopy provides a powerful contact-free means of measuring nanowire electrical properties. It can achieve accurate measurements of charge carrier transport and dynamics at room temperature with sub-picosecond temporal resolution, and yields key parameters such as electron mobility, ionised dopant density, charge carrier lifetime and surface recombination velocity. Being a contact-free technique, it overcomes many of the challenges associated with traditional contact-based measurements and provides fast feedback to growth experiments. This has enabled the optimisation of growth parameters for achieving nanowire heterostructures, doped nanowires and modulation-doped nanowires [3, 4]. This talk will discuss how THz spectroscopy is guiding nanowire growth, the cross-correlation of THz and contact-based measurements, and the engineering of nanowire-based devices, particularly devices operating at THz frequencies.


3:30 PM *NM03.14.01

Studying and Exploiting the Unique Properties of III-V Nanowires in the Terahertz Gap

By Hannah J. Joyce
University of Cambridge, Cambridge, United Kingdom; University of Oxford, Oxford, United Kingdom; University of Regensburg, Regensburg, Germany.

Between the microwave and infrared regions of the electromagnetic spectrum lies the so-called "terahertz gap," a band of terahertz (THz) frequencies which are difficult to access by conventional photonic or electronic technologies. Due to their high charge carrier mobilities and tunable charge carrier lifetimes, III-V semiconductor nanowires exhibit great potential for optoelectronic devices operating at these THz frequencies. For example, high performance nanowire-based photoconductive THz detectors [1] and ultrafast switchable THz polarisation modulators [2] have been recently demonstrated.

Just as III-V nanowires show great promise for THz devices, the THz spectral region is greatly promising for the development and optimisation of III-V nanowire materials. Specifically, transient THz spectroscopy provides a powerful contact-free means of measuring nanowire electrical properties. It can achieve accurate measurements of charge carrier transport and dynamics at room temperature with sub-picosecond temporal resolution, and yields key parameters such as electron mobility, ionised dopant density, charge carrier lifetime and surface recombination velocity. Being a contact-free technique, it overcomes many of the challenges associated with traditional contact-based measurements and provides fast feedback to growth experiments. This has enabled the optimisation of growth parameters for achieving nanowire heterostructures, doped nanowires and modulation-doped nanowires [3, 4]. This talk will discuss how THz spectroscopy is guiding nanowire growth, the cross-correlation of THz and contact-based measurements, and the engineering of nanowire-based devices, particularly devices operating at THz frequencies.


4:00 PM NM03.14.02

Ultrafast Lights up the Nanoscale—Pushing the Limits of THz Spectroscopy to Reveal Novel Nanowire Optoelectronic Properties with fs-Temporal and nm-Spatial Resolution

By Jessica L. Boland
University of Oxford, Oxford, United Kingdom; University of Regensburg, Regensburg, Germany; Lund University, Lund, Sweden; École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Accurate characterization of the electronic properties of semiconductor nanowires is essential for the development of novel nanowire-based devices. In order to harness the full potential of these materials, an in-depth understanding of key properties, such as charge carrier lifetimes, mobilities, doping concentrations, charge carrier recombination and scattering mechanisms, is vital. However, detailed studies still prove challenging, as the inherent quasi-one dimensional nanowire geometry impedes conventional electrical measurement techniques. Challenges in fabricating lateral Ohmic contacts for Hall effect measurements and uncertainty in the gate capacitance term for field effect measurements, render such techniques difficult. Therefore, non-contact, non-destructive techniques, such as terahertz and Raman spectroscopy, are highly desirable for obtaining the nanowire optoelectronic properties, providing a route for optimization and control of the nanowire transport properties for device optimization.

In this work, both far-field optical-pump terahertz-probe (OPTP) spectroscopy and near-field terahertz scanning optical microscopy (THz-SNOM) are presented as alternative techniques for accurate characterization of the charge carrier dynamics in semiconductor nanowires. First, OPTP spectroscopy is employed for InAs, Sb, nanowires. Photoconductivity lifetimes, carrier mobilities and scattering rates are obtained at room temperature and within the temperature range of 4 – 300K for a range of Sb contents. As Sb content is increased, the defect density within the NWs reduces, leading to an increase in electron mobility and carrier lifetime. For 35% Sb concentration, the highest ever electron mobility for III-V NWs is reported at ~7000cm²V⁻¹s⁻¹ at 300K, indicative of reduced impurity scattering in the NW due to reduced defect density offered by Sb incorporation. These results highlight the potential of OPTP as a powerful tool for characterising nanowire behaviour. Secondly, THz-SNOM is discussed as a near-field method for examining the local optoelectronic properties of a single nanowire and preliminary measurements on Bi₂Sₑ nanowires are presented. With this technique, the optoelectronic properties of semiconductor nanowires can be resolved with not only femtosecond temporal resolution but also nanometre spatial resolution. The technique is also surface-sensitive, allowing the transport and dielectric properties of the nanowire to be resolved at different depths within the nanowire, isolating contributions from the bulk and the surface to the nanowire conductivity.

4:15 PM NM03.14.03

Wavelength-Selective Reflection Enhancement Towards Rare-Earth Doped 1D-Nanolasers

By Maximilian Zapf
University of Jena, Jena, Germany; University of Regensburg, Regensburg, Germany.

Wavelength-selective (WS) reflection enhancement using rare-earth ions (REIs) in III-V nanowires is presented. A novel method for growth and post-growth processing to achieve WS reflection enhancement is described. WS reflection enhancement is shown to be a general method for REI activation and the realization of nano-scaled lasers. Nano-scaled lasers are essential for future optoelectronic applications in life sciences, chemistry, and physics for on-chip sensing, spectroscopy, and optical data communication. Optically one-dimensional nanolasers are currently realized using semiconductor nanowires (NWs) under intense optical excitation, as they inherently combine the required semiconductor optical gain and the beneficial NW morphology. This morphology allows efficient wave guiding and provides a nanoscale Fabry-Pérot-type cavity.
resonator structure, where the cavity is determined by reflections at the nanowire end facets due to refractive index contrast. Both the internal material gain and the end facet reflectivities strongly influence the lasing threshold. Distributed Bragg reflectors (DBRs), where the nanowire is periodically cut, have higher reflectivity than a single end facet at wavelengths pre-determined by the spacing of cuts. These wavelength-selective mirrors can be combined with gain from the semiconductor material or from dopants ion implanted into the NW to shift laser emission within a broad spectral range. Finite-difference time-domain calculations were performed to simulate the wavelength-dependent reflections occurring at an air - ZnO DBR structure. Such DBR structures were milled into ZnO nanowires using inert-gas focused ion beam providing the high refractive index contrast between the ZnO material and air. Subsequently, reflection and transmission properties of the DBR structures have been studied. Enhanced wavelength-dependent end facet reflections allow reducing laser thresholds in nanowire lasers as well as tailorable nanoscale wavelength filtering, and spectral emission tuning. This wavelength-selective reflection enhancement can be applied in order to realize sub-band gap nanolaser emission in arbitrary spectral regimes determined by the optical gain of the dopants.

4:30 PM NM03.14.04
GaAsSbN Based Core-Shell Nanowires with Photoluminescence Emission Reaching 1.55 μm Prithviraj Deshmukh1, Manish Sharma1, Surya Nalamati1, Lewis Reynolds2, Yang Liu2 and Shanthi Iyer1; 1Department of Electrical and Computer Engineering, North Carolina Agricultural and Technical State University, Greensboro, North Carolina, United States; 2Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; 3Nanoengineering, North Carolina Agricultural and Technical State University, Greensboro, North Carolina, United States.

Incorporation of nitrogen in the GaAsSb shell is studied to reduce the bandgap energy for realizing nanoscale optoelectronic devices in the telecommunication wavelength region. Bandgap tuning up to 1.55 μm in GaAsSbN nanowires (NWs) can be achieved using dilute amounts of nitrogen in the shell. Engineering the material composition and structure of the core-shell NW for bandgap reduction has not been fully explored in this quaternary system. Previous work on GaAsSb [1] and GaAsSbN [2] shell utilizes a GaAs NW as the core, which limits the amount of Sb to 10 at. % in the shell, due to NW bending and rough surface morphology. [2] In this work, we report on high density of vertical GaAsSb/GaAsSbN core-shell configured nanowires, with smooth surface morphology and Sb compositions exceeding 10 at. %, in the shell, grown on Si (111) substrates using plasma assisted molecular beam epitaxy. Nitrogen incorporation in the dilute nitride shell was optimized to produce high photoluminescence (PL) intensity. Effects of N incorporation on the morphology of NWs were studied to optimize a closely lattice-matched core-shell material configuration. Study of variation in shell thickness and V/III ratio are carried out to achieve NWs with reduced bandgap energy and smooth morphology. Room temperature PL emission of 1.55 μm has been achieved. Annealing in dilute nitrides is essential for annihilation of N-induced point defects and band tail states. [3] We have carried out rapid thermal annealing in N2 ambient at varying temperatures in order to eliminate point defects and to enhance the PL intensity. Changes in peak positions and spectral lineshapes in the Raman spectra of annealed samples have been used to ascertain the nature of the defects being annihilated. Study of structural quality of dilute nitride NWs using transmission electron microscopy will also be presented. We successfully demonstrate significant bandgap reduction in the core-shell NWs by engineering appropriate reduction in the lattice strain with the non-nitride core.

Acknowledgment: This work is based upon research supported by the U.S. Office of Naval Research under award number N00014-16-1-2720

References:

4:45 PM NM03.14.05
GeSn Mid-Infrared Nanophotonic Resonant Absorbers Siying Peng, Michael Braun, Andrew C. Meng, Zhengrong Shang, Alberto Salleo and Paul C. McIntyre; Geballe Laboratory of Advanced Materials, Stanford University, Stanford, California, United States.

Mid-IR wavelengths are technologically crucial for chemical sensing, thermal imaging and LIDAR communications. Having been shown to exhibit a direct bandgap, GeSn alloys hold great promise as a mid-IR light emitting and absorbing material, with the potential to be monolithically compatible with existing silicon technologies. Therefore GeSn can open pathways for miniaturization of mid-IR devices such as on-chip molecular sensors, optical interconnect and thermal cloaking. Previous research on GeSn films has shown mid-IR lasing at T<90K. It has also been shown that GeSn nanowires with high-Sn content exhibit strong direct-gap PL at room temperature. In principle, GeSn nanowires have several advantages over thin films. GeSn film suffers the inherent compressive misfit strain from coherency with a silicon growth substrate, while GeSn nanowires are not constrained to lattice match with the substrate. In addition, epilayer film growth of metastable Sn alloy compositions (~10%) required to modify the conduction band structure of Ge so to achieve a direct band gap is likely to produce defects due local Sn surface segregation and/or phase separation. In comparison, GeSn nanowires grown by catalyzed low-temperature methods may be able to achieve unusually high Sn contents by solute trapping. Therefore, GeSn nanowires may constitute a superior laser gain medium compared to GeSn thin films, whose emission characteristics are limited by substrate-induced strain and non-radiative combination centers from defects. We have synthesized and characterized mid-IR photonic crystals consisting of GeSn/Ge core-shell nanowires. FDTD simulations reveal Mie resonances of the high refractive index (n>4) GeSn/Ge structures can be tuned to the desired wavelength by varying radius and height of individual nanowires. GeSn/Ge nanowires arranged in hexagonal photonic crystal arrays can be designed to be highly absorbing, by varying periodicity and filling factor of the photonic crystal. Ebeam lithography was utilized to pattern Au catalyst arrays on [111] Ge substrate, followed by two step VLS growth to synthesize GeSn nanowire arrays, with periodicity of 1000 nm and radius from 60 nm to 300 nm, and yielding 90% vertical growth. We then spin coat PMMA to insulate the Ge substrate from the nanowires, followed by ITO spattering for top contact. At bottom contact was then evaporated onto the n-type Ge substrate. Room temperature PL characterization reveals emission peaks from 1600nm to 2100nm. Mid-IR reflectance of the GeSn photonic crystal arrays was measured with FTIR, showing 40% reflectance from photonic crystal arrays, with the reflectance peak tunable with radius of the nanowires. We also performed photocurrent characterization with a FTIR spectrometer. Room temperature photocurrent was observed at wavelengths from 1.2μm to 2μm, generated from a non-coherent mid-infrared source. Nanophotonics tuning of the wavelength and widths of the photocurrent peak will be discussed.
Single crystalline metal oxide nanowires are interesting nanostructures due to their abundant resources and robustness in air and water. In addition, metal oxides exhibit many fascinating physical properties, including high-Tc superconductors, ferromagnetism, ferroelectrics, memristive properties, photocatalytic properties, transparent conductors and others, which are not attainable to conventional semiconducting materials (group IV and III-V).

However, fabricating single crystalline metal oxide nanowires has been based on a rule of thumb, there has been no general principle to design metal oxide nanowires. The feasibility of functional oxide nanowires, whose physical properties are hardly attainable to other materials, has been also strongly limited. Here I demonstrate i) a fundamental design concept for creating single crystalline oxide nanowires via vapor-liquid-solid (VLS) pathway, and ii) a development to measure the physical properties of a single nanowire, including electrical and thermal transport properties. By comparing experimental VLS nanowire growth to MD simulations, we found that the difference between LS interface and VS interface on the critical nucleation size essentially allows us to perform VLS nanowire growth. This knowledge can be expanded to discover novel metal oxide nanowires via VLS mechanisms. In addition, we have shown the impact of crystal growth interface on the electrical properties of metal oxide nanowires. I believe that the presented approaches by utilizing meal oxide nanowires offers an important platform for investigating not only nanoscale physical properties of transition metal oxides but also exploring novel nanodevices with other materials, which had not been possible to be integrated onto Si and/or plastic substrate.

Next, vanadium dioxide (VO₂) has attracted much attention due to its distinct change of physical properties across the metal-insulator transition (MIT). Specifically, VO₂ will experience a dramatic strain up to 1% along the c-axis as a result of MIT, which is hundreds of times larger than the other material such as piezoelectric ceramics and bimetal actuators, which could only have strain of 10⁻³-10⁻⁴ more importantly. Young’s modulus of VO₂ can approach 140 GPa, which is rather lower than steel. These distinctive characteristics make VO₂ a promising material in actuator applications. As previously reported, most of micro-sized VO₂ bimorph actuators are fabricated by pulsed laser deposition (PLD). However, the equipment required for PLD process is complex and expensive, and the preparation is time consuming and results in micro-scale VO₂ films, largely restricting its developing. In addition, the obtained VO₂ films demonstrated a severely limited output work density of 0.63 J/cm², compared with the theoretical value of 7 J/cm², which was caused by the disordered polycrystalline structures of VO₂ in PLD process. Therefore, a novel synthesis method is urgently required.

To break these limitations, we propose a facile and scalable method to fabricate large-scale and high-performance actuator films. In this work, we firstly synthesized ultra-long VO₂ nanowires (>100nm) via a scalable hydrothermal process, then successfully assembled the nanowires into super-aligned arrays in the water-oil-vapor interface. Subsequently, carbon nanotube (CNT) thin films were combined with the VO₂ super-aligned arrays to obtain VO₂/CNT actuator in a macro scale (1-5cm², much larger than that fabricated by PLD method). The synthesized actuator demonstrated excellent performance close to single crystal with the ratio of actuation displacement/length up to 0.83 and work density up to 5.67 J/cm³. Furthermore, VO₂/CNT actuator exhibited strong anisotropy characteristics, namely, its actuation direction would significantly change with the orientation of VO₂ nanowires. Besides, several biomimetic devices based on VO₂/CNT actuator are developed, and these devices have the advantages of superior performance, long-time durability and multiple excitation sources. Overall, we have fabricated high-performance VO₂/CNT actuator and biomimetic devices based on super-aligned VO₂ nanowire arrays for the first time, which will definitely pay a way for research on actuators and biometrical devices.

9:15 AM NM03.15.03 Oxidation-Enhanced Si Self-Diffusion in Isotopically Modulated Nanopillars Ryotaro Kiga1, Sayaka Hayashi1, Satoru Miyamoto1, Yasuo Shimizu2, Tetsuo Endoh3, Yasushi Nagai2 and Kohei M. Itoh1; 1School of Fundamental Science and Technology, Keio University, Yokohama, Japan; 2Institute for Materials Research, Tohoku University, Sendai, Japan; 3JST-ACCEL, Sendai, Japan.

In advanced Si-MOSFETs, current leakage issues have been pronounced as a result of approaching downsizing limit. A vertical gate-all-around architecture offers great advantages for both low-power consumption and high-density integration [1]. While gate-oxide formation surrounding nanoscale Si pillars involves a high-degree controllability, substantial modifications from conventional planar oxidation may be required for a precise process modeling of surface-oxidized nanopillar geometry. Recently, taking the geometrical and stress effects into account, several paths of Si atomic transport are theoretically predicted for the inner Si and outer SiO₂ regions, respectively [2]. In this work, we present experimental investigation of Si self-diffusion in the oxidized nanopillars by means of atom probe tomography (APT).

Here, a periodic Si isostructure heterostructure composed of naturally abundant ⁵²Si and isotopically enriched ⁵⁷Si (99.92%) was epitaxially grown on a Si(100) substrate, which was followed by a top-down metal-assisted chemical etching for obtaining isotopically modulated Si nanopillars. The resulting nanopillars having a diameter of ~200 nm were subject to dry oxidation at 900 °C for 4 hours. For reference, a nanopillar sample annealed in an Ar ambient was also prepared. Individual nanopillars were then picked up from each sample and sharpened into needle-shaped APT specimens by focused ion beam technique. In order to acquire ⁵⁷Si concentration profile along a pillar or depth axis, 3D mapping of Si isotopes was carried out using a laser-assisted atom probe (LEAP4000XHR, Cameca). In parallel, second ion mass spectrometry (SIMS) was performed only for an unetched bulk region outside nanopillars. The comparison of isostructure layer thickness with the SIMS profile enabled APT-based evaluation of Si self-diffusivity on a calibrated depth scale [3]. For a bulk region of the Ar-annealed sample, the Si self-diffusivity obtained from the APT analysis indeed represented good agreement with the SIMS result. In addition, whereas the Si self-diffusion was obviously enhanced for both nanopillar and bulk under dry oxidation, the self-diffusivity in nanopillar was found to remain comparable with the result for the bulk Si. Although oxidation-enhanced diffusion is known to take place via Si interstitials created at the Si/SiO₂ interface, they are most likely to diffuse out of the pillar core into the deep bulk region. However, the oxidation-enhanced diffusion holds irrespective of the nanosized structures since more Si interstitials can be injected into the pillar core due to high interface-volume ratio.

This work was supported by JST ACCEL Grant Number JPMJAC1301, Japan, and in part by JSPS KAKENHI (No. 15H05413).

Like GaAs and GaSb, GaAsSb ternary alloys are not expected to show hot carrier effects. We use femtosecond pump-probe measurements (TRS: transient Rayleigh scattering) in single zinc-blende GaAsSb nanowires at both 10 K and 300 K to monitor the photoexcited carrier density and temperature as a function of time and so determine directly the energy loss rate. We confirm that hot carriers quickly thermalize to the lattice predominantly through optic phonon emission as expected. Similar measurements were performed on GaAsSb-InP core-shell nanowires. While the growth of the InP shell results in substantially longer lifetimes through passivation of surface defects, we found, surprisingly, that the growth of the shell had a dramatic impact on the thermalization of the photoexcited carriers. Using TRS measurements, we monitor the density and temperature of carriers to determine the energy loss rate. At both 10 K and 300 K the optic phonon emission rate is strongly suppressed resulting in strong hot carrier effects. This is surprising since the GaAsSb nanowire core is the same in both cases. The presence of the InP shell is impacting directly the thermalization dynamics of carriers confined to the GaAsSb core.

We acknowledge the financial support of the NSF through grants DMR 1507844, DMR 1531373 and ECCS 1509706, and the financial support of the Australian Research Council.

9:45 AM NM03.15.05
Adjusting the Surface Band Structure of Bottom-up Grown Silicon Nanowires
Tobias Dlugosch, Tanja Sandner, Ahmed Chnani and Steffen Strehle
Ulm University, Ulm, Germany.

Silicon nanowire ion-sensitive field-effect-transistors were highlighted within the last decade as nanoscale transducers for label-free molecule detection owing to their large surface to volume ratio. Hence, a reliable and well-controlled transducer response is intimately linked to the electronic surface band structure, but which is still insufficiently explored. Here, we discuss the electronic surface band structure of bottom-up grown silicon nanowires as well as strategies that allow to rationally adjust the position of the surface valence and conduction band edge as well as the surface Fermi-level position. The studies were carried out by using a Kelvin probe, ambient photoelectron spectroscopy, and ambient surface photovoltage spectroscopy allowing an absolute reconstruction of the electronic surface band structure as well as an estimation of the charge carrier lifetime. In principle, as-grown silicon nanowires showed frequently the well-known mid-band gap Fermi-level pinning, governed by surface states, which significantly limits the transducer sensitivity. Nevertheless, the surface band structure can be effectively controlled by suitable surface state passivation layers. Besides a hydrogen termination, a common surface functionalization, e.g. by (3-aminopropyl)trimethoxysilane and (3-mercaptopropyl)trimethoxysilane, is already sufficient to alter the surface states effectively. Furthermore, ultra-thin field-effect passivation layers such as thermal SiO2 and atomic layer deposited Al2O3 were intensively studied and allow to rationally adjust the surface band structure and therefore, the surface charge carrier concentration. In result, silicon nanowire surfaces exhibiting a charge carrier accumulation, depletion, inversion and even a degeneration can be created in this manner, which is highly relevant for any reliable and controlled nanowire device usage. The silicon nanowires for our study were synthesized bottom-up by using a SiH4-based and gold-catalyzed vapor-liquid-solid process. Besides unintentionally doped nanowires, p- and n-type doping of varying concentration were realized by admixture of either B2H6 or PH3, respectively.

10:00 AM BREAK

SESSION NM03.16: Epitaxy and Growth
Session Chairs: Jordi Arbiol and Takeshi Yanagida
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Back Bay D

10:30 AM *NM03.16.01
Epitaxy of Nanostructures for Device Integration
Heinz Schmid1, Johannes Gooth2, Stephan Wirths1, Philipp Staudinger1, Benedikt Mayer3, Siegfried F. Karg4, Heike Riel1, Svenja Mauthe1 and Kirsten Moselund1; 1IBM Research Zurich, Rueschlikon, Switzerland; 2MPI Dresden, Dresden, Germany; 3ABB, Baden Daetwil, Switzerland; 4MPI Berlin, Berlin, Germany.

Over the last 20 years many approaches for nanostructure synthesis have been pursued [1] which often resulted in exotic geometries from a wide range of materials, and triggered huge interest across many scientific disciplines. Translating these promising nano-structuring methods into a powerful device technology remains challenging up to now, also with competing technologies steadily improving. Here, we show our efforts on nanostructure synthesis specifically targeted towards device integration and illustrate challenges and opportunities. We focus on III-V compound semiconductors as these materials are well known, have outstanding properties, are universally used, but still face unsolved integration issues when combined with silicon. The device examples were all fabricated by local epitaxy in templates on Si substrates [2]. Epitaxy and resulting structural and electrical material properties are discussed in detail. Selected device results on field effect transistors and optical excited disk lasers [3] are shown and their integration potential addressed. Finally, devices targeted for 1D transport measurements [4] are discussed which are of interest in more fundamental oriented research.

Acknowledgements: This research received funding from the European Community’s Horizon 2020 projects: INSIGHT, SILAS, MODES, and PLASMIC.

References:

11:00 AM NM03.16.02
Oriented Semiconductor Nanostructure Generation with Phototropic Growth Control
Madeline Meier; California Institute of Technology, Pasadena, California, United States.

Photosynthetic plants, including palm trees and sunflowers, exhibit a phenomenon known as phototropic growth wherein the physical extension of the
biological system proceeds preferentially towards the time-averaged position of the sun. By capitalizing on anisotropies intrinsic to light-material interactions, a natural phototropism can be mimicked using photoelectrochemical deposition to effect the template-free generation of semiconductor nanoarrays. Photocatalytic electrochemical growth of semiconducting chalcogen films without any lithographic pre-processing or photomask yielded films comprised of highly anisotropic and ordered nanostructures. By controlling the angle of incidence of the light during deposition, the orientation and growth direction of the structures with respect to the substrate could be defined without relying on epitaxial growth. This manner of morphological evolution was observed as the growth was dictated by light capture: mass was spontaneously added most preferentially to the localized regions capturing the maximal light flux. Morphological complexity was generated by combining the use of inclined illumination with a series of defined polarization and wavelength inputs which allowed in-plane and out-of-plane orientation, spacing, and periodicity. Growth was simulated using a finite-difference time domain method to model the light-matter interactions and a Monte Carlo method for mass addition. The results of the simulation successfully reproduced the experimentally observed morphologies. The underlying optical basis was further investigated using a simplified light scattering model that corroborated the magnitude and direction of the empirically-observed phototropic responses.

11:15 AM NM30.16.03
Effects of Growth Conditions on the Preferential Orientation of Al-Catalyzed Silicon Nanowires
Mel Haine1, Xiaotian Zhang1, Ke Wang1 and Joan M. Redwing1; 1Pennsylvania State University, University Park, Pennsylvania, United States; 2Materials Process Engineering, Nagoya University, Nagoya, Japan.

Silicon nanowires grown in high energy growth direction such as <110>- and <100>- are of scientific interest because of their predicted improved conductivity and hole mobilities relative to <111>- wires. However, large-scale, controllable growth of these wires remains a challenge, limiting not only their potential application, but even attempts to experimentally verify their predicted properties. Additionally, the use of an aluminum catalyst is desirable because the incorporated Al acts as a p-type dopant instead of forming deep-level traps as with an Au catalyst.

In this report, we demonstrate the effect that hydrogen partial pressure, reactor temperature, and particularly precursor (SiH4) depletion have on the preferential growth direction of aluminum-catalyzed silicon nanowires grown by chemical vapor deposition (CVD) in a hot wall quartz tube reactor. The substrates used for growth consisted of Si (110) wafers coated with a 10 nm Al catalyst film. Previously, we have demonstrated that sub-eutectic growth temperatures and high hydrogen partial pressures promoted <110>- wire growth from Si (110) substrates. However, prior reports of Al-catalyzed <111>- wire growth suggested that these same temperatures and pressures should promote growth in the lower energy <111>- direction. To better understand how the same growth conditions can promote different preferential growth directions, long (~3 cm) Si (110) substrates were placed in the reactor using the previously described preferential <110>- growth conditions. At the front of the sample, closer to the gas inlet, nanowires grew exclusively in the <111>- direction. Moving further downstream in the reactor, a clear transition from preferential <111>- to preferential <110>- growth was observed without significant change in the nanowire growth rate.

Computational fluid dynamic simulations combined with a simplified gas phase and surface chemistry model of SiH4-decomposition and reaction along the length of the reactor tube suggests that the transition from <111>- to <110>- corresponds with gas phase depletion of SiH4. The transition from preferential growth in high-energy growth directions under SiH4-depleted conditions agrees with previous observations from Ge <110> nanowire growth, where decreased Ge flux to the catalyst droplet changed the preferential growth direction from <111>- to <110>-.

Finally, by using silane-depleted growth conditions, we demonstrate that <100>- wires can also be fabricated from Si (100) substrates. These results suggest that silane-depletion conditions can be used to fabricate wires in previously inaccessible growth directions.

11:30 AM NM30.16.04
Realization of Vertical GaN NW Static Induction Transistors
Matthew Hartensveld1, Cheng Liu1, Yu Kee Ooi1 and Jing Zhang2; 1Microsystems, Rochester Institute of Technology, Rochester, New York, United States; 2Electrical and Microelectronic Engineering, Rochester Institute of Technology, Rochester, New York, United States.

Nanowire (NW) transistors are emerging as replacement technology to planar devices due to better scaling and gate control. Vertical NWs, as opposed to planar NWs, allow for conventional fabrication techniques to be utilized to build the device once the NWs are formed. The gate length in these devices is defined by the metal thickness on the sidewalls which allows better scaling of those transistors. In addition, vertical NWs support higher transistor densities and allow for separate source and drain metalization engineering. Specifically, GaN has been explored to use in vertical NW transistors due to the wide bandgap along with high carrier mobility, which are important in high power applications. Several studies have explored GaN vertical NW transistors recently, which are mostly Metal Oxide Semiconductor Field Effect Transistors (MOSFETs). Those MOSFETs typically make use of a surface channel combined with a unique growth structure, which are difficult to implement. Alternatively, Static Induction Transistors (SITs) have a buried channel, straightforward vertical structure, and ability to support high voltages. Therefore, in this work, GaN-based NW vertical SITs have been realized in order to capitalize on these properties. Instead of a custom n-i-n structure from most GaN NW MOSFETs, this GaN NW SIT is fabricated from unintentionally doped GaN with a background doping concentration of 1×1016 cm-3. A top-down NW formation and a bottom-up fabrication process are utilized to fabricate the SIT. The NWs are formed through nanoscale lithography and Reactive Ion Etch (RIE), followed by KOH wet etch to crystal graphically shrink the diameter and to smooth the sidewalls of the NWs. Layers of metal are deposited to form the source, gate, and drain with Polydimethylsiloxane (PDMS) as the supporting insulating layers. In this study, a small gate length of 30 nm of aluminum is achieved solely through metal deposition. 20 nm of titanium is deposited as the source and drain contacts, followed by annealing in an N2 environment to produce nitrogen vacancies. These vacancies then act as donors that create an n-i-n structure through the wire. Both simulations and experimental results are obtained in order to electrically characterize the vertical SIT. The experimental results include the on/off ratio and the family of curves, recording six orders of magnitude difference for the on/off ratio. The effects of Drain Induced Barrier Lowering (DIBL) on the device are also electrically measured and show a shift to higher pinch-off values as the source to drain bias is increased. As the drain bias increases from 1 V to 1.5 V, the current level increases by 188 times. Device simulations have also been performed using Silvaco’s Athena, showing similar findings in experimental performance and DIBL. Due to the feasibility of the vertical GaN NW SITs, these power transistors can open the door to a number of new integration opportunities.

11:45 AM NM30.16.05
Optically Directed Bottom-Up Growth of Anisotropic Semiconductor Nanostructure Arrays
Azhar I. Carim1, Nicolas Bataara2, Anjali Premkumar2, Harry A. Atwater2 and Nathan S. Lewis1; 1Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States; 2Engineering and Applied Sciences, California Institute of Technology, Pasadena, California, United States.

Bottom-up growth of macroscale arrays of highly anisotropic nanoscale elements with significant periodic order was effected via photoelectrochemical deposition of a semiconducting chalcogen film. The exact nature of the optical excitation was the determinant of the features sizes, periodicities, anisotropies, and orientations of the arrays. Use of linearly polarized light resulted in the development of an array of highly-anisotropic components with a single set of extended axes that aligned along the E-field vector. The nanoscale component size and pitch was encoded by the illumination spectral profile.
A single pitch was observed regardless of the use of broadband and multimodal spectral profiles. The void space between the array elements could be tuned and this value could be tuned between ca. 20 nm to 100 nm by using ultraviolet to near-infrared wavelengths. Intersecting arrays with nonequal periodicities in the two orthogonal in-plane directions could also be generated and both periodicities could be independently controlled by orthogonally polarized inputs. “Stacked” arrays could be generated by using temporally-varying polarization and/or wavelength inputs.

The nanopatterning process occurred without the use of any type of physical or chemical templating agents: no photomask, patterned substrate nor surfactants/ligands were used to influence the morphology. Modeling of the growth using a combination of full-wave electromagnetic simulations of light absorption and scattering coupled with probabilistic simulations of mass addition successfully reproduced the experimentally observed morphologies and indicated that morphology development was a consequence of the fundamental light-matter interactions during growth.

SESSION NM03.17: Structural Properties
Session Chairs: Kimberly Dick Thelander and Heinz Schmid
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Back Bay D

1:30 PM *NM03.17.01
Structural Analysis of Stable Defects in III-V Semiconductor Nanowire
Ana M. Sanchez1, James A Gott1, H Aruni Fonseka1, Yunyan Zhang2, Huiyuan Liu2 and Richard Beanland1, 2
University of Warwick, Coventry, United Kingdom; 3University College London, London, United Kingdom.

The rapid improvement in semiconductor growth and new processing techniques has produced novel materials/structures with unique functionalities. Nevertheless, persistent obstacles, such as the constraints on lattice parameter and thermal expansion mismatch, have prevented the growth of a wide range of epitaxial layers on bulk substrates. These constraints cause dislocations and cracks making the devices unviable. Nanowires (NWs) avoid both of these problems, since they are only attached to the substrate at one small region – their base. Moreover, mobile defects with long-range strain field – i.e. dislocations – are unstable and get expelled from the NW by surface image forces.

Electron microscopy plays a key role in understanding the structure of these novel materials. In fact, aberration-corrected scanning transmission electron microscopy (ac-STEM) has provided some beautiful images and valuable insights into many materials, with resolution and analysis capability now truly at the atomic scale.

This work demonstrates that the nanopore defect microstructure is very different from bulk material. We analysed defects present in semiconductor nanowires in regions of imperfect crystal growth, i.e., at the nanowire tip formed during consumption of the droplet in self-catalyzed vapor–liquid–solid growth and subsequent vapor–solid shell growth. Various line defects have been observed either (i) trapped by locks or other defects (ii) arranged as dipoles or groups with a zero total Burgers vector and (iii) have a zero Burgers vector. We find two new line defects with a null Burgers vector, formed from the combination of partial dislocations in twinned material.

The most common defect is the three-monolayer high twin facet with a zero Burgers vector. These defects are \( \Sigma 3 \) (11-2) boundaries, having topological properties similar to those of dislocations, but no long-range strain field are stable and act as non-radiative recombination centers. Interestingly, if NW polarity is maintained across the (111) boundaries on either side of the step, i.e. an ortho-twin, the material on opposite sides of the \( \Sigma 3 \) (11-2) boundary is related by a mirror, and it must be a para twin. These interfaces are constituted by 5- and 7-membered rings that contain under-bonded and over-bonded atoms. Density functional theory calculations demonstrate that these \( \Sigma 3 \) (11-2) facets produce a shift in the band edge and a closing of the band gap. So they will act as non-radiative recombination centres, causing problems for minority carrier devices and deleterious effects on nanowire properties.

2:00 PM NM03.17.02
In Situ Studies on Layer-by-Layer Growth Kinetics of GaAs Nanowires
Carina Baba Maliakkal1, 2, Daniel Jacobsson1, 3, Marcus Tornberg1, 2, Axel R. Persson1, 3, Jonas Johansson1, 2, Reine Wallenberg1, 3 and Kimberly A. Dick1, 2, 3
1NanoLund, Lund University, Lund, Sweden; 2Solid State Physics, Lund University, Lund, Sweden; 3nCHREM and CAS, Lund University, Lund, Sweden.

Semiconductor nanowires (NWs) have emerged as a highly promising technology for next-generation electronics and photonics. Although the potential of these structures lies in the possibility to control and design their properties on an atomic scale, the current mechanistic understanding of the synthesis process is clearly insufficient for achieving the promised level of control. Semiconductor nanowires are mostly grown via vapor-liquid-solid mechanism using a catalytic liquid metal nanoparticle (typically Au). The process is broadly understood to occur by dissolution of semiconductor precursor species in the liquid metal followed by precipitation of the solid semiconductor once the precursor becomes supersaturated. NW growth occurs in two steps: formation of a critical nucleus followed by step-flow across the liquid-solid interface. Most theoretical models explaining NW growth assume the step-flow to be effectively instantaneous and the NW growth rate to be limited by the slow nucleation. In-situ imaging of nanowire growth demonstrated that the step-flow can also limit the overall growth rate.[1] We study, using in-situ TEM imaging combined with in-situ compositional analysis, the layer-by-layer growth kinetics of III-V NWs.

We have grown GaAs nanowires in a Hitachi HF3300S aberration-corrected environmental TEM connected to a CVD system. A SiNx-based MEMS heating chip was mounted on a holder with two separate microtubes running to the holder tip for supplying gases. We used trimethylgallium (TMGa) and arsine as the Ga and As precursors respectively. High resolution, high-frame-rate videos (20 fps) enable us to determine the growth rate for each bilayer (step flow time) as well as incubation times between layers. We studied the elemental composition of the catalyst by energy dispersive X-ray spectroscopy as a function of the growth parameters.

When growth temperature is increased for Ga-limited growth, the average Ga content in the droplet increases along with the incubation time. However, the step flow time is rather insensitive to temperature. When varying the TMGa flux, we identify two regimes: For TMGa flux below a critical value, the average concentration of Ga in the droplet is constant and Ga limits the average growth rate, while for TMGa flux above this value, the Ga content increases in the catalyst. The concentration of As in the catalyst droplet is small and below our detection limit. For the Ga-limited regime the long incubation time between bilayers limits the average growth rate. The incubation time decreases significantly with increasing Ga precursor flux. However, the step flow time is independent of Ga and we propose that this is limited by the arrival of As species in both regimes. For sufficiently high TMGa flux, the incubation time becomes shorter than the step flow time, and the arsine flux will limit the overall growth rate.


2:15 PM NM03.17.03
Semiconductor nanowires with high carrier mobility and controlled chemical composition, morphology, and size distribution offer great promise in designing novel electronic, thermoelectric, and photovoltaic applications. It is well known that III-V nanowires can grow in the wurtzite crystal structure, even if the bulk crystal structure of the same material is zinc blende. There is currently a lot of research about controlling the crystal structure of nanowires by fine-tuning the growth conditions and this is known as crystal phase engineering. The breakthroughs in this area open new horizons allowing the fabrication of nanowires with well controlled or modulated crystal structure along the growth direction. Previous attempts to control crystal structure control are mainly devoted to binary III-V nanowires. Crystal structure control in ternary nanowires is, on the other hand, poorly studied.

The aim of the current investigation is therefore to understand and predict the crystal structure of ternary nanowires. Among the various ternary material systems which are relevant for nanowire fabrication, the greatest attention has been paid to InGaAs [1] due to its excellent materials properties. We present an approach to understanding the zinc blende and wurtzite crystal structure formation in InGaAs nanowires growing from a quaternary gold-based liquid alloy. The model we have developed is based on two-component nucleation theory using realistic chemical potentials, calculated from an assessed thermodynamic database [2]. Using the model we calculate the probabilities of zinc blende and wurtzite phase formation in this materials system for different growth conditions. We compare our results with available experimental data and special attention is paid to analysis of the main trends in crystal phase control and the impact of the liquid composition on the final crystal structure. The developed model may help in optimization of the growth conditions for InGaAs nanowires with tailored crystal structure.

Finally, an interesting theoretical result of our analysis is that the wurtzite and zinc blende phases have different compositions, even if they are nucleated from identical conditions of the catalyst particle. We will show that this could open up for the possibility to fabricate nanowires with zinc blende and wurtzite segments having significantly different compositions even if the growth conditions are almost identical.


2:30 PM NM03.17.04
Light Trapping in Nanowire Geometric Superlattices Seokhyeun Kim1, Kyoung-Ho Kim1, David J. Hill1, Hong-Gyu Park2 and James F. Cahoon3; 1University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 2Physics, Korea University, Seoul, Korea (the Republic of).

All-optical operation holds promise as the future of computing technology, and key components will include miniaturized waveguides (WGs) and optical switches that control narrow bandwidths for logic operations and wavelength multiplexing. Nanowires (NWs) offer an ideal platform for nanoscale WGs, but their utility has been limited by the lack of a comprehensive coupling scheme with band selectivity. Controlled in-coupling of light to NW WGs thus still is problematic and has relied on scattering at NW end facets or end-on parallel coupling to the NWs. Mie resonances of NWs have been considered as a potential route to enable controlled coupling into guided modes, but the interplay of the two orthogonal modes remains yet unclear. Here, we introduce a NW geometric superlattice (GSL) that allows controlled, narrow-band guiding in Si NWs through direct coupling of a Mie resonance with a bound guided state (BGS) under normal incidence illumination with transverse-magnetic (TM) polarization. Periodic diameter modulation in a GSL creates a Mie-BGS coupled-excitation that manifests as a scattering dark state with a pronounced scattering dip in the Mie resonance envelope. We analyze scattering characteristics of NW GSLs using Temporal Coupled-Mode Theory (TCMT) and compare with numerical finite-element modeling. The coupling strength between the Mie and BGS modes, which is zero in the absence of the GSL geometry, becomes non-zero with periodic modulation and increases with an increasing modulation depth. Experimental extinction spectra of individual NW GSLs are measured by a home-built laser microscope and presented with numerically simulated spectra. The frequency of the coupled mode, tunable from the visible to near-infrared, is determined by the pitch of the GSL and exhibits a Fourier-transform limited bandwidth. Using a combined GSL-WG system, we demonstrate spectrally-selective guiding at telecommunication wavelengths with bandwidths of ~50 nm, which aligns with the spectral positions of the dips observed in extinction spectra. We also present optical switching characteristics of a GSL with an index change of the surrounding medium, highlighting the potential to use NW GSLs for the design of on-chip optical components.

2:45 PM NM03.17.05
2D to 1D Growth of Layered SnSe2—Morphological Control of CVD Grown Nanostructures Fionán Davitt1, 2, Samantha Hawkens1, Subhajit Biswas1, Gillian Reid1 and Justin Holmes1, 2; 1Materials Chemistry and Analysis Group, University College Cork and the Tyndall National Institute, Cork, Ireland; 2AMBER, CRANN, Trinity College Dublin, Dublin, Ireland; 3School of Chemistry, University of Southampton, Southampton, United Kingdom.

Bottom-up growth strategies offer the potential for precise control over the crystallinity, structure, composition, and morphology of nanomaterials. In this research, a liquid injection chemical vapour deposition method has been utilized to grow crystalline tin diselenide (SnSe2) nanostructures, from a distorted octahedral [SnCl4{BuSe(CH2)3SenBu}] single source diselenoether precursor.1 Most notably, careful adjustment of the growth parameters yielded great morphological control of the grown nanostructures; yielding structures from large 2D flakes, to large branched wire networks, and individual one-dimensional (1-D) nanostructures. With the custom designed single source precursor, SnSe2 nanostructures of only a few layers thickness were achievable, as well as 1-D growth with diameters between 60-240nm. The Sn:Se stoichiometric ratio of ~1:2 in all of the different morphologies was confirmed by energy dispersive X-ray analysis and Raman spectroscopy. The presence of the SnSe2 A1g Raman mode was clearly observed for all synthesized nanostructures.2 The Sn:Se stoichiometric ratio of ~1:2 in all of the different morphologies was confirmed by energy dispersive X-ray analysis and Raman spectroscopy.

The presence of the SnSe2 A1g Raman mode was clearly observed for all synthesized nanostructures.2 The morphology and crystal structure of the SnSe2 nanostructures was investigated through X-ray diffraction, atomic force microscopy, electron diffraction, and transmission electron microscopy. SnSe2 nanostructures demonstrate potential applications in phase change memory devices (PRAM), with films of SrTiO3 being previously reported as showing the reversible amorphous to crystalline switching needed in phase change memory applications.3,4
Electroluminescence from Photonic Crystal Cavities Based on III-V Nanowire Array on Silicon-on-Insulator

Conventionally, nanowire characterization with a high spatial resolution relies on electron microscopy techniques, which can provide a large variety of structural and compositional information with atomic resolution. Energetic electrons interact quite strongly with condensed matter so that the analyzing depth is limited and the Bremsstrahlung-background allows only a moderate detection limit of elements. Compared to electrons, X-rays interact less strongly with matter and are thus less invasive and have a higher penetration depth, enabling analysis even at ambient conditions of operating and/or functional devices. Even if the spatial resolution of X-ray based methods is clearly lagging behind the one obtained by electron based techniques, today one can focus X-rays below 30 nm at several synchrotron facilities. In addition to their high brilliance, third generation synchrotron radiation sources have wide energy tunability, a high degree of polarization, fast temporal structure, coherence and more. This opens up the possibility of studies at length scales relevant for the characterization of semiconductor nano-devices with energy dependent X-ray studies, such as X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS). In this presentation, we will show several combinatorial studies [1,2] demonstrating the beneficial use of X-ray nano probes for the characterization of single semiconductor nanowires and in-operando studies on devices thereof.


Electrical and Optical Characterization of GaN-Based Hybrid Nanowire and Microrod LEDs

Linus Kriegl, Stefan Leis, Angelina Jaros, Joergen Jungclaus, Florian Meierhofer and Tobias Voss; Braunschweig University of Technology, Braunschweig, Germany.

The oxidative chemical vapor deposition (oCVD) of ultrathin (<100nm) and highly transparent p-conductive polymer layers on arrays of vertically aligned semiconductor nanowires or microrods is a very powerful method for the fabrication of hybrid three-dimensional (3D) LEDs. In these hybrid LEDs, the p-doped part of the diode consists of a conformal layer of highly p-conductive poly(3,4-ethylenedioxythiophene) (PEDOT) for which literature values >3000 S/cm of the lateral conductivity have been reported. We have used oCVD of PEDOT for the fabrication of hybrid GaN-based nanowire and microrod LEDs. The inorganic part of the LED consists of n-type GaN rods grown by selective-area MOVPE on sapphire substrates. The active region is formed by a radial InGaN-based multi-quantum-well structure. Using the gaseous monomer EDOT and FeCl3 as oxidant, thin p-conductive polymer layers have been deposited on planar and 3D GaN structures to form full hybrid LEDs. Stable, blue electroluminescence is observed from the devices at ambient conditions for an applied voltage ~3V. We have studied the electronic properties of the hybrid pn-junction in temperature-dependent IV-measurements. The results are modelled in the frame of a thermionic emission model based on a bipolar Schottky junction yielding barrier heights of ~0.7-1.0 eV, breakdown voltages of ~-8 V, ideality factors of ~1.8-2 at room temperature and rectification ratios at ±4 V in the order of 106.

Our results demonstrate that oCVD of conductive polymer layers is about to become a powerful technique for the fabrication of highly p-conductive transparent polymer layers on nanowire devices with the layer thickness and doping level of the polymer being controlled by the deposition parameters.

Electroluminescence from Photonic Crystal Cavities Based on III-V Nanowire Array on Silicon-on-Insulator

Ting-Yuan Chang1, Hyunseok Kim1, Wook-Jae Lee2 and Diana Huffaker2; 1University of California, Los Angeles, Los Angeles, California, United States; 2Cardiff University, Cardiff, United Kingdom.

Epitaxial growth and heterogeneous integration of III-V optoelectronic devices on silicon photonic platform have been a potential building block for optical interconnect. Here, we demonstrate III-V arrayed nanowires (NWs) light emitting diodes (LEDs) monolithically integrated on silicon-on-insulator (SOI) substrate by selective area epitaxy (SAE) using MOCVD. This presentation will include the NWs LED design, growth and characterization in detail. NWs with axial p-GaAs / i-InGaAs heterostructure and in-situ InGaP passivation shell are directly grown on lattice mismatched n-type silicon substrate, while maintaining more than 98% yield and remarkable uniformity in NW dimensions. Due to small footprint, lateral strain releasing leads to lack of threading dislocation in NWs. Electroluminescence at photonic band edge in near infrared (NIR) region is observed, which can be utilized in in-plane waveguide coupling and low-loss propagation in silicon optical interconnect. It is worth noting that altering the design of NW array allows tunable emission wavelength for on-chip multi-wavelength optical network communication. Lastly, we show an advanced NW heterostructure in which diffusion barriers are incorporated to improve electrical confinement, enabling high carrier densities in the gain medium. These results provide great opportunities for achieving electrically injected NW-based photonic band edge lasers on silicon photonic platforms.
subsequently fluorescence-tagged with live-cell compatible labels targeting the cell membrane and filamentous Actin, respectively.

Within the cell, the nanowires form nanoscale ring structures of about 100 nm diameter, wrapping tightly around the nanostraws. On the other hand, the Actin cytoskeleton forms intricate, coil-like nanometric structures around the nanostraws; these structures strongly vary in diameters between 250-600 nm and appear to widen with increasing distance from the nanostraw substrate.

In addition, STED images of living cells stained for both membrane and Actin signal reveal a significant degree of co-localization at the apical cell membrane, i.e. further away from the nanostraws. This co-localization is almost entirely lost at the basal membrane close to the nanostraws which is due to a strongly reduced Actin signal on that side of the cell.

In conclusion, our sub-diffraction STED imaging based investigations of the behavior of single living cells cultured on nanostraws reveals a strong response of the cellular membrane and the Actin cytoskeleton – two of the main structure-giving features of the cell. In a next step, we will extend our studies to additional scaffolding proteins to arrive at a more detailed map of the topology of living cells at the interface to nanostructures of different geometries.

4:45 PM NM03.18.05
Preparation of 2D Bar Code Labeled Substrates for Nanowire Devices Yuki Hanamura, Grace G. Redivyk, Ryo Yamada and Hirokazu Tada; Engineering Science, Osaka University, Osaka, Japan.

Nanowire materials have been intensively studied in recent years because of the quantum confinement effect in one-dimensional structures of superconductor, metal, semiconductor, organic materials, and so on [1-4]. Their typical length to width ratio is greater than 10, which makes it possible for nanowire materials to connect with other macroscopic structures towards a functional device. There have been several works on the position control of nanowire structures, such as in-situ growth, electrophoresis alignment, and flow-induced shear force [5]. Preparation of an individual nanowire device using such methods requires a precise control of the position of the selected nanowire. However, direct observation of the nanowire position during electron beam lithography may cause structural deformation [6]. Therefore, atomic force microscopy (AFM) observation is typically used prior to the electron beam lithography to locate the individual nanowire. Here we report the development of 2-dimensional (2D) bar code as a position marker to determine the exact location of the nanowire and ensure the successful lithography of the electrode contact. The 2D bar code was made of Au thin film, with a thickness of 30 nm. One bar code was constituted by orientation markers and binary markers. The binary markers represent the coordinate of the 2D bar code relative to the alignment marker. We will show how we can utilize the 2D bar code from the AFM image to determine the nanowire position and create electrode contact successfully to the nanowire.

References:

SESSION NM03.19: Advanced Characterization and Structure
Session Chairs: Kimberly Dick Thelander and Ana Sanchez
Friday Morning, November 30, 2018
Hynes, Level 2, Room 207

8:30 AM NM03.19.01
Pinning Down the Structure/Performance Interplay in Nanowires with Electron Microscopy Sonia Conesa-Boj; Quantum Nanoscience, Delft University of Technology, Delft, Netherlands.

In the last decade, a significant progress has been made in controlling the growth and properties of low-dimensional systems such as nanowires. Their small radial dimension enables more freedom for the combination of different materials. The ability of nanowire systems to overcome existing limitations of heterostructures is one of the key ingredients for the design of next-generation devices. In turn, this requires a detailed understanding of the crystalline structure and the mechanisms for strain relaxation in these systems, in order to eliminate defect formation and thus to boost optical and electronic properties. Therefore, the characterization of their structure and chemical composition with atomic resolution is essential to achieve a full understanding of how their physical properties are correlated. In this context, transmission electron microscopy (TEM) provides a unique toolbox to achieve this goal. TEM is extremely versatile, combining within a single instrument the complementary capabilities of imaging, diffraction and spectroscopy. In this talk I discuss the crucial role that electron microscopy plays in mapping the structure, properties, and performance of nanomaterials and their mutual interplay, and then present the results of recent studies illustrating this important role for the specific case of core-shell nanowires. Finally, I motivate the impressive physics potential that can be exploited by pushing the boundaries of electron microscopy analysis for novel quantum materials.

9:00 AM NM03.19.02
Helium Ion Microscopy as a Novel High-Resolution Probe for Complex Quantum Heterostructures in Core-Shell Nanowires Christian Pöpsel1, Jonathan Becker1, Nari Jeon2, Markus Dixbinger3, Thomas Stettner1, Alexander Holleitner1, Jonathan Finley1, Lincoln J. Lauhon2 and Gregor Koblmueller1; 1Walter Schottky Institut, Technical University of Munich, Garching, Germany; 2Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 3Department of Chemistry, Ludwig-Maximilians-Universität München, Munich, Germany.

Over the years semiconductor nanowires (NW) have emerged as promising systems for many unique device applications in nano- and quantum-electronics, --photons and energy conversion. Simultaneously, they also became an excellent testbed for advancing ultrahigh-resolution imaging methods due to their rich palette of integrated quantum heterostructures, defined by either intentional polypeptide crystal phases or by accurately controlled modulations in alloy composition along their axial or radial dimensions. Ideally, the ultrahigh-resolution imaging techniques should enable examination of the specimens’ structure and material contrast at the sub- or few-nanometer scale with minimal damage and sample preparation.

Here, we demonstrate that scanning helium ion microscopy (ShelM) provides a powerful and straightforward method to map the unique material contrast of quantum heterostructures embedded in complex III-V semiconductor nanowires (NW) with an accuracy at the ~1-nm resolution level. By probing the

9:15 AM NM03.19.03 Growth and Characterization of Epitaxial, Anisotropic Ge$_x$Sn$_{(1-x)}$, Nanostructures as Direct Bandgap Materials Michael S. Seifner and Sven Barth; Institute of Materials Chemistry, TU Wien, Vienna, Austria.

Germanium can be converted into a purely group IV-based direct bandgap material with high light-emitting efficiency in the mid-IR range. However, the required and thus targeted Sn content of > 9 at% to convert Ge to a direct bandgap material exceeds the solid solubility limit of < 1% according to the binary phase diagram. [1,2] Conventional high-temperature approaches will therefore not lead to the desired metastable compound and alternative synthesis strategies using kinetically controlled growth conditions have to be established. We demonstrate that solution-grown Ge$_x$Sn$_{(1-x)}$ NWs show low resistivity values in single nanowire devices and determined the thermal stability for different chemical compositions of these germanium-tin nanowires. [3,4,5] The knowledge gained by these solution processes has been used to establish a strategy for the epitaxial growth of anisotropic, metastable Ge$_x$Sn$_{(1-x)}$, nanostructures with high Sn content in a vapor-phase process at very low temperatures. This procedure does not rely on a Ge nanowire support structure acting as a template. Independent and complementary methods including X-ray diffraction and STEM-EDX elemental mapping are used to determine the Sn content, while TEM confirms the single crystalline nature of the obtained products. We demonstrate a size and synthesis parameter dependence of the Sn content in the composition range of 8-15 at% Sn. Optical measurements confirm the formation of a low bandgap material without strain effects of the substrate material used for these metastable Ge$_x$Sn$_{(1-x)}$, nanostructures with Sn concentrations above the threshold of the indirect-to-direct bandgap material transition. [6] The results of this study will help to push the implementation of group 14-based direct band gap materials for novel optoelectronic devices.


9:30 AM NM03.19.04 Self-Assembled Ultrathin Gold Nanowires—Modeling to Reveal Their Structure and Reactivity Jorge Vargas1, Valeri Petkov1 and Guillaume Viau1; 1Physics, Central Michigan University, Mt. Pleasant, Michigan, United States; 2LPCNO, Université de Toulouse, Toulouse, France.

Ultrathin metallic nanowires and metallic nanorods exhibit unique structural and electronic properties due to their very small diameter and one-dimensional (1D) feature. In particular, ultrathin gold nanowires (Au NWs) are promising candidates for nanoelectronics, optics, electro-catalysts or as active materials in chemical sensors. Their synthesis and several measurements have been intensively reported over the last decade. In this contribution, Au NWs are studied using the atomic Pair Distribution Function (PDF) obtained from analysis of the ternary AlGaAs shell layers and of compositionally non-uniform GaAs/AlAs SLs reveals distinct alloy composition fluctuations in the form of Al-rich clusters with size distributions between ~1-10 nm. In the GaAs/AlAs SLs the alloy vanishing with increasing SL-period (> ~5-10 nm GaAs/4-5nm AlAs), providing insights into critical size dimensions for atomic intermixing effects in short-period SLs within a single NW [3]. The small-size alloy clusters correspond to previously identified sources of quantum-dot-like emitters in AlGaNAs-based NW shell layers that are otherwise only detectable by advanced, yet destructive APT methods [4]. Moreover, our SHEIM data also evidences first indications of atomic segregation at twin-plane defects in the AlGaNAs alloy shell system, illustrating excellent image contrast in the single monolayer level [3].

9:45 AM NM03.19.05 Atomic-Level Imaging and Structure Identification of Mo$_5$O$_{14}$ Nanowires by Advanced Electron Microscope Yi-Hsin Ting1, Ping-Hung Yeh1 and Wen-Wei Wu1; 1Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 2Department of Physics, Tamkang University, New Taipei City, Taiwan.

The Mo$_5$O$_{14}$-type structure is a very important and representative to the complex oxide in the selective oxidation of heterogeneous catalyst. However, the spatial resolution in the conventional technique of transmission electron microscopy (TEM) was insufficient to distinguish the real position of atoms. In this work, we aim at systematically analyzing and identifying the needle-like Mo$_5$O$_{14}$ nanowires fabricated by chemical vapor deposition (CVD) process. Utilizing high-angle annular dark-field (HAADF), annular bright-field (ABF) and enhanced annular bright-field (E-ABF) within scanning transmission electron microscope (STEM) revealed the real atomic-level images and large-scale special arrangement. Importantly, E-ABF could enhance the intensity of light atoms like oxygen atom, so the image demonstrated the overall structure of Mo$_5$O$_{14}$. We presented the ultra-high resolution images consistent with the network of MoO$_6$ octahedral and MoO$_7$ pentagonal bipyramids in theoretical model. Electron energy loss spectroscopy (EELS) analysis would also provide the information about binding energy of Mo$_5$O$_{14}$ and the element distribution through atomic-scale mapping. Besides, the ultra-high resolution images have provided the new insights to the [001] growth direction of needle-like Mo$_5$O$_{14}$ nanowires with quasi-2D structure and tunnel structure. The cross-section images showed the unique close-packed plane and highly periodic atomic arrangement with repeating pentagonal structure. Details of the atomic structure were analyzed. In addition, we used in-situ TEM to investigate electron beam radiation effect. It revealed that Mo$_5$O$_{14}$ structure transferred from crystal to amorphous. These results would benefit to the catalytic selective oxidation related with Mo$_5$O$_{14}$-type structure.

10:00 AM BREAK
In order to translate 1-D nanostructures from the laboratory into viable technologies, there is a need for efficient characterization tools, particularly for semiconductor nanowires with complex dopant profiles or heterostructures. Traditional measurement methods, because they require each nanowire to be electrically contacted, are laborious. Thus, they are unsuitable for statistically analyzing process – structure – property relationships of nanowire ensembles. Here, we advance electro-orientation spectroscopy (EOS) to characterize individual, vapor-liquid-solid-grown Si nanowires with axially programmed dopant profiles. EOS is a non-contact technique that can determine the structure and properties of individual nanowires based on their transient alignment under applied AC electric fields when suspended in a fluid. We demonstrate an ability to measure the length ratio of two segments of distinct carrier density in individual nanowires. We find that nanowire segment-length ratios exhibit much less variation than the segment conductivity, which can differ by more than an order of magnitude within an ensemble. We also show that nanowire carrier densities are strongly surface-dependent, with Al2O3 passivation via atomic layer deposition (ALD) able to increase nanowire conductivity by more than 4 orders of magnitude. Notably, the relative variation of the conductivity decreases with surface passivation. This advancement in EOS enables, for the first time, the high-throughput characterization of nanowires with structural heterogeneity, and serves as an important step toward the characterization of full devices.

**11:00 AM NM03.20.02**

**Properties, Challenges and Limits of Metallic Nanowire Networks—A Brief Overview**

Daniel Bellet; LMGP - Grenoble INP, Grenoble, France.

In recent years there has been a growing interest for metallic nanowire (MNW) networks as they exhibit very promising properties: high optical transparency, very good electrical properties and mechanical flexibility [1]. Such networks are mostly targeted to be used as transparent electrodes for many applications [1] such as solar cells, OLEDs, displays, transparent heaters [2] or smart windows. They could replace the currently well-known transparent electrode indium tin oxide (ITO) since indium scarcity and the lack of flexibility of ITO have prompted the search for alternative low cost and flexible materials.

Many researches worldwide deal with the optimization of the properties of MNW networks and the enhancement of their stability. Research focuses on i) the fundamental understanding of the physical phenomena taking place both at the network scale (macroscale) and at the nanowires scale (nanoscale); and ii) the integration of MNW networks as transparent electrodes in many devices. Our research mainly concerns Ag nanowires. In-situ electrical measurements performed during either thermal annealing [3] or voltage ramps [4] provide useful information regarding the evolution of AgNW networks properties. We have extensively investigated the influence of both length and diameter of AgNWs, as well as network density, on the physical properties of the networks [4]. At the network scale, the ability to distinguish the nanowires taking part in the electrical conduction (“electrical percolating pathways”) from the inactive nanowires is a critical issue for the application. By combining in situ experimental a discrete activation process of efficient percolating pathways through the network was evidenced [5]. We have lately reported that the electrical degradation of AgNW network is associated with crack occurrence and propagation that was observed in-situ [6]. We will address as well the stability issue associated to AgNW networks and will propose a solution for enhancing it thanks to Spatial Atomic Layer Deposition (SALD), an low cost, high throughput deposition technique which allows the deposition of very thin oxide layers onto AgNWs for preventing silver atomic surface diffusion and therefore the network degradation [7]. We will conclude by highlighting what appears to be the future most promising and innovative research directions in the field of transparent electrodes based on MNW networks.

Some references of our team:


**11:15 AM NM03.20.03**

**Exploring Pure and Mixed Metal Phases as Catalysts for Wurzite InP Nanowire Growth**

Mariana Zavarize, Murilo H. Moreira, Varlei Rodrigues and Monica A. Cotta; UNICAMP, Campinas SP, Brazil.

Free-standing semiconductor nanowires are currently under intense investigation, both as basic science, to understand the nanostructure formation dynamics, and for technological applications in areas such as optoelectronics and energy harvesting, among many others. However, their integration into current device processing technologies still poses a few challenges. Planar nanowires, on the other hand, show similar advantages with yet a more straightforward integration capability. For this reason, efforts to control and characterize planar nanowires have grown in the last few years. Also, most of the studies use Au catalysts in Vapor-Liquid-Solid (VLS) growth mode for semiconductor nanowire synthesis; however, some characteristics of this type of synthesis limit nanowire potential applications, such as integration with silicon, for example. So in order to find an alternative to gold, many other metals have been explored in nanowire synthesis the last few years, such as Cu, Sn, Ag and Pd.

In this work we explore Ag, Au and Ag/Au alloy nanoparticles as catalysts for planar and vertical InP nanowire growth. Both metals present many similar properties, such as crystal structure, melting point and ductility. The InP nanowires were grown by Chemical Beam Epitaxy in VLS growth mode. The metal nanoparticles were obtained by the gas aggregation method, which allows size and composition control (in case of alloys). These nanoparticles show a pure metal-phase, with no passivating cap layer from the colloidal chemistry. Substrates of InP and GaAs with different crystallographic orientations and polarity were used for each of the growth conditions. Scanning electron microscopy provided nanowire shape statistics while transmission electron microscopy was used to investigate chemical and structural properties of the nanowires. We observe that nanowires tend to grow in planar or vertical mode depending on the polarity and orientation of the substrate, for each type of catalyst used. Au-catalyzed InP nanowires tend to grow in planar mode on GaAs(111)A and vertically on GaAs(111)B. For Ag catalyzed nanowires, however, we observe the opposite behavior, i.e., nanowires grow in planar mode on GaAs(111)B and vertically on GaAs(111)A. GaAs(100) substrates exhibit mixed populations. Similar behavior was observed with InP substrates. When Ag/Au alloy nanoparticles are used, however, planar and vertical nanowire populations are present on both GaAs(111)A and GaAs(111)B substrates, but with different densities in each case. These results indicate the importance of the surface-chemistry mediated substrate-metal nanoparticle interaction to
determine nanowire growth mode.

**11:30 AM NM03.20.04 Earth-Abundant Semiconductor Nanowires for Energy Harvesting** Simon Escobar Steinwall, Luca Francaviglia, Mahdi Zamani, Elias Stutz, Jean-Baptiste Leran and Anna Fontcuberta i Morral; Laboratory of Semiconductor Materials, Institute of Materials, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Nanotechnology has allowed the utilisation of materials with limitations in their bulk form by utilising the processing and enhancing functionalisation. Nanowires in particular facilitate defect free epitaxial growth of systems with relatively large lattice mismatch through radial strain relaxation, and avoidance of mismatch dislocations at the interface if the diameter is small enough [1].

One material benefitting from this is zinc phosphate (Zn₃P₂). Despite exhibiting optoelectronic properties ideal for photovoltaic applications, such as a direct band gap at 1.5 eV, carrier diffusion lengths in the order of 5-10 um, and high absorption in the solar spectrum, it has found negligible use in modern photovoltaics [2-3]. The factors inhibiting its successful application are the lack of availability of lattice-matched substrates, impedes epitaxial growth, its high expansion coefficient compared to other semiconductors, causing strain and crack formation after processing, and doping, due to intrinsic p-doping by phosphorus interstitials and difficulty of homogeneously introducing extrinsic dopants.

Zn₃P₂ nanowires have been successfully grown on InP (001) substrates through the vapour-liquid-solid method using molecular beam epitaxy. It is observed that the zinc reacts with the InP substrate, generating In-Zn-P droplets, which act as the growth catalyst. Transmission electron microscopy (TEM) shows that the resulting wire is single crystalline and free of defects, and compositional analysis confirms that it is indeed composed of Zn₃P₂. It also shows that indium, proposed as an n-type dopant in Zn₃P₂, is incorporated throughout the wire. [4] This has the effect of doping the nanowire and slowly consuming the droplet, resulting in a tapered shape. Further studies also show how varying the zinc pre-deposition alters the size of the formed droplets, consequently determining the diameter of the nanowires. Micro-photoluminescence studies of these nanowires indicate an optical band gap at 1.40 eV, which is lower than the bulk value and closer to the maximum of the Shockley-Queisser limit. Power dependent measurements also indicate that the recombination is through acceptor-donor pair transitions rather than band gap transitions. Electrical measurements carried out in the 4-point configuration and back-gated transistor measurements will also be included, showing the electrical characteristics of the wires and their dominant charge carrier type.


**11:45 AM NM03.20.05 Synthesis and Characterization of Tellurium Nanowires Using Both Chemical and Green Routes and Their Comparison in Terms of Biocompatibility and Anticancer Properties** Ada Vernet Crua, David Medina and Thomas Webster; Northeastern University, Boston, Massachusetts, United States.

Traditional chemistry has undoubtedly enhanced the quality of life, but a price of the threat of the environment and the health of humans. Chemical processes are responsible for the contamination of all the known ecosystems all over the planet, to more or less extent. The traditional physics-chemical approaches for the synthesis of compounds are easy-to-get and straightforward. Nevertheless, there is a cost associated with the limitations that should be overcome from these approaches, such as the production of toxic by-products or the biocompatibility of the products. Therefore, new methods are needed, and the green chemistry offers a suitable answer.

Tellurium nanowires (TeNWs) were prepared using both chemical and green chemistry approaches. For the first one, sodium tellurite was dissolved in an aqueous solution of polyvinylpyrrolidone (PVP), hydrazine monohydrate and ammonia, and kept inside a hydrothermal reactor for several hours. The environmentally-friendly approach led to the use of telluric acid and starch as a unique reducing agent and kept inside a hydrothermal reactor for several hours. Both structures were characterized in terms of morphology and composition using TEM, SEM and EDX. Once purified, TeNWs were used as a template for the growth of metallic nanoparticles in a quick method with no need of additional reducing agent at room temperature. Besides, biocompatibility tests of the TeNWs with human tissue were accomplished, growing human dermal fibroblast (HDF) cells in media in the presence of both chemical and green-synthesized nanowires. Furthermore, anticancer studies were done using the tellurium nanowires with melanoma cells for 5 days.

It is demonstrated that green TeNWs can be used as a template for the in-situ preparation of nanoparticles. In vitro cytotoxicity assays were performed with human dermal fibroblasts (HDF) cells. The experiments showed that green-synthesized nanowires showed a higher cell proliferation of the cells than the experiments carried out with chemically-synthesized structures. Furthermore, after the incubation period, the growth of the cells was enhanced in comparison with the control and the chemically-synthesized nanowires. Anticancer studies showed an enhanced anticancer activity of green nanowires compared to the chemically-synthesized structures over a period of 5 days, causing a higher depletion of cell viability. Anticancer properties were examined: the presence of nanoparticles was able to delay the cell proliferation over the same range of nanoparticle concentration. Starch was able to synthesize tellurium nanoparticles in a rapid, cost-effective and entirely green approach that showed both antimicrobial and anticancer effect with low cytotoxicity for healthy cells.

Therefore, green TeNWs were compared with chemically-synthesized structures to show that the first ones have an enhanced biocompatibility and anticancer properties over the ones synthesized using traditional methods.

**SYMPOSIUM NM04/B101/ET14**
Environmental issues keep steadily increasing, thus there is a strong urge to discuss how materials scientists could more rapidly respond to the worldwide concerns. This joint tutorial effort would be organized by the three symposia together. To ensure the success of such synergistic efforts it is also urged a close dialogue with society so to establish guidelines for policymakers, thus this tutorial will incorporate both the societal and the engineering aspects of life cycle analysis (LCA) would be covered. The main objective of this tutorial is to explore communications pathways between companies and materials researchers that further elevate the profile and challenges of sustainability that represents a societal necessity and a viable and critical topic for research.

1:30 PM  
**Societal Aspect of LCA** Jean-Pierre Birat; ArcelorMittal

Materials are not simply the product of an engineering discipline, Materials Science, but also "social constructs" that have entertained a close relationship with society all through the historical timeline and remain a core element of our modern world, what is called a Key Enabling Technology. How this can be analyzed by parallel approaches of hard and soft sciences will be explained in the class as well as the trinity of economic, environmental and social values of materials. Examples reported in the 13 past SAM conferences will be used as examples.

2:45 PM BREAK

3:15 PM  
**Engineering Aspect of LCA** Alan Rae; IncubatorWorks, USA

The instructor will provide an overview on all the aspects considered in a life cycle analysis aimed to the engineering design of an industrial process. A part of the tutorial will involve the interaction with the audience in order to apply some of the concepts described in the first part of the tutorials to common objects.

4:15 PM **Sustainability Challenge** Alan Rae, IncubatorWorks

The symposia organizers will divide the participants into groups and a sustainability challenge will integrate the concepts presented by the instructors so to review and facilitate networking among participants and instructors

4:45 PM  
**Final Remarks**

---

**SYMPOSIUM NM04**

Nanomaterials and Nanomanufacturing for Sustainability  
November 26 - November 29, 2018

**Symposium Organizers**  
Babak Anasori, Drexel University  
Monica Jung de Andrade, The University of Texas at Dallas  
Maria Perez Barthaburu, University de la Republica  
Yin Ting Teng, Republic Polytechnic

**Symposium Support**  
American Elements
higher than reported data in the literature. Therefore, the current study reported a type of highly electrocatalytic efficient IrO2 nanostructures, but also a specific capacitance, total charge, most accessible charge, electrochemically active surface area, and roughness factor. Our IrO2 NRs demonstrated enhanced electrocatalytic OER activity in 0.5 M H2SO4 compared to the commercial IrO2 NPs. Moreover, compared to commercial IrO2 NPs and previous reports, our IrO2 NRs showed enhanced electrocatalytic activity for both OER and HER after passing either N2 or O2 gas in a 0.5 M KOH electrolyte, as confirmed by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Our results are comparable with, and in most cases, higher than reported data in the literature. Therefore, the current study reported a type of highly electrocatalytic efficient IrO2 nanostructures, but also a simplistic, reliable and scalable synthetic process for them. It is expected that these IrO2 NRs can serve as a benchmark in the development of active OER and HER (photo)electrocatalysts for various applications in the near future.

Electrocatalytic water splitting has been considered as a viable strategy to convert and store energy renewably, but has been hampered by the slow kinetics of the oxygen evolution reaction (OER). Hence there is an urgent need to improve the performance of currently used materials and/or develop new materials. Iridium oxide is an effective stable electrocatalyst with low over-potential and high current for efficient fuel generation technologies. To further improve its activity, we developed a facile one-step molten salt synthesis process to generate ultrafine iridium oxide nanorods (IrO2 NRs). The electrocatalytic performance of these IrO2 NCs for OER in acidic media was compared with that of commercial IrO2 nanoparticles (NPs) in terms of specific capacitance, total charge, most accessible charge, electrochemically active surface area, and roughness factor. Our IrO2 NRs demonstrated enhanced electrocatalytic OER activity in 0.5 M H2SO4 compared to the commercial IrO2 NPs. Moreover, compared to commercial IrO2 NPs and previous reports, our IrO2 NRs showed enhanced electrocatalytic activity for both OER and HER after passing either N2 or O2 gas in a 0.5 M KOH electrolyte, as confirmed by cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. Our results are comparable with, and in most cases, higher than reported data in the literature. Therefore, the current study reported a type of highly electrocatalytic efficient IrO2 nanostructures, but also a simplistic, reliable and scalable synthetic process for them. It is expected that these IrO2 NRs can serve as a benchmark in the development of active OER and HER (photo)electrocatalysts for various applications in the near future.

Gamma-radiation-induced synthesis of metal and metal oxide nanoparticles involves reactions of dissolved precursor metal salts with products of water radiolysis. When exposed to ionizing radiation water decomposes to form chemically reactive radicals and molecular species. The products of water radiolysis range from highly oxidizing, e.g. hydroxyl radicals to highly reducing, e.g. hydrogen radicals and solvated electrons. The oxidants and reductants produced upon radiolysis react then with solutes and change their oxidation state. These chemical changes lead to the formation and subsequent precipitation of insoluble species, since the solubility and reactivity of metal ions depend on their oxidation states. Synthesis of nanomaterials can be done by using either reductive or oxidative routes. To reach the controlled redox conditions and avoid the unwanted reactions one can add other organic or inorganic compounds which act as scavengers of the radicals. The amount of material obtained by gamma-radiation-induced synthesis can be controlled by the yield of reductive/oxidative radiolysis products formed in solution. Radiation-induced synthesis is a powerful tool to produce the materials of complex shape and compositions. It has the following advantages as compared to the other methods: The nanoparticles with very narrow size distribution and uniform shape can be synthesized; there are possibilities to synthesize the nanostructure in confined media, such as porous materials, nanotubes etc. The formation of radicals stops immediately when the solution is removed from the radioactive source. Therefore the amount of reacting radicals and thus the amount of obtained precipitate is controlled by the total radiation dose with a high accuracy. Moreover, the radiation-induced method is cost-effective processing, since it implies direct energy transfer without intervening media. It has low energy consumptions, since the radiation source does not require external energy supply. It requires minimal use of potentially harmful chemicals (initiators, crosslinking agents, acids etc.). Thus, radiation-induced synthesis can be considered as a green method.
In the current work we demonstrate how gamma radiation induced synthesis can be implemented to produce metal (Ag, Cu, Ni) and metal oxide (Cu2O, Co3O4, CuO) nanoparticles having narrow size distribution for different applications. The nanomaterials are produced both free standing and on solid supports. Metal nanoparticles are synthesized using the reductive route while metal oxide particles are produced using both oxidative and reductive routes [1, 2].

References

9:30 AM NM04.01.04
Photoelectron Spectroscopy Investigation of GaN/Si Heterostructures for Photocatalytic Water Splitting Srinivas Vankel1,2, Elisabetta Arca3, Glenn Teeter1 and Zeitian Mi4; McGill University, Montreal, Quebec, Canada; 2University of Michigan, Ann Arbor, Michigan, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States.

Surface, interface, and bandgap engineering play a pivotal role for designing tandem photoelectrodes for photocatalytic water splitting to potentially realize solar-to-hydrogen efficiencies >20%. III-nitride semiconductors, e.g. GaInN, have emerged as one of the most promising materials to realize high efficiency photocatalysts: their fundamental bandgap can be varied across nearly the entire solar spectrum by changing the alloy compositions and the band edge positions straddle water oxidation and reduction potentials under visible light irradiation. In this context, we have performed, both theoretically and experimentally, a detailed investigation of the structural, electronic, and photocatalytic properties of Ga(In)N/Si heterostructures. Detailed X-ray photoelectron spectroscopy (XPS) measurements reveal that the conduction band edge of GaN and Si are nearly-perfectly aligned, which enables efficient extraction of photo-generated electrons from the underlying Si wafer to GaN nanowires. Band diagrams were constructed from the measured valence band minimum (VBM) and the observed core-level shifts between different thickness GaN/Si samples. Deposition of 2-3 nm of GaN evidently passivates the Si surface and induces a small amount of upward band bending (BB). The interfacial valence-band-offset calculated from measured VBMs and core-level shifts was 2.52±0.1 eV. This value, in combination with the individual band gaps of Si and GaN, leads to a conduction band offset of 0.22±0.1 eV, where the negative sign indicates that the CBM of GaN is lower than that of Si. It is to be noted that in GaN acts like a hole blocking layer which helps in charge carrier separation and thereby reduce the surface recombination of the photo-generated carriers. With the incorporation of Pt co-catalyst nanoparticles on Ga(In)N surface, we have demonstrated solar water splitting on Ga(In)N/Si photocathode with a maximum current density of >35 mA/cm² and an applied bias photon-to-current efficiency >10% in 0.5 M H2SO4 under AM1.5G one-sun illumination. This work shows the use of GaN nanowires as a multi-functional protection layer as well as excellent charge extraction of the photogenerated electrons from the underlying Si wafer.

9:45 AM NM04.01.05
Structure and Reactivity of Zinc Oxide Nanoparticles—A DFT Study Takat B. Rawal1, 2 and Loukas Petridis1, 2; 1Department of Biochemistry and Cellular and Molecular Biology, University of Tennessee, Knoxville, Tennessee, United States; 2UT/DOE Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Zinc oxide (ZnO) nanoparticle, an active ingredient of bactericides, has potential applications in treating citrus greening disease owing to its unique properties. Here, employing density functional theory we study the structures and reactivity of sub-nanometer-sized ZnO nanoparticles. Examination on the propensity of binding of water, urea, salicylic acid and citric acid molecules to the surface of ZnO nanoparticle (diameter ~14Å), indicates that the molecules bind strongly at Zn atoms at the nanoparticle edges. Strikingly, the binding of urea, salicylic acid and citric acid through their O (O=C) atoms at the Zn sites can be traced to the electronic structures. We also investigate the solvation effects on the binding characteristics of these molecules. Finally, we compare the structures and energetics of molecules adsorbed on the nanoparticle with those on extended ZnO(10-10) surface, and find that the edge Zn sites of the nanoparticles are more active than the surface Zn sites of the extended surface. Overall, our results provide insights into the reactivity of ZnO nanoparticle in different local environments, and may offer guidelines to design the ZnO-nanoparticle-based material as an antibacterial agent for agricultural applications.

*This work is supported by USDA NIFA under grant FLAW-2014-10120.

10:00 AM BREAK

10:30 AM NM04.01.06
Hybrid Nanomaterials and Their Applications in Energy and Water Areas Pei Dong1, Yongjie Zhan3 and Jun Lou2; 1George Mason University, Fairfax, Virginia, United States; 2University of Texas, Texas, United States; 3Northwest University, Xi’an, China.

Water and energy are two of the world’s most valuable resources. In the near future, as the industrial sector expands, demand for water and energy will be even greater than it is today. Recently, advanced nanomaterials have been widely implemented in energy and water areas. Here, hybrid nanostructures composing of graphene-like film and bamboo-like carbon nanotubes have been synthesized in a simple, one-pot, catalyst-free chemical vapor deposition process. Pre-sputtered carbon coating on a copper substrate is considered as the key factor contributing to the final morphology. Furthermore, this hybrid nanostructure product has been shown to be a potential alternative material in solar cell and water desalination applications for sustainability.

10:45 AM *NM04.01.07
Smart Gel-Based Materials from Design to Application via Organic-Inorganic Hybrid Technology Meifang Zhu, Kai Hou, Peiling Wei, Tao Chen, Mengge Xia and Zhourui Meng; State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China.

Smart gels-based materials can respond external stimulus, such as temperature, pH value, light, electric, magnetic etc., via significant volume phase transition, have attracted a great amount of attentions.1 Recently, organic/inorganic hybrids have been developed as a novel platform for design of gels-based materials with diverse scales and dimensions, showing multi-functions to broaden their applications in smart sensing and biomedical fields. Here, we combing our long-term research, series of organic-inorganic hybrid gels-based materials with diverse dimensions to meet practical applications requirements have been designed and prepared. In details, we prepared zero-dimensional (0D) nanogels, functionalizing with photothermal agents and anticancer drugs to deal with cancer.2-4 As for 1D fiber, we obtained hydrogel fibers continuously with high efficiency based on a novel dynamic-crosslinking-spinning technology, the hydrogel fiber could be functionalized with conductive agents using a subtle coaxial spinneret, provide promising candidate for artificial nerves.5 Furthermore, several 3D smart bulk hydrogels were synthesized by in-situ introduction of functional nanoparticles into hydrogels, which could be used in fields of sensors including micro-channel valves and temperature switches.5-9

Acknowledgement: This work is financially supported by National Key Research and Development Program of China
Nanostructured Devices and Catalysts for the Solar-Driven Reduction of CO2 to Fuels

CO2-derived fuels present an attractive way towards a sustainable energy system. Mimicking natural photosynthesis by synthesizing carbon-based energy carriers using renewable energy allows for closing the anthropogenic carbon cycle and therefore represents an attractive way to store intermittent power, a challenge that has not yet found a satisfying solution. Using solar power as the energy source for fuel synthesis will require large surfaces of absorbers and efficient catalysts, which should be fabricated from abundant materials. In this context, we show the application of cheap and scalable CuO photocathodes in combination with molecular rhenium catalysts, both in solution and covalently bound to the nanostructured photoelectrode surface. Both systems feature substantial photocurrents and photovoltages, demonstrating protected CuO photocathodes as viable candidates for solar-driven CO2 reduction processes.

Moving from organic solvents into aqueous systems, we demonstrate the unassisted and sustainable splitting of CO2 into CO and O2 using perovskite demonstrating protected Cu2O photocathodes as viable candidates for solar-driven CO2 reduction processes.

Going beyond the production of CO, a novel approach was used to gain insight into the mechanism of hydrocarbon formation at copper electrocatalysts. Studying this process in nonaqueous electrolytes at low temperatures allows for fine-tuned control of the proton donor and the CO binding strength, enabling activation-controlled kinetic studies over an extended parameter range. From these measurements, we are able to show that the rate of methane and hydrogen formation is governed by the competition of CO and H for surface sites while ethylene formation remains weakly impacted by this effect.

Microkinetics on these electrodes indicate that the selectivity change is due to the suppression of H2 evolution, while the rate of CO production remains similar. Together with the use of a bipolar membrane, allowing for separating product gases while maintaining a sustained pH gradient, we used these electrodes demonstrate long-term solar CO production at an efficiency of 13.4 %, driven by a single 3-junction photovoltaic. Going beyond the production of CO, a novel approach was used to gain insight into the mechanism of hydrocarbon formation at copper electrocatalysts.

The presentation illustrates the pathway to ever more insight and to efficient catalysts and devices for the reduction of CO2, first to CO and subsequently to hydrocarbon fuels such as methane and ethylene.

11:30 AM Rapid Fire Presentation

SESSION NM04.02: Synthesis and Nanomanufacturing II
Session Chair: Meifang Zhu
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Back Bay C

Etched Metal Superhydrophobic Surfaces for Enhanced Condensation
Soumyadip Sengupta, Kalyan Boyina, Kazi Fazle Rabbi, Bassel Abu Jabal, Justin Olson, Longnan Li and Nenad Miljkovic, University of Illinois, Urbana, Illinois, United States.

Inspired from natural surfaces such as lotus leaves, water strider legs, the Namib desert beetle, and geckos’ feet, the past few decades have seen significant research and development in the design and manufacturing of water repellent or superhydrophobic surfaces. For superhydrophobicity, surfaces need to be fabricated in two steps, initially creating micro/nanostructures, thereby providing roughness to the primary substrate, followed by the deposition of a low energy surfactant coating. The low surface energy leads to higher advancing and receding contact angles with water droplets, lower contact angle hysteresis, and hence easy droplet removal, promoting dropwise condensation and enhancing heat transfer. Recent studies have focused on chemical oxidation of metallic surfaces to form conformal micro/nanoscale structured metal oxide layers at the solid-air interface. The process is usually self-limiting, with both the oxide layer thickness and structure length scale ranging from 10 nm to 100 µm. Despite efficient dropwise condensation, the metal oxide layers create a significant conduction parasitic thermal resistance due to their lower thermal conductivities (around 10 W/m.K) when compared to their pure metal counterparts (around 100 W/m.K). Furthermore, the application of metal oxide structures for industrial applications remains a challenge due to their poor durability. Here, we develop micro/nanostructured surfaces via direct electrolytic etching of metals. Different length scale surface structures and roughness are obtained by controlling the etching time and supply voltage of the electrolytic process. The etched metallic structures are made of the base metal, enabling higher thermal conductivity and lower parasitic resistance. Furthermore, the uniform metallic composition of the base metal and etched structure minimizes the thermal-mechanical stresses. Linear abrasion tests revealed greater durability of our etched metal structures when compared to metal oxides. After coating the developed surfaces with a low energy self-assembled monolayer using vapor deposition, these surfaces show water droplet contact angles greater than 160°. Our work not only develops metal etched structured surfaces for durable condensation of steam and enhancement of condensation heat transfer coefficient, it enables a scalable manufacturing technique for durable superhydrophobicity.

2:00 PM NM04.02.03
Periodic Step Nanostructure Evolution at the Thin Film Gold/Substrate Interface
Linfeng Chen, Maria Koifman Khristosov, Cecile Saguy, Alex
Nanoscale step structures have attracted recent interest owing to their importance in both fundamental and applied research, for example in adsorption, in catalysis, and in directing nanowire growth. In this in situ study, self-ordered vicinal-like surface structures were obtained by annealing of thin films of gold deposited on ultraflat Si/SiO$_2$ substrate. Annealing at temperatures ≥200 °C efficiently promoted the formation of vicinal-like structures on the inner gold/substrate interface. Gold grains near the inner surface exhibited an orientation with the [111] direction very close to the substrate normal. Furthermore, the step periodicity depended on the grain/substrate orientation angle. Smaller misorientation resulted in a larger average step periodicity, similar to that seen in regular vicinal surfaces of gold single crystals. Formation of low-index terraces and atomic steps at the inner gold interface (while the silica surface remains ultraflat) can be considered as a kind of solid–solid dewetting. We suggest that the formation of vicinal-like structures could be attributed to the thermally activated surface reconstruction by minimization of the total surface energy, which includes the gold/substrate cohesion energy and the GB energies. The process is controlled by diffusion of gold from the inner gold/substrate interface, most probably to the grain boundaries and then to the outer surface of the film. Substantial bulk diffusion across the film during annealing at 400 °C for 4 h can also provide a required mass transport from the inner to the outer surface. This work contributes to the understanding of the atomic step structure formation at the gold/substrate interface, which will be helpful in the use of vicinal-like surfaces as templates for growing of regularly spaced nanostructures. It also offers a method for the in situ investigation of both the grain orientation and the grain interface step periodicity in a given grain, and then can be utilized for further explorations of vicinal-like surfaces.

2:15 PM *NM04.02.04
Sustainable Hydrogen Solution Enabled Through Hydrolysis with Water-Reactive Nanoporous Metals

Eric Detsi, John S. Corsi and Jintao Fu; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Water-reactive nanostructured materials and metalloids such as nano-Mg, nano-Al, nano-Zn and nano-Si with minimum surface oxide coverage have a broad range of potential applications. They can serve as catalysts for combustion, as active materials in hydro-powered spaceship engines, and as materials for onboard hydrogen production to power portable devices and hydrogen fuel-cell vehicles. The degree of reactivity of this class of materials with water is linked directly to their nanoscale size and to the extent in which the surface of these nanomaterials is covered with oxide. For example, smaller nanostuctures exhibit faster kinetics in their reaction with water to produce hydrogen. Nearly oxide-free, ultrafine nanoscale structures with characteristic sizes in the range of 10-20 nm are commonly required for effective reactivity with water. Nanofabrication of these highly-reactive materials with such ultrafine structure sizes and minimum surface oxide coverage is still a fundamental challenge due to their high chemical reactivity. In this talk, I will present a novel, cost-effective, and scalable route to sustainable hydrogen for on-board application. Our new route involves: (i) the hydrolysis of neutral water with nanoporous aluminum to produce hydrogen and aluminum oxide without the typical use of catalysts, and (ii) the recycling of aluminum hydroxide back to aluminum metal without any CO$_2$ footprint. While over 95% of hydrogen used worldwide is produced by steam reforming of natural gas, this method is not sustainable because CO$_2$ is co-produced during the process. Sustainable hydrogen can be generated by electrolysis of water into hydrogen and oxygen, but this method is relatively expensive (~40-53 kWh of energy is needed to produce 1 kg of H$_2$) and not very efficient (40-60% yield). The new method presented in this talk requires only 24-47 kWh of energy to produce enough nanoporous aluminum to generate 1 kg of hydrogen with 50-85% yield by hydrolysis in neutral water. [1,2]

References:

2:45 PM NM04.02.05
High Temperature Nanomanufacturing for Emerging Technologies

Yonggang Yao; University of Maryland, College Park, Maryland, United States.

High temperature processing can provide sufficient activation energy for materials’ compositional, structural, and morphological evolutions, and is essential for various kinds of reactions, synthesis, and post-treatment. However, the current high temperature heating sources, mostly furnaces, are far from satisfying for nanomaterials processing owing to their bulky size and limited temperature and ramp range (~1300 K, ~10 K/min). Here we have focused on the study of electrical triggered Joule heating as a new route for high temperature engineering of nanomaterials toward nanomanufacturing. We developed facile, highly stable and controllable heating strategies for micro/nanoscale high temperature engineering. Ultrahigh temperature annealing (~2500 K) is applied to carbon nanomaterials to address the defects and poor interfacial problems. Ultrafast thermal shock (~2000 K in 55 ms) is applied to metal salt loaded carbon substrates for in-situ synthesis of ultrasmall, well-dispersed nanoparticles. The high temperature engineering on nanomaterials is highly facile, energy-efficient, and reliable toward scalable nanomanufacturing. More exciting results and products are expected for various nanomaterials during/after the unique high temperature engineering.

3:00 PM BREAK

3:30 PM OPEN DISCUSSION

3:45 PM NM04.02.07
Additive Manufacturing of Gold Nano-Dimers Under Ambient Conditions

Chenpling Zhao; University of Dayton, Dayton, Ohio, United States.

The terms “nanomanufacturing” and “nanofabrication” are often used interchangeably. Recently, Liddle et al. have distinguished between nanomanufacturing and nanofabrication by using the criterion of economic viability. Nanomanufacturing, which utilizes efficient and cost-effective nanofabrication methods to manufacture nanostructures and functional devices, has the characteristic of being a source of money, while nanofabrication is often a sink. Nanomanufacturing is indispensable in today’s “nano-world” as the devices keep shrinking in size. The functional devices with internal bond lengths of 10-20 nm scales have intriguing and extraordinary properties for many applications. For example, the color of gold nanoparticles distributed in a material does not appear yellow its familiar color for bulk gold, instead, the color of nano-gold changed to ruby red. The melting point of gold at the nanoscale is also significantly lower than its bulk counterparts.

There are a large number of nanofabrication approaches available, but only a few are suitable for large-scale nanomanufacturing. Therefore, the exploration of new technology is desperately needed to expand the nanomanufacturing toolbox. Here, we demonstrate a method that can be used for affordable nanomanufacturing at the ambient conditions. A low-cost continuous-wave (cw) laser is used to directly kick and transfer nanostructures from one substrate
to another in ambient conditions. Unlike the direct laser ablation method, where expensive pulsed lasers are typically used to ablate the materials disruptively, the method demonstrated here has no damage on the nanostructures, therefore, this method can maintain the geometry of nanostructures and transfer them selectively in an additive manner.

4:00 PM °NM04.02.08
Sustainable Nanomanufacturing Research at NSF* Khershed Cooper; Advanced Manufacturing, National Science Foundation, Alexandria, Virginia, United States.

Nanomanufacturing is the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures, and the integration of these into larger scale systems with manipulation and control at nano-scale. Typically, the scale ranges from 1-100 nm. Processes can be top-down (additive/subtractive) or bottom-up (self- and directed-assembly) or an integration of the two. Manufacturing processes need to be scalable, controllable, reproducible, efficient and low cost. The combination of large-scale production and nano-scale products raises environmental and sustainability issues. Questions needing answers are: 1) How can industry develop new nanotechnologies in a responsible and sustainable manner; 2) How can it be ensured that nanomanufacturing processes are safe for producers and products are safe for consumers and the environment. This talk discusses NSF-supported projects in sustainable nanomanufacturing that address life-cycle analysis, recycling, environmentally-benign nanomaterials and processing, green nanomanufacturing, clean energy, wastewater treatment, among others. It will conclude with a discussion on future directions and their implications.

4:30 PM RAPID FIRE PRESENTATION
efficient pathways for ion and electron transportation, as potential successor of current filtration membranes. While the pressure driven transport data on highly ordered continuous, thin films of multi-layered graphene oxide and holey graphene is expected to demonstrate faster transport for salt water, higher retention for charged and uncharged organic probe molecules with hydrated radii above 5 Å as well as modest retention of mono- and di-valent salts for ~150 nm thick membranes. The highly ordered graphene nanosheets and nanoscaled porous graphene in the plane of the membrane make organized, molecule-hugging cylindrical and spherical channels, respectively, thus enhance the permeability and hydrodynamic conductivity. The results illustrate that both the mesoscale and nanoscale pores are favorable for enhancing CDI performance by reducing the diffusion distance from external electrolyte to the interior surfaces and enlarging surface area analogous to electrochemical double-layer supercapacitors where in electrical energy storage is through concurrent surface ion adsorption and electron transfer. We determined the salt ion species rejection by composite CDI electrodes by > 65% for actual seawater in one cycle which can be further improved by use of nanoparticles for ion selectivity. This work is supported in parts by KY NSF EPSCoR and WKU Research Foundation internal grant.

NM04.03.04
3D Hierarchical Structure for Water Splitting with Extraordinarily Enhanced Photocactivity
Junho Jun, Sucheol Ju, Seungho Baek, Minseop Byun and Heon Lee; Korea University, Seoul, Korea (the Republic of).

As the need for renewable energy continues to increase, hydrogen, the most promising clean energy source, is receiving a great deal of attention. Solar water splitting, which is the most efficient way to produce hydrogen without any pollutants, has been actively studied since the discovery of the TiO2 photocatalyst by Fujishima in 1972. Nevertheless, the production efficiency of this method is still very low, making it impractical for commercial use, and many studies are underway to improve the efficiency of solar water splitting. The mechanism of the reaction at the photoelectrode can be roughly divided into three sub-categories: absorption (Eabs), electron separation (Esep), and surface reaction (Etrans), each with its own efficiency. In order to produce an efficient optical electrode, the material used for solar water splitting must be efficient for all three reactions. Especially, it is challenging to decouple the efficiency between light absorption and charge separation (Eabs x Esep). Nanostructuring is one of the most efficient method to overcome this coupling issue. By nanostructuring with one or more materials, nanostructured layer can have increased light absorption with even a thin layer, which is good condition for short carrier diffusion length of oxide materials such as BiVO4, Fe2O3.

Herein, We fabricate Au/BiVO4 3D nanostructured photoelectrode via nanoimprint lithography(NIL) and various deposition method. NIL has advantages on fabrication of nanostructure in large area. Using NIL, we can fabricate uniform nanostructure such as nanocone or high-aspect ratio pillar. After that, we deposit various materials on nanostructured template by Atomic layer deposition(ALD) or photo assisted electrodeposition (PED). This 3D hierarchical structure has an optical effects that can enhance light-matter interaction including anti-reflection and light-scattering, and also help generated electron-hole deposit various materials on nanostructured template by Atomic layer deposition(ALD) or photo assisted electrodeposion (PED). This 3D hierarchical structure has an optical effects that can enhance light-matter interaction including anti-reflection and light-scattering, and also help generated electron-hole.

NM04.03.05
One-step Flame Synthesis of W/Mo/N-Doped Titanium Dioxide Nanoparticles for Enhanced Photocatalytic Activity
Yujuan Zhang, Zhizhong Dong, Bernard Kear and Husnu E. Unalan; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

W/Mo/N-doped titanium dioxide (W/TiO2) nanoparticles are synthesized using a multiple diffusion flames setup, where tungsten mesh, molybdenum wire, and CNH2 is utilized as doping source and titanium isoproxopropoxide (TTIP) serves as precursor for TiO2. At relatively lower tungsten loading rates, nanoparticles are produced in W-TiO2 form with an obvious shift angle (0.15°) in the XRD pattern. However, at high tungsten loading rates, homogenous nucleation of WO3 occurs concurrently with homogeneous nucleation of TiO2, thereby leaving less tungsten ions to be doped into the TiO2 matrix. Molybdenum wire is placed on top of the tungsten mesh to achieve W-Mo co-doping of TiO2. Cyanamide solution is injected into the central flame to produce N-doped TiO2. UV-Vis spectroscopy shows that the as-synthesized doped nanoparticles possess enhanced absorbing ability in the visible light wavelength range compared with that for non-doped TiO2 nanoparticles. Photocatalytic activity of the doped nanoparticles are tested via batch phase water reduction with methanol as a sacrificial agent. As-synthesized samples having a higher H2 evolution meanwhile are more active under dark and UV illumination comparing to that for Pt25.

NM04.03.06
Ultra-Fast Additive Nano-Patterning Process and Its Applications with Large Area and Flexible Form-Factors
Hanul Moon1, Hyeonho Jeong1, Han-Jung Kim1, Min Yoon1, Chang-Goo Park2, Yong Suk Oh1, Dae-Geun Choi2 and Seunghyup Yoo1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Nano-scale patterns have been intensively studied in wide range of fields because they provide enhanced performance or new functions that cannot be observed in macro- or micro-scale patterns. However, conventional nano-patterning process based on lithographic methods has limited wide-spread of nano-patterns due to complex process steps requiring expensive equipment. To fully open the possibility of nano-patterns in various fields, an alternative method is required to fabricate nano-patterns in a facile way that secures significantly improved cost-effectiveness, and versatility allowing large-area fabrication or various form-factors such as flexibility. Here, we proposed an additive nano-patterning process from solution route using selective-wetting phenomenon in response to such requirements.

The proposed process proceeds to 1) nano-imprinting on to hydrophobic/hydrophilic bilayers and 2) solution dragging. Appropriate post-processes such as annealing can be followed. The former step results in 3D structures consisting of nano-scale engraved hydrophilic parts and embossed hydrophobic parts. Then, by dragging a solution on top of the surface, the solution is automatically confined in the engraved hydrophilic parts without residue on the embossed hydrophobic top surface by selective-wetting phenomenon. The 3D engraved structure is also essential to cause nano-patterns with sufficient amount of target materials. The results verified that the yield of the nano-patterning process is almost perfect once the imprinting onto the bilayer is successful. 150 nm-diameter dot arrays of Ag over the area of 10 cm × 10 cm were successfully fabricated with high yield, and was served as a plasmonic color filter of uniform magenta color. The mechanism of the proposed nano-patterning process was analyzed using fluid-dynamics simulation, and verified control parameters aiming at higher process speed and smaller pattern size.

Virtually, any kind of solutions can be applied to the process, and nano-patterns of Ag, metal-oxide, and organic materials could be fabricated by using a metal-nano-particle ink, a sol-gel solution, and organic solvent. In terms of throughput, the dragging speed of solution could be over 4.5 m/min. The selectivity-wetting phenomenon also enables self-aligned multiple deposition of nano-patterns, thus allows thickness controllability and multi-layer nano-patterns assembly of different materials. Thanks to the simple fabrication steps, the proposed method could open an access to make various substrates including plastics and papers. According to the aforementioned advantages, we believe the proposed process significantly improves the usefulness of nano-patterns in wide range of fields, especially if they require nano-patterns over large-area with various form-factors fabricated by a cost-effective way.

NM04.03.07
Investigation of Magnetic Properties of Electrodeposited Cobalt Ferrite Films with Control of Grain Size and Surface Morphology
Brent
Cobalt ferrite is a material which has been researched for its applications in spintronics, magnetic sensing, and catalysis. Though synthesis methods have been established for formulating films including pulsed laser deposition, chemical vapor deposition, and rf sputtering most of these methods need high vacuum and power sources to formulate a film. Within this work a facile method for synthesizing films through electron deposition without the need of high energy appliances. The main component for the process includes an aqueous solution which can be reused with reproducible results. Through varying Co:Fe content, time, potential, and ramp rates, control over grain size and morphology of the surface was established. X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) were used to confirm phase, composition and surface morphology. Variations in magnetic properties such as transition temperatures, magnetic saturation, coercivity, were observed from grain size ad surface morphology. The current research seeks to improve facile thin film methods which may be facilitated in a variety of magnetic applications.

NM04.03.08
On-Demand Band-Gap Tuning of Colloidal Perovskite Nanocrystals Enabled by Fast Anion-Exchange Reactions Kameel K. Abdel-Latif, Robert W. Epps, Michael Bowen, Corwin Kerr and Milad Abolhasani; Chemical Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Since the discovery of the colloidal perovskite nanocrystals three years ago, they have rapidly grown to become one of the most promising classes of nanomaterials for large-scale applications in optoelectronic devices. Anion exchange reactions of the highly luminescent cesium lead halide perovskites (CLHPs) provide a facile post-synthetic route for the tuning of the absorption/emission band-gap of CLHPs. These post-synthetic reactions allow the utilization of CLHPs in various optoelectronic applications including third-generation photovoltaic cells and light emitting diodes. Studies of anion-exchange reactions are typically conducted using the time- and material-intensive flask-based synthesis approach. Batch scale synthesis strategies are notorious due to (a) batch-to-batch variation, (b) inefficient and irreproducible mixing timescales, (c) manual sampling and characterization at room temperature, and (d) poor size distribution of the resulting nanocrystals after scale-up. Here, we present a modular multiphase microfluidic strategy with an in situ spectral monitoring capability that enables the systematic kinetic study of anion-exchange reactions of CLHP nanocrystals. Utilizing the microfluidic nanocrystal synthesis platform, we monitor absorption and emission spectra of CLHPs, in real-time, over residence times ranging between 100 ms and 17 min. In-situ monitoring of the optoelectronic properties of CLHPs over different synthesis conditions enables fundamental and applied studies of structural tuning of CLHPs via anion-exchange reactions. The enhanced mixing feature of the multiphase flow along with the novel anion-exchange framework using ZnX2 (X=I or Cl) facilitates on-demand bandgap tuning of high-quality CLHPs (i.e., narrow size distribution with high quantum yield) via a positive feedback loop in which synthesis parameters are varied until the target optoelectronic characteristics are achieved.

NM04.03.09
Corporate Responsibility—A Green Initiative to Reduce Chlorobenzene Based Chemistries in Semiconductor Processing Monique Farrell, Kevin Frey and John Mason; Northrop Grumman, Linthicum, Maryland, United States.

Climate change and an increase in endangered species, are examples of technological advances negatively impacting the environment. As technology demands increase, an earnest effort to reduce the environmental impact of processing and manufacturing related activities is critical. From a business perspective, minimizing or removing toxic chemicals from processes, is a high impact area that can increase work environment safety and decrease waste management costs. This work presents processing considerations when transitioning to greener alternative polymer resist solvents, for applications in nanomanufacturing with sustainability considerations. Within government contracting, process modifications that change product form, fit, or function require qualification and at minimum justification. This work presents the conversion from a chlorobenzene to anisole based solvent using a 495 kMW polymethyle methacrylate polymer resin, without impacting form, fit, or function of the intended device. Resist conversion is of interest as the difference in the substrates of the two solvents, impact the effective toxicity of the materials. Specifically, the oral median lethal dose (LD50) for chlorobenzene is 1110 mg/mL, while anisole is 3700 mg/mL. Developing a process that utilizes anisole as opposed to chlorobenzene, addresses this safety concern and contributes to green initiatives worldwide. Within this work, an electron beam lithography fabricated transistor consisting of a source, drain and gate were converted from a chlorobenzene based resist to a process utilizing an anisole solvent; while maintaining process of record specifications. The purpose of this work is to provide a starting platform for individuals seeking to convert from a chlorobenzene solvent to an anisole based resist, for sub-micron lithography steps.

Approved For Public Release #18-1367; Unlimited Distribution

NM04.03.10
The Role of the Counterion on the Crystal-Shape and Photocatalytic Properties of ZnO Nanostructures Grown via Hydrothermal Route Ariadne C. Canto1, Luis F. da Silva1, Mateus Ferrer2, Osmundo F. Lopes1, Valmor R. Mastelaro3 and Elson Longo1; 1Federal University of São Carlos, São Carlos, Brazil; 2University of São Paulo State–UNESP, Bauru, Brazil; 3University of São Paulo, São Carlos, Brazil.

Nowadays, a concern over environmental problems has enhanced our awareness of the need to develop alternative and environmentally friendly process aiming at increase environmental protection. For the treatment of waste water and pollutant degradation, photocatalysis is considered one of the most promising and sustainable way due to its high-efficient, eco-friendly, low toxicity and low cost. Zinc oxide (ZnO) exhibiting different morphologies and high surface/volume ratio exhibit many favorable optical, electronic and surface properties leading it a promising candidate in field of photocatalysis as a sustainable and eco-friendly technology. Motivated by these considerations, the goal of this study consisted to investigate the influence of zinc precursor on the structural, microstructure, surface and photocatalytic properties of nanostructured ZnO films grown under hydrothermal conditions.

The nanostructured ZnO films were grown via hydrothermal method using different zinc salts, including acetate (Zn(CH3COO)2·2H2O), nitrate (Zn(NO3)2·6H2O), and sulfate (ZnSO4·7H2O) under identical conditions. The crystalline structure and morphological features were investigated by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) measurements, while the surface properties were probed using X-ray photoelectron spectroscopy (XPS).

XRD patterns of the ZnO films were fitted to the wurtzite ZnO structure, however the sample synthesized from zinc sulfate also presented additional peaks assigned to the zinc hydroxy-sulfate-hydrate phase. FE-SEM analyses reveal that the morphology of the ZnO structures is strongly dependent on the zinc salt. The zinc nitrate provides the formation of the same morphology of the acetate, with an anisotropic growth preferentially along the (0001) direction resulting in hierarchical nanorod-like structures with an average diameter of ca. 90 nm. The average rod diameter was larger for ZnO samples synthesized using zinc acetate (ca. 2 times). Regarding the zinc sulfate, the change in microstructure was more significant, where SEM images revealed the formation of hexagonal microplate-like structures. In this case, the growth along (0001) was dramatically suppressed, producing a micrometric 2D morphology.

With respect to photocatalytic activity, the ZnO samples were studied for the degradation of methylene blue (MB), and rhodamine B (RhB) dyes under ultraviolet light. The ZnO film prepared from zinc nitrate exhibited the best photocatalytic activity compared to other samples, followed in turn by the
sample prepared with acetate, and sulfate. The enhancement of photocatalytic activity was attributed to structures size, surface morphology including the higher fraction of exposed (0001) ZnO polar facets, as well as the presence of oxygen defects.

NM04.03.11  
**High Volume Manufacturing of Boron Nitride NanoBarbs**  
Steve Wilcenski; BNNano, Inc., Cary, North Carolina, United States.

Boron nitride nanotubes have become a material of significant interest due to their unique combination of physical and chemical properties. Among the desirable properties are the high thermal stability, high thermal conductivity, electrical resistivity, very high strength and stiffness, and super hydrophobicity. This combination of properties makes boron nitride nanotubes an attractive material for use in wide-ranging markets from aerospace to automotive and defense to biomedical.

The most significant limitation to these potential applications has been the lack of supply of high purity boron nitride nanotubes in the marketplace. Recent advances in the manufacture of this material are now enabling additional research and product development. The high-volume NanoBarb process is uniquely positioned to manufacture and supply commercial volumes of high purity boron nitride nanotubes to fulfill this need.

NM04.03.12  
**Rational Design of Novel Dielectric and Photocatalytic Core-Shell Nanomaterials by a Sacrificial Template Method**  
Prabodha M. Balasinghawaka1, Swati Naik2, Liang Hong3, Robert Klie2 and Gabriel Caruntu1; 1Central Michigan University, Mount Pleasant, Michigan, United States; 2Physics, University of Illinois at Chicago, Chicago, Illinois, United States.

SrTiO3 has a well-known perovskite crystalline structure and exhibits excellent dielectric, electro-optic and catalytic properties, being the leading candidate in many cutting-edge technological applications. We report here on the rational synthesis of SrTiO3/TiO2 nanodimensional heterostructures by using TiO2 colloidal nanocrystals as sacrificial templates under different reaction conditions, with the main goal of achieving control over the morphology (size, shape), internal structure and surface composition of the resulting nanoparticles. Both the synthesis of TiO2 nanocrystals and their subsequent conversion into SrTiO3 were performed using a hydrothermal method. These nanocrystals were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrational spectroscopy (Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy) and optical absorption measurements. Various reaction parameters have been finely tuned in order to optimize the reaction conditions. A detailed characterization of the dielectric properties of these nanopowders was carried, revealing that dielectric permittivity has a value around 120 at room temperature with a low loss, which make these nanomaterials desirable for applications in energy storage and as dielectrics. Moreover, the photocatalytic properties of SrTiO3/TiO2 heterostructures were analyzed by using dye degradation method under ultraviolet light. An enhanced photocatalytic activity was observed, which can be ascribed to the improved charge separation between photogenerated electrons and holes in conduction and valence bands of SrTiO3 and TiO2. Thus, this synthesis strategy of nanoscale heterostructures is useful to develop functional materials with superior efficiency for implementation into functional electrical devices, as well as photocatalysts.

NM04.03.13  
**Hierarchical Porous Solvogel Monoliths—Synthesis and Application**  
Marie-Christin Röpert, Christoph Weidmann and Rainer Ostermann; Westphalian University of Applied Science, Recklinghausen, Germany.

Bimodal pore systems are of utmost importance for many high-tech applications, for example in chromatography or as carrier material for catalysts. A hierarchical structure with both micro/mesopores and macropores allows to obtain both high surface areas and good transport properties (accessibility of and low pressure drop in the porous structure). The inorganic sol-gel-chemistry offers reliable routes to synthesize materials with tunable pore sizes, most prominently via phase separation during condensation and solidification of silica precursors [1]. This concept was successfully transferred from inorganic to organic polymers, based on the radical polymerization of divinylbenzene [2]. In contrast to these studies, we extend this strategy to novel bicontinuous porous polymers, which form readily under mild conditions. Therefore, we use the cyclotrimerization of inexpensive diisocyanates to obtain materials with continuous macropores and very high adsorption capacities. The ratio of solvent, polymer and diisocyanate in the studied system can be varied over a wide range, allowing to independently control both pore size and volume. In addition, the isocyanate chemistry allows using tailored prepolymer to optimize the properties (e.g. shrinkage) or functionalizing the resulting solvogels for adjusting polarity and incorporating catalysts. Furthermore, the crosslinked polysiloxane network is thermally and mechanically stable and therefore suitable for applications involving high pressure or temperature.

We will present the considerations leading to systems of suitable solvents and polymers for controlled phase separation, focus on the parameters for synthesis and functionalization, as well as giving a first outlook on applications.


NM04.03.14  
**Effect of Surface Modification and Confinement Effect of Crystalline and Amorphous SiC for Sustainable Renewable Energy and Environmental Remediation**  
Akash Mathur1, Dipayan Pal2, Ajaib Singh1, Rinki Singh1 and Sudebha Chattopadhyay1, 2, *; 1MEMS, Indian Institute of Technology Indore, Indore, India; 2Physics, Indian Institute of Technology Indore, Indore, India; 3BSBE, Indian Institute of Technology Indore, Indore, India.

Silicon carbide (SiC) became an important material whose popularity has been constantly increasing due to its excellent mechanical, electrical, optical and chemical properties, which recommend it for cleaner, smaller, stronger and more efficient technologies for solar cell applications as well as for environmental monitoring and decontamination [1]. The occurrence of different polytypes of SiC makes it suitable for photocatalytic material for hydrogen generation and environmental remediation [2] in crystalline SiC forms and for solar cell applications as diffusion barriers, antireflection coatings in amorphous SiC form [3]. Herein, the confinement effects of the different polytypes of crystalline SiC particles and amorphous SiC thin films are being addressed. Here, we report the significant enhancement of photocatalytic activity and substantial bandgap narrowing of EG/SiC composites. Graphitization of SiC by high temperature thermal decomposition method [4] has been employed to grow epilayer graphene (EG) on silicon carbide (EG/SiC hybrid system) to modify the surface and interface structure in controlled manner. The systems have been characterized by Raman and UV–vis spectroscopies along with the XRD, SEM and HRTEM analysis. Significant enhancement of the photocatalytic activity (~1000%) and bandgap narrowing (~30%) of EG/SiC systems were observed, relative to the bare SiC, depending on the quality and quantity of the EG and heterojunction interface structures. Furthermore, we report on a dual ion beam sputtering assisted deposition (DIBSD) of confined SiC thin films (about 450 nm to 20 nm thickness range) with low surface roughness. The thin films have been characterized by Spectroscopic Ellipsometry technique along with AFM, XPS, XRD and XRR. Clear indication of systematic band gap variation was observed for the changes in surface roughness as an effect of confinement of DIBSD grown SiC films. The effect of different types of SiC (polytypes/amorphous) at their different confinement levels (thin films, nanoparticles) have been studied further to explore the potential application in photocatalysis for renewable energy and environmental remediation (e.g., waste water treatment) and for different...
optoelectronics and solar cell applications


NM04.03.16

Core-Shell Nanoparticle Synthesis—A Novel Strategy to Achieve Heterostructures at the Nanoscale using a Molten Salt Solvent

Benjamin Levitas1, Yuexing Zhu2, Katsuyoshi Kakinuma3 and Srikanth Gopalan3; 1Boston University, Boston, Massachusetts, United States; 2Fuel Cell and Nanomaterials Center, University of Yamanashi, Yamanashi, Japan.

In the last three decades, solid oxide fuel cells (SOFCs) have garnered significant interest for viable alternative energy systems owing to their high electrical efficiency and fuel flexibility. In this work, we introduce a novel synthesis of cathodes in SOFCs, wherein oxygen reduction occurs in two steps—adsorption and electronegation, and surface/bulk diffusion to incorporation sites. Transition metal oxides such as strontium-doped lanthanum manganite (LSM) and strontium-doped cobalt iron oxide (LSCF) have been used as cathode materials, however both individually lack the key characteristics to successfully complete oxygen reduction. Furthermore, the accumulation of chromium (chromium poisoning) on SOFC cathodes is known to significantly hinder the performance of the cells. Incorporating core-shell composites as the cathode material could alleviate this problem: effectively combining the functionalities of both materials and providing a nanoscale protection from Cr poisoning with a shell such as Cr-doped LSM (LSCM). Core-shell oxide composites have broad applications in fuel cells, catalysis, magnetic devices, spintronics, nanophotonics, and many more fields. However, synthesizing core-shell composites previously has proved difficult requiring multiple steps, resulting in non-uniform core-shell structures. In this work we propose utilizing a molten salt synthesis process to create core-shell composites with precise composition with relative ease. The core is synthesized using high-temperature calcination and ball milled with the precursors of the target shell material. The milled powder mixtures are added to a LiCl-KCl eutectic melt to form core-shell hetero-structures via heterogeneous nucleation. Prior results have shown the successful formation of LSM and LSCF using the molten salt synthesis, along with the formation of core-shell LSCF-LSM hetero-structures. Synthesis temperatures dropped from the conventional 1000 °C to 500 °C, with dwell times as low as 10 minutes. Furthermore, SOFC cathodes consisting of LSCM were found to have stable polarization resistances, whereas the polarization resistance in LSM cathodes steadily increased. This result provides a strong motivation to further explore LSCM as a shell for core-shell cathodes to ensure protection from chromium poisoning. In essence, this work demonstrates an inexpensive, sustainable method to synthesize core-shell cathodes that can simultaneously provide high power densities and low rates of degradation arising from Cr-poisoning.

NM04.03.17

All-Solution-Processed Transistors on Paper for Cheap Flexible Electronic Applications

Do Hoon Lee, Taewan Kim, Hyun Soo Kim, Ye Rim Lee and Byung Yang Lee; Korea University, Seoul, Korea (the Republic of).

Paper electronics is receiving great interest because it is one of the best candidates for next generation devices with many useful features such as low cost, disposability, and flexibility. In this work, we demonstrate the fabrication of zinc oxide nanowire (ZnO NW) field-effect transistors (FETs) on paper with facile, low-cost and large area manufacturing. This was achieved using the high absorption property of paper. By absorbing silver nanowire (AgNW) solution into the paper, AgNW network formed on the paper surface that acts as a gate electrode with low sheet resistance (9.5 Ω/μ) and low RMS roughness of 120±20 nm. Then, a dielectric layer was deposited by injecting poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) solution on top of the gate. This enabled precise control of the dielectric layer thickness by controlling the concentration of the solution according to pore size of the paper. As a result, a uniform thin dielectric layer of less than 10 nm was formed. The ZnO NWs were self-assembled on a dielectric layer by a simple dipping and pulling method. Afterwards, electrodes were formed via inkjet printer. The all-solution-processed flexible FETs on paper exhibit electrical performance with charge carrier mobility of 0.1 cm2 V-1 s-1, and current on/off ratio of 2×103. Furthermore, even after 100 bending cycles, only a 10% decrease in mobility was observed. By utilizing simple equipments such as a vacuum chamber and a syringe pump alone, we could produce outstanding FETs that are desirable for cheap flexible electronic applications.

NM04.03.18

Magnetic Separation and High Reusability of Chloroperoxidase Entrapped in Multi Polysaccharide Micro-Supports

Sonia García-Embíd 1, 2, Francesca Di Renzo1, Laura De Matteis 4, 2, Nicoletta Spreti3 and Jesús M. de la Fuente1, 2; 1Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC/University of Zaragoza, Zaragoza, Spain; 2CIBER-BBN, Instituto de Salud Carlos III, Madrid, Spain; 3Department of Physical and Chemical Sciences, University of L’Aquila, L’Aquila, Italy; 4Instituto de Nanociencia de Aragón, University of Zaragoza, Zaragoza, Spain.

The World Commission on Environment and Development introduced the term sustainable development, indicating the present need of modern industrial processes to optimize the use of raw materials, reduce waste and avoid the use of toxic molecules. Amongst the approaches used over the years to achieve this sustainability, biocatalysts, especially enzymes, have been in the spotlight due to their great properties. Sustainability of enzymatic catalysis is maintained through the whole cycle: from their production (living organisms) to the waste treatment.1 However, their present application at industrial scale is hampered by the high costs in their production that decrease cost-effectiveness of their application. Reutilization of the enzyme is therefore the tool to obtain more cost-effective and sustainable industrial processes. Immobilization of these biocatalysts allows an easy recovery of the material and protection from the reaction conditions in the different production steps.2 Nowadays, nanotechnology offers one of the most forefront approaches for enzyme immobilization. Magnetic nanoparticles allow an easy recovery of an immobilized enzyme using a simple magnet to separate the catalyst from the reaction product. To improve colloidal stability of the support, reduce interactions between the magnetic cores and prevent interactions with the environment that can affect both support and enzyme stability, a polymer coating is an easy and cheap approach.3 Using this approach, in this work we developed a hybrid, modular micro-support based on organic and inorganic nanocomponents. The easiness of tuning the composition of the support makes this system a potentially universal support for the immobilization of very different catalytic systems.

Here we present the application of the developed micro-support for the immobilization of chloroperoxidase (CPO), an enzyme able to catalyze many reactions of large-scale interest. A multipolysaccharidic shell containing the immobilized enzyme and obtained through a combination of chitosan and alginate, biodegradable polymers from natural sources, was used to stabilize a nanoemulsion core in which magnetic nanoparticles were embedded. Microsystems obtained through different combinations of nanocomponents were characterized and tested in terms of their chemical stability under reaction conditions.

An excellent reusability of the entrapped enzyme was observed opening the way to the immobilization of different catalytic systems and to the scale-up study in view of future industrial application.4

References
 NM04.03.19

**Synthesis and Characterization of Ferroic Materials, Introducing Perovskite and Pyrochlore Europium Titanate Nanocrystals Synthesized by Gel-Collection Nasim Farahmand**

Chemistry, The City University of New York, New York, New York, United States.

Europium Titanate is one of the most interesting materials used in various applications such as sensors, memory devices and energy storage. Its unique features are due to its rich properties, mostly in the area of magnetic properties, which is a result of its seven unpaired spins in its 4f orbital. There are several methods in synthesis Europium Titanate compounds, most of which are among solid state reactions. In this work we have synthesized Europium Titanate compounds both in Perovskite and Pyrochlore crystal structure using gel-collection method. The synthesized material was heat treated both in air and in Argon. XRD of the samples heated in different temperatures indicated interesting results. A dramatic change observed in X-ray diffraction at 750°C indicates a dramatic transfer from amorphous to crystal. While the heated samples in air proved to be pyrochlore structure with interesting electrical properties which make them good candidates as dielectric materials, the sample heated in tube furnace indicates a perovskite structure.

In conclusion we could make europium titanate both in perovskite and pyrochlore structure using the gel-collection method. PDF analysis was done and proved that our perovskite structure is likely to be cubic pm3m, while our pyrochlore structure is in good agreement with the refinement for cubic Fd3m.

 NM04.03.20

**Facile Solution Synthesis of V-VI-VII Inorganic Semiconductors and Their Potential for Applications in Electronic Devices Prashant Kompag Hendrik Faber, Kalaivanan Loganathan, Yuliar Firdaus, Emre Vengel and Thomas Anthopoulos; KAUST Solar Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.**

V-VI-VII compounds are semiconductor materials consisting of elements from group V, VI and VII of the periodic table. These materials usually consist of at least one metal, one chalcogen and one halogen. The recent discovery of Bi2S3 and Bi2S5 as efficient solar cell materials has stimulated research interest from different disciplines to explore various interesting (opto-)electronic properties and applications for V-VI-VII materials. Traditionally, V-VI-VII compounds are synthesized at high temperature following an elemental reaction/flux method using specifically designed and dedicated experimental apparatuses. Unfortunately, both the solid state as well as solution phase synthesis suffers from the formation of V-VI and V-VII phase binary products and phase pure material can only be synthesized under specific experimental conditions. Simultaneously, specific precautionary/safety conditions are required, making the synthesis of these systems only accessible to experts.

In order to further study of these materials in terms of applied, as well as fundamental research, the development of a robust synthetic methodology is therefore highly desirable. Specifically, a low temperature solution based synthesis route with easy-to-handle precursors will open up lots of research possibilities and will facilitate potentially more widespread practical uses in the future. Herein we report a low cost, energy efficient and less time-consuming solution-based synthesis of nanoparticles of various compositions in V-VI-VII materials using Bismuth-Sulfur-Iodine as the model system. In addition to separate precursors for all the required constituent elemental precursors, we have also employed a molecular precursor approach and summarized results will be presented. Synthesized nanoparticles can be dispersed well in organic/aqueous solvents and deposited in the form of homogeneous thin films. Electronic devices such as diodes, transistors and solar cells are used for a comparative study of the electronic transport properties of the synthesized materials.

 NM04.03.21

**UV-Enhanced Gas Sensors Based on SnO2: Nanoparticles Obtained via Microwave-Assisted Nonaqueous Method Luis F. da Silva1, 2, Mattia A. Lucchini2, Ariadne C. Catto1, Waldir Avansi Jr1, Sandrine Bernardin2, Caue Ribeiro de Oliveira2, Markus Niederberger2 and Khalifa Aguir1**

1Department of Physics, Federal University of São Carlos, São Carlos, Brazil; 2Department of Materials, ETH Zürich, Zürich, Switzerland; 1Institute of Physics of São Carlos, University of São Paulo, São Carlos, Brazil; 2Laboratory of Microsensors, Aix Marseille University, Marseille, France; 1Embrapa Instrumentation, São Carlos, Brazil.

Gas sensors based on semiconducting metal oxide (MOS) nanostructures have drawn the attention of researchers mainly due to their sensitivity and stability. Nowadays, these sensor devices are necessary for the detection of harmful gases arising from industrial processes, vehicle emissions, and environmental control. In last decades, several MOS have been used as sensitive layer, due to its excellent performance. Among them, tin oxide (SnO2) has been widely investigated as resistive gas sensors. Despite its remarkable properties, gas sensors based on SnO2 require thermal activation (<150°C) for an enhancement of their gas sensing performance. Recently, the use of UV-light irradiation to activate the gas sensors has been an efficient and inexpensive way for room-temperature stimulation and improvement of the gas sensing properties. In this work, we present an investigation on the influence of the experimental parameters (time and temperature) in the preparation of the SnO2 nanoparticles via microwave-assisted nonaqueous route. The SnO2 samples were evaluated as ozone gas sensors operating at room-temperature under continuous UV illumination. The structural (long-and short-range order), surface, and morphological properties were characterized by X-ray diffraction (XRD), X-ray absorption and, X-ray photoelectron spectroscopies, and high-resolution scanning transmission electron (HR-STEM) analyses. The XRD and Sn LIII-edge XANES measurements indicated an increase in crystallization degree with time and temperature treatment, where Sn4+ ions are in an octahedral coordination. Regarding the surface properties, XPS spectroscopy indicated a significant reduction of carbon species (from precursors) and oxygen vacancies on the samples surface. HR-TEM analyses showed an increase of particle size from 3 to 15 nm, as well as, the formation of necks between the particles, as function of time and temperature treatment. DC electrical measurements revealed that SnO2 nanoparticles were sensitive to sub-ppm ozone levels (80 to 1400 ppb) at room temperature under UV-light illumination, presenting a fast response, good reproducibility, and total reversibility. These findings demonstrate that this chemical method provides a fast and efficient route to manufacturing ozone gas sensor devices for practical applications.

 NM04.03.22

**All Gas-Phase Synthesis and Functionalization of Silicon Nanocrystals Zhaohan Li and Uwe R. Kortshagen; Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States.**

Silicon nanocrystals have attracted increasing attention as light emitting materials, luminescent downshifters, and imaging sensors. Among various quantum dot materials, silicon is earth abundant, biocompatible, and has low toxicity compared with group II-VI and III-V materials. Nonthermal plasma synthesis has been successfully applied for production of quantum confined, luminescence silicon nanocrystals with narrow size distribution. However, the relatively low luminescence efficiency of silicon nanocrystals will limit their use as light emitting materials. Engineering of silicon nanocrystal surfaces is usually necessary for enhanced luminescence performances, and this is typically done by functionalization of silicon surfaces with organic ligands.

In this work, we develop an all gas-phase synthesis route that integrates nonthermal plasma synthesis, plasma-assisted functionalization and in-flight heating of nanocrystals in a single flow stream. In this approach, ligands are attached to nanoparticle surfaces in the plasma afterglow, after which the gas stream carrying nanocrystals enters a tube furnace. With the appropriate furnace temperature, the as-produced silicon nanocrystals have photoluminescence quantum yield exceeding 20%. This is a five-fold increase relative to the case when no in-flight heating is applied. We attribute the enhanced photoluminescence to a reduction of dangling bond densities and a change of surface silyl species composition associated with heating. Compared with colloidal synthesis methods, the all gas-phase approach eliminates the use of solvents, produces no by-products, and has higher process yields. With gas-phase deposition methods, silicon nanocrystals can be directly deposited as nanocrystal thin films with densities approaching the theoretical limit of random close packing. We further demonstrate that it is feasible to control the average interparticle distance in nanocrystal films by using ligands with different lengths for functionalization. This work was supported by the DOE Energy Frontier Research Center for Advanced Solar Photophysics.

NM04.03.23
New Green Chemical Method for the Preparation of the Semiconducting FeCrO3 and NiO Nanoparticles Rajesh Kumar Rajagopal and Venimadhav Adyam; IIT Kharagpur, West Bengal, India.

In the recent years, focus on the nanoparticle synthesis has shifted towards the clean and eco-friendly methods, for: simple, cheap, nontoxic, reusability and ecofriendly green chemical synthesis. Here, a novel, environmentally benign method for the FeCrO3 and NiO nanoparticles is reported by using the gelling property of biopolymer pectin. The prepared powders are calcinated at different temperatures, from Transmission electron Microscope (TEM) analysis revealed the 300°C calcinated has the particle size of ~6 nm and uniformly distribution spherical shape nanoparticles. For the 500°C particle size was ~36 nm, UV-Vis spectroscopy confirmed the narrowing of the band gap for the nanoparticle. The proposing method is highly reproducible and simple for the preparation of the nanoparticles.

NM04.03.24
Variable Kinetic-Control Effect Towards Porous Nanostructures via Solvents Selection Amrita Sarkar and Morgan Stefik; Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States.

Controlled fabrications of porous nanostructured materials are pivotal for studying structure-property and performance relationships in energy storage and conversion devices. Regardless of great success, fully tunable nanostructures are remains elusive based upon block copolymer self-assembly. Fundamental studies of structure-performance relationship in energy devices require tunable materials with architecture control where one can tailor pore size and wall-thickness independently. A unique kinetic-controlled self-assembly based approach, termed as persistent micelle templating (PMT), recently reported establishing a custom-made block copolymer structure-directing agent, poly(ethyleneoxide-block-hexyl acrylate) and a solution processing guideline where the kinetic rates are regulated by adjusting cosolvent amount. It directs to formation of nanostructured materials with tunable 6-9 nm wall-thickness with ~2Å precision and constant pore diameters of 13 nm with a wide range of inorganic material addition. Also, interestingly, the nanoscale morphology remains constant throughout the addition of various amounts of inorganics. This approach launches a new era to fine-tune small architectural feature limiting micelle chain exchange. However, the excessive amount of cosolvent may cause the formation of secondary pores into the material wall. This is addressed by improving the PMT approach via adding major solvents of higher Hildebrand solubility parameters (6) and minimizing the cosolvent amount. This new approach not only avoids the formation of secondary pores, it also expands the PMT window tunability. PMT control with a range of solvents will be presented here.

NM04.03.25
Low Temperature Sintering Copper Fine Particle System Tetsu Yonezawa and Hiroki Tsukamoto; Hokkaido University, Sapporo, Japan.

We are now proposing low temperature sintering copper fine particle systems. Usually, in order to sinter metal components at very lower temperature than melting temperature, nano-sized objects are frequently used. Nanoparticles or other nano-sized objects show melting point depression, which are often used for low temperature sintering. Gold and silver nanoparticles have been proposed for low temperature sintering printed electronics materials. However, they are noble metals and these materials are very expensive. Therefore, low temperature sintering system of copper is eagerly desired. However, since copper is easily oxidized even under air, its surface is necessary to be coated with organic materials and inorganic materials to prevent oxidation, so even if stable copper nanoparticles are prepared, their sintering temperature cannot be lowered according to the passivate layer. Therefore, in order to perform low temperature sintering of submicron copper fine particles, we attempted to prepare the surface stable state of specially designed copper fine particles. Detailed discussion will be done at the site.

NM04.03.26
Controlling Morphology of Noble Metal Replica Nanostructures Using Silver Halide Templates for Sustainability and Environmental Applications Jang Ho Joo and Jae-Seung Lee; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

Noble metal nanostructures have been extensively investigated owing to their morphology-dependent physical and chemical properties. In particular, a number of synthetic methods have been widely used to synthesize the noble metal nanostructures because the morphology of the template can easily determine the shapes and sizes of the replicated nanostructures. Therefore, controlling structural properties of templates is essential to synthesize the replica metallic nanostructures having desired physical and chemical properties. Especially, nanometer-sized silver halide templates have been conventionally replicated into gold and silver nanostructures, and demonstrated excellent photocatalytic properties under visible light irradiation. In fact, the silver halide nanomaterials hardly generate hot electrons under visible light because of their wide band gap, which is a crucial disadvantage as visible light photocatalysts. On the other hand, the gold or silver metal nanoparticles on the surface of the silver halide templates can absorb light using localized surface plasmon resonance (LSPR), which consequently results in the generation of hot electrons in the silver halide templates. In spite of the aforementioned advantages of silver halides over conventional TiO2 catalysts, limited morphologies of the silver halide templates are hurdles for many applications. In this work, we present our systematic investigation of key factors to control shapes and sizes of AgCl templates, and demonstrate their replicated noble metal nanostructures. Not only the mole ratio of silver ion and chloride ion, but also the concentration and molecular weight of polyvinylpyrrolidone (PVP) dominantly affect the shape and size of the AgCl nanostructures. To precisely figure out the components, we analyzed several metallic replica nanostructures with different shapes and sizes using energy dispersive x-ray spectrometer. In addition, the surface-enhanced Raman scattering (SERS) properties of the replicated metallic structures were observed, which was additionally supported by theoretical simulation. Importantly, the synergistic effect of gold and silver was determined to be crucial for the SERS activity. Finally, we demonstrated the shape-dependent photocatalytic properties of the noble metal replica nanostructures under visible light for the removal of Cr(VI), which would be highly important for the environmental applications.

NM04.03.27
Excellent Acetone Sensor Based on Ordered Mesoporous In-SnO2 Loaded g-CN Ritu Malik1, Vijay Kumar2 and S.P. Nehra3;1University of Kiel, Kiel, Germany; 2National Chemical Laboratory, Pune, India; 3School of Chemistry, IIT Bombay, Mumbai, India.
Compared to mesoporous In-SnO$_2$, the g-CN supported In-SnO$_2$ nanocomposite shows ~2.8 fold increase in response to acetone gas while reducing the operating temperature by 50 °C. This outstanding response is due to easily accessible 3D mesoporous structure with higher surface area and their unique planar morphology of In-SnO$_2$/g-CN. The findings reported in this study shows promising glimpse for designing a novel strategy to the development of ultrasensitive VOCs sensors working at low operating temperature.

NM04.03.28
Controlled Synthesis of Transition Metal Doped Lead Sulfide Semiconductors Emmanuel Onche and David J. Lewis; Materials, University of Manchester, Manchester, United Kingdom.

Semiconductors are important materials for a wide range of scientific and industrial applications. Continuous effort are made to improve limitations in their electronic, optical and magnetic properties. These properties are dependant on chemical composition, the type and method of synthesis. Doping – an intentional introduction of impurities (dopant) into the semiconductor (host) is often used to improve properties. The optical properties can also be tuned by introducing different impurity atoms, the concentration of these dopants determine the degree to which the band gaps are tuned. In this work, imidodithiodiphosphinates complexes of Mn(II), Zn(II) and Pb(II) were synthesised and used deposit metal sulfide materials using melt reactions. Controlled doping of Zn$^{2+}$ and Mn$^{2+}$ into host PbS was carried out between 2 to 12 percent. Peak shifts in XRD and Raman indicated successful doping. The P-XRD peaks of the Mn$^{2+}$ doped PbS shifted towards lower 2θ angles while that of the Zn$^{2+}$ doped PbS shifted towards higher 2θ angles. The cubic structure of the PbS phase was not altered even at high dopant concentration.

References

NM04.03.29
Liquid-Crystalline Dendrons Modified Self-Assembling FeO$_x$ Nanoparticles Takehiro Yachi, Masaki Matsubara, Atsushi Muramatsu and Kiyoshi Kanie; Institute of Multidisciplinary Research for Advanced Material, Tohoku University, Sendai, Japan; National Institute of Technology, Sendai College, Natori, Japan.

Two- and three dimensional arrangement of magnetic nanoparticles (NPs) enables us to control the magnetic properties and novel functions since the magnetic properties of the NPs are affected by the interparticle interactions. Liquid crystalline dendritic molecules are representative organic materials with self-assemblying property by the change in the temperature. In our previous studies, precise modification of liquid crystalline dendrons on the surface of the functional NPs enables us to introduce self-assembling and dynamic structure-changeable abilities into the NPs.

In the present study, we focused on FeO$_x$ NPs to introduce the dynamic functions into the NPs by the surface dense modification by the liquid crystalline dendron. The FeO$_x$ NP-cores were synthesized by the thermal decomposition method in the presence of oleic acid and oleylamine as ligands. Then, oleic acid and oleylamine on the particle surface were changed to phosphonic acids by the ligand exchange reaction, followed by the introduction of the carboxyl group onto the NPs surface. In this case, dodecylphosphonic acid (DPA) and carboxyl group-terminated 16-phosphonohexadecanoic acid (PHDA) were used as a ligand. From the TEM observations, particle mean diameter of the phosphonic acid modified FeO$_x$ NPs was assigned as 7.1 ± 0.4 nm. It is to be noted that the interparticle distance was controlled to 9.0 ± 0.8 nm and that the phosphonic acids were bound to the surface of FeO$_x$ NPs, confirmed by the absorption at 1070 cm$^{-1}$ due to Fe-O-P bond. In addition, the ligand exchange was successfully performed with high efficiency because any peaks of oleic acid were not detected.

After modification by DPA and PHDA, amiation between carboxy group of NPs and amide group-containing dendron was carried out to obtain FeO$_x$NPs with double layers structure in which the inner was phosphonic acids and the outer dendron. The amount of COOH groups on the particle surface was controlled by change in the molar ratio of DPA and PHDA in feed. At the same time, the modified density of the dendrons layer was brought to form an ordered NPs array. FT-IR profile of the dendron-modified NPs showed the absorption at 1645 cm$^{-1}$ derived from the amidation bond between carboxy group of NPs and amide group-containing dendron. In conclusion, the modification by liquid crystalline dendron have successfully enabled FeO$_x$ NPs to control to give the ordered array.

References

NM04.03.30
Subtractive Laser Patterning of Silver Nanoparticle Ink by Marangoni Effect Saewoong Park, Wooseop Shin, Younggeun Lee, Seonje Park, Jaemook Lim, Junyeob Yeo and Sukjoon Hong; Optical Nanoprocessing Lab, Department of Mechanical Engineering, Hanyang University, Ansan, Korea (the Republic of); Novel Applied Nano Optics Lab, Department of Physics, Kyungpook National University, Daegu, Korea (the Republic of).

Patterned metal film is an inevitable component for wide range of electronic devices, and it is fabricated by standard photolithography and vacuum deposition methods in general. These conventional fabrication methods have achieved tremendous success to date, but also possess a number of limitations such as requirement of high vacuum environment, high processing temperature and the use of toxic chemicals. As a consequence, the need for alternative method is growing continuously in the area of low cost, large area electronics in particular.

Regarding this matter, selective laser sintering (SLS) of silver (Ag) nanoparticle (NP) ink has been reported recently to create metal pattern through all-solution process in low temperature and non-vacuum environment. In the previous studies, Ag NP ink is firstly coated on the target substrate and...
selectively sintered to create continuous metal patterns at micron scale by utilizing the focused laser as a localized heater, while the other NPs are removed by a simple cleaning procedure with the solvent. The entire process can be conducted in 0.3W power and 1mm/s speed with the smallest amount of heat affected zone. Through the proposed method, two types of negative photomask – single slit and alphabetic letters – which are difficult and time-consuming to achieve with the conventional SLS process are created successfully and tested through optical means.

NM04.03.31
Unique p-n Heterostructured Water-Borne Organic Semiconductor Colloids via PC60 Micelle Surfactants—Toward Extremely Efficient Photo-Induced Particle Activity

Yu Jin Kim, Xiaobing Zuo, Richard D. Schaller and H. Christopher Fry; Argonne National Laboratory, Lemont, Illinois, United States.

In the last a few years, research using water-borne organic semiconductor nanoparticles (NPs) has intensified as an eco-friendly route to electronic materials without toxic chlorinated-solvents. The water-processable NPs are so far the most environmentally friendly outcome. In syntheses of the NPs, typically sodium dodecyl sulfate (SDS) is used as a surfactant. However, they suffer limited charge carrier behavior particularly for the charge separation owing to their confined structure, a randomly blended core of p- and n-type materials surrounded by a surfactant shell. To overcome this phenomenon, we introduced a new surfactant, PC60, which comprises an n-type semiconductor fullerene molecule grafted with a polyethylene glycol (PEG) chain. We found that the PC60 has a spherical micelle structure with double-layer formation, which allows specific shell structure in the heterojunction NPs. Consequently, unique p-n heterostructured NPs with precisely phase-separated core (p-type)-shell (n-type) morphology were obtained when combined with p-type semiconductor polymer, and they showed superior photo-induced charge separation characteristics. Furthermore, we could control the shell morphology of the NPs through one- or two-phase methodology, and the resulting water-borne NPs showed not only shell-morphology-dependent carrier quenching effect but also ultra-stable colloidal property under thermal- and long-term conditions. Our NPs, thus, can open up and provide a new paradigm in the current fields of water-based organic semiconductor colloids.

NM04.03.32
Versatile Nanomanufacturing of Ternary III-V Nanostructure Arrays via Inverse Metal-Assisted Chemical Etching

Thomas S. Wilhelm1, 2, Zihao Wang1, Cody W. Soule1, Mohadesheh A. Baboli1, 2, Jan Yar1, Stefan F. Preble1 and Parisan Mohseni1, 2; Microsystems Engineering, Rochester Institute of Technology, Rochester, New York, United States; 3NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York, United States; 4Microelectronic Engineering, Rochester Institute of Technology, Rochester, New York, United States; 5Matrix Opto Co., Ltd., Suzhou, China.

Ternary III-V semiconductor alloys, such as InGaP and AlGaAs, play vital roles in many nanoelectronic, optoelectronic, and photovoltaic devices. However, these materials are often plagued by a variety of nanomanufacturing difficulties that stem from either detrimental or incompatable top-down etching, or expensive bottom-up growth techniques. Here, low-cost, high-throughput, and lean nanofabrication processes are demonstrated via metal-assisted chemical etching (MacEtch), with the potential to revolutionize wafer-scale III-V nanomanufacturing. Specifically, novel Au-catalyzed etching approaches are defined for fabrication of suspended InGaP nanofoils and ordered arrays of AlGaAs nanopillars. MacEtch methods show promise as robust, solution-based alternatives for fabrication of high aspect-ratio nanostructures with smooth surfaces. These methods rely on catalytic oxidation of a semiconductor directly beneath a metal catalyst layer, followed by site-specific dissolution of the selectively oxidized material. MacEtch techniques combine many of the advantages of other top-down etching approaches, such as the anisotropic nature of reactive ion etching (RIE), and the fabrication simplicity and cost-efficiency of conventional wet chemical etching. Additionally, many of the correspondingly advantageous disadvantages are not present, including surface damage from high-energy ion bombardment and use of hazardous gases associated with RIE, and the crystallographic dependences or isotropic nature of traditional wet etching. While MacEtch research has been predominantly focused on silicon processing, these techniques have been recently adapted to overcome fabrication challenges associated with III-V nanomaterials synthesis. In this work, Au-enhanced inverse-MacEtch (I-MacEtch) of heteropitaxial InGaP/GaAs systems is presented, and differential etch rates between epilayer and substrate are exploited as a viable method to produce suspended III-V nanofoils. A comparison of vertical etch rates (VER) between nominally undoped, p-type, and n-type InGaP is detailed, showing VER in the I-MacEtch regime is independent of doping type. Au-enhanced I-MacEtch of AlGaAs is also demonstrated, and the VER and lateral etch rates (LER) are shown to be tunable with Al fraction and etching temperature. Control over the VER:LER ratio allows for etch conditions to be tailored to provide ordered AlGaAs nanopillar arrays with predefined aspect ratios. The work detailed here provides efficient means to customize nanomanufacturing processes for specific needs, such as tuning MacEtch process parameters to achieve a desired ternary III-V nanoflament geometry. It is anticipated that these processes can be utilized for adaptable and versatile manufacturing of nanomaterials for LEDs, lasers, HEMTs, and multijunction solar cells applications.

NM04.03.34
Detecting Entrapped Humans with Nanostructured Gas Sensors

Nicolau J. Pineau, Andreas T. Günther and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Earthquakes are lethal natural disasters frequently burying people alive under collapsed buildings. Tracking entrapped humans from their unique volatile chemical signature with hand-held devices would accelerate urban search and rescue (USAR) efforts. Here, a compact and orthogonal sensor array has been designed to detect the breath- and skin-emitted volatile markers acetone, ammonia, isoprene, CO2 and RH, all together serving as sign of life. It consists of three nanostructured metal-oxide sensors (Si-doped WO3, Si-doped MoO3, and Ti-doped ZnO), each specifically tailored at the nanoscale for highly sensitive and selective tracer detection along with commercial CO2 and humidity sensors. When tested on humans enclosed in plethysmography chambers to simulate entrapment, this sensor array rapidly detects tracers of human presence with low parts-per-billion (ppb) level accuracy and precision, unprecedented by portable detectors but required for USAR. These results were validated by bench-top selective reagent ionization time-of-flight mass spectrometry (SRI-TOF-MS). As a result, an inexpensive microstructured sensor array is presented that can be integrated readily into hand-held or even drone-carried detectors for first responders to rapidly screen affected terrain.

One-Step Aqueous Synthesis of Zn-Based Quantum Dots as Direct Generators of Reactive Oxygen Species

Julio A. Rivera de Jesus1, Sonia J. Bailon2, Vinoth Kumar Jayaraman3, Agileo Hernandez-Gordillo and Monserrat Bizarro1
1Instituto Investigaciones en Materiales, Mexico City, Mexico; 2Department of Chemistry and Physics, University of Puerto Rico, Ponce, Puerto Rico; 3Department of General Engineering, University of Puerto Rico, Mayaguez, Puerto Rico.

Abstract

Semiconductors quantum dot (QDs) are fluorescent nanocrystals with a ranging diameter of 2 nm - 10 nm. Due to their intrinsic optical properties, which are dependent of their size, these nanoparticles have many industrial and bio-medical applications e.g. bio-imaging, diagnostic, LED’s (light emitting diode) production, and photocatalyst of organic compounds. More recent applications are based on their potential use as photosensitizer to generate cytotoxic reactive oxygen species (ROS) when activated by light. The factors that govern the cytotoxicity associated to the generation of ROS include: particle size, shape, surface chemistry, the presence of lattice defects, degree of aggregation, among others. Based on these considerations, the present work was focused on: (i) the development of a synthesis protocol of water dispersible pure and doped ZnS-based QDs, (ii) modify their surface chemistry with biocompatible molecules and, (iii) evaluate their potential capacity to generate ROS under light irradiation. QDs were synthesized in water using a microwave reactor system under controlled temperature and reaction time in presence of 3-mercaptopropionic acid (MPA) as sulfide supplier. ZnS QDs were also doped with Mn2+ or Cu2+. As-synthesized ZnS QDs, as evidenced by XRD, were optically characterized by X-ray Diffraction (XRD), HRTEM, UV-Vis and Photo-luminescence spectroscopy techniques. UV-Vis analyzes evidenced the presence of excitonic peaks around 310 nm, 314 nm and 315 nm for ZnS, Cu-ZnS and Mn-ZnS, respectively. The band gap energy of the pure ZnS QDs was estimated at 3.70 eV that indicates a strong quantum confinement effect, as evidenced by this high value compared to the bulk (3.54 eV). In addition, the photoluminescence analyses of the QDs showed a strong emission peak (438nm for pure ZnS) that was red-shifted when Mn2+ (487nm) or Cu2+ (521nm) were used as dopant species. The incorporation of these transition metals into the ZnS lattice should have created new intermediate energetic levels between the valence and conduction bands of the ZnS particle. The effect of doping on the crystal size and the corresponding intermediate capacity of ZnS-based QDs to generate ROS, via the photo-degradation of specific organic dyes, will also be presented and discussed.

Reference

[5] Güntner, A. T.; Pineda, N. J.; Mochalski, P.; Wiesenhofer, H.; Agapiou, A.; Mayhew, C. A.; Pratsinis, S. E., Anal Chem (2018), 100% discoloration of indigo carmine occurred for Ag-Ni co-doped ZnO thin films in less than one hour, whereas the Ag-doped ZnO, Ni-doped ZnO, and undoped ZnO achieved only 30-50% of discoloration in one hour. In this work, we propose the possible degradation mechanism of indigo carmine dye with respect to dopants type and their concentration.
80 °C, 1 h reaction time, 1 wt. % of the catalyst, using methanol:oil molar ratio of 20:1. The best results were obtained with the catalysts containing 3 and 5 wt. % of sodium carbonate, which gave methyl esters (ME) yields of 90-91 %. In the same conditions, the reference STN catalyst resulted only in a 53 % of ME yield. Such a strong increase in the catalytic activity of Na2CO3-containing sodium titanate nanotubes was attributed to a synergetic effect between the impregnated sodium salt and 1D nanostructured STN material.

NM04.03.39 Sustainable and Green Manufacturing of Diagnostic Iron Oxide Nanoparticles using Natural Products Isabel Gesner1, Lisong Xiao2 and Sanjay Mathur2; 1University of Cologne, Cologne, Germany; 2University of Duisburg-Essen, Duisburg, Germany.

During the last years, an enormous variety of nanomaterials with different shapes and compositions have been developed for a broad range of applications including optics and electronics but also for their employment in health care and foods. However, many of these fabrication processes still rely on the employment of toxic and environmentally hazardous substances, offering potential risks to manufacturers and customers. Therefore, alternative synthetic procedures are focus of current research to allow for the synthesis of nanomaterials under the important aspects of biosafety and environmental compatibility.

Herein we report a green and facile one-pot synthesis for the preparation and in situ functionalization of water-dispersible and biocompatible iron oxide nanoparticles (IONPs) for their employment as contrast agents for magnetic resonance imaging (MRI). Two classes of naturally available nutrients namely ascorbic acid (vitamin C) and green tea were employed. In the first approach, easily water-dispersible crystalline IONPs were produced in a hydrothermal synthesis using ascorbic acid as reducing agent whereby the oxidation product instantly formed a protecting and stabilizing layer around the particles. As-obtained particles were not only highly biocompatible, but demonstrated enhanced r2/r1 ratios compared to the clinically approved contrast agent Sinerem.

In this context we further developed the synthesis of iron oxide nanoparticles using green tea catechins. Green tea is a promising material which additionally exhibits beneficial antioxidative, antiinflammatory and anti-inflammatory effects. Similar to vitamin C, green tea functionalized IONPs were long-term stable in water and highly biocompatible. Moreover, in vivo studies revealed accumulations of the particles in tumor tissues similar to clinically approved contrast agents. Indeed, a strong contrast enhancement was visible based on high relaxivity values, which further support their employment as novel MRI contrast agents in clinics.

NM04.03.40 Nanostructured TiO2 Support Effect on Hydrothermal Stability of Platinum-Based Catalysts Xingyu Lu1,2, Wenyi Yang1 and Puxian Gao1,2, 1Institute of Materials Science, Storrs, Connecticut, United States; 2Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States.

Platinum (Pt) based catalysts are widely used in petrochemical refinery, automotive emission control, and fuel cell applications (1). However, the catalytic activity of Pt nanoparticles (NPs) catalysts tends to decrease drastically as a result of the loss of active surface area via sintering at high temperature (2). TiO2 is an earth-abundant and chemically stable material and has been extensively studied as support for Pt-based catalysts (3). However, for the precursors of TiO2, such as layered protonated titanates (LPTs), the sintering resistance effects on noble metal NPs are not well studied. The high surface area and cation exchange capacity of LPT make it the ideal supports for catalytically active materials (4). In this work, the promotional effects of the support structures on the hydrothermal stability of the TiO2 nano-array supported Pt catalysts were studied. Two types of TiO2 nano-array supported Pt catalysts were prepared with different initial support structures, namely the anatase TiO2 and LPT nanowires. Pt NPs were loaded onto both types of supports and went through the same hydrothermal aging at 800 °C for 50h. The evolution of the Pt NPs before and after the hydrothermal aging was studied by scanning transmission electron microscope and CO oxidation was employed as a probe reaction to compare the catalytic performance of these catalysts. According to the microstructural evolution of the Pt NPs and the catalytic activity of the sample before and after hydrothermal aging, the LPT-nano-arrays based Pt catalysts showed better hydrothermal stability than the crystalline anatase nano-arrays based ones. The better hydrothermal stability of the LPT nano-array supported Pt NPs might be due to the greater interaction between the Pt NPs and the LPT surfaces formed during the dip-coating process through ion-exchange. The sintering resistance of the Pt NPs is therefore enhanced by the potentially better anchoring effect from the LPT nano-array supports.

Considering the wide application of TiO2 supported Pt catalysts, this new finding may provide a new pathway to design highly stable Pt-based catalysts for different gas phase reactions.

Keywords: Pt-based catalysts; Hydrothermal stability; Layered protonated titanates; Sintering resistance; CO oxidation.

NM04.03.41 Enhanced Performance of Inverted Indium Phosphide Quantum-Dot Light-Emitting Diodes via Thermal Annealing Jinwoon Lee and Changhee Lee; Electrical and Computer Engineering, Seoul National University, Seoul, Korea (the Democratic People’s Republic of).

Indium phosphide (InP) quantum-dots (QDs) have attracted as most promising luminescent material for developing cadmium-free QD light-emitting diodes (QLEDs). However, the performance such as efficiency, maximum luminance and operational lifetime of InP QLEDs is still far behind that of CdSe QLEDs [1, 2]. This is mainly attributed to unoptimized synthesis of InP QDs and device structure. InP QDs have relatively low electron affinity (EA), so the electron injection barrier is quite large with conventionally available electron transporting materials, thereby resulting in low electron injection [2]. In this work, we will demonstrate that thermal annealing of zinc oxide nanoparticle (ZnO NPs) electron transport layer and the QD emissive layer can lead to enhanced QLED performance. The current density of electron-only devices with ZnO NPs increases and exhibits trap-free space-charge-limited-current (SCLC) characteristics after thermal annealing. Furthermore, the photoluminescence (PL) quantum yield of the QD layer increases with thermal annealing due to increased packing density of QDs, as previously reported [3]. Optimizing annealing temperature of inverted green InP QLEDs results in increased external quantum efficiency from 2.32 % to 3.61 % and maximum brightness over 10,000 cd/m2. The half-lifetime (LT50) at an initial luminance of 1000 cd/m2 increases up to nearly 2 hours. Therefore, thermal annealing process can be effectively utilized to optimize the device performance of InP QLEDs.

Reference
Efficient Photocatalysis with Biomimetic Hedgehog Supraparticles

Luiz F. Gorup, Gleiciania d. Silveira, Naomi S. Ramesar, Douglas G. Montjoy, Suwon Tung, Emerson R. Camargo, and Nicholas A. Kotov; 1 Federal University of Sao Carlos, Sao Carlos, Brazil; 2 Chemistry, Federal University of Grande Dourados, Dourados, Brazil; 3 Chemistry, University of Michigan, Ann Arbor, Michigan, United States.

Nanostructured hedgehog supraparticles (SPs) were formed by the self-assembly of erdite nanoparticles (NaFeS2·2H2O) into a remarkable functional geometry. The nanoscale corrugation with the particles allows for enhanced dispersion stability and leads to greater effectiveness for photocatalytic degradation. The self-assembly of nanoparticles is a promising strategy to fabricate hybrid biomimetic nanostructures that can be used as an innovative alternative to obtain superior properties from conventional material. In the present study, erdite hedgehog supraparticles were successfully synthesized using a cost-effective self-assembly method and employed as a photocatalyst for degradation of organic dyes. The nanostructures were formed by altering the ionic strength of the synthesis solution, resulting in SPs (6.62 μm ± 1.4) with spikes that provided a surface area greater than 8.2 m²/g. The structural morphology and optical features of the synthesized erdite SPs were confirmed by X-ray diffraction, electron microscopy and UV-visible spectrophotometry. The pollen morphology prevents aggregation of the particles and promotes high surface area. The supraparticles exhibit excellent photocatalytic activity under illumination of H2O2 (SP+ H2O2) in a fenton reaction, resulting in degradation of methylene blue (MB) (25 μg/mL) in 5 minutes under 302 nm light. Additionally, The SP+ H2O2 are very effective in the catalytic degradation of phenol red (PhR), nitrophenol (NP), and rhodamine B (RhB) under UV light, visible light, and dark condition. Finally, the erdite SP catalyst has excellent activity and recyclability for more than 55 cycles, with the addition of H2O2 on average every 13.8 ± 2.2 cycle. The excellent photocatalytic activity is owing to the synergistic interaction between the SPs and H2O2. The SPs exhibit high adsorption capacity and low recombination of the photogenerated electrons and holes due to the shape and erdite composition. This work showed how particles with singular morphology, such as hedgehog supraparticles are highly attractive because of their enhanced properties.

NM04.03.43

Defect Engineering of Low-Dimensional Heterostructures Toward an Efficient Electrocatalysts

Sehman Ozden; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Designing novel efficient and robust catalysts with enough active sites and excellent conductivity is one of the key parameters for water splitting devices to produce hydrogen as a clean energy source. Existing Pt-based noble catalysts have some issues with their relatively high-cost and limited abundance. In this regard, the development of novel catalysts that exhibit higher catalytic activity, longer durability and lower cost can significantly facilitate the realization of clean energy. Recently, low-dimensional materials such as nanotube, graphene, MoS2, and h-BN, have gain attention for hydrogen evolution reactions (HER), oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) etc. Although these nanostructures have been used for HER, ORR and OER, they need to be engineered to improve their catalytic activity for large scale industrial applications. Novel catalysts with unique properties can be fabricated by creating heterostructures of low dimensional nanomaterials with rich defect density. Here, we will discuss outstanding catalytic activity of metal-free low-dimensional carbon-based hybrid heterostructures with rich defect density as an efficient electrocatalyst. In addition, the role of increased defect density on the free-energy of hydrogen adsorption from density functional theory (DFT) calculations will be discussed.

NM04.03.44

Characteristics of Biogenic Sulfide Semiconductor Nanomaterials

Yoriko Tominoaga, Ryo Shimizu, Shachiko Maki, Makoto Maeda and Yoshiko Okamura; Hiroshima University, Higashihiroshima, Japan.

We report here the characteristics of PbS formed by bacteria. X-ray diffraction (XRD) measurements and transmission electron microscope (TEM) revealed clear diffraction peaks and lattice fringes, respectively, revealing that the bacteria synthesized polycrystalline PbS. Current-voltage (I-V) measurements showed that the electric current across the PbS increased linearly with increasing applied voltage, and the amount of the current increased with increasing the area of crystalline PbS. Bionimallization have been actively studied for more than 20 years. It can be performed to form such as magnetite, silica, calcium carbonate, hydroxyapatite, metal particles and so on under ordinary temperature and normal pressure. This can develop material synthesis techniques with low power consumption at low cost. Under this kind of circumstances, microbial synthesis for sulfide semiconductors such as CdS and PbS has been explored in some previous studies. The studies have already demonstrated the formation of nanocrystallite of these sulfide semiconductors by some yeasts. However, it has not been clarified whether they can have crystalline quality that may be applied to the semiconductor devices or not. In this study, we aim to reveal their crystalline qualities and semiconductor characteristics by focusing on PbS towards the future fabrication of the biogenic semiconductor devices. We established bacterial strains involved in PbS formations and confirmed micro structures and crystalline quality of PbS formed by the bacteria using a X-ray diffractometer and a JEOL JEM-2010 TEM equipped with an energy dispersive X-ray spectroscopy (EDS) system, operated at 200 kV. XRD spectra of the PbS samples exhibited clear diffraction peaks, and there were good agreements with experimental data and theoretical ones of polycrystalline PbS on peak diffraction angles on each crystal plane of PbS. TEM images and EDS analysis for the samples also showed that the materials consisted of Pb and S, and lattice fringes and electron diffraction patterns corresponding to crystalline PbS. I-V characteristics were measured using probe after Indium electrodes were formed on the surface of the PbS samples mounted on semi-insulated InP substrate. When the shape of PbS was formed to be spherical nanocrystallites, the amounts of the current were in the range between 0 and 17.5 pA with applied voltage was in the range between -1 and 1 V. On the other hand, the shape of crystalline PbS was changed to be thin film, the amounts of the current changed to be in the range between 0 and 18.5 μA. The former amounts of the current increased to be 0 - 25.0 pA under light irradiation. These results suggested that the biogenic PbS have bandgaps and it exhibited general fundamental characteristics of the semiconductors.

NM04.03.45

3D Cubic Ordered Mesoporous SnO2@SBA-16—A Highly Sensitive Humidity Sensor

Vijay K. Tomer, Ekta Poonia and Krishan Kumar; 1Berkeley Sensor and Actuator center, University of California, Berkeley, Berkeley, California, United States; 2Department of Chemistry, Deenbandhu Chhotu Ram University of Science and Technology, Sonipat, India.

The need for the development of highly sensitive humidity sensors for monitoring of indoor climatic conditions has always remained a challenging task. Myriads of study have been performed to formulate an ideal humidity sensor, wherein, the mesoporous materials are leading among the others in the quest for designing highly sensitive humidity sensor. Due to high surface to volume ratio, easy charge transportation, tunable geometry of pore structure and excellent capability in the role of a host matrix for a variety of dopants (metals and metal oxides), the mesoporous materials have emerged as the new hot-spot for designing humidity sensors. In the present study, we propose a simple and low-cost strategy to prepare 3D-cubic ordered mesoporous silica-nanohybrid impregnated with SnO2 nanoparticles. The relative humidity (%RH) sensing results in the 11–98%RH range reveal that the SnO2/SBA-16 nanohybrid sensor possesses fast response/recovery (4.2/3.5s), negligible hysteresis (0.8%), high sensitivity, wide range of applicability and high stability. The high resolution transmission electron microscopy (HR-TEM) confirms the porous nature of the nanohybrid. Field emission scanning electron microscopy (FE-SEM) revealed the long range network of these pores even after impregnation of SnO2 which is an essential facet for high performance %RH sensor. The N2 adsorption-desorption isotherms studies confirmed the high surface area (746m²/g) for the nanohybrid which suggests that the mesoporous nature remained intact even after impregnation of SnO2 in the SBA-16 matrix. The XRD and IR analysis further indicated that the inclusion of
SnO₂ does not disintegrate the 3D cubic channels of SBA-16. The present work not only highlights an efficient scheme for designing the high performance %RH sensors and but also advocates the promising applicability of mesoporous materials for gas sensing application.

SESSION NM04.04: Energy Harvesting and Storage I
Session Chairs: Raquel Ovalle-Robles and Maria Perez Barthaburu
Tuesday Morning, November 27, 2018
Sheraton, 2nd Floor, Back Bay C

8:15 AM NM04.04.01
Defect Enriched Fe Incorporated β-Ni(OH)₂ Nanosheets with Both High Total Electrode and Intrinsic Activity for Oxygen Evolution Reaction Tianyi Kou. University of California, Santa Cruz, Santa Cruz, California, United States.

Accompanied by the fast world population growth, the depletion of energy resources and environmental pollutions have become two major issues that pose serious threats to the survival of human beings. As a clean and renewable alternative, hydrogen has been given special attentions in the past decades and is believed to be a high gravimetric energy density carrier for fuel cells. Nonetheless, most of the hydrogen in earth is still generated through energy intensive industries such as steam reforming which unavoidably makes the energy resource shortage and environmental problems even worsen. In contrast, generating hydrogen in the cathode through water electrolysis is a green chemical route in which pollutant free and zero carbon emissions can be realized. Additionally, the energy sources driving water electrolysis can also be renewable, further making water electrolysis a promising strategy to produce hydrogen. However, the sluggish kinetics and high energy barriers of oxygen evolution reaction (OER) in the anode have largely restricted the overall efficiency of water electrolysis, and thus limited the hydrogen production. Different catalysts have been investigated so far to address the limitations of OER. Iridium oxides, for example, are found to exhibit a great OER activity but the high costs of iridium become the barrier of their large-scale application. Developing inexpensive catalysts is critical but to boost their activity it is still challenging, as most of the OER catalysts still require an overpotential around 250 to 300 mV to achieve the geometric current density of 10 mA/cm². In this work, we synthesized Fe incorporated β-Ni(OH)₂ nanosheets on macroporous nickel foam through a facile one-pot hydrothermal method. The as-synthesized Fe incorporated β-Ni(OH)₂ nanosheets are found to be composed of mixed crystal and amorphous structures. Along the boundary of crystal and amorphous structures are enriched defect sites. By virtue of these structural merits and electronic structure modification of Fe dopants, the as-prepared Fe incorporated β-Ni(OH)₂ nanosheets exhibit a low and competing overpotential of 219 mV at a geometric current density of 10 mA/cm², demonstrating a high total electrode activity. In addition, at the overpotential of 300 mV, a electrochemical surface area current density of 6.25 mA/cm² has also been obtained, which represents the highest value among the reported NiFe based OER catalysts at the same or higher overpotentials, indicating its high intrinsic activity.

8:30 AM NM04.04.02
Moving from Environmental Remediation to Energy—What We Learned about Nb₂O₅ Photocatalysts Caue Ribeiro de Oliveira. Brazilian Agricultural Res Corp, Sao Carlos, Brazil.

Literature has many examples of semiconducting materials as photocatalysts for degradation of water contaminants. Despite a large concentration in TiO₂ and TiO₂-based materials, other semiconductors have gained attention due specific aspects that promote higher photoactivity (e.g., in visible light, reduced electron-hole recombination) but few was done to understand the role of surface acidity in these process. A study-of-case is Nb₂O₅, which is a wide-band semiconductor, with similar electronic properties to TiO₂ but with very acidic surface. This feature indicates that the way that Nb₂O₅ plays its photooxidative role is different from other semiconductors, depending of the equilibrium of charges in degradation medium. We developed a method to produce this semiconductor through a peroxocomplex formation, which is further destabilized in hydrothermal conditions to promote oxide precipitation in a controllable manner. This synthesis, despite very simple, was easily controlled to produce different surface features, as well as heterostructures based on T/TT Nb₂O₅ phases. This material has showed a considerable photoactivity in UV light for degradation of different pollutants, but also a good versatility: the mixture with g-C₃N₄ (a polymeric semiconductor) in adequate pH conditions has lead to a self-organized heterostructure, with also remarkable photoactivity. However, these materials did not present only photooxidative activity: measuring their potential for photo reduction, we have observed that modifications with other semiconductors (e.g. CuO) allows this system to promote Cr(VI) reduction and, more interesting, promote the CO₂ reduction to CO in significant yields, despite the acidic surface suggest that this reaction would not be favored. Therefore, the knowledge about this material for environmental remediation is now opening other application for this material in renewable energy production, which needs be deeper investigated. 

Acknowledgements: FAPESP; CAPES; CNPq; FINEP; National System of Nanotechnology Laboratories – SISNANO/MCTI; Rede Agronano/Embrapa

9:00 AM NM04.04.03
Single-Source Precursors for Controlled Gas Phase Deposition of Iridium-Based Catalytic Coatings for Water Splitting Applications Lasse Jørgensen. Michael Frank, Jennifer Leduc and Sanjay Mathur; Inorganic Chemistry, University of Cologne, Cologne, Germany.

Investigation of the interplay of metal-organic chemistry will enrich the state-of-the-art of chemical vapor deposition (CVD) and atomic layer deposition (ALD) technology and open new possibilities for the applications of new Ir-based materials. Therefore new heteroleptic Lanxæs-types compounds exhibiting high volatility and defined thermal decomposition under CVD and ALD conditions are reported to elaborate the precursor chemistry – materials synthesis – functional property chain. The new precursors unify both reactivity and sufficient stability through its heteroleptic constitution to provide a precise control over compositional purity in CVD and ALD deposits. CVD- and ALD-grown materials were tested towards their (electro)catalytic applications, particular in the oxygen evolution reactions. In this work functional characterization of deposited materials will be reported and their catalytic behavior is examined. The deposition on various substrate materials without the need of additional reactant gases underlines the potential of this heteroleptic precursor class for CVD and ALD of metallic thin films. The presented CVD data opens new possibilities in the vapor phase synthesis of materials facilitating the application of such films, for example, as electro- or photocatalyst in oxygen evolution reaction (OER) and oxygen reduction reaction (ORR).

9:15 AM NM04.04.04
Nanostructured Co-Precipitated Cu₇Zn₄O₁₂ Catalytic Nanoparticles for Solar Driven Thermochemical H₂O/CO₂ Valorization Rahul R. Bhosale and Gorakh Nath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

Thermochemical splitting of H₂O and CO₂ generates a mixture of CO and H₂ i.e. syngas which can be used for the production of storable and transportable...
Reverse osmosis (RO) is one of the most widely employed technologies for water desalination. A drawback of this technology is high consumption of electricity by electric motors used for high-pressure water pumping. Energy consumption can account for up to 70% of the desalination costs. Due to the high-energy intensity, the carbon footprint of the process is substantial. Most of pumps and compressors including those used in RO desalination plants are driven by electric motors or internal combustion engines. Pumping systems account for nearly 20% of the world’s electrical energy demand and range from 25-50% of the energy usage in certain industrial plant operations. To improve economics of water desalination plants we propose innovative energy efficient, inexpensive, robust water pump powered by heat. The basic principle of the pump is the same as that of regenerative type external combustion engines. Generation of heat makes pumps of this type very energy efficient. The novelty of the pump comprises a new working cycle in combination with the use of a dense working fluid which is liquid in the cold space of the pump and gas or supercritical fluid in the hot space of the pump. Carbon dioxide, water-alcohols mixtures or mixtures hydrocarbons can be used as the working fluids. This pump does not have any high precision parts and even does not require super alloys and any other expensive materials. The pump can generate very high pressures (hundreds bars) and therefore can be used instead of modern plungers pumps driven by electric motors, thus eliminating completely the consumption of electricity for pumping in RO processes. Another important feature of the pumps is that no high temperature heat sources are needed. Heat sources with temperature of 200 – 300°C is sufficient to create pressure drops typical of RO processes. Therefore, renewable energy sources such as solar radiation can be used to power the pump. Replacement of fossil fuels with renewable energy sources in desalination processes will minimize greenhouse gas emissions. In addition, a substantial improvement of the economics of the RO processes is expected due to the use of solar power. In this study, we have attempted to improve the solar energy absorption capacity of the solar unit by adding metal oxide nanoparticles. These metal oxide nanoparticles are synthesized in our laboratory using sol-gel method. Due to the improvement in the solar energy absorption capacity, the overall efficiency of the desalination process is observed to be enhanced significantly. The detailed results will be presented.
characterized by X Ray Diffraction, nitrogen adsorption–desorption isotherms, Linear Sweep Voltammetry (LSV), Chronoamperometry, Scanning Electron Microscopy, Micro Raman and FTIR spectroscopy technics. The microscopy images reveal that the FeOx nanospheres decorated with extreme efficiency on the flower structure of ZnO. A significant increase in the surface area is observed with the addition of the α-FeOx in the ZnO flowers and also significantly alters the pore volume of this material. The LSV showed a high current density of the FTO/ZnO/FeOx (0.58mA.cm-2) film being superior to the FTO/ZnO (0.16mA.cm-2) film in light condition. The analysis showed that these materials are promising photoelectrode for DSSC applications, characterizing them FeOx nanoparticles improving the ZnO photoelectrochemical properties. Simultaneously with this the method that was used to produce the nanoparticles adds to the production process of the same, a methodology that does not require the need for high technology equipment, not have a high energy demand or time to run it and does not generate waste, that is, a highly practical, economically viable and environmentally friendly method.

11:00 AM NM04.04.08

The performance of concentrating solar power (CSP) receivers is limited by thermal losses, particularly at concentrations <100 suns. Existing CSP receivers rely on spectrally selective surfaces placed within vacuum glass enclosures to minimize heat loss due to radiation and convection. However, using spectrally selective coatings and maintaining a high-quality vacuum at high temperatures (400 °C) increases cost and significantly limits longevity. We have developed a high-temperature solar-transparent thermal insulation that enables high-efficiency heat collection and obviates the need for selective coatings and vacuum in CSP receivers. We use silica aerogels, a class of highly porous (porosity >90%) materials known for their thermally super-insulating properties, which we have engineered to achieve extremely high solar transparency. The optimized aerogel nanostructure has reduced pore sizes of 2-50 nm that minimizes scattering losses at low wavelengths, increasing the solar-weighted transmittance to >95% for an 8 mm thick sample compared to <85% typically reported in literature. The low near-UV scattering, high infrared absorption, and high porosity of our aerogels maximize solar transmittance and minimizes heat loss due to conduction, convection and radiation, enabling CSP receiver efficiencies >80% even at concentrations <50 suns. In this work, we report the results of optical and high-temperature thermal characterization of the fabricated solar-transparent silica aerogel. We compare experimental results with a numerical model based on the spectral equation of radiative transfer that predicts the optical and thermal properties of silica aerogel. Finally, we model the performance of a linear CSP receiver comprising of our solar-transparent aerogel and optimize its thickness, density and pore-size to maximize receiver efficiency.

11:15 AM NM04.04.09
Rational Design of Nanostructured Electrodes for Capacitive Energy Storage Husam N. Alshareef, Chuan Xia, Qiu Jiang and Narendra Kurra; Materials Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Electrochemical supercapacitors are important energy storage devices that bridge the gap between electrostatic capacitors and batteries. A critical component of supercapacitor design is the electrode material. We have been developing electrode materials and fabrication strategies for conventional electrochemical capacitors as well as micro-supercapacitors (in-plane devices fabricated on-chip). Pseudocapacitive materials in particular hold promise of significantly higher capacitance than carbon-based materials and hence have recently become a subject of intense investigations. These materials can store charge through both surface redox reactions and fast intercalation process leading to intercalation pseudocapacitance. We will discuss strategies that we have developed to rationally design pseudocapacitive materials, including oxide and chalcogenides. Material structure, conductivity, electrochemical activity, defect concentration, and dimensionality are critical parameters to maximize both ion and electron transport within the electrode material, and hence improve capacitor performance. Selected examples from our work will be presented to show how dramatic improvements in electrode performance can be achieved through rational approaches. For micro-supercapacitors, we also show that collector material type, geometry (e.g., 3D and macroporous structures), and microfabrication techniques can be used to improve the kinetics and capacitance of devices. Recent integration of microsupercapacitors in energy harvesting and sensing devices will also discussed.

11:45 AM RAPID FIRE PRESENTATION

SESSION NM04.05: Energy Harvesting and Storage II
Session Chairs: Husam Alshareef and Phoebe Tan
Tuesday Afternoon, November 27, 2018
Sheraton, 2nd Floor, Back Bay C

1:30 PM NM04.05.01
CSilk® Carbon Nanotube Sheet Based Origami Triboelectric Nanogenerators and Its Yarn Applications Jaeh Lee and Raquel Ovalle-Robles; LINTEC Nano-Science % Technology Center, LINTEC of America, Inc., Richardson, Texas, United States.

Due to an increase in demand, low-carbon and environmentally-friendly energy, as well as thin and lightweight portable electronic devices and wearables that can generate power has attracted great attention. We have here demonstrated origami triboelectric nanogenerator (origami-TENGs) using cSilk® sheets as the starting material, having a high degree of alignment, being lightweight, and having a high electric conductivity. Sandwich structure combined with cSilk® Sheets and PEDOT:PSS as a current collector were prepared via layer-by-layer coating and acid treatment. Two individual strips (cSilk® Sheets/PEDOT:PSS) were prepared and infiltrated with two different polymers having the positive and negative triboelectric affinity. The cSilk® Sheet-TENG can be fabricated from these two separate strips that are folded together to form a resilient structure that reversibly compresses in response to an applied compressive force and spontaneously returns to its uncompressed state, spring-like, when the applied compressive force is removed. The output short-circuit current (Isc) and open-circuit voltage (Voc) of this cSilk® Sheet-TENG can reach 20 μA and 1500 V, respectively. This generated electricity could directly light up 500 commercial light-emitting diodes (LEDs) connected in series without any energy storage devices. In addition, the as-fabricated cSilk® Sheet-TENGs are capable of harvesting mechanical energy from various kinds of human motions such as stretching, pressing, and bending. Furthermore, we have been developing TENGs using highly flexible, electrically conductive, and mechanically robust cYarn® fibers by providing twist-insertion to cSilk® sheets. cYarn®-TENG can be woven to make a textile and harvest energy from human motions such as rubbing, bending, and stretching. Also, cYarn®-TENG can harvest energy by hand-powered torsional actuation.

2:00 PM NM04.05.02
Computational Modeling of 2D Materials and Their Heterostructures for Sustainable Energy Storage—Opportunities and Challenges Kamalika Ghatak, Vidushi Sharma and Dibaker Datta; New Jersey Institute of Technology (NJIT), Newark, New Jersey, United States.
Because of the low gravimetric capacity of conventional graphite anode (theoretical value ~ 372 mAh/g), and massive structural changes and volume expansion of silicon anode (on the order of 300%); extensive research has been carried out during last few decades to develop stable and high-capacity anode materials. Moreover, large-volume expansion leads to stress built-up at the interface between the Si film and the current collector, leading to delamination at the interface. We, therefore, examined the possibility of 2D materials for application of high-capacity anode materials. By first-principle calculations based on density functional theory (DFT), we investigated the adsorption of lithium (Li), sodium (Na), and calcium (Ca) on graphene with divacancy and Stone-Wales defects. We find that with controlled defect topology, we can achieve a maximum storage capacity of approximately 1675, 1450 and 2900 mAh/g for Li-, Na-, and Ca-ion batteries respectively. However, despite enormous opportunities, we need to concern about several challenges such as adatom trapping at the defect sites, the effect of defects on adatoms diffusivity, microstructural changes, etc., mechanical degradation at defect sites, etc. In addition, our recent work shows that for the Si-based anode, we can achieve far better electrochemical stability by simply coating the current collector surface with graphene sheets. The combined DFT-MD work shows that graphene can be utilized as slippery interfaces to enhance the electrochemical stability of Si film anode in Lithium-Ion Batteries because of the less stress build-up and less stress cycling of the slippery substrate as opposed to a fixed surface. Our results indicate a new paradigm of 2D materials based energy storage. Besides graphene, several other 2D materials such as graphene allotropes, Transition Metal Dichalcogenides (TMD), etc. have tremendous potential in energy applications. Moreover, by building heterostructures (stacking of different 2D materials), it is possible to combine the advantage and eliminate the disadvantages of the individual sheet.

We need a computational genome to identify the optimal heterostructures for the energy storage. In this presentation, we will provide a detailed overview of opportunities and challenges of modeling of 2D materials and its heterostructures for the next-generation sustainable energy storage applications.

2:15 PM NM04.05.03
One-Dimensional Nanomaterials for Emerging Energy Storage  
Liqiang Mai; Wuhan University of Technology, Wuhan, China.

One-dimensional nanomaterials can offer large surface area, facile strain relaxation upon cycling and efficient electron transport pathway to achieve high electrochemical performance. Hence, nanowires have attracted increasing interest in energy related fields. We designed the single nanowire electrochemical device for in situ probing the direct relationship between electrical transport, structure, and electrochemical properties of the single nanowire electrode to understand intrinsic reason of capacity fading. The results show that during the electrochemical reaction, conductivity of the nanowire electrode decreased, which limits the cycle life of the devices. We have developed a facile and high-yield strategy for the oriented formation of CNFs from metal–organic frameworks (MOFs). The appropriate graphicitic N doping and the confined metal nanoparticles in CNFs both increase the densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. Then, we fabricated a field-tuned hydrogen evolution reaction (HER) device with an individual MoS2 nanosheet to explore the impact of field effect on catalysis. We also identified the exciting electrochemical properties (including high electric conductivity, small volume change and self-preserving effect) and superior sodium storage performance of alkaline earth metal vanadates through preparing CaV4O9 nanowires. Our work presented here can inspire new thought in constructing novel one-dimensional structures and accelerate the development of energy storage applications.

References

2:30 PM NM04.05.04
Correlating Nanoporous–Carbon Anode Materials Properties with Li-Ion Intercalation  
Matthaus Wolak, Katharine L. Harrison, Michael Siegal, Kyle Fenton and Dorina Sava-Gullis; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Graphite is the state-of-the-art anode material for Li-ion energy storage due to its low cost and high coulombic efficiency, enabling long term cycling. Alternative carbons can store more lithium than graphite (specific capacity ~ 370 mAh/g), likely due to increased interplanar spacing, defects, pores, and grain boundaries; however, they suffer from low coulombic efficiency, capacity fade with repeated cycling, and often do not allow precise control of the relevant structural properties. Nanoporous-carbon (NPC) films can grow directly onto anode current collectors without the complication of binder materials, allowing direct correlations between nanostructures and the electrochemical properties governing Li-ion intercalation. Graphite is fully dense and alternative carbons are disorganized with pores and varied interplanar spacings. NPC can bridge the gap between alternative carbon materials through exquisite control of the mass density and surface area and help provide greater mechanistic understandings.

Using pulsed-laser deposition of pyrolytic graphite at room temperature, NPC self-assembles into randomly oriented nm-sized graphene fragments only a few layers thick. NPC density is controlled via the deposition energetics from below 0.1 g/cm³ to 2.25 g/cm³ (near graphite). The density is homogeneous throughout a sample, i.e. NPC does NOT consist of dense graphicitic particles separated by voids. Such densities are due to expanded interplanar spacings between the graphene sheet fragments resulting from the deposition kinetics. NPC surface area increases with decreasing mass density, e.g. ~ 1300 m²/g for 1 g/cm³ NPC, so far only reported for foams with densities < 0.1 g/cm³.

NPC specific capacity increases above that for graphite with decreasing density, attributed to the plethora of grain boundaries, pores, and the greater interplanar spacings. NPC with densities < 1 g/cm³ have initial specific capacities 4 – 5X > graphite, higher than many alternative carbon materials. Coulombic efficiencies rise quickly after the first two cycles to a range between 98 and > 99%, indicating minimal initial SEI formation. Both specific capacities and coulombic efficiencies remain high beyond 100 cycles.

This work may lead to determining the optimal interplanar spacing between graphene sheets to maximize Li-ion accessibility while minimizing SEI formation for high cyclability, and may eventually lead to the development of appropriate bulk material fabrication processes.

We thank Lyle Brunke for assistance growing NPC films, Kyle Klavetter for discussions, and Carlos Gutierrez for programmatic guidance. This work is supported by the Laboratory Directed R&D program at Sandia National Labs, a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE National Nuclear Security Administration under contract DE-NA0003525.

2:45 PM BREAK

3:15 PM NM04.05.05
Bio-Inspired Supercapacitors: Francesco Soavi1, Federico Poli1, Antonio Terella1, Jacopo Seri1, Alessandro Brilloni1, Ruben Aldrin Albis Vasquez1, Francesca De Giorgio1, Catia Arbizzani1, Maria Letizia Focarete1, Davide Fabiani1, Clara Santato1, Carlo Santoro2 and Nicholu Manyala3; 1University of Bologna, Bologna, Italy; 2University of West of England, Bristol, United Kingdom; 3University of Pretoria, Pretoria, South Africa; 4Polytechnique Montréal, Montreal, Quebec, Canada.

Water and energy underpin the economic and social development of Countries. Water is needed for each stage of energy production, and energy is crucial for the provision and treatment of water. Within the so-called Water-Energy Nexus, smart and sustainable energy harvesters and storage technologies are required for an efficient managing of water and renewable energy sources. Within this context, microbial fuel cells (MFC) and supercapacitors (SC) are playing a key role. MFCs are bio-electrochemical devices that convert the chemical energy of wastewater organic compounds directly into electrical energy. SCs can store the energy harvested by the MFC and deliver it back at desired power. Strategies that lower the environmental and economic impact of disassembly and recycling of waste devices are mandatory. The use of water-processable electrode binders and new membrane production techniques like electrospinning are viable approaches to decrease cost and environmental footprint. A study on the development of bio-inspired supercapacitors, including natural binders, electrospun separators and eumelanine-based electrodes, as well their integration with MFCs is reported and discussed.

Acknowledgments
The research has been carried out under the Italy-South Africa joint Research Programme 2018-2020 and the Executive Bilateral Program Italy-Quebec 2017-2019, Italian Ministers of Foreign Affairs and of the Environment.


3:30 PM NM04.05.06
Simulated Nanoparticle-Functionalization Interface Towards High Energy Density Dielectric Capacitors: Joshua Shipman, Brian Riggs, Binod Subedi, Jianwei Sun and Douglas Chrisey; Tulane University, New Orleans, Louisiana, United States.

Increasing the energy density of high power density dielectric capacitors using nanoparticles (NPs) has often been attempted, but interfacial breakdown has often resulted in lower storage density, cancelling the effect of a higher dielectric constant, especially at higher loadings. We present work in optimizing the interface using a priori simulations combined with experimental verification and feedback. We began by simulating a system used previously that has mitigated some of the interfacial effects using covalent bonding. We modelled the interface of nanoparticle and surface functionalization using a vacuum slab containing a barium titanate NP surface and a surface functionalization molecule. Several different possible metrics for the efficacy of the surface functionalization in mitigating the concentrated electric field at the NP interface were calculated and compared, including the binding energy of the molecule, the HOMO-LUMO gap, and the local dielectric constant. Ultimately, combining the local dielectric constant with a Monte Carlo simulation of the location of NP-functionalization dielectric traps in the material proved to be the most accurate predictor of a NP- functionalization’s effect on the breakdown of the overall composite. 6 different functionalizations were examined both in silico and in spin coated and PulseForge (high energy pulsed Xe light illumination) cured samples. The overall energy density is presented and our model’s efficacy at predicting the highest energy density of our experimentally produced films. We also discuss how our modelling technique could be applied elsewhere where interface control is paramount, such as supercapacitor electrodes, surface functionalization for organometallic perovskite solar cells, and quantum dot solar cells.

3:45 PM *NM04.05.08
2D Materials as Binders for Electrodes of Electrochemical Capacitors: Bin Xu1 and Yuriy Gogotsi1; 1Department of MSE and A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; 2State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, China.

Carbon-based materials have attracted much attention as electrodes for electrochemical capacitors. However, they are usually made into free-standing films with the aid of polymeric binders which add electrochemically inactive weight. Fluorinated polymers used as binders produce toxic gases when incinerated. Here, we discuss manufacturing of freestanding supercapacitor electrodes made of highly porous carbide-derived carbon (CDC), highly accessible hierarchical porous carbon, and activated carbon fibers (ACF) using electrochemically active materials, such as reduced graphene oxide (rGO) and Ti3C2MXene2, as the binders. In these hybrid electrodes, the 2D layers hold carbon particles together, producing freestanding films. The sandwiched carbon particles prevent layer stacking and increase accessibility of the active material to the electrolyte ions, which improves electrochemical performance. As a result, electrodes with excellent capacitance, high-rate performance and good lifetime can be manufactured and operated in aqueous and organic electrolytes. These hybrid electrodes material design is greatly viable in high-power and high energy applications.


4:15 PM RAPID FIRE PRESENTATION
Ultra-Thin, Embedded High-Volumetric Density Capacitors with High Operating Frequency and Low Leakage Properties

Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Smart systems have continuously evolved with the integration of computing, communication, power, and sensing functions that utilize heterogeneous technologies such as digital, RF, analog, MEMS, sensors and optics in ultra-miniaturized form-factors with escalating component densities. This entails the use of multiple power converters for specific voltage and current applications. These power converters invariably utilize components such as capacitors and inductors to store and release the energy in specific intervals determined by the switch frequency. Today’s components with low volumetric density and thick form-factors are a major roadblock to miniaturization of the power modules. Moreover, such components are placed far away from the chips leading to large interconnect parasitics and lower operating frequencies. On the other hand, thin-film passive technologies are limited to low densities and would require a large area to meet the required capacitance or inductance values. Hence, novel thin-film technologies with high densities and small form-factors are required to enable miniaturization and performance at high frequencies. However, processing high surface area electrodes as thin-films with substrate-confined processes, and achieving low leakage currents and low ESR (equivalent series resistance) for high frequency stability are major challenges to accomplish these goals. Furthermore, novel packaging technologies are required to integrate these high-density passives as thin-films in substrates. This research work addresses these challenges with tantalum-based ultrathin high-density capacitors at higher operating frequencies with lower leakage properties and their integration in silicon substrates. The work focuses on the processing of high-density capacitors as thin-films based on tantalum with low leakage properties (< 0.01 µA/F) and for high-frequency applications in low power modules. The anodization kinetics and the underlying leakage current mechanisms are investigated to provide optimal process guidelines. The capacitors demonstrated high capacitance density of 0.1 µF/mm² at 1-10 MHz in form-factors of 50 µm, which corresponds to 6X higher volumetric density relative to the commercial capacitors. The aforementioned tantalum-based high-density capacitors are laminated as thin-films on silicon substrates followed by planarization, via-drilling, lithography and metallization to complete the integration process.

Reduced Graphene Oxide - Molybdenum Disulfide Aerogel Nanocomposite Electrodes for Supercapacitors

NM04.06.04

Reduced Graphene Oxide - Molybdenum Disulfide Aerogel Nanocomposite Electrodes for Supercapacitors

Alptekin Aydinli¹,², Ozgur Dogan¹, Serkan Koylan¹, Erhan Bat¹ and Husnu E. Unalan¹,², ¹Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey; ²Energy Storage Materials and Devices Research Center (ENDAM), Middle East Technical University, Ankara, Turkey; ³Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey.

Super capacitors have attracted extensive attention for their high specific power and moderate energy densities. Nanoscale structure and high surface area are the two main requirements for a supercapacitor electrode with high performance. We report on the fabrication and electrochemical characterization of hybrid aerogel nanocomposite supercapacitor electrodes composed of reduced graphene oxide and molybdenum disulfide nanosheets on nickel foams. Graphene oxide was produced using Tour Method. Reduced graphene oxide (rGO) aerogel was produced from graphene oxide dispersion via solvothermal technique followed by freeze-drying and thermal reduction. For the fabrication of hybrid electrodes, produced rGO aerogels were simply pressed onto nickel foams, which was followed by drop-casting of exfoliated molybdenum disulfide (MoS₂) nanosheets onto the rGO aerogel. Electrochemical properties such as specific capacity and capacity retention of the fabricated nanocomposite electrodes were examined through cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy in two electrode configuration. Results of the measurements were compared to that of control samples fabricated simply by pressing bare rGO aerogel and bare MoS₂ nanosheets directly onto nickel foils. In order to determine the effect of electrolyte type on the electrochemical properties of the hybrid nanocomposite electrodes, various environmentally friendly and neutral aqueous solutions, such as lithium sulfate (Li₂SO₄), sodium sulfate (Na₂SO₄), sodium chloride (NaCl) and potassium chloride (KCl) were investigated as the electrolytes. Fabricated hybrid supercapacitor electrodes showed encouraging results with a specific capacitance of 38.69 mF/cm² and a Coulombic efficiency of 83%. Following 1000 charge/discharge cycles, specific capacitance of the fabricated electrodes degraded to 94% of its initial capacitance value. A comprehensive analysis on the electrochemical properties of the fabricated supercapacitor will be presented.

Aqueous Phase Synthesis Method of Cu-In-S₂ Compound Solar Cell Nanoparticles by Controlling the Metal Complexes in Original Solutions

NM04.06.05

Aqueous Phase Synthesis Method of Cu-In-S₂ Compound Solar Cell Nanoparticles by Controlling the Metal Complexes in Original Solutions

Hideyuki Takahashi, Kohei Sato, Shun Yokoyama and Kazuyuki Toji; Graduate School of Environmental Studies, Tohoku University, Sendai, Japan.

CIS (CuInS₂) type solar cell is one of the most suitable photovoltaic devices with high stability and efficiency, since the bandgap of CIS is 1.5eV while ideal band gap for solar cell is 1.4eV. Moreover, it does not contain toxic materials, such as Se. In usual case, these CIS type solar cell is synthesized by gas phase method. However, since vaporizing temperature of four elements (Cu, In, Ga, Se) is extremely different, productivity under the gas phase is relatively low, which reads the large amount of waste of resources. Thus, to decreasing the cost of CIS type solar cell, synthesis method with high recovery rate should be developed. On the other hand, it is also well known that liquid phase reduction methods can be easily produced the nanomaterials with high recovery rate. However, in many cases, crystallinity of the products was relatively low, which reads the large amount of waste of resources. Thus, to decreasing the cost of CIS type solar cell, synthesis method with high recovery rate should be developed. In our presentation, detailed description of CIS₂ particles synthesis from Cu, In and Se was to be described. In this research, we aim to develop a new synthesis method for CIS₂ nanoparticles with high recovery rate and high crystallinity. We expected that CIS₂ nanoparticles with high crystallinity and high recovery rate can be synthesized using aqueous phase synthesis method. In this method, metal complex is dissolved in water and mixed with metal source (Cu, In and Se). After that, the reaction mixture is heated up to 120°C for 10 hours. In this reaction, CIS₂ nanoparticles were synthesized with high recovery rate and high crystallinity. These nanoparticles were characterized by XRD, SEM and TEM analysis.
Fossil fuels—coal, petroleum and natural gas—have provided more than 80% of total U.S. energy consumption for more than 100 years. To alleviate our dependence on fossil fuels, renewable energy sources such as solar, wind, and geothermal play an important role in the future. Among them, solar harvesting takes advantage of clean and abundant energy from sun by converting the solar energy to electrical or thermal energy. Considering the clean source and product, solar harvesting is a promising tool to utilize endless energy and reduce greenhouse gases in the environment. In a typical solar thermal conversion system, sunlight is absorbed in the form of heat at the absorber surface. To enhance the conversion, this absorber needs to strongly absorb the sunlight, while losing less heat to the environment by convection and radiation. Spectrally selective solar absorbers, having a strong solar absorptance and low infrared emittance, are now widely investigated for solar radiation capture in the form of heat. More specifically, Al2O3-based selective solar absorbers have been extensively investigated for their excellent optical properties and thermal stability. Several techniques, such as co-evaporation, reactive sputtering and solution-based methods, have been employed to fabricate Ni-Al2O3-based selective solar absorbers. The solution-chemical method is desirable due to its low cost and readiness. This method includes two steps: the generation of ordered anodic aluminum oxide pores and the impregnation of nickel. The anodic aluminum oxide with ordered pore geometry is typically fabricated by a two-step anodization in acid solution. The nickel impregnation can be performed under direct or alternating voltage. Salmi et al. carried out the impregnation in a nickel sulphate solution under alternating voltage, which resulted in a coating with a low emissivity (0.14 at 700 °C) and high solar absorptivity (> 0.9). To further improve the uniformity of nickel deposition, Nielsh et al. developed a pulsed electrodeposition (PED) method, which shows that nearly 100% of the pores were filled with nanocrystalline nickel with a very small fluctuation in growth rate.

Although the uniform deposition of nickel into porous alumina had been investigated before by using the PED method, the direct connection between porous geometry and surface optical properties has not been previously investigated. Also, by using more modern equipment (e.g. SEM, FIB) with higher resolution, details inside the materials can be characterized with higher accuracy. Understanding this connection and the detailed microstructure of Al2O3-based selective solar absorbers will lead to a better understanding and further improvement in solar conversion efficiency.

In this study, we refined the nickel deposition by using PED method and investigated the effects of various nickel deposition parameters on the optical properties of selective solar absorbers.

NM04.06.07

Microkinetic Analysis of Hydrogen Evolution Reaction on Graphene Coupled Molybdenum Carbide Heterostructure Timothy T. Yang and Wissam Saadì; Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Molybdenum carbides have shown high catalytic activity towards hydrogen evolution reaction (HER) by coupling with graphene supports. However, the atomistic mechanism for the enhanced activities is still lacking. Herein, we use first-principles calculations in conjunction with ab initio thermodynamics to investigate the HER on Gamma-phase MoC coupled graphene. Analyzing the reaction pathways and charge transfer events from first principles results, we develop a novel model to predict linear sweep voltammetry in electrochemical conditions based on Volmer-Butler kinetics. Particularly, this model shows that the heterostructure with graphene vacancies reaches its optimum for HER resulting in an overpotential of ~0.1 V vs. SHE for 10 mA/cm2 current density. We validate this kinetic model by demonstrating that the Volmer-Heyrovsky pathways on the heterostructure are mainly controlled by hydrogen adsorption Gibbs free energy, the descriptor which has been widely used to measure HER activities in the catalyst community.

NM04.06.08

IR-Driven Photoelectrochemical Properties and Band Structures of CdSe/ZnO Heterostructures Fabricated on the Up-Conversion Glass-Ceramics Joo-Won Lee, Joon-Soo Yoon and Yun-Mo Song; Korea University, Seoul, Korea (the Republic of).

We report the new approach for utilizing infrared (IR) light, which is differentiated from the established routes using heterostructures of up-conversion (UC) fluoride nanoparticles and semiconductor photocatalysts. We introduced the IR-driven photoelectrochemical (PEC) cells using UC glass-ceramics as substrates and this enabled the overcome of the natural instability of UC fluoride nanoparticles, the blockage of incident light, and the restricted exposure of photocatalysts to liquid electrolytes. Oxyfluoride glass-ceramics containing (Yb,Er)-doped and (Yb,Tm)-doped YF3 nanoprecipitates were verified to radiate UC green and UC ultraviolet/blue emissions, respectively under 980 nm illumination. High-density ZnO nanorod arrays were fabricated on the UC glass-ceramics substrates via the hydrothermal method and subsequently CdSe/ZnO heterostructures were realized with the chemical bath deposition method. CdSe nanoparticles with the bandgap of ~1.8 eV were activated by both the UC ultraviolet emission from Tm3+ ions and the UC visible emissions from Er3+ and Tm3+, whereas ZnO nanorods with the bandgap of ~3.2 eV absorbed the UC ultraviolet emission from Tm3+ mostly. Two distinct carrier transport mechanisms, so called sensitization and type-II cascade, turned up in the identical CdSe/ZnO photocatalysts originated from the difference in the UC emissions from Er3+ and Tm3+ ions. Eventually, the CdSe/ZnO fabricated on the UC glass-ceramics containing (Yb,Tm)-doped YF3 exhibited increased photocurrent density compared to that on the UC glass-ceramics containing (Yb,Er)-doped YF3 because of the charge separation activated by the type-II cascade transport mechanism.

NM04.06.09

Optically Transparent, Thermally Insulating Aerogels for Energy Efficient Window Applications Elise M. Strobach1, Bikram Bhatia1, Lin Zhao2, Sungwoo Yang2, Shaoing Lin1, Xuahne Zhao3 and Evelyn N. Wang1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Civil and Chemical Engineering, The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

The United States uses 14% of the total annual energy produced on heating, ventilation, and air conditioning in buildings. A large portion of this energy is lost through windows, a necessary but lossy portion of the building envelope. High-performance windows use exotic low conductivity gases, large frame footprints, low-emissivity coatings, and complex sealing strategies to achieve high performance, often leading to long payback periods. We propose using high-transparency silica aerogel developed in our lab to reduce energy losses via the super-insulating properties of its nanoporous structure. In this work, we have shown that by controlling density and pore/particle size, we can achieve a visible transmission of >98%, a visible haze <3.0%, and a thermal conductivity of <0.02 W/mK through a 3 mm monolithic slab in ambient conditions. This exceeds the highest clarity reported in literature for silica aerogels, allowing the material to be competitive with traditional window insulating materials at a relatively low cost ($2 per square foot). We also present an approach to optimize the high-transparency aerogel structure for optical, thermal, and mechanical performance critical to window applications. This is done using structure-property relationships developed in combination with a center-of-pane window performance model to identify the ideal achievable aerogel structure. This optimization approach creates a framework that allows the aerogel to maximize energy efficiency in windows for the varied performance needed in many different buildings and climates.

NM04.06.10

SnS2 Nanoparticles and P3HT Blends for Hybrid Solar Cells Maria E. Perez Barthaburu, Daniela Oreggioni, Loengrid Bethencourt, Mauricio Rodríguez Chialanza, Ricardo Santana, Lauro Maia and Laura Formaro; 1Departamento de Desarrollo Tecnológico, CURE - Universidad de la República, Rocha, Uruguay; 2Instituto de Física, Universidade Federal de Goiás, Goiania, Brazil.
Hybrid solar cells are among the studied technologies for the generation of electric energy from solar energy. In these solar cells, an inorganic electron acceptor of nanometer size must be developed, being a polymer is generally used as donor, while a NPs is used as the most common one. SnS$_2$ is a semiconductor with an energy band gap of 2.35 eV adequate for its use in hybrid solar cells. Many studies were performed for its application as sensor, in lithium batteries, photocatalysis, etc. In the present work, we synthesized Sn$_x$S$_y$ NPs (by the hydrothermal method. SnCl$_2$·H$_2$O and Thiouacetylmete were used as Sn and S sources. In all the syntheses citric acid was used as capping agent (CA). The ratio Sn:CA was varied to study its influence in morphology and size of NPs. For this purpose, the ratios [2:1], [1:10] and [1:15] were tested. All obtained samples were centrifuged with water and ethanol. The sample with a Sn:CA [1:10] ratio yielded the best results, with hexagonal NPs of 15-50nm and rounded NPs of 2-4nm in size, observed under Transmission Electron Microscope. This sample was selected to perform an exchange of CA. The sample was refluxed in pyridine or aniline during 6 hours (samples S-Py and S-Ani, respectively). They were washed following the same procedure described before. The success of CA exchange was studied by FTIR, confirming the presence of aniline in sample S-Ani and pyridine in sample S-Py. The stability of NPs suspension in chloroform was studied, being important for the preparation of P3HT/SnS$_2$ blends. It was proved that NPs capped with aniline were more stable than the pyridine ones, presenting a decanting coefficient of 0.02g/L.min. Blends and then layers of Sn$_x$S$_y$/P3HT were obtained with both samples, S-Ani and S-Py. Layers were deposited onto glass covered with ITO/PEDOT:PSS substrates, using the spin coating technique. The layers S-Ani and S-Py were studied by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). EDS results confirmed presence of SnS$_2$; NPs, while SEM showed that both layers have uniform distribution of NPs. Phoatoluminescence experiments were performed on S-Ani, S-Py, LS-Ani and LS-Py samples. Emission peaks of CA were observed for the samples S-Ani and S-Py; Sn$_x$S$_y$ emission is possibly included in these peaks. The layers also showed the characteristic emission peaks of P3HT. UV-Vis spectroscopy studies were carried out to the same samples and to substrates covered with P3HT only, observing two bands of P3HT. Results of layers prepared with different proportions of nanoparticles, proved that there is an electronic coupling between the polymer and the NPs. Our results show that the presence of aniline or pyridine are necessary for the suspension of Sn$_x$S$_y$, being aniline the best. Moreover, the spectroscopy results encourage us to further study the photovoltaic properties of layers for the development of hybrid polymeric-inorganic solar cells.

NM04.06.11

Gold Deposited Flexible Nickel Micro-Pillar Structured Substrate for Solar Steam Generator Soomin Son, PilHoon Jung, Jaemin Park, Dongwoo Chae, Sucehoel Ju and Heon Lee; Korea University, Seoul, Korea (the Republic of).

Solar steam generators are potential technologies that can be used in a variety of applications such as desalination and sterilization, and are emerging as promising technologies for solar energy harvesting. In recent years, various artificial structures have been developed for the purpose of improving the energy conversion rate by improving solar absorption, thermal localization, water supply and steam transportation. In this research, a solar steam generator was fabricated by depositing plasmon metal particles that can efficiently convert light into heat under sunlight, such as gold on a nickel micropillar (NiMP) structured substrate. The NiMP substrate was confirmed to have a high absorption of 98% or more in the broad spectrum of 300-2500 nm. As a result, we have fabricated the steam generator with high solar conversion efficiencies using high absorbance and light-to-heat efficient conversion under solar light illumination. This structure demonstrates the potential for future regeneration functions, portable solar energy generation and phase change applications, and solar energy based desalination.

NM04.06.12

Improving Ni-VSZ Cermet Anode Performance by Liquid Infiltration of Nickel Catalyst Particles with LSCM Yanchen Lu, Paul Gasper, Boshan Mo, Uday Pal, Srikanth Gopalan and Soumenendra Basu; Boston University, Brookline, Massachusetts, United States.

Hydrogen generation and storage are a critical part of a sustainable energy future; a key technology for the production of energy from hydrogen fuel is the solid oxide fuel cell (SOFC). Impregnation of nanoscale metallic catalysts into the anode electrode has been shown in many studies to improve SOFC performance in various ways, such as increase catalytic performance, improve sulfur tolerance, and mitigate coking. The goal of this study is to infiltrate nickel nanoparticles into both anode symmetric cells and anode supported button cells to increase electrochemical active site density and improve anode performance, and for catalytic energy conversion reactions such as water splitting. The synthesis of such compounds is commonly done in time and energy consuming batch processes. Alternatively, spray-flame synthesis (SFS) allows the formation of functional perovskite nanoparticles in a single step. Cost-efficient production requires the utilization of cheap and abundant precursors such as metal nitrates, which are more attractive than the organometallic precursors (acetates, carboxylates). However, the use of metal nitrates in SFS is often associated with the formation of particles non-homogeneous in size. Furthermore, the different melting/decomposition mechanisms and their different solubility in solvents such as ethanol cause the formation of undesired phases, e.g., La$_2$CoO$_4$, La$_2$O$_3$ and Co$_3$O$_4$, which are often obtained in parallel to the main perovskite phase. In order to improve the perovskite homogeneity in size and composition, mixtures containing the metal nitrate precursors and two different solvents, ethanol and 2-ethylhexanoic acid (2-EHA), were employed in this study. The incorporation of 2-EHA has been previously investigated and a positive effect toward narrow particle-size distributions has been observed. It is suggested that the addition of 2-EHA leads to the formation of micro-explosions in the droplets through superheating of ethanol and the formation of volatile metal carboxylates, which is investigated in this study. The LaCoO$_3$ and LaFeO$_3$ nanoparticles were synthesized from solutions of the respective nitrates in ethanol/2-EHA. To understand the effect of 2-EHA on the product properties, temperature-dependent liquid-phase ATR-FTIR studies were performed. It was found that an esterification of 2-EHA with ethanol occurred forming ethyl-2-ethylhexanoate (verified by GC/MS). We assume that the metal nitrates act as catalysts as reported for similar reactions. The nanoparticle products were characterized using XRD, XPS, TEM, SAXS, and Mößbauer spectroscopy. The measurements confirm that the incorporation of 2-EHA in the solution was effective for obtaining homogeneous, single-phase, and high-surface-area products (LaCoO$_3$: $d_p = 11$ nm, SSA $> 90$ m$^2$/g, LaFeO$_3$: $d_p = 15$ nm, SSA $> 88$ m$^2$/g). The LaFeO$_3$ and LaCoO$_3$ perovskites were evaluated for the catalytic oxidation of carbon monoxide, reaching a 50% CO conversion at temperatures lower than 206°C.

NM04.06.13

Spray-Flame Synthesis (SFS) of the Nanosized LaMO$_3$ (M = Fe, Co) Perovskites from Metal Nitrate Precursors—Influence of the Mixture of Ethanol and 2-Ethylhexanoic Acid on Materials’ Homogeneity Steven Angeli$^{1, 2}$, Mira Klinge$^3$, Hermann Nirschl$^3$, Klaus Friedel-Ortega$^4$, Yuan Wang$^1$, Hamidreza Arandiyan$^5$, Hartmut Wiggers$^{1, 2}$ and Christof Schulz$^{1, 2}$; 1IVG, Institute for Combustion and Gas Dynamics, University of Duisburg-Essen, Duisburg, Germany; 2CENIDE, Center for Nanointegration, University of Duisburg-Essen, Duisburg, Germany; 3Institute of Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Germany; 4Faculty of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Essen, Germany; 5Particles and Catalysis Research Group, University of New South Wales, Sydney, New South Wales, Australia; 6Laboratory of Advanced Catalysis for Sustainability, The University of Sydney, Sydney, New South Wales, Australia.

Perovskite nanomaterials composed of LaMO$_3$ (M = Fe, Co) are of current interest for environmental catalysis applications, e.g., oxidation of CO and CH$_4$, and for catalytic energy conversion reactions such as water splitting. The synthesis of such compounds is commonly done in time and energy consuming batch processes. Alternatively, spray-flame synthesis (SFS) allows the formation of functional perovskite nanoparticles in a single step. Cost-efficient production requires the utilization of cheap and abundant precursors such as metal nitrates, which are more attractive than the organometallic precursors (acetates, carboxylates). However, the use of metal nitrates in SFS is often associated with the formation of particles non-homogeneous in size. Furthermore, the different melting/decomposition mechanisms and their different solubility in solvents such as ethanol cause the formation of undesired phases, e.g., La$_2$CoO$_4$, La$_2$O$_3$ and Co$_3$O$_4$, which are often obtained in parallel to the main perovskite phase. In order to improve the perovskite homogeneity in size and composition, mixtures containing the metal nitrate precursors and two different solvents, ethanol and 2-ethylhexanoic acid (2-EHA), were employed in this study. The incorporation of 2-EHA has been previously investigated and a positive effect toward narrow particle-size distributions has been observed. It is suggested that the addition of 2-EHA leads to the formation of micro-explosions in the droplets through superheating of ethanol and the formation of volatile metal carboxylates, which is investigated in this study. The LaCoO$_3$ and LaFeO$_3$ nanoparticles were synthesized from solutions of the respective nitrates in ethanol/2-EHA. To understand the effect of 2-EHA on the product properties, temperature-dependent liquid-phase ATR-FTIR studies were performed. It was found that an esterification of 2-EHA with ethanol occurred forming ethyl-2-ethylhexanoate (verified by GC/MS). We assume that the metal nitrates act as catalysts as reported for similar reactions. The nanoparticle products were characterized using XRD, XPS, TEM, SAXS, and Mößbauer spectroscopy. The measurements confirm that the incorporation of 2-EHA in the solution was effective for obtaining homogeneous, single-phase, and high-surface-area products (LaCoO$_3$: $d_p = 11$ nm, SSA $> 90$ m$^2$/g, LaFeO$_3$: $d_p = 15$ nm, SSA $> 88$ m$^2$/g). The LaFeO$_3$ and LaCoO$_3$ perovskites were evaluated for the catalytic oxidation of carbon monoxide, reaching a 50% CO conversion at temperatures lower than 206°C.
NM04.06.14

Spray-Flame Synthesis of Ba$_{1-x}$Sr$_x$TiO$_3$ Nanoparticles for Photocatalytic Hydrogen Production

Alexander Tarasov$^{1,2}$, Marco Relohs$^2$, Frank Marlow$^2$ and Hartmut Wiggers$^{1,2}$; $^1$Institute for Combustion and Gas Dynamics – Reactive Fluids (IVG), University of Duisburg-Essen, Duisburg, Germany; $^2$Max-Planck-Institut für Kohlenforschung, Mülheim, Germany; $^3$Center for Nanointegration Duisburg-Essen, CENIDE, Duisburg, Germany.

Barium titanate (BaTiO$_3$) and strontium titanate (SrTiO$_3$) are oxide perovskites with large band gap values (~3.2 eV) suitable for hydrogen production via water splitting under UV light. These materials show high thermal and chemical stability, and the flexibility of the ABO$_3$ perovskite structure offers the possibility of substituting cations on both, A and B sites, therefore allowing to selectively adjust properties of interest such as band gap width and particle size. While nanoscale cubic SrTiO$_3$ has been shown a promising catalyst, BaTiO$_3$ is afflicted by the existence of multiple phases over a narrow temperature range. The cubic phase of BaTiO$_3$ can be stabilized by the introduction of smaller Sr-atoms, however, the influence on the catalytic activity is not known so far. Therefore, the formation of Ba$_{1-x}$Sr$_x$TiO$_3$ and its catalytic properties was investigated.

Nanosized barium strontium titanate was synthesized in the gas phase by means of spray-flame synthesis (SFS). This scalable method allows a continuous production of oxide nanoparticles and provides a good control over size, crystallinity, and phase composition. The SFS method is essentially a combustion process, whereby high temperatures of the burning spray lead to the evaporation of the dissolved metal precursors, gas-phase reactions, and subsequent particle formation. The applicability of the SFS technique to nanoparticle synthesis has been already demonstrated for many simple oxides (e.g., TiO$_2$, Al$_2$O$_3$). Once using this method to extend the SFS technique to oxide nanoparticles could enlarge the number of catalytically interesting materials.

As-produced (AP) and heat-treated powders (HT) were tested in UV light water splitting reaction with methanol and compared with commercially available BaTiO$_3$ powder. On average, the Sr-containing AP powders show 15% higher hydrogen production rate than the commercial sample. Surprisingly, HT samples show similar activity despite having less surface area as suggested by BET measurements. We attribute this to an initial decomposition of the adsorbents, which no longer hinder the catalytic reaction.

NM04.06.15

High-Efficiency, High-Temperature Cu and Mn Oxides Nanoparticle-Pigmented Anti-Oxidation Solar Selective Coatings via Spray-Coating Method

Can Xu, Eldred Lee, Xiaoxin Wang and Jifeng Liu; Dartmouth College, Hanover, New Hampshire, United States.

As an important component of concentrating solar power (CSP) systems, solar selective absorber coatings can help enhance the absorbance in the solar spectrum regime and reduce the emittance loss in the infrared (IR) range [1]. However, many of the current coating products are not capable of maintaining the solar selectivity as well as satisfying the thermal efficiency requirement (~90%) when undergoing high operating temperature [2]. Herein, we report Cu and Mn oxides nanoparticle(NP)-pigmented silicone solar selective coatings on Inconel substrates via a simple hot spray-coating method. The coatings can withstand a high temperature of 750 degrees C for future generations of CSP systems [3], and hence improve the thermal efficiency according to Carnot's Theorem. Based on theoretical modeling [4] and verified by experiments, these NP-pigmented coatings can tolerate a relatively large variation in the pigment NP concentration, diameter, as well as coating thickness, thereby enabling facile spray coating method without the need of stringent thickness control. By adequately selecting silicone precursors with low emissivity and high enough viscosity, the pigment NPs can be well dispersed in the solution for spray coating with excellent stability against precipitation of NPs. To further explore the impact of relevant factors, we varied parameters including type of silicone precursors, organic solvents, compositions and concentrations of NPs, and the thickness of the coatings. Our preliminary optimization effort has already achieved a high solar absorbance of 96.7%, a thermal emittance of 59.1%, and a record-high overall optical-to-thermal energy conversion efficiency of 93.0% for 1000x solar concentration ratio at 750 degrees C, exceeding that of the state-of-the-art Pyromark 2500 black paint (90%) at the same temperature [4]. These coatings also block the IR emittance losses of the thermal oxide layers on the Inconel substrates found in previous research [5]. Furthermore, they have already passed 100 h endurance testing at 750 degrees C in air without deterioration in efficiency or mechanical integrity, promising for long-term thermal stability at high temperatures. The high efficiency, high-temperature thermal stability, and simple and facile fabrication process make these Cu and Mn oxide NP-pigmented solar selective coatings especially promising for scaling up in CSP industry.


NM04.06.16

Cellulose Based Nanomaterials Synthesis for Sustainable Energy Conversion

Anand Kumar$^1$, Isna Ashraf$^4$ and Anchul Ashok$^1$; $^1$Department of Chemical Engineering, Qatar University, Doha, Qatar; $^2$Department of Mechanical and Industrial Engineering, Qatar University, Doha, Qatar.

Fuel cells (FCs) have long been considered as an alternative to fossil fuel energy for a sustainable growth and the protection of the ecosystem from harmful emissions. Direct methanol fuel cells (DMFCs) among various types of FCs, have been intensively studied because of their low-operating temperature, high-energy conversion efficiency, and environmental-friendly nature for micro-power energy strategy. However, Pt is the only commercially available anodic materials, that is reasonably active and stable, as it has shown low CO-poisoning in alkaline media. Alternative materials with low costs are still being sought as suitable catalysts to enable commercialization and widespread application of DMFCs. Here we explore a more sustainable approach that is based on the application of cellulosic materials for large-scale synthesis of transition metals and their alloys with noble metals for various catalytic applications, in particular, fuel cells. In this technique, an aqueous solution of metal nitrate and a reducing agent is impregnated on a thin cellulose paper. The paper is dried and locally ignited at one end to start combustion reaction that is self-sustained under optimum loading of reactive solution, continuously producing nanoparticles. The thin film helps in generating a quenching effect and limits nanoparticles sintering in post-combustion stages. This paper
describes the synthesis of Cu, Ni and Co based nanomaterials that are found to be active for sustainable hydrogen production from bioethanol, methanol that can be generated from bio-wastes. A detailed mechanistic study of nanoparticle evolution during synthesis process was conducted along with the reaction pathway analysis for hydrogen production from bioethanol. In-situ FTIR (DRIFTS) studies on the metal surfaces reveal the differences in their catalytic performance and help in explaining the observed product distribution.

ACKNOWLEDGMENTS
This publication was made possible by NPRP grant (NPRP6-509-2-209) from the Qatar national research fund (a member of Qatar foundation). The statements made herein are solely the responsibility of the author(s).

NM04.06.17 Sustainable CO2 Conversion Over Visible-Light-Responsive Perovskites via Artificial Photosynthesis Eduardo Morais1, Kristy Stanley1, James Sullivan1 and Ravindranathan Thampi2; 1School of Chemistry, University College Dublin, Dublin, Ireland; 2School of Chemical and Bioprocess Engineering, University College Dublin, Dublin, Ireland.

The bulk of energy generation on Earth derives from combustion of fossil fuels. This has undesired consequences including the depletion of fossil fuel resources (which are also the principal feedstock of the chemical industry) and the generation of CO2 (a greenhouse gas which has recognised the generation of which has implications for climate change implications). This reliance on fossil fuels is unsustainable and therefore it is imperative to find alternative cleaner energy sources.

This work aims to harness the energy available in solar radiation using photo responsive catalysts to carry out the reduction of CO2 into CO and/or CH4 using H2O as a co-reactant (i.e. the artificial photosynthesis reaction). The materials studied are a range of semiconductor Bi2WO6 quasi-perovskites Bi1-xCoxWO3. These were prepared via facile solvothermal methods at low temperatures and the use effects of surfactants, template agents and microwave radiation within the preparation mixture and surface modifications with amine groups on reactivity was investigated. Also, surface modifications with terminal amine moieties and doping were carried out on the parent materials with the aim of enhancing the photocatalytic activity. All the plain and modified catalysts were characterised using a range of techniques and applied in a batch reactor in the artificial photosynthesis reaction.

CO2 + H2O + hv → CH4 + CO + O2

The characterization techniques included XRD, UV Visible spectroscopy, TEM, BET, and XPS. X-ray diffraction showed both crystalline and amorphous Bi2WO6 depending on the synthetic route adopted. SEM and TEM studies revealed that nanoparticle morphologies also depended on the synthesis. The materials had relatively large BET surface areas and TPD experiments confirmed the adsorption / desorption of CO2 and H2O on (and from) the catalyst surface.

The catalysts were tested in the CO2 + H2O reaction under simulated solar radiation, evolving CO and CH4 as products. CO2 conversion and CO/CH4 product ratios were dependent on aspects such as surface area and functionalization and light absorption properties (which in turn were dependent on the morphology of the particles).

References

NM04.06.19 Photovoltaic and Photocatalytic Properties of Bismuth Oxyiodide-Graphene Nanocomposites Candy C. Mercado, Levannie A. Mabuti and Ian Kenneth Manding; Department of Mining, Metallurgical, and Materials Engineering, University of the Philippines Diliman - ANSYD Lab, Quezon City, Philippines.

Solar energy is considered to be the most viable solution for the future energy crisis and water pollution. In this study, we evaluate the photovoltaic and photocatalytic properties of chemical vapor deposited bismuth oxyiodide (BiOI) and bismuth oxyiodide-graphene (BiOI-GR) nanocomposite thin films.

They were characterized using XRD, SEM, UV-Vis spectrophotometer, and EIS. The BiOI thin film has an average thickness of 574 nm and a bandgap of 2.12 eV. The BiOI and BiOI-GR thin films exhibited nanoflake morphology. It was found that addition of graphene increases absorbance by causing vertical growth of nanoflakes, imparting anti-reflectance and light trapping and also suppresses recombinations due to its electron accepting nature. The photocatalytic activity of the thin films were evaluated by examining methylene blue (MB) degradation under visible light irradiation. BiOI-GR degraded 56-62% of MB in two hours while BiOI degraded 44.16%. Afterwards, FTO | BiOI | Graphite | Al and FTO | BiOI-GR | Graphite | Al solar cells devices were fabricated with photocurrent density values of 0.20 μA/cm² and 0.27 μA/cm², respectively. The improved properties of BiOI-GR are attributed to the anti-reflecting and light trapping properties of vertical BiOI-GR nanoflakes and the enhanced carrier separation due to graphene.

NM04.06.20 Oxide Anchored, Carbidie Supported Pt Nanoparticles for Oxygen Reduction Reaction Zishuai Zhang1, Amin Sadeghi1, Nicolas Brodusch1, Raynald Gauvin1, Jeff Gostick2, Siyu Ye1, Geraldine Merle1 and Jake Barral1; 1McGill University, Montreal, Quebec, Canada; 2University of Waterloo, Waterloo, Ontario, Canada; 3Ballard Power System Inc., Burnaby, British Columbia, Canada.

Transition metal carbides have attracted increasing attention recently as low-cost electrocatalyst supports for the oxygen reduction reaction (ORR) due to some conductivity and relative stability. Furthermore, transition metal carbides can promote electron transfer between the catalysts and supports. To further improve the carbide conductivity and stability, especially at higher potentials (T<1.5V), we developed a process for the formation of a cobalt oxide protective shell on Pt decorated TiC. The oxide was removed selectively at the location of the Pt thereby creating a protective layer for the carbide only. It had the unexpected advantage of pHsically anchoring the Pt to the carbide. We examined ORR activity and stability of these composite particles by chronoamperometry analysis in oxygen-saturated solution. The process method consists in depositing platinum before the cobalt layer, and 5 wt% hydrogen peroxide was used to burst the cobalt shell to expose platinum nanoparticles.

Electron microscopy confirmed that the platinum nanoparticles were in contact with both the carbide core and cobalt shell. These coated carbide nanomaterials had greatly improved stabilities as supports compared with pristine carbides (chronoamperometry curve showed no activity loss at 0.6 V vs
Nanoscale complex metal oxides have transformed how technology is used worldwide. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices. As the number of portable devices is projected to increase, so too will the inadvertent release of complex metal oxide nanomaterials into the environment. This is a pressing problem because the environmental and biological impact of complex metal oxide nanomaterials is most times unknown, since they are subject to transform rapidly with changes in pH and concentration. This brings us to a looming problem that needs to be solved on a global scale. There is a fundamental knowledge gap in developing sustainable nanotechnology because there is not yet a systematic method to predict how the properties of a complex metal oxide will change with changes in chemical environment. We have developed an analysis, based on Hess’s Law, which combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the surface dissolution of complex metal oxides. We focus on the materials found in a Li-ion battery cathode, namely LiCoO2 and compositionally tuned variants with general chemical formula Li(NiMnxCoy)O2. We find that adjusting surface terminations, compositions and pH will change the dissolution properties of this family of materials, and yields insights into the nanoscale transformations that may take place under a given set of conditions. Not only can these results be used to improve environmental fate and toxicity models, but we are able to use the results of our analysis to create a set of rational design rules to govern the creation of the next-generation of Li-ion battery cathodes that will be benign by design.

**NM04.06.22**

**Internal Polarization Modulation in Nanostructured Bi2MoO6 for Photocatalytic Performance Enhancement Under Visible Light Illumination**

Yan Chen¹, Weiye Yang¹, Shuang Gao², Linghang Zhu¹, Caixia Sun¹ and Qi Li²; ¹Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; ²Graduate School at Shenzhen, Tsinghua University, Shenzhen, China; ³Beihang University, Beijing, China; ⁴Qingdao Binhai University, Qingdao, China.

Recently, the introduction of a built-in electric field inside polar photocatalysts was proved effective for the improvement of their photocatalytic performances because the internal electric filed could provide the driving force for electrons and holes to move in opposite directions for their enhanced transport. Most research in polar photocatalysts is now focused on exploring polar semiconductors as novel photocatalysts, including GaN, ZnO, BaTiO₃, NaNO₂, Sr₂(Ta,Nb)₂O₇, Cu₂(OH)PO₄, BiOCl, BiOF, BiOIO₃, Na₃VO₂B₆O₁₁, and Bi₇Fe₃Ti₃O₂₁, while fewer efforts had been made on the modulation of its current efficiency, maximum luminance and FWHM from 3,300 nit to 31,700 nit, and FWHM from 41 nm to 37 nm. Refining the device structure by inserting hole suppressing interlayer further suppresses hole injection from HTL to QDs. We believe that our result is a step forward to make highly efficient InP QLEDs.
Strong Covalent Bonding Modulated Graphene Oxide/Epoxy Interfacial Enhancement and Advanced Corrosion Resistance

Recent interests in graphene-based polymer nanocomposites for structural applications have been driven by the expectation of enhancing the mechanical properties of composites. Although there has been a rapid growth of interest in graphene-based polymer nanocomposites, the mechanics of reinforcement in such materials has only recently become understood [1,2].

The modern structures employed in aerospace and automotive applications are becoming lighter and thinner, but still require high levels of aerodynamic and vibration stability, leading to the stiffness becoming a dominant design driver. Since graphene has high levels of stiffness and strength its use as a reinforcement in polymer composites shows huge potential of further enhancing the mechanical properties of composites. Although there has been a rapid growth of interest in graphene-based polymer nanocomposites for structural applications, the mechanics of reinforcement in such materials has only recently become understood [1,2].

It is shown that the addition of approximately 2% by weight of graphene to the matrix of a unidirectionally-reinforced carbon fiber epoxy composite can lead to a significant enhancement in mechanical properties. In particular, it is found that the axial stiffness of the composites can be increased by the order of 10 GPa accompanied by an increase in axial strength of 200 MPa. X-ray computed tomographic imaging and polarized Raman spectroscopy have demonstrated that the graphene is predominantly aligned parallel to the axes of the carbon fibers. Moreover stress-induced Raman band shifts showed that the self-aligned graphene is subjected to high levels of stress during axial deformation of the composite. The graphene is found to have an effective growth of interest in graphene-based polymer nanocomposites for structural applications, the mechanics of reinforcement in such materials has only recently become understood [1,2].

Chemically functionalized graphene oxide (MAGO) was achieved by building covalent bonds between graphene oxide (GO) and a small molecule containing benzene structure and multi-amino groups. FT-IR, XRD, X-ray photo electron spectroscopy and TEM-EDX results certified that the molecule was successfully grafted onto GO nanosheets. Subsequently, functionalized GO was incorporated into waterborne epoxy (EP) coating through ball-milling method. This molecular design can significantly improve the dispersion of MAGO in EP matrix, as well as the compatibility and interaction between MAGO and EP. Compared with GO/EP, the water absorption of MAGO/EP decreased from 4.38% to 2.59%, the adhesion strength of MAGO/EP increased from 4.72 MPa to 6.32 MPa after immersion of 40 days in 3.5% NaCl solution. Incorporation of 1 wt% of MAGO into EP matrix prominently improved the long-term corrosion resistance. The impedance modulus of GO/EP coating decreased by four orders after 40 day immersion, while that of MAGO/EP coating only decreased by one order. The impedance modulus was still $1.47 \times 10^8 \Omega \cdot cm^2$, and two-time constant wasn’t detected for MAGO/EP coating. This research developed a facile approach to prepare green anticorrosion coating with enhanced durability for metal protection. MAGO can also be utilized as nanofillers for other waterborne polymer matrixes to fabricate green anticorrosion coatings of high performance.

Real-Time Observation of Single CNT Fiber Subjected to Transverse Ballistic Impact

Axial Reinforcement of Unidirectional Composites by Self-Aligned Graphene

Our way of producing master alloy and dispersing them are thus key for the comprehensive superiority of the properties over other methods of making Al+CNT nanocomposites. This cold welding and rapid surface burying process were revealed by in situ transmission electron microscopy (TEM) experiments under similar vacuum conditions. Our way of producing master alloy and dispersing them are thus key for the comprehensive superiority of the properties over other methods of making Al+CNT nanocomposites.
Young’s modulus in the composite of around 825 GPa, approaching its theoretical value of 1050 GPa. This behavior has been modelled using the rule of mixtures and shear-lag analysis and it is demonstrated that highly-aligned graphene in a constrained environment between high-modulus fibers can give significantly better mechanical reinforcement than graphene in conventional polymer-based nanocomposites. It has been demonstrated the enhancement is due to three effects: (a) the alignment of graphene around the fiber by a ‘filtering’ effect; (b) confinement of graphene between the fiber gaps and (c) the matrix being stiffened by the carbon fibers. It shows the considerable potential of using graphene to enhance the mechanical properties of conventional carbon fiber composites even in the high-stiffness fiber direction.


10:00 AM BREAK

10:30 AM *NM04.07.06
Strong, Tough Graphene Sheets by a Low Temperature Sequential Bridging Process Sijie Wan1, Qunfeng Cheng2 and Ray H. Baughman1; 1The University of Texas at Dallas, Richardson, Texas, United States; 2School of Chemistry, Beihang University, Beijing, China.

We here show that infiltrated bridging agents can convert inexpensively fabricated graphene platelet sheets into high performance materials, thereby avoiding the need for a polymer matrix. Two types of bridging agents were investigated for interconnecting graphene sheets, which attach to sheets by either π-π bonding or covalent bonding. When applied alone, the π-π bonding agent is most effective. However, successive application of the optimized ratio of π-π bonding and covalent bonding agents provides graphene sheets with the highest strength, toughness, fatigue resistance, electrical conductivity, electromagnetic interference shielding efficiency, and resistance to ultrasonic dissolution. Raman spectroscopy measurements of stress transfer to graphene platelets allow us to decipher the mechanisms of property improvement. In addition, the degree of orientation of graphene platelets increases with increasing effectiveness of the bonding agents, and the interlayer spacing increases. When compared with other materials that are strong in all directions within a sheet, the realized tensile strength (945 MPa) of the resin-free graphene platelet sheets was higher than for carbon nanotube or graphene platelet composites, and comparable to that of commercially available carbon fiber composites. The toughness of these composites, containing the combination of π-π bonding and covalent bonding, was much higher than for these other materials having high strengths for all in-plane directions, thereby opening the path to materials design of layered nanocomposites using multiple types of quantitatively engineered chemical bonds between nanoscale building blocks. Y. Li, J. Mu, A. Aliev, S. Fang, N. A. Kotov, and L. Jiang also collaborated on this work.

11:00 AM NM04.07.07
Preparation and Nanostructure Analysis of Graphitic Carbon Infused Copper Alloys Beihai Ma1, Uthamalingam Balachandran1, Steve Dorris1, Tae Lee1, Jie Wang1, Jianguo Wen1, Yuzi Liu1, Jonathan Poplawsky2 and Adam J. Rondinone3; 1Argonne National Laboratory, Lemont, Illinois, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

We prepared graphitic carbon nanostructure infused copper alloys by electron-beam melting. This new class of materials, known as copper covetics, exhibit enhanced electrical and thermal conductivities. We observed up to 30% enhancement in electrical conductivity in covetic copper thin films deposited by electron-beam evaporation. Our results revealed remarkable promise for applications as interconnects in the next generation integrated circuits and memory devices. Understanding the nature of interaction between the carbon nanostructures and their host metal is critical to elucidate the origins for superior properties. We utilized atom probe tomography (APT), helium ion microscopy (HIM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) in the study of carbon nanostructures in copper covetics and thin films. APT revealed 3D distribution of carbon-rich nanoclusters; HIM provided unique opportunity to visualize carbon nanostructures in metal matrix due to its superior contrast and resolution; HRTEM and STEM elemental mapping verified the existence of carbon nanoparticles and networks in the copper metal hosts. Details of experimental results will be presented in this talk.

This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357. HRTEM and STEM were performed at the Center for Nanoscale Materials at Argonne, a DOE Office of Science User Facility. APT and HIM experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

11:15 AM NM04.07.08
Water-Processable Cellulose-Based Resist for Green Nanofabrication Camilla Dore1, Johann Osmond2 and Antonio Agustín Mih1; 1ICMAB-CSIC, Bellaterra, Barcelona, Spain; 2ICFO–The Institute of Photonic Sciences, Barcelona, Spain.

Cellulose is the most abundant polymer on Earth and for centuries has had a wide technological impact in areas such as textile, packaging or knowledge storage. Cellulose is biodegradable, biocompatible and possesses excellent mechanical characteristics that have raised the interest of many engineering fields. In our manuscript, we introduce an exciting new path for cellulose derivatives. We report a new lithographic process employing hydroxypropyl cellulose (HPC), a biocompatible and biodegradable cellulose derivative, and water as only chemicals. We use hydroxypropyl cellulose as a nanoimprinting and electron beam lithography resist and demonstrate its potential by fabricating photonic crystals and 2D metal nanoparticle arrays with up to 100 nm resolution over 1 cm² areas. Beyond its biocompatibility and abundance, we combine this cellulose with traditional resists non-soluble in water (PMMA), leading to advanced fabrication possibilities. We fabricated alternating stacks of HPC and PMMA in which each material is selectively removed with the proper solvent. Furthermore, when combined with nanoimprinting, sub-micrometric air cavities are left inside the PMMA, enabling a straightforward nanofabrication strategy for novel optofluiddic devices.

11:30 AM RAPID FIRE PRESENTATION
Cellulose nanofibers (CNFs) are high aspect ratio nanofibers (dia. ~10 nm) that have high specific stiffness and strength, and are also optically transparent and biodegradable. These properties make them attractive building blocks for bulk structural materials. However, to date, the overall dimensions of bulk materials comprised of CNFs are significantly limited by the development of residual stresses generated during the drying process. CNF solutions gel at low volume fractions (~1%), thus a significant amount of water must be removed during drying. Here, we overcome these issues by producing CNF films and structures by additive manufacturing (i.e., 3D printing) of a shear thinning aqueous CNF suspension under controlled drying conditions. The multistep layer-by-layer manufacturing process allows for control of drying and management of residual stresses. The fabricated materials have Young’s moduli and fracture strengths greater than 10 GPa and 70 MPa, respectively. Mechanical characterization is supported by additional characterization via atomic force, optical, and electron microscopy. This study demonstrates the ability to additively manufacture stiff, strong, and uniform materials comprised of sustainable cellulose nanofibro materials.

2:30 PM BREAK

1:30 PM NM04.08.01
Additive Manufacturing of Cellulose Nanofibril Materials
Kevin T. Turner, Lisa M. Mariani and John M. Considine; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2USDA, US Forest Service, Forest Products Laboratory, Madison, Wisconsin, United States.

Cellulose nanofibrils (CNFs) are high aspect ratio nanofibers (dia. ~10 nm) that have high specific stiffness and strength, and are also optically transparent and biodegradable. These properties make them attractive building blocks for bulk structural materials. However, to date, the overall dimensions of bulk materials comprised of CNFs are significantly limited by the development of residual stresses generated during the drying process. CNF solutions gel at low volume fractions (~1%), thus a significant amount of water must be removed during drying. Here, we overcome these issues by producing CNF films and structures by additive manufacturing (i.e., 3D printing) of a shear thinning aqueous CNF suspension under controlled drying conditions. The multistep layer-by-layer manufacturing process allows for control of drying and management of residual stresses. The fabricated materials have Young’s moduli and fracture strengths greater than 10 GPa and 70 MPa, respectively. Mechanical characterization is supported by additional characterization via atomic force, optical, and electron microscopy. This study demonstrates the ability to additively manufacture stiff, strong, and uniform materials comprised of sustainable cellulose nanofibril materials.

1:45 PM NM04.08.02
From Sol Gel Electrospun Composite Nanofibers to Ultralight and Flexible Aerogels
Tahira Pizzada and Saad A. Khan; Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States.

We present a facile and sustainable solid templating approach to fabricate highly porous and superhydrophobic aerogels of composite nanofibers of cellulose diacetate and silica which are produced through sol gel electrospinning. Scanning electron microscopy, contact angle measurement and attenuated total reflection-Fourier transform infrared spectrometry are used to understand the structural features of the resultant aerogels while thermogravimetric analysis and differential scanning calorimetry demonstrate their thermal stability as compared to cellulose diacetate. These aerogels exhibit a self-supportive three-dimensional network abundant in large secondary pores surrounded by primary pores resulting in a highly porous structure. Thermal crosslinking of the aerogels has further stabilized their structure and flexibility without compromising on the porosity. Ease of processing, thermal stability, high porosity and superoleophilic nature of these aerogels make them promising candidate for applications like thermal insulation and oil and water separation.

2:00 PM NM04.08.03
A High Concentration Approach to Magic-Sized Cluster Scale-Up

Magic-sized clusters (MSCs) are renowned for their identical size and precise composition, existing at an intermediate length scale between small molecule and conventional nanocrystal. Nanocrystal systems have been extensively studied and modeled to understand the synthesis, yet this knowledge does not directly translate upon scale-up and current production yields are miniscule. Furthermore, despite efforts, nanocrystals still possess a disparity in size, shape, and composition (although small) that in essence is a distribution of products. Hence, MSCs provide a quintessential framework to understand colloidal synthesis and assembly across length scales. Traditionally, the origin of the MSC stability was thought to derive from the “closed-shell” arrangement of atoms; this inhibits the continuous growth that is typically seen with nanocrystals. However, in semiconductor MSCs, we report that the MSC stability is strongly coupled to an organic-inorganic mesophase: a fibrous self-assembly of inorganic clusters passivated with organic ligands that form during high concentration (1000 mM) synthesis. This mesophase behaves as a large suspended network (~100 nm grains) that stabilizes and promotes a well-defined reaction pathway for the formation of high-purity MSC. Conversely, diluting precursor concentration (<500 mM) impedes mesophase formation and thus inhibits MSC formation. To identify the hexagonal mesophase where these MSCs persist, we utilized in-situ small and wide angle x-ray scattering, which also revealed that the rate of mesophase formation is proportional to the MSC nucleation rate. The MSCs still preserve their fibrous mesophase assembly after separation and purification. Akin to protein systems, these fibrous assemblies (secondary structure) of MSCs (primary structure) align into bundles (tertiary structure) that form banded (quaternary) structures under uniaxial shearing and drying. Polarization spectroscopy revealed that not only are the individual clusters strongly anisotropic with polarized emission, but also their assembly into highly ordered banded structures at the millimeter length scale yield polarized absorption. This high degree of polarization across magnitudes of self-assembled length scale enables investigation into novel optical properties, which previously has only been accomplished in metatomaterials. The high concentration synthesis of magic-sized clusters not only produces larger quantities of single-sized nanomaterials, but also deepens the understanding of nanosynthetic pathways and enables novel property development.

2:15 PM NM04.08.04
Lightweight Organosilica Foams Prepared from a Surface-Active Aminosilane and Cellulose Nanofibers
Korneliya S. Gordeyeva, Hugo Voisin, Niklas Hedlin, Lennart Bergström and Nathalie Lavonne; North Carolina State University, Raleigh, North Carolina, United States.

Organosilica foams are commonly obtained by elaborate multistep processes involving hydrolysis and condensation of organosilanes followed by solvent exchange and e.g. supercritical CO2 drying. Here, we report a novel, simple and energy-efficient approach for the preparation of hybrid organosilica foams from aqueous mixtures of a surface-active aminosilane (AS) and TEMPO-oxidized cellulose nanofibers (TCNF) that introduces air bubbles in the TCNF/AS dispersion by mechanical blending followed by ambient pressure drying to obtain the solid foam. The dry foams displayed low densities (25-50 kg/m3) and high porosities (96-99 %) with monodisperse macropore sizes of 150-300 µm. NMR showed that the hydrolysis and condensation of the surface-active AS was triggered by the increase of the temperature and solvent evaporation during the drying step. The influence of the pH and AS concentration on the foaming behavior and foam stability will be presented and correlated to the rheological properties and the interactions between the AS and TCNF. We will demonstrate that by variation of pH and AS concentration foams with defined density, homogeneity and porosity can be prepared.

2:30 PM BREAK

3:30 PM NM04.08.05
Nanocomposite Sensing Skins for Human and Structural Monitoring
Kenneth J. Loh; Department of Structural Engineering, University of California, San Diego, La Jolla, California, United States.
Both physical structures and human assets are susceptible to deterioration and damage that can degrade their performance, especially in challenging operational conditions. For example, the safety of aerospace, civil, and marine structures are jeopardized by damage due to excessive loading, corrosion, and impact. On the other hand, monitoring the health and physiological performance of the warfighter is necessary for ensuring their combat readiness. Therefore, the objective of this research is to develop a sensing platform that can be used for both structural health monitoring and human performance assessment. The approach is to design flexible and scalable coatings that are designed whose electrical properties are selectively sensitive to a certain type of external stimulus and can be deposited onto various structural surfaces. Here, these sensors are designed from a materials perspective stemming from a “bottom-up” design methodology. Nanomaterials and conductive polymers are judiciously chosen, and then assembled, to realized nanocomposite thin films that are sensitive to parameters such as strain or pH. First, this work begins with a discussion of how carbon nanotubes (CNT) and graphene nanosheets (GNS) could be used during spray-coating, micro-plotting, and screen-printing to form thin film strain sensors. Second, tensile-compressive tests were performed to validate their sensing behavior. Third, a percolation-based model was implemented to explain the nano/micro-scale mechanisms that enable their bulk film behavior, and the model was employed for determining fabrication parameters that enhanced sensing performance. However, even after optimization, a fundamental limitation was that they remained as discrete sensors, where one could only obtain information about the physical or human structure at the location where the sensor was instrumented. Thus, by coupling the films with an electrical impedance tomography (EIT) measurement strategy and algorithm, reconstruction of the two-dimensional resistivity or conductivity distribution of these materials was possible. These “sensing skins” could then be implemented to sense and localize damage features over large spatial domains. Distributed strain, impact, crack, and pH sensing was successfully validated.

4:00 PM RAPID FIRE PRESENTATION

SESSION NM04.09: Poster Session III: Nanocomposites
Session Chairs: Babak Anasori, Monica Jung de Andrade and Maria Perez Barthaburu
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Ihnes, Level 1, Hall B

NM04.09.01
Impact of Graphene Oxide Disparsity on Its Applications Harish V. Kumar, Thomas Francinc and Douglas Adamson; Polymer Program- Institute of Materials, University of Connecticut, Storrs, Connecticut, United States.

Graphene oxide (GO) is used in various applications due to its unique surface properties. One of the important features of GO is that it stabilizes oil-in-water emulsions by staying at the interface of the two phases. We harness this property of GO to act as a surfactant in order to characterize, fractionate, and use the system for various applications. Different batches of GO are composed of graphene sheets with different degrees of oxidation. We divide graphene oxide sample into differently oxidized fractions using emulsion based fractionation method. In this emulsion based method, more oxidized GO sheets suspend in a water phase, while the less oxidized material stabilizes the emulsion phase. This method provides the ability to control different properties of GO. These GO fractions are characterized by different techniques including XRD, UV/vis, elemental analysis, and Raman spectroscopy.

Further, we explore the property changes of polymer/graphite oxide (GO) nanocomposites as the degree of GO oxidation is changed. We have found that emulsifying a sample of GO separates the sheets into fractions of differing degrees of oxidation and we have demonstrated that this variation in degree of oxidation of GO plays a role in the improvement of tensile properties of GO based polymer nanocomposites. The interaction of GO sheets with the polymer matrix plays an important role in the mechanical properties of the nanocomposites. In addition, the mechanical properties are also dependent on the hydrophilic or hydrophobic nature of the polymers. We further investigate polymer nanocomposites made from oil-in-water emulsion systems stabilized by GO. The nature of the emulsion is controllable by replacing a part of GO with graphene sheets as well as by altering the type of GO used. This approach provides a route to control the shape and conductivity of these polymer nanocomposites.

In addition, we describe further merits of the fractionation method, as well as explain the impact controlling the extent of oxidation has on various other GO based applications.

NM04.09.02
Ultrasonic Deacetylation—A Rapid Method to Covert Cellulose Acetate into Cellulose Nanofibers Muzamil Khatri, Ick Soo Kim and Zeeshan Khatri; Shinshu University, Ueda City, Japan.

Electrospun nanofibers are getting more attraction because of their prominent applications such as light weight, permeability, breathability, filtration, biomedical, apparel and functional applications. Cellulose nanofibers because of high absrobency and high surface area is also considered one the efficient material for potential applications. Getting electrospun cellulose nanofibers is highly time consuming, conventionally deacetylation process takes upto 30 hours to convert cellulose acetate into cellulose. We attempted to use ultrasonication to enhance efficiency of deacetylation process. We successfully deacetylated cellulose acetate by using ultrasonic method which only took 1 hour instead of 30 hours. SEM showed smooth morphology before and after ultrasonic deacetylation. XRD showed increased crystallinity after deacetylation because cellulose substrate has more crystalline region. Wicking behaviour was also enhanced after deacetylation which is another evidence to justify conversion. FTIR showed chemically converted cellulose after deacetylation process.

NM04.09.03
Surface-Modified Cellulose Nanofibers for the Effective Reinforcing Materials of Poly(e-caprolactone) Composites Hiroki Ichimura, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama-shi, Japan.

Poly(e-caprolactone) (PCL) is one of the leading biocompatible and biodegradable polymers, having the great potential for an alternative material of polyolefins such as polyethylene and polypropylene. However, the mechanical property of PCL is relatively poor as compared with that of polyolefins, which has limited the active applications of PCL for an industrial material. In this study, to enhance the mechanical property of PCL, cellulose nanofibers (C-NF), compounding agents of several composites due to their high mechanical property, were investigated for the reinforcement material of PCL. The C-NF were fabricated via the electrospinning of cellulose acetate (CA) before the saponification of CA. The spinning solution was prepared by dissolving CA in the mixed solvent of acetone/dimethylacetamide (6/4 wt/wt) and the concentration of CA was set at 20 wt%. The electrospun CA nanofibers were saponified in a 0.05 M NaOH/ethanol solution to finally obtain C-NF. For the enhancement of the mechanical property of the PCL composite, the compatibility of C-NF and PCL was studied. The surface modification of C-NF was performed by the ring-opening polynamidation to graft PCL onto C-NF.
The RC-NF were compounded into poly(vinyl alcohol) (PVA) by the film-casting method to fabricate RC-NF/PVA composites. The mechanical properties such as modulus. However, it was found that the direct annealing of RC-NF resulted in no effect in increasing the crystallinity of the RC-NF. It was considered that annealing at higher temperature was necessary for improving the crystallinity of the RC-NF. By considering the Helpin-Tsai equation, it was found that the Young's modulus of the RC-NF increased from 11.2 to 28.0 GPa. The correlation between the crystallinity of the RC-NF and the annealing time at 50°C was observed and it reached ~3.0 GPa, when CA-NF were annealed at 75°C for over 4 h or annealed at 100°C for over 0.5 h. The Young's modulus of PVA with non-annealed RC-NF was ~2.1 GPa, and the modulus of PVA with annealed RC-NF increased from 37 to 41% up to the annealing time of 12 h, which became constant after 12 h. The CA-NF were annealed at 50°C, the crystallinity of the resulting RC-NF increased by 17% compared to that of PCL, while, compounded with CA-NF-g-PCL, it reached 25%. The fracture surfaces of the composites were analyzed by SEM. Through the image analyses, it was confirmed that the interfacial adhesion between PCL and CA-NF was successfully improved by the surface modification. The results demonstrated that the effective surface modification of CA-NF fabricated via electrospinning was realized by the CA-NF-g-PCL/PCL composites.

NM04.09.04
Enhancement of the Mechanical Property of poly(ε-caprolactone) Composites with Surface-Modified Cellulose Nanofibers Hiroki Ichimura, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama-shi, Japan.

The use of natural products as reinforcement materials of composites has recently been actively studied. Among the reinforcement materials, cellulose is attracting considerable interest because of its high mechanical property and high biocompatibility. In fact, the enhancement of the mechanical properties of the composites by reinforcing cellulose nanofibers (CNF) has already been reported. In this study, CNF fabricated via the electrospinning of cellulose acetate (CA) before the saponification of CA, were compounded into poly(ε-caprolactone) (PCL) to improve the mechanical properties. In the electrospinning method, the spinning solution with CA in the mixed solvent of acetone/dimethylacetamide (6:4 v/v) was concentrated at 20 wt% was prepared. The CA-NF were then introduced to a syringe with stainless needle. Then a high voltage of 12 kV was applied between the syringe needle and a ground collector to fabricate CA nanofibers. The obtained CA nanofibers were dried under vacuum at 50°C for 24 h and saponified in 0.05 M NaOH/ethanol solution for 24 h to convert CA nanofibers into CA-NF. In addition to the fabrication of CNF, the surface modification of the CNF was also performed to improve the compatibility with the PCL for the enhancement of mechanical properties of the composites. In order to graft PCL onto the CNF to make CNF-g-PCL, the ring-opening polymerization was carried out as follows: CNF, tin(II) 2-ethylhexanoate (a commonly used catalyst for the polymerization of lactones), ε-caprolactone, and super-dehydrated toluene were added to a flask in a glove box under argon atmosphere. The flask was then set into an oil bath and the polymerization was allowed to proceed in the flask at 130°C for 1 hour to obtain CNF-g-PCL. The Fourier transform infrared (FTIR) spectroscopy was used to determine the structures of the CNF and the CNF-g-PCL. The FTIR results indicated that the polymerization was successfully conducted. The compression molding method was employed to fabricate CNF/PCL or CNF-g-PCL/PCL composite films. CNF or CNF-g-PCL was inserted between two compression-molded PCL sheets, which was thermally compressed at the pressure of 8 MPa at 80°C. Tensile testing was performed to examine the mechanical property of the CNF/PCL and the CNF-g-PCL/PCL. At the fiber concentration of 15 wt%, the Young's modulus of PCL compounded with CNF-NF-g-PCL increased by 17% compared to that of the composite with neat CNF. The fracture surfaces of the composites were analyzed by the scanning electron microscopy (SEM). The image analyses confirmed that the interfacial adhesion between the PCL and the CNF was substantially improved by the surface modification.

NM04.09.05
Mechanical Properties of Poly(vinyl alcohol) Composites with Electrospun Cellulose Nanofibers Annealed at Different Temperatures Shunya Inukai, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama, Japan.

We synthesized highly crystallized regenerated cellulose nanofibers (RC-NF) through the annealing and the subsequent saponification of cellulose-acetate nanofibers (CA-NF) that were used as reinforcement materials for poly(vinyl alcohol) (PVA). We especially focused on the studies of the effects of the annealing temperature on the mechanical property of RC-NF/PVA composites. To enhance the mechanical properties of the RC-NF/PVA composites, annealing was first carried out for the RC-NF to raise the crystallinity. However, it was found that the direct annealing of the RC-NF did not affect the crystallinity. It was considered that the hydrogen bonding of the hydroxyl groups (-OH) in the RC-NF could be too strong to maintain the molecular movement of the cellulose required for the increase in the crystallinity. In this study, we investigated highly crystallized RC-NF through the annealing and the subsequent saponification of CA-NF. Cellulose-acetate (CA), a derivative of cellulose, possesses a smaller amount of hydrogen bonding as compared with cellulose, thus maintaining a sufficient molecular movement to obtain higher crystallinity. Therefore, highly crystallized RC-NF could be obtained via the saponification of the annealed CA-NF. CA-NF were fabricated by electrospinning, subsequently annealed at 50, 75, and 100°C for 0-12 h above the glass transition temperature of the CA. The annealed CA-NF were then saponified to obtain highly crystallized RC-NF. The crystallinity of the RC-NF was measured by the X-ray diffraction (XRD). The RC-NF were compounded into poly(vinyl alcohol) (PVA) by the film-casting method to fabricate RC-NF/PVA composites. The mechanical properties of the RC-NF/PVA were investigated by tensile testing. It was found that the CA-NF annealed at 50°C, the crystallinity of the resulting RC-NF increased from 37 to 41% up to the annealing time of 12 h, which became constant after 12 h. The CA-NF annealed at 75°C for over 4 h and at 100°C for over 0.5 h produced highly crystalline RC-NF reaching 41% in crystallinity at the maximum. The Young's modulus of PVA with non-annealed RC-NF was ~2.1 GPa, which increased as the annealed RC-NF annealing time increased. The Young's modulus eventually reached ~3.0 GPa at the maximum, becoming constant after 12 h of the annealing time at 50°C. It also reached ~3.0 GPa, when CA-NF were annealed at 73°C for over 4 h or annealed at 100°C for over 0.5 h. By considering the Helfin-Tsai equation, it was found that the Young's modulus of the RC-NF increased from 11.2 to 28.0 GPa. The correlation coefficients between the crystallinity and the Young's modulus of the RC-NF fabricated from the CA-NF annealed at 50, 75, and 100°C, were 0.970, 0.945, and 0.991, respectively. It was concluded that the maximum crystallinity and Young's modulus could be gained at shorter annealing time when annealed at higher temperature.

NM04.09.06
Annealing and Saponification of Electrospun Cellulose Nanofibers for a Reinforcement Material of Poly(vinyl alcohol) Composites Shunya Inukai, Naruki Kurokawa and Atsushi Hotta; Keio University, Yokohama, Japan.

Compounding relatively strong fibers into polymer materials has been one of the effective ways to enhance the mechanical properties of the polymers. It is well known that the higher aspect ratio of nanofibers in polymer composites could result in the increase in the specific surface area of the nanofibers, thus eventually improving the adhesion between the polymer matrix and the fibers. Electrospinning is also known as an effective way to make polymer nanofibers with high aspect ratios. Among the electrospun cellulose nanofibers, regenerated cellulose nanofibers (RC-NF) fabricated by the saponification of electrospun cellulose-acetate nanofibers (CA-NF), are attracting considerable interest as reinforcement materials. In fact, improvement of the mechanical property of RC-NF is the key to generate polymer composites with excellent mechanical property. For this purpose, an annealing process is an effective way to raise the crystallinity of the targeted polymers, hence improving the mechanical property, leading to the fabrication of fibers with higher tensile modulus. However, it was found that the direct annealing of RC-NF resulted in no effect in increasing the crystallinity of the RC-NF. It was considered that...
the hydrogen bonding of the hydroxyl groups (-OH) in the RC-NF was too strong, inhibiting the enough molecular movement of the cellulose required for the improvement of the crystallinity.

In this study, we, therefore, synthesized highly crystallized RC-NF through the annealing and the saponification processes of CA-NF. Cellulose-acetate (CA), a derivative of cellulose, possesses a smaller amount of hydrogen bonding as compared with cellulose, thus carrying sufficient molecular-movement characteristics to obtain higher crystallinity. In more detail, the CA-NF were first annealed, and acetyl groups (-OCOCH3) of the annealed CA-NF were then replaced with hydroxyl groups (-OH) to obtain highly crystallized RC-NF. The annealing time was changed, while the annealing temperature was kept constant at 50°C, which was above the glass transition temperature of CA.

The CA-NF were fabricated by electrospinning, which were then annealed and saponified to obtain highly crystallized RC-NF. The crystallinity of RC-NF was measured by the X-ray diffraction (XRD). By increasing the annealing time of CA-NF from 0 to 12 h at 50°C, the crystallinity of RC-NF increased from 37 to 41%, which became constant after 12 h. It indicated that highly crystallized RC-NF were successfully obtained by the annealing and the saponification of CA-NF. Finally, the RC-NF were compounded into poly(vinyl alcohol) (PVA) by the film-casting method to fabricate RC-NF/PVA composites. The mechanical properties of the RC-NF/PVA were investigated by tensile testing. The Young’s modulus of the RC-NF/PVA increased from 2.1 to 3.0 GPa by raising the annealing time from 0 to 12 h, after which it became constant, whereas that of pure PVA was 1.5 GPa.

NM04.09.07 Highly Stable Photoconductive Cellulose Paper—A Bright Future for Flexible Paper Electronics Naveen ul Hassan Alić, Samim Sardar, Xavier Crispin and Magnus Jonsson; Laboratory of Organic Electronics, ITN, Linköping University, Norrköping, Sweden.

These days cellulose paper is ubiquitous in our daily life. For thousands of years, cellulose paper has been a major medium for displaying and transmitting information in many parts of the world. Its chemical and mechanical stability under atmospheric conditions and ability to absorb ink readily remain unmatched by other materials used in large abundance. Cellulose, the major component of paper, can be obtained from plants and represents one of the most abundant organic materials on earth. Cellulose by itself is usually limited in functionalities. Recently, research on organic/inorganic cellulose composites has increased dramatically due to the potential applications in electronics, biosensors, and energy storage devices [1-4].

The integration of functional micro and nanostructures into the paper, such as zinc oxide tetrapods or nanoparticle powders, has opened up many opportunities for applications in advanced energy harvesting systems and electronic devices [5-6]. In this respect, one of the major challenges is to avoid leakage of the micro- and nanoparticles from the paper over time. This is a serious problem that is limiting their applications into the practical devices. In this work, we present a novel, environmentally friendly and fully scalable approach enabling the production of highly stable paper functionalized with zinc oxide nanotetrapods or nanoparticle powders, has opened up many opportunities for applications in advanced energy harvesting systems and electronic devices [5-6]. In this respect, one of the major challenges is to avoid leakage of the micro- and nanoparticles from the paper over time. This is a serious problem that is limiting their applications into the practical devices. The device shows a strong and repeatable 65 µA photocurrent signal under simulated sunlight. This is more than 100 and 10,000 times better than the photocurrent of our control samples fabricated using zinc oxide tetrapods and nanoparticles, respectively. In addition to the superior photoconductive properties, our paper is smooth and mechanically strong, allowing its applications in a range of flexible energy and electronics devices.


NM04.09.08 Effect of Surface Nanocrystallization on the Mechanical Properties of AISI 304 Stainless Steel Wire Temitope O. Olugbade and Jian Lu; City University of Hong Kong, Hong Kong, Hong Kong.

The effect of surface mechanical attrition treatment (SMAT) on the mechanical properties of 304 stainless steel (SS) wire was investigated using different ball materials and wire diameter. The surface characterization after SMAT was observed by scanning electron microscope (SEM) and X-ray diffraction (XRD). The mechanical properties were studied through yield stress, ultimate tensile stress, and fracture elongation. At different treatment time, the SMAT operation using the same amount of Tungsten Carbide (WC) and 304 SS balls significantly enhanced the strength of the material as well reduced the fatigue damage and other material-related failures such as crack. The tensile test, with a tensile speed of 1.5 mm/min at room temperature, indicated a marked increase in strength after SMAT. Compared to the untreated sample, the 304 SS wire subjected to SMAT experienced a great improvement in yield stress, ultimate tensile stress, and reduction in fatigue fracture. The type of ball used, and the wire diameter also has a significant effect on the mechanical properties. The surface characterization by SEM and XRD revealed an improvement in the yield and ultimate tensile stress of the SMATed samples using WC balls and 1.5 mm wire. The nanostructured material will find applications in biomedical and nanomanufacturing sectors.

NM04.09.09 Flame Retardant and Antiwetting Cellulose-Based Composite Aerogels as Sustainable Engineering Materials for Sound Adsorption Application Xianjing Gong; Materials Science and Engineering, City University of Hong Kong, Hong Kong, SAR, Hong Kong.

Cellulose nanofiber (CNF) is an attractive bio-material and has advantageous properties such as light weight, excellent mechanical property, high aspect ratio, good thermal stability, as well as relatively low cost. In this study, we demonstrate a sustainable composite aerogel with sound adsorption, flame retardant and antiwetting abilities, the structure of which is composed of modified CNF and aluminium hydroxide (Al(OH)3). Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to confirm the modification of CNF and the formation of Al(OH)3. Then scanning electron microscopy (SEM), sound-adsorption test, thermogravimetric analysis (TGA) and contact angle test were conducted. These results imply promising applications for practical engineering materials.

NM04.09.10 Strong, Flexible and Transparent Films of Lignocellulose Produced by Tailoring the Electrostatic Interactions Yingxin Liu; Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden.

The assembly of nature-based nanomaterials into complex architectures is both a design principle of biological composites, e.g., nacre with outstanding properties and a promising route for developing functional macroscopic materials. Our study aims to investigate the colloidal assembly behavior of nanocellulose in aqueous dispersions. Moreover, composite films of nanocellulose and nanoclay/lignin with diverse functionalities are fabricated by tailoring the electrostatic interactions of these building blocks.

Initially, optically transparent films of synthetic aminoclay (50 wt%) and cellulose nanofibril (CNF) were fabricated, of which tensile strength and strain to failure (205 MPa and 7.5%) were significantly higher than previously reported nacre-mimicking nanocellulose-based materials, e.g., montmorillonite-CNFM04.09.11
films, due to the formation of ionic bonding between the cationic clay and anionic CNF. On the other hand, anionic lignin nanoparticles were tested to enhance the colloidal stability and dispersity of carboxylated CNF in dispersions, and showed an effective strengthening and stiffening effect on the matrix of CNF. The mechanical properties of lignin-CNF films were superior to previously reported polymer/nanoparticle-CNF composites, such as polyvinyl alcohol-CNF films and even reduced graphene oxide-CNF films. The low cost of nanocellulose in combination with the excellent mechanical performance and functionalities of above composite films sheds light on potential applications such as substrates for optoelectronics.

**NM04.09.11**

**Mechanical and Microstructural Characterisation of Graphene Oxide Reinforced Aluminium Matrix Nanocomposites**

Fei Li1, Ian A. Kinloch1, Robert Young1, Shaojun Yan2, Qihu Hong2, Xiang Chen3, Xiaoyan Zhang2 and Shenglong Dai4; 1Advanced Nanomaterials Group, National Graphene Institute and School of Materials, The University of Manchester, Manchester, United Kingdom; 2Beijing Institute of Aeronautical Materials, Beijing, China.

Due to its low density and high Young’s modulus, graphene is able to make Aluminium (Al) matrix composites lighter and stronger. These materials are in demand for structural materials in airplanes, automobiles and other transportation applications. These structural materials can contribute to low carbon emissions, sustainable development and the overall economy. Al matrix nanocomposites reinforced with graphene related materials, have been developed well in the last decade. We have investigated the relationship between the mechanical properties and microstructure for Graphene Oxide (GO) reinforced Al matrix nanocomposites.

A powder metallurgy (PM) method was employed to produce GO reinforced Al matrix composites. We fabricated Al matrix composites with 0.3, 0.5, 1.0 wt. % loadings of GO, and pure Al as well for comparison. By using large area Raman mapping and SEM respectively, we found the GO flakes to be dispersed well and located at the grain boundaries of the Al matrix in the composite. In addition, GO was aligned well in the direction of extrusion, indicated by Raman orientation investigations. Interestingly, the GO can even hinder grain growth of the Al matrix. Grain refinement was observed in the composite, caused by the barrier effect of GO. Quantitative information of the grain orientation and grain size was obtained from the analysis of EBSD (Electron Backscatter Diffraction) results. Aluminium carbides were not detected by either X-Ray Diffraction (XRD) or Raman spectroscopy, and thus chemical reaction at the interface did not take place. Nanoindentation experiments were conducted to determine the mechanical properties of the pure Al and reinforced Al matrix composites as well. For macro mechanical properties, Young’s modulus and hardness of the Al matrix composite were improved by adding 0.3, 0.5 and 1.0 wt. % GO in comparison with pure Al. GO has the ability to improve the mechanical properties of Al matrix composite when it is dispersed uniformly in the composite. However, the composite with a loading of 0.5 wt. % GO, rather than with 1.0 wt. %, was found to have the most strengthening effect. We observed some agglomeration in the composite reinforced with 1.0 wt. % GO from SEM images, which induced more defects, more pores, less interfacial area, and a lower effective modulus. We believe these factors may explain why its Young’s modulus was not as high as expected. In addition, SEM (Scanning Electron Microscopy) was used to observe the microstructure around the indented areas. Indeed, the mechanical properties of the composites are closely linked to the microstructure. After indentation, we can see that the GO flakes between grain boundaries hinder the movement of the dislocations. Al matrix grains experienced their plastic deformation by slipping or twinning when the dislocations cannot move further due to obstruction by the GO. These microstructural changes resulted in better mechanical performance of the composites.

**NM04.09.12**

**A Novel Process to Fabricate Nano Carbon Reinforced Copper Matrix Composites Utilizing Self-Assembly of Bioinspired Polydopamine**

Yao Zhao, Filippo Di Carlo, Bosen Qian, Haoqi Li, Zhuohe Zhang and Fei Ren; Mechanical Engineering, Temple University, Philadelphia, Pennsylvania, United States.

Introduction of nanocarbons, such as graphene and carbon nanotubes, to metal matrices may enhance the electrical and thermal transport and mechanical properties of the composite materials. In this study, copper (Cu)-polydopamine (PDA) composite was fabricated by coating Cu powders with the bioinspired PDA polymer, which was then converted to graphite-like structure during the subsequent sintering. Structural characterization using SEM, TEM, and Raman spectroscopy demonstrated the formation of the graphite-like structure in the composite. Compared to the pure Cu sample, the Cu-PDA composite showed increased electrical conductivity, higher microindentation hardness, and enhanced wear resistance. These findings suggest inclusion of nanocarbon phase converted from PDA can simultaneously improve the electrical and mechanical properties of sintered Cu materials. Effect of coating time (carbon content) on the microstructure and properties of the composites will also be discussed.

**NM04.09.13**

**Mechanical Properties of Polydopamine Thin Films**

Haoqi Li, Qian Dong, Quiting Zhang, Yao Zhao, Zhuohe Zhang, Huijun Liu, Jie Yin and Fei Ren; Temple University, Philadelphia, Pennsylvania, United States.

Polydopamine (PDA) is a recently discovered bioinspired polymer. Coating and freestanding films of PDA can be fabricated via the self-assembly process of dopamine molecules in mild conditions. Many interesting properties of PDA have been reported. One potential application of PDA thin film is in soft and flexible devices, where the mechanical property of the film and adhesion to substrate are critical. By adding dopamine hydrochloride into alkaline solution, freestanding PDA films were synthesized at the air/solution interface, which was then transferred onto capillary tubes. The vibrational response of PDA freestanding film was investigated using acoustic impulse method, from which the elastic modulus was determined. Meanwhile, by studying the surface buckling behavior of PDA coating on PDMS substrate, the adhesion between the two materials was obtained. Furthermore, wear resistance of PDA films was evaluated using nanoscratch test. Effects of film thickness and metal ion doping were also investigated.

**NM04.09.14**

**Effect of Encapsulation of Citric Acid with Zeolite Nanoparticles on Its Heat Resistance in Polymer Composite**

Hye Mi Choi1, Young Min Lim1, Dong Soo Shin2, Gun Young Kwak1 and Tae Hwan Oh3; 1Yeungnam University, Gyeongsan, Korea (the Republic of); 2Clavis, Gyeongsan, Korea (the Republic of); 3Dyteec, Daegu, Korea (the Republic of).

Citric acid having low heat resistance was encapsulated by zeolite nanoparticles and zeolite/citric acid capsules were coated by titanium oxide (TiO2) to enhance the heat stability of the citric acid during melt processing of polymer/citric acid composite. The conditions to maximize adsorption of the citric acid were investigated for citric acid concentration, adsorption temperature and time. Reaction conditions for TiO2 coating onto zeolite were also investigated for enhancing the heat resistance of the citric acid during melt processing of polymer/citric acid composite. The presence of the citric acid after its adsorption into zeolite was measured by electrical conductivity change with concentration. By coating TiO2 on zeolite, the heat resistance of the citric acid increased and hence after melt extrusion, we could observe the survival of the citric acid after melt extrusion.

**NM04.09.15**

**Synthesis of Eco-Friendly Nano-Structured Biosurfactants from Vegetable Oil Sources and Characterization of Their Interfacial Properties for**
Cosmetic Applications: JongChoo Lim, DaNan Yea and SeonHui Jo; Dongguk University, Seoul, Korea (the Republic of).

The enormous market demand for surfactants is currently met by numerous synthetic, mainly petroleum-based, chemical surfactants. These compounds are usually toxic, non-biodegradable and environmentally hazardous. Tightening environmental regulations and increasing awareness for the need to protect the ecosystem have effectively resulted in an increasing interest in biosurfactants as possible alternatives to chemical surfactants. They have advantages over their chemical counterparts in specificity, relative ease of preparation, mildness, and effectiveness even at extreme temperature or pH. Biosurfactants also have the merit of diversity, environment friendly nature such as nontoxicity and excellent biodegradability, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection. Due to their unique functional properties, biosurfactants have been used in various industries including agriculture, fertilizers, petroleum, petrochemicals, cosmetics, pharmaceuticals, personal care products, food processing, beverages, textile manufacturing, metal treatment and processing, pulp and paper processing, paint industries and many others. They can be used as emulsifiers as well as demulsifiers, wetting agents, foaming agents, spreading agents, environmental cleanup of pollutants, functional food ingredients and detergents. In this study, 3 types of zwitterionic phospholipid biosurfactants were prepared using 3 different raw materials such as rapeseed oil, coconut oil, and cottonseed oil respectively and the structure of the resulting products was elucidated by FT-IR, 1H NMR, and 13C NMR spectroscopies. Biodegradability, acute oral toxicity (LD₅₀), acute dermal irritation and acute eye irritation tests revealed that the newly synthesized biosurfactants possess excellent mildness and superior environmental compatibility as well as superior interfacial properties, indicating the potential applicability in cosmetic product formulations. The patch test has been performed with 0.1 mL of 0.5 wt% surfactant solution and the result has shown that the newly prepared biosurfactants indicated no allergic inflammation on a skin during 48 hrs. The prescription test in shampoo formulation prepared with the newly synthesized biosurfactants indicated excellent sensory feeling and foam ability compared with conventional hydrocarbon and silicon surfactants. In particular, CDP(S) surfactant can be considered as a strong candidate for the potential applicability in cosmetic product formulations since the newly synthesized CDP(S) surfactant is highly surface active, mild, nontoxic, non-irritating and readily biodegradable.

ACKNOWLEDGEMENTS
This work was supported by "the Technology Innovation Program"(10063387, Development of aryl phenol surfactants and paint additives for the replacement of nonyl phenol) funded by the Ministry of Trade, Industry & Energy, Korea.

NM04.09.16
Mechanical Properties of Rubber Composite Reinforced by Cellulose Nanofiber: Tomoyuki Sakai; The Yokohama Rubber Company Ltd, Kanagawa, Japan.

Yokohama Rubber Company Ltd. has been researching on sustainable materials for rubber as an environmentally friendly company. We prepared NR and SBR reinforced with TEMPO oxidized cellulose nanofibers (TOCN), which were modified from wood pulp, instead of traditional carbon black derived from petroleum. The Wood-derived TOCN can contribute to an effective use of forests and to a recycling-based society. They have average 3 nm in diameter and high aspect ratio. The wear resistance and viscosity of the rubber-TOCN composites were investigated for the application of automotive tires. Their tensile stress was larger than that of the same amount of carbon black reinforcement. We will discuss how to improve their mechanical property by examining the rubber on the interface of cellulose nanofibers.

This research was supported by grants from the Project of the NARO Bio-oriented Technology Research Advancement Institution (R&D matching funds on the field for Knowledge Integration and innovation)

NM04.09.17
Manganese Incorporation on Structural, Optical and Photocatalytic Properties of ZnO Nanofibers: Ilyas Savkilyildiz1, 2, Elif Baylam2 and Ozlem A. Yildirim1, 1: 1Selcuk University, Konya, Turkey; 2Konya Technical University, Konya, Turkey.

There is currently intense interest in the elimination of the organic dye compounds in the water via photocatalytic reactions. Zinc oxide (ZnO) nanofibers are known to act as a promising photocatalyst for its high catalytic activity, low cost, and environmental friendliness. Visible-light photocatalytic properties of ZnO nanofibers can be improved with metal doping. To improve photocatalytic activity of ZnO nanofibers, manganese-doping (ZnO:Mn) is appreciable because manganese behaves highly reactive catalyst in the photocatalytic reactions. Furthermore, synthesis of ZnO:Mn nanofibers with well-controlled size and morphology have been also attracted great attention to enhance photocatalytic efficiency. In this study, we aimed to improve visible-light photocatalytic activity of Mn doped ZnO nanofibers via electrospinning technique to eliminate interparticle interactions. The effects of doping level and aspect ratio of nanofibers, on the band structure of ZnO and finally photocatalytic properties of ZnO:Mn nanofibers were investigated through XRD, XPS, HRTEM, FESEM and UV-Vis spectroscopy. The results showed superior photocatalytic activity for 1.5 at.% Mn doped ZnO nanofibers and the complete decomposition of Methylene Blue has been achieved after 120 minutes UV illumination.

NM04.09.18
Polymerization of Valerolactone Derived from Biomass for Eco-Friendly Powder Coating: Lim Hanwhyu1, 1: 1Yonsei University, Seoul, Korea (the Republic of); 2Green Chemistry and Materials Group, Korea Institute of Industrial Technology, Cheonan, Korea (the Republic of).

Valerolactone is a biomass material that can be obtained through catalysis from mevalonic acid obtained by fermentation of glucose. It is used as an environmentally friendly application material and it also can be applied as powder coating material without organic solvent. In order to use valerolactone as a coating material, it is necessary to polymerize by ring opening transesterification polymerization (ROTEP) reaction, and it have to be optimized according to the type, amount of catalyst and reactant conditions. As a result, ROTEP polymer was successfully synthesized using valerolactone using 0.75 wt% TBD catalyst. The result is 30,000 g/mol, Mw and PDI = 1.2 confirmed by GPC. Furthermore, we also discussed the application of additional functional groups to enhance the biomass ratio. After replacing the terminal of the polymerized polymer with hydroxyl groups, molecular weight could increase with bio-based content. The synthesized compounds were applied to coating material as the powder form.

NM04.09.19
Flammability and Structural Characterization of LDPE/EVA Blend Composites Containing Keratin Fibers and DNA as a Flame Retardant: Saul Sanchez, Eduardo Ramirez, Jorge Albitre, Yuresis Nuñez and Rogelio Ramirez; CIQA, Saltillo, Mexico.

The combination of keratin fibers obtained from feathers, with deoxyribose nucleic acid (DNA) applied as a coating with a segregated structure on filler dispersion and flame retardant properties of low-density polyethylene-ethylene vinyl acetate (LDPE/EVA) blends was investigated. A maleic anhydride modified polyethylene (PEGMA) was used as compatibilizer. The thermal stability and flame retardant properties were evaluated by Limiting Oxygen Index (LOI), Cone calorimeter determinations and Flammability test (Underwriters Laboratory - UL-94). The structural characterization was carried out by
FTIR and scanning electron microscopy in transmission mode (STEM). The mechanical properties were also evaluated. The effect of coating procedure, directly affecting segregated structure deposition, on DNA dispersion and flame-retardant behavior was discussed. The results indicated that the DNA deposition method of segregated structure promoted the best flame retardant behavior and that the incorporation of keratin fibers enhanced the mechanical performance of the nanocomposites. It was demonstrated that DNA induced a char foam layer that was able to quite efficiently protect the blend polymer matrix against heat, reducing the combustion kinetics. The thermal stability of PE/EVA blends increased to a higher extent when using these filler combinations.

NM04.09.20
Materials Engineering—Controllable Defect Nanomaterials for Electrical and Biological Application
Li Wei Huang1, Chun-Yen Lai2, Lin M. Ling1, Ping-Hung Ye1 and Wen-Wei Wu2; 1Tamkang University, New Taipei City, Taiwan; 2National Chiao Tung University, Hsinchu City, Taiwan.

For materials engineering, the various electrical properties of Poly-SnO$_2$ nanofiber can be obtained by controlling fabrication processes. By well controlling fabrication processes, there are several specific materials can be found, such as defect-free, defect-rich and defect-controlled SnO$_2$ nanofiber. In this research work, defect-free sample has strong reaction with UV light. But if the defect amount was increased by changing formation process, the defect-rich poly crystal nanofibers can be obtained to make an ultra-sensitive nano-sensor. Because the nano-sensor has huge defect that will give the device to has ultra-high sensitivity; the current of the nano-sensor can be easily varied by light and surrounding gas. This property can make our nano-sensor as room temperature gas (50 ppb NO) detector. This nanomaterial also can control the defect amount to fit the biological antibacterial purpose by well controlled the fabrication process. In a well-controlled defect amount, the nanomaterial can provide Hydroxyl by specific light in moisture solution to prevent bacterial infections. In our work, the E-coli can be effectively reduced by our nanomaterials substrate due to the Hydroxyl.

SESSION NM04.10: Toxicology, Monitoring and Depollution I
Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Back Bay C

8:30 AM *NM04.10.01
Nanotoxicology and Environmental Impact of Carbon Nanomaterials—A Focus on Double-Walled Carbon Nanotubes

Carbon nanotubes (CNTs) are often the emblematic figure of nanoparticles in general, promoted by many for their exceptional physico-chemical properties which have led to applications in almost all fields, and criticized by the others for their potential toxicity toward human health and the environment. After a general introduction to the toxicity of nanoparticles, we will focus on the case of CNTs and in particular of double-walled CNTs (DWCNTs) [1] which represent a unique category at the interface between single-wall CNTs and multi-walled CNTs. The interaction of DWCNTs with the immune system [2, 3] will be described, showing that if these CNTs activate this defence mechanism, there are also potential ways to moderate this through appropriate surface functionalisation. Some examples of interaction of DWCNTs with cancer cells [4] or bacteria [5] will also be given as illustrations of potential biomedical applications.

Finally, we will summarise our recent work on the question of the choice of the most appropriate metric in order to allow the comparison of the results obtained for different kinds of nanocarbons (different carbon nanotubes, few-layer graphene, nanodiamonds) as well as a sample of carbon black, in the case of their environmental impact [6]. Experimental results obtained using an amphibian larvae model (xenopus), very relevant for the aquatic compartment and especially the water column, clearly show that only the specific surface area allows the plot of all the data on the same "master curve", even making possible to become predictive and to propose a "Surface effective concentration" SEC$_{50}$. These results have also been recently extended to the comparison of nanocarbons dispersed in water by either covalent (oxidation) or non-covalent (addition of a surfactant) functionalisation, confirming that the specific surface area is still the relevant parameter.

Acknowledgement
The research received funding from the European Union 7th Framework Program under grant agreement N°785219 Graphene flagship.

References
Sustainability should be an objective of every future technology. Especially nanotechnology has shown that worries and concerns of consumers may hamper the development of nanomaterials. In the face of the conflict between immediate marketing of innovative products containing engineered nanoparticles (ENP) and the precautionary principle regarding the potential environmental and human risks we established a multidisciplinary consortium of 10 academic, industrial and regulatory partners, which worked on manifold questions within project. For a sustainable production of goods containing ENPs it is crucial to have no adverse effects on the environment. Therefore, the project focused on the study of the long-term characteristics of ENPs under various environmental conditions. Silicon dioxide nanoparticles (SiO\textsubscript{2} -NP) and cerium dioxide nanoparticles (CeO\textsubscript{2} -NP) were selected because of their prevalence and commercial relevance. Utilization oriented aspects were studied on SiO\textsubscript{2} -NP spiked lubricants as an exemplary application. On the other hand innovative functionalized variations of SiO\textsubscript{2} -NP and CeO\textsubscript{2} -NP (e.g. doped) are produced by lab- and pilot scale gas phase reactors. For these materials an enormous marketing potential is expected due to their presumed low toxicity and multiple application possibilities.

On the other hand we detected, tracked and modeled the life cycles of the ENPs in the lab and the near-natural environment to enlarge the knowledge of ENPs ecotoxicological potentials and to fill methodological gaps concerning their environmental exposures. The environmental fate and pathways of the ENPs were studied using numerous methods on different levels: characterization of the ENPs, environmental exposure and fate modeling. The effects of ENPs on organisms representing different trophic levels and environmental compartments were addressed for the identification of early warning indicators required for the long-term risk assessment of ENPs. The bilateral approach of DENANA addresses the interests of all stakeholders (producer, user and consumer). The identification of early warning indicators of the long-term risk potential supports the progress in the statutory approval of new ENPs; the generation of data on the environmental exposure provides a basis for regulatory measures and, finally, materials risk quantification. We present methods (e.g. Europium doping) to tune particle morphology, which allows to trace, track and identify particles in biological systems. Furthermore, the exposure of nanoparticle into soils and the effect of plant growth are shown. Results of end of life cycle assessment using new models of nano particle distribution scenarios are displayed. The project ended with the collective evaluation of obtained results required for the identification of design criteria of sustainable ENPs. Finally, the selected test materials did not reveal any ecotoxicological potentials to organisms.

9:45 AM NM04.10.01
Design Criteria for Sustainable Nano Materials (DENANA) Philipp Altmann\textsuperscript{1}, Juliane Filsber\textsuperscript{1}, Bernd Giese\textsuperscript{1}, Martin Hoppet\textsuperscript{1}, Tim Hauelner\textsuperscript{1}, Marcus Lukas\textsuperscript{2}, Lutz M"{a}ddler\textsuperscript{3}, Sunan Pokhrel\textsuperscript{4}, Karsten Schlicht\textsuperscript{5} and Sophie M. Schnurr\textsuperscript{6}; Kl"{u}ber Lubrication M"{u}nchen SE & Co. KG, Munich, Germany; Center for Environmental Research and Sustainable Technology (UFT), University of Bremen, Bremen, Germany; Department of Technology Development and Design, University of Bremen, Bremen, Germany; Federal Institute of Geoscience and Natural Resources (BGR), Hannover, Germany; Particle Process Technology and Characterization, Institute of Energy and Environmental Technology e.V., Duisburg, Germany; Federal Environment Agency (UBA), Berlin, Germany; Foundation Institute of Materials Science (IWT), Bremen, Germany; Ecotoxicology, Fraunhofer Institute for Molecular Biology and Applied Ecology (fgo), Schmallenberg, Germany.

9:45 AM NM04.10.05
Portable Ultra-low Power Smart Electronic Nose System Based on Three-Dimensional Tin Dioxide Nanotube Arrays for Multiple Gases and Mixture Detection Jiaqin Chen\textsuperscript{1}, Zhiqiang Luo\textsuperscript{1}, Douglas Bousfield\textsuperscript{2} and Philip Demokritou\textsuperscript{2}; 1Center for Nanotechnology and Nanotoxicology, Harvard University, Boston, Massachusetts, United States; 2Department of Chemical and Biological Engineering, University of Maine, Orono, Maine, United States.

Cellulose is the most abundant natural polymer, is readily available, biodegradable, and inexpensive. Recently, interest is growing around nano-scale cellulose due to the sustainability of these materials, the novel properties, and the overall low environmental impact. The rapid expansion of nanocellulose uses in various applications makes the study of the toxicological properties of these materials of great importance to public health regulators. However, most of the current toxicological studies are highly conflicting, inconclusive, and contradictory. The major reason for these discrepancies is the lack of methods to and to characterize nanocellulose in various forms. In order to address these issues, industry-relevant synthesis platforms were developed to produce nanocellulose with controlled properties that can be used as reference materials in toxicological studies. In this work we report the synthesis and characterization of CNF and CNS reference ENMs and outline some of the most important challenges in our efforts. Among the greatest challenges is to characterize the CNF length and thus to obtain the complete morphology of CNF. We developed a new method that utilizes Scanning Electron Microscopy (SEM) to resolve these issues. Furthermore, another issue is the characterization in liquid in particular when DLS is not suitable. In our work we have developed a method to image the cellulose aggregates in various biological media.

9:45 AM NM04.10.04
Challenges in Characterizing Nanocellulose for Toxicological Studies Zhenyuan Zhang\textsuperscript{1}, Georgios Pyrgiotakis\textsuperscript{1}, Dimitrios Bitounis\textsuperscript{1}, Ana Stavanovic\textsuperscript{1}, Wing Luu\textsuperscript{2}, Douglas Bousfield\textsuperscript{2} and Philip Demokritou\textsuperscript{2}; 1Center for Nanotechnology and Nanotoxicology, Harvard University, Boston, Massachusetts, United States; 2Department of Chemical and Biological Engineering, University of Maine, Orono, Maine, United States.

Nanostructures (including gold nanoparticles, AuNPs, and nanorods, AuNRs) using real and mimetic membrane models. The interaction of the nanomaterials with the lipidic membrane models was studied using Langmuir monolayers, revealing that incorporation of AuNRs into the mimetic cell membrane was more pronounced compared to nanoparticles (AuNPs), as revealed by the adsorption kinetics and surface pressure measurements. We also evaluated the toxic effects of graphene-oxide (GO) on aquatic organisms, in vivo, after exposure to sub-lethal concentrations. Flow cytometric analysis showed that sub-lethal GO exposure led to an increase in the number of gill cells that were in early apoptotic and necrotic stages in zebrafish. The toxic mechanism of GO to zebrafish was attributed to an increase in the oxidative stress level, as observed by the enzymatic biomarkers that showed significant increases in the activity of superoxide dismutase (SOD) catalase (CAT) and lipid peroxidation after sub-lethal exposure. We showed that both gold and carbon-based nanostructures may be harmful to human cells and aquatic species. In the latter, such effects could be permanent, threatening the aquatic food chain balance. Our results may help in the determination of environmentally safe concentrations of nanomaterials for regulatory purposes.
target gas or gases mixture discrimination. Multiple gases (H₂, NO₃, benzene and water vapor) and gases mixtures (H₂ and ethanol, H₂ and acetone, H₂ and methanol) have been tested, and benefiting from the excellent repeatability of the sensor array, the developed classification algorithm, bagging decision tree, could reach a very satisfied classification performance (more than 95%) for both single gas and gases mixtures. Such a robust smart E-nose system can address the imperative needs for distributed environmental monitoring in smart homes, smart buildings and smart cities in the form of a portable or wearable device.

10:00 AM BREAK

10:30 AM NM04.10.06
Highly Selective Formaldehyde Detection with Microporous Zeolite Membranes for Environmental Monitoring
Andreas T. Güntner, Sebastian Abegg, Jan van den Broek, Karsten Wegner and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

A major challenge in environmental sensing is the detection of trace-level pollutants (e.g. carcinogenic formaldehyde) in complex gas mixtures. Devices based on chemo-resistive gas sensors would offer sufficient sensitivity and low detection limit down to ppb, but lack selectivity. Here, we combine nanomanufactured ensors with highly selective zeolite membranes pre-separating gas mixtures. Zeolites - broadly applied in catalysis and gas separation - effectively separate molecules based on kinetic diameter, sorption and diffusion characteristics. Therefore, zeolite membranes are suitable filters for gas sensors removing undesired species from indoor air. As proof-of-concept, a zelite MFU-Al₂O₃ membrane is placed upstream a highly sensitive but weakly selective Pd-doped SnO₂ sensor. Their combination exhibits exceptional selectivity (>100) for formaldehyde down to 30 ppb at 90% relative humidity, outperforming state-of-the-art detectors by more than an order of magnitude. This novel concept is readily extendable to other tracers, as manifold combinations of widely tunable microporous membranes and gas sensor types can be realized in the modular sensing device. This could enable a new class of highly sensitive and selective environmental monitors.

(1) International Agency for Research on Cancer, IARC classifies formaldehyde as carcinogenic to humans. IARC: Lyon, 2004; Vol. 15.

10:45 AM NM04.10.07
Environmental Transformation and Biological Impact of LiCoO₂ and LiNixMnyCo(1-x-y) (NMC) Lithium-Ion Battery Cathode
Silica Based Hybrid Colloidosomes and Pickering Emulsions and Their Implantation For Single Cell Microencapsulation
Xiaowei Xu1, 2, Liping Zhu1 and Shuguang Yang1, 2; 1Center for Advanced Low-dimension Materials, Donghua University, Shanghai, China; 2State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China.

The mixture of dye/salt generated from digital ink-jet printing industry is not only a crucial source of pollution but also a huge waste of materials. Recently, polymer complex membranes (PCMs), as a nano-filtration membrane, have drawn a considerable attention in treatment of the dye/salt mixture in order to recycle dye due to its inherent ionic cross-linking structures and high hydrophilic property. The preparation of polymer complex membrane usually requires the protonation and de-protonation of certain functional groups to make the solution homogeneous and processable in a large scale. In this work, in order to avoid the adjustment in the amount of ionic groups after complexation, a new solution preparation method is developed to maintain the viscosity and homogeneity of solution, and thus to skip the common and necessary precipitation process existed in most of the membrane preparation methods. Partially hydrolyzed poly (2-ethyl-2-oxazoline) (PEO-E) which is consisted of poly (2-ethyl-2-oxazoline) and polyethyleneimine (PEI, as cation polyelectrolyte, and poly(acrylic acid) (PAA), as anion polyelectrolyte, are selected to prepare PCMs by solution-casting first, then followed by an interfacial polymerization process. The structural characteristics and surface properties are then systematically investigated. The number of hydrogen-bonding sites can be easily manipulated with solution pH, which provides an opportunity to efficiently clean the membrane and make it reusable under extremely conditions. A high water permeability and good antifouling ability are expected due to the hydrophilicity of membrane provided by the excess amount of carboxyl groups. Though the dye barrier ability is currently lower than the commercialized nano-filtration membrane systems, the overall performance of the as prepared PCMs, including facile fabrication process, high selectivity for the dye/salt mixture, high permeability and good antifouling ability, find them a promising future in separation of dye/salt mixture.

11:00 AM NM04.10.08
PEOs-EI/PAA Complex Nano-Filtration Membrane for Dye/Salt Separation
Xiaowei Xu1, 2, Liping Zhu1 and Shuguang Yang1, 2; 1Center for Advanced Low-dimension Materials, Donghua University, Shanghai, China; 2State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China.

This research presents an in-situ functionalization of silica nanoparticles in oil-in-water (o/w) biphaseic system with two equimolar organosilanes of antagonistic polarity. Homogeneous and stable Pickering emulsions have been obtained, where droplet size can be tuned according to the silica particle concentration and the o/w ratio used. The micro and nano-structure was analysed by optical and fluorescence microscopy and cryo-SEM. The introduction of carbon nanotubes (CNT) to the silica based Pickering emulsion enabled us to prepare electrically conductive CNT/silica nanohybrid colloidosomes with controlled porosity. CNTs and silica nanoparticles both are located in the interface, as evidenced by confocal laser scanning microscopy and cryo-SEM. After drying, hierarchical porous structures have been generated spanning the micro, nano, and macropore range. The emulsions have shown high stability against coalescence and sedimentation. Additionally, a highly tunable bio compatible Pickering emulsion system enabled us to develop a new approach for
successful single cell encapsulation of fungal spores of *Metarhizium anisopliae*, which is implemented in efficient biopesticide formulation for arthropod pest control in agricultural applications. This successful single cell encapsulation system led to a significantly higher distribution of conidia cells on the leaves. The Pickering emulsion based formulation exhibited significantly higher pest control against *Spodoptera littoralis* larvae, thus making it a promising cost effective, innovative approach to tackling the pest control challenge.

11:30 AM RAPID FIRE PRESENTATION

1:30 PM *NM04.11.01*

**Advancing Nanocellulose Technologies for Water Purification**

Benjamin S. Hsiao; Stony Brook University, Stony Brook, New York, United States.

The fabrication of nanocellulose can be accomplished by chemical and mechanical treatments of any natural biomass, including agricultural waste, weeds and shrubs, where some sources can provide "effortless extractability" with very low energy consumption. Nanofibrous scaffolds have very unique properties including interconnected pores, a very large surface-to-volume ratio and a high capacity for surface modifications, making them ideal candidates for fabrication of high throughput separation membranes (e.g. microfiltration and ultrafiltration) and/or highly efficient sorptive media. Directed water channels in the barrier layer of reverse osmosis and nanofiltration membranes can also be formed through the formation of interface between the nanofibers and barrier layer polymer matrix, while the gap thickness can be regulated by physical interactions or chemical bonding. In the present context, advances in fundamental studies on cellulose microfibrils, the building blocks from the cell wall of any plant, and their interactions with metal ions by means of synchrotron x-ray and neutron techniques have provided us with new insight into the design and fabrication of highly permeable nanofibrous membranes, having a hierarchically tiered structure, that can enable higher flux, higher retention and lower energy consumption water purification. Nanocellulose may serve as a revolutionary platform technology for the design and fabrication of low cost, sustainable and highly efficient filtration and sorptive media.

2:00 PM NM04.11.02

**Design and Development of Process for Wastewater Treatment Using Sustainable Adsorbents**

Nathan Grishkevich1; Nishil Mohammed1, Richard Berry2 and Michael K. Tan1; 1Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada; 2Celluforce, Montreal, Ontario, Canada.

This study describes the design and development of a continuous process for use in textile effluent remediation. The system utilizes an adsorbent prepared from eco-friendly materials derived from renewable sources, cellulose nanocrystals (CNCs) and sodium alginate (ALG). The ability of the adsorbent to remove a model cationic dye, methylene blue (MB), was studied in detail.

Equilibrium batch adsorption experiments provided information on the equilibrium uptake of MB dye from water as well as the adsorption kinetics. In addition, the impact of ionic strength, pH, and temperature on the equilibrium uptake were examined. Continuous experiments were conducted in a fixed bed vessel to study the impact of flow rate, initial MB concentration and packing height on the capability of the process to remove MB. A self-sustained system that could produce this adsorbent in-situ was also developed.

From the batch experiments we determined a theoretical maximum adsorption capacity for MB by the adsorbent to be 431.6 mg/g, and additional experiments demonstrated that the adsorbent could undergo repeated adsorption–desorption cycles, achieving ~97 % dye removal efficiency after 5 cycles. From lab scale continuous experiments we determined the influence of flow rate, initial MB concentration and packing height on breakthrough curve and shape of the breakthrough curve, allowing for the scale-up of the system for field tests. Continuous tests also validated theoretical predictions of maximum adsorption capacity obtained from batch adsorption experiments, achieving an MB loading of 391.7 mg/g.

Following this, a pilot scale fixed bed was developed to treat wastewater generated at a batik textile mill in Yogyakarta, Indonesia. However, the influence of other contaminants in the wastewater impacted the adsorption of MB onto the adsorbent, resulting in a lower projected performance. Following this, the influence on divalent salts during the start up of the fixed bed process on the adsorption of MB dye and the swelling of the adsorbent was studied. The CNC–ALG hydrogel beads were determined to be effective adsorbents for the removal of organic dyes from wastewaters in both batch and continuous processes, and their development for use in industrial water treatment systems is progressing well.

2:15 PM NM04.11.03

**Tension Gradient Self-Assembly to Facilely Fabricate Polytetrafluoroethylene Nanofibrous Coating for Oil-Water Separation**

Dong Feng, Jiadao Wang and Ding Wong; Tsinghua University, Beijing, China.

Oil-water mixtures, which result from food processing, metal finishing, petrochemical and so on, have become the most common contaminant all over the world. Thus, oil-water separation is an important challenge in the field of scientific research and environment protection. Traditional methods for the oil-water separation, including air flotation, ultrasonic separation and biological treatment, have difficulty in practical applications due to the limitations of low separation efficiency and the generation of secondary pollutants. Recently, the superhydrophobic and superoleophilic materials for selectively adsorbing or filtrating oil from oil-water mixtures have flourished with advantages of high separation efficiency and wide applicability. Numerous preparation methods are developed, such as electrochemical deposition, electrosprinning and vapor phase deposition. However, they are complex, high-cost, or inapplicable for large-area fabrication.

Here, we present a facile method to create durable superhydrophobic and superoleophilic coating on the porous metal fiber sintered felt (PMFSF) via tension gradient self-assembly. Firstly, PMFSF was immersed into ethanol and then pulled out vertically. A thin film of ethanol formed on the surface of PMFSF. Secondly, PMFSF was vertically placed into polytetrafluoroethylene (PTFE) solution (6 wt%) at a speed of 1 cm/s. The tension gradient appeared as a result of the dissolution of ethanol into water, and induced the Marangoni convection and the relative motion between the solution and the PTFE nanoparticles. The particles moved towards the surface of PMFSF and a PTFE nanoparticle coating formed. Thirdly, the sample was heated to 380 °C for 40 min, followed by cooling down in air. During the sintering process, the PTFE particles melted and rearranged to form nanofibers. As a result, the PTFE nanofibers not only offered low surface energy, but also provided nanoscale roughness, which was beneficial for the oil-water separation. After a series of
tests, the PMFSF coated with nanofibers could separate a series of oil–water mixtures with an efficiency over 98%. The separation efficiency was still stable after the sample was reused for 30 times. Moreover, the sample worked well under extreme environmental conditions of strong acidic or alkaline solution, high temperature and ultraviolet irradiation. In summary, we have demonstrated a simple, low-cost and rapid method to fabricate larger-area PTFE nanofibrous coating on PMFSF for oil-water separation based on tension gradient self-assembly. The coated PMFSF has the advantages of high-efficiency, durability and good environmental adaptability, which is suitable for industrial application.

2:30 PM BREAK

3:00 PM NM04.11.04

Nanofluidic Channels and Electrokineti Energy Generation on Two-Dimensional Boron Nitride Membrane Si (Alex) Qin, Zhiyu Wang, Dan Liu, Weitwei Lei and Joselito Razal; Deakin University, Geelong, Victoria, Australia.

Recent research show that two-dimensional (2D) membrane can provide unprecedented large number of nanofluidic ion channels through economic and easy fabrication processes. However, constructing a 2D membrane suitable for harsh environment such as highly acidic or alkaline solutions is still a challenge. Boron nitride (BN) membranes constructed from highly stable, acidic and alkaline resistant functionalised BN nanosheets are promising alternatives for organic or GO membrane. Herein we show BN membranes which allow ions to pass through intra-layer spaces. Measurement across the BN membrane showed a surface-charge-governed ionic conductivity in a variety of salt solutions (KCl, NaCl and CaCl₂) at low salt concentrations (<10⁻⁴ M). Moreover, due to outstanding chemical and thermal stability of BN nanosheets, the ionic channels remain fully functional in harsh conditions and at elevated temperatures. The BN membrane can operate in highly acidic and basic environments, and does show degradation after immersing in solutions with extreme pH (pH close to 0 or 14) for one week. More interestingly, pressure gradient results in a current response across the membrane. Current in the range of 8–13 nA can be generated on a 5 mm² membrane with a pressure gradient of 5 kPa in 0.1 M NaCl solution. The electrokineti electric generation can be scale up by connecting multiple devices. Those excellent properties make the BN membranes suitable alternative to organic or GO membranes and attractive for applications in nanofluidic devices and membrane separation.

3:15 PM NM04.11.05

Ultrahigh Performance of Novel Energy-Efficient Capacitive Deionization Electrodes Based on 3D Nanotubular Composites Nageh K. Allam; American University in Cairo, New Cairo, Egypt.

Capacitive deionization (CDI) is being progressed as an auspicious ions removal technique from brackish and seawater. Herein, we introduce a novel one-step facile chemical approach to fabricate tubular architecutured composite electrodes made of both Titania and Multi-walled carbon nanotubes (TNTs/MWCNTs). The composites have been exploited, for the first time, as the electrode materials for capacitive deionization. The composite electrodes were fully characterized via Field Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy, X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) techniques, and Nitrogen Sorption. The electrochemical response was investigated by using Cyclic Voltammtry (CV), Galvanostatic Charge and Discharge (GCD), and Potentio-Electrochemical Impedence Spectroscopy (PEIS) measurements. The fabricated composite electrodes containing 5 wt% TiO₂ nanotubes showed a remarkable specific capacitance, conductivity, reversibility, and durability compared to pristine MWCNTs and other MWCNTs-based composite electrodes reported in the literature. The desalination capability of the composite electrode was investigated using batch mode operation. The electrosorption capacity of the composite electrode containing 5 wt% TiO₂ nanotubes (13.2 mg/g) is approximately two folds of magnitude larger than that of pristine MWCNTs (7.7 mg/g), indicating an improved desalination efficiency. Therefore, the fabricated TNTs/MWCNTs composite electrode is a promising candidate for CDI technology.

3:30 PM NM04.11.06

Using Nickel Sulfide Nanoparticles Incorporated PMMA-Zirconia Membranes as Efficient Adsorbent for Ultra Deep Desulfurization of Thiophenes Adnan Miahial1, Tuba Choudhury1, Tajmal Hussain1 and Sadia Zafar Bajwa2; 1Institute of Chemistry, University of the Punjab, Lahore, Pakistan; 2National Institute of Biotechnology and Genetic Engineering, Faisalabad, Pakistan.

Ultra deep desulfurization of liquid fuels such as gasoline/diesel has attracted considerable attention of modern clean fuel research due to strict environmental regulations. Apart from that, SO₂ produced during combustion, poison the catalytic converter and exhaust emission system. Comparing to conventional catalytic and hydrodesulfurization techniques, adsorptive method for removal of sulfur bearing compounds e.g. thiophene derivatives is a promising approach which does not require hydrogen, or high temperature and pressure. In this study, we used nickel sulfide nanoparticles as a potential affinity material for adsorptive extraction of thiophene derivatives i.e. thiophene, benzothiophene and dibenzothiophene from n-hexane. The functionality and surface morphology of synthesized material was examined by Fourier transformation infrared (FTIR) and atomic force microscopy (AFM) images, respectively. The quantitative data regarding adsorptive removal of thiophene derivatives was determined by monitoring the absorbance values of their standard solutions before and after treating with synthesized material under ambient conditions. It was noticed that nickel sulfide nanoparticles exhibited excellent rebinding response for removal of dibenzothiophene down to 0.5ppm which is useful concerning ultra deep desulfurization. The prepared nickel sulfide nanoparticles were incorporated in poly(methylmethacrylate-zirconia) matrix for adsorptive desulfurization of tedious thiophenes from liquid fuels without using hydrogen gas or any other catalyst.

3:45 PM NM04.11.07

Chemically Functionalized Laminar MoS₂ Membranes for Nanofiltration Mark A. Bissett, Wisiit Hirunpinyopas, Eric Prestat and Robert A. Dryfe; University of Manchester, Manchester, United Kingdom.

Environmental pressures, along with the discovery of two-dimensional (2D) materials such as graphene, have combined to provide renewed interest in the development of membrane technologies. Laminar membranes of two-dimensional materials are excellent candidates for applications in water filtration due to the formation of nanoapillaries that can exhibit a size and charge sieving effect, while allowing high water flux. Laminar membranes of 2D materials have been demonstrated previously in the case of graphene oxide, however these membranes suffer from swelling when exposed to liquid water, leading to low ionic rejection and reducing their applicability for desalination applications.

In this work, we demonstrate that thin (~5 μm) laminar membranes of exfoliated molybdenum disulfide (MoS₂) can be modified by a simple chemical functionalization step and can efficiently reject (~99%) of the ions commonly found in sea water (e.g. Na⁺, K⁺, Ca²⁺, and Mg²⁺), while maintaining water fluxes significantly higher (~5 times) than those reported for graphene oxide membranes. These chemically functionalized MoS₂ membranes exhibit long-term stability with no swelling, and consequent decrease in ion rejection, when immersed in water for periods exceeding 6 months. Similar stability is observed when exposed to organic solvents, indicating that they are ideal for a variety of technologically important filtration applications.

We also performed ion transport measurements through the chemically functionalised MoS₂ membranes as a function of applied electric potential to
differenct between the effects of size and charge. Hydrated and non-hydrated cation permeability was measured for various mono-, bi-, and trivalent ions, demonstrating that higher charge density has a greater effect on the permeability of the inorganic cation than on the organic cation of comparable radii. The method presented here, based on non-toxic organic-functionalized MoS2 laminar membranes, demonstrates impressive potential for application in water purification technologies such as desalination, ion exchange, electrodialysis, reverse osmosis, and electrodeionization (EDI).


4:00 PM RAPID FIRE PRESENTATION

SESSION NM04.12: Poster Session IV: Toxicology, Monitoring and Depollution
Session Chairs: Babak Anasori, Monica Jung de Andrade and Maria Perez Barhaburu
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM04.12.01
Coffee Waste as Biocleaning Agent for Polluted Water Reservoirs
Pedro Perdigon-Lagunes1, Sofia Aguillera-Barraza2, Alejandro Isaza-Orozco2, Pablo A. Cano-Martinez3, Lorena Arreguin-Lozano3, Humberto Pro White3, Daniel David Nehmad4, Diego Delgado Fajardo4 and Raul Herrera-Becerra1; 1Universidad Nacional Autonoma de Mexico, Mexico City, Mexico; 2Instituto Tecnológico y de Estudios Superiores de Monterrey, Ciudad de Mexico, Mexico.

Fresh water reserves are being depleted quickly in the last century and the rest of them are being contaminated. Different types of pollutants are released in the environment from various industries, specially, heavy metals in water reservoirs are a harsh task to solve. This is because these types of materials bound strongly to water molecules; hence, it is necessary to use different methods such as electro-Fenton reactions, advanced oxidation processes and nanotechnology to remove them [1]. An interesting approach is to use living microorganisms or fungi as bioremediating agents, because in the native these organisms work as caretakers of water and soil. However, in this case the contaminants surpass their resilience to toxic waste. In our case, we decided to solve this problem using nanotechnology approach [2], utilizing a common waste as our main reduction agent: Coffee waste. Despite the fact it is used as a compostable waste, we used it as a biocleaning agent instead. Coffee extracts have demonstrated their capability to bioreduce metals into nanostructures [3]; therefore, we obtained a bioactive extract from used coffee capable of quickly reducing metallic ions into nanoparticles. Then, we tested our extract to collect heavy metals from polluted water. In this experiment, metal-oxide nanoparticles of different composition were precipitated at the bottom of the test tube. Then those nanoparticles were analyzed to determine their composition. This technique is a promising one, because it is simple to escalate, it uses small nanoparticles as their main reagents, and small nanoparticles can be recovered to be used in technological applications.

References

NM04.12.02
Synthesis of Nanoporous Adsorbents Showing High CO Selectivity to CO2 and High CO2 Selectivity to CH4, Based on Systematic Study on Effect of Physico-Chemical Properties of Nanoporous Materials to Adsorption of Each Component
Kanghee Cho, Jong-nam Kim, Sang Sup Han, Jong-ho Park, Hee Tae Beum, Jongkee Park and Sun Hyung Kim; Korea Institute of Energy Research, Daejeon, Korea (the Republic of).

We synthesized two types of nanoporous adsorbents: one for CO-selective separation from CO2/CH4 mixture, and the other for CO2-selective separation from CO2/CH4 mixture. For the synthesis of the CO-selective adsorbent, we impregnated CuCl species which shows strong interaction with CO on suitable alumina-type nanoporous supporting material. The driving force of CO-selective adsorption is strong interaction between the CuCl species and CO molecules. For the synthesis of the CO2-selective adsorbent, we modified zeolite to tune finely the size of micropore aperture of the zeolite to certain size between the molecular sizes of CO2 (0.33 nm) and CH4 (0.39 nm). The driving force of the CO2-selective adsorption is the size-selective effect (molecular sieving effect) of the micropores in the zeolite. For both cases of the adsorbent syntheses, it is highly important to choose suitable nanoporous supporting material and to modify the nanoporous supporting material, in order to enhance adsorption capacity and selectivity of target component. For this purpose, it is necessary to understand the effect of the physico-chemical properties of the nanoporous materials to the adsorption of each adsorbate. In the case of the CO-selective adsorbent, nanoporous supporting material is desired to disperse well the CuCl species to increase CO adsorption capacity, and it is simultaneously desired to show weak interaction with CO2 to enhance CO selectivity. Zeolite 13X which has been normally used for the preparation of CO-selective adsorbent shows high CO2 adsorption capacity owing to electro-static interaction with CO2 and zeolite microporosity, even though it shows high surface area which is good for high dispersion of CuCl. We used mesoporous alumina as a supporting material for the CuCl, and the mesoporous alumina has weaker electrostatic interaction than zeolite and no microporosity. We confirmed that our new CO-selective adsorbent 35 cm3 g−1 of CO2 adsorption at 293 K under 100 kPa of each gas. In the case of the CO2-selective adsorbent, the adsorbent is desired to show nanopore size between the sizes of CO2 and CH4 to have size-selective effect. When the size of micropore aperture of the zeolite is reduced to desired range, CH4 molecules cannot enter the micropore aperture. However, the adsorption speed of CO2 becomes inevitably too low to use fully the size-selective effect of the zeolite in CO2 separation. In order to resolve such a problem of slow adsorption, we generated additional mesopores in the zeolite crystals by using organosilane surfactant as a mesopore generating agent. The adsorption of CO2 into the micropores is still slow in the case of the mesoporous zeolite, but the mesopore generation increases the number of micropores exposed to external surface. The mesoporous zeolite shows high CO2/CH4 selectivity, and is shows much higher CO2 adsorption rate than solely microporous zeolite counterpart.

NM04.12.03
Dielectric Mirrors for Vapor Sensing and the Study of Time-Resolved Response
Shuai Gao, Karen Forberich and C. Brabec; University of Erlangen-Nuremberg, Erlangen, Germany.
Organic solvent and water vapor detections play an important role in industrial and life areas. Predictable and selective sensing shows a large number of applications. Dielectric mirrors (DMs), also known as Bragg stacks or one-dimensional photonic crystals, have certain reflection bands, and the position of the reflection band can be controlled by changing the thicknesses or the refractive index of the stacked layers. Polymers or organic-inorganic materials are popular in vapor sensitive dielectric mirrors, and the variation of refractive index or thickness is easily controlled because polymers show the property of swelling. The tunable reflection bands enable the mirrors to work as vapor sensors. In most research, polymers are deposited as the active layer and oxide nanoparticles are deposited as the other porous layer to improve the permeability and increase the refractive index contrast in the bilayer structure. However, due to the specific properties of the polymers, they can only respond to either water or organic solvents.

In this work, dielectric mirrors based on bilayers are fabricated for the purpose of vapor sensing, which are made of polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene (SEBS) and polyvinyl alcohol (PVA)-zirconium dioxide (ZrO2) nanocomposites. The specific reflection bands of dielectric mirrors depend on the refractive indices and thicknesses of the alternating layers. When dielectric mirrors are exposed to solvent vapor, layers swell which causes a shift of the reflection band. Since SEBS and PVA respond to organic solvents and water, respectively, these mirrors can be used as sensors for a large variety of different solvents. Hydrophilic ZrO2 nanoparticles are introduced to increase the porosity of the PVA layers, and the ratio of ZrO2 nanoparticles was optimized to achieve the optimum effect. The time-resolved response is studied to understand the swelling processes. Time-resolved measurements show that the mirrors with nanoparticles have a significantly faster response compared with those without nanoparticles. Due to the different Flory-Huggins interaction parameters between materials and solvents, the dependence of the responses on the relative humidity and on the type of solvents is studied, which provides an approach to make responses predictable and selective. The swelling of the mirrors is reversible upon thermal annealing so that the response of the vapor sensors shows good reproducibility. The combination of good properties such as selectivity, predictability, and reversibility with the simple fabrication procedure is promising in the development and application of the dielectric mirrors as vapor sensors.

**NM04.12.04**

**TiO2 Encapsulated AIOOH Dual Nanostructures with Robust Anti-Oil Fouling**

Sun Mi Yoon1,2; Hyebin Lee1, Young Cheol Park1, Sahn Nahm3 and Myoung-Woon Moon3, 1Materials and Life Science Research Division, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Department of Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

More researches are under progress for developing an oil-water separation or recovery method as oil spillage accidents continuously occurs. Technology for removing oil spilled in the sea or the river includes adjusting surface energy like hydrophilicity and hydrophobicity as well as the structures in nano- or microstructures or their hybridization. Among functional materials, the hydrophilic/underwater oleophobic materials have advantages in the various applications such as self-cleaning, oil transportation or oil-water separation. However, the hydrophilic or superhydrophilic surfaces are still required for the long-term durability in mechanical and chemical stability.

In this work, we present a durable superhydrophilic and underwater superoleophobic mesh filter with dual nanostructures of nanoflake and nanoparticle clusters. The aluminum (Al) mesh surfaces show the long-term superhydrophilicity/underwater superoleophobicity induced by hydrothermal treatment in containers having Al mesh and TiO2 nanofluid. As Al is immersed in boiling TiO2 nanofluid, the Al surface reacts hydroxyl ion decomposed water to form flake-like AIOOH nanostructure encapsulating TiO2 nanoparticles inside. Al ions are diffused out from the Al2O3 matrix, leaving Al depletion zone, then the Al ions in TiO2 nanofluid can be precipitated on the surfaces of Al depletion zone and TiO2 nanoparticles. Pristine Al mesh filter without TiO2 nanoparticles showed mild hydrophilic but not lasted for longer duration, while the mesh filter with dual nanostructures has long-term stability in superhydrophilicity more than 10 weeks due to dual scale roughness in nanoscale as well as TiO2 effect. The hybrid nanostructures have very low wetting angle of near 0° degree in air and superoleophobic underwater long-lasting anti-oil property. We applied this surface to oil collecting filter by separating oil/water, which are required for the spontaneous oil detachment at the water surface for cyclic oil-water collection-separation-release process with the crude oil over 5,000 times.

**NM04.12.05**

**Cost-Effective Fabrication of Metal Oxide Nanoparticles (WO3, ZnO) Based Gas Sensor for Selective Detection of NO2 and CO Environmentally Hazards Gases**

Sapana Ranwa, Vikas Sharma, Habeebur Rahman and Bodh R. Mehta; Department of Physics, Indian Institute of Technology Delhi, New Delhi, India.

In today’s era, real-time monitoring of toxic pollutant gases is vital for domestic sector as well as automotive sector to uphold human health and safety. The selective detection of most common and hazardous gases CO and NO2 at low operating temperature is one of the critical challenges in the area of environmentally sensitive sensors. Metal oxide nanoparticles (ZnO, WO3) based gas sensor provides an opportunity to fabricate cost-effective environmental gas sensor with low concentration gas detection possibility even at moderate operating temperature. In this study, a WO3 nanoparticles based sensor able to give ~36.3% sensor response towards 10 ppm NO2 gas even at 50 °C operating temperatures. This sensor shows highly selective sensor response towards 10 ppm NO2 gas in comparison to other air pollutant gases (10 ppm CO ~ 2% and 10 ppm NO ~ 3%) at a low operating temperature (50 °C). Furthermore, doping of Ga (1% to 5%) into ZnO based sensor could provide the possibility to solve the selectivity problem for NO2 gas concentration among other common environmental pollutants (CO, NOx). 2.5% Ga doped ZnO based sensor able to depicts 10 fold increased sensor response with high selectivity towards 10 ppm NO2 gas at 150 °C operating temperature in comparison to pristine ZnO based sensor for other hazards gases (CO, NO). ZnO nanoparticles and Ag loaded ZnO Nanoparticles based chemical sensor performance have been further studied for selective detection of 10 ppm CO gas concentration at operating temperature ranging from 50 °C to 150 °C. Functionalization of ZnO sensor with surface decoration of Ag nanoparticles (5-20 nm) has been achieved by a continuous gas phase deposition method. Gas sensing response of Ag loaded ZnO sensor shows significantly enhanced sensor response ~40% in comparison to ZnO sensor response ~9% for 10 ppm CO gas concentration at 150 °C operating temperature. This improved sensor response towards reducing gas (CO) for Ag loaded ZnO sensor could be explained by electronics as well as chemical gas sensing mechanism. Ag loaded ZnO sensor also has been able to depict selective sensor response towards 10 ppm CO gas with ~40 % sensor response in comparison to other air pollutants (10 ppm NO with ~10% and 10 ppm NO2 with ~20%) at 150 °C operating temperature. This current approach enables us to fabricate cost-effective and low operative temperature (50 °C) gas sensor with high selectivity for the detection of CO and NO2 gases. These studies also motivate us to record both NO2 and Ag loaded ZnO based sensor response at the same time which gives selective detection of NO2 and CO gases without changing sensor from the chamber.

**NM04.12.06**

**Photocatalytic activity of Ce doped SnO2 nanoparticles for the degradation of organic toxic pollutants**

Akanksha Gupta1, Sunjeet K. Yadav2, Prateek Saini2, Ayesha Seth1 and Vinod Kumar2; 1Chemistry, Sri Venkateswara College, Delhi, India; 2Chemistry, KIIT Mal College, Delhi, India.

Water pollution by different harmful compounds is becoming an increasing global concern. Most industrial dyes, pesticides are toxic, carcinogenic, and mutagenic, and have low biodegradability. Moreover, dye-containing effluents are highly colored, so discarding these effluents into natural water bodies affects the balance of aquatic ecosystems because they can prevent the penetration of sunlight into the water, which results in a reduction in dissolved oxygen content. Therefore, the removal of dyes and pesticides prior to the discharge of wastewater from industries is of great importance. The inadequate treatment and inappropriate disposal of these toxic carcinogenic organic compounds pose a considerable threat to the environment [1].

Water pollution by different harmful compounds is becoming an increasing global concern. Most industrial dyes, pesticides are toxic, carcinogenic, and mutagenic, and have low biodegradability. Moreover, dye-containing effluents are highly colored, so discarding these effluents into natural water bodies affects the balance of aquatic ecosystems because they can prevent the penetration of sunlight into the water, which results in a reduction in dissolved oxygen content. Therefore, the removal of dyes and pesticides prior to the discharge of wastewater from industries is of great importance. The inadequate treatment and inappropriate disposal of these toxic carcinogenic organic compounds pose a considerable threat to the environment [1].
Several binary oxides such as TiO₂, ZnO, SnO₂ etc. have been recognized as preferable materials for photocatalytic activities due to their high photosensitivity, low cost, and chemical stability and hence, they have been investigated for the degradation of these pollutants in waste water [2]. Little information is available in the literature regarding the SnO₂-RE (RE=rare earth) system [3].

Tin dioxide (SnO₂) is a n-type semiconductor that has a wide range of potential applications in gas sensors, catalysts, batteries, transistors, and transparent electrodes. The structure, band gap, and chemical stability of SnO₂ are similar to those of titanium dioxide (TiO₂), which is a widely used photocatalyst. Moreover, SnO₂ has no adverse health effects and is poorly absorbed by the human body when injected or inhaled. Thus, SnO₂ is potentially an ideal photocatalyst and possess large surface area. Semiconductor photocatalytic processes are based on the generation of electron-hole pairs by means of band gap radiation. SnO₂ has also been used as a component of composite photocatalysts such as SnO₂/TiO₂, SnO₂/ZnO, and SnO₂/ZnO/TiO₂ [4]. Doping of rare earth ion in metal oxide introduce defects lowering the effective optical gap and hence leading to a better photocatalytic. Ce doped SnO₂ is a promising material and several scientists have reported its gas sensing properties for various harmful gases but to the best of our knowledge its photocatalytic activity has not been explored much.

Herein, we present the synthesis and structural characterization of varying concentration of Ce-doped SnO₂ nanoparticles. Detailed characterization have not been explored much. Material and several scientists have reported its gas sensing properties for various harmful gases but to the best of our knowledge its photocatalytic activity has not been explored much.

In this study, we report the synthesis and electrochemical characterization of varying concentration of Ce-doped SnO₂ nanoparticles. Detailed characterization are attempted based on the PXRD measurements, FTIR, Raman, UV-visible spectroscopy etc. We have successfully degrade the organic dyes and pesticides under UV irradiation, which might be helpful for the wastewater treatment in future.

References

NM04.12.07
High Performance Single Magnéli Phase Reactive Electrochemical Nanoporous Membrane for Waste Water Treatment Sasmita Nayak and Brian P. Chaplin; University of Illinois at Chicago, Chicago, Illinois, United States. Reactive electrochemical membrane (REM) based on Magnéli phase titanium oxides (T₄O₇₋₃n, n = 4 to 10), are attractive, because of their high conductivities, chemical stability, and low cost with unique functionality to produce OH via water oxidation. Most of the present Magnéli phases based REM are limited to formation of high-quality, the most conductive and single magnéli phase, i.e., TlO₂. This study reports the synthesis and electro-oxidation capabilities of Magnéli Tl₄O₇ REM using probe molecules and organic compounds through both direct oxidation (oxalic acid) and interaction with OH (terephthalic acid). High membrane fluxes of (1736 L/M².hr) resulted in a convection-enhanced rate constant for Fe(CN)₆₄⁻ oxidation of 8.13 × 10⁴ m²/s⁰ and that for Fe(CN)₆₃⁻ reduction of 10.84 × 10⁴ m²/s⁰ that approaches the kinetic limit. Batch experiments were also performed for electrochemical destruction of N-nitrosodimethylamine (NDMA) in flow-through electrode for single-pass sequential reduction–oxidation.

NM04.12.08
Highly Efficient Adsorption of Heavy Metal Ion from Wastewater Using Hollow Carbon Coated with Fe₃O₄ Hybrid Composites Byeong Seok Lim, Bongkyun Kang and Woo Seok Yang; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

The presence of hazardous heavy metals in water is an important issue in environmental pollution management with crucial effects on human health. Heavy metal can cause several serious health problems and skin cancer. Iron oxide based materials are very effective in the removal of heavy metal. However, Fe₃O₄ nanoparticles are actually prone to aggregate by spontaneous magnetization that decreases specific surface area. Additionally, heavy metal adsorbed Fe₃O₄ nanoparticles are difficult to separate in water owing to their low magnetic properties and nanosize. In this work, we synthesized the hollow carbon coated with Fe₃O₄ hybrid composites via SiO₂@dopamine core shell. The hollow carbon coated with Fe₃O₄ hybrid composites did not aggregate well compared to other Fe₃O₄ materials because the hollow carbon structure had a three dimension (3-D) sphere shape and high outer surface area with inner surface. Consequently, the hollow carbon coated with Fe₃O₄ hybrid composites exhibited more heavy metal adsorption capacity compared to pure Fe₃O₄ and other materials with Fe₃O₄.

NM04.12.09
An Intelligent Dual Mode Reversible Filtration Device for Separation of Immiscible Oil/Water Mixtures and Emulsions Parul Raturi and Jitendra P. Singh; Physics, Indian Institute of Technology Delhi, Delhi, India.

For the treatment of oily wastewater strategies used for oil/water separation, including immiscible light/heavy oil water mixture, both oil in water and water in oil emulsions are of great demand. Recently, materials with specific wettability properties have become interesting due to their importance in the field of oil/water separation. Herein, we report intelligent mesh for dual mode reversible separation of immiscible heavy/light oil water mixture and both oil- in-water as well as water-in-oil emulsions. ZnO nanowires coated stainless steel meshes with pore size of 50 μm and 10 μm were fabricated successfully. The wettability of mesh can be reversibly switched between “oil-blocking” and “water-blocking” modes by alternative exposure and removal of low surface energy material. The “oil-blocking” mode was suited for the efficient separation of light oil/water mixture and oil-in-water emulsion, while “water-blocking” mode was found to be suitable for the separation of heavy oil/water mixture and water-in-oil emulsion. This work provides a simple, cost effective, eco-friendly and time saving approach applicable for separation of both form of oil/water mixture, free as well as surfactant stabilized emulsions, irrespective of the types of oil involved. The separation efficiency of the mesh was found to be more than 99% for free as well as emulsified mixtures. Even after cyclic usage in both modes alternatively, the separation efficiency of the mesh remained relatively unchanged, showing anti fouling property and excellent recyclability of the mesh.

NM04.12.10
Recyclable and Multifunctional 3D Hybrid Networks for Adsorption, Detection and Decomposition of Environmental Pollutants Yajieong Lee, Seungki Lee, Chang Min Jin, Hye Sil Kim and Inhee Choi; Department of Life Science, University of Seoul, Seoul, Korea (the Republic of).

Monitoring and removal of environmental pollutants have been regarded as important tasks nowadays due to global and public health issues. For this purpose, efficient materials that can adsorb, detect, and decompose such pollutants have been consistently sought after. Even for such an essential necessity, there are only a limited number of reports on suitable platforms or materials that can allow combining multiple roles of adsorption, detection, and decomposition of VOCs. Herein, we present a simple, inexpensive and eco-friendly fabrication method of recyclable and multifunctional three-dimensional (3D) network with functional nanoparticles (hybrid network). Water-soluble crystals (e.g., sugar and salt) and photocatalytic nanoparticles (e.g., TiO₂ nanoparticles) are utilized to construct porous templates where liquid polydimethylsiloxane (PDMS) mixture (base and curing agent) is filled. For more sensitive detection of pollutants, metal precursors (e.g., HAuCl₄ and AgNO₃) can be added into the liquid PDMS mixture to form the plasmonic nanoparticles such as Au and Ag nanoparticles in the porous PDMS network. After curing the PDMS, porous network structures with the self-integrated nanoparticle are finally obtained by dissolving the templates by water. To demonstrate the performance of the hybrid network, we quantitatively and qualitatively detect the pollutants such as organic dyes and volatile organic compounds (VOCs) via molecular-specific and label-free Raman scattering.
Furthermore, we show the recyclability by achieving photocatalytic decomposition of the adsorbed pollutants by using the TiO$_2$ hybrid networks. We believe that the developed hybrid 3D networks could be widely utilized in managing organic pollutants in aquatic and atmospheric environments.

**NM04.12.11**

**Enhanced Aqueous Copper(II) Ion Adsorption Efficiency of Polyaniline Nanofibers via Phytic Acid Doping**

Hyeyeong Jin Kim and Young Joon Hong; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).

Scavenging discarded metal in aquatic environment has been of note in both polluted water purification and mineral mining, which have been usually processed using various methods. Among the diverse methods, adsorption/metal-organic complexation by ion exchange has gained a great deal of interest for low processing cost, energy saving, and greener chemical technology. Because of the ability of the technique to reuse the adsorbent and the discarded metal, as of late, many types of meso-porous and nanostructured have been developed for high efficiency collection of aqueous metal ions, due to the high surface-to-volume (s/v) ratio. In particular, nanostructure adsorbents are thought to be ideal for high-efficiency metal adsorption, but high density surface ionic functional groups are further needed to strongly attract aqueous metal. Especially, polymer has a structural advantage of being viable to modify surface chemical properties via doping chemical functional groups to backbone, enabling it to substantially raise the aqueous metal adsorption efficiency. Also, many polymers are deformable such that they can be structurally designed to form desirable shapes in demand. In addition, considering the significance of reuse of adsorbed metals.

Here, we report on radical polymerization synthesis of phytic acid-doped polyaniline nanofibers (Ph-PAni NFs) and enhanced adsorption of aqueous Cu$^{2+}$ after the doping. To pose a higher negative charge, the dopant of phytic acidic molecules with phosphoric acid functional groups was employed. The Cu$^{2+}$ adsorption efficiency of Ph-PAni NFs was markedly increased after the doping, presumably due to high ionic attraction feature of phosphoric acid group in phytic acid. The adsorption efficiency of Ph-PAni NFs is discussed in terms of Langmuir and Freundlich adsorption models. We further investigated the pH-dependent adsorption efficiency of Ph-PAni NFs and found much higher Cu$^{2+}$ adsorption capability under high pH conditions owing to spontaneous deprotonation by the basic solution. Furthermore, Ph-PAni NFs showed stable, high Cu$^{2+}$ adsorption efficiency, irrespective of Co$^{3+}$ concentration in the bi-metallic Cu and Co aqueous solution. Surface modification and/or doping to enhance the adsorption efficiency of Cu(II) introduced in this study will provide a great venue for expanding the use of many other polymeric nanostructures for reclamation in metal mining as well as the conventional environmental applications such as water purification.

**NM04.12.12**

**Smart Metal Mesh to Simultaneously Harvest Atmospheric Fog and Remove Pollutants**

Ritwick Ghosh$^{1,2,3}$, Rakesh P. Sahaj$^{4}$, Igor Zhiltominrsky$^{1}$, Ranjan Ganguly$^{2}$ and Ishwar K. Puri$^{4}$; $^{1}$Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; $^{2}$Power Engineering, Jadavpur University, Kolkata, India; $^{3}$Mechanical Maintenance, NTPC Ltd., Farakka, India; $^{4}$Mechanical Engineering, McMaster University, Hamilton, Ontario, Canada.

Water harvesting from fog-laden atmospheric and industrial wind streams is finding increasing application. Since fog often contains SO$_x$, NO$_x$, and VOCs, use of the harvested water is limited by its quality. We describe an integrated approach that simultaneously harvests fog and removes pollutants from the collected water. A stainless steel (SS) mesh is coated with TiO$_2$/ZnO nanoparticles through electrophoretic anodic deposition. These two types of nanoparticles used to coat the meshes are correlated with this mesh efficacy. This technology can potentially be used to improve the local air quality by arresting smog in large complexes, such as hospitals, schools and public arenas.

**NM04.12.13**

**Gas-Phase Interrogation Module For Lower-Power Chemical Collection (GIMLI)**

Myeongseob Kim, Michael J. Bowers, Don Ahmasi Harris and Pierre-Alain Auroux; FAST Labs, BAE Systems, Columbia, Maryland, United States.

In this presentation, we provide partial results of IARPA supported MAEGLIN (Molecular Analyzer for Efficient Gas-Phase Low-Power Interrogation) program. The MAEGLIN program intends to develop an ultra low power chemical analysis system for remote site detection and identification of explosives, chemical weapons, industrial toxics and pollutants, narcotics, and nuclear materials in the presence of significant background and interferents. The system should be traceable to a package fitting within 0.5 L and 2.5 kg. The power threshold is < 7.5 J per analysis run with a goal of < 1.5 J per analysis run. The autonomy of the systems shall be at least 730 cycle sampling performance (one sample per day for two-year use). To accomplish this task, BAE SYSTEMS utilized its open cell proprietary foam as a low pressure drop broad-based adsorbent medium which enables sampling at high rates (liters per minute or lpm) utilizing a computer fan or blower. Upon collection the analytes are thermally desorbed from the foamed sorbent material and delivered directly to a GC column without use of a cryo-focusing system. Currently our system is able to collect over 50 targets (among 100 background compounds and with 5 true unknowns) with a compound mass range of 30-350 amu. With energy per sample 1.248J, system volume 0.82 L, and reusability is >730 times.

**NM04.12.14**

**Ultra-Durable Superhydrophobic/Superoleophilic Mesh Prepared by Spray-Coating for Oil/Water Separation**

Chuang Cheng, Ding Weng, Aways Mahmood and Jiaoda Wang; Tsinghua University, Beijing, China.

Nowadays, the efficient separation of oil/water mixtures has become an urgent challenge all over the world. Superhydrophobic/superoleophilic materials have been widely employed to separate oil/water mixtures due to its high efficiency, high flux and high selectivity. However, the poor mechanical durability of superhydrophobic materials has always been a common drawback, which limits their applications in real industry. Here, we propose a facile method to fabricate superhydrophobic mesh by spraying commercial adhesives and PTFE nanoparticles. The adhesives were used to bond the PTFE nanoparticles to the substrates and enhance its durability. The PTFE nanoparticles were used as building blocks to decrease the surface energy of substrates and promote hydrophobicity. The coated mesh exhibited superhydrophobic/superoleophilic properties with water contact angle of above 155$^\circ$ and oil contact angle of 0$^\circ$. Moreover, the as-prepared mesh can be applied to separate not only immiscible oil/water mixtures, but also water-in-oil emulsion with high separation efficiency. The coated mesh also exhibited good hydrophobicity and possessed high separation efficiency for various oil/water mixtures even after over 600 abrasion cycles, showing ultra-durable property. Furthermore, this method could be flexibly applied to almost any soft and solid substrate such as fabric, sponge, glass and so on, which could have significant application in industries.
NM04.12.15
Toxicity Evaluation of Boron- and Phosphorous- Doped Silicon Nanocrystals Towards *Shewanella oneidensis* MR-1
Bo Zhu1, Sadhana Mishra2, Natalie V. Hudson-Smith1, Uwe R. Kortshagen2 and Christy L. Haynes1; Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; 3Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Silicon nanocrystals, also known as silicon quantum dots, are regarded as green alternatives to traditional quantum dots composed of heavy metal elements. While the semiconductor properties of these materials can be tuned by doping with p-type dopants (*i.e.*, boron and phosphorous), little is known about the potential environmental impacts of these doped nanocrystals. This work demonstrates that introduction of dopants, especially phosphorus, causes the doped silicon nanocrystals to produce reactive oxygen species, resulting in significant toxicity to a model microorganism, *Shewanella oneidensis* MR-1. In addition, the interaction between bacteria cells and silicon nanocrystals was investigated using hyperspectral dark field microscopy and TEM. Interestingly, likely due to Lewis acid-base interactions, the boron-doped silicon nanocrystals tend to attach to the bacterial cell surface while this phenomenon was not observed for undoped or phosphorous-doped silicon nanocrystals. This mechanistic understanding of nanocrystal-bacteria interactions yields critical insight for future design of sustainable nanomaterials.

NM04.12.16
Surface Modification of Polymer Filters by Etching and a PDA Coating for Oil-Water Separation
Pei Zhao, Ning Qin, Carolyn Ren and John Wen; Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada.

Oil-water separation has been a global challenge due to extensive oily wastewater from industry and oil leakage. The polymer filters possessing underwater oleophobicity have been used for oil-water separation, which selectively allow water to flow through while resist oil. Those filters have been achieved either by the surface etching or by using novel coatings, as the wettability depends on the nature of the surface materials as well as the topography. Here, we developed a two-step strategy to modify polymer meshes and nonwoven fabrics for oil-water separation, where an underwater oleophobic PDA bio coating was applied onto a pre-etched polymer surface that had a large roughness. This strategy combines the required wettability of the coating and the large roughness that could further enhance the wettability.

Such modified polymer filters possessed superoleophobicity (>150°) in water and were capable of separating various oil-water mixtures with a high efficiency (>98.5%). These filters also showed increased intrusion pressure than the only coated or only plasma treated filters. The rugged surface created by the etching reinforced the coating stability and prevented the coating from peeling off of the substrate. Then the two-step modified filters were more durable than the only coated ones. Different from other durability investigations, in our work, for each cycle of use the filter was intruded (contaminated) by oil in order to measure its intrusion pressure. After 6 cycles of uses, the nonwoven filter was no longer underwater oleophobic due to severe oil contamination, and thus came to a failure in oil-water separation. After 19 repeated uses, the mesh filter was still capable of separating a certain amount of oil-water mixture but presented a decreased intrusion pressure due to slight oil fouling. Filters with different structures had different oil fouling levels during repeated uses that affected their durability for oil-water separation. The nonwoven with complex layers of pores was less durable than the mesh with a simple one layer porous structure, due to the much heavy oil fouling of the nonwoven. A way to efficiently clean the viscous oil residual in the filters could benefit the durability. The recoverability of the filter from oil fouling should be considered for practical applications. The two-step method of surface modification for polymer filters and the durability investigations give a new insight for filter design.

NM04.12.17
Electroimpedance Sensor for Detection of Cd with a Low-Cost Solution-Processed Sensing Layer
Priya Vinayak, Henam Sylvia Devi, Soumen Saha, Madhusudan Singh and Bhaskar Mitra; Indian Institute of Technology Delhi, New Delhi, India.

Cadmium is a trace metal in the Earth’s environment that presents with significant toxicological and carcinogenic effects in multiple organs in humans. The Centers for Disease Control (CDC) prescribe a maximum daily Cd exposure limit of 9 mg/m3. In this work, we have used chemical bath deposition to deposit CdS on gold for sensing Cd ions in test solutions. A Cr/Au layer (15nm/40nm) was deposited on glass under vacuum (4.2 x 10−6 Torr) using thermal evaporation. Subsequently, this substrate was immersed in an aqueous solution consisting of triethanolamine, cadmium acetate and thiourea (sulfur excess) at a pH of 12 using ammonium hydroxide, for over one hour at 50°C under constant stirring. Thin film X-ray diffraction (XRD) revealed CdS (111) deposition, while the absorption of resulting film was consistent with published data. The composition of the film was verified using energy dispersive X-ray spectroscopy (EDX) to reveal a Cd:S ratio of approximately 1:1. Electroimpedance measurements were carried out using a Biologic SP-150 potentiostat using an AC bias of 50 mV peak to peak on a DC ramp, with a Pt counter electrode and Ag/AgCl reference. Spiked Cd(NO3)2·4H2O solutions with concentrations 1M to 10−4M were used to characterize the operation of the sensor. The sensor showed linearity below 10−6M, with a detection limit of 2 x 10−5 M.

NM04.12.18
Functionalized Single Walled Carbon Nanotubes as Novel Nanoresin for Fast, Safe and Sustainable Water Purification
Abhinav Sahu and Jordan C Poler; Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina, United States.

Ground water & surface water quality in rural & urban areas are affected by natural & anthropogenic contamination. These water resources are being contaminated by pervasive Low Molecular Weight Organic Compounds (LMWOCs) which are not effectively removed by the current wastewater technologies. The US Environmental Protection Agency (USEPA) is focused on the removal of many classes of LMWOCs from drinking water & wastewater including; disinfection byproducts (DBP) precursors, pharmaceuticals, personal care products, heavy metals & perfluoroalkylated substances. In order to address removal of these pervasive compounds, an anion exchange resin polymer (AEP) functionalized Single Walled Carbon Nanotubes (SWCNTs) in the form of nanoresin has been developed. The large surface area of SWCNTs increases the availability of active ion exchange sites of the AEP. These nanoresins have higher & faster adsorption capacity compared to other current commercialized materials like magnetic ion exchange resins, DOWEX, etc.

This nanoresin was synthesized by modified activator regenerated electron transfer atom transfer radical polymerization technique in aqueous media. The hydrodynamic diameter of the purified AEP & nanoresin was 1.660 ± 0.10 nm & 194.9 ± 11.3 nm, respectively. The ratio between D & G bands, measured using Raman Spectroscopy, increased by 100% compared to pristine carbon nanotubes which is indication of covalent functionalization of the AEP. The proton nuclear magnetic resonance of the growing AEP showed 99.8% conversion from monomer to polymer in 69.30 hours. The scanning electron microscopy of nanoresin films fabricated on mixed ester cellulose (MCE) membrane for performance testing showed a smooth morphology of mesh of SWCNTs with conformal polymer coating. The step height of the fabricated film determined under atomic force microscopy was 142.31 nm. The measured membrane resistance of the thickest nanoresin film was determined to be $R_m = 2.1 \times 10^{12} \text{ m}^{-1}$ which is smaller than typical ultrafiltration membranes with $R_m = 2 \times 10^{10} \text{ m}^{-1}$.
We demonstrate the removal of several types of pharmaceuticals (viz., tetracycline hydrochloride and carbencimillin sodium), pesticides (viz., bentazon, terbutryn, Dithiopyram, DBCP, benomyl, chlorpyrifos, and clomazone) and PFAS (viz., perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS)), from water via adsorption capacity measurements. The percentage removal of PFOA and PFOS, for a starting concentration between 2-4 mg/L of contaminant, was 92.67% and 95.8%, respectively. The regeneration studies performed upto 20 cycles, showed a slope of -0.23 ± 0.18% per cycle which demonstrates that the nanorein could be regenerated. The green synthesis of nanorein, the ability to remove different classes of pervasive contaminants & the regeneration capacity corroborate an effective & sustainable solution to water purification & enhancement of water quality.

NM04.12.19 Microbial Platinum/Carbon Based Anode for Wastewater Treatment Andres F. Gonzalez, Myreisa Morales-Cruz and Carlos R. Cabrera; University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico.

The recycling of human urine has become a main area in wastewater treatment due to the increased demand of water. Urine is composed of 95% of water and 2% of urea and the rest are organic and inorganic salts. Urea is a toxic molecule that may cause renal failure and gastrointestinal bleeding. It is difficult to remove urea by common methods since it is a small uncharged molecule. In this work we develop a microbial carbon brush anode for the removal of urea. The bacterium uses urea and generates ammonia as a byproduct, subsequently oxidized by platinum at the carbon fiber surface. To improve the efficiency of the system we prepared carbon brush electrode as the anode material since it has been used to provide high surface areas for bacterial growth and high power densities in microbial fuel cells and modified with platinum for better catalytic properties. We synthesized platinum nanoparticles in our laboratory and attached it to the carbon fiber brush surface by impregnation. We tested unsupported and supported with Vulcan platinum nanoparticles synthetized in our laboratory and commercial platinum black and platinum nanoparticles in order to compare the catalytic activity for ammonia oxidation. The Pt-based catalysts were characterized by cyclic voltammetry and SEM to compare their capability and adhesion to the carbon fibers. We obtained better ammonium oxidation currents using the synthetized Pt nanoparticles than by using commercial platinum. Also we did a series of modification experiments with the bacteria in the anode surface to find the best modification conditions among temperature, voltage and time. These results were characterized by SEM imaging to compare the amount of carbon fiber surface covered by the bacteria. In our results the modifications of the carbon with bacteria were best when we didn’t use any voltage at 37°C.

NM04.12.20 A Scalable Approach for Manufacturing Nanoporous Silicon Membranes for Unconventional Separations Rahul Ramakrishnan, Brendan D. Smith and Jeffrey C. Grossman; Department of Materials Science and Engineering, Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts, United States.

Thermal separations are extremely energy-intensive processes integral to many industries worldwide, and are responsible for 12% of all energy use in the United States. By switching from thermal to membrane separations, over 70 TWh could be conserved. Traditional polymer membranes, which are commonly used for filtration, possess high chemical sensitivity as well as an inability to withstand temperatures above 40 °C. Ceramics are a second class of membrane materials which offer chemical and thermal resilience. Their high cost, however, deters their popular use. Nanoporous silicon (NPSi) membranes have recently been shown to provide excellent performance and enhanced chemical and thermal stability, but have only been produced on the millimeter scale.

Here, we present a scalable method for the production of NPSi membranes via a modified metal-assisted chemical etching (MACE) process that allows for catalyst-dependent control over pore morphology. Through a simple three-step process involving selective chemical thinning of standard silicon, sputter-deposition of metal catalysts, and MACE of ultrathin aspect ratio nanotubes, a novel membrane is produced using common commercial materials and processes.

The core advancement of metal catalyst sputter-deposition allows for greatly improved avoidance of nanoscale catalyst aggregation and sintering on the surface prior to MACE, translating to well-dispersed individual nanotubes which cannot exceed aspect ratios of 1000:1. SEM and TEM images reveal pore diameters of less than 5 nm and surface porosities greater than 5%. In terms of membrane performance, we also demonstrate that the NPSi produced via our method is suitable for water filtration, achieving 92% rejections of 2 nm gold nanoparticles while exhibiting minimal permeability loss with respect to pure water as measured by UV-Vis spectroscopy and flow rates. These results suggest that NPSi membranes produced via this process can remove bacteria, viruses, emulsified oils, and even heavy metals from water in one step. We demonstrate that even after harsh chemical and thermal treatment via immersion in nitric acid (pH < 0) and high temperature environments (over 200 °C), NPSi membranes created via our method remain able to conduct filtrations with the same rejections and permeabilities. Our simple and innovative approach can also be modified for health care applications such as hemodialysis, as well as numerous other applications in the food and beverage and biopharmaceutical spaces, among others.

NM04.12.21 High Performance Capacitive Deionization via Manganese Oxide-Coated, Vertically Aligned Carbon Nanotubes Wenbo Shi1, Xuechen Zhou1, Jinyang Li1, Eric R. Meshot1, André Taylor1, Shu Hu1, Jaehong Kim1, Menachem Elimelech1 and Desiree Plata2; 1Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States; 2School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, China; 3Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California, United States; 4Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, New York, United States.

The growing population and corresponding rise in clean water scarcity create appeal for transformative and sustainable desalination technology development and innovations. The capacitive deionization (CDI) desalination, where salt is removed by an electrochemical method, has emerged to tackle the limitations of poor energy efficiency, complex infrastructure, and high cost of other well-developed desalination technologies. Discovering electrode materials with exceptional capacitance, an indicator of the ability of a material to hold charge, is critical for CDI device development. Manganese oxides (MnOx) have shown promise, but exhibit a trade-off of lower active MnOx loading, coming at a cost of lower conductivity. To address this challenge and achieve high salt adsorption, we designed and fabricated carbon nanotube (CNT)-MnOx core-shell vertically aligned array electrodes using atomic layer deposition (ALD) to coat thin films of MnOx onto vertically aligned CNTs (VACNTs). The hierarchical, anisotropic, 3D macroporous structure of VACNT-MnOx and the unique tunable coating hallmark of ALD enabled the co-optimization of the hybrid material’s specific capacitance in dimensions of mass and geometric area, with an exhibited optimized mass-specific and geometric area-specific capacitance at 215 ± 7 Fg and 1.1 ± 0.1 Fcm², respectively. This co-optimized, outstanding capacitance not only positions them as candidate materials for traditional usage as energy storage devices, but also exhibits promise with a remarkable salt adsorption capacity (29 ± 1 mg NaCl/g material; two-fold higher than pristine VACNTs) to enable water desalination via CDI.

NM04.12.22
Highly Efficient Oil/Water Separation by Superhydrophobic/Superoleophilic Sponges Based Oil Skimmer

In recent years, nanotechnology has been proven to offer promising biomedical applications for in vivo diagnostics and drug delivery, stressing the importance of thoroughly investigating the biocompatibility of potentially translatable nanoparticles (NPs). Herein, we report the cellular responses of uncoated chitosan NPs (CS NPs) and hyaluronic acid-coated chitosan NPs (HA-CS NPs) when introduced into Chinese hamster ovary cells (CHO-K1) in a dose-dependent manner (2.5, 0.25, 0.025, 0.0025, and 0.00025 mg mL−1) at two time points (24 and 48 h). MTS assay, cell proliferation, showed a decrease in the viability of cells when treated with high doses of CS NPs (0.25 and 2.5 mg mL−1). When exposed to high doses of CS NPs, the lactate dehydrogenase (LDH) enzyme started to leak out of the cells and the cellular levels of mitochondrial potentials were significantly reduced accompanied by a high production of intracellular reactive oxygen species (ROS). Our study provides molecular evidence of the biocompatibility offered by HA-CS NPs, through ROS scavenging capabilities rescuing cells from the oxidative stress, showing no observed cellular stress and thereby revealing the promising effect of cationic hyaluronic acid to significantly reduce the cytotoxicity of CS NPs. Our findings are important to accelerate the translation and utilization of HA-CS NPs in drug delivery, demonstrating the pronounced effect of surface modifications on modulating the biological behaviors.

NM04.12.23

Formation of Metal Nanoparticles Directly from Bulk Sources Using Ultrasound and Application to E-Waste Upcycling

We present a method for creating nanoparticles directly from bulk metal sources using ultrasound, therefore bypassing high energy and potentially toxic intermediates and increasing atom efficiency. Nanoparticle formation occurs in water, in the presence of a bilayer forming surfactant system. Implosive collapse of cavitation bubbles occurs asymmetrically near the bulk metal surface, which generates powerful microjets leading to material ejection. This liberated material is captured by the surfactant bilayer and stabilized in the form of nanoparticles. The method is first characterized in detail using gold, but is also demonstrated on other metals and alloys, and is generally applicable. We show that nanoparticles can be produced from a number of different bulk metal form factors, as long as there is a sufficiently large planar surface to induce asymmetric bubble collapse. We then extend the method to an environmentally important problem, the reclamation of gold from an electronic waste stream.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

NM04.12.24

Highly Efficient Oil/Water Separation by Superhydrophobic/Superoleophilic Sponges Based Oil Skimmer

Functional materials inspired from lotus leaves possess outstanding water repellency and oil affinity simultaneously, which refers to superhydrophobicity and superoleophilicity, respectively. By utilizing the contrary extreme wettability to water and oil, such bio-inspired functional materials can be used for oil/water separation. In recent years, oil/water separation has received extensive attention owing to the growing oil pollution problem caused by oil spills, domestic sewage and industrial effluents. Therefore, the fabrication of functional materials for oil/water separation has been a research hotspot. However, most of the methods to fabricate the extreme wettability materials involve the use of toxic chemical reagents and complex processes. Herein, a simple and efficient immersion method is presented to prepare superhydrophobic/superoleophilic sponges for sustained separation of oil/water mixtures. The sponge with super-wettability is fabricated by dipping common polyurethane sponge in cupric stearate solution. The introduced micro/nanostructures and long-chain alkyl group of cupric stearate enable the sponge to be superhydrophobic and superoleophilic in air. Water droplets can be supported as spheres with contact angles above 158° and can easily roll off from the surface, while oils can spread completely on the sponges. The prepared sponge can maintain its superhydrophobicity after being fixed under water for more than 4 hours, showing good durability and stability. By employing the as-prepared superhydrophobic/superoleophilic sponges, a large-scale oil skimmer is designed to collect oil spills with a wide range of kinematic viscosities (0.42–74.4 cSt at 40 °C). Results show that the floating oils can be successfully separated from the mixtures with separation efficiencies above 90% for different oils. Additionally, no water is observed in the separated oils, demonstrating high purity of the collected oils. This facile, environmentally friendly and efficient method could offer a new perspective on practically solving pollution caused by oily industrial/domestic wastewater and oil spills.

NM04.12.25

Aldehyde Gas Detection Based on Cellulose Colorimetric Films

Aldehyde gas detection based on cellulose colorimetric films is of great importance for monitoring environmental gases. We demonstrate that cellulose-based colorimetric films can be utilized for the detection of aldehyde gases from food deterioration, especially the rancidity of fat. The film is fabricated by cellulose and nanocellulose fibers on a reflectant metal surface such as Au or Ag. By simple dip and pulling method, cellulose-based films with diverse colors from dark blue to yellow are formed. The color range can be controlled by changing the layer thickness from 46 nm to 165 nm with the pulling speed (from 1 mm/min to 10 mm/min) and drying conditions (from 58 to 60% relative humidity) during the self-assembly of cellulose fibers. Afterwards, the films are functionalized with amine groups to make them sensitive to aldehyde gases. When the film is exposed to the target gas, this functionalization intensifies structural color change and makes it possible to detect aldehyde gas down to several ppm. We demonstrate that sensing data analysis with a phone camera and discriminant analysis algorithms can tell apart the different gases to which the sensor is exposed. We expect that our results will be utilized in providing a low-cost and low-power systems for the monitoring of environmental gases.
covered CdTe/CdS QDs are facilely decorated with the low cost sulfur tolerant [Mo3S13]2− nanoclusters to exhibit enhanced visible-light photocatalytic H2 generation than the CdTe QDs catalyzed with classical cocatalysts of Pt. In all, the combination of sulfur tolerant [Mo3S13]2− nanoclusters and CdTe/CdS core/shell structure significantly enhance the activity and stability of CdTe QDs for visible-light photocatalytic hydrogen evolution.

Detection of Environmental Imidacloprid Using a Molecularly Imprinted Polymer Sensor Alyson G. Michael and Joseph J. BelBruno; Dartmouth College, Hanover, New Hampshire, United States.

A sensor for the environmental detection of the neonicotinoid pesticide imidacloprid has been designed by leveraging the selectivity of molecular imprinting and the sensitivity of conductive polyaniline nanowires. Imidacloprid is a widely used pesticide that has been linked to declines in bee populations. Imidacloprid from solution hydrogen bonds with imprinted PMMA-co-PMAA, and de-dopes the surrounding polyaniline nanowires, thereby increasing the resistivity of the system. The success of the system is justified by LCMS, FTIR spectroscopy, and resistance measurements. The sensor permits straightforward monitoring of the presence of imidacloprid in the environment and the assessment of sustainable bee keeping practices.

SYMPOSIUM PM01
Architected Materials—Synthesis, Characterization, Modeling and Optimal Design
November 26 - November 29, 2018

Symposium Organizers
Katia Bertoldi, Harvard University
Tobias Schaadler, HRL Laboratories, LLC
Lorenzo Valdevit, University of California, Irvine
Martin Wegener, Karlsruhe Institute of Technology

* Invited Paper

SESSION PM01.01: Shape Morphing and Origami/Kirigami Materials I
Session Chairs: Katia Bertoldi and Lorenzo Valdevit
Monday Morning, November 26, 2018
Hynes, Level 1, Room 102

8:00 AM *PM01.01.01
Shape Morphing Metamaterials Damiano Pasini; McGill University, Montreal, Quebec, Canada.

Thermal expansion can be challenging to control in applications that require thermal stability, yet it can be exploited to generate shape transformations that are highly predictable. In this talk, I will first present compliant building blocks that can deform under temperature, and then illustrate how their sequence can be encoded to attain macroscopic reconfigurations that are reversible. Investigated through theory and computations, the metamaterial behaviour is tested through proof-of-concept prototypes that show promise for deployable satellites, morphing components, and actuation devices.

8:30 AM PM01.01.02
Mechanical Instability Tuning in Architected Magnetoelastomers Vincent Chen1, 2, Artemii Goshkoderia3, Matthew Robinson1, 2, Carson Willey1, 2, Stephan Rudykh4, Abigail Juhi1 and Phil Buskohl1; 1Air Force Research Laboratory, WpaFB, Ohio, United States; 2UES, Inc., Dayton, Ohio, United States; 3Technion–Israel Institute of Technology, Haifa, Israel; 4University of Wisconsin–Madison, Madison, Wisconsin, United States.

Magnetoelastomers (MAEs) are an important class of soft, strain tolerant materials that generate a stiffness increase in response to a magnetic field. Stiffness tuning under magnetic field is advantageous due to the fast, reversible and non-contact control of the material properties, which is relevant for applications such as soft actuators, adaptive vibration dampers and acoustic filters. Architected MAE composites, such as laminates and periodic MAE inclusions in a non-active matrix, have been predicted to possess novel mechanical instabilities, due to the spatial distribution of stiffness mismatch and the ability to tune the mismatch with magnetic field. To demonstrate these concepts experimentally, we fabricated MAE composites using a commercial silicone as the non-responsive soft matrix and a silicone loaded with carbonyl iron particles for the stiff, magnetoactive regions. The silicone matrix underwent several modifications to increase the stiffness ratio between the soft encapsulating matrix and the stiff MAE regions, including tuning of the crosslinker to polymer ratio, incorporation of hydride-terminated silicone to promote a linear network, and addition of silicone oil to further reduce crosslinking. Laminates and 2D periodic MAE architectures were constructed through a series of drop casting and molding steps using 3D printed molds. A custom compression test jig was developed to systematically load the laminate specimen in the presence of a magnetic field. The study provides feedback on the sensitivity of the buckling strain to experimental specimen sizing/edge effects and provides broader insight on the practical integration of MAE instabilities into functional devices.

8:45 AM PM01.01.03
Field Responsive Architected Materials Julie A. Mancini1, 2, Mark Messner3, William L. Smith1, Logan Bekker1, Bryan Moran1, A. M. Golobic1, Andrew Pascale1, Eric B. Duoss1, Kenneth J. Loh2, 4 and Christopher M. Spadaccini1; 1LLNL, Livermore, California, United States; 2Mechanical Engineering,
We present a method of creating field responsive architected materials by combining additive manufacturing with magnetorheological (MR) fluid. MR fluid, a fluid that commonly consists of oil and magnetic particles, goes through a change in its rheological properties under a magnetic field. This rheological change observed in the MR fluid is on the order or milliseconds and is highly reversible. We demonstrate these field responsive architected materials by infilling tubular cuboctahedron unit cells and lattices with MR fluid. The result is a dynamically tunable structure that can rapidly and reversibly change its effective stiffness through the simple application of a magnetic field without changing its overall form. We will also discuss a predictive model that we have created to aid in future design of these field responsive architected materials. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Supported by LDRD Strategic Initiative 14-SI-004. LLNL-ABS-753060.

**PM01.01.04**

**3D Uniaxial Chiral Metamaterials with Ultra-long Characteristic Length Scale**

Patrick Ziemke* and Peter Gumbsch1, 2; 1Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Fraunhofer Institute for Mechanics of Materials, Freiburg, Germany.

Ordinary linear elastic materials do not exhibit a chiral mechanical response. This means that they do not convert a stretch or a compression into a twisting deformation mode. Recent research into the fabrication and design of metamaterials has made this degree of freedom accessible. By stacking 3D laser printed unit cells in each spatial direction, Frenzel et al.[1] created samples of a chiral mechanical metamaterial and successfully mapped its behavior onto a micropolar continuum[2]. Micropolar continuum theory predicts that the magnitude of the twist decreases inversely proportional to the ratio of the sample size to the size of one unit cell. To maintain the global chiral response for larger samples, the scaling behavior must be manipulated to minimize the decay of the twist.

This can be approached by either increasing the intrinsic chiral response of the material or by decreasing the coupling strength for the chiral component of the distortion. We attempt the latter and approach it with three-dimensional lattices based on a geometrically simple uniaxial chiral unit cell. Such simple structures can be modeled with reduced-order finite element formulations (cf. [3]) yielding an efficient numerical technique which allows the execution of extensive parameter studies with large three-dimensional samples.

We combine chiral unit cells with non-chiral coupling elements to form different lattices. Chiral and non-chiral elements can then be arranged just like in binary crystals forming CsCl or NaCl structures and the like. By testing different structures and tuning the properties of the different unit cells, we have designed lattice structures exhibiting an ultra-long decay-length compared to previously presented chiral mechanical metamaterials. In fact, some of our structures show an increasing chiral response at small numbers of unit cells and do not show a significant decay in the chiral response up to an edge length of 20 unit cells.


**9:15 AM PM01.01.05**

**Deployable Multi-State Structures via Pre-Strained, Multistable Elements**

Jochen Mueller1, 2, Jennifer Lewis1, 2 and Katia Bertoldi1, 2; 1John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 2Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, Massachusetts, United States.

Inspired by the shape memory of crumpled sheets and prior art on multistable structures, we present a new type of architectural metamaterial that can be fabricated flat and buckle out-of-plane to form complex shapes with defined load bearing capacity. The material is composed of discrete elements, of which the sides are exposed to different levels of pre-strain, locally induced during fabrication. Through experiment and simulation, we show that the elements buckle out of plane into different, stable states when exposed to small, orthogonal loads. The resulting, global shape can be pre-programmed via local pre-stress levels or changed by the fly via the activation sequence. By adding additional hierarchy levels, large displacements are achieved. All deformations are elastic and, hence, reversible. This reprogrammable and versatile material is expected to find application in a range of small and large-scale structures, such as deployable space frames and robotic manipulators.

**9:30 AM BREAK**

**10:00 AM PM01.01.06**

**Morphing Sheets into Freeform Objects, at the Micro- and Macro-Scales**

Chiara Daraio; California Institute of Technology, Pasadena, California, United States.

Morphing two-dimensional sheets into three-dimensional objects is a classical problem in mechanics, mathematics and art. Today, the ability to manufacture two-dimensional materials with an almost arbitrary microstructure, architecture and pre-stress distribution opens the door to new approaches for bending sheets into complex forms. In this talk, I will review recent progress in the design of micro- and macro-scale, nonuniform sheets that can bend into freeform objects. Engineering the distribution of residual stresses, stiffness gradients and/or cut patterns, we control the buckling of sheets at both local and global scales. The designed distribution of responsive materials within the sheets provides a time dependent control of the developing shapes. I will discuss examples of sheets that change shape in response to environmental stimuli or the application of point loads. Programming 2D sheets into rigid, 3D geometries expands the potential of existing manufacturing tools for efficient and versatile production of 3D objects.

**10:30 AM PM01.01.07**

**Atomic Origami—A Technology Platform for Nanoscale Machines, Sensors and Robots**

Itai Cohen; Cornell University, Ithaca, New York, United States.

What would we be able to do if we could build cell-scale machines that sense, interact, and control their micro environment?
In Richard Feynman’s classic talk “There’s Plenty of Room at the Bottom” he foretold of the coming revolution in the miniaturization of electronics components. This vision is largely being achieved and pushed to its ultimate limit as Moore’s Law comes to an end. In this same lecture, Feynman also pointed to the possibilities that would be opened by the miniaturization of machines. This vision, while far from being realized, is equally tantalizing. For example, even achieving miniaturization to micron length scales would open the door to machines that can interface with biological organisms through biochemical interactions, as well as machines that self-organize into superstructures with mechanical, optical, and wetting properties that can be altered in real time. If these machines can be interfaced with electronics, then at the 10s of micron scale alone, semiconductor devices are small enough that we could put the computational power of the spaceship Voyager onto a machine that could be injected into the body. Such robots could have on board detectors, power sources, and processors that enable them to make decisions based on their local environment allowing them to be completely untethered from the outside world.

In this talk I will describe the work our collaboration is doing to develop a new platform for the construction of micron sized origami machines that change shape in fractions of a second in response to environmental stimuli. The enabling technologies behind our machines are graphene-glass and graphene-platinum bimorphs. These ultra-thin bimorphs bend to micron radii of curvature in response to small strain differentials. By patterning thick rigid panels on top of bimorphs, we localize bending to the unpatterned regions to produce folds. Using panels and bimorphs, we can scale down existing origami patterns to produce a wide range of machines. These machines can sense their environments, respond, and perform useful functions on time and length scales comparable to microscale biological organisms. With the incorporation of electronic, photonic, and chemical payloads, these basic elements will become a powerful platform for robotics at the micron scale. As such, I will close by offering a few forward looking proposals to use these machines as basic programmable elements for the assembly of multifunctional materials and surfaces with tunable mechanical, optical, hydrophobic properties.

11:00 AM PM01.01.08
Reconfigurable Rotationally Symmetric Kirigami Structures and Their Applications
Erin Evke, Dilara Meli, Tristan Blanzy and Max Shelnit; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Kirigami design principles increasingly are being used to engineer auxetic materials and structures to achieve 2D to 3D transformations and precisely tune their physical properties. Here, we design, fabricate, and characterize rotationally symmetric kirigami (RSK) structures with complex elasticity, allowing for deformations of planar sheets to approximate curved surfaces and reversibly undergo large deflections. A combination of theory, finite element modeling, and experiments are used to depict the relationship between the cut pattern and the structure’s cross-plane deformation. We classify the RSK structures based on the order of rotational symmetry, defined by the number of sides and cuts along the perimeter. While in the planar, relaxed state, RSK structures exhibit inversion symmetry; this is broken upon cross-plane deformation, a property that may be of interest in controlling wave propagation. The deformed state can be interpreted as a superposition of deformed sub-units, in which the total deflection is a summation of the individual rings’ displacements. The rings can further be partitioned into beams that correspond to the cut geometry, which strongly influences the mechanical properties. We find the effective spring constant decreases with radial cut density but increases with azimuthal cut density, resulting in a theoretical 200-fold reduction in stiffness over the noncut membrane. To demonstrate the electrical characteristics and feasibility of RSK structures for flexible electronic applications, we fabricate conductive nets that maintain electrical properties even under large strains, well beyond 100,000% of the original profile. We also show the reconfigurability of the structures using thermally activated shape memory polymers and analyze their fatigue mechanism.

11:15 AM PM01.01.09
Inflatable Origami-Inspired Structures
David Melancon1, Chuck Hobern1, 2, Jason Ku3, Erik Demaine4 and Katia Bertoldi1, 3; 1John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; 2Graduate School of Design, Harvard University, Cambridge, Massachusetts, United States; 3Wyss Institute, Boston, Massachusetts, United States; 4Computer Science and Artificial Intelligence Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Origami has long been used as a source of inspiration to design creative and esthetic constructions, from the iconic paper swan to facades of multi-story buildings. More recently, the rules of folding have been applied to fabricate architectured materials with functional properties such as compactness, self-foldability, and multi-stability. These properties highlight the potential of origami to become a new design paradigm for rapidly deployable structures. Whereas multiple origami-inspired deployable surfaces have been reported in the literature, there is a lack of research on enclosed deployable geometries. In this work, we introduce a novel type of inflatable origami-inspired structure comprised of a polyhedron with triangular faces and elastic hinges. From simple geometry principles, this star-shaped structure possesses two compatible configurations – flat-folded and deployed – giving rise to a bi-stable behavior. Based on experiments of prototypes and simulations of an energy-based model, we characterize the mechanics of the deployment and explore the design space of this origami-inspired structure. The insights gained from the study of this simple geometry enable understanding the enabling of the folding principles of a novel class of enclosed origami-inspired structures that can be deployed to different stable configurations through inflation.

11:30 AM PM01.01.10
Kirigami Inspired-Metamaterials—From Morphable Structures to Soft Robots
Katia Bertoldi; Harvard University, Cambridge, Massachusetts, United States.

In recent years kirigami has become an emergent tool to design programmable and reconfigurable mechanical metamaterials. Kirigami-inspired metamaterials allow the practitioner to exploit cuts in addition to folds to achieve large deformations and create 3D objects from a flat sheet. Therefore, kirigami principles have been exploited to design highly stretchable devices and morphable structures.

In this talk I will show that precreased folds are not necessary to form complex 3D patterns in kirigami, as mechanical instabilities in flat sheets with an embedded array of cuts can result in out-of-plane deformation. Furthermore, by largely stretching the buckled perforated sheets, plastic strains develop in the ligaments. This gives rise to the formation of kirigami sheets comprising periodic distribution of cuts and permanent folds. As such, the proposed buckling-induced pop-up strategy points to a simple route for manufacturing complex morphable structures out of flat perforated sheets. Finally, I will also show that kirigami principles enable the design of morphable and transformable skins that facilitate the design of soft robots capable of locomotion.

11:45 AM PM01.01.11
Kirigami Inspired Self-Folding
Aref M. Abdullah1 and K. Jimmy Hsia2; 1Mechanical Science and Engineering, University of Illinois at Urbana–Champaign, Urbana, Illinois, United States; 2Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Realization of complex programmable metamaterials where the structural characteristics and functionalities could be tuned beyond their original, as fabricated design remains as one of the challenging problems within the research field of architectured materials. To that end, Kirigami - the art of cutting and folding flat sheets of paper, provides scalable routes to generate intricate three-dimensional shapes from thin, planar (two-dimensional) sheets of materials. Researchers have utilized mechanical force actuated Kirigami structures in functional disciplines as diverse as energy harvesting, actuation, optics, stretchable electronics, and soft robotics. Achieving shape reconfiguration of freestanding, Kirigami-cut sheets in a stimuli-responsive, autonomous manner would not only enable new functionalities but also contribute to self-assembled...
This work aims to understand the self-folding behavior of Kirigami-cut bilayers where one layer isotropically expands with respect to the other in response to an external stimulus. We investigate two distinct types of cut geometries namely squares with radial cuts and rectangles with side cuts through a combination of nonlinear finite element modeling and experiments with soft polymeric systems. The Kirigami cuts decompose the pristine squares and rectangles into interconnected beams (length >> width) and plates (length ~ width) of varying aspect ratios. Our finite element calculations reveal that it is possible to tune both the bending direction and curvature values of each individual geometric units within the Kirigami-cut structures and thus transform the bilayers into complex three-dimensional architectures with spatially varying bi-directional curvatures in an on-demand manner. To experimentally demonstrate the potential of our approach, we design planar bilayered samples with side cuts and swell them in organic solvents to generate letters from the English alphabet to make up "UIUC" (University of Illinois at Urbana-Champaign) and "MRS" (Materials Research Society). We also design bilayers with radial cuts, and as they transform shapes with varying mismatch strains (solvent concentrations), we show that it is possible to use them as freestanding tunable optical systems where the transmission and reflection windows for incident light could be controlled through the deformation behavior of individual geometric units between the cuts. We also use a combination of the cuts to realize polyhedral shapes (such as tetrahedron and cube) through the self-folding of planar bilayers. The design principles proposed in this work would be applicable to a variety of material systems across length scales and contribute toward the development of smart programmable metamaterials.

SESSION PM01.02: Shape Morphing and Origami/Kirigami Materials II
Session Chairs: Damiano Pasini and Martin Wegener
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 102

1:30 PM *PM01.02.01
Sequential Mechanical Metamaterials Martin Van Hecke; Leiden University, Leiden, Netherlands.

Ordered sequences of motions govern the morphological transitions of a wide variety of natural and man-made systems, while the ability to interpret time-ordered signals underlies future smart materials that can be reprogrammed and process information. Here we introduce two novel classes of mechanical metamaterials, that can (1) exhibit sequential output and (2) are sensitive to sequential input. To obtain metamaterials that translate a global uniform compression into a precise multistep pathway of reconstructions, we combine strongly nonlinear mechanical elements with a multimodal hierarchical structure, and demonstrate multi-step reconstructions of digitally manufactured metamaterials. To obtain metamaterials that are sensitive to a sequence of mechanical inputs, we introduce the notion of non-commuting metamaterials, and show their capability for storing and processing information. Our work establishes generic principles for infusing metamaterials with sequential input and output.

2:00 PM PM01.02.02
In Situ Tunable Stiffness Using Multistable Kirigami Metamaterials Yi Yang1, Marcelo Dias2 and Douglas Holmes3; 1Boston University, Boston, Massachusetts, United States; 2Aarhus University, Aarhus, Denmark.

Materials with in situ tunable stiffness are needed for engineering programmable materials, shape-shifting structures, artificial muscles, and soft robotic actuators. While most examples of materials with in situ tunable stiffness focus on stimulus-responsive material properties, recent investigations on reconﬁgurable mechanical metamaterials opened another door to attain tunable material properties by systematically programming the microstructure of a constituent material. The mechanical properties of these architected materials depend on the topology of the substructure regardless of the constituent materials used. By introducing morphological structures into the unit cell, reprogrammable and reconﬁgurable metamaterials can be attained. Among various types of mechanical metamaterial, kirigami and origami metamaterials attracted tremendous attention due to its robust and straightforward ability to transform 2D sheets into 3D structures. Compared with its sister, origami metamaterials which have been extensively studied, understanding the mechanical behavior of kirigami metamaterials is limited. In this study, through a combination of experiments, simulation, and theoretical analysis, we demonstrate how a multistable microstructure inspired by kirigami provides a new design approach. By changing the spacing between the adjacent slits in the conventional linear parallel cutting patterns, we obtain multistable kirigami lattice structures composed of repeating unit cells whose structure is endowed with a bistable snap-through mechanism. Each stable state of the mechanical metamaterial exhibits a corresponding stiffness. By switching unit cells between the two stable states, we can tune the stiffness of this kirigami metamaterial in situ by a factor of five. Since this multistable kirigami approach is material independent, it could be integrated with stimulus-responsive materials, 3D printing technique, or combined with origami structures to be applied in multifunctional materials, deployable space structures, soft robotics, and biomedicine.

2:15 PM PM01.02.03
Observation of Mechanical Activity in a 3D Chiral Metamaterial Tobias Freznel1, Muamer Kadic1,2 and Martin Wegener3,4; 1Institute of Applied Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany; 3FEMTO-ST, Université de Bourgogne Franche-Comté, Besançon, France.

In a medium exhibiting optical activity, an incident transverse linear polarization of a light wave rotates because the eigenpolarizations of the chiral medium are not linear but rather circular, with a lifted degeneracy between left- and right-handed circular modes. Therefore, a linear incident polarization must be decomposed into the two circular eigenpolarizations, which propagate with different phase velocities. The resulting phase difference accumulated during propagation leads to a periodic rotation of the linear polarization axis versus the propagation coordinate. A rotation by 90 degrees corresponds to mode conversion.

Regarding elasticity, a different kind of mode conversion has recently been observed in two-dimensional (2D) centrosymmetric metamaterials [1]. There, the conversion between in-plane longitudinal (compression) and in-plane transverse (shear) modes did not require chirality. Chirality is crucial in quasi 2D monolayers of non-centrosymmetric tungsten diselenide crystals, for which the presence of chiral phonons [2] was deduced via selection rules of optical transitions.

In this contribution, we report the first experimental observation of mechanical activity, the elastic counterpart of optical activity, in 3D chiral polymer microlattices [3]. We have previously investigated related 3D chiral micropolar metamaterial samples made by 3D laser nano imprinting in the static regime [4]. Our present experimental approach in the dynamic regime is based on cross correlations of microscopy images taken under phase-delayed synchronized stroboscopic illumination with a light-emitting diode and sinusoidal excitation of the sample with a piezoelectric actuator. This approach is distinct from the established mapping of out-of-plane surface excitations by interferometric laser detection and laser excitation (see, e.g., [5]).

For an incident linearly polarized transverse elastic wave, we demonstrate the polarization rotation by 90 degrees at 225 kHz frequency over as few as 10
unit cells in the axial direction, with 3-by-3 unit cells in the cross section. The experimental results are in good agreement with numerical finite-element calculations for finite beams as well as with band structure calculations for fictitious infinitely extended beams. These experiments pave the road for molding the polarization and the propagation direction of elastic waves in three dimensions by micropolar mechanical metamaterials.

Architected Nanocomposites as Model Materials for Armor Systems
Anna Guell Izard, Jens Bauer and Lorenzo Valdevit; Mechanical and Aerospace Engineering, University of California, Irvine, Irvine, California, United States.

Armor systems must be carefully designed to mitigate two threats: blast and penetration. A successful armor dissipates the kinetic energy of the blast via plastic deformation while being able to resist the penetration of a projectile. These functional requirements require a material with high toughness and hardness, two properties that are generally mutually exclusive in monolithic materials. Current armor solutions consist of multi-layer systems encompassing one or more metallic or polymeric phases for energy absorption and a ceramic phase for penetration resistance. Here we propose a novel strategy based on the optimal design of functionally graded micro/nano-architected ceramic/polymer or ceramic/metal composites. The optimal intertwining of the two phases at the nanoscale has the potential to vastly outperform current solutions, while reducing weight. In this talk, we will present the performance of ceramic/metal and ceramic/polymer architected nanocomposites based on ordered lattice topologies and spinalod architectures.

4:15 PM PM01.03.03
Mechanical Behaviour of Architected Auxetic Hybrid Lattice Structures
Frédéric Albertini1, Justin Dirrenberger1, André Molotoiak2 and Cyrille Solligoub1; 1PIMM, CNRS, Paris, France; 2Material Science and Engineering, Monash University, Clayton, Victoria, Australia.

Architected Materials are an emerging class of advanced materials that bring new possibilities in terms of functional properties, filling gaps in Ashby’s material performance maps. The term architected materials describes any heterogeneous material that exhibits improved specific properties due to a thoughtful and predetermined morphology and/or topology design. This usually induces characteristic length-scales comparable to the size of the final component being produced, i.e. the millimetre scale in the case of lattice structures. Different strategies have been studied in the literature for mitigating the surface defects of additively manufactured metallic lattices: chemical etching, electro-erosion, mechanical polishing. A new proposition is presented in this work: polymer coating or embedding of metal struts, by analogy to the soft-hard turtle-like strategy for mitigating crack propagation. Besides processing of such architected lattice structures, the present work brings experimental and numerical results concerning the mechanical behaviour in compression for negative Poisson’s ratio lattices, also known as auxetics. As a matter of fact, one engineering challenge is to predict the effective mechanical properties of architected materials; computational homogenization using finite element analysis is a powerful tool to do so when considering quasi-static behaviour; difficulties arise when analysing the effective damping behaviour. A straightforward solution is to rely on full-field finite element dynamic simulation, accounting for the intrinsic viscoelastic damping of the constitutive material, as well as the structural damping due to the geometrical definition of the lattice structure considered in the present work. Homogenized behaviour of architected materials can thus be used in large structural computations, hence enabling the dissemination of such materials in the industry. Comparison is made between the metal and hybrid lattice structures.

4:30 PM PM01.03.04
Architected Viscoelastic Impact Attenuators for Sports Padding Applications
Eric C. Clough1, 2, Zak Eckel1, Alvin Escobar1, Jacob Hundleby1 and Tobias Schaedler1; 1HRL Laboratories, Malibu, California, United States; 2Materials, University of California Santa Barbara, Santa Barbara, California, United States.

Mitigating injury as a result of an impact between multiple players or between a player and the ground presents a significant challenge to the sports protective equipment designer. These designs must consider multiple injury criteria (e.g. concentrated loads, peak acceleration, peak torque) for multiple successive impacts, while balancing human factors such as comfort and player mobility. For padding components, maximal volumetric energy absorption is key to achieving impact attenuation performance without sacrificing player mobility. Typical padding materials include urethane and vinyl nitrile closed-cell foams which attenuate impacts through the collapse of internal pores when compressed. The stochastic internal geometry of foams limits optimal design of foam pads to essentially two design variables: composition and apparent density. Conversely, lattices provide the designer with a host of architectural degrees of freedom enabling the optimal design of lattice pads that can significantly outperform foams through tuning of buckling and post-buckling response. The open-celled architecture of lattices additionally affords improvements in airflow for comfort or enhanced energy absorption. In this talk, we will present our recent work on the design, fabrication, and optimization of lattice padding materials fabricated via HRL’s rapid and scalable self-propagating photopolymer waveguide process. We demonstrate that by optimal design of the architecture, in conjunction with tuning the viscoelastic properties of the parent solid, lattice pads with impact attenuation performance exceeding 1.3X that of state-of-the-art foam padding can be achieved.

4:45 PM PM01.03.05
Plate Mechanical Metamaterials and Their Applications
Igor Bargatin; Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Wynnewood, Pennsylvania, United States.

Recently, we introduced the concept of plate mechanical metamaterials—cellular plates with carefully controlled periodic geometry and unique mechanical properties—as well as its initial realization in the form of freestanding corrugated plates made out of an ultrathin film. We used atomic layer deposition (ALD) and microfabrication techniques to make robust plates out of a single continuous ALD layer with cm-scale lateral dimensions and thicknesses between 25 and 100 nm, creating the thinnest freestanding plates that can be picked up by hand. More recently, we also fabricated and characterized plate metamaterials made from multiple layers of nanoscale thickness, whose geometry and properties are reminiscent of honeycomb sandwich plates or corrugated paper cardboard. The two layers are offset from each other but at the same time are connected using vertical-wall webbing, which prevents shear of the two layers with respect to one another. As a result, these “nanocardboard” plates orders-of-magnitude higher bending stiffness than the single-layer structures we reported earlier, while still possessing extremely low weight (as low as 0.5 g/m²) and mechanical robustness. The increase in the bending stiffness is expected, and its mechanism is similar to that used in conventional honeycomb sandwich plates, which offer the best possible combination of high bending stiffness and low mass. However, in contrast to sandwich composite plates, our nanoscale two-layer mechanical metamaterials can sustain extremely large deformations without fracture, fully recovering their original shape and not displaying any signs of internal damage.

Like the nanotuss-based mechanical metamaterials reported by other groups, plate mechanical metamaterials are extremely lightweight and resilient due to their nanoscale thickness and microscopic cellular structure. However, in contrast to the cube-shaped metamaterials that typically form a lattice easily penetrated by the ambient air, our plates form continuous flat plates. Ultralow weight, mechanical robustness, thermal insulation, as well as chemical and thermal stability of alumina make plate metamaterials attractive for numerous applications, including structural elements in flying microbots and interstellar light sails, high-temperature thermal insulation in energy converters, photophoretic levitation, as well as ultrathin MEMS/NEMS sensors and resonators. I will briefly discuss our experimental progress on all these applications, including demonstration of extremely robust thermal insulators that can sustain a temperature difference of ~1000 C across a micron-scale gap, macroscopic plates that levitate when illuminated by light, and hollow AFM cantilevers that offer greatly enhanced sensitivity and data acquisition rates.
8:00 AM *PM01.04.01* 
**Materials by Design—Three-Dimensional (3D) Nano-Architected Meta-Materials** Julia R. Greer, Andrey Vyatskikh, Carlos M. Portela, Xiaoxing Xia and Arturo J. Mateos; California Institute of Technology, Pasadena, California, United States.

Creation of extremely strong and simultaneously ultra lightweight materials can be achieved by incorporating architecture into material design. We fabricate three-dimensional (3D) nano-architectures, i.e. nanolattices, whose constituents vary in size from several nanometers to microns or even centimeters. These nanolattices can exhibit superior thermal, photonic, electrochemical, and mechanical properties at extremely low mass densities (lighter than aerogels), which renders them ideal for many scientific pursuits and technological applications. The dominant properties of such meta-materials, where individual constituent size at each relevant scale (atoms to nanometers to microns) is comparable to the characteristic microstructural length scale of the constituent solid, are largely unknown because of their multi-scale nature. To harness the beneficial properties of 3D nano-architected meta-materials, it is critical to assess properties at each relevant scale while capturing the overall structural complexity.

We describe the fabrication and synthesis using Additive Manufacturing (AM) techniques, as well as the mechanical, biochemical, electrochemical, and thermal properties of nanolattices made of different materials with varying microstructural detail. Attention is focused on uncovering the synergy between the internal atomic-level microstructure and the nano-sized external dimensionality, where competing material- and structure-induced size effects drive overall response and govern these properties. Specific discussion topics include the nanofabrication and characterization of (often hierarchical) three-dimensional nano-architected meta-materials and their applications in chemical and biological devices, ultra lightweight energy storage systems, damage-tolerant fabrics, and photonic crystals.

8:30 AM PM01.04.02 
**Nanocrystalline Aluminum Truss Cores for Lightweight Sandwich Structures** Tobias Schaedler¹, Lisa Chan², Eric C. Clough³, Morgan A. Stilke³, Lawrence J. Masur² and Jacob Hundle³; ¹HRL Laboratories, LLC, Malibu, California, United States; ²Xtalic Corporation, Marlborough, Massachusetts, United States.

Substitution of conventional honeycomb composite sandwich structures with lighter alternatives has the potential to reduce the mass of future vehicles. Here we demonstrate nanocrystalline aluminum - manganese truss cores that achieve 2 - 4 times higher strength than aluminum alloy 5056 honeycombs of the same density. The scalable fabrication approach starts with additive manufacturing of polymer templates, followed by electrodeposition of nanocrystalline Al-Mn alloy, removal of the polymer, and facesheet integration. This facilitates curved and net-shaped sandwich structures, as well as coating of the facesheets, which eliminates the need for extra adhesive. The nanocrystalline Al-Mn alloy thin -film material exhibits high strength and ductility and can be converted into a three-dimensional hollow truss structure with this approach. Ultra-lightweight sandwich structures are of interest for a range of applications in aerospace, such as fairings, wings, and flaps, as well as for the automotive and sports industries.

8:45 AM PM01.04.03 
**Additive Manufacturing and Design of Multi-Functional 3D Architected Metamaterials** Xiaoyu Zheng; Virginia Tech, Blacksburg, Virginia, United States.

Rapid progress in additive manufacturing methods has led to the creation of a new class of ultralight, stiff and strong 3D architected metamaterials comprised of a network of hierarchical, stretch-dominated, micro-scale unit cells. The performance of these micro-architected metamaterials, spanning across multiple length scales, will ultimately be limited by their tolerance to damage and defects, yet an investigation of their fracture toughness has remained elusive. Here, we provide the first experimental observations of different crack initiation modes activated by model -loading of notched low density, hierarchical metamaterials. We find that, through hierarchical micro-architected features, the low density, stretch-dominated metamaterials can achieve simultaneously higher fracture toughness and strength: properties that are usually mutually exclusive. Numerical and scaling relationships are also reported that accurately capture the measured fracture toughness and strength values. These are then used to develop design maps for the optimal hierarchical architectures as functions of the density of the metamaterial and failure strain of the parent material.

9:00 AM PM01.04.04 
**Subtractive Post-Processing to Create Delicate Nano-Scale Structures** Andrew Gross and Katia Bertoldi; Harvard University, Cambridge, Massachusetts, United States.

Two photon polymerization (TPP) has become a popular technique for testing new devices and designer materials at the nano and micro scales. This technique provides much of the flexibility of a desktop 3D printer with access to physics that are uniquely scale dependent. Like every additive manufacturing technique, TPP is limited to a minimum achievable size for the voxel that can be rastered to create a structure. The constraint on reducing the size of the voxel is a practical limit arising from both the spatial photon density distribution within the diffraction limited focal volume of the laser illumination and the contrast curve of the photoreisit that describes the degree to which it polymerizes in response to exposure at a certain dose. Here, we present an approach for achieving smaller feature sizes that is accessible to researchers without specialized equipment. This approach leverages the high resolution of a piezo stage to precisely raster the voxel into shapes that upon isotropic etching allow access to a smaller length scale. Free-standing fully three-dimensional structures with feature sizes under 100 nm are demonstrated. Additionally, this technique allows for the fabrication of structures which are otherwise too delicate to make. This is achieved both by simply etching a structure of interest to impart more slender features, and also by including secondary support material to create complex structures that cannot be fabricated by any other method at this length scale.

9:15 AM PM01.04.05 
**Carbon-Based Nanolattice Materials** Jens Bauer, Anna Guell, Cameron Crook and Lorenzo Valdevit; University of California, Irvine, Irvine, California, United States.

From a traditional perspective, there is little room for further expansion of the accessible material property space by classical material fabrication methods.
Single one- and two-dimensional nanoscale objects, such as nanowires and thin films, are known to exhibit exceptional physical properties. Yet, their properties are intrinsically coupled to their small size and, therefore, can hardly be accessed in actual materials of practical volume. If nanowires and thin films are simply scaled up, many of their exceptional properties, which relate to surface to volume effects, drop dramatically; similarly, if nanoscale objects are clustered in a composite material, interfaces dominate the overall behavior, again substantially reducing performance. Nanolattice materials, regular three-dimensional networks constructed from nanowires or thin films, can potentially resolve this dilemma. Nanolattice materials can be thought of as metamaterials which can scale up beneficial size effects by topological design of their architecture.

In our work, we have fabricated carbon-based nano-architected lattice materials by direct laser writing (DLW) and pyrolysis. The combination of DLW and pyrolysis facilitates complex three-dimensional carbon-based ceramic structures of uniquely high resolution, with feature dimensions below 100 nm. This enables to take advantage of pronounced size-dependent effects on material strength. We systematically investigate the effects of processing parameters, dimensional scale, topology and topology-dependent strain during pyrolysis on the mechanical and functional properties of nanolattices. Here, we offer an overview of manufacturing routes, with emphasis on the key processing parameters. The interplay of size-dependent effects with different topological and material design approaches is emphasized.

9:30 AM BREAK

10:00 AM PM01.04.06
Designing and Manufacturing Cellular Mechanical Metamaterials
Carolin Körner1,2 and Maximilian Wormser2; 1Chair of Materials Science and Engineering for Metals, FAU Erlangen-Nuremberg, Fürth, Germany; 2Joint Institute of Advanced Materials and Processes (ZMP), FAU Erlangen-Nuremberg, Fürth, Germany.

The geometrical structure of a material can drastically change its mechanical behavior. Mechanical metamaterials are architected structures with extreme properties that surpass the capabilities of conventional bulk material. Periodic cellular structures lend themselves to be used as metamaterials because of their high variability. In the past, manufacturing methods limited the possibility to create intricate three-dimensional cellular structures. This changed with the advent of additive manufacturing technologies. Nowadays, cellular structures can be printed as polymers, ceramics or metals. Finding new shapes for cellular materials can be difficult. We developed a new method to find interesting unit cell designs by using eigenmode analysis on a basic unit cell. The eigenmode shapes of the basic cell then serve as new unit cell for further simulations. Cellular materials can have an excellent ratio of stiffness to weight, making them highly suitable for lightweight construction. By adding additional metamaterial functions to these structures, we get a so-called intelligent or smart material. An example for such a feature is auxetic behavior, i.e. a negative Poisson ratio. Therefore, if the structure is compressed, it will also compress laterally to the applied force and reduce its volume as opposed to regular materials that expand laterally.

Other metamaterial effects influence the way structures interact with mechanical waves. Given the right geometry, a structure can be unable to resonate in a certain frequency band. This effect is called phononic band gap and it can be used for wave guiding and filtering. Selective Electron Beam Melting (SEBM) is a powder-based additive manufacturing technology that enables us to produce complicated structures on a millimeter scale with very few limitations. We used this technology to create auxetic structures as well as phononic band gap structures using the above mentioned eigenmode analysis method and tested their properties. A new measurement method for mechanical wave transmission in lattice materials was developed. Piezoelectric transducers were used to create and measure the incoming and outgoing signal. The experimental results were compared to numerical simulations and were found to be in agreement with each other. By further improving the design based on gradient based optimization the phononic band gap of a macro-level unit cell could be pushed into the audible range below 20 kHz.

10:30 AM PM01.04.07
Single Atom Scale Fabrication by Scanning Transmission Electron Microscopy
Ondrej Dyck1,2, Sergei V. Kalinin1,2 and Stephen Jesse1,2; 1Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Fabrication of atomic scale structures remains the ultimate goal of nanotechnology. The reigning paradigms are scanning probe microscopy (SPM) and synthesis. SPM assembly dates to seminal experiments by Don Eigler, who demonstrated single atom manipulation. However, stability and throughput remain issues. The molecular machines approach harnesses the power synthetic chemistry to build individual functional blocks, yet strategies for structural assembly remain uncertain.

In this presentation, I discuss research activity towards a third paradigm — the use of the atomically focused beam of a scanning transmission electron microscope (STEM) to control and direct matter on atomic scales. Traditionally, STEM’s are perceived only as imaging tools and beam induced modifications as undesirable beam damage. Our team and several groups worldwide have demonstrated that beam induced modifications can be more precise. We have demonstrated ordering of oxygen vacancies, single defect formation in 2D materials, and beam induced migration of single interstitials in diamond like lattices. What is remarkable is that these changes often involve one atom or small group of atoms and can be monitored real-time with atomic resolution. This fulfills two out of three requirements for atomic fabrication. I will introduce several examples of beam-induced fabrication on the atomic level, and demonstrate how beam control, rapid image analytics, better insight through modelling, and image- and ptychography based feedback allows for controlling matter on atomic level.

This research is supported by and performed at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, BES DOE.

10:45 AM PM01.04.08
Facile Electrochemical Fabrication Route for Multicomponent and Multifunctional Inverse Opaline Films for Highly Sensitive VOC Detection
Pei-Song Hung1, Ju-Szu Chou1, Shih-Cheng Chou2, Guang-Ren Wang1, Chuan-Jyun Wang2, Yu-Ting Cheng2, Pochun Chen1, Tsung-Eong Hsieh1, Kuei Tsong Tang3 and Pei Wu1; 1National Chiao Tung University, Hsinchu, Taiwan; 2National Taiwan University of Technology, Taipei City, Taiwan; 3National Tsing Hua University, Hsinchu City, Taiwan.

Non-invasive diagnosis for early detection of diseases have drawn considerable attention during past few decades. Earlier, several biomarkers have been identified in exhaled breath specimens using GC-MS technique. However, the GC-MS analysis is a tedious process requiring high-end instruments, spacious facility, and well-trained personnel. With rapid development of artificial intelligent e-nose system, there is a promising potential serving as a portable alternative to the aforementioned analytical technique. With ultra-high specific surface area and activities, numerous nanomaterials have been explored for sensing applications. However, a dilemma often exists as researchers trying to increase the amount of materials used for enhanced sensitivity and meanwhile maintaining accessible surface area. Unlike 2D thin film sensors, 3D nanostructured sensing materials provide a larger surface-to-volume ratio with enhanced mass transfer due to their open cell configuration. Several architectures have been proposed and designed for these purposes. Among them, inverse opal (IO) is considered as a promising candidate as it possesses ordered and monodispersed porous scaffolds with numerous interconnected channels for superior permeability.
Ideally ordered nanohole array of TiO₂ has attracted attention due to its wide applicability based on the periodicity of the nanoholes, high refractive index and semiconductor properties of TiO₂. Various types of optical devices based on an ideally ordered nanohole array of TiO₂ have been proposed, such as photonic crystal, photocatalyst, solar cells and so on. Until now, several kinds of fabrication process of nanohole array structure of TiO₂ have been proposed. By applying semiconductor microfabrication process using electron beam lithography and focused ion beam etching apparatuses, an ideally ordered nanohole array could be obtained. However, this process is time consuming. By anodization process, porous TiO₂ could be obtained in large sample area. However, it is difficult to obtain ideally ordered nanohole array structure because the nanoholes in anodic porous TiO₂ usually form multi domain structure. In this presentation, fabrication process of anodic porous TiO₂ having ideally ordered nanohole array and its application to photonic crystal will be presented [1–4]. Prior to the anodization of Ti, concaves were fabricated onto the surface of Ti through a texturing process. In subsequent anodization, each concaves acted as a starting point of the formation of nanoholes, resulting in the formation of an anodic porous TiO₂ having ideally ordered nanohole array. Photonic crystal properties of the anodic porous TiO₂ were evaluated by measuring reflection spectra. In this study, we have demonstrated that photonic crystal properties were significantly enhanced by the photonic crystal fabrication process using anodization, and that these results could be applied to various optical devices.

**References**

Self-assembly of particles into long-range, three-dimensional, ordered superstructures is crucial for the design of a variety of materials, including plasmonic sensing materials, energy or gas storage systems, catalysts and photonic crystals. This kind of structures have been demonstrated mostly with spheres that, owing to their entropically favoured fcc packing, form the densest structures possible.[1] Polyhedra have been tested but so far only with metals and oxides.[2]

Here, we have combined experimental and simulation data to show that truncated rhombic dodecahedral particles of the metalorganic framework (MOF) ZIF-8 can self-assemble into millimetre-sized superstructures with an underlying three dimensional rhombohedral lattice with photonic crystal properties.[3]

These superstructures feature a photonic bandgap that can be tuned by controlling the size of the ZIF-8 particles and is also responsive to the adsorption of guest substances in the micropores of the ZIF-8 particles. Superstructures with different lattices can also be assembled by tuning the truncation of ZIF-8 particles, or by using octahedral UiO-66 MOF particles instead. These well-ordered, submicrometre-sized superstructures might ultimately facilitate the design of three-dimensional photonic materials for applications in sensing.

References

SESSION PM01.05: Micro/Nano-Architected Materials III
Session Chairs: Jens Bauer and Andrew Gross
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 102

1:30 PM *PM01.05.01
Robust Architected Materials—Deformation and Failure of Microlattices Under Cyclic Loading Ruth Schweiger: Karlsruhe Institute of Technology, Karlsruhe, Germany.

Cellular materials with designed nanoarchitectures have redefined the limits of the accessible material-property space throughout different disciplines.

Having characteristic features in the micro to nanometer regime, such architected materials exhibit exceptional mechanical properties at low density, including ultrahigh strength, damage tolerance, and stiffness. However, the design of lightweight structures that are both strong and damage tolerant is still a challenge and requires a better understanding of cyclic deformation and failure of the strength-optimized structures. Not only the absorbed energy during one loading cycle is important, but also the ability of the lattices to recover, maintain the strength, and be able to absorb energy during additional cycles. The highest resolution in manufacturing is currently achieved by 3D direct laser writing, which enables the fabrication of highly customized polymeric microlattices. We then apply additional processing steps, such as additional heat treatments and ceramic or metal coatings, to further improve or tailor the effective mechanical properties. While a ceramic coating in general results in enhanced strength, the failure mechanisms depend on the coating thickness. Brittle fracture of the struts rather than buckling is observed, when comparing the effect of 10 nm and 100 nm thick alumina coatings. However, in addition to high strength our solid-beam microlattices exhibit significant energy dissipation during cyclic loading experiments. Overall, the energy dissipation is a function of progressively failing ligaments, while upon multiple loading cycles to the same strain stable cyclic behavior is approached. In situ experiments showed that post-yield softening was induced by plastic buckling and crushing of individual ligaments. The contributions of the different deformation and failure mechanisms to the specific dissipated energy were quantified through progressive cyclic loading of the microlattices.

2:00 PM PM01.05.02
Architected Interfaces with Enhanced Fracture Toughness Kevin T. Turner1, Simon Heide-Jørgensen2, Sumukh Pande1 and Michal K. Budziszek1; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Aarhus University, Aarhus, Denmark.

Additive manufacturing has opened new opportunities for engineering the mechanical properties of materials via geometry. While there have been significant efforts in the architected materials field to exploit geometry to realize materials with unique properties such as high specific stiffness and the ability to recover from large deformations, the engineering of fracture properties and crack growth resistance via geometry is less studied. Here, we use a combination of experiments and computational modeling to investigate the role of geometric structuring on the toughness of interfaces containing arrays of pillars. Specifically, we establish quantitative relationships between toughness and geometry and to demonstrate how compliance introduced by structuring can reduce the strain energy release rate at crack tip, resulting in higher effective toughness. Toughness of architected interfaces made via laser patterning as well as additive manufacturing were measured using double cantilever beam experiments. Measurements on a relatively brittle acrylic (PMMA) and higher toughness ABS structured specimens were performed. The experimental results are in agreement with model predictions. A key and significant finding of this work is that less material can lead to higher toughness when the geometry of the interface is designed based on an understanding of the mechanics of the interface. The experiments, mechanics modeling, and an overall design strategy for using geometry to enhance interface toughness will be presented.

2:15 PM PM01.05.03
Control of Interfacial Crack Behavior via Architected Cellular Materials in 3D Printed Structures Chengyang Mo and Jordan R. Raney; Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Natural materials, with their remarkable fracture toughness and low density, have long been a source of inspiration to engineers. In recent years, researchers have made great strides in cataloging the specific mechanisms by which these properties are attained. These mechanisms arise from the very complex microstructures that are observed in natural materials, including mechanisms that arise due to internal geometric parameters (e.g., structural hierarchy, interface density, interface angle, etc.) and due to material parameters (e.g., interfacial adhesion between two distinct material types). It is often difficult to isolate the respective contributions, particularly in an experimental context, where it is difficult to precisely and uniformly control the interfacial properties between two materials along an internal interface. As one example, the Conch Shell has three different levels of hierarchy to prevent shell
fracturing under puncture loading allowing dissipation of a large amount of energy by crack divergence, with characteristic hard calcium carbonate sheets separated by soft protein layers where initial cracks form during loading. The goal of this research is to separate the effects of geometry from that of the material interface, and thereby determine how toughness can be maximized purely through a structure’s internal geometry. To do this, we fabricate structures (from a single material) that contain internal lattices, which act as weak interfaces due to their decreased relative density. Rather than relying on a material interface, internal cellular structures act as crack arresting regions with variable effectiveness based on such properties as relative density and lattice shape. We experimentally characterize fracture behavior, measuring properties such as fracture toughness, energy dissipated, and crack path in 3D printed single edge notched bend samples (SENB). We study geometric parameters including defect region orientation, lattice density, and lattice shape for crack diversion to occur and maximize energy dissipation. The effect of lattice parameters to critical defect region orientation is studied analytically and compared with experiments. Numerical simulation is also implemented to better predict the critical angle taking account of differences in fracture toughness of cellular materials under different modes.

2:30 PM PM01.05.04

Selective Laser Melting of Ti6Al4V Lattice Structures with Hollow Struts—Processability, Mechanical Behaviour and In Vitro Response

Ezgi Onal1, Wencheng Liu2, Bernard Chen3, Jessica E. Frith1, Xinhua Wu1 and Andrey Molotnikov1; 1Department of Materials Science and Engineering, Monash University, Melbourne, Victoria, Australia; 2Department of Mechanical and Aerospace Engineering, Monash University, Melbourne, Victoria, Australia; 3Monash Centre for Additive Manufacturing, Monash University, Melbourne, Victoria, Australia.

Advances in additive manufacturing are enabling fabrication of multitude of complex cellular structures for numerous applications in aerospace and biomechanical fields. Among periodic lattice structures hollow lattice structures are gaining popularity due to their improved mechanical properties, such as higher flexural and inelastic buckling strength [1] and higher compressive strength due to greater resistance to plastic buckling when compared to the solid lattice structures [2]. Furthermore, additional channels provided by hollow struts provide ample space for tissue ingrowth and cell colonization. The latter aspect is of a particular interest since our recent study demonstrated [3], that pore size and distribution significantly affect the cell migration in the lattice scaffolds.

In this work, we explore the potential use of hollow lattices for bone implant scaffolds. We have designed and fabricated Ti6Al4V hollow body centered cubic (BCC) lattice structures with different hollow thicknesses and unit cell pore sizes using selective laser melting process. We also included additional hollow z-struts at the nodes and centres of each BCC unit cell to study the effect of vertical channels. The mechanical properties and failure behaviour of the obtained scaffolds are investigated using compression testing. Furthermore, in-vitro studies with pre-osteoblast cells are conducted to study cell migration and colonization behaviour in channels and hollow struts. This study explores the use of novel lattice structure designs for orthopaedic implants and contributes to understanding of mechanical and biological response of hollow architectural materials.


2:45 PM PM01.05.05

Collective Magnetic Behavior and Domain Formation in Magnetite Nanoparticle Assemblies

Nils Neugebauer1,2, Alexander Fabian1,2, Matthias T. Elm1,2, Michael Czernecki1,2, Christian Heilig1,2 and Peter J. Klar1,2; 1Institute of Experimental Physics I, Justus-Liebig-Universität Gießen, Gießen, Germany; 2Center for Materials Research, Justus-Liebig-Universitat Gießen, Gießen, Germany; 3Institute of Theoretical Physics, Justus-Liebig-Universität Gießen, Gießen, Germany; 4Institute of Physical Chemistry, Justus-Liebig-Universität Gießen, Gießen, Germany.

Ferromagnetic nanostructures, such as arrays of magnetic nanodots, are of high interest for applications on the field of high density storage media, non-volatile logic or spintronic devices, as the magnetic properties of the arrays can be tuned by their shape and their arrangement. An alternative approach to patterning magnetic thin films is the fabrication of arrangements of ferromagnetic nanoparticles. Such low dimensional assemblies show collective magnetic behavior due to dipolar coupling between the nanoparticles, which offers an additional degree of freedom in manipulating the magnetic interactions inside the magnetic elements. However, in order to tune the magnetic interactions of the assemblies a detailed understanding of the magnetic coupling phenomena is necessary.

Here we present the investigation of the magnetic properties of magnetite nanoparticle assemblies using angle-dependent ferromagnetic resonance measurements [1]. Nanoparticle assemblies of different shape were prepared using the meniscus force deposition method. For this, electron beam lithography was used to prepare PMMA openings. In a horizontal dip-coating process the nanoparticles with an average diameter of 20 nm are arranged in these openings by self-assembly. To investigate the influence of the shape on the magnetic interactions between the particles, rectangular assemblies with different aspect ratio varying from 1:1 to 1:1000 were prepared. The angle-dependence of the resonance was described using the Smit-Suhl formalism. For assemblies with aspect ratios below 1:10 the demagnetization factors obtained are in good agreement with the values expected from the aspect ratio revealing a single magnetic domain behavior due to dipolar coupling. For larger aspect ratios the ratio of the demagnetization factors is much smaller than the expectation indicating the formation of a magnetic domain structure inside the assemblies. This assumption is further supported by magnetic simulations of the magnetic structure and probably arises due to inhomogeneities in the filling of the openings. Furthermore, magnetic coupling between the arrangements was investigated by varying the distance between circular shaped arrangements. Due to their shape, isolated arrangements reveal an isotropic behavior of the angle-dependence of the resonance field in in-plane geometry. However, below a critical distance between the arrangements occurs which is manifested by an angular dependence of the resonance field.


3:00 PM BREAK

3:30 PM *PM01.05.06

Nano to Macro Architected Materials and Structures—Processing Challenges and Opportunities

Haydn N. Wadley; University of Virginia, Charlottesville, Virginia, United States.

The development of light metals and ceramics with internal topologies that offer novel combinations of properties has been greatly accelerated by the recent development of additive methods for their fabrication. These enable the fabrication of complex shaped structures containing internal features with length scales that range from a few tens of nanometers to the centimeter scale. However, each of the processing methods suffer from various deficiencies such as a limited materials palate, difficult to control internal surface roughness, the presence of residual stresses and distortions of structure, and properties of the solid material that are sometimes inferior to those of conventionally processed counterparts. As a result, innovative applications of traditional fabrication-processing methods can still compete with additive approaches in many areas. Here three approaches for making microarchitected materials are described and the challenges confronting their further development discussed. At the centimeter scale, we describe the use of electron beam melting approaches for making Ti-6Al-4V octet lattice structures and show how surface roughness of the trusses impact mechanical performance, especially as the
Octet nanolattices to be 2.1-7.2 MPa g\(^{-1}\) cm\(^3\), which is comparable to that of metal lattices with 0.1-1.0 mm beam diameters fabricated using alternative methods, with shape diversity at the micro-scale. Then, bubbles are strategically assembled into meso-scale 3D structures. Subsequently, these structures are used to demonstrate a new class of carbon-based, ultralight, strong, and superelastic closed-cellular network structures. In contrast to conventional top-down approaches such as three-dimensional (3D) printing, the building units are prepared by a multi-scale design approach starting from the controlled alignment of Barium Titanate Platelets for Textured 3D Piezoelectric Architectures Using Direct Writing. Direct writing textured piezoelectric ceramics can allow for increased flexibility of 3D designs for a variety of applications through greater geometric possibilities, as well as novel orientations of crystallographic alignment. Generally, direct writing of ceramics and ceramic composites involves the extrusion and deposition of a ceramic containing paste which is then gelled to maintain its shape. Some studies on the alignment of platelets using a circular nozzle have explored the densification of textured ceramic as a function of position in the filament cross-section and length of the deposition nozzle. This work will highlight the fabrication of textured Pb(In\(_{1/2}\)Nb\(_{1/2}\)O\(_3\))-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\))-PbTiO\(_3\) ceramic designs with crystallographic orientations that are difficult to fabricate with traditional forming techniques. The effect of shear field shape and duration and ceramic paste rheology on the alignment of barium titanate templates and the fidelity of the printed geometries will be explored. Increasing the magnitude of the shear field in the nozzle during direct writing and controlling the rheology of the paste via pH control of the aqueous phase allows for the fabrication of dense, textured Pb(In\(_{1/2}\)Nb\(_{1/2}\)O\(_3\))-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\))-PbTiO\(_3\) ceramics with varied geometries and alignment directions.

Alignment of Barium Titanate Platelets for Textured 3D Piezoelectric Architectures Using Direct Writing

We used additive manufacturing methodologies to fabricate impact resistant composites. Similar to natural materials, such as mantis shrimp dactyl club, these lightweight synthetic analogues display superior structural properties and functionalities – such as fracture toughness and impact resistance. The present study is based on the hypothesis that synthetic impact resistant materials with extraordinary fracture toughness can be obtained and tuned by the 3D hierarchical micro-architected molecular structures – often enabled with nanoscale sub-structures – and that such 3D structures and mechanical properties could be enabled by additive manufacturing approach, especially with an integrated electrosprinning technique that combine multi-length scale fabrication capabilities. Further, more specifically, this study investigated the fracture toughness and impact resistance properties of the 3D helicoidal architecture inspired by the mantis shrimp dactyl club and elucidate the associated deformation mechanisms. Having layers of multiscale fibers with rotated alignments in each layer, the 3D helicoidal architecture could potentially lead to very efficient (high rate) as well as highly tunable damage dissipation mechanism. We further explore the effect of 3D hierarchy micro-architected structures and the possible size effects of the substructures on the fracture toughness and impact resistance properties of the resulting composite materials as well as the associated damage mechanisms. In this study, we fabricated structures by controlling the orientation of the polymer fibers within the composites. This is enabled by recent advances in additive manufacturing technologies. We plan to use electrosprinning further as well as a novel integrated approach involving melt near-field electrosprinning (NFES) technique and another deposition method called the fused deposition modelling (FDM). The 3D architecture would enable the composites to absorb mechanical energy before they fracture. Ultimately this high performance, impact-resistant composite technology will have other widespread technologically important applications, such as in aerospace, space, military/defense to automotive and biomedical/prosthetics. We also aim to enable design of such advanced composite materials through creation of new manufacturing technologies for micrometer and nanoscale materials and for their assembly and integration at larger scale.

Complete Space Filling Cellular Network of Graphene Bubbles for Ultralight, Strong and Superaesthetic Materials
Seon Ju Yeo1, Min Jun Oh2, Hyun Min Jun3, Minhwon Lee1, Jung Gun Bae1, Yeseul Kim2, Kyung Jin Park2, Seungwoo Lee2, Daeyeon Lee4, Byung Mook Woon2, Won Bo Lee1, S. Joon Kwon1 and Pil J. Yoo2; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Sungkyunkwan University, Suwon, Korea (the Republic of); 3Seoul National University, Seoul, Korea (the Republic of); 4University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Advanced materials with low density and high strength will have transformative impacts in construction, aerospace and automobile industries. These materials can be realized with assembling well-designed modular building units into interconnected structures. This study uses a hierarchical design strategy to demonstrate a new class of carbon-based, ultralight, strong, and superaesthetic closed-cellular network structures. In contrast to conventional top-down approaches such as three-dimensional (3D) printing, the building units are prepared by a multi-scale design approach starting from the controlled synthesis of functionalized graphene oxide nanosheets at the molecular- and nano-scale, leading to the microfluidic fabrication of solid-shelled bubbles with shape diversity at the micro-scale. Then, bubbles are strategically assembled into meso-scale 3D structures. Subsequently, these structures are transformed into self-interconnected and structurally-reinforced closed-cellular network structures through post-treatment, leading to the generation of a 3D graphene lattices with rhombic dodecahedral honeycomb structure at the centimeter-scale. The 3D graphene suprastructure simultaneously exhibits the Young’s modulus above 300 kPa while retaining a light density of 7.7 mg/cm\(^3\) and sustaining the elasticity against up to 87% of the compressive strain benefited from efficient stress dissipation through the complete space-filling closed-cellular network. The fabricated 3D graphene closed-cellular structure opens a new pathway for designing lightweight, strong, and superaesthetic materials.
Recent advances in Additive Manufacturing (AM) enable the fabrication of complex 3D lattice structures at many scales and with many materials. Through computational design optimization methods for AM lattice structures, it is possible to control the distribution of materials and structure within objects with a high degree of precision. This has the potential to dramatically improve structural performance and even enable new functionalities that can not be realized with conventional manufacturing. However, this is highly challenging for designers due to the vast design space of new possible shapes, materials and structures and often unknown AM fabrication constraints.

To address these challenges, a Design for Additive Manufacturing (DiAM) framework is developed that starts with AM material and process characterization from which quantitative models are created. These models are then used within design optimization methods for discrete lattice structures considering design variables of material, member size, shape and topology. Two methods are focused on including a Generalized Optimality Criteria (OC) method for multi-material optimization and optimization for anisotropy considering displacement, local yield stress and Euler buckling constraints. A Sequential Linear Programming (SLP) method is also discussed for the efficient optimization of member size and shape of truss lattice structures considering local yield stress and Euler buckling constraints. While the methods are process and material independent, results are shown for the characterized materials of the multi-material polyjet printing process. The results highlight the necessity of including AM fabrication constraints and tested material properties in the optimization process and the tight coupling needed among material understanding, the AM process and optimization methods to achieve optimized results.
The Representative Cellular Element (RCE) Method – Model, Implementation and Validation with Additive Manufacturing

Dhrub Bhat, Arizona State University, Mesa, Arizona, United States.

Material modeling approaches for cellular materials broadly fall into three different categories, depending on the level of discretization at which the property of interest is modeled. In order of the scale at which material behavior is represented, these models can operate at either the level of the material point (bulk property models), the connecting member (member models) or finally, at the level of the cell (homogenization models). Bulk property models are often not representative of the microstructure and surface effects at the scale of the members that constitute cellular structures in Additive Manufacturing. Member models are challenging to characterize due to the small sizes of the structures involved and the specimen geometries do not always accurately capture behavior of the cellular material. Homogenization models, while efficient to implement computationally, are shape and size dependent and are unlikely to represent irregular and stochastic cell shapes and distributions accurately.

In this work, being presented for the first time, we propose a Representative Cellular Element (RCE) method for modeling cellular materials. Our approach follows from the concept of the Representative Volume Element (RVE) developed for heterogeneous materials. The RCE method essentially involves the identification of a structural element that represents the cellular material for the property of interest. For the model to be both valid and accurate, we show that it must represent the cellular material in three critical ways: geometry, processing history and the physics of its deformation and failure. We assess the performance of the RCE model against prismatic cellular structures (honeycombs) in a wide range of conditions: different shapes (regular, graded and stochastic), Additive Manufacturing processes and materials (ABS with Fused Deposition Modeling, Inconel 718 with Laser Powder Bed Fusion, and Ti6Al4V with Electron Beam Melting) and strain rates (ranging from 10⁰ to 10⁶ s⁻¹). The model is also evaluated against a multi-material hexagonal honeycomb made with a nylon composite and Kevlar continuous fiber. In each case, we examine the model's predictability of the nonlinear stress-strain response in the elastic and plastic regimes. Three different design strategies for the RCE are compared under these conditions to identify the ones that yield the best results. Challenges in implementation and limitations of the RCE approach are also discussed.

Multi-scale Geometric Design Principles Applied to 3D Printed Architected Materials

Seyed Mohammad Sajadi1, Peter S. Owoor1, Cristiano F. Woelbing2, Varlei Rodrigues2, Robert Vajta1, Jun Lou1, Douglas S. Galvao2, Chandra S. Tiwary2 and P. M. Ajayan2; 1Materials Science and NanoEngineering, Rice University, Houston, Texas, United States; 2Applied Physics Department, State University of Campinas, Campinas, Brazil.

The emergence of 3D printing has enabled scientists to innovate complex geometrical designs in materials which were unattainable using conventional synthesis methods. The topological material design is becoming a common occurrence aided by 3D printing. Here we use inverse methods (function-to-structure) to design multifunctional materials. This work reports 3D porous structures with negative Gaussian curvatures, which forms a rigid foam-like architecture (including the network topology, truss geometry and base materials). Enabled by advances in additive manufacturing, large arrays of periodic, hierarchical or functionally graded truss unit cells have been assembled at the micro- to nanoscales, producing new ultra-lightweight cellular solids. With enhanced experimental capabilities comes the need for new theoretical and computational tools to describe and predict the performance of truss networks containing millions and more of individual struts and junctions, where classical approaches such as direct numerical calculations incur prohibitive computational expenses. We show that such truss networks can be described efficiently by advanced constitutive models and numerical tools that replace the discrete truss network by an equivalent continuum. Our formulation captures nonlinear and inelastic material behavior as well as finite deformations. We discuss the theoretical and numerical techniques (involving nonlocal homogenization based on both translational and rotational degrees of freedom), and we present representative examples of truss lattices undergoing not only homogenous deformation but also instabilities such as buckling and shear banding. Finally, we combine the methodology with topology optimization to predict optimal cellular networks with spatially varying truss architecture. Unlike classical multi-scale optimization, this approach results in compatible non-uniform truss architectures that can readily be fabricated by methods of additive manufacturing and offer opportunities for lightweight metamaterials with optimized mechanical properties.

Fracture Toughness of Truss and Shell-Based Architected Materials

Meng-Ting Hsieh and Lorenzo Valdevit; University of California, Irvine, Irvine, California, United States.

The fracture toughness of brittle 2D lattices, such as triangular and kagome lattices, has long been investigated using elastic K-field approaches. However, much less is known about the fracture toughness of 3D cellular materials, particularly those built from ductile components. Here, we numerically investigate the linear elastic and elasto-plastic fracture toughness of octet lattices and spindal shell-based architected materials. We address the issues of mesh dependence where stress singularity arises by incorporating a characteristic element size. To extract R-curves for cellular materials, local damage is modeled using the Johnson-Cook criterion and fracture toughness is obtained by the J-integral compliance with SENB (single-edge notched bend) specimens. We compare the performance of truss and shell-based architected materials in terms of scaling laws and R-curve behavior, and extract design principles. Numerical results are verified by fracture toughness experiments.
On the Correlation Between Topology and Elastic Properties of Imperfect Truss-Lattice Materials Panos Pantidis1, Andrew Gross2, Katia Bertoldi1 and Simos Gerasimidis1; 1Civil Engineering Department, University of Massachusetts, Amherst, Amherst, Massachusetts, United States; 2Harvard University, Boston, Massachusetts, United States.

The pursuit of new materials with properties superior to the current state of the art, has led many investigators to examine the behavior of materials with a truss-lattice microstructure which accommodates member sizes in the range of micro- and nanometers. Aided by the immense progress of 3D additive manufacturing techniques, such as self-assembly (bottom-up techniques), material scientists have been enabled to fabricate novel materials with complex architectures which can attain unique, unprecedented and tunable properties. However, defects of various forms and concentrations are unavoidable in any fabrication process, and it is anticipated that the application of self-assembly techniques to larger three-dimensional volumes will increase the concentration of defects. Of particular interest for the self-assembly of truss-lattice materials is the influence of struts that are missing from the network, in various defect forms such as missing blocks (clusters) or randomly missing members. In this study, the dependence of the elastic properties on the concentration and distribution of missing struts is investigated for several three-dimensional lattice-truss materials of varying coordination number. This work constitutes a systematic experimental and numerical approach to examine and identify the mechanical elastic regime of defected architected metamaterials. The experimental part of this project is conducted with a two-photon lithography approach, an advanced additive manufacturing technique capable of printing struts with sub-micron cross-sectional dimensions, while the numerical part utilizes finite element simulations accounting for the randomness of the damage spatial distribution through exhaustive Monte Carlo simulations. Focusing on a variety of elastic mechanical properties (Young’s, bulk and shear modulus), their evolution is monitored as the total defect percentage increases in magnitude, providing a comprehensive picture of the defected architected metamaterials elastic property space. Finally, this work thoroughly explores the connection between defected truss-lattices and well-established homogenization techniques for composite mediums, elaborating on the applicability of the latter methods to accurately describe the response of defected lattice-based materials.

11:15 AM OPEN DISCUSSION

Analysis of a Three-Dimensional Spider Web Architecture Isabelle Su1, Zhao Qin1, Tomás Saraceno2 and Markus Buehler1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Studio Tomás Saraceno, Berlin, Germany.

Spiders are abundant in most ecosystems in nature, making up more than 47,000 species. This ecological success is due to the web architectures and the exceptional mechanical properties of spider silk. Silk’s combination of strength, elasticity, toughness, and robustness originates from its hierarchical structure and has been a template for high-performance material design. In particular, spiders have optimized and adapted their web architecture to survive in their environment.

The most studied and familiar spider web is the 2D orb web which is composed of radial and spiral threads. However, 3D webs, such as sheet, funnel, or cob webs, are more common in nature. In contrast to 2D webs, where the spider is vulnerable to attacks, 3D webs surround the spider and offer a defensive advantage by warning the spider of intruders, blocking its predators and entangling prey.

Here, we investigate the architecture and mechanical properties of a Cyrtophora citricola 3D web. For the first time, we build a model of the 3D spider web generated through automatic laser scanning. The web is scanned by taking a high resolution picture of slices of the web illuminated by a sliding sheet laser. Using image processing algorithms, we construct a 3D fiber network. We study the response of a realistic web structure to mechanical loads using a coarse-grained bead-spring models based on the network model created through scanning and image processing. Using this new method to trace the fiber network, we can study the connection between material and performance of numerous 3D spider webs. Understanding the roles of structure and material in the functionality and evolutionary fitness of spider webs could lead to innovative 3D spider web-inspired structures such as high performance light-weight long-span structures or fiber reinforced composite materials.

Harnessing Design Principles from Glass Sponges for Structurally Robust Lattices Matheus C. Fernandes1, James Weaver2; 1Harvard University, Cambridge, Massachusetts, United States; 2Wyss Institute, Cambridge, Massachusetts, United States.

Glass sponges are predominately deep sea sponges that live in ocean depths of 100-2000m. Beyond their fracture propagation inhibiting material composition, these sponges are perceived to exhibit large structural rigidity and strength against buckling. Since these sponges are primarily made of ‘brittle silica’, buckling strength may be a crucial property in making them resistant to impact and environmentally applied stresses. Structurally, they exhibit a base square-grid architecture and regular ordering of vertical and horizontal struts that form the skeletal system. Furthermore, their base structure is overlaid with double diagonal reinforcement struts, which create a checkerboard-like pattern of open-closed cell structure. This diagonal reinforcement design is conjectured to give the sponge greater buckling resistance and strength to localized damage then it would experience having a single diagonal reinforcement strut (while allocating the same amount of mass to the diagonal reinforcement.) Analogous to the sponge, many engineering structures, such as buildings and bridges, exhibit diagonal reinforcement struts as a stability mechanism. Based on this similarity, we explore the following research question: Can we generate design principles for diagonal reinforcements of square beam lattices that are optimally designed to avoid global structural buckling? Here, we present a numerical analysis of the structure deformation under various loading conditions as well as survey different arrangements within similar design space of the sponge. Furthermore, we present experimental evidence that supports our numerical analysis. Through the various design iterations we look for the critical buckling strain and the elastic load caring capacity. Finally, we compare the results from the sponge design to what is typically used in engineering of structures such as buildings and bridges.

1:30 PM *PM01.07.01
Advancing Acoustic Application with Architectured Metamaterials Nicholas Fang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Today, sound is an indispensable component in numerous industrial and consumer products, such as musical instruments, cars, building technology, medical diagnostics, and many others. Acoustic characteristics are among their most important properties, greatly influencing their function and our society.
at large. Recent development of acoustic metamaterials opens a door to an unprecedented large design space for acoustic properties such as negative bulk modulus, negative density, and refractive index. These novel concept expands pave the way for the design of a new class of acoustic materials and devices with great promise for diverse applications, such as broadband noise insulation, sub-wavelength imaging and acoustic cloak from sonar detection.

In this invited talk, I will present our development of advanced design and micro/nanofabrication techniques, to enable exploration architecture of meta structures for acoustic waves. These structures show promise on focusing and rertoing ultrasound through broadband metamaterials. As example, our study on the sound absorption of thin composite aerogel foams using a bimodal porous structure predicts a possible route to perfect thin film absorber by increasing the amount of epoxy resin. In a second case, stimuli responsive acoustic metamaterials are demonstrated to be able to extend the 2D phase space to 3D through rapidly and repeatedly switching signs of constitutive parameters with remote magnetic fields. Lastly I will report our study on a prototype hydraulic hydrogel transducers with excellent optical and sonic transparency.

2:00 PM PM01.07.02
Design of a Resonant Laser Beam Scanner Based on a Topologically Protected Twist Edge State Julian Köpfler1, 2, Tobias Frenzel2, Muamer Kadic1, 2, 3, Jörg Schmalian1, 5 and Martin Wegener2, 1; 1Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Institute of Applied Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany; 3FEMTO-ST, Université de Bourgogne Franche-Comté, Besançon, France; 4Institute for Theoretical Condensed Matter Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany; 5Institute for Solid-State Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany.

The concept of band gaps in periodic mechanical systems allows, for example, the design of waveguides and cavities. However, the corresponding modes are often fairly sensitive with respect to perturbations. Therefore, the more recent idea of topologically protected boundary modes has provided a new twist. Aiming at applications as one-way waveguide architectures, recent work [1,2] designed and realized mechanical structures exhibiting topological two-dimensional (2D) band gaps. 1D topological band gaps exhibiting longitudinal and bending interface modes were achieved using a beam composed of a 1D periodic arrangement of elastic unit cells [3].

In this paper, we present an application of topological mechanical band gaps that specifically takes advantage of chirality. We design a 1D chain of two different alternating 3D elastic chiral unit cells [4]. The individual unit cells have been inspired by our previous work [5]. The chain’s topological band gap, a result of the alternation of unit cells combined with their chirality, guarantees a protected edge state at one end of the beam, corresponding to a resonant localized twist mode. This mode can be excited by an axial motion at the other end of the beam, via evanescent modes in the gap. The topological robustness of the edge state allows us to add a micro-mirror, turning the arrangement into a resonant laser beam scanner with scalable operation frequency and adjustable quality factor.

Our work starts from calculations based on a simplified 1D mass-spring model, which we solve analytically. The system resembles two Su-Schrieffer-Heeger (SSH) models [6], one for the longitudinal displacement and one for the twist, which are chirally coupled via additional springs. We justify this model by the fact that the longitudinal (or pressure) and the twist mode on the one hand, and the two transverse (or shear) modes on the other hand, live in orthogonal subspaces according to micropolar continuum theory for chiral media. Within this model, the topological protection is due to a combination of time-reversal and a mirror symmetry, generalizing the classification of mechanical metamaterials [2]. The results of the model are verified by numerical finite-element calculations for the complete 3D microstructures. These microstructures should be amenable to laser nanoprinting.

2:15 PM PM01.07.03
Dynamically Tunable Topological States in Soft Elastic Metamaterials Shuaifeng Li and Jianfeng Zang; Huazhong University of Science & Technology, Wuhan, China.

Topology describes the properties of space under continuous deformation in mathematics. The concept has been used to explain band structures in condensed matter physics, resulting in the theoretical prediction and experimental observation of topological insulator in electronic system, and recently also in photonic and phononic systems. Topological elastic metamaterials offer insight into classic motion law and open up opportunities in quantum and classic information processing. Theoretical modeling and numerical simulation of elastic topological states have been reported, whereas the experimental observation remains relatively unexplored. Here we present an experimental observation and numerical simulation of tunable topological states in soft elastic metamaterials. The on-demand reversible switch in topological phase has been achieved by changing filling ratio, tension, and/or compression of the elasstic metamaterials. By combining two elastic meta-materials with distinct topological invariants, we further demonstrate the formation and dynamic tunability of topological interface states by mechanical deformation, and the manipulation of elastic wave propagation. Moreover, we provide a topological phase diagram of elastic metamaterials under deformation. Our approach to dynamically control interface states in soft materials paves the way to various phononic systems involving thermal management and soft robotics requiring better use of energy.

2:30 PM BREAK

3:30 PM *PM01.07.04
Non-Reciprocal Wave Phenomena via Mechanical Modulation of Discrete and Continuous Elastic Lattice Systems Samuel P. Waller2, Benjamin M. Goldsberry1, 2 and Michael R. Haberman1, 2; 1Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States; 2Applied Research Laboratories, The University of Texas at Austin, Austin, Texas, United States.

Non-reciprocal acoustic and elastic wave propagation is of significant interest due to its potential to enable direction-dependent devices that augment mechanical wave sensing and transmitting capabilities. They also open up the possibility for the construction of novel materials or structures for isolation from vibration and impacts. However, non-reciprocity can only occur under very specific circumstances, many of which are very difficult to achieve in practice. This work considers mechanical modulation as a potential means to obtain non-reciprocal elastic wave propagation in architected materials. The specific case studied is the application of a slowly-varying, large amplitude, mechanical pump wave whose motion is orthogonal to the direction of wave propagation. This pump wave acts as a spatio-temporal modulation of the mechanical structure, resulting in time and space varying effective material properties and non-reciprocal elastic wave phenomena. The mechanical system of interest is modeled using both discrete and continuous mechanical
Acoustic metasurfaces that can manipulate and control sound waves at two-dimensional subwavelength scales open new avenues to unusual applications, such as sound barrier, super-resolution imaging, and particle manipulation. However, the long-standing goals of pushing frontier metamaterials research into real practice are still severely constrained by cumbersome configuration and rigid structure of the existing metamaterials. Here we fabricate an ultrathin metasurface (10-300 μm in thickness, up to 1/650, λ the wavelength) that is capable of imparting sound wave with a non-trivial phase shift with high transmittance (>80%) in the range of 5 kHz and 30 kHz by electrospinning method. Besides, we incorporate the traditional paper-cutting art to carve the ultrathin metasurface into hollow-out patterns, resulting in a variety of remarkable functions, including acoustic vortex, focusing, and super-resolution. Our hollow-out patterning approach innovates the traditional one-step metadevice fabrication process into two separated steps: (1) fabrication of ultrathin metasurfaces; (2) hollow-out patterning of metasurfaces. Our strategy opens an avenue to mass production of acoustic metadevices, shedding light on the applications of the metamaterials in architectural acoustics.

Moreover, benefited from the flexibility of our hollow-out patterning metasurfaces, we propose the unprecedented non-planar acoustic metasurface. Actually, most objects and occasions refer to non-planar surface in nature. Non-planar metasurface is sorely in need to match these application scenarios but there has been hardly thought or design about non-planar acoustic metasurface so far. We demonstrate a high-efficiency focusing on nearly arbitrary non-planar surface and design an "umbrella structure" to implement focusing with dynamic tunable focal length.

Two-Step Manufacturing of Ultrathin Acoustic Metasurfaces and Non-Planar Acoustic Metasurfaces

James Blondeau1, Vitalyi Gusev1, Katia Bertoldi2 and Vincent Tournat1; 1LAUM, CNRS, Le Mans Université, Le Mans, France; 2John A Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

Assessing nondestructively the elastic properties of micro-scale architected materials is of key importance in several applications. Here we propose a method based on the laser generation and detection of ultrasound to extract the vibrational mode frequencies of 3D-printed micro-truss samples. Experimental results show that the first bending and compressional modes of the truss systems can be monitored in the MHz frequency range. The corresponding frequencies are then compared to finite element simulations results, which allow to assess the effective elastic parameters, Young's modulus and shear modulus, of the micro-scale trusses. Capabilities and limitations of this laser ultrasonic characterization method will be discussed in the context of micro-scale architected materials, and some prospects in wave control problems at the micro-scale will be proposed.

Additively Manufacturable Micro-Mechanical Logic Gates

Yuanming Song1, Robert Panas2, Samira Chizari2, Lucas Shaw2, Julie Jackson1, Jonathan Hopkins1 and Andrew Pascall1; 1Lawrence Livermore National Lab, Livermore, California, United States; 2Department of Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Early examples of computers were almost exclusively based on mechanical devices. Although electronic computers became dominant in the past 60 years, recent advancements in 3D micro-additive manufacturing technology provide new fabrication techniques for complex microstructures which have rekindled research interest in mechanical computations[1-3]. The authors propose a new digital mechanical computation approach based on additively-manufacturable micro-mechanical logic gates. The proposed mechanical logic gates (i.e., NOT, AND, OR, NAND, and NOR gates) utilize multi-stable micro-structures that buckle to perform digital computations based purely on mechanical forces and displacements with no electronic components. Unprecedented properties have been achieved simultaneously including functional completeness, continuous operation, scalability, and near-zero energy consumption. A key benefit of the proposed approach is that such systems can be additively fabricated as embedded parts of microarchitected metamaterials[4] that are capable of interacting mechanically with their surrounding environment while processing and storing digital data internally without requiring electric power.

Additive Manufacturing of Lightweight Mirrors

Nikola Dudukovic, Logan Bekker, Wen Chen, Jesus Partida, Bryan Moran, Eric B. Duoss, Christopher M. Spadaccini, William Steele, Tayyab Suratwala and Rebecca Dylla-Spears; Lawrence Livermore National Laboratory, Livermore, California, United States.

Additive manufacturing offers new routes to lightweight optics inaccessible by conventional methods by providing a broader range of reconciled functionality, form factor, and cost. Predictive lattice design combined with the ability to 3D print complex structures allows for the creation of low-density metamaterials with high global and local stiffness and tunable response to static and dynamic loading. This capacity provides a path to fabrication of lightweight optical supports with tuned geometries and mechanical properties. Our approach involves the simulation and optimization of lightweight stretch-dominated lattices for anticipated stresses due to polishing and mounting loads via adaptive mesh refinement. The designed lattices are 3D-printed using large area projection microstereolithography (LAPuSL), coated with a metallic plating to improve mechanical properties, and bonded to a thin (1.25 mm) fused silica substrate. We demonstrate that this lightweight assembly can be polished to a desired flatness using full aperture polishing under a load, and subsequently treated with a reflective coating. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program. LLNL-ABS-738806.
SESSION PM01.08: Additive Manufacturing
Session Chairs: Tobias Schaedler and Martin Wegener
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 102

8:15 AM PM01.08.01

title: 3D Printed Transparent Glass with Gradient Properties
authors: Timothy Ye1, Do Nguyen1, Joel Destino2, Nikola Dudukovic1, Michael Johnson1, Koroush Sanas1, Lana Wong1, Paul Ehrmann1 and Rebecca Dylla-Spear1; Lawrence Livermore National Laboratory, Livermore, California, United States; Creighton University, Omaha, Nebraska, United States.

We present an approach to fabricating glass with a gradient refractive index profile by combining additive manufacturing and conventional ceramic processing techniques. Silica and silica-titania nanoparticles are synthesized and formulated into a slurry, which is tuned rheologically to enable extrusion through a nozzle via direct ink writing. During printing, two feedstocks of different compositions are fed at variable flow rates and mixed inline, allowing for controlled compositional profiles in the printed part. After printing, an optimized heat treatment is performed to ensure the removal of organic material and the formation of fully dense, transparent glass. We demonstrate 3d-printed gradient index lenses, and we show that our 3d-printed glasses have comparable properties to commercial glasses. This approach is promising for the development of optics with new functionality that cannot be accessed through conventional methods.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program 16-SI-003. LLNL-ABS-937900.

8:30 AM PM01.08.02

title: Design and Electrohydrodynamic Jet Printing of Layered Periodic Photopolymers
authors: Brian Iezzi1, Zahra Afkhami2, David Hoelzle3, Kira Barton2 and Max Stien2; Materials Science and Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; Mechanical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio, United States.

Periodic layered mirrors and filters are used for wavelength selection in spectroscopy and imaging. These mirrors have long relied on inorganic materials that have the refractive index contrast necessary to obtain desired electromagnetic wave interference patterns but require cumbersome and expensive manufacturing processes. Photopolymers have been formulated with refractive indices ranging from 1.3 to 1.7, and are, in principle, compatible with versatile, low-cost additive manufacturing processes. We use commercially available high (n=1.70) and low (n=1.38) refractive index photopolymers to create periodic layered mirrors and filters. We design mirrors having fewer than 15 alternating index layers with reflectance exceeding 60% in the visible range and complementary Fabry-Perot filters using a polymer resonant cavity with narrow transmission peaks of 15 nm FWHM with fewer than 30 layers. Experimental validation of these constructs is done using electrohydrodynamic jet (e-jet) printing; achieving individual layer thicknesses between 50-150 nm and well-defined filter “pixels” below 100 square micrometers. The reflectance/transmission characteristics of the printed mirror/filter “pixels” are measured using custom microspectrophotometry. Initial transmission results of five-layer samples are shown to be within 5-30% of prediction in the 500 to 700 nm wavelength range. Various printing parameters, such as utilizing continuous versus pulse printing and their effect on layer interfaces are discussed, along with how this information is used in the multi-physics design of monolithically-integrated organic imaging devices with predictable external quantum efficiency characteristics.

The authors would also like to acknowledge Aaditya Hambarde, Parag Deotare, and Steven Morris for their contributions to the work.

8:45 AM PM01.08.03

title: Fabricating Nanostructured Ceramics via Block-Copolymer Soft Templates
authors: Lisa M. Rueschhoff1, Luke Baldwin1, Robert Wheeler1,2, Hilmar Koerner1, Matthew Dalton1, John D. Berrian1, Michael Cinibulk1 and Matthew Dickerson1; Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States; UES, Inc., Dayton, Ohio, United States.

Ceramics and ceramic composites architected at the nanoscale can exhibit extraordinary mechanical properties, including elastic deformation and high toughness, but are difficult to fabricate using scalable production methods. The ability to control bottom-up templates for preceramic polymers (PCPs) allows for the production of polymer-derived ceramic components with desired nanostucture and mechanical properties. The combination of block copolymers (BCPs) and PCPs allows for the templating of the PCPs as a result of the self-assembly of the BCPs. Subsequent pyrolysis of the material converts the PCP into a structural ceramic material while removing the self-assembled BCP fugitive template. Using this method we have created novel silicon carbide based ceramic structures with nanoscale features and porosity. Insight into the relationship between polymer chemistry and structure in thin films of a novel and relatively inexpensive BCP/PCP system, as well as in-situ mechanical characterization of porous ceramic micropillars, will be presented.

9:00 AM PM01.08.05

title: Improved Strength and Functionality in Polymer Lattice Additive Manufacturing
authors: Joshua DeOtte1, 2, James Oakdale1 and Eric B. Duoss1; Lawrence Livermore National Lab, Livermore, California, United States; University of California, Davis, California, United States.

Polymer lattices produced with stereolithography additive manufacturing often have mechanical performance lower than expected from bulk properties. During fabrication, oxygen inhibits polymerization at pattern edges, which is oftentimes exploited to reduce adhesion to the print window. For small structures, this region of reduced polymerization could include entire features, dramatically reducing stiffness. Typically, a UV post-cure step is used to finish polymerization at the surface, but improvement in stiffness is minimal. Raman spectroscopy was used to measure the conversion ratio along the radius of a 500um diameter, additively manufactured cylinder, which showed that conversion ratio begins decreasing 100um from the surface. UV post-cure was insufficient to complete polymerization over the full region, so simultaneous thermal analysis was used to probe the temperature required to initiate acrylate polymerization as well as the temperature for thermal degradation. After thermal post-processing, the average conversion ratio increased, improving stiffness in an additively manufactured lattice by an order of magnitude.
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:15 AM PM01.08.06
3D Printed Ultrastrong and Ultratough Metallic Architectures Wen Chen1, Cheng Zhu2, Thomas Voisin2, S. K. McCall2, Andrew Pascale2, Joshua Kunz2, Eric B. Duoss2 and Christopher M. Spadaccini2; 1Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States.

Ultrafine grain metals are a class of advanced structural materials with superior mechanical properties due to the inherent refined microstructure. Processing of ultrafine grained metals is however very challenging and often lacks versatility and scalability. Here, we introduce a novel approach that allows fabricating a variety of ultrafine grained metal 3D architectures by combining direct ink writing based additive manufacturing with nanocrystallization of a metallic glass precursor. The developed 3D ultrafine grained metal architectures demonstrate unprecedented mechanical performance such as high strength and energy absorption compared with other metallic architectures. More generally, our finding offers a new routine to achieve high performance complex metallic architectures with high precision, scalability, and versatility.

Prepared by LLNL under Contract DE-AC52-07NA27344.

9:30 AM PM01.08.07
Print Path Optimization and Computation of Machine Motions for Direct Ink Writing on Non-Planar Substrates Eric B. Duoss, Adam Jaycox, Christopher M. Spadaccini, Seth Watts, Todd Weisgraber and Thomas Wilson; Lawrence Livermore National Laboratory, Livermore, California, United States.

Recent work in direct ink writing (DIW) of elastomers on planar substrates has shown that different lattice morphologies display interesting characteristics, including tunable compressive and shear response. A natural question is whether we can achieve the same characteristics when printing on non-planar substrates. This presents two challenges: first, the curvature of such substrates induces distortion on planar designs, preventing a direct translation of these lattices; and second, determining the machine motions necessary to print lattices on non-planar substrates via DIW is non-trivial. We discuss our approach, which uses optimization techniques to address both challenges. Specifically, we pose the mapping of lattices to non-planar substrates as a minimization of areal distortion subject to constraints on angular distortion, and we determine the machine motions by solving an inverse problem using a forward kinematics model of a six-axis DIW machine to determine the translations and rotations necessary to print the lattices of interest.

9:45 AM BREAK

10:15 AM PM01.08.08
Designing Elastomeric 3D Printed Architectures with a Mechanical Reduced Order Model Todd Weisgraber, Ward Small, Jeremy Lenhardt, Christopher M. Spadaccini, Robert Maxwell, Eric B. Duoss and Thomas Wilson; Lawrence Livermore National Laboratory, Livermore, California, United States.

Direct ink writing of silicone elastomers enables printing with precise control of porosity and mechanical properties of ordered cellular solids, suitable for shock absorption and stress mitigation applications. With the ability to manipulate structure and feedstock stiffness, the design space becomes challenging to parse to obtain an architecture with a desired mechanical response. Here we derive an analytical design approach for structure and feedstock. Results from finite element simulations and quasi-static mechanical tests of two different parallel strand architectures were analyzed to understand the structure-property relationships under uniaxial compression. Combining effective stiffness-density scaling with least squares optimization of the stress responses yielded general response curves parameterized by resin modulus and strand spacing. An analytical expression of these curves serves as a reduced order model, which, when optimized, provides a rapid design capability for filament-based 3D printed structures. To demonstrate the capability, we present computed optimal architecture designs that satisfy prescribed loading conditions and porosity constraints along with validating mechanical characterization data.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-752767.

10:30 AM PM01.08.09
Redox-Based EHD-Printing—Chemically Architected Metals with Submicron Chemical Resolution Alain S. Reiser, Marcus Lindén and Ralph Spolenak; ETH Zurich, Zurich, Switzerland.

The concept of architected materials, i.e., the design of properties through architecture, is of widespread interest, e.g., for the fabrication of optical and mechanical metamaterials, advanced microelectromechanical systems or biological scaffolds. Two-photon lithography (TPL) of polymeric materials is currently the major enabling technology for additively manufactured (AM) small-scale architected materials, i.e., architectures with a smallest feature size <1 μm. TPLs combination of submicron feature size and high fabrication speed is unmatched by any competing AM technology, and post-print coating- or pyrolysis-techniques extend the accessible materials range towards metals and ceramics. Nonetheless, multi-material capabilities of TPL are currently very limited, especially for inorganic materials, and property design mostly relies on design through cellular geometries – an approach that invariably renders porous materials, with absolute properties that are typically inferior to dense designs. Microscale multi-material AM has great potential to advance the synthesis of complex 3D chemical architectures with properties or functionalities that go beyond those of cellular designs. Yet, while multi-polymer approaches are relatively advanced, similar techniques for inorganic materials face serious limitations: because almost all methods are variations of ink-based, multi-nozzle strategies, the resulting as-deposited materials-quality is typically low, the chemical voxel-size, i.e., smallest feature of a fixed chemical composition, is large, and alignment can be demanding.

Here, we introduce redox-based EHD-printing. This ink-free, electrochemical technique can overcome the before-mentioned limitations of multi-material microscale AM for the case of metals: it offers multi-metal printing from a single print-head with a chemical voxel-size of 250 nm, switching of the printed chemistry at a frequency of 10 Hz, and smallest geometrical feature size <100 nm. We show that the underlying electrochemical principle enables as-deposited materials quality that compares well with that of PVD-deposited metals, e.g., a flow-strength of 1 – 1.5 GPa for Cu, or a resistivity of 8 x bulk Cu. At the same time, redox-based EHD-printing offers a deposition speed of several μm s⁻¹, which is more than an order of magnitude faster than that of other electrochemical microscale AM methods. We demonstrate the synthesis of bi-metallic Cu-Ag 3D geometries with complex, embedded chemical
3D Direct Laser Writing of Efficient X-Ray Lens Nano-Architectures

Kahraman Keskinbora, Umut T. Sanli, Hakan Ceylan, Julija Bykova, Markus Weigand, Metin Sitti and Gisela Schütz; Max Planck Institute for Intelligent Systems, Stuttgart, Germany.

Focusing optics used in X-ray microscopy often have very demanding geometries from a fabrication point of view due to extremely small features, sub-mm scale apertures, extremely tight tolerances and high aspect ratios [1]. Such X-ray optics range from Fresnel zone plates (FZP) to three-dimensional kinoforms and several types of stacked lenses [2]. Generally, top-down subtractive methods are used for fabricating diffractive X-ray optics such as binary FZPs. Fully 3D optics, on the other hand, can be fabricated only in approximated forms by resorting to subtractive methods [2] including optical lithography, direct-write ion beam lithography or e-beam lithography followed by etching and electroplating. While these methods produce binary X-ray FZPs with the highest resolution today, they fail when high aspect ratios are required for focusing harder X-rays or optics with overhang structures such as tilted, wedged or curved lenses are desired towards high-efficiency focusing at high resolutions.

Two-photon polymerization (2PP) emerged as a versatile route for manufacturing three-dimensional complex geometrical structures on the nano-scale. 2PP is an expanding field of research with a long list of technological applications in micro-robotics [3], photonics [4,5], metamaterials [6,7], and MEMS/NEMS [8] to name a few.

Here, we employed direct-write 3D femtosecond laser lithography to fabricating a highly efficient type of X-ray optic called kinoform lens, with parabolic surface profiles [9]. Then, we thoroughly characterized the focusing/imaging performances of the lenses by mounting them in a scanning transmission X-ray microscope (STXM) located in the synchrotron radiation facility BESSY II. The demonstrated an efficiency of up to 20 % efficiency, a remarkable value for soft X-ray energies. Using the fabricated lenses, we resolved 240 nm and 30 nm features via direct scanning and ptychographic imaging, respectively.

Finally, we discuss the potential application of 2PP for printing other types of X-ray optics with integrated wavefront shaping elements and nano-focusing lenses.

References

11:00 AM PM01.08.11

Additive Biofabrication of Elastic 3,4D Constructs for Human Repair and Enhanced Future Ways of Living

Raymond Oliver and Chawisa Deesomboon; Northumbria University, Newcastle upon Tyne, United Kingdom.

Humans are innovative beings that have successfully created new materials that are so durable and so efficient in so many different ways. One material in particular has been embedded into our daily lives is synthetic polymer in the form of plastic. Collectively, we can agree that we can't fully live without it, but we can probably agree on the huge negative impact that it generates through single use application. For example, it is logical to use a material for a single, brief use, but on throwing it away, it doesn't biodegrade for many hundreds of years. We therefore report on a Design:STEM approach to explore new material forms derived from natural abundant sources such as polysaccharides, responsive materials in the form of hydrogels and cellular materials such as bio-based aerogels or foams. The first area of research activity we report is based on options to facilitate a shift away from synthetic polymers to natural ones and at the same time, create additional and useful functionality. The second part of this investigation we report on is the use of additive manufacture with insights into the ease and constraints associated with 3,4D microfabrication which provide soft, elastic, bioreilient and bioeompatible characteristics for both human repair and 'smart' consumer products.

The work was carried out using an Envisiontec bioplotter or extruder to create material constructs that has allowed a comparison between different natural biomaterials under a measured range of rheological, thermal and mechanical properties associated with polysaccharide, hydrogel and organic aerogel examples. The initial experimental programme using the bio-plotter generated a range of elastic and responsive 3D constructs using PU and Acrylic elastomers which required no post work differentiating the bioplotter from other traditional 3D printers. Initial studies concentrated on creating optimal thermal, curing, mechanical and rheological conditions for the formation of reproducible 3D elastic structures. This was followed by the development of bio-elastomeric sample materials and the current state of play has been the introduction of hydrogel components into the bioplotter formulations to yield a 4D bioelastic construct. The techniques employed to achieve this included working with Rhino software and digital fabrication methods to transfer designs from laser scanned 3D images to a 3D computer controlled robotic plotting head to generate the desired complex structures. The subsequent constructs and their behaviour was filmed and recorded to create digital records of both the fabrication kinetics and the form of the various 3,4D elastic constructs. The results to date indicate that it may be possible to generate natural alternatives to synthetic polymers which have applications ranging from human repair i.e. the replacement of prosthetics with potential bio-resorbable tissue engineered constructs and industrially relevant structures for automotive and aerospace applications.

11:15 AM PM01.08.12

Controlling Architecture Through Active Mixing Processing

A. M. Golobic1, 2, Jason Ortega1, Jeremy Lenhardt1, Eric B. Duoss1 and Thomas Wilson1; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2University of California, Davis, California, United States.

The mixing process of multimaterial systems can impart microstructure that can affect the overall material performance. This is especially true when mixing materials with vastly different densities, rheological behavior, and mechanical properties. The use of an active mixing printhead in 3D printing processes requires an understanding of how the processing dictates the microstructure, which in turn influences the material properties. The architectures formed during mixing were investigated with an active mixing printhead and siloxane inks with different rheology and mechanical behavior. The mixing was varied by controlling the rotating impeller speed and the resulting structure was studied with spectroscopic methods. The mechanical behavior was tested and correlated to microstructure. The experimental findings were compared with simulations of the mixing process and mechanical response.
Additively Manufactured Metallic Cellular Materials—Energy Absorbing Characteristics

Morphology and Composition of Magnesium Calcium Phosphates Prepared in a Multiple Emulsion

The Effect of Adhesion Strength Between Steel and Polymer on the Formability of Their Composites

11:30 AM PM01.08.13
Additively Manufactured Metallic Cellular Materials—Energy Absorbing Characteristics

Metallic cellular materials such as lattices and honeycombs are of interest for blast and impact protection, due to their ability to dissipate energy efficiently during dynamic crushing. High-performance energy absorbing materials find applications in a wide range of industry sectors: e.g., aerospace, rail, automotive crashworthiness and structural blast protection.

Additive manufacturing (AM) processes enable new cell wall material-geometry combinations for the design of high performance cellular materials for impact energy absorption. This is of interest, for example, in the space industry, where high performance but light-weight materials that can protect structures from impact are sought.

To date, optimisation of AM cellular materials for high-strain rate loading scenarios remains relatively under-developed. Design of AM materials requires an understanding of the relationship between the AM process parameters and the properties of the resulting material across different scales: from the microstructure, to the geometric feature rendition, to the overall dynamic performance. Challenges include: (i) understanding process-property interactions for high strain rate behaviour; (ii) developing methodologies to navigate the wide design space enabled by AM processes, and hence optimise high strain rate properties; and (iii) modelling challenges spanning a range of length scales. These gaps in understanding hinder the exploitation of AM to deliver solutions for the most demanding impact protection problems.

First, focusing on the selective laser melting of a well-established alloy (316L), the influence of the laser heating strategy was investigated, specifically, the influence on defects, properties, microstructure and energy absorption. The laser power and the exposure time were varied, while maintaining a fixed total heat input. Also considered was the effect of five cellular material geometries: square honeycomb (SHC), lattice-wall square honeycomb, octet lattices (two variants), and origami.

It was found that a 125W laser power produces material with fewer porosity defects, which resulted in a higher yield strength and higher ductility. For the five geometries tested, the 125W power gives the cellular material with the greatest strength and energy absorbing capacity. However, the relative performance of the different geometries is insensitive to the laser power - SHC performs best in all cases. If we increase the strain rate, the same performance ranking holds between cellular geometries and laser powers. In all cases, a dynamic elevation in strength is observed.

11:45 AM PM01.08.14
Laser Power Optimization Using Feed Forward Control on the Overhang Geometry for 316L Stainless Steel

Arbitrarily complex architectures in metal additive manufacturing can be improved by using physics modeling and analysis to optimize the laser power throughout the scan path. Predicting the transient evolution of the thermal field to prevent overheating is critical for printing parts that meet quality criteria. This study investigates control of the laser power during selective laser melting (SLM) of 316L stainless steel to build an overhang geometry. Diablo, a parallel finite element code that models the heat transfer is used with a control algorithm to optimize the laser power across the overhang. This study investigates strategies to use predicted physical quantities for feed forward control of the laser power. Parts printed using the feed forward control strategy are analyzed and simulation results are used towards the development of a geometry based model. Prepared by LLNL under Contract DE-AC52-07NA27344.

11:00 AM PM01.08.15
The Effect of Adhesion Strength Between Steel and Polymer on the Formability of Their Composites

Due to global pressure to enhance energy efficiency, automotive industries have endeavoured to develop new lightweight structural materials. Steel/polymer/steel hybrid composites have been researched for this purpose because the weight of steel structure can be reduced maintaining its performance, e.g., the hybrid composites with a volume fraction of polymer of 30% theoretically shows that the flexural rigidity is maintained at 97%, but the weight is reduced to 75%, compared with the same volume of steel. In addition, these hybrid composites have showed improved damping and soundproof properties compared to pure steel structure. In order to apply those hybrid composites to industrial fields, their formability must be investigated in order to prevent the deterioration of mechanical properties of the hybrid composites during the forming process in various shapes. Therefore, experimental studies have been conducted to evaluate the formability of hybrid composites have recently been conducted. However, there are few studies to predict the formability of the hybrid composites because the physical properties of core polymer and interfacial characteristics cannot be considered properly in simplified model. In this study, first formability tests were carried out for evaluating the forming limit diagram of the hybrid composites. After that, the formability test of the hybrid composites was simulated considering the viscoelastic properties of the core polymer and the interfacial properties. Finally, the effect of the interfacial adhesion on the formability of the hybrid composites was investigated, from which an optimal condition was explored for the interfacial adhesion strengths that can ensure the formability of the hybrid composites for specific applications.
Inorganic hollow microspheres can be prepared by interfacial reaction (IR) in a W/O/W multiple emulsion. For controlling their morphology, it is worthwhile to know the transfer mechanism of the reactant ions from the outer aqueous (W_o) phase through the oil (O) phase to the inner aqueous (W_i) phase. In this study, calcium phosphate microspheres containing Mg were prepared by IR, and the effects of the solution concentration on the morphology and composition were investigated. Solution reaction (SR) was also carried out for discussing the transfer mechanism in IR.

2. Experimental

-Solutions- K_2HPO_4 solution was used as W_i phase. Solutions of CaCl_2 and MgCl_2 at a Mg molar ratio X=Mg/(Ca+Mg) of 0.05–0.6 were used as W_o phase, containing Tween20. O phase was a Span80-cyclohexane solution.

-Interfacial reaction- W_i phase at C_o=0.3 mol/kg was poured into O phase and agitated to form a W/O emulsion. This was mixed with W_o phase at C_o=0.5 mol/kg to form a W/O/W multiple emulsion. The stirring was kept at 323 K for 18 h to prepare microspheres.

-Solution reaction- At 323 K, 100 cm³ of W_i phase at C_o=0.05–0.5 mol/kg was added dropwise for 1 h into 300 cm³ of W_o phase at C_o=0.03–0.3 mol/kg, and the stirring was kept for 18 h.

-Characterization- The crystalline phase was identified by XRD. The morphology was examined by TEM. The Ca and Mg concentrations were measured by ICP-AES after dissolving in nitric acid. The relative deviation was defined as RD=(x_s–x_i)/x_i, where x_s and x_i are the Mg ratios prepared by IR and SR, respectively.

3. Results and discussion

The crystalline phase of the product prepared by IR was predominantly Mg-TCP. A hollow morphology was observed, in which primary nanosheets assemble at the interface between W_o and O phases. As X was increased, primary round shaped particles were increased. x_s was as significantly low as one-tenth or less of X. On the other hand, x_s by SR was almost the same as X, whereas the predominant phase was also Mg-TCP. This result means that Mg at a given concentration can be taken in the product when reactant ions are mixed at a given concentration. Less x_s may be due to a lower concentration of the reactants at a reaction site. Therefore, it is thought that the mixing state of both the aqueous phases in IR should be inferred if the combination of C_i and C_o by which x_s becomes equal to x_i by IR could be found.

SR was carried out at a fixed C_i. The resulting x_s was similar to X. Under any condition, RD was much greater than unity. It was not consistent with the results by IR. Next, SR was carried out at a fixed C_i. Lower C_i resulted in less x_s. Regardless of X, RD at C_i=0.03 mol/kg was almost zero, which means consistent with IR. This result suggests that a low concentration of phosphate ions are mixed at a reaction site with a given concentration of Ca and Mg ions.

In the presentation, we will propose a transferring mechanism by assuming some carrier for ions.

PM01.09.04

Challenges for the Additive Manufacturing of Shape Memory Ceramics Virag S. Raut¹, Tom Glen², Hang Yu³ and Steven T. Boles¹; ¹Electrical Engineering, Hong Kong Polytechnic University, Kowloon, Hong Kong; ²University of Edinburgh, Edinburgh, United Kingdom; ³Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia, United States.

The multiplicity of phases (cubic, tetragonal, monoclinic, etc.) in zirconia-based systems has produced many opportunities for new applications and research directions. Interestingly, zirconia doped with ceria in certain compositions gives rise to a shape memory effect (SME) and superelasticity when exposed to applied stress and/or temperature. In this work, we have investigated SME behaviour in 12% ceria-doped zirconia (Ca_{12}Zr_{10}O_{37}, CZ). CZ undergoes a martensitic transformation upon application of an applied stress which is marked by a phase change between tetragonal (T) and monoclinic (M) phases. The monoclinic content (MC) generated from the applied stress can subsequently undergo a thermally induced reverse phase transformation from M to T. The findings from our experiment suggest that the shape and morphology of CZ powder influences the MC generated during stress-induced transformation.

A higher MC in pellets is produced after stress-induced transformation despite of a reduced MC i.e. fewer nucleation sites after annealing the CZ powder. The behaviour is split into two regimes: for lower temperature treatments, the morphology give rise to stress concentrations and contribute to a higher growth in MC; for higher temperature treatments, sintering and grain growth seemingly dominate the morphology and applied stress has a limited ability to increase MC. These results suggest conventional processing steps for bulk ceramics may be challenging. To avoid deleterious thermal treatments, a slurry based additive manufacturing approach is employed to produce porous ceramic structures. Infiltrating porous CZ with polymer materials using architectured topologies and new design methods may lead to optimization of SME properties for meta-materials research and applications.

PM01.09.05

Precise Synthesis for Designed Polymer Gel Networks from the Star Polymers and Its Properties  Kwon Dowoo, Yuto Jochi, Yukikazu Takeoka, Takahirou Seki, Kotoro Satoh and Masami Kamigaito; Nagoya University, Nagoya, Japan.

Polymer gels have been continuously studied by researchers, because they exhibit useful functions for various applications. Also from an academic point of view, polymer networks of polymer gels have attractive properties both theoretically and experimentally. Generally, polymer networks can be easily prepared by free radical polymerization using monomers, initiators, and crosslinking agents. However, because the reaction process is extremely complicated in the reaction solution for preparing polymer gels, the resultant conventional gels have inhomogeneous and entangled polymer networks. While the structures of the polymer networks are closely related to the properties, the network structures including homogeneity, monomer sequence, and crosslinking points have been difficult to control by the methods so far. To design optimal network structures for applications, it is necessary to clarify the relationship between the structures of the polymer gels and those physical properties in an appropriate manner.

In this research, we introduced precise strategy to control the network structures and investigated thermal and mechanical properties of the network designed gels. Two types of preparative methods for synthesizing star-shaped polymers are sequentially employed. Firstly, star-shaped polymers are synthesized using ‘Core-first method’ by living radical polymerization utilizing tetra-functional initiator. The Atom transfer radical polymerization (ATRP) system of N-isopropylacrylamide(NIPA) was selected, because highly controllable polymerization system was essential to the detailed control of the networks. By the ‘Core-first method’, tetra-branched polymers with narrow polydispersity index (<1.1) were successfully synthesized. Secondly, according to ‘Linking methods’, the resultant star-shaped polymers are converted to the polymer networks by adding linking agents in one-pot. After adding the crosslinking agents when the monomer conversion reached over 95%, the polymer gels were obtained in 5 minutes. The combination of these methods facilitates to control the homogeneity and the sequence of monomers on the polymer networks.

Considering the experiment data, we have expected that the polymer gels have repetitive structure units composed of two types of sparse or dense star-shaped polymers, which are originated by the tetra-branched polymers and the crosslinking agents. Comparing with polymer networks prepared by free radical polymerization, there might be no inhomogeneity except for a few dangling chains derive from unreacted polymer chains. The physical properties of the polymer gels were investigated on the conventional gels and the network designed gels. On the poster presentation, we would like to discuss about the detail of the synthesis data of the novel structure gels and the consideration about the structure-properties relationship.

PM01.09.06

Optimizing Process Parameters in Commercial Micro-Stereolithography for Forming Polymer Microparticles in Non-Planar Microfluidic Devices Max Männel¹, Ricardo Bernhardt², Julian Thiele²; ¹Leibniz-Institute of Polymer Research e.V., Dresden, Germany; ²Technische Universität Dresden, Dresden, Germany.

Inorganic hollow microspheres can be prepared by interfacial reaction (IR) in a W/O/W multiple emulsion. For controlling their morphology, it is worthwhile to know the transfer mechanism of the reactant ions from the outer aqueous (W_o) phase through the oil (O) phase to the inner aqueous (W_i) phase. In this study, calcium phosphate microspheres containing Mg were prepared by IR, and the effects of the solution concentration on the morphology and composition were investigated. Solution reaction (SR) was also carried out for discussing the transfer mechanism in IR.

2. Experimental

-Solutions- K_2HPO_4 solution was used as W_i phase. Solutions of CaCl_2 and MgCl_2 at a Mg molar ratio X=Mg/(Ca+Mg) of 0.05–0.6 were used as W_o phase, containing Tween20. O phase was a Span80-cyclohexane solution.

-Interfacial reaction- W_i phase at C_o=0.3 mol/kg was poured into O phase and agitated to form a W/O emulsion. This was mixed with W_o phase at C_o=0.5 mol/kg to form a W/O/W multiple emulsion. The stirring was kept at 323 K for 18 h to prepare microspheres.

-Solution reaction- At 323 K, 100 cm³ of W_i phase at C_o=0.05–0.5 mol/kg was added dropwise for 1 h into 300 cm³ of W_o phase at C_o=0.03–0.3 mol/kg, and the stirring was kept for 18 h.

-Characterization- The crystalline phase was identified by XRD. The morphology was examined by TEM. The Ca and Mg concentrations were measured by ICP-AES after dissolving in nitric acid. The relative deviation was defined as RD=(x_s–x_i)/x_i, where x_s and x_i are the Mg ratios prepared by IR and SR, respectively.

3. Results and discussion

The crystalline phase of the product prepared by IR was predominantly Mg-TCP. A hollow morphology was observed, in which primary nanosheets assemble at the interface between W_o and O phases. As X was increased, primary round shaped particles were increased. x_s was as significantly low as one-tenth or less of X. On the other hand, x_s by SR was almost the same as X, whereas the predominant phase was also Mg-TCP. This result means that Mg at a given concentration can be taken in the product when reactant ions are mixed at a given concentration. Less x_s may be due to a lower concentration of the reactants at a reaction site. Therefore, it is thought that the mixing state of both the aqueous phases in IR should be inferred if the combination of C_i and C_o by which x_s becomes equal to x_i by IR could be found.

SR was carried out at a fixed C_i. The resulting x_s was similar to X. Under any condition, RD was much greater than unity. It was not consistent with the results by IR. Next, SR was carried out at a fixed C_i. Lower C_i resulted in less x_s. Regardless of X, RD at C_i=0.03 mol/kg was almost zero, which means consistent with IR. This result suggests that a low concentration of phosphate ions are mixed at a reaction site with a given concentration of Ca and Mg ions.

In the presentation, we will propose a transferring mechanism by assuming some carrier for ions.
Droplet-based microfluidics is an established technique for fabricating microemulsions, microparticles and vesicles with tailored physicochemical properties for a broad range of applications in biology, chemistry, and material science. The state-of-the-art technique for fabricating flow cells to prepare microprobes is a combination of photo-lithography and soft lithography based on poly(dimethylsiloxane) (PDMS), where a PDMS replica of microchannels is bonded to a glass slide, followed by post-processing steps, such as surface modification. While this multistep process yields microfluidic devices with feature sizes of a few micrometers in a parallelized fashion, each processing step is prone to experimental errors, which can make it challenging to reliably obtain high yields of functional microflow cells. Additive manufacturing based on micro-soft-lithography (μSL) is a promising alternative approach for fabricating microfluidic flow cells. This one-step three-dimensional (3D) printing technology is characterized by its high resolution and short process time. Utilizing a digital light processor, the 3D computer-aided design of a microflow cell is built up in a layer-by-layer fashion by exposing a liquid resin bath with stacks of xy-illumination patterns. Several parameters are optimized to make functional microflow cells, including the layer thickness, exposure time and energy, and the tilting up and down speed after each exposure. The high resolution and comparable to conventional PDMS-based fabrication methods and ultimately replace them, we have evaluated three key printing parameters in μSL: resin viscosity, alignment of the flow cell with respect to the printing direction, and the voxel compensation adjustment in the xy-plane. The same 3D-printed flow cell can be employed for forming both oil-in-water (o/w) and water-in-oil (w/o) emulsions, with respective diameters of approximately 100 µm and 50 µm. The emulsions then serve as templates for preparing hydrophobic or hydrophilic polymer microparticles with frequencies of up to 2.8 kHz in a single 3D-printed microflow cell without requiring additional steps for controlling microchannel wettability. In contrast to conventional multistep microfluidic device fabrication by photo- or soft-lithography, we report the preparation of non-planar microfluidic flow cells in a single processing step that can be used for fabricating both hydrophobic and hydrophilic microparticles without requiring surface modification.

PM01.09.07
Bio-Inspired, Metal Based, Layer-by-Layer Structured Composites with Exceptionally High Toughness Yunya Zhang and Xiaodong Li; University of Virginia, Charlottesville, Virginia, United States.

Nature’s wisdom resides in constructing delicate architectures from limited constituents and achieving superior performances by the constructed structures. As exhibited in nacre, hard CaCO3 platelets are cemented by soft biopolymers, forming laminated architecture. The hard CaCO3 platelets act as main load bearers while the soft biopolymer layers dissipating energy and redirecting cracks. Such hard-soft-hard design enables a joint enhancement of strength and toughness, which are considered mutually exclusive in engineering materials. Therefore, nature inspires us that the dilemma between strength and toughness can be overcome by rational design of microm-scale architectures. In order to mimic nacre’s structures, graphene, a single layer of carbon atoms with extremely high strength, was used to composite with metals. In one study, graphene oxide sheets were incorporated with Al flakes. After freeze drying, sintering, and rolling, nacre’s three identifying features (laminated structure, nanosuperstructures, and mineral bridges) were effectively emulated in the composite. Graphene oxide released oxygen-containing gases during high temperature annealing and the gases reacted with Al, forming Al2O3/graphene/AlOx sandwiched layers at interfaces. The confluence of multiple strengthening and toughening mechanisms resulted in a joint improvement in hardness (210%), strength (223%), stiffness (78%), and toughness (30%). In another study, Ni powders were coated with graphene layers via shear mix and freeze dry. Carbon reacted with Ni at high temperature, forming rectangular NiC2 second phase particles. The brick-and-mortar structure coupled with dissolved carbon atoms led to 97% improvement of strength with a minor reduction of ductility.

PM01.09.08
Fabrication of Electroactive ZnO Nanomesh via Vapor-Phase Materials Infiltration in Self-Assembled Pyridine-Based Diblock Copolymer Thin Films Ashwathn Subramanian1, Kim Kisslinger1, Daniel Yi2, Robert B. Grubbs3, Gregory Doerk4 and Chang-Yong Nam5; 1Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 2Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States; 3Department of Chemistry, Stony Brook University, Stony Brook, New York, United States.

Thin film nanoarchitectures can offer enhanced materials properties, such as large specific surface areas that amplify the structures’ interaction with environments, making the nanostructures useful for various sensing applications. Infiltration synthesis, a new-type of organic-inorganic material hybridization technique derived from atomic layer deposition, relies on the vapor-phase inorganic precursor infiltration into polymeric matrix. When applied to self-assembled templates of diblock copolymer (BCP) thin films and combined with the subsequent removal of polymer matrix, the technique enables a reliable large-scale inorganic material nanoengineering. Although the infiltration synthesis of alumina (Al2O3) nanostructures using self-assembled poly(2-vinylpyridine)-block-poly(methylmethacrylate) (PS-b-PMMA) BCP thin films has been well documented, the generation of more useful semiconductor nanostructures, such as those made of zinc oxide (ZnO), has been relatively scarce, unless the pre-infiltration (i.e., priming) of Al2O3 is applied, due to the weaker interaction of Zn precursor with polymers in general. Here, we demonstrate the successful infiltration synthesis of pristine ZnO nanostructures without resorting to the Al2O3 priming, by taking advantage of more chemically reactive self-assembled polystyrene-block-poly(2-vinylpyridine) PS-b-P2VP BCP thin films as well as the newly developed, micro-dose infiltration synthesis protocol. By exploiting the self-registrering phenomenon between successively coated self-assembled BCP thin films, we generate the electroactive, stacked ZnO nanomesh thin film architecture with the controlled number of stacked layers. The electrical characterization under dark and illuminated conditions reveals an enhancing electrical conductance with increasing number of nanomesh stack layers. The results not only illustrate the first demonstration of electrical functionality based on the ZnO nanoarchitecture generated by the infiltration synthesis in self-assembled BCP thin films but also present a new, large-area scalable, metal oxide thin film nanoarchitecture fabrication method utilizing industry-compatible polymer solution coating and atomic layer deposition. The fabricated ZnO nanomesh architecture also promises potential applications as an efficient active sensing medium for chemical and optical detectors.

PM01.09.09
Investigating the Conformality of Shell Structures on GLAD Growth Rod Core Structures by Monte Carlo Simulation Mesut Yunkur1, Serkan Demirel1 and Fatma Merve Yurtsever2; 1University of Arkansas, Little Rock, Arkansas, United States; 2College of Computer and Information Sciences, Regis University, Denver, Colorado, United States.

Shell-core nanorod array geometry can offer enhanced durability for polymer electrolyte membrane (PEM) fuel cell electrodes, and increased surface-volume ratio for high efficiency for batteries, solar cells, sensors if a structured shell is conformally coated around the nanorod support base. The quality of volume ratio for high efficiency for batteries, solar cells, sensors if a structured shell is conformally coated around the nanorod support base. The quality of shell coating around nanorod is as crucial as the quality of the nanowires in device applications. In this study, we performed an experimental investigation of different physical vapor deposition (PVD) techniques to discover the most efficient deposition technique for a conformal shell coating around nanorods. To assess the PVD conditions to produce conformal shell coatings, Monte Carlo simulation method (MC) can provide useful guidance as well as helping investigate fundamental growth dynamics during shell-core nanorod array fabrication. Monte Carlo simulations were conducted to determine a simple and scalable fabrication technique for conformal and uniform shell coatings. We conducted Monte Carlo simulation (MC) and investigated the conformality of PVD shell layers on nanorods of the same length to predict the different materials. Our results show that high pressure with normal angle deposition can generate better conformal shell coating inside all others. The results suggest that an atomic flux with an angular distribution which can be easily maintained by sputtering at high working gas pressure can form conformal and uniform coatings. Our results indicate that...
conventional PVD techniques, which offer low cost and large scale thin film fabrication, can be utilized for highly conformal and uniform shell coating formation in shell-core nanostructures. In our previous works, the pre-patterned template was used to run the shell coating simulations. In this paper, we investigated the shell conformality on in situ grown GLAD rod structures by Monte Carlo simulation. This work will give the reader an understanding of how significant the geometry and the design of the rod structured arrays play a role in core-shell PVD coating device applications.

PM01.09.10
Study on Array Transmittance Improvement of Thin-Film Transistors Chengzhi Luo; Wuhan University, Wuhan, China.

Transparent electronics, such as thin film transistors, is one of the most advanced topics for a wide range of device applications. The key components are wide bandgap semiconductors, not only as passive component but also as active component, similar to what is observed in conventional semiconductors like silicon. Transparent electronics has gained special attention during the last few years and is today established as one of the most promising technologies for leading the next generation of flat panel display due to its excellent electronic performance. In order to achieve the high performance, TFTs need to possess high light efficiency. Transmittance improvement is the main method to improve light efficiency of TFT array substrate.

In this paper, multilayer thin films of low temperature poly-Si array transmission area is made to study the effect of thin films and structure on transmittance. The results show that the transmittance of TFTs is greatly affected by different refractive index surface after inter layer dielectrics finished. We also find that that the effect of planarization layer thickness on transmittance is not obvious. Transmittance is decreased with the increasing of ITO thickness. By decreasing the film numbers, changing the film component, the inter surface with great difference of refractive index was reduced and transmittance can be improved by 7% approximately.

PM01.09.11
Autonomous Printing of Functional Contact-Stylus Circuits Annika Muehlbradt and Gregory Whiting; University of Colorado Boulder, Boulder, Colorado, United States.

Printing enables the fabrication of flexible, lightweight, and low-cost electronic devices with potential application in batteries [2], displays [1, 7], sensors [3, 6], and actuators [4]. Printing processes offer high-throughput production capabilities, but well-known printing methods, like inkjet and gravure printing, require different ink parameters (e.g. viscosity), substrate parameters (e.g. paper), and environmental parameters (e.g. humidity), and support variable throughput, uniformity, accuracy, and resolution [5]. These requirements make it difficult to fabricate functional printed electronics quickly and at scale. Printing methods to create devices “on-the-fly” in ambient conditions are needed to fully exploit the potential of printed electronics.

We introduce a novel, automated printing process for scalable manufacturing of flexible, multi-material electronics. The printing process comprises two phases: (1) an analysis of the circuit sketch, ink, and substrate, and (2) fabrication of the circuit. The circuit sketch is processed using a nearest-neighbor classifier with a geometric template matcher to extract key features. The ink and substrate parameters are inferred from a test print in which we measure electrical properties. Using these parameters as guidelines, our printing algorithm fabricates the circuit by iteratively printing circuit components and validating their electrical properties, making adjustments “on-the-fly” to achieve a functional circuit. This autonomous printing technique is universal and can be extended to a number of different inks, multi-material prints, and printing devices and offers a flexible fabrication process for printed electronics.


PM01.09.12
Optimization of 3D Printed Low-Density Foams for Inertial Confinement Fusion Matthew Worthington, James Oakdale, Monika Biener, Daniel Malone, Chantel Aracne-Ruddle, Jean-Baptiste Forien, Salmaan Baxamusa, Jianchao Ye, William L. Smith, Todd Weisgraber, Michael Stadermann and Juergen Biener; Lawrence Livermore National Lab, Livermore, California, United States.

A complex and diverse set of materials and material processing techniques enable a wide range of high energy density (HED) physics endeavors at Lawrence Livermore National Laboratory. One such experimental platform seeks to achieve inertial confinement fusion through symmetrical implosion of a capsule containing deuterium-tritium atoms. Here, a series of laser beams are focused into the inside cavity of a cylindrical gold hohlraum creating an x-ray drive field. One issue with this method is that there is significant hohlraum “wall movement” (i.e. generation of partially ionized plasma) that interferes with the path of the lasers leading to asymmetric capsule implosion. A low density foam liner on the interior of the hohlraum has been proposed as means to retard the motion of this plasma plume. Our approach to this problem of liner fabrication is to first 3-D print a polymeric lattice-based template using direct laser writing via 2-photon polymerization (DLW-TPP), followed thereafter by atomic layer deposition (ALD) to apply a high-Z coating of tantalum oxide (Ta2O5) and finally polymer template removal to arrive at a low-density hollowed-out tubular lattice composed of the desired material. This work will focus on the 3D-printing aspect of this project and will discuss our efforts to create a customizable, uniform polymer template that will fit snugly inside the gold hohlraum. 3D-printing, or additive manufacturing foam liners offers several advantages in addition to rapid design prototyping, including the ability to make complex density gradients or architectures that would otherwise be difficult/impossible to machine. DLW-TPP enables the ability to print sub-micron features, which is important for achieving density uniformity (i.e. >10 um sized pores). The density of the polymer template is 0.1 g/cc and after ALD/etching the desired Ta2O5 foam with a density of 0.02 g/cc is achieved (solid fraction < 1/400). When printing these templates, we have to account for shrinkage while drying with shrinkage during the ALD process. It is important to make sure these values are accounted for, as the foam must fit perfectly inside the hohlraum. During insertion stress on the liner is tracked using a modified nano-indenter. This data and its relevance to the liner diameter vs. hohlraum diameter vs. fidelity during template etching will be presented.

The work was performed under the auspices of the US Department of Energy by LNL under contract No. DE-AC52-07NA27344. The project was supported by the Laboratory Directed Research and Development (LDRD) programs of LNL (18-ERD-064).

PM01.09.13
The Size Effect for Low-Temperature Synthesis of Graphene on Porous Silicon Kurbangali B. Tynyshtykbayev1 and Zinetula Z. Insepov2,3,; 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan.

It has been shown that reducing the size of nanocrystallites on the surface of porous silicon (PS) fabricated via electrochemical etching leads to a significant increase of the surface energy of PS and to a decrease of the melting point of the nanocomposite. This effect was used for low-temperature synthesis of a graphene-like carbon by carbonization of the porous silicon surface using a CVD method, at temperatures as low as 350 – 500 °C [1]. This...
work demonstrates that synthesis of graphene-like carbon nanocomposites in form of spatially-oriented graphene modified with small additives of carbon nanotubes CNT and SiC inclusions occurs on the surface of graphene nanocrystallites on PS surface at 1050°C. We also demonstrated that the surface of a single c-Si crystal is not carbonized at 1050°C. A low-temperature synthesis of graphene-like carbon nanocomposites in form of graphene oxides and CNT with inclusions of various carbon allotropic forms occurs at 350 ± 500°C. The temperature of the low-temperature synthesis of graphene and graphene-like structures is related to the growth of surface energy of nc-PS nanocrystallites formed during pore formation in electrochemical etching. It has also been shown that the carbonized surface of PS-C=C preserves a high chemical stability.


PM01.09.14 Liquid Crystal-Templated Synthesis of Porous Polymeric Membranes with Predetermined Pore Alignment Asli Karausta and Emre Bukusoglu; Chemical Engineering Department, Middle East Technical University, Ankara, Turkey.

Liquid crystal (LC) is a phase of material which is intermediate to a crystalline solid and an isotropic liquid such that the molecules flow but retain a degree of long-range orientational ordering. LCs, due to their long range orientational ordering and fluidic properties, can be used in templated synthesis of polymeric materials. In the past studies of oil-in-water emulsion based polymeric microparticle synthesis, it was showed that control over the particle shape, organization of polymer chains and incorporation of porosity can be achieved when LCs were used as the oil phase[1]. In this study, we indicated that polymer films templated from liquid crystals provide basic design principles for the synthesis of films with predetermined pore alignment. For the synthesis of the material, we photopolymerized the mixture of reactive (4-[3-acryloyloxypropoxy]benzoic acid 2-methyl-1,4-phenylene ester (RM257)) and nonreactive (4-cyan-4'-pentylbiphenyl (5CB)) mesogens confined in film geometries with thickness of 20-200 μm, and then extracted the unreacted mesogens with solvent to yield polymeric films of area in the order of 10 cm2. The crucial point of this study was that, when we constrained the polymer films to an area either through a mechanical or a configurational constraint, open pores were incorporated into the films. The average diameter of the pores was found to be in the range 10-40 nm, and can be tuned by varying the reactive monomer concentration. In fact, the average direction of the pores was found to be determined by the nematic director which can further be controlled by the functionality of the contacting surfaces. Having control over the sizes and directions of the pores has enabled the material to be involved in many application areas. We found that the range of the pore sizes and the alignment behavior of the pores can potentially be used for the ultrafiltration purposes as one of these applications. We also demonstrated a successful separation of protein molecules and solid nanoparticles from aqueous media using polymeric films templated from liquid crystalline media, the mass transfer performance of which was also dependent on the alignment direction of the pores with respect to the surfaces. For the synthesized polymeric materials, we used characterization methods such as thermal, optical, mechanical properties, nitrogen adsorption porosimetry and electron microscopy. Overall, the outcomes of this study provide basic tools for the synthesis of porous polymeric films with predetermined pore directions that can potentially be suitable for separation purposes, drug delivery, catalysts, etc.


PM01.09.16 Additive Manufacturing of Hierarchical Three-Dimensional Micro-Architected Graphene Aerogels Xiaoyu Zheng; Virginia Tech, Blacksburg, Virginia, United States.

Graphene foams, despite having one of the stiffest base materials ever measured, suffer incredible degradation in mechanical properties with decreasing density, so much so that polymer foams can outperform graphene foams at low-densities, despite the polymer base material being significantly less stiff than a graphene sheet. Until now there were few predictable means with which experimental approaches to alter this paradigm had been developed. A light-based 3D printing process to rapidly create three-dimensional graphene lattices of essentially any desired structure with graphene strut microstructure having pore sizes on the order of 60 nm. This flexible technique enables printing 3D micro-architected graphenes with complex, high-resolution form factors unparalleled by previous graphene 3D printing techniques. We utilize this ability to demonstrate improved mechanical properties when scaling to lower densities due to control of its three-dimensional hierarchical micro-architecture. These 3DGs are ultra-light, possess large surface area, and maintain good electrical conductivity, while greatly expanding the micro-architectural design space that 3DGs can realize.

PM01.09.17 One Pot Synthesis of a Gel with a Homogeneous Network Structure by Combining Two Methods of Synthesizing Star Polymers Yusuke Baba, Kwon Dowoo, Yuto Jochi, Yukikazu Takeoka, Takahiro Seki, Kotaro Satoh and Masami Kamigaito; Graduate School of Engineering, Nagoya University, Nagoya, Japan.

A polymer having a three-dimensional network structure and absorbing a solvent is called a gel. A gel is expected to be applied to many functional materials because of their simple adjustment method and various functionalities. Generally, when a gel is synthesized by free radical polymerization, the gel has an inhomogeneous network structure. The inhomogeneity of the network structure of the gel influences the properties of the gel. However, the relationship between the homogeneity of the network structure and the properties of the gel has not been investigated in detail. This is because there are few methods for synthesizing a gel with a homogeneous network structure. In order to investigate the relationship, our research group succeeded in synthesizing a PNIPA (poly(N-isopropylacrylamide)) gel with a homogeneous network structure by combining two methods of synthesizing star polymers. One method is a core-first method in which star polymers are synthesized by living polymerization using multifunctional initiators. Another method is a linking method in which star polymers are synthesized by adding divinyl compounds to linear living polymers and crosslinking the polymer terminations. In our study, a star polymer is synthesized from a 4-branched initiator by living radical polymerization (core first method), and then the polymer chain ends are crosslinked by adding divinyl compounds (linking method). Thereby, a gel with a homogeneous network structure can be obtained. We believe that research on how inhomogeneity affects the properties of a gel will proceed on this gel. In this study, in order to investigate the correlation between the network structure and various physical properties in a solvent-free elastomer, a monomer in which the polymer becomes liquid at room temperature was used. So we prompt to synthesize a P(2-(2-methoxyethoxy) ethyl methacrylate) gel which can take an elastomer state with a homogeneous network structure and measure the mechanical properties. First, we prepared 4 branched star-shaped P(2-(2-methoxyethoxy) ethyl methacrylate) gel using 4 branch initiator, CuCl for catalyst, and bipy for ligand in anisole. As a result, we obtained 4 branch P(2-(2-methoxyethoxy) ethyl methacrylate) gel which can take an elastomer state with a homogeneous network structure and measure the mechanical properties. Finally, by combining these star polymer synthesis methods, a homogeneous polymer network consisting of MEO2MA was successfully synthesized.
The high hardness or yield strength of an alloy is known to benefit from the presence of small-scale precipitation, whose hardening effect is extensively applied in various engineering materials. Stability of the precipitates is of critical importance in maintaining the high performance of a material under mechanical loading. The long period stacking ordered (LPSO) structures play an important role in tuning the mechanical properties of a magnesium alloy. Here, we report (10-12) deformation twin inducing decomposes into lamellar LPSO structures and their re-precipitation in an Mg0.5Zn0.5Y (at. %) alloy. Using atomic resolution scanning transmission electron microscopy (STEM), we directly illustrate that the misfit dislocations at the interface between the lamellar LPSO structure and the (10-12) deformation twin are corresponding to the decomposition and re-precipitation of LPSO structure, owing to dislocation effects on redistribution of Zn/Y atoms. This finding demonstrates that deformation twinning could destabilize complex precipitates. An occurrence of decomposition and re-precipitation, leading to a variant spatial distribution of the precipitates under plastic loading, may significantly affect the precipitation strengthening. Regarding the compression deformation twin, we uncovered the interaction between (10-13) twin and stacking faults (SFs) occurrence of decomposition and re-precipitation, leading to a variant spatial distribution of the precipitates under plastic loading, may significantly affect the precipitation strengthening. The high hardness or yield strength of an alloy is known to benefit from the presence of small-scale precipitation, whose hardening effect is extensively applied in various engineering materials. Stability of the precipitates is of critical importance in maintaining the high performance of a material under mechanical loading. The long period stacking ordered (LPSO) structures play an important role in tuning the mechanical properties of a magnesium alloy.
introduces a new energy loss mechanism at low strains of only 1-5%. This loss mechanism, known as the Payne Effect, is one of the mechanical hallmarks of filled rubbers and is a major contributor to rolling friction in tires.

We create a model filled rubber which exhibits the rheological hallmarks of traditional filled rubbers, but can be optically imaged. Optical transparency is achieved by matching the refractive index of our filler, fumed silica, and our polymer, PDMS. Visualizing the deformation of the filler subnetwork requires a contrast mechanism with sufficient spatial resolution to resolve the filler microstructure. Fluorescent silica nanoparticles, whose physical size is comparable to the smallest length scales in the filler subnetwork, provide the desired optical contrast. With this system we can directly observe microstructural changes of filler particle aggregates during *in situ* shear deformation. We complement these observations with bulk rheological tests to gain new insight into the microscopic deformations underlying the Payne effect. By controlling filler loading and crosslink density, we can tune the microstructure of our composite to better understand the relation between its structure and mechanical properties.

**PM01.09.22**

**Jellium Phase-Field Crystal Model—The Thermodynamic Influence of Electronic Contributions**

Salvador Valtierra1, Nan Wang1, Nana Ofori-Opoku1, 2, Nikola Provatas1 and Kirk H. Bevan1; 1McGill University, Montreal, Quebec, Canada; 2Canadian Nuclear Laboratories, Chalk River, Ontario, Canada.

In an effort to systematically engineer the performance of multiphase materials we have developed a new electronic-ionic based coupled phase-field crystal (PFC) methodology.1,2 Our results are underpinned by a deep analysis of the free energy functional formulation which leads to the addition of an electronic free energy term in PFC.3,4 This functional is normally constructed based on an atomic number density in classical density functional theory (CDFT).5,6 Through a series of approximations from CDFT and a mean-field approach, PFC permits the modeling of multiple phases and observe microstructural features in materials. In this work, a jellium system is employed as framework to formulate a free energy which allows the visualization of the electron energetics that modify the stability of liquid and crystalline phases modeled in PFC. We present a profound discussion of the physical implications behind the construction of the free energy functional and architected microstructural consequences. This formulation would extend the model to study the influence of electronic features and external forces acting on the microstructure in order to tailor the multi-functional properties of materials. The aim of this study is to provide a new perspective on PFC, that will permit the inverse design of new phenomena in materials science modeling.

---


**PM01.09.23**

**Optical Properties of an Exciton in a AlN/GaN/AIN Spherical Core/Shell Quantum Dot Under Pressure**

Mustafa Sadoglu1, Noreddine Aghoutane2, Mohamed El-Yadri1, Amsaa El Haouari1, Elmustapha Feddi1, F. Dujardin1, Chuong V. Nguyen4, Nguyen N. Hieu1, Huynh V. Phu1 and Gen Long1; 1Saint John's University, Jamaica, New York, United States; 2Group of Optoelectronic of Semiconductors and Nanomaterials, ENSET, Mohammed V, Rabat, Morocco; 3LCP-A2MC, Institut de Chimie, Physique et Matériaux, Université de Lorraine, Metz, France; 4Institute of Research and Development, Duy Tan University, Da Nang, Viet Nam; 5Division of Theoretical Physics, Dong Thap University, Dong Thap, Viet Nam.

This work is based on our recent theoretical investigation of the effects of the hydrostatic pressure and core/shell sizes on the optical properties associated with the transition from the ground state into the first excited state (1s-1p), of the exciton in a spherical core/shell quantum dot (SCSQD). Our calculations are performed in the framework of the effective mass approximation and the energies are obtained by using a Ritz variational method. We have computed the linear, third-order nonlinear and total absorption coefficients (AC) and refractive indices (RI) as a function of photon energy for different sizes of SCSQD under the influence of the hydrostatic pressure. Our results show that the optical absorption is strongly dependent on the incident optical intensity and sensitively influenced by the confinement and pressure effects. We have found that, by increasing pressure, the AC and RI curves move toward the higher energies (blue shift). Our calculation also shows that the AC and RI are affected by the core/shell quantum dot sizes.

**PM01.09.24**

**Direct Ink Writing of Polymide Composites with Density/Dielectric Tunability**

H. Clive Liu1, 2, James O. Hardin1, 2 and John D. Berrigan3; 1UES Inc., Beavercreek, Ohio, United States; 2Air Force Research Laboratory (AFRL), WPAFB, Ohio, United States.

Polymide has been an important engineering material with excellent oxidative- and thermal-stability, mechanical performance, and dielectric properties that can be employed in harsh environments. However, architectural design and exploration of novel polymide composites are still hindered by the limited manufacturing and property-tailoring strategies. Currently, hierarchical construction of polymide can be achieved through imidizing the additive-manufactured precursor polyamic acid or photo-curing a chemically modified polyimide. Yet these 3D process-ability are reported at the respective expense of significant shrinkage (≥ 40%) accompanied by the imidization reaction or a pronounced decrease (100 – 200 °C) in degradation temperature compared to other polymide analogues.

In this study, we present 3D polymide architectures through direct writing of fully-imidized polymide ink without photo-crosslinking or post-print thermal/chemical imidization. The printed structures are programmed with intrinsic micro-porosity through a simple formulation strategy that acts to suppress density, dielectric permittivity, and dissipation. Moreover, the development of composite ink formulations allow tailoring of functionality (e.g., electrical/thermal conductivity, high-$k$ dielectric) into the structures. These micro-porous and composite polymide materials enable the investigation of cellular and graded architectures to manipulate mechanical response, structural mechanics, and electromagnetic wave steering efficiency for future 3D printed antenna applications.

**PM01.09.25**

**3D Direct-Nozzle Printing of Ceramic Magnetic Core for Transformers with Viscoelastic NiZn-Ferrite Paste**

Taekyu An and Jihoon Kim; Kongju National University, Cheonan, Korea (the Republic of).

3D printing technology recently attracts a significant amount of attention due to its potential to easily fabricate complex designs of diverse products. This
technical convenience leads to the step where 3D printing technology is considered an innovative and simple way of manufacturing ceramic-based electronic components. In this study, 3D direct-nozzle printing was introduced to fabricate various shapes of the NiZn-ferrite soft magnetic core for transformers. The NiZn-ferrite paste for 3D direct-nozzle printing was formulated by incorporating various functional additives to impart viscoelastic property. This viscoelastic property of the paste plays a critical role in printing and maintaining the 3D shape of the transformer core. The correlation of viscoelastic property with 3D printability will be addressed in depth in this presentation. The 3D-printed magnetic cores of different designs were sintered at an elevated temperature. The volume shrinkage and magnetic functionality were investigated after sintering. Finally, we printed EFD type transformer cores and compare their performance against commercial transformers with the same type. Our successful demonstration implies the importance of viscoelasticity in 3D printing ink and the potential of 3D printing as a manufacturing process for ceramic-based electronic components.

PM01.09.26
Application of Box Benhken Experimental Design in the Fabrication of Anodized Aluminium Oxide Templates from Low Purity Substrates and Its Escalation to Extended Areas
Line M. Castro and Carlos Ostos; Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, Medellin, Colombia.

In the last years, the scientific community has developed multiple variations of the aluminium anodization process, with the goal to prepare nanostructures to be adapted for new technologies. The controllable microstructural parameters, self-organized pore-arrangement, parallel nanochannels, narrow pore-size distribution, and high pore density, open a wide range of possibilities for nanomaterial synthesis and the opportunity to module the properties of the periodic nanostructures. Therefore, an optimization of the experimental conditions is mandatory to achieve the desired dimensions and best arrangements of pore features; hence providing the best performance of derived nanostructures [1].

In this work, the influence of the most important operating parameters, such as potential (30V-60V), temperature (10°C-20°C), and concentration of electrolyte (0.3M-0.6M), on the structural features of alumina was investigated by means of Box-Benken experimental design (BBD). A low purity aluminium foil, 99.06%, was selected to accomplish the experiments because of its low cost and high suitability when addressing real applications. The aluminium foils were first machined with an area of 1 cm² and degreased using a mixture solution of acetone/ethanol; afterwards, the foils were processed using oxalic acid solutions with concentrations from 0.3 M to 0.6 M, temperature range from 10°C to 20°C, and potential from 30V to 60V, these parameters were used as input factors for the BBD design. The obtained models granted us the possibility to understand the individual and interaction effects of the three operational parameters on the steady state current and pore features, such as regularity ratio (R₃₅), pore diameter (Dₚ), eccentricity (Ecc), aspect ratio (AR), pore density (ρₚ), interpore distance (Dₓ), and porosity percentage (%P). Potential and temperature were found to significantly affect most of the assessed geometrical pore features of the Box-Benben design. The regularity ratio was optimized with a value of 2.0134 under the next conditions: 46V-10°C-0.6M.

The optimized set of conditions were used for the scaling up of the process in 78 cm² aluminium foils. We have found that anodization under these conditions can produce porous alumina templates with a highly ordered cell configuration, even from inexpensive aluminium substrates and without the necessity of advanced equipment, an important fact that widen its applications at industrial scale. The fabrication of the extended AAO surfaces is important to proceed with the large-scale assembly of one-dimensional structures, which must be considered to boost the development of new technologies.


PM01.09.27
Monolayer-to-Thin-Film Transition in Supramolecular Assemblies on Graphene—The Role of Topological Protection
Alexander J. Marsden, Zachary Laker, Oreste De Luca, Ada Dell’Aia, Luis M. Perdigão, Giovanni Costantini and Neil Wilson; 1Materials, University of Manchester, Manchester, United Kingdom; 3Chemistry, University of Warwick, Coventry, United Kingdom; 4Physics, University of Warwick, Coventry, United Kingdom.

Supramolecular assembly is a promising route for the bottom-up synthesis of nanomaterials. The resulting structure is guided by the non-covalent forces between molecules, and those between a substrate and the molecules. The interactions with the substrate can template up through the film: successive layers of molecules are influenced by earlier ordering, and the resulting structure can be different from its expected bulk form. These structured nanomaterials show promise for applications in electronics and optoelectronics. Here we study the supramolecular assembly of benzene-1,4-dicarboxylic acid (terephthalic acid, TPA), and benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA) on graphene. The thin film structure is investigated using low-dose, aberration-corrected transmission electron microscopy (TEM) as the film thickness increases, and is compared to the monolayer structure found using scanning tunneling microscopy (STM).

At the monolayer, both molecules display a structure dictated by hydrogen bonding between molecules: TMA forms a hexagonal chicken-wire structure, and TPA, a brickwork pattern. The orientations of these 2D monolayers are influenced by the graphene substrate through van der Waals epitaxy, although this is stronger in the case of TMA. Above a monolayer, TMA and TPA behave differently. The chicken-wire structure of TMA templates up through increasing film thickness, until after a certain critical thickness when the film becomes polycrystalline with random in-plane orientations. On the other hand, after a monolayer, TPA forms fibre-like islands, with the in-plane lattice parameters gradually changing with increasing thickness to those consistent with the bulk structure. These differences are thought to be anachronisms in the differences between the 2D and bulk structures for the two molecules. TPA can transition from its 2D structure to its bulk form through tilting and compacting of the lattice. However, TMA’s 3D structure consists of interleaving planes, which cannot be smoothly transitioned to as the film thickness increases. This idea of topological protection could be used to help design supramolecular assemblies in the future.


PM01.09.28
Bioinspired Design of Cement-Polymer Composites
Jessica Rosewitz, Habibehe Choshali and Nimra Rahbar; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Recent advances in the design of structural composites often mimic natural microstructures. Specifically, the structure of abalone nacre with its high stiffness, tensile strength, and toughness is a source of inspiration from the process of evolution. The inspiration from nacre can lead to design of a new class of architected structural materials with superb mechanical properties. This work presents a combined experimental and computational study on a set...
of bioinspired architected composites created using a cement mortar cast with brick-and-mortar and auxetic polymer phases. The impact of this unit-cell architecture on polymer phase on the flexural and compressive strengths, resilience, and toughness is thoroughly studied as a function of microstructural geometry. All mechanical properties of the architected composite specimens are found to be greater than those of control samples due to prevention of localized deformation and failure, resulting in higher strength. The microstructurally designed composites showed more layer shear sliding during fracture, whereas the control samples showed more diagonal shear failure. After initial cracking, the microstructurally designed composites gradually deformed plastically due to interlocking elements and achieved high stresses and strains before failure. Results also show that microstructurally designed composites with the architected polymer phase outperform control samples with equal volume fraction of a randomly oriented polymer fiber phase. Extensive computational studies of the proposed unit cells are also performed and the results suggest that the orientation of cells during loading is critical to achieve maximum performance of a cementitious composite. The implications of these results are immense for future development of high performing construction materials.

PM01.09.29
Fabrication of Photo-Activating Acryl-polyurethane Through Short Curing Time
Hyo Jinn Jung, PilHo Huh, Kyung Soek Kang, Jihong Bae, Chanhyuk Lee, WonBin Lim and Byeongoo Kim; Pusan National University, Busan, Korea (the Republic of).

Thermoplastic photo-activating PU was successfully synthesized by the additional reaction of methylene diphenyl disocyanate (MDI), poly(tetramethylene ether) glycol, and tri-acrylate derivatives as a crosslinking point. The crosslinked PU-acrylate elastomers were fabricated by the exposure to 200–400μm UV radiation. DMF was used as a solvent for the synthesis, but THF with low UV cut off was used to crosslinked the PU-acrylate in order to reduce crosslinking time. The structures and properties of the resulting acryl-PUFs were evaluated by fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), ultra violet spectroscopy (UV-Vis), differential scanning calorimetry (DSC), and universal testing machine (UTM). The increase of acrylate concentration in acryl-PUFs elastomers led to higher tensile strength and hardness due to the increased crosslinking density and the enhanced interchain hydrogen bonding. The application as a 3D printing material was verified according to the shortened crosslinking time.

PM01.09.30
The Effects of Dynamic Transformation on the Formation of Pt-Ni Nano-Octahedra
Yiliang Luan1, Can Li2, Bo Zhao3, Amar Kumbhar3, Jun Zhang4, and Jiye Fang1; SUNY Binghamton, Binghamton, New York, United States; 2Texas Tech University, Lubbock, Texas, United States; 3University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 4China University of Petroleum, East China, Qingdao, China.

Colloidal synthesis has been widely used in the development of nanomaterials including metals, alloys, and semiconductors, as it can produce uniform, size-controlled and shape-controlled nanoarchitectures. It is usually desired for shape-controlled products to expose exclusive facets, correlating a collective property such as reaction activity or selectivity with the specific surface crystal face. Compared with other conventional approaches such as the hydrothermal method, the solution-based synthesis has more variable factors that govern the formation of the nanocrystal products, due to the kinetic and thermodynamic effects in the nucleation and crystal growth processes, such as a competition between the deposition and diffusion of “free atoms” on a nanocrystal. These factors greatly impact the morphology evolution of the products with some in-depth mechanistic insights to uncover. In our synthetic system, a non-polar organic solvent is usually chosen as the reaction medium to facilitate a formation of shape-controlled nanocrystals at an elevated temperature through the hydrophobic interaction between the solvent and the hydrocarbon chains in the selected capping ligands. Thus, the mass and heat transfer that is closely associated with the progress of the nanocrystal evolution could be greatly influenced by some intrinsic properties of the solvent such as the viscosity and by some tunable conditions. In the latter, stirring rate and the ramp rate of heating are identified as two of the significant factors that could alter the balance between the deposition and diffusion of “free atoms” on a nanocrystal. Nevertheless, there are limited reports of studying these factors. Herein, we present our progress of such a study using a synthesis of Pt-Ni octahedral nanocrystals in the presence of W(CO)6 as an example. A slow stirring rate (~200 rpm) and high ramp rate for heating (8 °C/min) resulted in pod-like Pt-Ni nano-products, whereas their counterpart conditions (~400 rpm and 5 °C/min) generated uniform Pt-Ni nano-octahedra when other experimental parameters remained the same. Based on our observation, a plausible mechanism is proposed. One hand, the slow stirring rate and high ramp rate of heating can promote the atom deposition on a nanocrystal, leading to pod-like products due to an accumulation of the ad-atoms on the same planes of a seed. On the other hand, the relatively high stirring rate and slow ramp rate of heating can preserve sufficient time to allow the deposited atoms to re-distribute to those thermodynamically stable sites. In other words, the dominative diffusion, in this case, is the driving force of the nano-octahedron formation.

PM01.09.31
Cement Mortar Reinforced with Polypropylene Mesh
Charles Nikou1, Konstantin Kornev1, Jeffery R. Owens2 and Igor Luzinov1; 1Materials Science and Engineering, Clemson University, Clemson, South Carolina, United States; 2AFCEC CXAE, Air Force Civil Engineer Center, Panama City, Florida, United States.

Concrete is one of the world’s most widely used building materials for many reasons including: relatively low cost, moldability, and high compressive strength. This high compressive strength is perfect for most construction applications where the building is subjected to constant and well known static forces. However, due to concrete’s brittle nature, crack formation and ultimately failure will occur when it is exposed to dynamic or tensile loading; concrete is often subjected to such conditions in highway and military applications. Polymeric fibers, namely Polypropylene (PP), are often added to the concrete mix in order to provide toughness and impact resistance, improving the survivability of concrete under such loading conditions. In this work we consider PP mesh in lieu of fibers as impact modifier for cement based structures. In brief, we have studied the effect of the mesh addition to cement mortar on physical properties, including impact resistance. It is suggested that mesh reinforcement can offer better improvements to toughness due to its connectivity and, therefore, ability to serve as macro scale reinforcement. Samples were prepared using a cement mortar mixture of constant composition (large aggregates were excluded due to the cm-scale sample size) and reinforcement with ~ 2% by volume of varying sized PP meshes. The samples were subjected to compression, tensile splitting, and impact testing in order to quantify their mechanical properties. The effect of mesh geometry and distribution on sample properties were investigated. Additionally, the properties of mesh reinforced samples were compared to those of fiber reinforced and non-reinforced samples. In the future, hybrid geometry reinforcements will be investigated alongside with mechanical modeling of the composite systems.

PM01.09.33
Polymer Templating for Metallic Foam Fabrication with Wide-Ranging Compositional Control
Chang-Eun Kim1, Raheleh M. Rahimi1, Ioannis Mastorakos2, and David F. Haley1; 1Purdue University, West Lafayette, Indiana, United States; 2Clarkson University, Potsdam, New York, United States.

Metallic foam structures can be fabricated using a wide range of techniques; at the nanoscale de-alloying forms nm-sized ligament/pore foams in noble metals, while gas foaming at the meso-scale enables bulk material formation in engineering alloys. Capturing both length scales, mm-level porosity to sub-mm porosity, is challenging, and compositions accessible by these particular techniques are often mutually exclusive. This presentation addresses a new model of metal foam creating, using electrospun polymer fibers containing soluble metal acetate. Using a combination of oxidation and thermal reduction on electrospun fibers allows for multiple length scales of structural feature control, with meso-scale pores dominated by the fiber diameter and spacing, and
PM01.09.34
Additive Manufacture of Hierarchically Porous Materials with High Resolution Siwei Liang1, Cheng Zhu2, Christopher M. Spadaccini1, Eric B. Duoss1, Theodore Baumann1 and Yat Li2; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2University of California, Santa Cruz, California, United States.

A ink system for additive manufacturing hierarchically porous materials with high resolution (ligament size < 100 μm) has been prepared by sol-gel approach. In this ink system, a resol polymer precursor was first synthesized and then mixed with other components including pluronic block-copolymer, other precursors, solvents and catalyst. The resulting clear and powder-free ink was direct-ink written into different structures and gelled at elevated temperature. The printing parts were further calcinated or carbonized to afford 3D hierarchically porous materials. The 3D products were characterized by SEM, SAXS, BET, TEM, Instron, FTIR/Raman spectroscopy and dielectric spectroscopy. They demonstrated potential application in energy storage and catalyst field.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

IM release number: LLNL-ABS-753108

PM01.09.35
Parameterized Lattice with High Stiffness Through Engineered Functional Gradients Joshua DeOtte1,2, Nigel Morris1, Adrian Butscher1, Erin Bradner1 and Eric B. Duoss1; 1Lawrence Livermore National Lab, Livermore, California, United States; 2University of California, Davis, California, United States; 3Autodesk, San Rafael, California, United States.

Topology optimization enables automated constraint-based design of structures. If a parametric lattice unit cell is used to construct the structure, a subsequent optimization pass can be run to redistribute mass within the generated topology and improve performance. A two-phase optimization scheme was used to generate a structure with a material gradient for supporting a cantilevered load. An isotropic unit cell with an effective modulus linearly dependent on relative density was used to populate an optimized cantilever structure. The second optimization pass then adjusted the beam diameters of each unit cell to improve stiffness. The resulting lattice structure was fabricated using a custom projection stereolithography system and mechanically tested. Four structures were used: 1) solid beam cantilever, 2) uniform lattice cantilever, 3) shape-optimized uniform lattice cantilever, and 4) shape- and material-optimized cantilever. Structures were cleaned and thermally post-processed to achieve high conversion. Mechanical testing showed that the flexural stiffness increased between the solid beam and the uniform lattice with additional gains for both shape-optimized and the shape- and material-optimized cantilevers.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

LLNL-ABS-753016

PM01.09.36
Polypropylene and PETG 3D Printed Hybrid Structures Erik L. Antonio, Pu Zhu and Igor Luzinov; Clemson University, Clemson, South Carolina, United States.

With the rise of 3-D polymer based printing, especially with the potential of the mass industrial utilization of the technology, there is a need for a better understanding for fabrication of hybrid structures utilizing the materials commonly used. To this end, using fused deposition modeling (FDM) 3D printing technique we fabricated Polypropylene (PP) and Polyethylene Terephthalate Glycol-modified (PETG) hybrid samples and analyzed their properties. The properties are directly related to the printing temperature, viscosity, and percentage within the print of the two components. Our studies confirmed that the hybrid samples have lower mechanical characteristics than the samples printed from either pure material. We associate the decrease in properties with adhesive issues at PP/PETG interface. To improve these properties, PP fiber was mixed with small amount of PETG to create diffusive bonding at the hybrid samples have lower mechanical characteristics than the samples printed from either pure material. We associate the decrease in properties with adhesive issues at PP/PETG interface. To improve these properties, PP fiber was mixed with small amount of PETG to create diffusive bonding at the interface. Our approach is expected to be transferable to similar 3D printed polymer hybrid/composite systems that also face poor mechanical properties.

PM01.09.37
Additive Manufacturing of New Structures for Heat Exchange Philip DePond1, Du Nguyen1, Pratana Roy1, Victor Beck1, Omer Dogan1, Dan Tortorelli1, Eric B. Duoss1, Manyalibo Matthews1 and Joshua Stolaroff2; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2National Energy Testing Laboratory, Albany, Oregon, United States.

Recent advances in manufacturing are enabling a new range of material properties and product performance. Additive manufacturing of metals and alloys, specifically laser powder bed fusion (LPBF), allows for the production of large, robust and highly complex structures. Here we describe the development and testing of a heat exchanger for sCO2 power cycles with radically improved material efficiency and higher temperature tolerance than current technology. Triply Periodic Minimal Surfaces (TPMS) are chosen as candidate structures as previous work shows an expected order of magnitude improvement in heat transfer performance over tubes and flat plates. The project combines additive manufacturing of nickel superalloys with new, efficient hierarchical geometries, which are common in nature to achieve high interfacial area with low pressure drop, and are now achievable in synthetic with advanced manufacturing techniques. Focusing on the Schwarz-O geometry, flow characteristics and temperature fields were modeled to compare heat transfer coefficients. Thermal stress modeling was performed to couple heat transfer with solid mechanics. The process development of 5 candidate nickel super alloys is described, along with ambient and high temperature mechanical testing results. Bench scale measurements of mass transfer, pressure drop and device robustness are performed for comparison and to aid design of a viable process.

PM01.09.38
A Hydrogel-Elastomer Hybrid Fabricated via 3D Printing Xinrui Niu and Yuexing Zhan; City University of Hong Kong, Kowloon, Hong Kong.
Mechanical integrity of hydrogel-elastomer hybrids is limited by the fracture toughness of hydrogel which disables the usage of many useful but fragile common hydrogels. This work fabricated a new hydrogel-elastomer hybrid with the help of 3D printing technique. The two materials are physical engaged into each other. Peeling test demonstrated that the new hybrid had superior mechanical integrity over the conventional hydrogel-elastomer anchored by chemicals. This method enables the mechanical integrity of hydrogel-elastomer hybrid to go beyond the fracture toughness of hydrogel.

**PM01.09.39**

**3D Printing of Bicontinuous Hierarchical Porous Carbons and Metal Oxides**

Cheng Zhu¹, Siwei Liang¹, Bin Yao², Marcus A. Worsley¹, Yat Li², Eric B. Duoss¹ and Christopher M. Spadaccini¹; ¹Lawrence Livermore National Lab, Livermore, California, United States; ²University of California, Santa Cruz, California, United States.

Hierarchically porous materials are becoming promising candidates for biomedical, catalytic, and energy storage applications for their unique combination of low density, exceptional mechanical properties, large surface area, and excellent electrical conductivity. Recent research has focused in the topological design of cellular materials in order to satisfy multiple design objectives. Unfortunately, these design advances have not been met with similar advances in cellular material manufacturing as existing techniques constrain a designer to a predetermined part mesostructure, material type, and macrostructure. In an effort to address these limitations, we utilized 3D printing techniques to create designed architectures with bicontinuous hierarchically pores from 10nm to 1000 microns. 3D printing is one of emerging additive manufacturing techniques, which has been successfully commercialized for both prototyping and distributed manufacturing with industrial applications in architectures, automobile, aerospace, engineering, food, and biomedical areas. The key point is to develop a printable phase separable inks from precursor polymers. With this approach, we aim to demonstrate multi-scale (e.g., from the nano- to macro-length scales) assembly of arbitrarily complex, hierarchical 3D structures composed of carbons or metal oxides.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

IM Release number: LLNL-ABS-752998

**PM01.09.40**

**Structure and Energetic Characterization of Reactive Material Structures Formed by Kinetic Spray**

Jungsu Park and Sang-Hyun Jung; Agency for Defense Development, Daejeon, Korea (the Republic of).

Reactive Material Structures (RMSs) are a new group of materials designed to have simultaneously the features of structural materials and energetic materials [1]. Their typical applications are considered for military uses like reactive fragments, respective bullets and reactive casings. This paper describes the manufacturing method for structurally robust RMSs, and shows the structural and energetic characteristics of the acquired RMSs. To acquire robust RMSs, we attempted kinetic spraying (i.e. cold spraying) of reactive material powders that is consisted of various compositions. As a results, we obtained tough RMSs of thickness over 1cm. The prepared RMSs were microscopy (SEM), X-ray diffraction (XRD) and universal testing machine (UTM). All RMSs show a porosity of less than 5% and a compressive strength of more than 250 MPa. To characterize energy releasing features under the environment of explosive detonation, the exothermic energy of each RMS was also analyzed using detonation calorimetric Analyzer (DCA). As a results, surprisingly, we found that RMSs can release more energy than conventional explosives.

References


**PM01.09.41**

**Multifunctional Foam Synthesis—Paradigm Shift Towards Next Generation 3D Printable Composites**

Maria A. Torres Arango²-¹, Domenic T. Cipollone² and Konstantinos Sierros²; ¹National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States; ²Flexible Electronics and Sustainable Technologies (FEST) Laboratory, Mechanical & Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States.

Engineering photonic properties represents an important milestone in the synthesis of new composite materials with potential applications in photo-electronic devices. Moreover, it is pivotal for their sustainable processing and reliability, while providing a new window to explore and further understand fundamentals. Here, we will discuss our approach to novel materials synthesis, focussing on hierarchical-cellular-heterostructured-photonic composites, with control over their multifunctionality, for additive manufacturing. Particularly, we will present our most recent results on Ag-decorated TiO₂ heterostructures’ one-pot synthesis. We believe that this route is the foundation towards a series of multi-material-based 3D printable composites. Such multifunctional composites will trigger great advances in direct-write additive manufacturing, while leading to unprecedented developments in multi-functional materials and 3D processing for optoelectronics, environmental and energy related applications, and even regenerative medicine.

**SYMPOSIUM PM02**

Conductive Materials Reliability in Flexible Electronics

November 27 - November 29, 2018

**Symposium Organizers**

Aram Amassian, King Abdullah University of Science and Technology
Alon Gorodetsky, University of California, Irvine
Jesse Jur, North Carolina State University
Jennifer Lewis, Harvard University
Recent Progress on Flexible, Intrinsically Stretchable and Healable Organic Electronics

Qibing Pei; University of California, Los Angeles, Los Angeles, California, United States.

The emergence of devices that combine elasticity with electronic or optoelectronic properties offers exciting new opportunities for applications, but brings significant materials challenges. This presentation will describe our latest results in the materials efforts in developing intrinsically stretchable conductors, semiconductors, dielectric polymers, and demonstrating integrated stretchable electronic devices. Specific examples include a polymer composite comprising surface-embedded silver nanowires with high transparency, high surface conductivity, and low surface roughness. The mechanical properties of the transparent composite electrode are determined by the polymer matrix employed, and demonstrated properties include flexibility, shape memory, self-healing, and rubbery deformation. Results on the healing efficiency of the healable composite with failure induced by both mechanical and electrical loading will also be presented. Touch panels were fabricated to demonstrate the applicability of the AgNW healable composite material.

Enhancing Flexibility of Highly Conductive and Transparent Platform with Buffered Conducting Polymer Layer

Devendra Singh and Gilles Lubineau, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The design of new electronic system featuring flexibility and stretchability requires using advanced materials and microstructure. Classical inorganic materials are conductive but brittle in nature. On another side, organic materials are flexible but comparatively less conductive and are sensitive to environmental conditions. Here, we propose a novel approach to integrate the advantages of both inorganic (Indium tin oxide) as well as organic materials, here PEDOT:PSS (poly-(3,4 ethylenedioxythiophene): poly (styrene sulfonic acid)) as conducting polymer, for their conductive and flexible intrinsic properties, respectively. In this work, a PEDOT:PSS buffer layer is used between ITO layer and PET [polyethylene terephthalate] substrate such that during the deformation of the film, the stacked system retains its high conductivity with strong stability. The reason for using a PEDOT:PSS buffer layer is to substantially reduce the detrimental effects of cracks in the ITO layer in terms of an overall conductivity of the system. The highly conductive and transparent ITO films were sputter deposited on PET substrates at room temperature, and different configurations (with and without annealing and/or an intermediate layer of PEDOT:PSS) has been studied extensively. Structural, optical, mechanical and morphological studies have been carried out to understand the behavior of involved layers qualitative and quantitatively. We find that integration of an ITO thin film with PEDOT:PSS buffer layer results in robust synergetic behavior, showing a relatively low initial electrical sheet resistance that is very stable even under strong bending (value of bending radii down to 2.5 mm, repeated cycles up to 1000 cycles). This high stability can be attributed to an improvement of the electrical transfer at the delaminated interfaces due to supporting buffer layer. Results show that this highly conductive, flexible and transparent platforms can be used for advanced flexible devices.
suitable operations as defogging/deicing systems for an automobile side-view mirror and camera lens, transparent heating block systems for polymerase chain reaction (PCR) devices, and particulate matter (PM) detecting systems for PM2.5 sensors.

3:00 PM BREAK

3:30 PM OPEN DISCUSSION

3:45 PM PM02.01.07
High Dielectric Constants of Transparent and Flexible Cellulose Hybrid Films Using Multidimensional Metal Nanostructures for Flexible Touchscreen Panels Sangyoon Ji, Jiuk Jang and Jang-Ung Park; UNIST, Ulsan, Korea (the Republic of).

Various forms of wearable electronics have been developed, including wrist bands, smart glasses, and watches, which are exposed extensively to outdoor activities. The key metrics for these rapidly-emerging, wearable electronics are high touch sensitivity and good mechanical and thermal stability of the flexible touchscreen panels (TSPs). The dielectric constants (k) of their protective cover layers are very important because they can determine touch sensitivities. Thus, studies on cover layers that are flexible and transparent and that have high-k dielectric films with outstanding mechanical and thermal reliabilities are essential for the success of future wearable electronics. Herein, we report an unconventional approach for forming flexible and transparent cellulose nanofiber (CNF) films. These films are used to embed random networks of ultra-long metal nanofibers that serve as nanofillers to increase the value of k significantly (above 9.2 with the high transmittance of 90%). Also, by controlling the dimensions and aspect ratios of these metallic fillers, we studied the effects of the fillers’ nanostructures and contents on the optical and dielectric properties of the resulting films. The length of the metal nanofibers can be controlled precisely using a stretching method locally to break the highly-aligned, ultra-long nanofibers. These nanofiber-embedded, high-k films are mechanically and thermally stable, and they have a better Young’s modulus and better tensile strength with lower thermal expansion than commercial transparent plastics. Our demonstration of highly-sensitive, flexible TSPs using high-k CNF film for smartphones suggested that this film has significant potential for use in next-generation, portable electronic devices.

4:00 PM PM02.01.08
High Performance Flexible Transistors and Thin Film Heaters via Simple Solvent Treatment of Ag Nanowire Networks Imnu Jin and Jaewoong Jung; KyungHee University, Yongin-si, Korea (the Republic of).

Silver nanowires (Ag NWs) have been extensively studied as the material of the transparent conductive electrode (TCE), as a promising replacement of conventional indium tin oxide (ITO). However, a typical polyl synthesis of Ag NWs employs insulating polymers as surfactants for the growth, stability and dispersion of silver, which limits efficient electron transport between each nanowire. Although the conventional post-treatments such as thermal welding process could improve transmittance and sheet resistance of Ag NWs networks, they usually require high temperature or complicated process that may limit the choice of substrate. In this presentation, we demonstrate the simple solvent treatment to enhance the optoelectronic properties of Ag NW networks. The solvent treatment effectively washes out the surrounding insulating polymer, which results in significantly improvement of transmittance and sheet resistance of Ag NW networks. By the optimization of the solvent treatment, we successfully fabricated a high performance TCE with a sheet resistance of 12.95 Ω/sq and a transmittance of 81.25% at 550 nm. The solvent treatment was also suitable for flexible substrate, leading to 16.29 Ω/sq and a transmittance of 78.76% at 550 nm. For the practical applications, transparent thin film heaters (TFHs) made of Ag NW networks followed by the solvent treatment was also fabricated. The TFHs exhibited a good performance of 155 °C at a bias of 5 V. In addition, the flexible TFHs based on Noland Optical Adhesive 63 as a substrate afforded a high performance flexible TFHs with a quick response time (15 s). This TFH exhibits good optoelectronic properties and outstanding mechanical robustness against deformation, such as flexibility and deformability. Therefore, this substrate can be used as a flexible and deformable heater and the temperature can exceed 110 °C at a bias of 4 V. This work clearly demonstrates the efficacy of simple solvent treatment for practical use of Ag NWs and to be formed into various shapes for TCE and TFHs.

4:15 PM PM02.01.09
Highly Conducting Transparent and Stretchable PEDOT:PSS Electrodes—Investigation of the Role of Additives Emilie Dauzon1, 2, Ahmed E. Mansour1, Fabrice Goubard2 and Aram Amassian1; 1King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Laboratoire de Physicochimie des Polymères et des Interfaces, Cergy, France.

Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is a potential candidate as a transparent soft conducting electrode for electronic and bio-electronic devices. It has also recently emerged as a potentially stretchable electrode when prepared under certain conditions. Despite a significant growth of the interest in this material, there is still significant debate about the causes and mechanisms involved in significant conductivity improvements in PEDOT:PSS films when processed in presence of certain additives, such as dimethylsulfoxide (DMSO) and Zonyl-FS300. Understanding the effects of these additives is crucial to further progress in the field, as it pertains to the design of even better electrode materials with finely tuned functionalities. The addition of DMSO co-solvent significantly improved the conductivity and the carrier concentration by several orders of magnitude, as confirmed by Hall effect transport measurements. Addition of the Zonyl elastomer also improved the electrical properties, but to a slightly lesser extent. Importantly, it softens PEDOT:PSS significantly by reducing its Young’s modulus over more than an order of magnitude, making it increasingly stretchable and mechanically compliant. We show that these benefits can be combined to achieve excellent electrical, optical and mechanical properties. To understand the effect of these additives in isolation and in combination with each other, we have investigated the relationship between the transport properties of PEDOT:PSS and the morphology and microstructure of these films by performing atomic force microscopy (AFM) and grazing incidence wide-angle X-ray scattering (GIWAXS). Our analysis reveals distinctive impact of the two additives on the PEDOT and PSS components in the solid-state PEDOT:PSS films. The DMSO enhances the aggregation of PEDOT, while Zonyl introduces order into PSS domains. Both additives induce fibrillar formation in the film and the combination of the two additives only enhances the fibrillar nature and the aggregations of both PEDOT and PSS components of the film. In situ GIWAXS investigation performed during the spin-coating and annealing steps showed that the presence of the additives influenced the aggregation behaviors of the PEDOT and PSS components directly during the transition from wet to dry film, i.e., during solvent removal, and do not evolve further during subsequent annealing. These results indicate that the additives directly influence the self-assembly behaviors of PEDOT and PSS during the ink-to-solid phase transformation.

4:30 PM PM02.01.10
Modification of PEDOT:PSS with Triblock Copolymer and Sulfuric Acid for Stretchable Transparent Electrode Jinho Lee and Jeong Sook Ha; Korea University, Seoul, Korea (the Republic of).

In this study, we report on the fabrication of a highly conductive, stretchable, transparent electrode based on modified poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) with triblock copolymer (PEO30-PPO90-PEO30, Phorone® P123) and post-treatment via sulfuric acid. Sulfuric acid post treatment is well known to increase the electrical conductivity of PEDOT:PSS via crystallization of PEDOT, conductive part of PEDOT:PSS. Since the sulfuric acid treated PEDOT:PSS film is not stretchable, however, we introduce P123 as a secondary dopant and plasticizer.
to enhance the stretchability via crosslinking as well as the electrical conductivity of PEDOT:PSS. The fabricated electrode shows high transparency of 89%, high electrical conductivity of ~1,700 S/cm, and minimal change in resistance of ~4% during repetitive stretch–release cycles by 40% tensile strain. By utilizing the high transparency and low resistance change with stretching of the electrode, a stretchable transparent touch sensor array with light emitting diodes is fabricated and it exhibits mechanical stability upon stretching by 30%. This work demonstrates the facile chemical modification to develop PEDOT:PSS based stretchable electrode with high transparency and high electrical conductivity.

4:45 PM PM02.01.11
Mechanically-Durable Printed Transparent Electrodes for Ultra-Flexible Organic Photovoltaics Zhi Jiang¹,², Kenjiro Fukuda¹,³,⁴, Sangjun Park³ and Takao Someya¹,²,³; ¹Thin-Film Device Laboratory, RIKEN, Hirosawa, Wako, Saitama, Japan; ²Electrical and Electronic Engineering and Information Systems, The University of Tokyo, Tokyo, Japan; ³Center for Emergent Matter Science, RIKEN, Saitama, Japan; ⁴Japan Science and Technology Agency, Saitama, Japan.

Conformable large-area optoelectronic devices are necessary for self-powered ultra-flexible applications to realize multi-functional systems, such as sensing, imaging, and healthcare-monitoring [1, 2]. Since conventional transparent electrodes, such as ITO, are brittle, novel transparent conductors owning good mechanical robustness are indispensable to these ultra-flexible photonic devices. Printing technology will make these novel ultra-flexible transparent electrodes closer to the step of their real application [3]; however, it remains challenging to obtain feasible printed transparent electrodes with ultra-thinness, good uniformity over a large area, and high conductance simultaneously [4]. There exists a trade-off between thickness and conductance. Highly conductive Ag mesh electrodes usually have a thickness in the range of 2-20 μm, which can limit the flexibility and inhibit utilization in ultrathin photonic devices. Reducing the thickness and keeping a high conductivity simultaneously is needed for ultra-flexible photonic devices.

Here, we present ultra-flexible and mechanically durable Ag mesh transparent electrodes fabricated by a reverse offset printing technique, which simultaneously achieved high conductance, high transparency, and good mechanical properties. Reverse-offset printing technology enabled high resolution (100 nm and 5 μm in thickness and width, respectively) and high uniformity of Ag mesh over a large area. The high uniformity comes from the good quality of Ag nanoparticle ink (good dispersion, ultrathin diameter, and uniformity of Ag nanoparticles), and small roughness of both glass cliché and PDMS transfer blanket. Consequently, the printed transparent electrodes exhibited a 17 Ω/sq sheet resistance at 93.2% transmittance. Furthermore, they showed an insignificant resistance increase (10.6%) after 500 cycles of 100% stretch/release deformation. The key mechanism for the mechanical robustness is the ultrathin thickness and buckling structure. Due to the total thickness of our printed ultrathin Ag mesh transparent electrodes is less than 1.5 μm, they can be easily used in ultra-flexible photonic devices. As a demonstration, organic photovoltaics (OPVs) are fabricated using our printed Ag mesh transparent electrodes, which showed a comparable power conversion efficiency (8.3%) to those using traditional ITO electrodes (8.6%).

The insight gained from the ultra-flexible printed Ag mesh transparent electrodes and their application in ultrathin organic photovoltaics will help to apply such novel transparent electrode into other ultrathin photonic devices, and even ultra-flexible systems.

Reference:
controlling ink spreading and penetration. This is shown to be more important than the larger scale inter-tow porosity governed by the weave. The importance of the fibre surface properties in controlling ink behaviour is further demonstrated through a comparative study of the interaction of a nanoparticle silver ink with cotton and polyester textile surfaces. The more hydrophilic cotton fabric shows greater spreading and infiltration of the ink than is observed with the polyester materials. Further hydrophobic chemical treatment of the fabrics using commercial water repellent finishes reduces the fabric surface tension, leading to reduced ink spreading and smoother ink deposition on the surface with higher areal ink concentration and improved electrical conductivity. Fibre architecture is shown to influence ink penetration and spreading in the longitudinal and transverse directions of a fibre tow with tighter fibre structures reducing lower levels of spreading.

Printed electronics has attracted considerable interest as an alternative manufacturing process to realize circuits or devices on paper or plastic considering its low material consumption and fast accessibility. Using metallic nanoparticles to create conductive traces for lower cost and faster process has been extensively investigated, but often limited by the sintering process. Plasma sintering is widely employed given its lower processing temperature and lower extent of damage caused to the substrate by avoiding the high temperatures of sintering. In spite of its advantages, the process suffers from skin effect due to the top-down treatment process which can hinder sufficient curing throughout the entirety of the printed patterns imposing either long-last processing times or the use of high-power plasma with potential for damage to the substrate.

Inkjet printing, a relatively new and promising technology for fabrication; its major advantages, compared with traditional photolithography, rely on fabrication costs reduction, reduced material waste output, and simpler manufacturing steps. This technology has gained increasing interest in the fabrication of thin films for flexible and stretchable electronics using new functional nanomaterial inks. Despite the established advantages of this technology, the electromechanical reliability of the fabricated material systems is still a key point to achieve competitive devices. In particular, bendable and stretchable electronics require electromechanical reliable interconnects as they are subject to mechanical loading which jeopardize the integrity of the material itself (the electrical interconnects) or that of the interfaces.

This work is focused on the electromechanical reliability of bendable and stretchable interconnects obtained through ink-jet printing by using a Dimatix material itself (the electrical interconnects) or that of the interfaces.

Here, we demonstrate a direct-write patternable water-based poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) composite ink consisting of PEDOT:PSS, graphene oxide nanosheets and anionic polyurethane does readily not permeated into hygroscopic fabric, which resulted in an enough electrical pathway for charge carriers even though only 2.9 wt% of PEDOT:PSS existed in the composite film. The PEDOT composite film exhibited electrical conductivity of 4.6 S/cm, extremely high stretchability.
of 375% rupture strain, and high durability for repeated washing process with strong bleaching agent. Light emitting diode incorporated on the stretchable spandex with interconnects of the PEDOT composite pattern showed that LED light intensity was almost maintained even with stretching of PEDOT interconnects to 290%.

10:00 AM BREAK

10:30 AM PM02.02.06
Direct Photochemical Deposition of Metallic Patterns on Polyimides for Development of Flexible Transparent Conductive Films
Kensuke Akamatsu, Yuma Yoshikawa, Yohei Takashima and Takaaki Tsuruoka; Konan University, Kobe, Japan.

Demand for the development of novel strategies for polymer metallization has been rapidly growing in the field of various flexible electronics applications, such as the liquid crystal displays, electronic paper, and solar cells. Polyimide film has been widely used to date for such applications as a low-k substrate, due to its chemical and thermal stability, and outstanding dielectric properties. Therefore, various processes for the metallization of polyimide films have been investigated for the development of flexible circuit elements in microelectronics applications. Additionally, adhesion strength between metal films and underlying polymer substrates becomes much more important when the device dimensions are in a sub-micrometer scale. The conventional approach to the fabrication of metal patterns on polyimide substrates utilizes a subtractive-based strategy, i.e., lamination metal films on polyimide films followed by patterning through lithographic methods, but this approach requires stringent environmental control, costly equipment, and complex, multistep processes such as resist-coating, lithography, and etching.

In order to sustain the demand for generating multichip packaging systems for future flexible electronic devices, it would be exceedingly useful to develop an additive-based strategy with high-throughput capability that would allow site-selective, direct metallization of flexible low-k substrates. In this contribution, we present surface modification-based strategy for the direct fabrication of microscopic silver circuit patterns on polyimide surface.

Deposition of silver patterns has been achieved by using ion-doped precursor films, through the process of chemical hydrolysis of polyimide by alkali treatment, doping of silver ions into the modified films followed by UV irradiation using photomasks. The high sensitivity of silver ions to UV light allows for direct area-selective photochemical reactions without the use of photocatalysts, providing granular nanostructures consisting of silver nanoparticles at metal/polymer interface. This granular structures ensure high adhesion between deposited metals and underlying polymer substrates. Subsequent electroless copper deposition provides copper circuit patterns on polyimide substrate, providing effective methodology for direct fabrication of circuit patterns on flexible polyimide substrate in fully additive based strategy. Specifically, the use of photomasks with square patterns (negative photomasks) provided flexible, transparent conductive films, which can be used as flexible displays and electronic papers.

10:45 AM PM02.02.07
Flexible, Foldable, and Wearable Carbon-Based Electronic/Electrochemical Devices on Paper
Muriel Santhiago, Mariane P. Perera, Cátia C. Corrêa and Carlos C. Bufon; Brazilian Nanotechnology National Laboratory, Campinas, Brazil.

In this work we will describe the fabrication of flexible, foldable, and wearable electronic/electrochemical devices using carbon-based materials. The first fabrication route is based on a direct, simple, and dry transfer method of graphite onto paper with unprecedented electrochemical features on paper. We have selected soft pencils to transfer graphite onto paper and achieved comparatively low sheet resistances. The sluggish electron transfer observed on bare pencil drawn surfaces was enhanced by two steps. The surface was first electrochemically oxidized and reduced. The origin of such unprecedented performance was characterized by atomic force microscopy, laser scanning confocal microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, and contact angle measurements. We observed that the oxidation process causes the formation of a few microcracks on the electrode surface. Also, different chemical groups are formed and reduced due to the electrochemical treatment. Some of the weakly attached graphite particles and carbon nanodebris are detached from the electrode surface after the electrochemical treatment. Our results suggest that oxidation process leads to chemical and structural transformations on the electrode surface, and these transformations are responsible for the electrode response improvements.

The second route to fabricate carbon-based devices on paper is based on the use of sacrificial adhesive layers. It is extremely challenging to fabricate carbon-based nanostructures on paper that has the potential to meet some of the recent demands of paper-based devices, namely: (i) low sheet resistance, (ii) high folding stability, (iii) flexible electrochemical cells with high performance and (iv) tunable electric properties to fabricate motion and wearable sensors. With this method it is possible to print different compositions of binder/carbon black with no extra care related to viscosity, particle size and solvent composition. The carbon black tracks have low sheet resistance and a high-record folding stability. I will also demonstrate the fabrication of a 3D paper-based electrochemical cell made from a single carbon-black track. Moreover, the ink was tailored in order to electrochemically detect biologically relevant molecules at low potentials. Flexible circuits can be fully crumpled and operated again with no significant response loss. Finally, we have created bioinspired motion and wearable devices by locally tuning the electrical properties of the conductive tracks.

11:00 AM OPEN SLOT

11:30 AM PM02.02.09
Three-Dimensional Organic Conductive Networks Embedded in Paper for Flexible and Foldable Devices
Muriel Santhiago and Carlos Cesar Bufon; Brazilian Nanotechnology National Laboratory, Campinas, Brazil.

Flexible and foldable devices have gained much attention in the field of low-cost electronics and wearable devices. Among the flexible materials used as substrates, paper is an exciting candidate with several attractive advantages. For instance, paper is a natural polymer broadly available worldwide, lightweight, disposable, portable and foldable. Also, paper has the unique porous structure formed by cellulose fibers, which can drive solutions by capillary action. Here, we described the fabrication of three-dimensional (3D) conductive tracks through the porous structure of paper [1]. We combined paper microfluidics and gas-phase pyrrole monomers to synthesize polypyrrole-conducting channels embedded in-between the cellulose fibers chemically. By using the proposed method, foldable conductive structures can be created across the whole paper structure, allowing the electrical connection between both sides of the substrate. Our approach is a step forward towards the development of 3D-electronic devices on paper. As a proof of concept, Top-Channel-Top (TCT) and Top-Channel-Bottom (TCB) conductive interconnections, as well as all-organic paper-based touch buttons are demonstrated. By functionalizing the conducting tracks, we also created paper-based sensors to assess the local humidity changes in fully-enclosed paper microfluidic elements. The sensors exhibit excellent mechanical stability, with more than 600 bending cycles achieved. Additionally, we observed that the electrical resistance increases with relative humidity (RH) increase. Most importantly, the humidity sensor response is reversible. Our work essentially paves the way toward 3D fabrication of electrochemical devices [2], including sensors, capacitors, and energy harvesting systems. Several devices can be manufactured in parallel, and the fabrication process allows high-volume production.

Acknowledgments:
We would like to thank National Center for Research in Energy and Materials (CNPEM), Brazilian Nanotechnology National Laboratory (LNNano), CNPq and FAPESP.

References:
Cellulose-based electronic textiles has promised as an interesting approach for the development of novel technologies, given its unique properties. Printed paper-based electronics have been usually accomplished by using standard printing methods, such as screen and inkjet printing. Some materials of interest for this field, however, are insoluble, hindering its use with solution-based direct printing techniques. This is the case, for example, of poly(P-phenylene vinylene) (PPV), a material that presents outstanding electrical, photo-luminescent and electro-luminescent properties, with great potential for applications. In this work we demonstrate the use of femtosecond laser induced forward transfer for creating high-resolution patterns of the conductive polymer PPV onto bacterial cellulose (BC) substrate, advancing the use of cellulose-based materials for printed flexible electronics, by offering a new approach for solid materials patterning. Such approach successfully allowed transferring PPV with resolution on the order of 10 µm and without materials degradation, which was subsequently doped to improve the electrical conductivity and exploited in the fabrication of functional devices. Our results open new avenues in the fabrication of paper-based devices, by combining high resolution and new classes of patterning materials.

Producing flexible, wearable circuitry relies on having robust electrical connectivity between components. The electrical traces must provide low resistance and predictable properties, especially over time, where a garment will see washing cycles and repeated mechanical stresses. Screen printing is a widely-used technique for making the conductive traces. Designing optimal inks in combination with various substrates for these applications requires control over several aspects of composites: 1) maintaining percolative conductivity; 2) control of the viscoelastic properties of the polymer binder and the substrate; 3) control over the adhesive interaction between the ink and the substrate; and 4) understanding the fracture behavior of this complex system. Industrial-academic partnerships, combined with internal research, provides a full context for working on and solving these problems. This presentation will show how the mechanical properties of the substrate and inks are interrelated and how that relationship affects electrical conductivity. We will also show the evolution of materials to more reliable, conductive compositions by applying lessons learned from extensive testing. Finally, we will discuss the current issues and where future work needs to be done.

The rising clinical and basic research interest in personalized and precision medicine promises to revolutionize traditional medical practices. This presents a tremendous opportunity for developing wearable devices toward predictive analytics and treatment. In this talk, I will introduce fully-integrated flexible biosensors for multiplexed in-situ perspiration analysis, which can selectively measure a wide spectrum of sweat analytes (e.g., metabolites, electrolytes, heavy metals, drugs and other small molecules) and allow us to gain real-time insight into the sweat-secretion and gland physiology. I will also demonstrate an integrated wearable sweat extraction and sensing system which can be programmed to induce sweat on demand with various secretion profiles. To demonstrate the clinical value of our platform, human subject studies were performed in the context of the cystic fibrosis diagnosis. These wearable and flexible devices open the door to a wide range of personalized diagnostic and therapeutic applications.

Cardiovascular disease is the leading cause of death in the United States. As a result, wearable health monitoring devices have become a heavily researched area. In order to provide long term monitoring of patients with heart-related diseases, electrocardiogram (ECG) studies employing textile-based wearable technologies. Concerns exist in these wearables in terms of data quality, power consumption, human design and manufacturing design. This work presents a systems-level approach towards the design of a self-powered ECG textile garment that seeks to resolve these issues. These garments are battery-less, open architecture sensor platforms that utilize continuous energy harvesting to ensure vigilant cardiac monitoring. Key stakeholder needs such as comfort, passive user-experience, accuracy, and data streaming were discovered during the NSF I-Corps program after interviewing patients, doctors, hospitals, and doctors. Component level integration and testing strategies are presented in the use of flexible interconnects, durable connectors, printed ECG electrodes, and energy harvesting integration. Finally, the garment design is considered based on understanding the use-cases in real-time cardiac monitoring health monitoring.

With the rise of wearable technologies there has been an unprecedented demand in finding suitable power supplies. As an alternative to conventional battery supplies, on-body energy harvesting is a promising avenue due to its ability to provide the location specific energy harvesting that is possible during long term (full day to multi-day) use, a key necessity to self-powered wearable systems.

In this paper, a high-sensitivity wide-range wireless strain gauge system is presented for simple structural health monitoring. The strain gauge contains a printable strain gauge, which is operated using a wireless system, can contribute to the inspection of deterioration rates in large-area infrastructure at low cost 

Biometrics are an effective way for technology to use signature indicators of a user’s body, such as the iris, facial features, or fingerprint, to create secure access methods. Especially, the recognition of fingerprints is one of the most popular techniques for mobile security applications. Capacitive fingerprint sensors have been widely used for contemporary portable electronic devices, including smartphones, with opaque sensor structures implemented in activation buttons or behind the phone. In the design of a device, the display occupies a relatively larger area of the total device size for improved usability. Except for the display, it would be optimal to reduce or completely remove other components (e.g., bezels, buttons, and sensors), from the front side of a product. As such, there has been a strong push for the development of invisible fingerprint sensors that are embedded in the display. However, the sheet resistance of conventional transparent electrode materials, such as indium tin oxide (ITO), carbon nanotubes, graphene, metal nanowires, or fine metal mesh patterns, are too high to allow high-frequency signals to drive the capacitive fingerprint sensors against noise from mobile devices. Here, we developed a transparent and flexible, capacitive fingerprint sensor array with multiplexed detection of tactile pressure and finger skin temperature for mobile smart devices. In our approach, random networks of hybrid nanostructures using ultra-long metal nanofibers and finer metal nanowires were formed as transparent and flexible electrodes of a multifunctional sensor array. The sensor array exhibited excellent optoelectronic properties (~ 1.03 Ohm/sq with an optical transmittance of 91 % in the visible light region) and outstanding reliability against mechanical bending. This resulting fingerprint sensor array has a high resolution (318 capacitors per inch) with good transparency (89%). This sensor offers a capacitance variation (between a ridge and valley) ~ 17 times better than the variation for the same sensor pattern using ITO electrodes, instead of the transparent hybrid electrode. This sensor with the hybrid electrode also operates at a high frequency (1 MHz) with negligible degradation in its performance against various noise signals from mobile devices. Furthermore, this fingerprint sensor array can be integrated with all transparent forms of tactile pressure sensors (sensing range from 10 kPa to 1.6 MPa) and skin temperature sensors (from 30 °C to 45 °C), to enable the detection of a finger pressing on the display. This will allow for the complete removal of any activation buttons on smart devices. Additionally, the capability to recognize artificial fingerprints further improves security. These results suggest the future promise of transparent and flexible devices for next-generation, interactive electronics.

This work proposes a printable strain gauge that exhibits high sensitivity (gauge factor < 100), a wide range (0.001% to 20% strain), and high durability (< a million strain cycles). The printable strain gauge is capable of detecting microcracks and microstrains simultaneously for long-term while conventional gauges lack the characteristic. A wireless system is installed, which further simplify structural health monitoring for maintenance, inspection, triage, and infrastructure remediation via the Internet of Things (IoT).

Current strain gauges are utilized to monitor microdeformation in concrete structures and to detect the risk of structural failures. Conventional reinforced concrete has a material breakdown limit of -10%–20% strain [1]. However, it deforms by -0.2%–0.2% strain per day. Conventional gauges do not provide a sufficiently wide measurement range [2]. The optimal gauge is selected as a function of strain range.

In this paper, a high-sensitivity wide-range wireless strain gauge system is presented for simple structural health monitoring. The strain gauge contains 83wt% of graphite. It was fabricated through screen printing on a polyimide substrate with a width of 0.5–2 mm and a scalability of < 1 m. A printed track was composed of highly conductive graphite fillers and a blended binder of poly-N-vinylacetamide (PNVA) and cellulose; this resulted in an electrical resistivity of 0.3 ohm cm. The printed track acts as a resistance-type strain sensor with the same sensitivity as that of a conventional gauge (correlative factor: over 0.99). Experimental results showed that PNVA, whose molecular structure consists of a strong network of hydrogen bonds, acted to improve performance under cyclic strain. As a consequence, the printable strain gauge exhibited high durability and retained its high sensitivity and wide measurement range even after < 1,000,000 strain cycles. It achieved long-term wireless monitoring in actual structural objects for over a month. Our printable strain gauge, which is operated using a wireless system, can contribute to the inspection of deterioration rates in large-area infrastructure at low cost.


All-Climate Aqueous Fiber-Shaped Supercapacitors with Record Areal Energy Density and High Safety Bin Wang and Jianli Cheng: China Academy of Engineering Physics, Chengdu, China.

Flexible fiber-shaped supercapacitors (FSSs) are promising energy storage candidates for wearable electronics. However, most of reported FSSs are flexible at room temperature and used the toxic flammable organic electrolyte or corrosive strong acid or base which may have safety hazards especially for wearable textiles directly sticking on the human skin at harsh environmental temperatures. Here we reported a new kind of aqueous symmetric FSSs with high safety and record high areal energy density at wide operating temperature ranging from -60 (14.2 µW h cm⁻²) to 75 degree (22.9 µW h cm⁻²) based on aqueous LCE-PVA based gel electrolyte and core-shell nanocrystalline polymer fiber electrode. The fabricated aqueous FSSs demonstrate high flexibility, high areal/volumetric energy density and stable cycle life at different operating temperatures, showing the potential application in all-climate.
work demonstrates the photoresist-etching-inspired new screen-printing technique that combines flexible conductive composite ink, water-soluble applications of graphene and derived structures for flexible electronics. CMOS devices. These array structure uses crosspoints as four-terminal switch and enables high complexity for logic synthesis compared to two-terminal structure can be applied for various switch designs. Nano-crossbar arrays are emerging structures as an area efficient state-of-art alternative to conventional integration of various printed devices such as batteries, supercapacitors, biofuel cells and sensors into stretchable and mechanical durable device can be created. This novel fabrication technique brings technological advantages of the inclusion of wide selection of materials in composite inks. Hence, a one-step to substrate and guided buckling by thickness control, complex 3D structures buckled from 2D planar design can be easily fabricated in few simple steps. Sacrificial material and mechanical buckling, allowing printed circuits to be stretchable and high-strain-enduring. Furthermore, utilizing selective bonding to substrate and guided buckling by thickness control, complex 3D structures buckled from 2D planer design can be easily fabricated in few simple steps. nanostructured flakes of rGO were produced from graphene oxide (GO). GO was prepared with modified Hummers’ method by chemically exfoliation and oxidation reactions. GO was washed, filtrated, centrifuged and vacuum-dried to obtain solid GO residue. Dry GO then powdered and sifted for further steps. Thermal treatment is applied for reduction of organic groups and expansion of GO into rGO, which took place in pure nitrogen flow (1 l/min.) with high heating rate and kept at high temperature (800°C) to form C:O structure with reduced oxygen content and high defects to be used in four-terminal switch device. The changes in structure and particle properties were investigated with scanning electron microscopy (SEM) for morphology, energy dispersive spectroscopy (EDS) for composition, X-ray diffraction (XRD) for crystal structure and stack layer quantifications, Brunauer-Emmett-Teller (BET) surface area analysis for effective surface area, Raman spectra for lattice distortions and defect structures and FTIR to identify functional groups. Besides that, fabrication of these switches require careful design features to perform symmetrically and accordingly. In this study, nanostructured flakes of rGO were produced from graphene oxide (GO). GO was prepared with modified Hummers’ method by chemically exfoliation and oxidation reactions. GO was washed, filtrated, centrifuged and vacuum-dried to obtain solid GO residue. Dry GO then powdered and sifted for further steps. Thermal treatment is applied for reduction of organic groups and expansion of GO into rGO, which took place in pure nitrogen flow (1 l/min.) with high heating rate and kept at high temperature (800°C) to form C:O structure with reduced oxygen content and high defects to be used in four-terminal switch device. The changes in structure and particle properties were investigated with scanning electron microscopy (SEM) for morphology, energy dispersive spectroscopy (EDS) for composition, X-ray diffraction (XRD) for crystal structure and stack layer quantifications, Brunauer-Emmett-Teller (BET) surface area analysis for effective surface area, Raman spectra for lattice distortions and defect structures and FTIR to identify functional groups. Products are then used in inkjet suitable ink for device fabrication. rGO-inks printed on PET and PI substrates as transistor channel between metal electrodes. I-V characteristics are measured to obtain the saturation region and channel effects between terminal switch options. Results show promising applications of graphene and derived structures for flexible electronics.

SESSION PM02.04: Flexible Electronics Processing II
Session Chairs: Jesse Jur and Chengyi Xu
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 109

8:30 AM PM02.04.01
Formation of Printable Granular and Colloidal Chains through Capillary Effects and Dielectrophoresis Zbigniew Rozyniec1,2, Ming Han3, Filip Dukta1, Piotr Garstecki1, Arkadiusz Jozefczak and Erik Luijten11, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland; 2Faculty of Physics, Adam Mickiewicz University, Poznan, Poland; 3Applied Physics Graduate Program, Northwestern University, Evanston, Illinois, United States; 4Faculty of Physics, University of Warsaw, Warsaw, Poland; 5Departments of Materials Science & Engineering, Engineering Sciences & Applied Mathematics, Physics & Astronomy, Northwestern University, Evanston, Illinois, United States.

One-dimensional conductive particle assembly holds promise for a variety of practical applications, in particular for a new generation of electronic devices. However, synthesis of such chains with programmable shapes outside a liquid environment has proven difficult. Here we report a route to simply ‘pull’ flexible granular and colloidal chains out of a dispersion by combining field-directed assembly and capillary effects. These chains are automatically stabilized by liquid bridges formed between adjacent particles, without the need for continuous energy input or special particle functionalization. They can further be deposited onto any surface and form desired conductive patterns, potentially applicable to the manufacturing of simple electronic circuits. Various aspects of our route, including the role of particle size and the voltages needed, are studied in detail. Looking towards practical applications, we also present the possibility of two-dimensional writing, rapid solidification of chains and methods to scale up chain production.

8:45 AM PM02.04.02
From 2D to 3D—A Mechanistic Deterministic Approach for Stretchable Printed Electronics Lu Yin and Joseph Wang; Nanoengineering , University of California, San Diego, La Jolla, California, United States.

The world of electronics is shifting away from rigid, bulky and fragile to flexible, miniaturized and sturdy, underlining the need for stretchability in the design form factors. Screen printing, as the most widely used manufacturing technique for circuit boards, is low cost, high throughput and versatile. This work demonstrates the photosensitive-etching-inspired screen-printing technique that combines flexible conductive composite ink, water-soluble sacrificial material and mechanical buckling, allowing printed circuits to be stretchable and high-strain-enduring. Furthermore, utilizing selective bonding to substrate and guided buckling by thickness control, complex 3D structures buckled from 2D planer design can be easily fabricated in few simple steps. This novel fabrication technique brings technological advantages of the inclusion of wide selection of materials in composite inks. Hence, a one-step integration of various printed devices such as batteries, supercapacitors, biofuel cells and sensors into stretchable and mechanical durable device can be realized. Several fabrication examples including the reversible buckling of several 3D structures and the free-standing serpentine interconnected battery group is demonstrated, which exhibited minimal performance change even under 100% stretching deformation. The successful implementation of such fabrication technique offers a promising route for the wide adaption of stretchable device.

9:00 AM PM02.04.03
Direct Fabrication of Flexible and Stretchable Conductor by Electrohydrodynamic (EHD) Printing Jingyan Dong; North Carolina State University, Raleigh, North Carolina, United States.

Direct printing of flexible and stretchable conductors provides a low-cost mask-less approach for the fabrication of next generation electronics. In this work, an electrohydrodynamic (EHD) printing technology was studied for a number of functional materials (e.g. low-melting-point metal alloys, 1D silver nanowires) that are hard to be printed with traditional print methods. We successfully achieved high-resolution printing of these materials, which enables low-cost direct fabrication of metallic conductors with sub-30μm resolution. The EHD printed microscale metallic conductors represent a promising way to create conductive paths with metallic conductivity and excellent flexibility and stretchability. A stable electrical response was achieved after hundreds of bending cycles and during stretching/releasing cycles in a large range of tensile strain (0-70%) for the printed conductors with properly designed 2D
patterns. When using low-melting-point metal alloys as functional inks, due to their low melting point, the printed conductor demonstrated excellent self-healing capability, which recovered from failure simply by heating the device above the eutectic temperature of the metal ink and applying slight pressure. A few device demonstrations, including a high-density touch sensor array and AgNW heaters and electrocardiogram (ECG) electrodes, were fabricated to demonstrate the high-resolution capability of the EHD printing for the direction fabrication of flexible and stretchable devices.

9:30 AM *PM02.04.04
Accelerating Design Through Flexible Hybrid Electronics Materials Data Collaboration Scott M. Miller, NextFlex, San Jose, California, United States.

Flexible Hybrid Electronics encompasses a rapidly growing set of technology and manufacturing capabilities that enable the creation of electronics with previously impossible form factors. The field combines printed electronic materials, additive processing, traditional semiconductor integrated circuits, and substrates that can bend, flex, and stretch. NextFlex, established in 2015 as America’s Flexible Hybrid Electronics (FHE) Manufacturing Innovation Institute, is a Public Private Partnership between the US Department of Defense and the private sector. The Institute brings together more than 85 companies and universities and 17 government organizations to shape the future of FHE, accelerate its development and commercialization, catalyze the manufacturing workforce of tomorrow, and ensure American manufacturing competitiveness in FHE. The Institute does this through a variety of mechanisms – jointly developing technology roadmaps; funding projects to advance the technology; performing technical projects to develop components, devices, and manufacturing processes; operating a low-volume production and prototyping fab; convening members of the ecosystem to collaborate; and developing education and training programs for both the next generation of talent and the current workforce.

One key challenge in FHE arises from one of its strengths – the abundance of materials that are available to use in designing and fabricating FHE devices. The material properties of common FHE materials are often dependent on the fabrication processes employed and the specific operating parameters used in those processes. The consequence is that a designer cannot look to a single data source for properties needed to conduct design, modeling, and simulation, and often requires an intimate knowledge of the fabrication process. In practice, design and fabrication often become linked by an iterative loop to arrive at the final design. This slows the design cycle for FHE devices. Furthermore, test methods are not standardized for FHE devices that undergo high strain, and these devices therefore require customized qualification testing.

This talk will present work that NextFlex has undertaken to address the data and design challenge by creating means for researchers, developers, and designers to collaborate. Tools like the NextFlex Material & Process Database provide a searchable repository for property data linked to specific labs or manufacturers, and specific processes. Examples of the use of this tool will be included. NextFlex funded projects that are developing design tools, test methods, and reliability testing will also be discussed.

10:00 AM BREAK

10:30 AM *PM02.04.05
Polymer-Assisted Metal Deposition for Soft Electronics Zijian Zheng, Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Metal electrodes are indispensable element for most future soft electronic devices. One critical challenge in this field is how to fabricate highly conductive, adhesive, smooth, and soft metal conductors at low temperature under ambient conditions, and preferably in a roll-to-roll manner. Our laboratory recently develops Polymer-Assisted Metal Deposition (PAMD) to address this issue. PAMD allows ambient fabrication of flexible, foldable, stretchable, compressible, and wearable metal (especially Cu) conductors with very high conductivity. Importantly, PAMD is compatible with versatile substrates and different printing technologies at ambient conditions. This seminar will discuss the materials chemistry of PAMD and demonstrate their applications in several important soft electronic devices including circuits, solar cells, supercapacitors, and transistors.

11:00 AM PM02.04.06
Undercooled Liquid Metal Particle Inks for Flexible Conductive Traces Using Direct Writing Andrew Martin1, Christophe Frankiewicz2, Zach Martin2, Dipak Paramanik1, Ian Tevis2 and Martin Thuo1, 3, 4; 1Material Science and Engineering, Iowa State University, Ames, Iowa, United States; 2Safi-Tech LLC, Ames, Iowa, United States; 3Dep-All LLC, Ames, Iowa, United States; 4Microelectronics Research Center, Iowa State University, Ames, Iowa, United States.

Flexible electronics offer the promise of comfortable and less-intrusive bio-interfacing devices and affordable and rugged displays in packaging. Thermal sensitivity of the typical substrates used, however, makes it challenging to mount components or create conductive lines on these devices. Silver nanoinks have emerged as a lower-temperature processing alternative; although curing temperatures significantly above ambient eliminates use of a significant number of heat sensitive substrates. Advances in synthesis of core-shell undercooled metal, and associated heat-free lead-free solders, offers a new approach to ambient fabrication of conductive lines and component soldering. Herein, we demonstrate the adoption of undercooled liquid metal particles in fabrication of flexible electronic devices via direct write or screen printing. Devices ranging from MEM sensors, Wheatstone bridge, conductive traces and LED arrays are used to demonstrate versatility of this heat-free fabrication technique.

11:15 AM PM02.04.07
Hierarchical Self-Assembly in 3D Printable Carbon Nanotube (CNT) Based Links Shayandev Sinha, Yanbin Wang and Siddhartha Das; University of Maryland, College Park, Maryland, United States.

Compared to the traditional metallic materials CNT is known to have superior thermal and electronic conductivity. Printability of such CNT based inks thus can change the way we make electronic devices, composite materials etc. For any large-scale manufacturing, a chemical binder free CNT based ink will be useful but the bottleneck is the solubility of CNT in water - which is very low. Here we include graphene oxide (GO) which increases the dispersion of CNT inside the water. This ink is then printed using a syringe 3D printer with optimized pressure on a 3D printed soft surface made of an UV curable adhesive material (NEA 121) and sintered at 150 °C for 8 hours. The water evaporation during sintering causes the CNT and GO particles to assemble on the soft solid. A detailed electron microscopy study reveals a very interesting feature- hierarchical self-assembly of CNT and GO where CNTs self-assembled over nanoscale is sandwiched between layers of GO self-assembled over microscale. GO covers the whole printed line and exhibits flake-like behavior covering the internal CNT layers. Thus, the composition of CNT: GO ratio changes the whole procedure of self-assembly and reveals various highly intriguing internal structures. This also effects the electrical conductivity and the overall printability of the ink. We believe that such kind of inks will be key for fabricating embedded electronics inside the conformable composites.

11:30 AM PM02.04.08
Junction-Modulated Silver Nanowire-Elastomer Composite Films for Stretchable Transparent Conductors Jae-Chan Lee, Soyeon Lee, Philip Won,
Recent demand of reducing physical distance between devices and human have attracted considerable interests in flexible and stretchable devices for wearable electronics. Nanostructured metals, especially silver nanowires (AgNWs) have emerged as most promising transparent electrodes for stretchable and wearable devices owing to their high mechanical endurance. Many research groups have examined fracture strain of freestanding single nanowire. To develop commercially available AgNW films in stretchable and wearable electronics, it is necessary to investigate on the factors such as junctions and interaction between nanowires and elastomeric substrates on stretchability of entire AgNW films. However, there have been few researches on the factors affect to reliability of entire AgNW films in stretching conditions instead of single nanowire for transparent electrodes. Here, we investigate the effect of post treatment on tensile reliability by in situ tensile testing within scanning electron microscope (SEM).

Our results showed the potential of the use of Ag NWs in energy storage devices and the structures presented in this work is highly plausible and can be easily extended to other metal nanowire, metal oxide and conducting polymer systems.

11:45 AM PM02.04.09
Flexible Supercapacitor Electrodes with Silver Nanowire Networks
Recep Yuksel, Sahin Coskun and Husnu E. Unalan; Middle East Technical University, Ankara, Turkey.

Silver nanowires (Ag NWs) are appealing candidates for supercapacitor electrodes due to their high conductivity in addition to their allowance for all active materials to be in close contact to facilitate charge transport. All are very important to attain maximum charge accumulation provided that Ag NWs are electrochemically stable within the utilized potential window. In this work, high aspect ratio Ag NWs are used within a coaxial and/or network-like flexible nanocomposite structure in supercapacitor electrodes. Utilization of Ag NWs as conductive templates also results in rapid deposition of electrode active materials. We have fabricated supercapacitors using Ag NWs and their nanocomposites with molybdenum oxide (MoO3) (50.7 F g⁻¹) [1], nickel hydroxide (Ni(OH)₂) (1165.2 F g⁻¹) [2], polypyrrole (Ppy) (509 F g⁻¹) and some PEDOT derivatives (61.5 F g⁻¹). Highly conductive Ag NWs were utilized as the only current collectors and templates for these electrode active materials. Electrochemical properties of the fabricated Ag NW based flexible nanocomposite supercapacitor electrodes were investigated through galvanostatic charge-discharge, cyclic voltammetry, and electrochemical impedance spectroscopy. We will present a detailed analysis of utilization of Ag NWs in the fabricated supercapacitors to underline their charge transport behavior.

This talk introduces a technology platform for the development of large-area, ultrathin and lightweight electronic and photonic devices, including solar wraps and "sixth-sense" magnetoception in electronic skins. Air stable perovskite solar cells, only 3 µm thick, endure extreme mechanical deformation and have an unprecedented power output per weight of 23 W/g. Highly flexible, stretchable organic light emitting diodes are combined with photodetectors for on-skin photonics and pulse oximetry, providing electrical functionality in yet unexplored ways. Tactile sensor arrays based on active-matrix organic thin film transistors can be operated at elevated temperatures and in aqueous environments as an imperceptible sensing system that ensures the smallest possible discomfort for patients requiring medical care and monitoring. Combined with organic amplifiers and biocompatible conductive gels, we demonstrate in vivo recording of vital signals. E-skins with GMR-based magnetic field sensors equip the wearer with an unfamiliar sense that enables perceiving of and navigating in magnetic fields. These large area sensor networks build the framework for...
other attractive characteristics. The nano-patched graphene was exploited to demonstrate soft electronic skin sensors and organic field-effect transistors that have superior electrical properties. We believe that this nanopatch method would have a wide range of applications and contribute to development of soft organic devices that are robust and practical.

Mechanical deformability underpins many of the advantages of organic semiconductors in applications from flexible solar cells to wearable devices for healthcare and virtual touch. The mechanical properties of these materials are, however, diverse, and the molecular characteristics that permit charge transport can render the materials stiff and brittle. In this talk, I describe the ways in which molecular structure and solid-state packing structure govern the mechanical properties of organic semiconductors, especially of π-conjugated polymers. In particular, I describe how low modulus, good adhesion, and absolute extensibility prior to fracture enable robust performance, along with mechanical “imperceptibility” if worn on the skin. The discussion focuses on the mechanisms by which mechanical energy is either stored (i.e., elastically) or dissipated (i.e., by plastic deformation or fracture). Mechanical energy is mediated at the level of both the molecular structure (determined by synthesis) and solid-state packing structure (determined by processing techniques). Development of metrological methods are critical for the accurate determination of the mechanical properties of thin films of materials for which only small quantities are available from laboratory-scale synthesis. We often find that the interplay between the semiconducting polymer and the substrate influence the mechanical properties and the fracture behavior. Computational molecular dynamics simulations have been particularly helpful in predicting the molecular mechanisms responsible for deformation. The talk concludes with applications of organic semiconductor devices in which every component is intrinsically stretchable or highly flexible.

Recent research in organic electronics has focused on developing next-generation practical soft devices that use graphene materials, which are a single-atom-thick sheet of sp2-hybridized carbon atoms. However, currently-available graphene materials are too fragile to meet industrial requirements for mass production, but also for use of electrodes in soft organic devices. Therefore, a main challenge in this field is to increase the strength and chemical stability of such material without degrading its electronic properties. In this talk I will present our recent study about nanoscale organic layers to strengthen metal graphene sheets. We found that alkylthiol molecules can self-assemble on flaws in the surface of graphene and form nanometer-thick patches on them, in a phenomenon that resembles suturing of wounds. This process dramatically improves graphene’s mechanical durability while preserving its other attractive characteristics. The nano-patched graphene was exploited to demonstrate soft electronic skin sensors and organic field-effect transistors that have superior electrical properties. We believe that this nanopatch method would have a wide range of applications and contribute to development of graphene-electrode-based soft organic devices that are robust and practical.

Recent research in organic electronics has focused on developing next-generation practical soft devices that use graphene materials, which are a single-atom-thick sheet of sp2-hybridized carbon atoms. However, currently-available graphene materials are too fragile to meet industrial requirements for mass production, but also for use of electrodes in soft organic devices. Therefore, a main challenge in this field is to increase the strength and chemical stability of such material without degrading its electronic properties. In this talk I will present our recent study about nanoscale organic layers to strengthen metal graphene sheets. We found that alkylthiol molecules can self-assemble on flaws in the surface of graphene and form nanometer-thick patches on them, in a phenomenon that resembles suturing of wounds. This process dramatically improves graphene’s mechanical durability while preserving its other attractive characteristics. The nano-patched graphene was exploited to demonstrate soft electronic skin sensors and organic field-effect transistors that have superior electrical properties. We believe that this nanopatch method would have a wide range of applications and contribute to development of graphene-electrode-based soft organic devices that are robust and practical.

We believe that this nanopatch method would have a wide range of applications and contribute to development of graphene-electrode-based soft organic devices that are robust and practical.

Robust flexible conductors are essential for the development of wearable electronics and soft robotics. While there are various types of compliant polymers such as elastomers that are highly flexible and moderately stretchable, the number of flexible functional materials is very limited. To address this challenge, we have developed stretchable thin-film conductors suitable for wearable electronics. The newly synthesized metallic conductors are composed of silver nanoparticles (AgNP) and eutectic gallium indium (EGaIn) alloy. This talk covers design, fabrication, and characterization of stretchable thin-film metallic conductors with applications in integrated electronic devices. The rapid manufacturing method developed for these flexible electronics is based on printing silver ink on a temporary tattoo paper (with a thickness of 5 microns) followed by deposition of EGaIn to the printed circuits. With a thin layer of EGaIn, the electrical conductivity and mechanical failure strain of the printed silver traces significantly improved. A volume conductivity of 4.8 × 10^6 Sm⁻¹ was achieved while the stretchability of circuits was enhanced as much as 20 times when compared to traces with pure silver ink. Extensive electromechanical characterization on the printed traces will be presented to demonstrate the practical potential of printed AgNP-EGaIn traces. Furthermore, functioning circuits with surface mounted microelectronic chips will be presented to show the performance of AgNP-EGaIn traces as soft, stretchable, skin-like electronics.

In the past two decades, the use of metallic thin films as principal conductive material has been extended from Silicon-based microelectronics to electronic circuitry on flexible substrates. This spans from bendable sub-micron sensors to meter-long displays. For commercial applications and wearable or implantable healthcare devices, however, one key point that is yet to be thoroughly addressed is their long-term reliability. Indeed, the lifetime of flexible devices is limited by performance degradation often due to fatigue failure of metallic conductors. In our work, we introduce a new concept for healing of metal films on flexible substrates while in operation. Integrating Ni/Al multilayers as latent heat sources, we demonstrate that the self-sustained solitary heat wave generated by the intermetallic-forming reaction can be harvested to locally heal cracks. Damage repair is activated on-demand at room temperature by a low energy current pulse that is compatible with standard current-voltage operation conditions of electronic circuitry. After healing, which is completed in a single microsecond, in-situ electrical probing shows a conductivity recovery as high as 90% for crack opening up to 500 nm in different metals, such as copper and gold. Intrinsic heat source healing represents a unique concept for rapid repair of metallic thin films, which can be applied to flexible electronics or even integrated in temperature-sensitive components in Si-based microelectronics.

In this talk I will present our recent study about nanoscale organic layers to strengthen metal graphene sheets. We found that alkylthiol molecules can self-assemble on flaws in the surface of graphene and form nanometer-thick patches on them, in a phenomenon that resembles suturing of wounds. This process dramatically improves graphene’s mechanical durability while preserving its other attractive characteristics. The nano-patched graphene was exploited to demonstrate soft electronic skin sensors and organic field-effect transistors that have superior electrical properties. We believe that this nanopatch method would have a wide range of applications and contribute to development of graphene-electrode-based soft organic devices that are robust and practical.

Robust flexible conductors are essential for the development of wearable electronics and soft robotics. While there are various types of compliant polymers such as elastomers that are highly flexible and moderately stretchable, the number of flexible functional materials is very limited. To address this challenge, we have developed stretchable thin-film conductors suitable for wearable electronics. The newly synthesized metallic conductors are composed of silver nanoparticles (AgNP) and eutectic gallium indium (EGaIn) alloy. This talk covers design, fabrication, and characterization of stretchable thin-film metallic conductors with applications in integrated electronic devices. The rapid manufacturing method developed for these flexible electronics is based on printing silver ink on a temporary tattoo paper (with a thickness of 5 microns) followed by deposition of EGaIn to the printed circuits. With a thin layer of EGaIn, the electrical conductivity and mechanical failure strain of the printed silver traces significantly improved. A volume conductivity of 4.8 × 10^6 Sm⁻¹ was achieved while the stretchability of circuits was enhanced as much as 20 times when compared to traces with pure silver ink. Extensive electromechanical characterization on the printed traces will be presented to demonstrate the practical potential of printed AgNP-EGaIn traces. Furthermore, functioning circuits with surface mounted microelectronic chips will be presented to show the performance of AgNP-EGaIn traces as soft, stretchable, skin-like electronics.

In the past two decades, the use of metallic thin films as principal conductive material has been extended from Silicon-based microelectronics to electronic circuitry on flexible substrates. This spans from bendable sub-micron sensors to meter-long displays. For commercial applications and wearable or implantable healthcare devices, however, one key point that is yet to be thoroughly addressed is their long-term reliability. Indeed, the lifetime of flexible devices is limited by performance degradation often due to fatigue failure of metallic conductors. In our work, we introduce a new concept for healing of metal films on flexible substrates while in operation. Integrating Ni/Al multilayers as latent heat sources, we demonstrate that the self-sustained solitary heat wave generated by the intermetallic-forming reaction can be harvested to locally heal cracks. Damage repair is activated on-demand at room temperature by a low energy current pulse that is compatible with standard current-voltage operation conditions of electronic circuitry. After healing, which is completed in a single microsecond, in-situ electrical probing shows a conductance recovery as high as 90% for crack opening up to 500 nm in different metals, such as copper and gold. Intrinsic heat source healing represents a unique concept for rapid repair of metallic thin films, which can be applied to flexible electronics or even integrated in temperature-sensitive components in Si-based microelectronics.

In this talk I will present our recent study about nanoscale organic layers to strengthen metal graphene sheets. We found that alkylthiol molecules can self-assemble on flaws in the surface of graphene and form nanometer-thick patches on them, in a phenomenon that resembles suturing of wounds. This process dramatically improves graphene’s mechanical durability while preserving its other attractive characteristics. The nano-patched graphene was exploited to demonstrate soft electronic skin sensors and organic field-effect transistors that have superior electrical properties. We believe that this nanopatch method would have a wide range of applications and contribute to development of graphene-electrode-based soft organic devices that are robust and practical.

Robust flexible conductors are essential for the development of wearable electronics and soft robotics. While there are various types of compliant polymers such as elastomers that are highly flexible and moderately stretchable, the number of flexible functional materials is very limited. To address this challenge, we have developed stretchable thin-film conductors suitable for wearable electronics. The newly synthesized metallic conductors are composed of silver nanoparticles (AgNP) and eutectic gallium indium (EGaIn) alloy. This talk covers design, fabrication, and characterization of stretchable thin-film metallic conductors with applications in integrated electronic devices. The rapid manufacturing method developed for these flexible electronics is based on printing silver ink on a temporary tattoo paper (with a thickness of 5 microns) followed by deposition of EGaIn to the printed circuits. With a thin layer of EGaIn, the electrical conductivity and mechanical failure strain of the printed silver traces significantly improved. A volume conductivity of 4.8 × 10^6 Sm⁻¹ was achieved while the stretchability of circuits was enhanced as much as 20 times when compared to traces with pure silver ink. Extensive electromechanical characterization on the printed traces will be presented to demonstrate the practical potential of printed AgNP-EGaIn traces. Furthermore, functioning circuits with surface mounted microelectronic chips will be presented to show the performance of AgNP-EGaIn traces as soft, stretchable, skin-like electronics.

In the past two decades, the use of metallic thin films as principal conductive material has been extended from Silicon-based microelectronics to electronic circuitry on flexible substrates. This spans from bendable sub-micron sensors to meter-long displays. For commercial applications and wearable or implantable healthcare devices, however, one key point that is yet to be thoroughly addressed is their long-term reliability. Indeed, the lifetime of flexible devices is limited by performance degradation often due to fatigue failure of metallic conductors. In our work, we introduce a new concept for healing of metal films on flexible substrates while in operation. Integrating Ni/Al multilayers as latent heat sources, we demonstrate that the self-sustained solitary heat wave generated by the intermetallic-forming reaction can be harvested to locally heal cracks. Damage repair is activated on-demand at room temperature by a low energy current pulse that is compatible with standard current-voltage operation conditions of electronic circuitry. After healing, which is completed in a single microsecond, in-situ electrical probing shows a conductance recovery as high as 90% for crack opening up to 500 nm in different metals, such as copper and gold. Intrinsic heat source healing represents a unique concept for rapid repair of metallic thin films, which can be applied to flexible electronics or even integrated in temperature-sensitive components in Si-based microelectronics.
Reliability of printed devices within the field of textile electronics is a significant roadblock to their widespread market adoption. This problem is further exacerbated by the lack of test methods for evaluating the failure modes of printed devices such as interconnects under mechanical strain. A simple but effective thermo-electro-mechanical method for identifying cracks within printed conductive pathways on textiles and on planar films laminated on textiles is presented. This method utilizes resistive Joule heating to isolate conductive areas where cracks can form in-situ. It requires only a DC power source, thermal imaging device, tensile testing setup, and printed conductive samples. It has been shown that along a printed interconnect, cracks can form along print directions that endure high localized strain such as at curved junctions or at connection points for many sinusoidal based interconnect geometries.

Compared to post visual inspection utilizing optical microscopy, SEM microscopy, or atomic force microscopy which can be time-consuming and expensive, our method is simple and cost-effective as a first pass for identifying the localized area wherein a crack has formed in-situ. In this talk we will show results for printed devices on films and conductive pathways ‘embedded’ into a textile by direct-write printing.


3:45 PM PM02.05.07
Tensile and Fatigue Ductility Testing of Free Standing Cu Films and of Cu Films on Polyimide Substrates Ulrich R. Memmert and Roland Herold; Aitech Deutschland GmbH, Berlin, Germany.

Mechanical properties like the ductility of Cu structures are often discussed in the context of reliability considerations. Often experimental data for free standing films of around 50 µm thickness are used. The influence of the layer thickness or of the interactions with the substrate or the surrounding materials is often not known.

Thin Cu films were investigated as free standing films (Cu thickness 10 µm – 60 µm) and deposited on polyimide (PI) substrates (Cu thickness 2 µm – 60 µm) by tensile testing. The ductility and the yield strength were determined. Both sample types were also investigated for Cu thicknesses between 10 µm and 50 µm by a cyclic bending test. From these data the fatigue ductility was determined. For some of the samples the grain structure was investigated before and after tensile testing by secondary electron microscopy (SEM).

The measured tensile ductility varies significantly with layer thickness and is, at least for low layer thickness, also significantly affected by the presence of the PI substrate. For low layer thickness it decreases in the case of free standing films while it is significantly enhanced when in being contact to a PI substrate. The fatigue ductility decreases with decreasing layer thickness and shows no strong sensitivity to the presence of the PI substrate. SEM imaging shows the grain structure for the original layers to be rather independent of the layer thickness. After tensile testing a clear refinement of the grains is found.

4:00 PM PM02.05.08
Fatigue-Free and Self-Healing Stretchable Transparent Electrodes Chuanfei Guo¹ and Zhifeng Ren²; ¹Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China; ²University of Houston, Houston, Texas, United States.

Flexible transparent electrodes are key elements in flexible electronics and soft robotics. Stretchability is one of the most demanding mechanical modes of flexibility. A material that is optically transparent and electrically conducting is often not stretchable. However, a transparent conducting film can become stretchable if it is tailored to a network. In addition, one-dimensional materials that are intrinsically stiff can become stretchable when tailored to serpentine structures. We used a method that we call grain boundary lithography and successfully fabricated Au nanomeshes with curved ligaments, exhibiting indium tin oxide (ITO) level sheet resistance and transparency, together with exceptionally large stretchability.

We also demonstrate quantitative characterization of adhesion performance of conductive hydrogel on diverse substrates. This method will provide a simple yet truly useful and powerful tools for the fabrication of unprecedented devices in diverse fields.

References

4:15 PM PM02.05.09
Tough Bonding of Conductive Hydrogel to Diverse Substrates Akihisa Inoue¹, ², Hyunwoo Yuk¹, Baoyang Lu¹ and Xuanhe Zhao¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²JSR Corporation, Tokyo, Japan.

Conductive polymer, such as poly(3,4-ethylene dioxythiophene)(PEDOT) have been attracting great attention because of their biocompatibility, relatively softness and highly conductivity. In addition, conductive polymer hydrogel which have properties both conductivity and hydrogel, based on PEDOT or another conjugated polymer are highly attractive materials in biomedical application, soft robotics and sensors. However, there is limitation to fabricate them into such applications with reliability to use due to poor adhesion to another materials. There are a few known approaches to achieve better adhesion of PEDOT on substrate, but those methods require special EDOT monomer for adhesion improvement. Therefore, to provide useful and general method for tough bonding of conductive hydrogel to diverse substrates has remained as grand challenge in this field.

Here, we report a useful and remarkable promising tough bonding method of conductive hydrogel to diverse substrates, such as glass, PDMS, polyimide and metal. We also demonstrate quantitative characterization of adhesion performance of conductive hydrogel on diverse substrates. This method will provide a simple yet truly useful and powerful tools for the fabrication of unprecedented devices in diverse fields.
Reliability Assessment of Conductive Interfaces for Flexible Electronics

Kyunjin Kim, Gabriel Cahn, Saresh Sitaraman, Olivier Pierron and Samuel Graham; Georgia Institute of Technology, Atlanta, Georgia, United States.

Flexible electronics are next generation devices due to thin and light features that results in low manufacturing, installation and maintenance costs. These can be applied to wearable technology by allowing devices to conform to bodies while offering great utility. Additionally, silver ink applications have been developed recently as potential flexible circuits for consumer electronics, medical devices and alternative-energy solutions. In each case, reliability assessment is important at every stage of development to ensure reliable functionality for an adequate period of service. In this study, we focused on conductive materials that are (1) used in wearable flexible electronics or (2) fabricated on polymer substrates for flexible circuits. We first demonstrated the wearable conductive interfaces’ degradation under various in environmental and mechanical conditions and analyzed the data. A Garmin conductive pad, Zephyr conductive fabric, Polar T-shirt conductive pad were kept in deionized (DI) water, 3.5% NaCl solution and simulated perspiration, and conductance measurement were recorded until they completely degraded. Simulated perspiration was found to be the harshest condition for the Zephyr fabric, while the pad types were not affected by any of the solutions. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were performed on the Zephyr fabric to image the surface degradation and predict the chemical reaction in NaCl and simulated perspiration conditions as compared to DI water. In addition to the above, the degradation of conductive inks on polymer substrates and the effect of barrier coatings on their degradation were studied further. A comparative in-situ microscopy tensile test and resistance measurement of a flake and a sintered-silver electric circuit pad on polymer substrate were conducted. The development of cracks in various types of polymer substrates was compared and analyzed using a depth-profiling technique in laser scanning confocal microscopy. The effect of atomic layer deposition (ALD) encapsulation layer on the development of cracks in the silver inks’ surface was also examined.

Fatigue Damage in Ag Nanowire Networks

Chongruang Liu, William Sampson and Brian Derby; University of Manchester, Manchester, United Kingdom.

Transparent conductive thin films (TCF) are widely used in electrical devices, especially for organic light-emitting diodes (OLED), screens & displays, solar cells and touch panels. TCFs must have low sheet resistance and high light transmittance. Generally, the materials used to make TCFs should behave as low sheet resistivity and high light transparency, typically the sheet resistance, $R_s$, should be $\leq 100 \Omega$ m² with optical transmittance, $T \geq 90 \%$. The current industry standard material that is used to define these standards is indium tin oxide (ITO). For applications in flexible and stretchable electronics, such films must be resistant to damage after significant strain, a requirement that cannot be satisfied using ITO TCFs. Potential replacement materials include conductive polymers, carbon nanotubes, metallic grids, graphene, and metallic nanowires. Silver nanowire networks (AgNW) can show lower sheet resistance with higher light transmittance than ITO thin films; they also display a much greater strain to failure and greater resistance to mechanical damage. This study investigates the optoelectric properties and flexibility of AgNW networks with the objective of developing a fuller understanding of their behaviour, damage mechanisms and how these can be developed into predictive models for their properties and lifetime.

Silver nanowires have been deposited onto flexible polymer substrates by spray coating to form a continuous stochastic network. Post-spraying treatment of either a low temperature anneal or a normal pressure is used to improve wire-wire electrical contact and reduce the network sheet resistance while maintaining optical transparency. The structural integrity of the film under repeated environmental service conditions has been assessed through repeated bending tests in a high cycle fatigue environment. Film electrical properties degrade with increasing cycle number, leading to a 40% increase in sheet resistivity after 5 × 10⁶ cycles through a strain of ± 1.7%. This change in film electrical properties is correlated with observations of distributed local fracture events observed after testing by SEM studies of the fatigued networks. The fibre fracture events visible on SEM images can be quantified using an image analysis routine to count the number of fibres fractured during the bending process. These data can be used in conjunction with a model for the sheet resistance of stochastic conducting networks to predict the increase in resistance as a function of mean fibre length and hence correlated with the number of fractured fibres.

Changes in the Conductivity of FDM Printed Commercial Graphene-Infused PLA Under Short and Long-Term Electrical Stresses

Adam Krajewski; Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States.

The Graphene-Infused PLA is a material made by melt blending commonly used Polyactic acid (PLA) with a few weight percent reduced graphene oxide (r-GO) to create an electrically conductive filament for polymer additive manufacturing. Among the other possible uses, it allows printing conductive circuits inside 3D printed PLA models using dual-extrusion with no change in mechanical properties of the model and printing flexible conductive circuits on fabrics using a standard FDM printer. In the recent years there were multiple successful studies on adjusting its composition and processing methods to achieve high conductivity. However, none of the studies have investigated how this property change over time when the material is used in a working device, what can be crucial to reliability of such device.

In the course of this study, we have investigated changes in the conductivity of as-printed Graphene-Infused PLA under electrical stress conditions that could be found in the target applications. Over 60 samples of additively manufactured tracks with 1.26mm x 4mm cross-section and 90±5μm layer height were prepared on non-conductive PLA substrate using popular Ultimaker 2+ FDM printer. Samples were studied in two separate experimental setups. In the first one, 36 samples underwent long-term study in which they were placed in groups, with different constant potentials applied and monitored for multiple weeks. The goal was to investigate reliability, variability and performance changes that would happen over lifetime of low-power devices like wearable electronics. In the second experiment, samples underwent short-term 6 hour long tests in which conductivity was measured with higher frequency and electrical stress characteristics were varied over broader spectrum, in order to well investigate the process of conductivity change and help formulate a theory explaining it.
Indium Tin Oxide (ITO) is a widely used transparent conducting oxide (TCO). TCO films have been deposited by solution deposition process using ITO nanoparticle. However, it is difficult to obtain high quality ITO film at less than 200°C because of high contact resistivity. The electrical properties of nanoparticle TCO films deposited by solution process should be strongly affected by the residual surface acting agent. Therefore, in order to obtain the high-quality nanoparticles TCO films by solution process with low resistivity, the after annealing temperature should be higher than 300°C. In this study, ITO films were deposited on substrates by mist deposition process. The deposition rate was almost equal to the one deposited by conventional sputtering depositions. The mist deposition process using a nanoparticle should be one of the most possible techniques for atmospheric pressure deposition, because these films were consist by high crystalline crystal grain.

ITO nanopaticles were dispersed in H2O solution with surface acting agent by ultrasonic dispersion (20kHz). H2O solution which include the ITO nanoparticle was atomized by ultrasonic transducer (2.4MHz). The solution mist were transported to substrate by carrier gas such as Ar or N2. The sheet resistivity was around 100 Ω/sq, where the post annealing temperature was 150°C. All the films showed more than 80% transmittance in the visible region. The transmittance increased in the near-infrared region where the reflectance was decreased. Moreover, the electrical resistivity decreased in the near-infrared region. The reflectance is increased. This behavior can be explained in terms of the variation in plasma oscillation in the near–infrared region, which is well known in highly degenerate TCO films. Capacitive touch-sensing device was fabricated by Nanoparticle ITO. Lozenge-patterned ITO films were created by FPD Lithography Systems.

PM02.06.03
Highly Sensitive Crack-Based Strain Sensor on Elastomer Fabricated by Laser Transfer of Silver Nanoparticles

Wooseop Shin1, Younggeun Lee1, Suwoong Park1, Seongie Park1, Jaemook Lim1, Junyeo Yeo2 and Sukjoon Hong1; 1Optical Nanoprocessing Lab, Department of Mechanical Engineering, Hanyang University, Ansan, Korea (the Republic of); 2Novel Applied Nano Optics Lab, Department of Physics, Kyungpook National University, Daegu, Korea (the Republic of).

Precise detection and control of strain at micro-nano scale is important for upcoming technologies such as robotics, automation factory and wearable medical applications. Fabrication of sensitive strain sensor on elastomer is key to monitor physiological information like human voice. Among various elastomers, polydimethylsiloxane(PDMS) has been studied for wearable devices since PDMS has a number of advantages such as biocompatibility, cost-effectivity, transparency in visible region and conformal adhesion to versatile geometries given that the PDMS is sufficiently thin. However, preparation of a sensing unit on the PDMS has been remained as a difficult task to date because of its low surface energy and poor wettability.

In order to fabricate a sensitive strain sensor on the PDMS, we suggest a facile method to fabricate unstable metal micro lines on a PDMS by selective laser transfer of silver (Ag) nanoparticle (NP) ink. This instability enables controllable generation of cracks on the metal micro lines whose gap, or its overall electrical resistance, is easily changed by small external disturbance such as external pressure/strain or vibration. The detailed experimental methods are summarized in the following section.

Firstly, prepare sufficiently thin PDMS with ~500 μm thickness to be adhered to substrate conformally. Secondly, coat Ag NPs ink on a separate glass by spin coater at 1000 rpm for 60 seconds. Thirdly, attach the PDMS on the top of Ag NP ink coated glass and irradiate 532 nm continuous wave (CW) Nd:YAG Gaussian laser at 0.21W power and 130mm/s scanning speed through 5X objective lens. Finally, detach the PDMS film from the glass. Sintered Ag patterns are transferred to the PDMS along the scanned path as a resultant.

Given that the laser power is sufficient, it is observed that the transfer of the sintered Ag NP to the PDMS film only happens when the scanning speed exceeds certain threshold, and we presume this result is stemmed from rapid thermal expansion and contraction of PDMS film. Thermal expansion coefficient of PDMS (907X10^-6/K) is known to be much larger than that of Ag (19X10^-6/K) or glass substrate. (4X10^-6/K) Consequently, large temperature gradient induced by rapid scanning is expected to cause a shear stress between these layers to promote the transfer of Ag NP towards the PDMS film.

The performance of the resultant sensor is related to the configurations of cracks which are derived from the detaching process. Among various factors, it is known from the previously reported that the crack spacing can affect the performance of the sensor in a controllable manner. In this study, the crack density is altered by exploiting the cylinders with different diameter to attain various bending curvature radii for the detaching process. The resultant crack-based strain sensor on elastomer at its optimum crack density has proven to be compatible to highly sensitive applications such as sound wave recognition.

PM02.06.04
Highly Stretchable/Bendable Skin-Mimic Organic Transistors

Hwasung Lee; Hanbat National University, Daejeon, Korea (the Republic of).

Stretchable electronics have recently been extensively investigated for development of highly advanced human-interactive devices, by using elastomeric templates. However, mechanical properties of transistor components cannot keep up with the high stretchability of the elastomeric substrate, resulting in a problem that the device electrical performances are drastically decreased. Herein, a hard parylene-C layer was deposited on the pre-strained Ecoflex surface to fabricate a corrugated substrate which is a structure that can prevent damage against the external force. The metal electrode, the dielectric (parylene-C), the organic semiconductor (DNTT) layers were formed thereon. As the results, a maximum and average field-effect mobilities of 0.83 and 0.65 cm2/Vs, respectively, were measured, and these device performances were maintained up to 30% strain. In particular, the results remained stable even when 20% tensile was repeatedly applied 1000 times.

PM02.06.05
Investigation of Charge Transfer Ability of Nanocomposites Based on Cellulose Nanowhiskers, Silver Nanoparticles and Electrospun Nanofibers

Keileane B. Teodoro1, Flavio Shimizu2, Vanessa P. Scagioni1 and Daniel S. Correa1; 1Nanotechnology National Laboratory for Agriculture (LNNA), Embrapa Instrumentacao, Sao Carlos, Brazil; 2Sao Carlos Institute of Physics, University of Sao Paulo, Sao Carlos, Brazil; 1PPGQ - Department of Chemistry, Federal University of Sao Carlos, Sao Carlos, Brazil.

Novel sensors and biosensors have been fabricated with nanostructured materials in order to provide specific chemical functionalization and enhance their sensing properties. For instance, cellulose nanowhiskers (CNW) has been combined with functional materials as silver nanoparticles (AgNP) to application in sensor devices [1]. Combining these nanostructures with polymeric nanofibers becomes interesting once CNW can work as scaffolds for nanoparticles deposition. In this work, polyamide 6 electrospin nanofibers were combined with CNW and AgNP employing distinct strategies and were deposited onto fluorine doped tin oxide electrodes (FTO) surface. A hybrid material composed of CNW and AgNP resultant of previous study was also employed as strategy (CNW/Ag) [2]. The distinct nanocomposites were produced as follows: i) neat polyamide 6 fibers - (PA6), ii) PA6 fibers containing CNW in the bulk - (PA6/CNW)bulk, iii) PA6 fibers containing CNW/AgNP in the bulk - (PA6/CNW/AgNP)bulk, iv) PA6 fibers coated with CNW/Ag - (PA6/CNW/AgNP)sheet, v) fiber coated with AgNP (PA6/CNW/AgNP)sheet. Samples (i – iii) were produced by electrospinning from PA6 solution (10% w/v) and a mixture of PA6 solution and CNW or CNW/Ag (1 %w/v), using formic acid as solvent. Experimental parameters used for electrospinning were: feed rate of 0.02 ml h⁻¹, electrical field of 20 kV, working distance of 5 cm, interval deposition of 7 minutes. Otherwise, samples (iv – v) were resultant of 2 hours-immersion of
Air-Liquid Interfacial Polymerization of Lacey Polypyrrole Thin Films by Luciano Santino1 and Julio M. D'Arcy1, 2; 1Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States; 2Institute of Materials Science and Engineering, Washington University in St. Louis, St. Louis, Missouri, United States.

Conducting polymers are commonly thought of as rigid materials with high glass transition temperatures, making them less attractive for flexible electronics. We report on developments in the vapor-liquid interfacial synthesis of a large area lacey (macroporous) polypyrrole films with submicron thickness. These lacy films are translucent, conductive, and continuous. Their porosity keeps them flexible under extreme conditions like immersion in liquid nitrogen, bypassing the limitations imposed by the high glass transition temperature of polypyrrole. The polypyrrole laces float on water due to the surface tension created by the wetting of their segregated pores, allowing for easy deposition onto substrates from solution. The freestanding films can be manually twisted into micron-diameter strings of highly porous and conductive polypyrrole, which exhibit exemplary tensile strength. A detailed mechanistic investigation shows the initial nucleation and polymerization of pyrrole vapor on aqueous oxidant forms an interconnected polymer skeleton. As the reaction progresses, the skeleton grows laterally, confined by Langmuir-Blodgett forces at the air-liquid interface. Lacey polypyrrole is shown to have impressive electrochemical energy storage abilities without the use of any conductive substrate backing.

Printed Biocompatible and Bioinspired Electrodes for Flexible Light-Emitting Chemical Cells by Martin Held1, 2, Daniel Ehjejij1, Johannes Zimmermann1, 2, Stefan Schlische1, 2, Tobias Rödlimier1, 2 and Gerardo Hernandez-Sosa1, 2; 1Light Technology Institute, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Innovation Lab, Heidelberg, Germany; 3Heidelberg University, Heidelberg, Germany.

Electrodes in light-emitting chemical cells (LEC) do not supply the necessary drive current, but need to provide sufficient transparency for the emission. Designing the entire device to be fully printed, biodegradable and compatible with the human body presents an additional challenge. While PEDOT:PSS electrodes are transparent and considered biocompatible, their relatively high sheet resistance produces high turn-on voltages in fully biodegradable printed LECs. To overcome this limit, inkjet printed gold grids are imprinted into the substrate below the PEDOT:PSS electrodes in various symmetric, deterministic and nature-inspired patterns. Inkjet printing supports full freedom of pattern design and scalability to industrial processes. Their contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed. Different stretchable substrates with increasing ultimate strain from thermoplastic cellulose acetate to parylene to biodegradable elastomers are utilized to test the benefits and contribution to the conductivity and reduction in transmittance is estimated with a simple model and experimentally confirmed.
The inks used are characterized by their electrical conductivity. The electrical performance of these inks varies significantly with substrate properties. For example, when supported by TPU, with a modulus of 100 MPa, the trace resistance was measured to triple. This disparity only increases with recovery after strain-induced damage. PI supported inks showed decreasing recovery, from approximately 100% after 1% strain, to 50% after 15% strain. By PI and PET, which have elastic moduli of 2.5 GPa and 3.5 GPa, respectively, at 5% strain the measured resistance approximately doubles from a mean strain or strain rate. Given these findings, there is a strong link between electrical performance of 5025 and its supporting substrate. Designers must be aware of these relationships when selecting supporting materials for specific applications.

**PM02.06.10**

Influence of Semiconductor Deposition Pattern in the Fabrication of Organic Field-Effect Transistors by Inkjet Printing Technique

Cristina Stefanello, João Henrique Rocha Matos, José Alberto Giacometti and Roberto M. Faria; São Carlos Institute of Physics, University of São Paulo, São Carlos, Brazil.

In the last years, the organic electronics has attracted great efforts at fundamental and technological researches. The organic electronics enables large-area fabrication, the use of flexible substrates, solution processing at low temperatures, and deposition by printing techniques. Moreover, several technological devices, such as, flexible displays, disposable sensors, RFID tags and wearable electronics can be produced using organic materials. To make possible these applications, is needed the production of field-effect transistor, an essential circuit component, which is used to amplify and switch digital and analog signals. Due to its importance, there is great interest at fabrication of field-effect transistors (OFETs). Among the developed printing technologies, inkjet is one of the most appropriate for microelectronics. It is a noncontact technique which uses low amount of material to print defined patterns, avoiding waste; furthermore it enables to change the printed pattern with easiness. Here, we present OFETs fabricated at the bottom gate-top contact architecture with the semiconductor deposited by inkjet printing technique. The semiconductor used was the 6,13-bis(trisopropylsilylethyl)pentacene (TIPS-pentacene), a promising material as p-type semiconductor, due to its high mobility, air stability and solution processability. In this work, the transistor performance was evaluated changing the distance between drops and printing patterns. The semiconductor was deposited on the organic dielectric layer. Different printing patterns of parallel lines were deposited with respect to direction of electronic conduction. Transistors presented higher performance for the pattern with same dispensing direction, achieving mobilities on the order of 10^2 cm^2/V.s and on/off ratio of 10^4. Similar features were obtained for the distance between drops of 250 µm. The better OFETs performance is associated with the printed film morphology, due to homogeneous semiconductor layer and oriented crystallization on the direction electronic conduction.

**PM02.06.11**

Strain Effects on Electrical Performance of Polymer Supported Dupont 5025 Conductive Ag Ink

Gabriel Cahn, Samuel Graham and Olivier Pierron; Georgia Institute of Technology, Atlanta, Georgia, United States.

Improvements in materials science and precision printing technologies have given rise to flexible hybrid electronics, allowing for the creation of components that are lightweight, and able to conform to non-planar and amorphous surfaces. Unlike conventional rigid printed circuit boards, the application space of flexible electronics includes high strain use cases. Polymer supported conductive inks have become principle building blocks of flexible electronic assemblies, and ongoing academic research endeavors to optimize electrical performance of such inks against induced strain. This work investigates DuPont’s 5025 ink, comprised of 80% by volume silver flakes in a polymer matrix. The ink is separately screen printed onto Kapton Polyimide (PI), Thermoplastic Polyurethane (TPU), and Polyethylene Terephthalate (PET), and subjected to strains in tension while measuring resistance of a circuit trace pattern. As strain increases, resistance rises at a rate dependent upon the stiffness of the supporting substrate. For example when supported by PI and PET, which have elastic moduli of 2.5 GPa and 3.5 GPa, respectively, at 5% strain the measured resistance approximately doubles from a preloaded condition. When supported by TPU, with a modulus of 100 MPa, the trace resistance was measured to triple. This disparity only increases with strain. In-situ optical microscopy revealed channel cracking of the ink as the primary cause of the increase in resistance, over that of length and cross-sectional area changes in the conductor due to the Poisson Effect. Of particular note is that cracking did not occur within the Ag flakes themselves, but rather at the flake/matrix interface. Post-mortem SEM imaging confirmed these findings. Furthermore, these channel cracks were observed to nucleate and grow more rapidly in inks supported by the softer TPU substrate. After loading, specimens were unloaded to assess the potential of electrical performance recovery after strain-induced damage. PI supported inks showed decreasing recovery, from approximately 100% after 1% strain, to 50% after 15% strain. PET samples decreased in a similar manner from 100%, but stabilized at approximately 65% recovery beyond 10% strain. TPU, having proved the most susceptible to strain damage, was shown to only recover 80% of its original performance after 1% strain, decreasing rapidly to a 25% recovery rate beyond 10% strain. Strain cycling conducted on PET supported inks indicates that strain amplitude has the greatest impact on electrical performance, above that of mean strain or strain rate. Given these findings, there is a strong link between electrical performance of 5025 and its supporting substrate. Designers must be aware of these relationships when selecting supporting materials for specific applications.

**PM02.06.12**

Preparation of Cu Nanoparticle Colloid from a Cu Ion Solution by Using Protein Surfactant

Masatoshi Sekiizuchi, Kei Oikawa, Mizuki Nakahara, Yuusuke Inaba, Taiyo Maeda, Akinori Matsui and Hiroki Ishizaki; Saitama Institute of Technology, Fukaya, Japan.

Recently, metal nanoparticles colloid had many problems such as the aggregation of nanoparticles, oxidation resistance and non-uniformity of nanoparticles. In order to dissolve many problems mentioned above, we support that oxidation and aggregation will be improved by using casein contained in milk as a polymeric surfactant. In this investigation Cu nanoparticle colloid will be grown from the aqueous solution containing Cu ion and casein. Also, high purity water by liquid phase reduction method was used. As a preparation method, copper sulfate, citric acid, and urea were dissolved in ultrapure water, and an aqueous copper ion solution was made strong alkali with an aqueous sodium hydroxide solution. Next, the copper ion aqueous solution, the surfactant solution and the reducing agent were stirred to prepare a copper nanoparticle precursor solution. The copper nanoparticle precursor solution was kept at 80 ° C. for 20 minutes to prepare an aqueous copper nanoparticle colloid solution. For the actual results, the concentration of the nanoparticle colloid will be controlled by the surfactant concentration. Since the wavelength of the absorption spectrum shifts to the shorter wavelength side, the size of the nanoparticle colloid is considered to be smaller.

**PM02.06.13**

Preparation of Cu Nanoparticle Colloid from a Cu Ion Solution by Using Protein Surfactant

Masatoshi Sekiizuchi, Kei Oikawa, Mizuki Nakahara, Yuusuke Inaba, Taiyo Maeda, Akinori Matsui and Hiroki Ishizaki; Saitama Institute of Technology, Fukaya, Japan.

Recently, metal nanoparticles colloid had many problems such as the aggregation of nanoparticles, oxidation resistance and non-uniformity of nanoparticles. In order to dissolve many problems mentioned above, we support that oxidation and aggregation will be improved by using casein contained in milk as a polymeric surfactant. In this investigation Cu nanoparticle colloid will be grown from the aqueous solution containing Cu ion and casein. Also, high purity water by liquid phase reduction method was used. As a preparation method, copper sulfate, citric acid, and urea were dissolved in ultrapure water, and an aqueous copper ion solution was made strong alkali with an aqueous sodium hydroxide solution. Next, the copper ion aqueous solution, the surfactant solution and the reducing agent were stirred to prepare a copper nanoparticle precursor solution. The copper nanoparticle precursor solution was kept at 80 ° C. for 20 minutes to prepare an aqueous copper nanoparticle colloid solution. For the actual results, the concentration of the nanoparticle colloid will be controlled by the surfactant concentration. Since the wavelength of the absorption spectrum shifts to the shorter wavelength side, the size of the nanoparticle colloid is considered to be smaller.

**PM02.06.14**

Improved Stability and Adhesion of Printed Graphene and Silver–Copper Composites for Circuits on the Foldable Substrates

Hui Jae Choi, Gyeong Seok Hwang, Ohyoung Kim, Dong Hyun Lee and Byung Doo Chin; Dankook University, Yongin, Korea (the Republic of).

Soft conductive materials, such as graphene and silver-based composites, are ideal for the electronic components of circuits and electrodes on the flexible, foldable, and even stretchable devices. Recently, stability against significantly smaller curvature and larger mechanical stress for repeated operation became a key factor to obtain a successful manufacturing of the commercial application of foldable electronic devices. Here, we have demonstrated the printed circuits on the foldable substrate with graphene ink and silver-copper nanocomposites. Few layer graphene powder nano-platelet, Angstrom materials graphene N002-PDR, was dispersed in solvents with appropriate binders to formulate a screen-printable paste. The paste was also modified for an electro-hydrodynamic jet printing toward a fabrication of fine line patterns on the foldable paper substrates and flexible polynime films. In order to modify the surface toward smoothness at foldable operation, poly(4-vinylphenol) coating on the commercial paper substrate was employed. In case of graphene/silver composites printed, circuit showed superior performance as well as folding stability; decrease of relative conductance for -90° and -180° folding (toward inside direction) was only 5% and 12%. Moreover, the conductance was maintained about 80% of initial value after 1000 cycle of continuous folding. For higher conductance circuit, silver-copper composite inks were printed and compared with graphene-based composites. In order to further improve the stability against continuous folding and unfolding deformaition, paper and plastic substrates were treated with primer containing the Joule-heater and touch screen panel.
flexible additive, poly(ethylene glycol) diacrylate (PEGDA). The folding stability of circuit conductance, employed as auxiliary electrode of green organic light emitting diode, was significantly improved by the enhancement of adhesion between PEGDA primer layer, foldable paper, and printed circuits.

**PM02.06.15**

*Fabrication of Ultra-Light Porous Boron Nitride/Polyimide (BN/PI) Composite Films with High Thermal Diffusivity and Low Dielectric Properties*

Yang Kwansoo1,2, Dong Gyun Kim2, No Kyun Park1, Jong Chan Won1,2 and Yun Ho Kim1,2; 1Korean Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2University of Science and Technology, Daejeon, Korea (the Republic of).

As modern electronic devices become functionalized, miniaturized, more integrated, and exhibit higher performances, one of the most important issues is to efficiently remove heat generated by high-power integrated circuits. In addition to the high thermal conductivity, the low values of dielectric properties such as the dielectric constant (\(\varepsilon\)) and dielectric loss (\(\tan \delta\)), are another important factors for future electronic devices using a high-frequency band, particularly for the 5G communications using frequencies above 2.8 GHz.

Here, we report a simple fabrication of ultra-light porous boron-nitride-(BN)/polyimide-(PI) composite films with high thermal diffusivities and low dielectric constants by combining high-internal-phase Pickering emulsification (HIPPE) and subsequent hot-pressing. BN nanoparticles in composite foams were well dispersed and three-dimensionally connected following the surface of the PI skeleton used as the polymer matrix. The BN contents in the BN/PI composite foams were adjusted in the range of 20–80 wt%. The porosities of the composite films were controlled according to the hot-pressing conditions such as the temperature. The internal porous morphologies of the BN/PI composite foams and films were characterized by scanning electron microscopy. The 400°C-hot-pressed BN/PI composite films had higher thermal diffusivities than those of BN/PI composite films prepared by the conventional solution blending method, despite the presence of internal air pores reducing the thermal conductivity. In addition, the internal pores provided lower dielectric constants of the BN/PI composite films.

The porous BN/PI composite films exhibited high thermal diffusivities of 0.059–1.033 mm²/s and low dielectric constants of 2.08–3.48 at 1 GHz for BN contents of 20–80 wt%. In particular, our porous BN/PI composite films had extremely low dielectric loss values, close to zero (< 0.002) at high frequencies regardless of the BN content and pressing conditions, which is essential for the 5G communication technology. Therefore, our porous BN/PI composite films with high thermal diffusivities and weak dielectric properties are promising for applications as packaging materials for integrated and miniaturized microelectronic devices.

**SYMPOSIUM PM03**

TUTORIAL: Flexible Hybrid Electronics
November 25 - November 25, 2018

* Invited Paper

**TUTORIAL**
Flexible Hybrid Electronics
Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 206

Flexible Hybrid Electronics promises to deliver high performance and reliable systems in novel forms and functions. It is achieved by utilizing high performance silicon based semiconductor devices assembled on flexible (flex) substrates using optimized materials and additive processes. Integration of electronic devices on flexible substrates is starting to enable dramatically new approaches to traditional applications including: information displays, lighting, sensors, solar energy conversion and diagnostic medicine. The course will look at the fundamental aspects of three approaches: coating and printing (Mastropietro), chip-on-flex and micron scale thin-film devices on flex (Poliks) and sub-micron scale self-assembled/imprinted device based coatings on flex (Watkins).

1:30 PM
**Coating and Printing** Michael A. Mastropietro; ACI Materials

Selecting the right print method for additively manufactured circuits require a fundamental understanding of performance metrics of printed conductors and functional materials. The selection of the appropriate printing method is also key. This section will review the fundamentals of direct write methods: inkjet, aerosol-jet, extrusion, micro-dispensing; printing methods requiring a master: screen printing, flexo, gravure, gravure offset; and coating methods: slot-die and Meyer rod, as well as the technical challenges of drying and curing functional inks.

3:00 PM BREAK

3:30 PM
**Chip-on-Flex and Micron Scale Thin-Film Devices on Flex** Mark D. Poliks; Binghamton University, The State University of New York
In the second section emerging methods for integration of thin semiconductor devices, sensors and transducers, including creation of thin die, thin die handling, die attach, interconnection and encapsulation on flexible substrates will be presented. Die function can also be integrated into micron scale thin-film electronic device fabrication directly on flexible non-silicon-wafer surfaces. Engineered polymer films such as PET, PI, PEN, as well as thin flexible metal foils and glass are all viable substrates for this technology. Key substrate properties include: dimensional and thermal stability, low moisture uptake, ultra-low gas and moisture transmission rates and nano-scale surface roughness. This part of the talk will examine how some of the basic semiconductor manufacturing processes can be adapted for use with flexible substrate materials and suggest a means for roll-to-roll manufacturing of flexible hybrid electronics. Advancements in manufacturing processes such as roll-to-roll handling, slot-die coating, vacuum deposition, photolithography and wet processing will be described.

4:15 PM
Sub-Micron Scale Self-Assembled/Imprinted Device Based Coatings on Flex James J. Watkins; University of Massachusetts-Amherst

The third part of this course, will discuss emerging technologies in printed and flexible electronics that can enable next generation performance. Nano-scale fabrication techniques, including the self-assembly of hybrid (inorganic/organic) materials and imprinted patterning using polymers, hybrid polymer/inorganic resists and crystalline nanoparticle ink systems, can resolve challenges associated with large area production of sub-micron device features leading to very high integration densities as well as cost-effective production of functional device components. Applications include printing of 2-D and 3-D crystalline inorganic structures for light and energy management, printed micron scale transistors and printed microfluidic sensors. In addition, printing of functional structures to modify the performance and behavior of adjacent components.

SYMPOSIUM PM03
Hierarchical, Hybrid and Roll-to-Roll Manufacturing for Device Applications November 26 - November 29, 2018

Symposium Organizers
Nikos Kehagias, Catalan Institute of Nanoscience and Nanotechnology
Shelby Nelson, Mosaic Microsystems
Mark D. Poliks, Binghamton University
James Watkins, University of Massachusetts

Symposium Support
Binghamton University, Center for Advanced Microelectronics Manufacturing, New York Node -- NextFlex Manufacturing USA
University of Massachusetts, Institute for Hierarchical Manufacturing, Massachusetts Node -- NextFlex Manufacturing USA

* Invited Paper

SESSION PM03.01: Transistors and Devices
Session Chairs: Nikos Kehagias and Shelby Nelson
Monday Morning, November 26, 2018
Hynes, Level 1, Room 108

8:15 AM PM03.01.01
Homojunction Transistor with Superior Electrical Characteristics Hinting the Feasibility of Solution for Roll-to-Roll Process Junhee Lee1, Jinwon Lee1, Jintaek Park1, Sung-Eun Lee1, Keon-Hee Lim1 and Yoon Sang Kim1; 1Seoul National University, Seoul, Korea (the Republic of); 2University of Illinois at Urbana Champaign, Urbana, Illinois, United States.

Growing attention has been given to solution deposition techniques, considered as one of the promising deposition procedures for roll-to-roll process due to its properties of a continuous and large-scale deposition processing. However, further research is needed to apply a solution process into roll-to-roll process because of its several drawbacks such as inferior electrical characteristics of solution-grown electronics such as thin film transistors compared to vacuum-processed ones. To date, various efforts have been made on eliminating causes of lowering electrical performance such as impurities and a small number of orbital overlap. While the outcomes exhibit a moderate increase in electrical characteristics, their performance still does not reach that of vacuum-processed thin film transistors. In order to address this issue, thin film transistors with double-stacked layers hold great promise among other approaches because of their superior electrical performance. Recent studies have proposed heterojunction transistors showing an average high field effect mobility of 30 cm²V⁻¹s⁻¹, an analogous performance with devices made by vacuum process. However, further development of double-stacked transistors is hindered by limitations particularly with regards to their turn-on voltage of ~40 V which is unsuitable for the switching devices. Herein, we overcome this restraint by proposing a renovated structure called homojunction thin film transistors consisting of a channel layer and a channel electron modulation layer. Not only do we achieve the highest field effect mobility of approximately 50 cm²V⁻¹s⁻¹, but a turn-on voltage of the device can also be effectively controlled from -80 V to 0 V through modifying each layer. Moreover, this exceptional electrical performance of homojunction transistors are maintained more than 50 days under ambient conditions, and other device traits such as uniformity and reliability are validated. Through five analyses, including x-ray diffraction, atomic force microscopy, x-ray reflectivity, x-ray photoelectron spectroscopy and transmission electron microscopy, the solution-grown thin films in our structure have few electron trap sites and thus afford fast electron transportation, showing unprecedented field effect mobility and excellent hysteresis characteristics. These outstanding results are attributed to the high film quality of oxide films with a thickness less than 6 nm. On the contrary, thick oxide films of more than 6 nm forms a relatively poor film quality because an oxidation process at ambient conditions is
disturbed. Lastly, we have also demonstrated the n-type metal oxide semiconductor inverter making up of the homojunction transistors. Our solution-based electronics with superior electrical performance suggest the possibility of a low-cost and manageable solution process being applicable for future deposition techniques including roll-to-roll process.

8:30 AM *PM03.01.02
Free-Standing and Transparent Printed Organic Field Effect Transistors and Integrated Circuits with Sub-10 V Operation Elena Stucchi1,2, Giorgio Dell’Erba1 and Mario Caironi1,1, Istituto Italiano di Tecnologia, Milano, Italy; 2Politecnico di Milano, Milano, Italy.

Organic electronics enables the fabrication of flexible and lightweight electronic circuits, creating a clear path toward the realization of portable and wearable devices. In the last decades, organic field effect transistors (OFETs) have been extensively studied, aiming at the development of low cost, large area, flexible electronic systems, fabricated by means of industrially scalable techniques onto cheap plastic substrates.

In this work, we show the successful fabrication of organic transistors and circuits onto different substrates, namely 125 µm-thick polyethylene naphthalate (PEN) and 3 µm-thick parylene films. In the latter case, devices have been encapsulated with a parylene film of the same thickness, thus allowing for the realization of free-standing, conformal devices with improved stability in air.

We fabricated OFETs in a top-gate/bottom-contact (TG/BC) configuration with inkjet printed PEDOT:PSS source and drain electrodes. Inkjet printing has been used also for patterning poly(N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl)-alt-5,5'-(2,2'-bithiophene)) (PNDI2OD-T2) and poly[2,5-bis(7-decylnonaaddexy)pyrrolo[3,4-c]pyrrole-1,4,2(H,5 H)-dioneÊ–(E)-1,2-di(2,2'-bithiophen-5-yl)ethene] (29-DPP-TVT), which have been employed as p- and n-type semiconductors.

One of the factors hindering the diffusion of these devices onto the market is related with their high operating voltages, affecting their power consumption and stability. We addressed this issue by focusing on the development of a thin dielectric layer for low voltage, transparent, flexible OFETs. We used parylene C as gate dielectric material, both alone and combined with other low-k dielectrics into multi-layered structures, limiting in all cases the thickness of the dielectric layer to 100 nm.

The employed dielectric allows transistor operation in the sub-10 V regime, with very low leakage current density despite the reduced thickness of the dielectric layer. An array of optimized OFETs has been fabricated and the devices show high yield, uniform performances, high transparency and stable output characteristics up to at least 1000 bending cycles.

We have successfully demonstrated the integration of p- and n-type devices onto the same substrate, and we have been able to fabricate well-balanced CMOS inverter logic gates. These devices have been further integrated into more complex circuits, such as ring oscillators and D-Flip-Flops, and their correct operation has been demonstrated with voltages as low as 2 V.

The results presented in this work, exploiting scalable deposition processes, offer a viable and cost-effective path for the fabrication of all-polymer, transparent, flexible electronic devices operating at low voltages, which can easily be integrated into consumer products.

8:45 AM *PM03.01.03
High-Speed, High-Resolution Printing of Inorganic Devices Vivek Subramanian and William J. Scheideler; University of California, Berkeley, California, United States.

In recent years, there has been increased interest in printed inorganic devices. This has been driven by the high performance that has been demonstrated in these systems, with field-effect mobility >10 cm²/V-s having been achieved in several solution-processed FETs based on inorganic semiconductor materials. Some of these materials are additionally attractive due to their optical transparency. Printing is a key issue in these systems. Due to the material constraints of these systems, inks formulated from these materials are often limited in their rheological tenability. Here, we review our work developing materials and processes for printing of inorganic devices, and present the resulting device data showing the achievement of high-performance devices using a range of high-speed and high-resolution printing techniques. We have realized transparent conductors and fully transparent FETs using these techniques. We have also developed material system and inks that enable fabrication of such devices at low-temperature, enabling the use of a wide range of substrates.

We report on our development of printed thin film transistors, conductors, and sensors based on these materials.

9:15 AM *PM03.01.04
Zone-Cast Printed Crystalline Organic Thin-Film Transistors and Circuits with High Mobility Paul Heremans1,2, Robby Jameck1,2, Dimitrios Karagiannis1,3, Thomas Nowack1,2, Hany Ali1,2, Florian De Roose1,2, Jan Genoe1,2, and Cedric Rolin1, imec, Leuven, Belgium; 2ESAT, KU Leuven, Leuven, Belgium; 3KU Leuven, Leuven, Belgium.

We develop a meniscus-guided printing technique for organic transistors with high mobilities. In our zone-casting technique, a solvent meniscus with dissolved organic semiconductor is formed, that coats a crystalline thin-film of semiconductor in a continuous way. We acquire in-depth understanding of the process by modelling the film formation for different solvents, solute concentrations, temperatures and printing speed, and correlating the results with experimental findings for two different small molecules C8-BTBT and TIPS-pentacene. Next, printed crystalline films of C8-BTBT with charge carrier mobility exceeding 5 cm²/Vs are used to fabricate TFTs, both in top contact geometry and in bottom contact geometry. We show a reproducible and accurate process for patterning the semiconductor by photolithography and etch down to channel lengths of 3 micron. The patterning process does not impact the transistor performance. Using the bottom-contact geometry, robust 19-stage ring oscillators with 5-micron transistors are shown that comprise 80 TFTs, having an operating frequency of 630 Hz at an operating voltage of 10 V.

9:45 AM BREAK

10:15 AM *PM03.01.05
Horizontal Alignment of Carbon Nanotubes Using Roll to Roll Processing Ken R. Carter; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

One-dimensional objects which have aspect ratios greater than 5 such as carbon nanotubes (CNTs), microtubes nanowires, microfibers, fibers, nanorods, microrods, whiskers, and the like, are generally bundled or entangled into aggregates or agglomerates when disposed on a surface. It is difficult to separate these objects and to orient them because their high aspect ratios permit them to overlap with one another when they are stored. This overlapping is generally random and often results in entanglements which produce the aggregates and agglomerates. The entanglements make it difficult to separate the one-dimensional objects from one another and to orient them in any particular direction.

Oriented one-dimensional objects can find utility in a variety of applications in electronics, conductive plastics, catalysts and the like. It is therefore desirable to find a method of orienting one-dimensional objects. We report a method where CNTs can be directed to horizontally align when coated on a patterned substrate. A dispersion of one-dimensional objects in a liquid mixture is deposited on a substrate that has channels create by NIL or Roll-to-Roll NIL techniques. The CNTs orient in a direction that is perpendicular to the walls of the channel. By changing the shape of the channel, different orientations of the one-dimensional object can be obtained. The orientation of the one-dimensional objects can therefore be controlled by controlling the shape of the channels. Using this method, large areas of horizontally aligned CNTs can be fabricated with ease and high throughput.
During the drying process, the magnitude is determined by the surface free energy (SFE) of the substrate and surface tension (ST) of the ink. This interaction mainly affects the contact angle (CA) of a single drop and thus the smallest possible printed feature size. For these reasons, substrates need to be chosen carefully. Therefore, the interaction between the ink and the substrate has a strong influence on the wetting behavior, pinning effect and film formation. A particular ink is usually developed for a particular set of surface properties and generally has to be reformulated when changing the substrate.

Light emitting diodes (OLED) or organic field-effect transistors (OFET) are to be deposited on non-porous and non-ink-absorbing substrates. Therefore, we introduce a controlled nanoscale roughness onto the substrate surface to define wetting and pinning properties without changing the ink. The deposition of solution processable functional materials with printing techniques offers the possibility to prepare low-cost electrical devices like organic light emitting diodes (OLED) or organic field-effect transistors (OFET). These devices are to be deposited on non-porous and non-ink-absorbing substrates. Therefore, the interaction between the ink and the substrate has a strong influence on the wetting behavior, pinning effect and film formation during the drying process which magnitude is determined by the surface free energy (SFE) of the substrate and surface tension (ST) of the ink. In addition, this interaction mainly affects the contact angle (CA) of a single drop and thus the smallest possible printed feature size. For these reasons, a particular ink is usually developed for a particular set of surface properties and generally has to be reformulated when changing the substrate.

Increasing Organic Semiconductor Crystal Width with the Dimensions of Inorganic Polymer Micropillar

Jeongchan Lee and Steve Park; Korea Advanced Institute of Science and Technology, Daegon, Korea (the Republic of).

Solution coating process using organic semiconductors (OSCs) are a promising technique for large-area, low-cost and flexible transistor application. Therefore, a variety of solution coating processes have been developed over the past few decades such as spin coating, slot-die coating, ink jet printing and solution shearing. The key requirement of organic electronics is the formation of high quality organic semiconductor thin-film over a large area in a facile manner. However, the crystal orientation, crystallinity and crystal size of OSCs, which affects the performance of transistors, are difficult to control because of uncontrollable nucleation and chaotic fluid flow. Therefore, the system is needed that controls the nucleation process during the solution coating.

Herein, we demonstrate that organic crystal size can be manipulated simply by changing the shape and dimensions of the microstructures on the blade during solution shearing. We tuned the shape of the meniscus by tuning the micropillar shape and size, by which nucleation rate was controlled. The mobility of the thin-films increased with increasing crystal size to as high as 3.56 cm²/Vs. Such a new way to manipulate the crystal size adds another useful parameter that can be utilized to tune the property of organic thin-films and is potentially applicable to other materials systems. We also demonstrate for the first time the use of an inorganic polymer (AHPCS) as the microstructured blade for solution shearing. Currently, microstructured silicon is used, which is expensive and difficult to fabricate, and is very brittle. On the other hand, AHPCS can easily be microstructured via molding and is mechanically durable. Furthermore, unlike elastomers such as PDMS, AHPCS is highly resistant to various organic solvents. The use of AHPCS for microstructured blade is therefore highly advantageous for industrial applications where low cost and durability are of great importance.
Another important aspect is the master fabrication and its upscaling to large-area imprint tools. Here we introduce a Step & Repeat UV-NIL technique.

For optical polymer components such as free-form micro-lenses or light outcoupling / reflecting structures the tenability of the refractive microfluidics are a sufficiently high surface energy to allow for a fast and long distance filling of analytes, the ability to be bio-functionalized and low wicking) energy surfaces and it should have low enough viscosity to allow for large-area coating. Special requirements for the channel forming resin in this scenario. It should be tunable in terms of elasticity and surface tension to account for easy demolding and for low (water-repellant) as well as high (water-reflecting) effect coatings.

In this study we report the set-up of a custom made R2R-UV-NIL pilot machine which is able to convert 10 inch wide polymer web with velocities up to 50 m/min. For imprint as well as polymer working stamp material UV-curing resins based on urethane acrylates and thiol-ene chemistry were designed to meet the requirements of R2R-UV-NIL processes being strong adhesion to polymer substrates, fast curing speed and high imprint fidelity. The mechanical properties, surface chemistry and refractive index of these UV imprint resins can be tuned over wide ranges by choice and ratio of urethane acrylate oligomers and acrylate or thiol monomers – and surface active dopants. We have achieved Young’s moduli between 5 MPa and 5 GPa, refractive indices nD25 between 1.4 and 1.7 and surface energies between 15 mN/m and 60 mN/m. Furthermore, new strategies have been developed to achieve excellent abrasion resistance and utmost weathering stability of the nanoimprinted biomimetic polymer surfaces in harsh outdoor applications.

Roll-to-Roll UV imprint lithography (R2R-UV-NIL) gains increasing industrial interest for large area nano- and micro-structuring of flexible substrates because it combines nanometer resolution with many square meter per minute productivity. Besides the classical application fields of nanoimprint lithography like micro-electronics and micro-optics currently biomimetic micro- and nano-structured surfaces get increasing attention for e.g. viscous drag reduction (shark skin effect), water and dirt repellence (lotus effect) and anti-reflection (moth-eye effect) coatings.

In this study we report the set-up of a custom made R2R-UV-NIL pilot machine which is able to convert 10 inch wide polymer web with velocities up to 50 m/min. For imprint as well as polymer working stamp material UV-curing resins based on urethane acrylates and thiol-ene chemistry were designed to meet the requirements of R2R-UV-NIL processes being strong adhesion to polymer substrates, fast curing speed and high imprint fidelity.

The mechanical properties, surface chemistry and refractive index of these UV imprint resins can be tuned over wide ranges by choice and ratio of urethane acrylate oligomers and acrylate or thiol monomers – and surface active dopants. We have achieved Young’s moduli between 5 MPa and 5 GPa, refractive indices nD25 between 1.4 and 1.7 and surface energies between 15 mN/m and 60 mN/m.

Furthermore, new strategies have been developed to achieve excellent abrasion resistance and utmost weathering stability of the nanoimprinted biomimetic polymer surfaces in harsh outdoor applications.

Roll-to-Roll UV Nanoimprint Lithography for Large Area Manufacturing of Bionic Surfaces

Dieter Nees, Johannes Goetz, Stephan Ruttillof, Ursula Palfinger and Barbara Stadlober; Joanneum Research, Graz, Austria.

Roll-to-roll UV nanoimprint lithography (R2R-UV-NIL) gains increasing industrial interest for large area nano- and micro-structuring of flexible substrates because it combines nanometer resolution with many square meter per minute productivity. Besides the classical application fields of nanoimprint lithography like micro-electronics and micro-optics currently biomimetic micro- and nano-structured surfaces get increasing attention for e.g. viscous drag reduction (shark skin effect), water and dirt repellence (lotus effect) and anti-reflection (moth-eye effect) coatings.

In this study we report the set-up of a custom made R2R-UV-NIL pilot machine which is able to convert 10 inch wide polymer web with velocities up to 50 m/min. For imprint as well as polymer working stamp material UV-curing resins based on urethane acrylates and thiol-ene chemistry were designed to meet the requirements of R2R-UV-NIL processes being strong adhesion to polymer substrates, fast curing speed and high imprint fidelity.

The mechanical properties, surface chemistry and refractive index of these UV imprint resins can be tuned over wide ranges by choice and ratio of urethane acrylate oligomers and acrylate or thiol monomers – and surface active dopants. We have achieved Young’s moduli between 5 MPa and 5 GPa, refractive indices nD25 between 1.4 and 1.7 and surface energies between 15 mN/m and 60 mN/m.

Furthermore, new strategies have been developed to achieve excellent abrasion resistance and utmost weathering stability of the nanoimprinted biomimetic polymer surfaces in harsh outdoor applications.
structures. Due to the improved light outcoupling the chemiluminescence signal was increased by about 20% as tested in a portable read-out device of a commercial chip testing platform. Another example is the R2R fabrication of freeform microrelief with small height that enable a homogenous distribution of light from discrete LED sources in ultra-thin direct lit luminaire.


Acknowledgement:
Parts of this work have been performed within the H2020 EU-funded project “R2RBiofluidics”, Grant Agreement number 646260 and the RSA project Green Photonics (FFG Austria)

3:00 PM BREAK

3:30 PM PM03.02.04

Replication and Surface Properties of Structures with a Novel 3D Topography Namrata Salunke1, Douglas McBain2 and Alamgir Karim3, 4, 5; 1The University of Akron, Akron, Ohio, United States; 2Chemical and Biomolecular Engineering, University of Houston, Houston, Texas, United States; 3Laird Technologies, Cleveland, Ohio, United States.

Surface texture is known to play an important role in altering and potentially improving surface properties of the material for different applications related to hydrophobicity, cleanability, heat transfer, lubrication, adhesion and friction. Traditionally, it is believed that the alterations in properties arise from increased roughness and waviness, but understanding in more specific terms is lacking. In the past decade, the importance of pattern shape has been gaining recognition. Several studies have focused on how patterns of various shapes (cubes, channels, cylinders) with similar surface roughness values show dissimilar properties. Recently, there has been an increased effort in developing technologies to fabricate patterns with increased geometrical complexities. In this talk, we discuss such a complex and a less conventional pyramidal pattern shape. A study using various processing techniques to obtain this less conventional pattern in the millimeter and micron range is reported. We will discuss traditional milling techniques and its limitations and proceed towards new innovative additive manufacturing and lithographic techniques.

3:45 PM PM03.02.05


Wrinkling is a ubiquitous surface phenomenon that occurs at a wide range of length scales from kilometers to nanometers. Particularly, micro/nano-scale wrinkles have found applications in stretchable electronics, tunable optics and coatings with controlled wettability and adhesions [1,2]. Although various techniques including thermal treatment [3], swelling [4], mechanical stretching [5], and UV curing [6], have been developed for wrinkle fabrication, little attention has been paid for continuous manufacturing over large scale. Bearing this in mind, here, we investigate wrinkling on a roller, both experimentally and theoretically, with the aim of developing a scalable roll-to-roll (R2R) manufacturing process. This technique takes advantage of the various geometrical shapes and curvatures defined by the 3D printed rollers to induce well-defined strain fields to manipulate the final wrinkle patterns on compliant polymer substrates. First, we study wrinkle formation on a thick polydimethylsiloxane (PDMS) film wrapped around a roller, followed by oxygen plasma. The wrinkle features show a strong dependence on the geometrical parameters of the roller, thickness of the film, and other processing parameters. We then explored to achieve continuous wrinkling under ambient conditions by applying a UV-curable polymer onto PDMS as the skin layer, followed by UV curing along with rotation of the roller. Based on this principle, we demonstrate one-dimensional (1D) gratings, two-dimensional (2D) herringbone and labyrinth patterns over large areas using different roller shapes, and the wrinkle wavelengths span from hundreds of nanometers to tens of microns. The use of rollers to control the generation of wrinkles paves the way for R2R manufacturing of surface wrinkles for a wide range of applications.


4:00 PM PM03.02.06

Transition to Superwetting for a Nanostructured Surface Nikolai K. Mandberg1, Agnieszka Telecka1, Tao Li2, Emil Ludvigsen3, Sokol Ndomi4, Rosa Di Mundo5, Fabio Falumbo5, Jackie Fiutowski5, Serguei Chirita6 and Rafael Taboryski6; 1DTU Nanotech, Kongens Lyngby, Denmark; 2Dept. of Electronic and Electrical Engineering, University College London, London, United Kingdom; 3Dept. of Chemistry, Politecnico di Bari, Bari, Italy; 4NANOTEC, National Research Council, Bari, Italy; 5Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark.

According to traditional Wenzel theory, superhydrophilicity emerge when introducing roughness on an intrinsically hydrophobic surface. However, recent studies have shown a deviation from this behavior [1]. Understanding the failure mechanism will aid the design of surfaces that exhibit superhydrophilic behavior. In particular, moderately hydrophilic materials, such as polymers and other low energy materials, need a careful design, as they are particularly prone to failure.

In this study, we employed block copolymer nanolithography [2] with a subsequent injection molding replication in poly(methyl methacrylate). Compared to the flat reference, the roughness increased the water contact angle (from 67.6° to 99.4°); a contradiction to the traditional Wenzel theory. For moderately hydrophilic substrates, a nanoscopy pillar-built surface has a Laplace pressure barrier that prevents droplet spreading. Increasing intrinsic hydrophilicity could lower the barrier to allow superwetting. Consequently, we characterized the transition by applying a low-pressure Argon plasma to increase the surface free energy in a continuous fashion. Using apparent contact angle to probe the transition, we found a threshold of 55°.

Furthermore, we demonstrate how macro- and microscopic wetting phenomena are interconnected. As an example of the barrier implications, we study the condensation of water on both sides of the threshold. While flat surfaces and untreated, structured surfaces both show indelible dropwise condensation, the plasma treated, structured surface gives rise to filmwise condensation. Using a transparent polymer and designing structures to be below the diffraction
limit for visible light, the threshold defines the emergence of anti-fogging properties relevant to a plethora of optical applications such as endoscopy [3].

References:
[1] D. Kim et al., Wetting theory for small droplets on textured solid surfaces, Scientific Reports (2016) 6, 37813

4:15 PM PM03.02.07

Rapid, high throughput patterning in three dimensions with nanoscale resolution has long remained an elusive target for materials scientists. Optical interference lithography has been an attractive technique to cheaply and rapidly pattern three dimensional features in polymer photoresists despite both resolution and feature size being limited by diffraction. In the past few years, Stimulated Emission Depletion Microscopy (STED) inspired lithography schemes have shown the ability to direct-write features well below the diffraction limit using visible light. However, the high light thresholds required for effective photoinhibition renders them unsuitable to be used for interference lithography and limits their use to point by point writing. Recently, we have shown that combining the reversibly saturable photoisomerization of spirothiopyran with thiol-Michael addition chemistry can be used to formulate a super-resolution writing system with desired low light thresholds for photo inhibition, thus enabling them to be used for parallel patterning using interference lithography. Adapting the spirothiopyran writing chemistry for self-assembled monolayers on glass substrates allows us to fabricate switchable photosensitive surfaces that can be activated and deactivated for patterning with maleimide functionalized molecules using UV (365 nm) and green (532 nm) light respectively. By exploring the kinetics of photoisomerization of bound spirothiopyran and subsequently tuning their chemical environment, we experimentally demonstrate large area nanopatterning with sub-diffraction resolution and molecular thickness using a 2-color interference lithography setup. The lateral feature size of the written patterns is shown to be tunable by controlling the relative intensity of the initiation and inhibition wavelengths. The resultant nanopatterns formed are characterized using super-resolution microscopy. Secondary conjugation on regions patterned with bifunctional maleimide linker molecules can be used to tailor the nanostructured surfaces to desired chemical functionalities. These experiments demonstrate the versatility of spirothiopyran based writing systems for rapid high-throughput nanopatterning. Efforts are currently underway in our laboratories to apply spirothiopyran mediated 2-color interference lithography for 3D nanopatterning in bulk polymeric gels.

4:30 PM PM03.02.08
High Resistive State Retention in Room-Temperature Solution-processed Biocompatible Memory Devices for Health Monitoring Applications Aishita Mishra, Henam Sylvia Devi, Soumen Saha, Abhishek Dixit and Madhusudan Singh; Indian Institute of Technology Delhi, New Delhi, India.

Wearable and bio-implantable health monitoring applications require flexible memory devices that can be used to locally store body vitals prior to transmission or to support local data processing in distributed smart systems. In recent years, non-volatile resistive random access memories composed of oxide-based insulators such as hafnium oxide and niobium pentaoxide have attracted a great deal of interest. Unfortunately, hafnium and niobium are not low-cost materials and may also present health challenges. In this work, we have explored the alternative of using titanium dioxide as the insulating oxide using a low-cost solution-phase deposition process. Aqueous sol deposited titanium dioxide thin films were deposited on standard RCA-cleaned commercial thermal silicon dioxide (500 nm) wafer (500 um). Patterned bottom contacts Cr/Au (~200/300Å) using shadow masks were deposited on the substrate using successive DC sputtering, and thermal evaporation, respectively at 5 x 10-6 Torr. A sol was prepared using titanium (IV) butoxide as precursor hydrolyzed under water and ethanol to form a colloidal solution (sol) at 50°C under constant stirring. Powder X-Ray Diffraction (PXRD) scans of calcined (from sol at 750°C) nanoparticles show a mixture of anatase and rutile phases, confirming the composition of the material. The sol was slowly cooled to room temperature before being spin coated at low rotational speeds on the substrate in multiple steps involving several spin coating and drying steps to form a uniform film. Top contacts (Ag) of thickness (~500Å) were deposited on the sol-deposited thin films using thermal evaporation. The resulting devices were coated with a thick layer of polydimethylsiloxane (PDMS) using a 10:1 ratio of base elastomer and curing agent respectively. After drying the PDMS, resistance measurements were carried out using Keithley 6514 electrometer. A high resistance state was detected prior to electroforming in the air at ~27 GΩ, which remains nearly unchanged (~24 GΩ) when dipped in a pH 7 buffer solution (equivalent to human blood’s pH reference value ~7.4). Unencapsulated devices were further characterized in air using a Keithley 4200-SCS semiconductor parameter analyzer in dual sweep mode to observe repeatable hysteresis behavior with a large difference between trace and retrace R-V characteristics (~50:3% over a pristine device), which compares favorably with recent data in the literature on high-performance sputtered TiO2 memristors. Unchanged retention ratio using biocompatible device materials and encapsulation suggests that these devices can be used for biomedical implantable sensor electronics.

SESSION PM03.03: Integration
Session Chairs: Shelby Nelson and Mark D. Poliks
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 108

8:00 AM PM03.03.01
Flexible Nanogap Diodes for GHz Radio Frequency Energy Harvesting Applications Kalaivanan Loganathan, Emre Yengel, Hendrik Faber, Zainab Felemban, Emre Yaral, Thomas D. Anthopoulos; Material Science & Engineering (MSE), King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

The emergence of the Internet of Things (IoT) device ecosystem is expected to impact many aspects of our daily lives including health via accurate sensing & monitoring of our environment, transportation, logistics, and entertainment, to name but a few. Despite the tremendous potential, however, numerous technological and economic barriers still exist. One such technology roadblock with significant economic implications is how to reliably power the myriad of these IoT devices without increasing the environmental impact (e.g. battery disposal/recycling). Among the various green options is harnessing the omnipresent radio frequency (RF) energy using Wireless Energy Harvesting (WEH) systems. The most crucial components of a WEH system is the rectifier circuits and the RF antenna as they determine the frequency of operation, operating distance, and ultimately the power conversion efficiency of the system. In order to satisfy these requirements, the rectifier circuit should be inexpensive to manufacture and able to operate at frequency ranges compatible
with the widely available RF networks (>1 GHz). This is the reason why recently considerable effort focused on the development of diode technologies that can satisfy both the performance and cost requirements. Here, we report the development of sub-20 nm co-planar asymmetric nanogap electrode Schottky diodes manufactured on arbitrary substrate materials using adhesion lithography (a-Lith) as an alternative nano-patterning technique. As the semiconductor we employ different metal oxides as they combine solution-processability with excellent electron mobility while as the electron Ohmic contact we employ Ti as its native oxide (TiO₂), which forms spontaneously upon semiconductor deposition, is thin (~2 nm) and semiconducting and as such does not compromise electron injection. For Schottky contacts, we find that both indium tin oxide (ITO) or Au yield large electron injection barriers and serve as good blocking materials. Using this rather simple nano-gap device architecture in combination with the attractive properties of metal oxides, we demonstrate diodes with operating characteristics significantly higher than 1 GHz. The manufacturing of the diodes can be further simplified through the use of an innovative photonic processing scheme that allows sub-10 second conversion of the metal oxide precursor to a highly polycrystalline semiconducting layer even on temperature sensitive substrates materials such as plastic, without compromising the diode’s performance. Our work paves the way to a radically new diode technology that has the potential to significantly impact the IoT device ecosystem.

8:15 AM *PM03.03.02
Site-Specific Growth and In Situ Integration of Different Nanowire Materials on a Single Chip for Electronic Nose Applications Guillem Domènech-Calí, Lukas Harachowina, Antonio Pardo, Michael S. Seifner, Isabel Gràcia, Carles Cané, Sven Barth and Albert Romano-Rodriguez; *1University of Barcelona, Barcelona, Spain; *2In2UB, Barcelona, Spain; *3TUW, Wien, Austria; *4CNM, Bellaterra, Spain.

Many of our daily habits contribute to disperse toxic and harmful gases to the atmosphere, both in indoor and outdoor environments. For this reason, there is an increasing concern about the presence of these gases in the ambient and the need to fabricate systems to monitor them. There are many types of gas sensors for this application and among them, solid state gas sensors are an excellent choice. These sensors offer low manufacturing cost and low power consumption thanks to MEMS technology. Even though gas sensors based on semiconducting nanowires offer remarkable performances in terms of sensitivity and response time, they usually lack in selectivity, showing cross-sensitivities with environment conditions (e.g. humidity or temperature) and being only able to distinguish among oxidizing or reducing gases. A way to solve this issue is using pattern recognition from arrays of sensors with different materials or operating at different temperatures, giving rise to an electronic nose (e-nose) configuration. Based on a modification of the chemical vapor deposition method, a new procedure to site-selective synthesize nanowires on top of micromembranes has been developed. This method allows to grow the material with nanowire morphology and different compositions on one single chip surface and can be easily tailored offering an adjustable fabrication process for the direct integration of different nanowire-based resistive multifunctional devices. The use of chemical vapor deposition techniques is compatible as a CMOS post-processing and, therefore, the impact of preparing gas sensors on any kind of chips for multifunctional devices is unimaginable. In this work, we demonstrated for the first time the site-specific growth and in-situ integration of different materials in form of nanowires for sensing applications on a single chip in a well-defined geometry, with little interference on the growth parameters caused by the prior deposition of other nanostructured material. This proof-of-concept is exemplified by the deposition of SnO₂, WO₃ and Ge nanowires on the membranes of one single chip and their gas sensing responses towards different concentrations of CO, NO₂ and humidity diluted in synthetic air are presented. The measured responses allowed to discriminate between all three analytes using the well-known Principal Component Analysis (PCA) representation, as it allows gas separation and identification and, thus demonstrate that the system is suitable for environmental monitoring.

8:30 AM *PM03.03.03
Scalable Manufacturing for Flexible Hybrid Electronics Benjamin Leever; Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States.

Flexible Hybrid Electronics (FHE), which combine additive manufacturing processes with silicon chips, will enable applications such as wearable, assistive soft robotics, conformal and embedded sensors for condition-based maintenance, and wear-and-forget medical monitoring devices. The Department of Defense along with industrial and academic partners established NextFlex in 2015 to move these concepts from the lab to the manufacturing floor in the United States by developing or maturing key manufacturing processes in the areas of device integration & packaging and printing. This presentation will describe our roadmaps, which detail the capabilities identified by the FHE community over the next five years to enable the variety of envisioned applications. In addition, the presentation will highlight the FHE design and manufacturing flow through examples such as an FHE Arduino as well as specialized manufacturing tools developed through NextFlex projects such as modular systems that combine surface pre-treatment, inkjet printing, and encapsulation. Finally, the talk will address future prospects for applying roll-to-roll processes to FHE manufacturing.

9:00 AM *PM03.03.04
Hydration Sensor Patch for Human Performance Monitoring Azar Alizadeh; GE Global Research, Niskayuna, New York, United States.

GE Global Research, Niskayuna NY 12309

Maintaining proper hydration is paramount for maximizing performance and minimizing health risks for laborers, warfighters, and athletes. Currently, there are no commercially high resolution solutions for accurate, non-invasive and continuous assessment of hydration in a wearable device format. Laboratory gold standards for hydration assessment are based on total body water and plasma osmolality under controlled conditions of stable and equilibrated body fluids. In practice, body mass losses are used as an indirect measure of fluid content, but continuous assessment of an individual’s body mass fluctuations in the field during a mission is unrealistic. Similarly, blood (or urine) osmolality measurements are invasive and require sophisticated equipment and training for analysis. In this talk, we will present our approach towards developing a fully wearable system composed of bio-impedance and sweat sensors for dynamic and non-invasive assessment of hydration. The presentation will also include recent results from field testing of these devices at the U.S. Air Force Academy in Colorado Springs.

This work is sponsored by NextFlex, NBMC and AFRL and is a collaborative effort between GE Global Research, AFRL, UES, Dublin City University, University of Connecticut, University of Massachusetts, American Semiconductors Inc., and University of Arizona.

9:30 AM *PM03.03.05
Printed Image Sensors Based on Organic Phototransistors Ana C. Arias; University of California, Berkeley, Berkeley, California, United States.

Image sensors are ubiquitous and used in a wide variety of applications ranging from consumer products to healthcare and industrial applications. The signal-to-noise ratio (SNR) of an image increases with larger pixels, which is costly to scale using silicon and wafer-based microfabrication. Solution-processed phototransistors can substantially advance the performance of image sensors. Phototransistors exhibit large photoconductive gain and a sublinear responsivity to irradiance, which enables a logarithmic sensing of irradiance that is akin to the human eye and has a wider dynamic range than photodiode-based image sensors. A solution-processed phototransistor composed of a heterostructure between a high-mobility organic semiconductor and an organic
bulk heterojunction is presented here. The device efficiently integrates photogenerated charge during the period of a video frame then quickly discharges it, which significantly increases the signal-to-noise ratio compared with sampling photocurrent during readout. Phototransistor-based image sensors processed without photolithography on plastic substrates integrate charge with external quantum efficiencies above 100% at 100 frames per second. In addition, the sublinear responsivity to irradiance of these devices enables a wide dynamic range of 103 dB at 30 frames per second, which is competitive with state-of-the-art image sensors. The fundamental operation of image sensors using intra-pixel charge integration will be introduced and the figures of merit for these systems reviewed.

10:00 AM BREAK

10:30 AM PM03.03.06 Roll-to-Roll Fabrication of Conductive Copper Patterns on Flexible Substrates Using Maskless Lithography and Electroless Plating \textsuperscript{U} Okoroanyanwu, N. Mehta, S. Brandso, M. Lepine, J. Morse and James Watkins; Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

We report scalable roll-to-roll manufacturing processes for fabricating conductive copper patterns on flexible polyimide and PET substrates using a combination of maskless lithography and two approaches for patterning the seed layer, followed by electroless plating. A roll-to-roll processing platform comprising in-line surface cleaning, corona treatment, coating (gravure), and direct write lithography modules was used to pattern positive tone photoresist-coated polyimide and PET substrates. In the first approach, silver nanoparticle ink was deposited within the resist patterns and then sintered by photonic curing, to obtain silver seed layer for subsequent electroless copper plating steps. In the second approach, reactive Cu(II)-bearing ink and reducing ink were simultaneously deposited into the resist patterns and air-dried at room temperature to obtain a verifiable reactive catalyst for subsequent electroless copper plating. Immersion of the silver seed layer and the catalyst bearing substrates into electroless copper plating baths resulted in deposition of conductive copper patterns over the lithographically defined silver seed layer and reactive copper catalyst patterns, respectively. Lastly, the photoresist pattern was lifted off the substrate in acetone, resulting in well-defined copper patterns. The obtained copper patterns were characterized with optical and scanning electron microscopy, X-ray diffraction spectroscopy, and energy dispersive X-ray spectroscopy. The resistivity, solderability and adhesion strength of the copper patterns obtained with the two approaches were determined and compared, and will be presented, as will the performance of the copper patterns on an actual flexible hybrid electronic device.

10:45 AM *PM03.03.07 Novel Substrates for Applications of Roll-to-Roll Printed and Hybrid functionalities Jukka Hast, Markus Tuomiskoski, Jussi Hiltunen, Marja Välimäki, Olli-Heikki Huttunen, Johanna Hiitola-Keinänen, Marko Juvansuu and Tiina Pöldör; VTT Technical Research Centre of Finland ltd, Oulu, Finland.

In this presentation, we discuss opportunities of novel substrate materials for roll-to-roll (R2R) printed and hybrid electronics and diagnostics applications as well as future production aspects. Traditionally standard substrates have been PET, PEN, PC, PMMA etc or stretchable polyurethane films. However, application requirements, especially wearable electronics and diagnostics, and sustainability issues are setting new demands for the future. Firstly, we present R2R thermal imprinting method to fabricate integrated polydimethylsiloxane (PDMS)-paper micro-fluidics for molecular diagnostics, which demonstrated in on-chip amplification of viral ribonucleic acid (RNA) with loop-mediated isothermal amplification (LAMP). Secondly, we discuss about new bio-based and recycled materials that include introduction of novel interactive cellulose fibre acoustic RGB-LED panel that is manufactured using R2R printing, chip assembly and foam forming technique. Moreover, to improve the sustainability, performance and consumer acceptance of printed and hybrid electronics we will introduce these functionalities on recycled, bio-based and biodegradable substrates and compare their functionality against traditional PET/PEN substrates. Third part of the presentation introduces PrinToNode industrial internet platform, which has been ramped-up recently. The aim of the PrintoNode is to explore challenges and solutions how to utilize collected process data in printed and hybrid electronics manufacturing and product lifetime towards novel data based business models.

11:15 AM *PM03.03.08 High Resolution Screen Printed Circuits for Low Cost Hybrid Systems Goran Gustafsson\textsuperscript{1}, Peter Andersson Ersmann\textsuperscript{1}, Roman Lassnig\textsuperscript{1}, Jan Strandberg\textsuperscript{1}, Robert Forchheimer\textsuperscript{2}, Deyu Tu\textsuperscript{1}, Isak Engquist\textsuperscript{1} and Magnus Berggren\textsuperscript{1}; \textsuperscript{1}RISE Acreo, Norrköping, Sweden; \textsuperscript{2}ISY, Linköping University, Linköping, Sweden; \textsuperscript{3}ITN, Linköping University, Norrköping, Sweden.

Printed electronics devices and systems built up from organic and inorganic electronic inks, promise for a low-cost technology platform that enables widely distributed electronics possible to add onto stickers, labels, posters, packages, smart cards, construction elements, solar cells etc. However, the functionality and reliability that can be achieved is still not enough for most products. Hybrid Printed - Si labels have the potential to fulfill the requirements above but are still awaiting their breakthrough. One reason for its slow market evolution is that the price is too high for low margin products, e.g. packaging. There is a strong need for a strategy to make such hybrid integration cost effective. We will present a technology platform that merges Si-based components with printed electronics, aiming at twinning the benefits of the two. The technology includes printed, low voltage, devices and circuits such as drivers and MUX/DEMUX that release Si from expensive input/output circuitry, thus making Si-labels into a low-cost technology. The technology platform is based on electrochemical devices such as transistors and displays printed at high resolution, by standard screen printing equipment. The major advantages of these printed electrolyte-based components are that the manufacturing can be performed outside the clean room facility that typically is used for most other transistor and display technologies. The resulting devices are operated at low voltages, less than 3 V, and are thereby compatible with printed batteries. The device manufacturing is further simplified by that only a small set of materials is employed, for instance is the very same conducting polymer utilized as the active material in both the electrochemical transistors and the electrochromic displays. In the presentation we will describe this platform in detail and also hybrid product demonstrators at different levels of integration.

11:45 AM PM03.03.09 Silver Nanowire Inks for Direct-Write Electronic Tattoo Applications Nicholas Williams\textsuperscript{1}, Steven Noyce\textsuperscript{1}, Jorge Cardenas\textsuperscript{1}, Matthew Catennacci\textsuperscript{2}, Benjamin Wiley\textsuperscript{2} and Aaron D. Franklin\textsuperscript{1,2}; \textsuperscript{1}Electrical and Computer Engineering, Duke University, Durham, North Carolina, United States; \textsuperscript{2}Chemistry, Duke University, Durham, North Carolina, United States.

Integrating electronics with biological systems is a critical step toward ubiquity for the ever-growing field of wearable electronics. The ultimate in custom integration will be to print functional electronics onto biological surfaces without any buffer or transfer layers – a directly written electronic tattoo. However, the development of such direct-write capabilities is severely limited by the absence of a conductive ink capable of printing directly onto biological surfaces. Current ink formulas typically require significant post-processing to achieve conductive traces, such as sintering at temperatures incompatible with living organisms (~40°C), ultraviolet curing, or rinsing with hazardous solvents. In addition, the electrical performance of printed traces
designated for low-temperature curing generally degrades rapidly when the substrate is flexed, even when the curvature is minor. Silver nanowires offer a promising solution to these challenges as their high aspect ratio allows for the high conductivity of traces to be retained when the supporting substrate is flexed. In this work, we demonstrate room-temperature aerosol jet printing of highly conductive silver nanowire traces onto both biological and non-biological substrates, including Kapton and an oak leaf, with near-identical electrical performance on both substrates. The printed traces maintain a conductivity within 10% of its initial value when the substrate is completely folded (bending radius <0.1 mm). We also show that the resistance of the printed traces was independent of nanowire length. As a result of these unique characteristics, we demonstrate how our water-based, silver nanowire ink is capable of providing direct-write electronic tattoos on sensitive biological surfaces, such as the petal of a flower. These results open the way for the tattooing of functional electronic components, from antennas to circuits, directly onto the surface of virtually any organism, such as the skin of an animal.

References

2:00 PM *PM03.04.01
Roll-to-Roll Processing of Perovskite Photovoltaics

Maikel van Hest; National Renewable Energy Laboratory, Golden, Colorado, United States.

Metal halide perovskites have emerged as a highly promising solar cell technology with high light to electric power conversion efficiency and low processing cost due to their solution processability. However, to make perovskite solar cells commercially viable, particularly to compete with or build upon the traditional silicon dominated photovoltaic market, substantial progress is needed in improving their process techniques and scalability. Fabricating perovskite devices and modules in a roll-to-roll process on flexible substrates will enable high throughput manufacturing, and it will also allow the application space to be extended beyond what is available to rigid geometries. We developed chemistries, contact and absorber layers, that can be deposited in a roll-to-roll fashion using scalable slot-die coating. As part of this development we investigated the performance of flexible perovskite solar cells with various transparent conductors, including flexible indium tin oxides (ITO) and indium zinc oxides (IZO), on thin (100μm) flexible glass substrates. Progress of scaling up perovskites to larger area, sheet-to-sheet and roll-to-roll, on flexible substrates will be reported. Insight will be given in module performance and the stability of such modules. For device structures of flexible glass/ITO/TiO2/mixed cation perovskites/Spiro-OMeTAD/MoOx/Al, a power conversion efficiency of 18% has been demonstrated.

2:30 PM *PM03.04.02
Flexible Glass Applications and Process Scaling

Sean Garner, Sue Lewis, Gary Merz, Alexander L. Cuno and Ilia Nikulin; Corning Research & Development Corporation, Corning, New York, United States.

Substrate choice is critical for overall flexible electronic device and process optimization. Flexible glass, ≤200μm thick, offers several advantages for web manufacturing of electronic devices. Compared to alternatives, glass substrates offer advantages of dimensional and thermal stability, hermeticity, transparency, and surface quality. Similar to other web materials, flexible glass is appropriately conveyed through fabrication equipment using roller systems. This paper discusses flexible glass properties that enable high-performance devices using roll-to-roll (R2R) processes. With a specific focus on mechanical reliability, use of glass web has been demonstrated in key R2R building block processes such as: vacuum deposition, lamination, laser patterning, printing, photolithography, and solution coating.

A disruptive industry ecosystem for flexible glass manufacturing is emerging with new equipment sets being specifically optimized for glass R2R processing. This paper provides specific examples of scaled-up glass web processing at manufacturing widths, lengths, and conveyance speeds for glass web. New demonstrations of flexible glass R2R microreplication, flexographic printing, and high temperature vacuum deposition are discussed. These processes go beyond the previous lab scale activities and highlight glass web R2R processing at 1m-width, 100m-length, and 30m/min conveyance speed.

References


3:00 PM BREAK

3:30 PM PM03.04.05
Ambient Roll-to-Roll Slot-Die Fabrication of Flexible Organic Photovoltaics with Non-Fullerene Acceptor

Yu-Ching Huang¹, Hou-Chin Cha², Yun-Ming Sung², Tsui-Yun Chung² and Cheng-Si Tsao²;¹ Ming Chi University of Technology, New Taipei, Taiwan;² Institute of Nuclear Energy Research, Taoyuan, Taiwan; ³Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan.

Solution-processed organic photovoltaics (OPVs) have shown a dramatic progress in enhancing power conversion efficiency (PCE) by using non-fullerene acceptors. The non-fullerene based OPVs recently achieved over 14% PCE [1-3], and the promising PCE demonstrated the great potential of commercialization. One of the most attractive advantages of OPVs is the printable capability into large-area devices. The high throughput slot-die coating process is the most suitable candidate for the mass-production technology. Our previous study has developed a universal roll-to-roll (R2R) slot-die coating approach to fabricate high-PCE OPVs [4]. Here, we demonstrate the promising photovoltaic characteristics of flexible OPVs based on a combination of PBDB-T and non-fullerene ITIC. We successfully R2R slot-die coated the flexible OPVs devices with high PCE over 9% under irradiation of simulated sunlight (AM 1.5G, 100 mW/cm²). In this study, we present systematical research on the morphology evolution of PBDB-T:ITIC bulk heterojunction (BHJ) films deposited by spin and slot-die coating processes. Our results indicates that the processing parameters significantly affect the morphology and nanostructure of PBDB-T:ITIC BHJ film. These results provide significant insights into the essential knowledge towards highly-efficient OPVs for R2R slot-die process.

References
Meniscus Guide Slot-Die Coating for Roll-to-Roll Fabricated Perovskite Solar Cells

Daniel Burkitt, Peter Greenwood, David Richards, David Beynon and Trystan Watson; Swansea University, Swansea, United Kingdom.

Slot-die coating has been proposed as a potential fabrication method for many of the layers of perovskite solar cell stacks and a growing number of publications are emerging on this topic. Slot-die coating is a versatile coating technique able to coat a range of ink rheologies and as a pre-metered coating method slot-die coating results in little ink wastage. It is compatible with both flexible and rigid substrates and can be used in both roll-to-roll or batch processes, is capable of simple patterning, such as stripes or patches and can achieve considerable line speeds. The use of a meniscus guide as part of the slot-die head, to help bridge the gap between the coating head lips and substrate, has been reported to improve stripe definition [1] and has often been employed in the fabrication of both organic photovoltaic and perovskite devices. To help understand the role of the meniscus guide and how it’s dimensions impact on coating quality we have performed coating trials and produced process windows with a range of inks and assessed if the onset of coating defects, low flow limits- ribbing, discontinuous films, can be predicted using the visco-capillary model of slot-die coating proposed by Carvalho [2]. We also present observations regarding the onset of flooding/leaking for different meniscus guide lengths and how these can be used to control stripe definition under different coating conditions and ink rheology.

We present results of how this understanding is used to develop improved roll-to-roll slot-die coating methods for perovskite solar cells in a P-1-N configuration using a sequential deposition process for the perovskite layer. The lead iodide ink used in the perovskite layer is formulated in a non-toxic solvent and results in a film readily converted to perovskite through slot-die coating of methylammonium iodide without any other pre-treatments. The choice of solution for the MAI ink is optimised by considering how the rheology and volatility of the formulation impact on the conversion to perovskite.

Finally, these developments will be used to demonstrate how slot-die coating can be used to produce the full perovskite device stack in a continuous roll to roll process.

References:


Scalable Strategies to Enhance Mechanical Stability in Efficient, ITO-Free, R2R Printed OPV Devices Processed in Ambient Conditions on Flexible Substrates

William Greenbank, Elodie Destouesse, Jani Lamminaho and Morten Madsen; The Mads Clausen Institute, University of Southern Denmark, Sonderborg, Denmark.

Organic photovoltaic (OPV) solar cells have been explored by research groups across the world as a promising form of next-generation solar energy technology. In addition to their potential to reduce the costs of PV solar energy, they also open up a range of new applications to solar energy. The major point of difference for OPV is that they can be fabricated using roll-to-roll (R2R) printing processes onto flexible substrates in ambient conditions, drastically reducing the energy payback time of the device. Despite all this promise, OPV are only just beginning to be commercialised on any significant scale, and efforts to scale up OPV production have been slow. Much of this stems from issues of low efficiencies and short lifetimes of devices – particularly when attempts are made to replicate laboratory-scale studies at commercial scales. In recent years, laboratory-scale OPV device efficiencies as high as 15% have been reported, and while this represents remarkable progress, devices with such high efficiencies are often produced using techniques that do not translate well to commercial production, and do not retain their high efficiency over time. This is compounded when attempts are made to replace expensive components of the device like indium tin oxide (ITO), or deposit on flexible plastic substrates.

At the SDU NanoSYD nanoscience centre at the University of Southern Denmark we explore an integrated approach to OPV research, spanning the spectrum from highly controlled, small scale device studies, to medium-scale slot-die coated modules, to large-scale R2R printed modules. In this way our work aims to help bridge the gap between the laboratory scale and the industrial scale. This strategy has already proven successful. Recently we successfully produced ITO-free OPV devices incorporating non-fullerene acceptors (NFAs) that were entirely air-processed on flexible polyethylene terephthalate (PET) substrates with 6% PCE using scalable slot-die coating. These devices showed impressive stability when properly encapsulated, demonstrating a viable route for the implementation of a highly efficient polymer-NFA system in industrial-scale OPV production.

One of the key areas that we focus on is improving the lifetime of OPV modules, in particular the mechanical stability of flexible modules. This is often an under-researched area for OPV stability, but vitally important for many of the anticipated applications of OPV technology. Much of the mechanical instability in devices arises from poor adhesion between chemically-incompatible layers that then easily delaminate when only small amounts of stress are applied to the device. In our work we explore strategies to improve layer compatibility without compromising device performance that can be easily applied to commercial-scale production. Although our focus is principally on OPV devices, the techniques we employ have the potential to be applied to any solution-processed organic electronic device.
investigated a hybrid approach which combines the polymer and ceramic into a composite electrolyte to achieve both processing and performance requirements. There is a significant need to understand how we can tailor the solid electrolyte to promote effective transport. Herein, we demonstrate a custom-made benchtop multi-material slot-die system that can print solid electrolytes with graded structures. Initial results have shown that the nano-scale interactions in the ink phase impact the macroscopic ink properties and the coating structure [1, 2]. This work focuses on demonstrating the fine feature capabilities in slot-die coating system and understanding how pathways can be engineered for efficient transport.


4:30 PM PM03.04.09
A Scalable Dry-Powder Spraying to Manufacture Lithium-Ion Batteries from Electrodes Towards the Entire Battery

Jin Liu1, Yan Wang1, Heng Pan2, Brandon Ludwig3, Yangtai Liu4 and Zhangfeng Zheng1; 1Worcester Polytechnic Institute, Worcester, Massachusetts, United States; 2Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

An advanced power-based spraying technology was developed by us to fabricate electrodes for the lithium-ion batteries to analytically lower 20% of the manufacturing cost. Gas-driven spraying guns were chosen to address a direct dry-powder laminating of the electrode structures onto the current collectors without involving solvents. Through removing the usage of these organic solvents and related recycling procedures, the entire processing of electrodes is shortened and found to be more precisely controlled, which results in product electrodes with higher bonding strength, structural integrity, and materials homogeneity. We have demonstrated this technology with a wide range of compatibility on producing electrodes, including cathodes (LCO, LMO, NCM), anodes (Graphite), advanced architecture designs (Ultra-low binder recipe (<1%), high-energy thick electrodes (>280um), hierarchical micro-structured).

In addition, the flexible arrangement strategy of spraying guns promoted the development of hierarchical designs to be practically available to the lithium-ion market. Dry-powder sprayed electrodes with a multi-layered structure, outperformed single layer ones at electrochemical performance and mechanical properties. This technology is currently developing to be grafted onto the existing roll-to-roll fabrication of electrodes for lithium-ion batteries at the pilot scale, and finally aiming to achieve an integrated direct manufacturing of the entire energy storage devices (batteries) accustomed to flexible designs.

4:45 PM PM03.04.10
Roll-to-Roll Fabrication of High Performance Conformal Thermoelectric Generators

Yining Feng1, 2, Zamaan Bagban1 and Na Lu1, 2, 4; 1Lyles School of Civil Engineering, Purdue University, West Lafayette, Indiana, United States; 2Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States; 3School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana, United States; 4School of Materials of Civil Engineering, Purdue University, West Lafayette, Indiana, United States.

Thermoelectric generator (TEG) is a solid-state technology that can convert thermal energy directly into electricity through the Seebeck phenomenon. Over 2.5 quadrillion BTU/year of energy generated in US is wasted as a form of heat, which can be reclaimed as electricity using flexible TEG to power sensors and other microelectronics for civil communications and Internet of Things (IoT) technologies. Unfortunately, the current TEG technology is suffering from its rigid device structured, low efficiency and high cost in both device fabrication and installations.

In this work, a novel roll-to-roll production line of conformal thermoelectric generator (cTEG) will be reported. In-line fabrication includes several micro-deposition processes on a roll-to-roll equipment for a continuous manufacturing platform. The specific activities include: (a) depositing top metal contact layers using screen printing technique; (b) creating micro-porous channels on polymer substrates using pulsed laser irradiation system; (c) filling of micro-channels with p- and n-type TE materials using pipet dispensing systems or similar technique for nanoparticles depositions; (d) laser sintering of p- and n-type TE materials for in-situ crystallization with minimal thermal damage, followed by screen printing the top layer metal contacts to achieve high power output of conformal TEG as power sources for sensors. Thermo-plastics with low thermal conductivity (i.e. kapton, PDMS, polyamide etc.) will be used as substrate and insulating materials between p-n legs.

The cTEG with polymer substrate and insulating materials lead to maximum heat gain to reach high efficiency at the device level for power generation. The performance of cTEG will be discussed with regards to the materials quality and manufacturing process. The fundamental science developed here will have a broad interest to flexible electronic and nanomanufacturing community.

SESSION PM03.05: Lighting and Optical
Session Chairs: Shelby Nelson and Barbara Stadlober

Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 108

8:15 AM *PM03.05.01
Hybrid Roll-to-Roll Manufacturing of OLEDs

Pim Groen1, 2; 1Holst Centre, Eindhoven, Netherlands; 2Aerospace engineering, TU Delft, Delft, Netherlands.

Hybrid production methods offer the possibility to exploit the benefits of different technologies in a single manufacturing process. In this contribution, this strategy will be highlighted using the example of the roll-to-roll (R2R) production of large area organic light emitting diodes (OLEDs) on flexible polymer substrates. Two opposing strategies are available to deposit the functional layers in an OLED device stack: The “dry” approach uses vacuum based methods such as thermal evaporation and sputtering, whereas the “wet” approach relies on the coating and printing of functional inks. The R2R production of OLEDs based solely on vacuum techniques has been demonstrated and can provide efficient and stable devices. By contrast, preparing OLEDs exclusively by R2R “wet” methods is generally hampered by the limited materials purity and undesired interactions between the functional layers during deposition. A number of R2R production steps from solution, however, are already well established and allow the high throughput production with good control over the resulting layer quality. We have designed an OLED architecture which can be prepared in a hybrid manner by combining elements of wet and dry R2R processing technologies. Starting with a roll of barrier substrate, indium tin oxide (ITO) is first deposited uniformly by R2R magnetron sputtering as a transparent conductor. Hereafter, an insulator is applied from solution with patterned slot die coating to separate the electrodes. This eliminates the need to pattern the ITO. A conductive and semiconducting inks is then employed, to enable the external power supply and planarise the ITO surface, respectively. These steps have been demonstrated at web speeds of 10 m/min and above. The slot die coated planarisation layer allows the following step (R2R evaporation of the active OLED materials) to be carried out targeting significantly lower layer thicknesses, thereby saving precious materials and speeding up the entire process. At current state, the efficiencies of the hybrid OLEDs still lag behind compared to fully evaporated reference
devices (20 vs. 45 lm/W at 1000 cd/m²), but with further process optimisation, it is foreseen that the increased process speed and more efficient materials use can compensate for a somewhat lower performance.

8:45 AM PM03.05.02
OLED Manufacturing on Flexible Substrates Towards Roll-to-Roll Christian May; Fraunhofer FEP, Dresden, Germany.

Besides to display technology, OLED also has unlikely potential for lighting applications. Where extremely thin, flexible or transparent light sources are desired, OLED can exploit its potential as a supplement to the LED. The improvement of flexible OLED is currently the focus of worldwide research activities. Thin substrates of primarily barrier-coated polymer films, but also metal foils or ultra-thin glass, were tested for use in OLED production and have advantages and disadvantages. OLED prototypes on polymer substrates as well as ultra-bright glass were realized by Fraunhofer FEP. The main development areas are the improvement of device stability and brightness. This includes intensive work on encapsulation as well as the development of stacked OLED architectures on flexible substrates.

Metal foils have also been utilized for several years as substrates for thin-film photovoltaics and batteries. Now metal foils are getting interest as substrates for flexible organic electronic devices. In contrast to substrate materials like glass or plastic web an extra smoothing layer on typically rough metal foils are necessary to reach sufficient device stabilities, in particular for large area OLED lighting. An advantage of metal foils in the organic electronics is the comparatively good electrical and thermal conductivity. This allows for homogenous large-area lighting surfaces with current densities of more than 10 mA/cm². Additionally, metal foils can be applied as top encapsulation on OLED devices on glass or plastic substrate to improve the temperature management during device operation, combined with excellent barrier properties of metal foils. Those benefits of improved temperature management on the OLED device lifetime and better illumination homogeneity will be outlined in the presentation. First results on a full roll-to-roll process chain enabling later high throughput production will be presented.

In future, the focus will be on the development of integration solutions in functional devices and surfaces using established technologies. Fraunhofer FEP works on processes along the entire value chain to produce flexible OLEDs in both, sheet-to-sheet and roll-to-roll processes. The requirements for the materials and technologies as well as the associated challenges will be introduced using latest results by Fraunhofer FEP. Solutions and application possibilities will be presented.

9:15 AM PM03.05.03
High Volume Manufacturing of Advanced Optical Elements Theodor Nielsen¹, Alicia Johansson¹, Iija Czolkos¹, Niklas Hansson² and Brian Bilenberg¹; ¹NIL Technology ApS, Kongens Lyngby, Denmark; ²NILT Sweden Filial, Gothenborg, Sweden.

Advanced optical element such as diffractive optical elements (DOEs) are expected to revolutionize the compact optics market for imaging and non-imaging systems by enabling low weight and low cost optical systems. Today we are in the beginning of a transition period when bulky optical systems consisting of classical lenses are going to be replaced by advanced optical elements using only a single flat optical element with an advanced micro- and nanostructured surface topology.

NIL Technology ApS specialises in supplying high-quality nanostructured masters and nanoimprinting solutions for customers worldwide. The key to high-volume and low cost production is replication and NIL are experts in replication techniques such as nanoimprint lithography, hot embossing and injection moulding.

Since 2010, NIL Technology has developed methods to implement advanced micro-and nanostructures on steel inserts for injection moulding of low-cost polymer parts. The applications range from super-hydrophobic lenses to consumer products with structural colors and lab-on-chip systems. Over 100,000 nanostructured parts have been replicated by injection moulding without any degradation of the nanostructured mould surface which demonstrates the potential for production of very high volumes at low cost.

In this presentation, NIL Technology will demonstrate advanced multi-level DOEs replicated in low cost materials suitable for high volume applications. Methods for future in-line quality control will also be presented. Focus will be on nanostructured steel injection moulding tools made by nanoimprint and the tools use in injection moulding process.

9:45 AM PM03.05.04
3D Printed Polymer Photodetectors Ruitao Su, Sung Hyun Park and Michael C. McAlpine; Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

Organic optoelectronic devices have witnessed significant advances in both material development and device performance over the past several decades. Recently, additive manufacturing has been applied to the fabrication of optoelectronic devices via utilizing various functional inks that are compatible with an extrusion-based 3D printing process. This has enabled the ability to additively print complex 3D optoelectronic architectures without the need for any traditional microfabrication processing techniques. Here, polymer photodetectors with high performance are fully 3D printed and thoroughly characterized. Specifically, functional inks are carefully selected for the constituent layers of the photodetector and semiconducting polymer ink is optimized for the active layer, achieving an external quantum efficiency of 25.3% and a specific detectivity of $8 \times 10^{12}$ cm$\cdot$Hz$^{1/2}$/W. Significantly, these metrics are comparable to those of traditionally spin-coated counterparts, yet are fabricated solely via a one-pot custom built 3D printing tool housed under ambient conditions. The devices were integrated into image sensing arrays with high sensitivity and wide field-of-view, by 3D printing interconnected photodetector arrays onto flexible substrates and directly onto hemispherical surfaces. It is further demonstrated that this approach can be extended to create fully integrated multifunctional devices consisting of optically coupled photodetectors and light emitting diodes which are both fully 3D printed on a single platform, showing for the first time the multifunctional integration of multiple semiconducting device types on an integrated platform. The 3D printed optoelectronic devices introduced here simplify fabrication procedures by eliminating the need for any conventional microfabrication facilities, enhancing the flexibility for the design and manufacture of next-generation wearable and 3D structured optoelectronics, and validating the potential of 3D printing to achieve integrated active electronic materials and devices.

10:00 AM BREAK

10:30 AM PM03.05.05
Digital Printing of Organic Photodiodes Comprising Non-Fullerene Acceptors—Device Architecture and Ink-Formulation Noah Strobel¹,², Felix Lindheimer¹,², Tobias Rödlmeier¹,², Mervin Seiberlich¹,², Stefan Schliske¹,², Manuel Pietsch¹,², Uli Lemmer¹,² and Gerardo Hernandez-Sosa¹,²; ¹Light Technology Institute, Karlsruhe Institute of Technology, Karlsruhe, Germany; ²Innovation Lab, Heidelberg, Germany; ³Institute of Microstructure Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Organic photodiodes (OPDs) have in recent years reached a level of performance comparable to inorganic devices. This has considerably fueled the development of printing processes for the fabrication of single and multi-device systems. However, in order to achieve adequate rheological properties
while maintaining optical and electrical device functionality, heavy investment into ink-formulation and process parameter evaluation is necessary even for small changes in material properties like the absorption range. For instance, in systems comprising a polymer donor and a fullerene acceptor the viscoelastic and optical properties are mostly defined by the polymer and are thus intrinsically coupled. To overcome this challenge, we are working with non-fullerene acceptors, which offer an additional adjustment screw to tune the optical properties of our devices without strongly affecting the viscoelastic behavior.

First, we present OPDs comprising poly(3-hexylthiophene) (P3HT) and the non-fullerene acceptor (NFA) IDTBR, having an indacenodithiophene core with benzo[k][1,2,5]thiadiazole and rhodanine flanking group. The devices show a photo-response up to 800nm and reach record responsivities of 400mA/W as well as cut-off frequencies surpassing 4MHz. To combine the gained spectral flexibility with the freedom of design, the fabrication is transferred to digital printing techniques (i.e. ink- and aerosoljet printing) to process opaque and transparent devices of comparable performance. Furthermore, we demonstrate successful decoupling of the optical and rheological properties by using visibly transparent polymer donors and color-selective non-fullerene acceptors. This approach offers spectral flexibility without the need for a variation in process parameters. By the selection of NFAs with energetic compatibility, we fabricated devices with color selectivity in the range of 400-600nm as well as 500-800nm.

10:45 AM *PM03.05.06
Novel and Scalable Concepts for Efficient, Bright and Low-Cost Light-Emitting Electrochemical Cells
Ludvig Edman; Umea University, Umea, Sweden.

The light-emitting electrochemical cell (LEC) features mobile ions in the active material, and it is the action of these ions that distinguishes the LEC from other light sources such as the OLED, and which enables for a number of attractive properties. For instance, it is possible to fabricate LECs from solely air-stable materials and employ a relatively thick single-layer as the active material. These attributes promise to pave the way for an unprecedented low-cost fabrication, and we have demonstrated how functional LEC devices can be fabricated by slot-die coating, inkjet printing, and spray-sintering directly on a wide variety of substrates -- including paper, metal, and textile -- under uninterrupted ambient-air conditions. We have also performed a cost analysis that predicts that solution-based high-volume R2R fabrication methods can allow for the realization of flexible LEC patches at a low cost of ~11 €/m², which deliver bright light emission at 3.6 mcd/1.7

The redistribution of the mobile ions during the initial operation of LECs causes electrochemical doping of the active material (p-type at the positive anode and n-type at the cathode), so that a light-emitting p-n junction forms at steady-state. It is thus in-situ formed doping structure that allows for the simple device structure and the low-cost fabrication, but at the same time it has represented a significant challenge from both a conceptual and performance perspective. More specifically, the doping regions comprise high concentrations of electron and hole polarons, and the direct interaction of these polarons with excitons formed in the p-n junction region will result in a quenching of the excitation before light emission. Thus, it has been questioned whether an LEC ever can become efficient at strong light emission. However, in a recent study we have demonstrated that this issue can be resolved with a triplet-emitting host-guest active material, designed with equally deep electron and hole traps, a balanced hole and electron mobility, and an optimized concentration of mobile ions. Such a carefully designed single-layer LEC featuring air-stable electrode materials and equipped with an outcoupling structure delivers strong green luminance of 1910 cd/m² at a efficiency of 99.2 cd/A, which corresponds to a record-high external quantum efficiency of 27.5 %.8

References
6 Lanz et al. Flexible and Printed Electronics 1, 025004 (2016).

11:15 AM PM03.05.07
Inkjet Printing of Small Molecular Phosphorescent Emitters at the Controlled Surface of Confined Geometry
Youjung Kang, Ji-lye Kim, Robert Bail and Byung Doo Chin; Polymer Science and Engineering, Dankook University, Yongin, Korea (the Republic of).

Significant progress has been achieved in the area of full color organic light-emitting diodes (OLEDs) in terms of their high performances. However, stable ink materials and accurate fine line patterning by printing is an essential core as an alternative candidate of expensive fine metal mask-aided RGB side-by-side patterning or multi-stack (tandem) high efficiency white technology for the large area OLEDs. We have prepared a suitable combination of soluble host material compounds with an effective ink formulation technology. The bipolar phosphorescent host materials based on diphenyl phosphine oxide, pyrroloindole, and carbazole-based structure were dissolved in a solvent mixture, and various conditions for the solvent composition and drying of films were examined. Homogeneous dot and line patterns with controllable surface condition at the confined geometries of light emitting pixels were obtained, where the precise pinning at the coverage of light emitting region was accomplished by use of the photo-patternable pixel define layer. Proper thickness and smooth surface were obtained from a mixture of chlorobenzene and other organic solvent with higher viscosity than chlorobenzene. During the inkjet process, several issues such as control of drop injection density, reduction of line-edge roughness, and the role of the mixed solvent properties were studied in detail. These results show the potential power of inkjet printing as a low-cost patterning method for low molecular weight emitters at high resolution or large area OLEDs.

11:30 AM PM03.05.08
Polychromatic Quantum Dot Light-Emitting Diode Array Fabrication Using Omni-Resolution Immersion Transfer Printing Technology
Tae Won Nam and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Diverse integration of depositing and patterning colloidal quantum dots (QDs) to demonstrate individual red-green-blue (RGB) QD pixels has been developed in past years to realize electroluminescent QD light-emitting diodes (QLEDs) as next-generation displays. Among numerous display products from televisions to mobile displays, the inception of virtual reality (VR) display demands for sub-micrometer pixel resolution due to the requirements of extremely high pixels per degree (PPD) far above those of the conventional displays. However, previously reported patterning technologies have limitations in demonstrating large area, full-color pixel arrays of sub-micrometer feature size with high fidelity and pixel quality such as edge-roughness. Here we present a novel transfer-printing technique which allows patterning and printing of QD array in omni-resolution scale; QD array in single-particle resolution to entire film can be fabricated and transfer-printed. Polychromatic array with unprecedented resolutions up to 200 PPD is demonstrated by utilizing sequential aligning and printing of individual RGB pixel arrays. Conventional transfer-printing techniques adopt flexible polydimethylsiloxane (PDMS) mold on which topological pixel information is written; expensive high resolution patterning on flexible media cannot
extend its functionality from prototype to industrial fabrication because the repeated use of soft PDMS transfer mold at pressure-assisted stamping step is no-longer possible due to accumulated deformation. Conversely, we used the pattern information on hard Si master template to control the capillary-force self-assembly patterning process of colloidal QDs occur in single step. After the ordered QD arrays are delivered to transfer media, hard master template can be reused permanently. Another advantage of using hard master is extremely low edge-roughness of QD pixels as the QDs are strictly confined in hard master trench with minimal edge-roughness when they undergo capillary-force self-assembly. At the final delivery stage of QD pixels, mere minimal contact between the pixels on transfer media and final substrate is necessary therefore avoiding pressure induced defect formation at QD solid. Our transfer-printing technique effectively reduces trade-offs of conventional QD patterning method thereby suggests possibilities for fabrication of full-color electroluminescent QLED displays in industrial scale.

11:45 AM PM03.05.09
Direct-Write Assembly of Freeform Colloidal Structures Alvin Tan, Justin Beroz, Mathias Kolle and A. John Hart; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Evaporative self-assembly can be used to assemble colloidal building block particles with varying degrees of order and scale. These particles, when assembled into a solid, can attain emergent properties, such as an electronic or photonic band gap. However, to date, self-assembly of colloidal materials is limited to planar films on substrates. Extending colloidal self-assembly to three dimensions would enable new applications uniquely enabled by macroscale colloidal crystals. Here, we demonstrate a direct-write technique capable of on-chip assembly of colloidal particles into centimeter-scale freestanding structures. Using a custom-built liquid dispense apparatus, we precisely extrude an aqueous polystyrene particle suspension from a fine needle onto a temperature controlled substrate. By balancing the rate of dispense with the rate of water evaporation, the polystyrene particles are continuously assembled into a crystalline solid. We propose that direct-write assembly has the potential to be adapted to a vast library of building blocks for building functional materials such as photonic crystals, quantum dot solids, and metamaterials.

SESSION PM03.06: Device Fabrication
Session Chairs: Mark D. Poliks and James Watkins
Wednesday Afternoon, November 28, 2018
Hynes, Level 1, Room 108

1:30 PM *PM03.06.01
Stretchable Hybrid Packaging for Skin Electronics and Electronic Textile Takao Someya1, 2; Hanbit Jin3 and Tomoyuki Yokota1; 1Electrical and Electronic Engineering and Information Systems, The University of Tokyo, Tokyo, Japan; 2RIKEN Center for Emergent Matter Science, Saitama, Japan.

In this talk, we will report recent progress of stretchable hybrid packaging for skin electronics and electronic textile. First, we have fabricated a skin display, which is an array of micro LEDs embedded in a thin rubber sheet. The display is stretchable by 45 percent of its original length. A skin display is much more durable to stretching and twisting than previous wearable displays. It is built on a novel structure that minimizes the stress resulting from stretching on the junction of hard materials, such as the micro LEDs, and soft materials, like the elastic wiring—which is a typical reason of damage in the past. Similar stretchable hybrid packaging is used to integrate rigid electronic elements and stretchable wires on textiles for smart apparel. Finally, we will describe remaining issues and future prospects of stretchable hybrid packaging.

2:00 PM *PM03.06.02
R2R Gravure as an Additive Manufacturing Technology for the Fabrication of Large Area Flexible and Inexpensive Devices Gyoujin Cho;
Sunchon National University, Suncheon, Korea (the Republic of).

Over the last decade, roll-to-roll (R2R) printing has been pursued with the expectation of developing a commercially viable, high throughput technology to manufacture flexible, disposable and inexpensive printed electronics. However, in recent years, pessimism has emerged due to the barriers faced when attempting to fabricate and integrate thin film transistors (TFT) using R2R printing. In this presentation, for the first time, I will report a way of manufacturing TFT based large area, flexible and inexpensive devices via a fully R2R gravure printing process with Ag nanoparticle based conducting ink, BaTiO3 nanoparticle based dielectric ink and single walled carbon nanotubes (SWCNT) based semiconducting ink. Using R2R gravure system including those inks and poly(ethylene terephthalate) (PET) as the substrate, we obtained about a 92 % device yield in 15 x 0.25 m2 of PET roll with the printing speed of 6 m/min and extracted the scalability factors needed for a feasible manufacturing process. The R2R gravure printing process addresses several barriers in the fabrication and integration of printed TFTs, circumventing or surmounting challenges associated with the alignment of source-drain and gate electrodes, threshold voltage (Vth) shift, stability and overall device yield, proving that R2R printing is indeed a viable advanced manufacturing technology that can enable high throughput production of inexpensive smart packaging.

2:30 PM BREAK

3:30 PM *PM03.06.03
Flexible and Printed Organic Electronics Development for IoT Sensor Applications Shizuo Tokito, Yamagata University, Yamagata, Japan.

Flexible and printed organic electronics technology has garnered increasing attention and resources in research and development because of its potential for low-cost, environmentally-friendly electronic devices. In particular, there is an immense need to deploy sensor frameworks for the so-called Internet of Things (IoT). These applications are envisaged as thin-film transistor (TFT) devices with various types of sensors fabricated using a variety of printing processes on thin plastic film substrates. Here, we report briefly on recent advancements in printable electronic materials, printed OTFT devices used in integrated circuits and IoT sensor applications. We have successfully fabricated pseudo-CMOS inverters using p-type OTFT devices, as well as NAND logic gates, which exhibited ideal characteristics at low operating voltages and high gains. True CMOS inverters using both p-type and n-type OSC materials are essential for low-power, high-speed operation, and for circuit designs with compact layouts. Using our newly developed n-type OSC material (TU-3) and a commonly used p-type OSC material (dI-F-TE-ADT), we successfully demonstrated a CMOS inverter that employed a stacked TFT device construction. Based on this CMOS inverter design, an operational amplifier, as well as ring oscillators and D-flip flop circuits, were also fabricated. To realize very short-channel OTFT devices and higher performance integrated circuits, we employed the reverse-offset printing method to form narrow channel lengths below 10 µm, resulting in good electrical characteristics. Pressure sensors based on ferroelectric polymer (PVDF-TrFE) materials are superior in detecting vital signs for the human body. We previously succeeded in the precise detection of pulse waves with a wearable patch-type sensor, which was fabricated on a plastic film substrate using printing methods. Our goal is to develop a smart sensor device that can be connected wirelessly to the
Internet, which combines printed integrated circuits and one or more sensors. More recently, we are developing flexible hybrid electronic (FHE) devices, which use silicon-based LSI die for the signal processing and wireless communication circuits and are integrated onto a flexible plastic film substrate. We patterned the sensor element, interconnect layer, and antenna with screen or inkjet printing methods, after which we mounted Si-LSI die and resistors on the same flexible film substrate, whereby we employed both Near Field Communication (NFC) or Bluetooth Low Energy (BLE) wireless communication protocols. We successfully demonstrated a wearable temperature sensor using a PEDOT:PSS sensor element.

4:00 PM PM03.06.04
Rapid Production of Large-Area, Transparent and Stretchable Electrodes Using Metal Nanofibers for Wearable Electronics
Jiuk Jang, Sangyoon Ji, Byeong Wan An and Jang-Ung Park; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Recently emerging electronic devices, including displays, light-emitting diodes (LEDs), touch screens, smart windows, and heaters requires transparent electrodes with high optical transmittance (T) and low sheet resistance (Rs). Although the indium tin oxide (ITO) shows the excellent electrical and optical properties, its brittleness limits many potential applications in stretchable and wearable electronics. There are numerous studies for high-performance, stretchable and transparent electrode to substitute the ITO-based transparent electrode, however, most of them are virtually unavailable to the industry because of their low production rates, high process temperature and lack of reliability.

Here, we report the rapid electrosprinning process that can directly form one-dimensional (1D), ultra-long Ag nanofibers (AgNFs) as a large-area, and continuous network for stretchable electrodes. The electrosprinning process is simple and cost-effective because AgNFs can be formed directly on a substrate while minimizing the waste of functional inks. Since this process is based on a roll collector, it enables the roll-based rapid production of a large-area and transparent electrode film that is composed of AgNF network. In this work, the electrode film exhibits superb electrical characteristics (Rs of ~1.3 ohm/sq) with high optical transmittance of ~90% in a visible regime and outstanding mechanical properties (90% stretchability and minimum bending radius of curvature of 70 μm). In addition, the annealing temperature of AgNF network relatively low (~150 °C), suggesting that the polymer substrate such as polyethylene terephthalate (PET) can be used directly without any transfer process. For a continuous roll-to-roll process, a photonic annealing of functional inks has been utilized and the production speed was 4.5 to 12 m/min. As an application of this high-performance transparent electrode, we fabricated a stretchable and transparent heater in a large area (300 mm x 300 mm) using the roll-to-roll process. The heater presents high temperature (250 °C) at a low operating voltage and excellent temperature reliability under large strain. Furthermore, we integrated the heater with wireless operation system by connecting Bluetooth module so that the temperature is controlled directly using smart devices. According to the target purpose, temperature also can be automatically controlled by applying logic circuit to the micro-controller unit. We believe that this approach presents a promising strategy for future wearable electronic devices.

4:15 PM PM03.06.05
Laser Patterning of Flexible Nanogap Schottky RF Diodes Via Adhesion Lithography
Hendrik Faber, Kalaiavanan Loganathan, Zainab Felemban, Emre Yengil and Thomas Anthopoulos; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

A major part of the envisioned Internet of Things device ecosystem will rely on wireless smart tags and sensor nodes for application areas as diverse as health care, wearables or logistics. All these devices rely on radio frequency (RF) signals for communication or wireless energy harvesting, and a crucial component for that are rectifying diodes capable of operating at the required frequencies typically beyond 1GHz. Therefore, developing novel manufacturing paradigms that successfully combine the ability to produce such RF diodes over large areas and flexible substrates, can truly make a substantial impact.

We have recently introduced adhesion lithography (a-Lith) as an innovative patterning technology that enables the fabrication of ultrafast planar RF Schottky diodes based on a variety of semiconductors [1-3]. A first metal layer (M1) is deposited and patterned via standard lithography procedures. Afterwards the M1 surface is treated with a self-assembled monolayer to weaken the adhesive forces towards a subsequently deposited second metal film (M2). Due to the weak adhesion, the second metal can then be peeled off where it overlaps M1 using a liquid glue or adhesive tape, resulting in the formation of a small inter-electrode gap of typically ~15nm at the boundary between M1 and M2. Because of the nm-sized gaps and the possibility to use dissimilar metals for M1 and M2, a-Lith is perfectly suited to create fast coplanar Schottky diodes. Such devices have been demonstrated using solution processed ZnO in Al-Au nanogap electrodes, reaching cut-off frequencies well above 20MHz [2]. For a-Lith the most involved step is the use of photolithography to structure M1. In this work we therefore investigated an alternative patterning approach to streamline the whole diode manufacturing process. Using a commercial laser scriber system (~1080nm), the desired pattern is achieved by selectively removing areas of M1 via laser ablation with sub-50 micron precision. With optimized process parameters the metal film can easily be patterned according to digital designs that can be realized quickly followed by the a-Lith steps. Using this innovative combination of laser ablation and a-Lith 50nm-nanogap coplanar ZnO diodes with on-demand size and shape are realized. Despite the simplicity of the approach, resulting diodes are found to exhibit excellent operation including high current rectification (~104) and cut-off frequency (~1GHz). Most importantly, the proposed manufactured methodology is compatible with a wide variety of electrode materials including Al, Au, Ti, ITO, Cu, as well as substrate materials such as glass and plastic. The easy adaptability of the diode designs and compatibility with flexible substrates makes the combination of laser ablation and a-Lith an ideal tool to prototype advanced RF devices and circuitry.

References:

4:30 PM PM03.06.06
Wafer-Recyclable, Environment-Friendly Transfer Printing Methods for Fabricating Large-Scale Thin-Film Nanoelectronics
Bongjoong Kim1, Dae Seung Wie1 and Chi Hwan Lee1, 2; 1Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; 2Biomedical Engineering, Purdue University, West Lafayette, Indiana, United States.

Thin film nanoelectronics that can offer performances beyond traditional bulk systems but on diverse substrates or surfaces in lightweight, low-cost, and/or flexible forms could enable many emerging applications. Example devices include flexible complementary metal oxide semiconductor (CMOS) systems, multifunctional nanosensors and optoelectronics, and high-speed nanowire circuits. Conventional approaches in transferring thin film nanoelectronics from their fabrication wafer to arbitrary surface of interests commonly requires chemical etching on the sacrifice of wafer, but also is limited by defects with a low yield. Here, we introduce a high-fidelity transfer printing process that enables the wafer-scale separation of high-performance thin film nanoelectronics from their fabrication wafer in a defect-free manner that allows multiple reuse of the wafer. This interfacial delamination is enabled through a controllable cracking phenomenon triggered by liquid at room temperature or electrochemical reactions. The physically liberated thin film nanoelectronics can be then pasted onto arbitrary places of interest, thereby endowing the particular surface with desirable add-on electronic features. Systematic experimental and theoretical studies reveal the underlying mechanics mechanism and guide manufacturability for the transfer printing process in terms of scalability, controllability, and reproducibility.
Aerosol jet printing (AJP) offers a promising digital, direct-write printing technology for device applications with broad materials compatibility, high resolution, and versatile integration capabilities. Despite its potential, ink design and printer operation for AJP has relied to date on empirical methods for highly curved surfaces. So far, very few efforts have been made to realize devices over a curved surface. Fabrication of optimized direct printed on inductor coil, these soft ferrite layer in WPT module plays important roles in (a) enhancing magnetic coupling between the inductor coils transmitting and receiving the magnetic field, and (b) preventing the magnetic field from reaching any conductive object, electronic devices, or human bodies near the WPT module. Laser annealing using an IR laser with various laser fluences was applied to enhance the magnetic property of the soft ferrite layer printed on the highly curved surface. The performance of the printed WPT module on the highly curved surface was demonstrated by transmitting wireless power to various electronic devices through the magnetic resonant coupling. This work may find potential applications, including wearable electronics, optoelectronics, biomedical devices, sensors, and Three-Dimensional (3D) electronics.

Guided Ink Design for Aerosol Jet Printing Ethan B. Secor; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Aerosol jet printing (AJP) offers a promising digital, direct-write printing technology for device applications with broad materials compatibility, high resolution, and versatile integration capabilities. Despite its potential, ink design and printer operation for AJP has relied to date on empirical experimentation with limited theoretical understanding or guidance. Recent work has examined fundamental principles governing this technology, revealing general guidelines for ink and process design. This work leverages those findings, examining several case studies in guided ink design spanning organic and aqueous solvent systems for printing colloidal dispersions, polymer solutions, and UV-curable monomers.

In each case, general principles of ink design derived from a simple numerical model are applied to identify suitable solvent systems. Standard calibration

Direct Printing of Wireless Power Transfer Module with Metal-Coil/Ferrite Layer/Capacitor Configuration on Highly Curved Surface Rajaram Kaveti and Jihoon Kim; Kongju National University, Cheonan, Korea (the Republic of).

Direct printing on curved surfaces is a newly emerging challenge in printed electronics due to the difficulties in developing the suitable inks and fabrication methods for highly curved surfaces. So far, very few efforts have been made to realize devices over a curved surface. Fabrication of optimized direct printing inks is highly significant for the production of high-quality printing on curved surfaces. The effect of solid, solvent, and dispersant on the printability and ink rheological properties such as viscosity, storage modulus, yield stress, thixotropy and viscoelasticity of various inks were tuned and investigated by rheological tests under steady and dynamic shear conditions. Here, for the first time, we demonstrate the direct printing of magnetic resonant coupled wireless power transfer (WPT) modules and ceramic layers directly onto the highly curved surfaces (hemispherical glass substrates with a radius of curvature ~ 50) with viscoelastic conductive, ceramic, and magnetic inks designed for the highly curved surface printing. WPT module consists of an inductor coil (Ag), and capacitors (Ag/BaTi2O3/Ag) are used to realize a parallel resonant LCR circuit. Furthermore, a soft ferrite layer (NiZn-Ferrite) direct printed on inductor coil, these soft ferrite layer in WPT module plays important roles in (a) enhancing magnetic coupling between the inductor coils transmitting and receiving the magnetic field, and (b) preventing the magnetic field from reaching any conductive object, electronic devices, or human bodies near the WPT module. Laser annealing using an IR laser with various laser fluences was applied to enhance the magnetic property of the soft ferrite layer printed on the highly curved surface. The performance of the printed WPT module on the highly curved surface was demonstrated by transmitting wireless power to various electronic devices through the magnetic resonant coupling. This work may find potential applications, including wearable electronics, optoelectronics, biomedical devices, sensors, and Three-Dimensional (3D) electronics.

Guided Ink Design for Aerosol Jet Printing Ethan B. Secor; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Aerosol jet printing (AJP) offers a promising digital, direct-write printing technology for device applications with broad materials compatibility, high resolution, and versatile integration capabilities. Despite its potential, ink design and printer operation for AJP has relied to date on empirical experimentation with limited theoretical understanding or guidance. Recent work has examined fundamental principles governing this technology, revealing general guidelines for ink and process design. This work leverages those findings, examining several case studies in guided ink design spanning organic and aqueous solvent systems for printing colloidal dispersions, polymer solutions, and UV-curable monomers.

In each case, general principles of ink design derived from a simple numerical model are applied to identify suitable solvent systems. Standard calibration
routines are presented to systematically identify a processing window and optimal printing conditions for specific applications. This framework establishes a useful toolbox for translating basic principles of AJP into practical guidelines, achieving stable printing over several hours with controlled deposition rate and resolution. By analyzing several materials systems, including silver nanoparticles, polyimide, and UV-curable acrylates, general considerations for ink design are clarified. By leveraging an understanding of AJP mechanisms, more systematic and robust ink design and printer operation is realized with general utility for this promising technology.


PM03.07.05
Architected Porous Media Designed for Flexographic Printing

Michael A. Gallegos1, 2, Chelsea M. Garcia2, Madeline Van Winkle1, Kristianto Tjiptowidjaja2 and Bryan Kaehr1, 2; Sandia National Laboratories, Albuquerque, New Mexico, United States; Dept of Chemical and Biological Engineering, The University of New Mexico, Albuquerque, New Mexico, United States.

The development of printed and unconventional electronic devices to meet application-specific needs requires innovation in printing technologies. Flexography (flexo), a rubber-stamping method developed in the 19th century, has proven scalable (meters per second) for graphic arts but is underdeveloped for printed electronics, particularly transistor and transparent electrode applications, due to limited feature resolution (>50 µm).

Although much work has gone into understanding the structural and fluid mechanics of the ink transfer processes, little attention has been paid to the actual stamp, typically fabricated via polymer replication of a hard master. The elastomeric stamp is top-side inked and compressed on a substrate, a process that has inherent limits for materials transfer and results in uneven pixel quality (poor feature resolution) due to compression-induced spreading. However, consider a porous stamp that undergoes precise deformation such as negative Poisson’s ratio (NPR) during this process. Here, ink transfer could be a metered process with the pore-space being the reservoir and the mechanical deformation being the “metering pump”. Moreover, a stamp that exhibits a slight NPR may allow for controlled expulsion and sharper transfer foot print (minimal line-edge roughness). Only recently has it been feasible to produce such engineered structures at high resolution, for example, using multiphoton-induced, direct laser writing (DLW). Here we investigate how precisely architectured (e.g., NPR and a structured pore size distribution), 3D porous media can control the fluid saturation/capillary pressure characteristics upon mechanical compression to enable high fidelity/metered material transfer for high speed printing. In this study, we systematically investigate the effects of porosity, pore size distribution and microstructure compression on flexographic ink transfer using iterative arrays of high-resolution (<1 µm feature size). DLW structures converge on optimized forms. Fluid dynamics simulations of defined poroelastic media provide further insight into metering ink transfer during compression. Overall, this work illustrates the design flexibility and precision control of micro-features/fluid dynamics enabled using form-fabrication of flexographic forms.

PM03.07.06
Engineered Nanocomposite Material Properties Through Embedding of Smaller Nanoparticles in a Polymer Matrix

Sanjoo Gupta, Alex Henson and Brendan Evans, Western Kentucky University, Bowling Green, Kentucky, United States.

Organic and inorganic nanoparticle reinforcements have garnered widespread attention for polymer nanocomposites to yield properties enhancement useful for wide ranging modern technologies including photovoltaics, catalysis, optics, and renewable energy. Recent experiments and computational simulations revealed the macroscopic properties are governed by mesoscale structure and interfacial layer dynamics due to the interactions between the polymer matrix (host) and nanoparticle reinforcements (guest). However, a clear fundamental understanding of the role of size, shape, loading (volume fraction) in controlling the structure and dynamics of polymer-nanoparticle interfacial layer is limited. Moreover, “forward” engineered polymer-nanoparticle composites targeting specific applications often require higher volumetric density and better dispersions remains a challenging task. We report on developing polymer nanocomposites engineered to minimize dielectric losses and investigating structure and dynamics of interfacial layer to predict macroscopic properties. The nanocomposites will consist of poly(2-vinylpyridine) (P2VP) polymer matrix with (~2-5 nm diameter) and (2) planar nitrogereated graphene nanoribbons (~20 nm wide), having dimensions comparable to polymer matrix characteristic length i.e. gyration radius (Rg = 5 nm). This approach will enable improved nanocomposites and identify key molecular parameters governing non-linear dielectric loss mechanisms while studying structured deposition using broadband dielectric spectroscopy and wide-angle X-ray scattering. The transmission electron microscopy will reveal microscopic structure and the lattice bonding, interfacial stress transfer and conjugation length will be determined from micro-Raman spectroscopy. The exact loading and glass transition temperature, Tg, will be obtained using thermogravimetric analysis and differential scanning calorimetry, respectively. We will gain fundamental insights into the interfacial layer and diffusion dynamics above and below Tg and establish quantitative structure-property correlations, while predicting macro-scale properties. We acknowledge KY NSF EPSCoR REG subaward Grant.

PM03.07.08
Polyaniline/Carbon Nano Hybrid Composites for Monitoring and Detection of Flexible Alkali Sensor

Do Hun Kim, Jin Sun Yoo, O Hwan Kwon and Woo Seok Yang; Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

As the safety has been emerged as a major interest in chemical industry facilities, there have been many researches about sensors for detecting hazardous chemicals. In this study, especially, the sensor for detecting alkaline solution was developed and evaluated. The sensor was composed of carbon materials and polyaniline, which is a conductive polymer. The candidate carbon materials for sensor such as graphite and graphene nano platelet were examined. When graphene nano platelet was used, it showed insensitive reactivity to basic material. Also sensor films can better overcome sensor errors in moisture and water when using graphite than GNP. Finally, it was confirmed that the graphite was the best carbon material for the alkali sensor and it was coated on PET to enable flexible sensor.

PM03.07.09
Enhanced Photo-Luminescence from Highly Interconnected Porous QD/BCP Nanocomposites Formed via Controlled Spinodal Decomposition of Block Copolymer

Geon Yeong Kim, Yeon Sik Jung and Duk Young Jeon; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

In this poster, highly interconnected porous QD/BCP nanocomposites was demonstrated in order to achieve enhancement of photo-luminescence. The QD/BCP nanocomposites with strong emission has the potential to be used in photo-luminescence devices of display application with simple and cost-effective fabrication method. Block copolymer (PS-b-P4VP) forms highly interconnected porous structure via the mechanism of spinodal decomposition
during the evaporation of solution when dimethylformamide (DMF) and water exist together. Here, the composite film was fabricated by simple spin-coating with the humidity control. The porous QD-BCP nanocomposites effectively enhanced absorption of quantum dots inside the block copolymer matrix by the multiple light scattering and trapping effect inside film, resulting in enhanced photo-luminescence. A one of current obstacles towards high-performance QD devices is reducing energy transfer nearby quantum dots, which is called Fluorescence Resonance Energy Transfer (FRET). The quantum dot was functionalized with hydroxyl ligand for the conjugation with BCP. The hydrogen bonding between hydroxyl ligand and nitrogen atom of P4VP block was successfully established. Consequently, by the self-assembly properties of block copolymer, the dispersion of quantum dots was induced, which indicated reduced Fluorescence Resonance Energy Transfer (FRET) effect. With the synergetic effects of light scattering from porous structure and dispersion of quantum dots from conjugation effect, the 21-fold enhancement in photo-luminescence was achieved compared to reference quantum dot film.

PM03.07.10 Fabrication of Robust Superhydrophobic Surfaces with Modified Siloxane Resin Kibeom Nam and Dong Yun Lee; Kyungpook National University, Daegu, Korea (the Republic of).

The superhydrophobic surfaces have received a significant attention for decades because of their wide spectrum of applications such as self-cleaning, anti-icing, separation of liquids, and anti-corrosion. We achieved durable water repellent surface through a spray coating method. This technique is possible to fabricate superhydrophobic surfaces with multiscale of roughness over large area. Spray coating is conducted by spraying the nanoparticles (NPs) onto the substrate with some binders in it; The NPs are gathered each other and form multiscale structures on the substrate and the binder which has low surface energy acts as an adhesive. This superhydrophobic surfaces has not only an excellent water repellency and superb solidity. In addition, it shows a heat resistance even at 300 celsius degree, and solvent resistance. To achieve such superhydrophobic surface through spray coating, we should consider various factors that influence on degree of superhydrophobicity, for example NPs size and content, binder content and the amount of coating solution. Especially, it is important to control the aggregated size of NPs in solution, that highly affect the surface morphology after coating process. The superhydrophobic surface means the surface that has high contact angle over 150° and low slide angle under 10°. It is well established that the superhydrophobic surfaces came from an association of low surface energy and multilevel of surface roughness (i.e., hierarchical structures). It is explained by two theoretical models (Wenzel and Cassie-Baxter); Both models explain a superhydrophobic surface that has rough surface with low surface energy. If liquid drops on Wenzel model, liquid fills up all grooves however, air pockets are formed between the surface and water droplet in Cassie-Baxter state. Because of such differences, they show different wetting properties, water droplet can be pinned on the Wenzel surface and do not roll off easily. By contrast Cassie-Baxter drops are fall form the surface because they sit partially on air. These structures are vulnerable to mechanical forces form the surrounding like water impact, or finger touching. When the structures are demolished, it lost its hydrophobic property. However, we introduce a method for fabricating the mechanically durable superhydrophobic surfaces by spraying robust siloxane resin as a binder. The resin can be synthesized through hydrolysis-condensation reaction of silanes and cured with amino-silanes. Furthermore, surface morphology is controlled by adjusting distribution and mount of NPs in the coating solution.

PM03.07.11 Superhydrophobic Functionalization of Textile Surface Using Roll-to-Roll Chemical Vapor Deposition Mehmet Gursoy; and Mustafa Karaman; Selcuk University, Konya, Turkey.

In most cases, functional polymeric thin films are essential parts for the production of many devices with electronic or other advanced functionalities, including transistors, memories, physical and chemical sensors, photovoltaic cells, photo detectors, energy storage devices, displays, lighting, biomimetic surfaces and flexible-hybrid electronic devices. Today, the interest in wearable devices is increasing rapidly, making it necessary to integrate device parts on flexible textile surfaces. Usually, the surfaces of textiles are not compatible with the other parts of the devices, which could be overcome by imparting a functional thin film on textile surface. The desired properties of a device-quality textile include flexibility, breathability, durability, ease-of-manufacturing, aerium and mechanical properties. To achieve such a high-throughput production, making it as a suitable mass production equipment such as roll-to-roll process. In this study, a pilot roll-to-roll iCVD system was designed and operated to produce thin films of poly(hexafluoro butyl acrylate) on bamboo fabric surfaces. In this way the surface of bamboo was modified with silver and copper nanowires are used to make transparent heaters because of their high electrical conductivity as well as high optical transmittance in the near infrared spectrum. The superhydrophobic surfaces have received a significant attention for decades because of their wide spectrum of applications such as self-cleaning, anti-icing, separation of liquids, and anti-corrosion. We achieved durable water repellent surface through a spray coating method. This technique is possible to fabricate superhydrophobic surfaces with multiscale of roughness over large area. Spray coating is conducted by spraying the nanoparticles (NPs) onto the substrate with some binders in it; The NPs are gathered each other and form multiscale structures on the substrate and the binder which has low surface energy acts as an adhesive. This superhydrophobic surfaces has not only an excellent water repellency and superb solidity. In addition, it shows a heat resistance even at 300 celsius degree, and solvent resistance. To achieve such superhydrophobic surface through spray coating, we should consider various factors that influence on degree of superhydrophobicity, for example NPs size and content, binder content and the amount of coating solution. Especially, it is important to control the aggregated size of NPs in solution, that highly affect the surface morphology after coating process. The superhydrophobic surface means the surface that has high contact angle over 150° and low slide angle under 10°. It is well established that the superhydrophobic surfaces came from an association of low surface energy and multilevel of surface roughness (i.e., hierarchical structures). It is explained by two theoretical models (Wenzel and Cassie-Baxter); Both models explain a superhydrophobic surface that has rough surface with low surface energy. If liquid drops on Wenzel model, liquid fills up all grooves however, air pockets are formed between the surface and water droplet in Cassie-Baxter state. Because of such differences, they show different wetting properties, water droplet can be pinned on the Wenzel surface and do not roll off easily. By contrast Cassie-Baxter drops are fall form the surface because they sit partially on air. These structures are vulnerable to mechanical forces form the surrounding like water impact, or finger touching. When the structures are demolished, it lost its hydrophobic property. However, we introduce a method for fabricating the mechanically durable superhydrophobic surfaces by spraying robust siloxane resin as a binder. The resin can be synthesized through hydrolysis-condensation reaction of silanes and cured with amino-silanes. Furthermore, surface morphology is controlled by adjusting distribution and mount of NPs in the coating solution.

PM03.07.12 Direct Write of Micro-Circuitry via Micro Cold Spray Ryan Mocadlo1, Victor Champagne1, Jianyu Liang2 and Richard Sisson2; 1U.S. Army Research Laboratory, Aberdeen, Maryland, United States; 2Materials Science & Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Micro-cold spray (MCS) is a process that can achieve the solid-state deposition of metal powders through capillary focusing. In this process, metal powders are accelerated, using high pressure helium, through a capillary nozzle to impact on a substrate, and subsequently deposit in micrometer lines. Fine feature sizes have been a long-standing aspiration of the cold spray community, but have remained elusive despite extensive efforts. Recent developments in micro powder feeding has enabled the use of the MCS as a direct-write technology to deposit conductive materials for use in printed electronics. In addition, the MCS process has shown the ability to deposit materials on flexible substrates, allowing for the possible use in the fabrication of flexible electronics. This work describes the extensive effort on understanding the impact of nozzle design, and process gas temperature on the final deposition. Computational fluid dynamics models were employed in the preliminary design of the capillary nozzles, with the goal of maximize particle velocity, while minimizing the particle beam diameter. The insights gained through experimental studies were used to help optimize the computational models for future use.

PM03.07.13 Transparent Thin-Film Heaters Based on Atomic Layer Deposited Oxides onto Copper Nanowire Networks Dogançan Tigan, Sevim Polat Genlik, Bilge İmer and Husnu E. Unalan; Middle East Technical University, Ankara, Turkey.

Transparent heaters utilizing random metallic nanowire networks received great attention in recent years due to their significant performance. Commonly, silver and copper nanowires are used to make transparent heaters because of their high electrical conductivity as well as high optical transmittance in the near infrared spectrum.
In this study, we succeed in patterning the anodized aluminum oxide layer by the photolithography technique. The minimum resolution of the patterning is less than 10 μm. To pattern the anodization oxide layer, first we patterned the photo resist on the connection wires. By covering the connection wire with copper nanowires, we successfully fabricated transparent thin film heaters using copper nanowires with oxide shells through simple means.

PM03.07.14 Reducing Fresnel Reflection Losses in Chalcogenide Based Infrared Optical Fibers via Direct Nanoimprinting Mikkel Lotz, Christian R. Petersen, Christos Markos, Ole Bang, Mogens Jakobsen and Rafael Taboryski; 1DTU Fotonik, Technical University of Denmark, Kongens Lyngby, Denmark; 2DTU Nanotech, Technical University of Denmark, Kongens Lyngby, Denmark.

Fresnel reflection at the glass-air interface in chalcogenide glass based optical components generally constitutes a significant portion of the overall losses due to the high refractive index (2-3) of the glass. In arsenic triselenide (As$_2$Se$_3$) based mid-infrared optical fibers the Fresnel reflection losses surmount to about a 40% reduction in transmitted power. Traditionally, mid-infrared optical systems have relied on antireflective dielectric coatings to solve this problem, but only a limited number of materials are chemically and thermo-mechanically compatible with chalcogenide glass. Nevertheless, we recently reported on the progress towards fabricating broadband mid-infrared antireflective moth-eye nanostructures on the surfaces of commercially available As$_2$Se$_3$ optical windows by thermal nanoimprinting. We now present a study into a more cost-effective method of reducing the Fresnel reflection losses in As$_2$Se$_3$-based optical fibers by nanoimprinting antireflective nanostructures directly on the end-facets.

Based on a simulation approach using rigorous coupled-wave analysis we first design a hexagonal array of moth-eye nanostructures optimized for the mid-infrared. A silicon master containing the moth-eye nanostructures is then fabricated using DUV lithography to create an etching mask and dry-etching to fabricate the structures in the silicon substrate. A nickel mold is then made by depositing a nickel-vanadium seed layer to the silicon master and subsequently electroforming it with nickel. The nickel mold is released by dissolving the silicon master in a potassium hydroxide solution. The negative relief mold of nickel (Ni shim) is then coated with Perfluorodecyltrichlorosilane (FDTS), which acts as an anti-stiction coating using Molecular Vapour Deposition (MVD).

Using a mid-infrared supercontinuum laser source with a radiation spectrum from 2.4-2.6 μm, we observe >30% improvement to the transmitted optical power (from 56% to almost 90% of incident power) as a result of nanoimprinting the input and output facets of a As$_2$Se$_3$ multi-mode fiber and a single-mode fiber, using the fabricated Ni shim.

PM03.07.15 Damage Induced Surface Texturing of PDMS Composites, a Single Fiber Insertion Study Navid Namdari and Reza Rizvi; Mechanical Engineering, The University of Toledo, Toledo, Ohio, United States.

Damage and mechanical failure are detrimental for materials in engineering applications. However, recent studies have shown that properly designed debonding and pullout phenomena in composite fractures can be implemented to introduce added functionalities by damage induced surface texturing (DIST). In this approach, randomly oriented or aligned fibers are incorporated in a polymeric matrix, followed by transversal shearing of the surface. As a result, the shear-fractured surface will have protruded fibers on it because of the debonding followed by subsequent pullout. The protruded fibers play a key role in imparting new functionalities to the cut surface. To date, two important applications have been affected by the introduction of DIST. The first application is in enhancing the ice friction coefficient by as much as 900% in carbon-based styrene butadiene styrene (SBS) composites. Furthermore, DIST has also shown a significant potential in hydrophobic surfaces where the water droplet contact angle increased by 30% in SBS reinforced with carbon fiber (CF) composites. DIST is a simple, economical, and a scalable method compared to lithography, hot embossing, and laser ablation. In addition, there is no need to use costly and time-consuming post-processing stages to introduce anisotropic properties into the material. Tailoring the pullout length can directly affect the functionality of the surface. Thus, selecting appropriate process parameters plays a key role in designing an optimized surface. The aim of this study is to investigate the effect of fiber type, polydimethylsiloxane (PDMS) modulus of elasticity, fiber stiffness, and fiber/matrix interface on the pullout length of the fiber. A PDMS with varying hardness of 10, 20, 30, and 50 was selected as the compliant material that will incorporate carbon and poly[p-phenylene-2,6-benzobisoxazole (PBO)] fibers. A single fiber insertion method was carried out with a sequential alignment of eight single fibers on a frame placed in a cubic mold before casting the PDMS. The samples were cut transversely to the direction of alignment with a custom-built cutter once the PDMS was cured. The protrusion lengths were measured with an image processing software (ImageJ) from the scanning electron microscopy (SEM) micrographs of the cut surface. Smaller protrusion lengths were observed by increasing the matrix modulus, according to the predictions of the model proposed by Wells and Beaumont [1]. Moreover, using regular and high-modulus PBO fibers brought to light the fact that increasing the fiber stiffness can enhance the pullout length. Finally, we evaluate the effect of epoxy sizing, plasma treatment, and no sizing on the pullout length of the carbon fiber.


PM03.07.16 Anodization Patterning for Organic Electronic Circuits with Low Operation Voltage Tomovski Yokota, Hirosi Jinno and Takao Someya; The University of Tokyo, Tokyo, Japan.

Organic circuits are much attracted in realizing the flexible and bendable electronics such as flexible display and flexible sensor systems. The important technology for realizing the high yield and high performance organic circuits with low operation voltage is anodized oxide gate dielectrics. Recently, many groups reported the low operation voltage organic transistor with anodized oxide gate dielectrics layer [1, 2]. Compare with a plasma-formed aluminum oxide layer, an anodized alumina oxide layer shows higher mechanical durability [1]. One of the biggest problems of anodization process is patterning. Normally, anodization process needs to connect the all electrodes to form the oxide layer. For this reason, it is very difficult to make the complicated circuit with anodized oxide gate dielectrics. Although some novel method of anodization patterning were developed [3], it is still difficult to apply these methods to organic integrated circuits.

In this study, we succeed to pattern the anodized aluminum oxide layer by the photolithography technique. The minimum resolution of the patterning is less than 10 μm. To pattern the anodization oxide layer, first we patterned the photo resist on the connection wires. By covering the connection wire with...
Automated Fabrication of Uniaxially Aligned Nanofibers via Beltspinning

Dave Jao and Vince Beachley; Rowan University, West Berlin, New Jersey, United States.

This study proposes a continuous and straightforward method for fabricating suspended micro- and nano-diameter polymer fibers by using an automated single step drawing system. Tangled beltspinning, fiber alignment, diameter, and morphology can be controlled by varying draw ratio, rotational belt speed, and polymer solution properties. The belt spinning device is inexpensive and simple to operate as it does not require an electric field. The device can draw single or multi-filament arrays of nanofibers from any kind of polymer and solvent. Fibers are continuously spun by the direct contact and mechanical drawing between the two rotating belts. The automated track can produce continuously aligned fibers along a single linear axis, which is advantageous for building uniaxially aligned scaffolds for tissue engineering. To demonstrate, fibers were manually pulled from polymer solutions containing 10, 20, and 30% w/v PVAc and 7, 10, and 13% w/v PE. As the system rotates and cycles, the viscous liquid polymer solution applied to the belt begins to evaporate and form semi-solid fiber bridges. The polymer bridges then proceed down the angled track where the fiber is further stretched and elongated over a wide range of fiber diameters. Polymer nanofibers with diameters as small as 400 nm with a length of 30 cm were produced using this technique. Controlling the drawing parameters, all kinds of polymeric materials (polymer melts and solutions), and biopolymers (protein materials), and polymer composite materials. The setup is inexpensive to implement, nozzle-less, easy to scale up, and the tracks can be patterned/textured for aligned fiber arrays. The ability to draw various materials into uniaxially aligned nanofibers opens the door to applications associated with 3D nanostuctures and development of new nanodevice configurations, while also providing opportunities in a wide variety of 3D substrate geometries that have been difficult or impossible to obtain, such as tissue engineering scaffolds. The preferential alignment of nanofibers can also lead to the formation of nanostructured materials with highly anisotropic behavior and new features, such as electrical, magnetic, ferroelectric, ferromagnetic, and structural mechanical. For example, drawing polymeric fibers can increase chain alignment and crystallinity, it is a conventional method to improve the thermal conductivity of the polymer along the axial direction of the nanofibers. While electrospraying has been successfully used in preparing many kinds of polymer fibers with high thermal conductivity, it has some disadvantages, such as the need for polar solvent carriers that are relatively high in electrical conductivity to spin highly resistive polymer materials, such as PE. Since studies have shown that the thermal conductivity of the mechanical drawn PE nanofiber is comparable to the electrosprun PE nanofiber, the automated drawing process can be implemented via beltspinning.
fabricated on Si substrates using a ZrO₂ gate dielectric and In₂O₃ semiconductor that are converted with a total annealing time of just 2 minutes. The devices exhibit a high carrier mobility (μ > 9 cm²V⁻¹s⁻¹) and on/off ratio (Ion/off > 10⁶) than the same TFT device structure made using a UV-ozone assisted metal oxide conversion plus thermal annealing at 250 °C with a total processing time of 3 hours (μ = 1.4 cm²V⁻¹s⁻¹, Ion/off = 10⁴). The sol-gel to metal oxide transformation process is characterized by XPS, FTIR, and ellipsometry. Photonic curing is further explored to convert sol-gel oxide films on polyethylene naphthalate (PEN) substrates. The increase in processing speed will be crucial to enabling high-throughput roll-to-roll manufacturing of metal oxide electronic devices.

8:15 AM PM03.08.02
Roll-to-Roll Ion Beam Assisted Deposition of Single-Crystalline-Like Conductive TiN Buffer Layer Directly on Metal Substrate for Thin-Film Optoelectronic and Electrical Applications  Sicong Sun, Ying Gao, Yongkuan Li and Venkat Selvamanickam; Department of Mechanical Engineering & Texas Center for Superconductivity and Advanced Manufacturing Institute, University of Houston, Houston, Texas, United States.

Single-crystalline-like buffer layers made by ion beam assisted deposition (IBAD) have been used to grow highly epitaxial functional layers on inexpensive metal and flexible glass substrates. Most commonly-used single-crystalline-like buffer structures consist of oxide materials such as LaMnO₃/MgO. While such oxide layers have led to high-performance epitaxial superconductor tapes, GaAs photovoltaics and Si and Ge-based flexible electronics, they isolate the active layers from the substrate. This architecture has a few drawbacks including possibility of thermal destruction in the event of an overcurrent situation and the need to fabricate lateral back contacts by etching and photolithography. Single-crystalline-like buffer structure of a conductive material is a very desirable design since they allow electrical and thermal contact between the active layers and the substrate which allows high thermal dissipation ability and the ability to fabricate back contacts on the substrate without the need to etch the active layers. TiN has been reported as a promising material for developing conductive buffer layer to replace oxides because of its good electrical conductivity and high thermal stability. Here we report a new method to grown biaxial-textured single-crystalline-like TiN thin film on polished metal tape by continuous roll-to-roll ion beam assisted deposition. Single-crystalline-like TiN has been directly realized on low-roughness metal tape surface (Rₘₐₓ 0.35nm, 1µm scale) without any seed layer at room temperature. In-plane texture Δφ of 5.6° and out-plane texture Δω of 1.8° are achieved in the homoepitaxy TiN on IBAD TiN. Such electrically- and thermally-conductive single-crystalline-like TiN have been used for epitaxial growth of active layers for photovoltaics, flexible electronics and superconductor applications by roll-to-roll manufacturing.

8:30 AM PM03.08.03
Ultra-Rapid Transformation of Materials Characteristics via Photonic Processing  Demosthenes Koutsogeorgis, School of Science and Technology, Nottingham Trent University, Nottingham, United Kingdom.

Humankind has always been fascinated by light. But, besides just mesmerising us, light can also be a powerful tool for manipulating matter and its characteristics. Light is no longer limited to just a diagnostic for probing materials’ characteristics, but has also become an engine for manipulating materials’ properties. This presentation is about using light in order to process thin films and manipulate their characteristics. As an alternative to conventional thermal annealing, photonic processing enables the use of temperature sensitive substrates without any loss in the effectiveness of a high temperature treatment. Photonic processing is amenable to the demands of R2R, providing a highly localised and ultra rapid thermal treatment, which targets the material of choice only and has minimal influence onto the surrounding materials. The 10 parameters that affect the outcome of photonic processing will be presented in detail, offering a description of how they may affect the outcome of the processing and transform the characteristics of thin film materials. Several examples of successful application of photonic processing to thin film materials will be presented. Examples include the processing of materials for effective dopant activation, control of crystalline structure, creation of ohmic contacts, fabrication of plasmonic nanoparticles, localised photo-chemical conversion of sol-gel precursors.

SESSION PM03.09: ALD and Printing
Session Chairs: Gyoujin Cho and Shelby Nelson
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 108

9:00 AM PM03.09.01
Roll-to-Roll Atmospheric Atomic Layer Deposition Technology for Thin Films and Flexible Electronic Applications  Kamrun Ali1 and Kyung H. Choi2; Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar; 1Department of Mechatronics Engineering, Jeju National University, Jeju, Korea (the Republic of).

Since the inception of Atomic Layer Deposition (ALD) Technology in 1974 by Dr. Tuomo Suntola, it has been adopted by numerous industries for variety of applications. ALD has earned a reputable status in electronic industry especially in the sectors of solar cells, displays, and energy storage devices etc. Although, the conventional ALD technologies are quite capable to produce good quality thin films of wide variety of materials, yet the sequential introduction and purging of precursors and inert gases prevent their application for mass production under atmospheric conditions. In this research work, a novel technology of roll-to-roll atmospheric atomic layer deposition (R2R-AALD) has been implemented for the increased production of Al₂O₃ thin films on movable web of polyethylene terephthalate (PET) substrates at low temperatures (< 100 °C), and the films were also implemented for the encapsulation of organic Poly (4-vinylphenol) (PVP) flexible memristor devices as for their life time enhancement. Trimethylaluminum (TMA) and water has been used as precursors. A compact multiple silt gas source head has been used to transport the precursors and the inert gas to the surface of the substrate and to efficiently remove the bye products and the unreacted gases from the reaction zone. The films deposition has been carried out under the working pressure of 740 Torr, which is very near to the atmospheric pressure. Thin films were developed under a promising growth rate of ~1 Å/cycle at a carefully optimized web velocity of 7 mm/second. The deposited Al₂O₃ thin films showed good morphological, chemical, and optical properties. The films demonstrated very low root mean square roughnesses (Rq) of ~1.73 nm. The fabrication of Al₂O₃ thin films was confirmed through X-ray photoelectron spectroscopy (XPS) analysis and its characteristic peaks of Al 2p, Al 2s and O 1s were appeared at the binding energies of 74 eV, 119 eV and 531 eV, respectively. The compositional study was also supported by conducting Fourier transform infrared spectroscopy (FTIR) analysis. The optical transmittance of more than 85 % in the visible region was observed for the films. The electrical characterization of memristor devices showed that the Al₂O₃ encapsulation has a prominent influence on their performance, and life time. The results reveal that the R2R-AALD technology has a great potential for mass production of thin films and has a promising future in the field of flexible electronics.

9:15 AM PM03.09.02
Hybrid Thin Films Prepared by Solution Processing and ALD for Ambipolar Thin-Film Transistor Devices  Jaspreet Kainth1, Martyn A.
Hybrid active layers comprising of both inorganic and organic semiconducting materials are becoming more promising due to the ability to produce inexpensive, versatile and tailored electronic devices such as thin film transistors (TFT) or photovoltaic (PV) devices. By combining the advantages of the single components, it becomes possible to produce devices with the high stability of inorganic and the mechanical flexibility of organic materials. TFTs generally exhibit unipolar behaviour, where the dominant charge carrier in the channel is either electrons or holes. However, recent work has demonstrated the use of a hybrid layer consisting of poly(3-hexylthiophene-2,5-diyli) (P3HT) on top of ZnO in TFTs which exhibits ambipolar behaviour. These solution processed devices exhibit lower saturated mobilities compared to their single component counterparts, however well-balanced electron and hole mobilities are achieved in their hybrid devices. There is scope for further optimisation of these devices, including reversing the active layer order and exploring alternative deposition techniques.

Atomic layer deposition (ALD) is a thin film deposition technique which produces thin, conformal films due to the precise control over the thickness and composition of films on the atomic scale. The ability to grow ZnO films with such precision and at low temperatures results in ALD having good compatibility with organic materials. The growth of ZnO relies heavily on the surface chemistry therefore varies with the type of substrate. As a result, the nucleation and growth of ZnO on different polymers results in variations in morphology and electrical properties. Previous studies have explored the growth mechanism of ZnO onto P3HT via ALD, showing that the precursors are able to vapour diffuse into amorphous regions of the polymer thin film resulting in incorporation of ZnO within the polymer nanostructure. Such hybrid structures have also been successfully incorporated into PV devices. In this contribution we investigate the well-studied P3HT/ZnO systems to develop the growth of oxide layers directly onto polymer thin films in TFT devices, comparing their performance with their single component counterparts. Our methodology is simple, first depositing P3HT from solution and subsequently ZnO by ALD. We demonstrate an ambipolar charge transport for these hybrid TFTs. Following this, the growth behaviour of ZnO onto alternative p-type semiconducting polymers, such as poly[p-phenylene vinylene] and poly(9,9-diocetylfluorene-alt-benzothiadiazole), are explored. The observed effects of polymer variation is investigated by examining the crystallographic and morphological characteristics, and their potential ambipolar properties are studied by investigating their electronic properties.

Hierarchically structured solid scaffolds are often used to improve light absorption and carrier collection in thin-film photovoltaics. The structure can simultaneously optimize the rates of light absorption, carrier collection at the semiconductor-liquid junction, and mass transport of reactants to improve the effective energy conversion properties of the material. However, the scaffolds require a continuous transparent, conductive coating to function as an electrode and maintain electrical contact to the entire, tortuous surface. The electrochemically robust transparent conducting oxide (TCO) fluorine-doped tin oxide (FTO) can only be grown by line-of-sight physical deposition methods such as RF sputtering or spray pyrolysis, which in general prevents the deposition of uniform thin coatings of FTO on the interior of a hierarchically structured scaffold. Other TCOs (tin-doped indium oxide (ITO), aluminium-doped zinc oxide (AZO)) can be grown conformally by surface specific methods such as atomic layer deposition (ALD). ITO and AZO films are only stable at near-neutral pH, limiting their use in photocatalytic energy conversion. Here, we describe a strategy for improving the stability of ALD-deposited AZO films for anodic operation in alkaline electrolytes. The addition of a conformal, nanoscale TiO2 coating preserves a conductive AZO film for more than 24 hours at pH > 13. This is an improvement of several orders of magnitude compared to the lifetime of pure AZO films. Although the TiO2 coating is not significantly conductive alone, we observed an improvement in the conductivity of the layered AZO/TiO2 film. The TiO2-coated AZO film can be used as an electron collector on hierarchically porous scaffold formed from close-packed inorganic silica spheres. The improved electrochemical stability suggests that this approach will greatly benefit the fabrication of ultra-thin film photoanodes based on alkaline-stable semiconductors, such as the ternary metal oxide systems NiMnO4 and BiVO4.

Atmospheric Pressure Plasma Enhanced Spatial ALD of Silver from a New Halogen-Free Precursor

Plasma enhanced atomic layer deposition (PE-ALD) affords excellent-quality thin-films for various applications [1]. However, conventional ALD is vacuum based and imposes limits toward high-throughput and low cost manufacturing. To overcome these limits, spatial PE-ALD at atmospheric pressure has been introduced [2]. We have shown outstanding gas diffusion barriers and semiconductor thin-films grown by spatial PE-ALD, recently [3,4]. For the PE-ALD of metals, reducing plasmas are needed. As of yet, work on spatial PE-ALD of metals at atmospheric pressure is very limited, as is the choice of suitable Ag precursors. In this work, we report on the growth of Ag by spatial PE-ALD at atmospheric pressure from a novel halogen-free, monomeric and volatile carbene-based Ag precursor at substrate temperatures as low as 80°C. The results are compared to those obtained from the more established precursor [Ag(fod)(Pet3)] (FOD), which contains fluorine, phosphorous and oxygen. An atmospheric pressure dielectric barrier discharge with Ar/H2 as working gas is used as reducing agent for both compounds. Using Rutherford backscattering spectrometry, a growth rate of 2.1 * 10^11 atoms cm^-2 cycle^-1 (corresponding to an equivalent of 0.36 Å cycle^-1) was obtained for the new precursor, as opposed to 0.3 Å cycle^-1 for the FOD precursor.[5] The slightly enhanced growth rate could probably be attributed to the higher reactivity of the carbene based Ag precursor. X-ray photoelectron spectroscopy confirmed that Ag films from the FOD precursor deposited by atmospheric pressure spatial PE-ALD contained a high level of fluorine residues. These residues could be efficiently avoided by using the new carbene-based precursor. Furthermore, growth characteristics in dependence of process parameters like deposition speed and substrate temperature as well as saturation of the precursor were investigated. The substrate temperature was reduced to temperatures as low as 80°C to reduce the mobility of the silver atoms on the substrate surface and thus the percolation threshold. The prospects to use these grown Ag layers to create semi-transparent electrodes for thin-film optoelectronic devices are discussed.

References:
During the last few years, atomic layer deposition (ALD) has been highlighted in the semiconductor industry. As device performances have been enhanced, the topography of the device structures have become more complex, and consequently, the requirements on the step coverage have become much more important. ALD is one of the best techniques to deposit conformal films on topographically complex structures. Also, the dimensions of the features have become smaller and narrower. Consequently, the required thickness of the films becomes less, thus low growth rate, one of the main drawbacks of ALD, is becoming less important. When the ALD technique was in the research phase for semiconductor applications, almost all studies were executed with single-wafer processing type reactors. However, as ALD is finding their way into high volume semiconductor manufacturing, the processing cost becomes an important factor to be taken into account. This has resulted in an introduction of batch-type ALD systems, particularly in dynamic random-access memory and flash memory fabs that are cost-sensitive.

As increasing the volume of the batch-type ALD reactor to enhance throughput, it became more difficult to deposit uniform films over the whole wafers, i.e., decreased within-wafer (WIW) uniformity and wafer-to-wafer (WTW) uniformity. We observed that the WIW and WTW uniformities are affected by the pulse step in ALD process. In this study, we developed a dynamic purging process and achieved excellent WIW and WTW uniformities at more than 80-wafer batch size. The dynamic purging process is composed of cyclic steps with purging and vacuum pumping. As comparison studies, we also checked the WIW and WTW uniformities with normal purging processes. We deposited Al2O3 films using tri-methyl aluminum (TMA) and ozone as Al and O sources, respectively, with N2 as a purge gas. With the dynamic purging process, we obtained enhanced WIW and WTW uniformities more than 50%. The dynamic purging process can be applied to all types of ALD reactors to increase uniformity, resulting in enhanced throughput.

Assembly of microscale objects with ever-decreasing sizes is essential for automated production of integrated electronic devices such as micro-LED displays. Here, we introduce a new engineered surface, comprising carbon nanotube (CNTs) forests coated with nanometer-scale ceramic layers, for dexterous pick-and-placement manipulation solid objects using electrically switchable adhesion. We describe the electromechanical contact behavior of the nanosurface components, which are mechanically soft, have low intrinsic adhesion, and can be rapidly switched using with 100x greater adhesion by application of an electric potential to the CNTs. The large range of tunable adhesive strength accompanied by the low intrinsic adhesion allows manipulation of objects whose small sizes dictate surface forces dominate over gravity. We demonstrate pick-and-place manipulation of a variety of objects including colloidal particles (metal, ceramic, polymer) with diameters from 0.5-30 μm, silver nanowires (~12 μm long), and unpackaged light emitting diode (LED) chiplets (~170 μm). These manipulations do not require chemical/thermal surface modification or additional adhesives, demonstrating the versatility of this new approach.

There is a growing industrial need for manufacturing technologies that can print devices with high resolution (< 10 microns) and at high throughput. Conventional flexography is limited in resolution due to the instabilities in the ink loading and transfer mechanisms. A recent invention from our research group, engineered nanoporous stamps composed of polymer coated carbon nanotube (CNT) forests, are highly porous (~90%) and can retain the ink within their volume rather than on their surface only and has been used to print micro-scale features with highly uniform ink layer thickness.

In this talk, we explore the liquid transfer behavior from engineered nanoporous printing stamps using a high-speed visualization system and discuss the governing physics enabling the high-resolution high-speed printing. We conducted experiments using a custom-built printing apparatus which enables printing on flat and curved substrates by precisely controlling the force and printing speeds while observing the printing process in the time scales of milliseconds using a high magnification high speed imaging system. We observe all the steps in printing and describe the details of liquid meniscus evolution that lead to the ink transfer. Then we theoretically and experimentally study the dynamics of liquid spreading and receding, emphasizing the effects of approaching and retraction speeds. Finally, we discuss how our understanding of ink transfer physics can be applied to the process control of contact printing for the precision electronics manufacturing.

Large-area, layer-by-layer transfer molding requires an adhesion strategy that facilitates transfer to the substrate by maximizing interlayer bond strength while minimizing stamp demolding force. A size dependence on transfer rate was observed for plasma bonding at the nano-scale in both batch and continuous processes using a conventional plasma cleaner and corona treatment, respectively. We study the possible contributions to this size dependence by transferring poly(dimethylsiloxane) (PDMS) lines with periods down to 140 nm into woodpile structures from perfluoropolyether (PFPE) stamps at 10-30 sec exposure times of 1-3 seconds showed successful bonding, while brittle delamination occurred at the more conventional longer exposure times of 30-60 seconds. In addition, demolding force displayed significant anisotropy depending on peel orientation with respect to the line direction. The results presented here offer insights into plasma bonding at the nanoscale and offer a pathway to rapid, scalable bonding strategies for printing and microfluidics applications.

Technologies for Multi-Material Additive Manufacturing of Embedded Heating Devices for Printable Sorbent in Life-Support Systems in Space Travel Applications

Jamie Thompson1, 2, 3, Charlotte Bellejean4, Camille Petit5 and Gregory Whiting4; 1NASA Ames Research Ctr, Moffett Field, California, United States; 2Materials, Imperial College London, London, United Kingdom; 3EMDL, Xerox PARC, Palo Alto, California, United States; 4Mechanical, University of Colorado at Boulder, Boulder, Colorado, United States; 5Chemical Engineering, Imperial College London, London, United States.
Kingdom.

Life support is the most essential process in human space flight. Currently, on board the International Space Station (ISS), carbon dioxide is removed via a four-bed molecular sieve system. The involved processes are heavily dependent on heating large containers of sorbent material during sorbent regeneration at a large energy cost. Therefore, any technologies that minimize the power requirements or turnover time of life support processes are invaluable for human space exploration.

Printed sorbent heater composites produced via additive manufacturing can be used for in-space CO2 capture and conversion processes. Through the development of multi-material printing technologies for ceramics and conductors, a heating element was successfully embedded within a printed sorbent device, allowing for more efficient and quicker localized heating from within the sorbent material. Embedded heaters will significantly minimize energy consumption during sorbent regeneration. Devices are manufacturable with a single print process and only require a post-printing heat treatment before being ready for use in a sorbent bed system. The processes are compatible with both terrestrial and space manufacturing techniques.

The evolution of these technologies explored the use of both metallic and nonmetallic conductor inks, as well as ceramic-conductor composite inks. Binders were also explored as part of the ink development to assess their role in both extrusion and drying/curing post processes. Pre-printing ink preparation methods capable of producing foams directly from homogenous solid phase solutions were developed to allow tunable porosity with minimal effects on printability. Changes to the nano, micro, and macrostructure of the sorbent materials were characterized to assess the extent of activation/deactivation caused by preparation, printing, and heat treatment steps.

11:45 AM PM03.09.10
Development of a Conductive Biodegradable Ink for Multi-Process Additive Manufacturing Madhur Atreya1, Gabrielle Marinick2 and Gregory Whiting3; 1Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 2Chemical and Biological Engineering, University of Colorado Boulder, Colorado, United States.

Widely distributed electronic systems for environmental monitoring can enable the collection of large data sets useful for resource optimization in areas such as agriculture. However, the use of such sensor systems is limited by a number of factors including unit cost and the potential for creating significant amounts of persistent electronic waste in the environment.

Continued research into transient electronic materials and devices has led to a number of available options for biodegradable conductive materials. However, development of biodegradable high-conductivity materials suitable for digital additive manufacturing under ambient conditions remains a challenge.

Building on previous work, we have created solution-based, conductive direct-write inks consisting of various metal particles (such as tungsten) and biodegradable polymeric binders (such as poly(lactic acid)). These printed conductors degrade under a combination of microbial action and water solubility in a predictable manner. Combining the direct-ink writing (DIW) process of these conductors with other digital additive processes, such as fused-deposition modelling (FDM), allows for the fabrication of three-dimensional electronic structures and complex geometries that enable the control of degradation time and mechanical properties.

Based on these materials and processes, a degradable sensor package for examining soil moisture was evaluated, with electronic properties, degradation characteristics and ecotoxicity of resulting by-products systematically analyzed.

1:30 PM PM03.10.01
Processing and Characterization of Reinforced Polymer Matrix Nanocomposites with Graphene and h-BN Nanoflakes Arab H. Hussein, Assimina Pelegri, Stephen D. Tse, Bernard Kear and Zhizhong Dong; Rutgers University, Piscataway, New Jersey, United States.

In this study, graphene (G) and hexagonal boron nitride (h-BN) microscale powders are exfoliated to nanoscale flakes in a liquid phase of poly-methyl methacrylate (PMMA) solution by an in-situ high shear process. G and h-BN are separately investigated for exfoliation and improvement of performance properties with the polymer. With pure PMMA as a reference, mechanical characterization, including nanoindentation test (strength and stiffness) and dynamic mechanical analysis (DMA), were conducted on the reinforced polymer matrix nanocomposite systems. The surface morphology and nanoflake interface within the polymer matrix are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Raman spectroscopy is used to determine the number of layers and the dispersion of the 2D flakes in the matrix, via the distribution of peak positions and intensities as a function of wavelength. The results demonstrate improvement in the final mechanical properties. During processing, changes in the viscoelastic behavior during exfoliation of graphene in the polymer is noted, along with G being more reactive than exfoliated h-BN within the polymer matrix.

1:45 PM PM03.10.02
Characterization of Hierarchical Composites with Glass Fiber/Carbon Nanotube using Alternating Current Electrophoretic Deposition Dae Han Sung1, Sagar Doshi1, Andrew Rider1 and Erik Thostenson1; 1Department of Mechanical Engineering and Center for Composite Materials, University of Delaware, Newark, Delaware, United States; 2Defense Science and Technology Group, Melbourne, Victoria, Australia.

The introduction of nanomaterials like carbon nanotubes (CNT) to conventional fiber-reinforced composites creates hierarchical structures where reinforcing fibers, which usually have diameters in the micrometer scale, are surrounded by nanoscale materials. In this research, we used an alternating current electrophoretic deposition (AC-EPD) technique to deposit CNTs directly onto the glass fibers. We expected that AC-EPD would reduce the influence of water electrolysis by which trapped hydrogen or oxygen bubbles made the gap between substrate fibers and electrodes, thereby facilitating a denser CNT network within fiber bundles and filaments as compared to direct current EPD. We compare two different aqueous CNT dispersions, anodic and cathodic, using a novel ozonolysis and ultrasonication technique that results in dispersion and functionalization in a single step. In the anodic solution system, ozone oxidation makes CNTs negatively charged (anions) with functional groups such as hydroxyl and carbonyl groups. On the other hand, in the cathodic system CNTs were functionalized with a polyethyleneimine (PEI) dendrimer where the amine groups protonate under acidic conditions and, in turn, became cations. Anions and cations moved to positively charged electrode (anode) and cathode, respectively, when electric potential was applied in each system. Characterization of the coated fiber surfaces and composites revealed a uniform coating of carbon nanotubes and penetration between the bundles. AC-EPD is novel and simple approach to modify interface properties of CNT hierarchical composites and has great potential to scale
up hybridizing process of nanomaterials which can be utilized as multifunctional applications.

2:00 PM PM03.10.03
Continuous Production of Carbon Nanotube-Grafted Carbon Fibres—A Route to Manufacture Hierarchical Composites

Hugo De Luca1, David B. Anthony2, Chengyin Liu1, Suresh Kumar Raman Pillai3, Emile Greenhalgh1, Alexander Bismarck1, M. B. Chan-Park1 and Milo Shaffer1; 1Materials, Imperial College London, London, United Kingdom; 2Chemical Engineering, Imperial College London, London, United Kingdom; 3Aeronautics, Imperial College London, London, United Kingdom; 4School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore.

The mechanical properties of fiber-reinforced composites depend on the properties of the fiber/matrix interface where stress concentrations prevail. Grafting of carbon nanotubes to produce a “hairy” or “fuzzy” carbon fiber creates hierarchical reinforcements, combining two different reinforcement length scales, in this instance micrometer and nanometer. This approach improves the interaction between fibers and polymer matrices, and can enhance thermal and electrical functionality of the final composite. Generally, hairy fiber production is limited to batch processes due to harsh synthesis conditions (e.g. high temperature, inert environment) inherent to chemical vapor deposition, and have only recently been scaled-up to continuous production. Carbon nanotube-grafting finally meets industry prerequisites for its implementation in carbon fiber production lines. In this work, the continuous production of carbon nanotube-grafted-carbon fibers was performed in an open chemical vapor deposition reactor with continuous in-line catalyst deposition. This patented technology can be adapted to different fibre types, including as whole tows, while ensuring that the substrate's initial mechanical properties are retained. At the single fiber level, the presence of a uniform 200 nm long carbon nanotubes coverage on the surface of carbon fibers led to an increase in interfacial shear strength of up to 7.5% (96.7 MPa) when compared to the baseline unsized material (89.4 MPa). Epoxy, stiffened through the addition of single-walled carbon nanotubes (up to 1 wt.%), dispersed with an epoxide containing tri-block (PMACEP-PI-PMACEP), showed a further improvement in interfacial shear strength of up to 3.5% (100.2 MPa) when compared to carbon nanotube-grafted carbon fibers in neat epoxy. The use of a nano-engineered epoxy, with continuously produced “hairy fibres” effectively displaces the weaker phase from the surrounding matrix interphase directly to the CNT/carbon fibre interface, demonstrating a synergistic effect and improved interfacial properties.

2:15 PM PM03.10.04
Multifunctional Structural Energy Storage and Stiffening of Fibre-Reinforced Polymer Composites Through Aerogel Addition

David B. Anthony1, Sang N. Nguyen1, Hui Qian1,2, Shi Xu1, Aryaman Singh1, Alexander Bismarck1,2, Milo Shaffer1 and Emile Greenhalgh1; 1Imperial College London, London, United Kingdom; 2Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong; 3Chemistry, University of Vienna, Vienna, Austria.

The desire to reduce overall weight in devices is a key driver for development; the ability to combine composites with energy storage which provide, simultaneously, structural integrity has the potential to replace single function components. To achieve this ambition, the multifunctional component must perform both functionalities sufficiently, but often there is a trade off in performance which is a significant challenge to overcome.

The performance and application of polymer-matrix fibre composites is often limited by matrix-dominated failures, both mechanical and functional. There is, therefore, considerable interest in the use of nanocomposite matrices, for example using resins filled with carbon nanotubes or graphene, to introduce both intralamellar and interlamellar reinforcement of the resulting hierarchical composites. The objective is to improve delamination resistance, through-thickness properties, and compression performance, without compromising the in-plane tensile response. The potential to improve thermal, fire retardance, as well as solvent and electrical conductivity, offers additional opportunities especially for multifunctional materials. However, due to processing constraints, the nano-reinforcements are typically present only at low loading fractions and in discontinuous form, limiting the level of enhancement.

Here, we present an alternative strategy, to form a rigid bicontinuous reinforcing network throughout the matrix volume. A suitable precursor is first infused into a structural fibre weave or other preform, then converted to form a porous monolithotic aerogel/xerogel matrix, with characteristic lengthscales around a few tens of nanometres. The presence of the reinforcing fibres allows the aerogel/xerogel to form a stable, handleable, structure. Both the rigid network and the porosity are bicontinuous, allowing a second matrix resin phase to be infused. This second phase may be a soft multifunctional phase, for example, one that can support ion conductivity for use in structural supercapacitors.

Pore purely mechanical properties can be investigated when the second phase is a conventional structural epoxy resin. We have studied two analogous systems, one combining carbon aerogel with carbon fibres, and one combining silica aerogel/xerogel with glass fibres, in both cases adding a secondary epoxy resin. In the carbon system, there are increases in compressive and tensile stiffness respectively, but drops in interlaminar, compressive and tensile strengths, due to poor fibre-matrix interfaces after processing. Measurements focussing on matrix performance, using +/-45° tests indicate intrinsic improvements. In the glass system, the interface quality is retained, such that interlaminar and compression properties are all maintained or improved. These initial studies highlight a family of bicontinuous nanostructured matrix systems for hierarchical composites, which have great potential and are worthy of further study.

2:30 PM PM03.10.05
Ultraitlight Xylem-Like Conductive 3D Porous Composite with Cellulose Nanofiber and Ag Nanowire

TaeGeon Kim1, Jongbeom Kim1, Seungmin Hyun2 and Seung Min J. Han1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Ultra-light porous structures demonstrating high strength-to-weight ratio and large surface area and porosity has been of recent interest especially due to their potential application as structural material such as the framework of airplane or vehicle (high strength to weight ratio), catalyst supports (large surface area), thermal insulation, and shock damping or acoustic absorption (high porosity). In order to fabricate such a structure, direct foaming of the melt or powder metallurgical (PM) technique is commonly used by blowing a gas in the liquid alloy or by admixing of foaming agents with reactive sintering. However, Metallic foam made by PM techniques represent only 65 - 90 % of the porosity that showed limitation of lightweight in the structure. Recently, freeze casting method was suggested to solve the limitations of conventional fabrication methods, which uses ice crystal as a template instead of light-induced polymer templates. Pore orientation of the structure can easily be controlled by directional freeze casting method to yield geometrically patterned structures. Therefore, in this study, we propose a xylem-like structure using a composite of cellulose nanofiber and Ag nanowire that satisfies both the high strength enhancement of metal and ultra-light weight of organic with small relative density.

To fabricate the xylem-like 3D porous structure, a mixture of cellulose nanofiber (CNF) and Ag nanowire solution was used in the one-step freeze casting process. CNF (diameter: ~20 nm, length: a few microns) is a fibrous material that demonstrates significantly higher modulus compared to conventional polymer or organic materials that makes CNF more suitable as a structural support for free standing structure. In addition, CNFs can form continuous 2D wall via strong hydrogen bonds and van der Walls forces as they fill in the empty remaining space in between the ice crystals, and thus CNF is chosen as a backbone in the 3D composite, which is further strengthened by the addition of Ag nanowires. This study successfully fabricated a CNF + Ag nanowire porous structure in the bulk form with controlled pore orientation through a low cost process of directional freeze casting. The strengthening effect of the amount of the Ag nanowire addition was achieved 14.3 times higher compressive strength (from
7 kPa to 100 kPa) below 1% of total relative density for xylem-like CNF + Ag nanowire structure. Especially, addition of 0.29% of relative density for Ag nanowires in xylem-like CNF structure showed same order of compressive strength with higher scalability compared to Ni metallic microlattice in micro scale. In addition, more than 5mg/cm3 of Ag nanowire embedded 2D CNF wall is also able to offer sufficient conductivity that maybe suitable for a variety of electronics applications such as battery or supercapacitor electrode.

**SYMPOSIUM PM04**

High-Entropy Alloys  
November 26 - November 28, 2018

Symposium Organizers  
Easo George, Oak Ridge National Laboratory  
Haruyuki Inui, Kyoto University  
Dierk Raabe, Max Planck Institute for Iron Research  
C. Cem Tasan, Massachusetts Institute of Technology

Symposium Support  
JEOL USA, Inc.  
Kyoto University  
Thermo-Calc Software Inc.

* Invited Paper

**SESSION PM04.01: Mechanical Properties and Cryogenic Phenomena**  
Session Chair: Peter Liaw  
Monday Morning, November 26, 2018  
Hynes, Level 1, Room 105

8:30 AM *PM04.01.01*  
**Damage-Tolerance in Medium- and High-Entropy CrCoNi Alloys**  
Robert O. Ritchie1, 2, Jun Ding2, Mark Asta1, 2, Bernd Gludovatz3, Easo P. George1 and Qing Yu1; 1Materials Science & Engineering, University of California, Berkeley, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 4University of New South Wales, Sydney, New South Wales, Australia; 5Zhejiang University, Hangzhou, China.

Damage-tolerance is an essential characteristic of structural materials as it defines the combination of strength and toughness, properties that are often mutually exclusive. Certain medium- and high-entropy alloys, the equiatomic Cantor alloy CrMnFeCoNi and its derivatives such as CrCoNi, all of which are single-phase, fcc solid solutions, display exceptional combinations of strength (~1 GPa), ductility (~60-90%), and toughness (~200 MPa.m1/2), properties which are further enhanced at cryogenic temperatures. *In situ* TEM observations of fracture at 293K and 93K identify multiple deformation mechanisms, associated with these alloys' high friction stress yet low stacking-fault energy (SFE), that are activated at different stages of deformation and act synergistically to contribute to strength, ductility and toughness. For example, TEM studies on CrCoNi show that a hierarchical twin network is established at 293K associated with its low SFE. This network generates substantial 3-D barriers to dislocation motion, contributing to high strength and marked strain hardening, yet at the same time, the network provides multiple pathways for the easy dislocation motion, which provides for ductility - the perfect ingredients for exceptionally high damage-tolerance. We further examine the fundamental origin of these exceptional damage-tolerant properties by focusing on the potential effect of local chemical ordering in these alloys. Although difficult to observe experimentally, our DFT-based Monte Carlo simulations show that variations in the state of local chemical order can have a profound effect on the SFE, the twin boundary energy, the energy difference between the face-centered cubic and hexagonal-close packed phases (which affects the occurrence of transformation-induced plasticity), and even the energy of formation of vacancies and interstitials, all features that can have a marked influence on the mechanical properties. These results highlight the possibility of “tuning order in disorder” to ultimately achieve the science-based design and optimization of new high-entropy alloy systems with specifically desired combinations of macroscale mechanical properties.

9:00 AM PM04.01.02  
**Low-Temperature Deformation Pathways of a High-Entropy Alloy by In Situ Neutron Diffraction**  
Muhammad Naeem1, Haiyan He1, Bing Wang1, Stefanus Harjo1, Takuro Kawasaki2, Si Lan1, Zhenduo Wu1, HaiLong Huang1, Fan Zhang1, Zhouping Lu1 and Xin-Li Wang1; 1Department of Physics, City University of Hong Kong, Kowloon, Hong Kong; 2Japan Proton Accelerator Research Complex, Japan Atomic Energy Agency, Tokai, Japan; 3State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing, China.

High-entropy alloys, which consist of five or more alloying elements in equal molar ratios, are among the most promising new class of structural materials. Despite the complex chemistry, they can form a single phase solid-solution with an incredibly simple lattice, CrMnFeCoNi is a face-centered cubic (FCC), for example. Several deformation mechanisms are known to operate in high-entropy alloys. At room temperature, CrMnFeCoNi deforms like a conventional FCC alloy, showing clear stages of dislocation slip and dislocation entanglement. At liquid-nitrogen temperature, the dominant deformation mechanism changes from dislocation to twinning, leading to high strength and large ductility. Here we show that, at even lower temperature, the serrated deformation dominates. Deformation behavior of CrMnFeCoNi high-entropy alloy was studied at 15K by *in-situ* neutron diffraction, to obtain insights of the effect of low temperature on the underlying deformation mechanism and the corresponding evolution of structure. Due to the highly penetrating power of neutrons,
Bulk Cantor alloys were successfully manufactured through spray forming and yttrium oxides were introduced into Cantor alloys, exhibiting clear grain rich particles with size of 150 nm were observed in Cantor alloys. Additional yttrium oxides serve as pinning points to dislocation movement, and further refining and strengthening effect. Further research will focus on investigating creep resistance and irradiation response of HEAs and y-doped HEAs.

Nano scale yttrium oxides and chromium-rich particles were observed with bimodal size respectively in y-doped Cantor alloys. Whereas only chromium-rich particles were observed with bimodal size respectively in y-doped Cantor alloys. Furthermore, the effect of grain size on yield strength, both alloys show good combination of strength and ductility.

A yttrium-free and yttrium-doped (y-doped) Cantor alloys both displayed equiaxed FCC structure with average grain size of 10 and 5 μm respectively. A yttrium together with oxygen source is known to form dispersed yttria, leading to grain refinement and oxide dispersion strengthening in alloys. Y-24 (high mass flow rate) and powder metallurgy (refined microstructure) and is thus well-suited for manufacturing complex compositional alloys. Addition of yttrium to HEA (which is also called Cantor alloy), is the most extensively investigated one and exhibits many unique properties (e.g. good combination of strength and ductility down to 77 K, exceptional fracture toughness, and good ultimate tensile strength. Based on the alloy composition or thermo-mechanical processing, solid solution strengthening, precipitation strengthening, transformation-induced plasticity (TRIP) effect, twinning-induced plasticity (TWIP) effect can each contribute to strain hardening in FCC HEAs. The relative contributions of each of these mechanisms, however, have not been systematically investigated. In the current work, we designed two new FCC HEAs with high strain hardening rates but different solid solution strengthening levels. The deformation substructures of the two HEAs at specific strain levels were investigated by using electron channeling contrast imaging (ECCI) combined with electron backscatter diffraction (EBSD). The HEA with higher solid solution strengthening level showed not only higher strength but higher ductility as well. We attribute this abnormal solid solution strengthening effect to the different defect evolution behaviors of the two FCC HEAs. The origins of this observation were systematically studied and will be presented in this talk.

High strain hardening rate plays a key role in enabling face centered cubic (FCC) high entropy alloys (HEAs) to have excellent ductility, high fracture toughness, and good ultimate tensile strength. Based on the alloy composition or thermo-mechanical processing, solid solution strengthening, precipitation strengthening, transformation-induced plasticity (TRIP) effect, twinning-induced plasticity (TWIP) effect can each contribute to strain hardening in FCC HEAs. The relative contributions of each of these mechanisms, however, have not been systematically investigated. In the current work, we designed two new FCC HEAs with high strain hardening rates but different solid solution strengthening levels. The deformation substructures of the two HEAs at specific strain levels were investigated by using electron channeling contrast imaging (ECCI) combined with electron backscatter diffraction (EBSD). The HEA with higher solid solution strengthening level showed not only higher strength but higher ductility as well. We attribute this abnormal solid solution strengthening effect to the different defect evolution behaviors of the two FCC HEAs. The origins of this observation were systematically studied and will be presented in this talk.

SESSION PM04.02: Local Structure and Mechanical Properties
Session Chair: Alice Hu
Monday Morning, November 26, 2018
Hynes, Level 1, Room 105

Universal Relation Between Critical Resolved shear Stress and Mean Square Atomic Displacement in Random High Entropy Alloys Shigenobu Ogata; Haruyuki Inui; Wei Wang; Osaka University, Osaka, Japan; ESISM, Kyoto University, Kyoto, Japan; Kyoto University, Kyoto, Japan;
High-entropy alloys (HEAs), are multi-component random solid solution alloys with nearly an equiatomic composition, have been receiving tremendous attention due to the excellent cryogenic temperature ductility, superior mechanical strength and good wear resistance, exceptional damage tolerance. Design and development of new HEA having further excellent mechanical properties is one of the challenges in these days. Since trial and error methods take long time and need cost, a general rule predicting mechanical response based on computable value by first-principles is truly desired. In our current study, we focus on critical resolved shear stress (CRSS) of HEA. It is well-known that CRSS of HEA is much higher than single element pure metals. Using molecular dynamics (MD) simulations with root-mean-square atomic displacement (RMSAD) tunable Jennard-Jones potential, we computed a normalized CRSS by shear modulus as a function of a normalized RMSAD by Burgers vector length for different concentration and component of random alloys at zero temperature. The results uncover that almost linear one to one relation between the normalized CRSS and RMSAD, which stands over very wide RMSAD range, in addition the relation depends quite weakly on the concentration and component of alloys. The universality of relation is also confirmed by MD using more realistic EAM potential and available actual experimental data. This implies that RMSAD computable by first-principles can be a general CRSS predictor of random alloys, that may strongly support high-throughput design of high strength random alloys.

11:00 AM PM04.02.02 Property Targeted Quantitative Design of Complex Concentrated Alloys Hyunseok Oh1, SangJun Kim1, Khoroglkhhus Odbudakhirh2, Wookha Ryu1, Kookhoon Yoon1, Sai Mu1, Fritz Körmann2, Yuji Ikeda1, C. Cem Tasan1, Dirk R. Raabe1, Takeshi Egami2 and Evun Soo Park1; Seoul National University, Seoul, Korea (the Republic of); 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany; 3Joint Institute for Computational Sciences, University of Tennessee and Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 4Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 5University of Tennessee, Knoxville, Tennessee, United States.

Despite their unique combinations of mechanical and functional properties the property targeted quantitative design of complex concentrated alloys (CCAs) is difficult due to the complex local atomic environment. Here we present an effective quantitative design approach predicting the solid solution strength of complex concentrated alloys based on the quantum mechanically driven atomic level pressure approximation. We show that the dominant factor for the solid solution strengthening in single phase face-centered cubic complex concentrated alloys consisting of 3d transition metal elements is the variation in the atomic level pressures and discuss (i) which alloy constituents dominate the atomic level pressure, and (ii) how to rationalize configurational fluctuations of the atomic-level pressure. Finally, we establish a design recipe which uses elemental atomic-level information without explicit electronic-structure calculations as an efficient vehicle for more systematic and constitutive structure-property design of CCAs.

11:15 AM PM04.02.03 Variable Chemical Order Opens a New High-Entropy Playground Ong-Jie Li1, Howard Sheng2 and Evan Ma1; 1Johns Hopkins University, Baltimore, Maryland, United States; 2Department of Physics and Astronomy, George Mason University, Fairfax, Virginia, United States.

High-entropy alloys (HEAs) were presumed to have a configurational entropy as high as that of ideally mixed solution of multiple elements in near-equal proportions. However, inevitable enthalpic interactions render such chemically disordered solid solution (SSs) rare and metastable, except at very high temperatures. Here we highlight a different “high entropy” signature that sets HEAs apart from traditional solvent-solute SSs. We show that HEAs can be defined as concentrated SSs offering an unusually large configurational space for (local) chemical ordering (LCO) and hence rich property possibilities. Our atomistic simulations with realistic empirical interatomic potentials for NiCoCr demonstrate that at a given overall composition the LCO changes conspicuously with alloy processing. The variable LCO gives rise to a broad spectrum for any generalized fault energy, in terms of both its sample-average and spatial variation (local fault energy on nanometer scale), significantly influencing the dislocation mechanisms and strength. As such, the partial chemical order in a single-phase HEA opens a vast playground not accessed by either random SSs or ordered intermetallics.

11:30 AM PM04.02.04 Tunable Stacking Fault Energies by Tailoring Local Chemical Order in CrCoNi Medium-Entropy Alloys Jun Ding1, Qin Yu1, Mark Asta1,2 and Robert O. Ritchie1,2; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2University of California, Berkeley, California, United States.

High-entropy alloys (HEAs) are an intriguing new class of metallic materials due to their unique mechanical behavior. Achieving a detailed understanding of structure-property relationships in these materials has been challenged by the compositional disorder that underlies their unique mechanical behavior. Accordingly, in this work, we employ first-principles calculations to investigate the nature of local chemical order and establish its relationship to the intrinsic and extrinsic stacking fault energy (SFE) in CrCoNi medium-entropy solid-solution alloys, whose combination of strength, ductility and toughness properties approach the best on record. We find that the average intrinsic and extrinsic SFE are both highly tunable, as the degree of local chemical order increases. The state of local ordering also strongly correlates with the energy difference between the face-centered cubic (fcc) and hexagonal-close-packed (hcp) phases, which affects the occurrence of transformation-induced plasticity. This theoretical study demonstrates that chemical short-range order is thermodynamically favored in HEAs and can be tuned to affect the mechanical behavior of these alloys. It thus addresses the pressing need to establish robust processing-structure-property relationships to guide the science-based design of new HEAs with targeted mechanical behavior. This work was supported by DoE-BES-DMSE, under Contract No. DE-AC02-05CH11231.

11:45 AM PM04.02.05 Lattice Distortion Measurement Using HR-STEM Yi Chou1, Chanho Lee2, Peter K. Liaw2 and Yi-Chia Chou1; 1Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan; 2Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

High entropy alloys (HEAs) have attracted attention for its excellent mechanical properties, such as very high yield strength even at elevated temperature or radiated condition,[1] which can be applied to high temperature (up to 1000 celsius degree) casting and nuclear application. HEA are alloys containing 5 or more elements in equal or near equal atomic percent to maximize the mixing entropy. Lattice distortion results from the atomic configuration of HEAs is expected to contribute effects on mechanical properties. In this paper, we examine and measure the lattice distortion two HEAs, NbTaTiV and NbTaTiVZr. Average lattice distortion factor is the commonly used factor to describe the magnitude of lattice distortion, and it is related to effective distance of two atom d0 and the average of effective distance d. Both d0 and d can be obtained from theoretical calculations. The measurement can be carried out in synchrotron or neutron diffraction, where d is the experimental data collected from diffraction peaks. Here we perform the imaging in STEM and the measurements from STEM images to evaluate the average lattice distortion factor. The STEM samples were prepared using FIB equipped with in-situ pick up system, and the thin HEAs were attached to grids with platinum deposition to fix the position for reducing the drift. HR STEM HAADF images were taken when the drift rate is below 0.5 Å/min and fitted with 2D Gauss equation to
specify the atomic position and intensity. The intensity guides to calculation of the Z contrast of HAADF images, and it clarifies that the atoms distributes randomly. The atomic position provides the guide to measure the lattice distortion by calculating the atomic displacement from two orthogonal plane which was defined as \(d^{\text{st}}\), and the standard deviation was taken from the displacement which in turn was the average lattice distortion \(u^{\text{st}}\). With the method, average lattice distortion is directly obtained from STEM images. The average lattice distortion factor of NbTaTiV and NbTaTiVZr are in good agreement with theoretical and synchrotron diffraction results.

Reference:

SESSION PM04.03: Elementary Deformation Mechanisms
Session Chair: C. Cem Tasan
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 105

1:30 PM *PM04.03.01
In Situ TEM Characterization on Deformation of NiCrCo Alloy at Room and Cryogenic Temperature Qian Yu1, Robert O. Ritchie2, Easo P. George1, Scott X. Mao1, Hongbin Bei1 and Bernd Gludovatz2; 1Zhejiang University, Hangzhou, China; 2University of California Berkeley, Berkeley, California, United States; 3Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 4University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

NiCrCo alloy shows good combination of strength and ductility at both room and cryogenic temperature. To understand how the strength-ductility trade-off can be defeated, we apply in situ, and aberration-corrected scanning, transmission electron microscopy to examine deformation mechanisms in the medium-entropy alloy CrCoNi that exhibits one of the highest combinations of strength, ductility and toughness on record. We find that a three-dimensional (3D) hierarchical twin network forms from the activation of the three twin systems. This serves a dual function: conventional twin-boundary (TB) strengthening from blockage of dislocations impinging on TBs, coupled with the 3D twin network which offers pathways for dislocation glide along, and cross-slip between, intersecting TB-matrix interfaces. The stable twin architecture is not disrupted by interfacial dislocation glide, serving as a continuous source of strength, ductility and toughness. However, as temperature deceases, multiple deformation mechanisms are activated which was thought unlikely since reduce of temperature usually increase the competition between different deformation modes.

2:00 PM PM04.03.02
In Situ TEM Straining Experiments in A3S and Cantor’s HEA Alloys at Liquid Nitrogen and Room Temperature Marc Legros1, Michal Mroz2 and Anna Fraczkiewicz2; 1CEMES CNRS, Toulouse, France; 2Ecole des Mines de Saint Etienne, Saint-Etienne, France.

The yield stress of a non-equiatomic HEA from the CoCrFeMnNi family (A3S® grade) is significantly increased compared to the equiatomic (Cantor’s) alloy of the same family. This behavior comes from a stable nanostructure, easily formed in the material after classical hot thermomechanical treatment (forging and annealing).

In situ TEM straining experiments were carried out in both alloys at liquid nitrogen and room temperature. Dislocations movements are analyzed with respect to the applied stress that is measured locally using dislocation curvature. Size effects due to the thin foil configuration are discussed. Strengthening mechanisms arise from classical dislocation/ obstacle (grain boundary, forest dislocations, twinning) interaction, but also from local distortions of the interface to the applied stress that is measured locally using dislocation curvature. Size effects due to the thin foil configuration are discussed. Strengthening mechanisms arise from classical dislocation/obstacle (grain boundary, forest dislocations, twinning) interaction, but also from local distortions of the interface. The atomic position provides the guide to measure the lattice distortion by calculating the atomic displacement from two orthogonal plane which was defined as \(d^{\text{st}}\), and the standard deviation was taken from the displacement which in turn was the average lattice distortion \(u^{\text{st}}\). With the method, average lattice distortion is directly obtained from STEM images. The average lattice distortion factor of NbTaTiV and NbTaTiVZr are in good agreement with theoretical and synchrotron diffraction results.

Reference:

The transformation induced plasticity (TRIP) effect is an ideal deformation mechanism for designing and tuning high-strength and yet ductile metallic materials. A recently developed dual-phase high entropy alloy (HEA) with a nominal composition of Fe50Mn30Co10Cr10 (at.%) shows an extraordinary combination of strength and ductility mainly owing to its TRIP effect, i.e. a sequential displacive transformation from the face-centered cubic (FCC) matrix to the hexagonal close-packed (HCP) phase [1-3]. In this study, we reveal the fundamental mechanisms of the displacive transformation in the dual-phase HEA at atomic scales. A combination of transmission electron microscopy (TEM), scanning TEM (STEM) and in-situ experiments unravels the detwinning and formation of hierarchical nanolaminated structures in the dual-phase HEA. The in-situ experiments conducted under low angle annular dark-field (LAADF)-STEM imaging reveals that the detwinning effect, i.e. formation of coherent \(\Sigma_3\) boundaries, induces a displacive transformation preferably at coherent \(\Sigma_3\) boundaries. In addition, owing to the positive and yet very low stacking fault energy of this specific dual-phase HEA (\(\sim 5.2 \text{mJ/m}^2\)), reversible displacive transformation from the HCP back into the original host FCC phase can also be induced during mechanical loading, in addition to the forward transformation from the FCC to the HCP. This complex sequence associated with the forward and backward transformation creates a hierarchical nanolaminated structure, which is strengthening the HEA without sacrificing any ductility.

Reference:

2:30 PM PM04.03.04
Light Weight High Entropy Alloys for Cryogenic Applications Kooknoh Yoon, Hyunseok Oh and Eun Soo Park; Seoul National University, Seoul, Korea (the Republic of)
High entropy alloy (HEA) has been studied due to its great mechanical properties such as strength, toughness, and so on. Moreover, it is reported that Cantor alloy, FCC HEA, shows extremely high toughness at cryogenic temperature due to nano-size twins that is formed under dynamic stress. In this context, many researchers are trying to utilize this novel material under cryogenic environments such as the Arctic, the outer space and so on. Meanwhile, cryogenic applications are closely related with weight-lightening, because materials for LNG carrier, space shuttle are used for transportations. Thus, in this study, we will report about an alloy design of TWIP/TRIP HEAs by controlling the stacking fault energy (SFE). In this, we developed a multiscale modeling approach for the simulations of mechanical behavior of HEAs. In the first step, the vacancy energy and stacking fault energy are calculated with density functional theory (DFT) methods. Based on the DFT calculations, we have developed an accurate embedded atom model (EAM) potential for large-scale molecular dynamics simulation of Al$_{0.1}$CrCoFeNi HEAs. The DFT calculation results for Al$_{0.1}$CrCoFeNi HEAs show that there is a large variation in stacking fault energy in a range of -79 to 46 m/Å$^2$, depending on the local atomic environments. The origin of the negative stacking fault energy is discussed from the thermodynamic metastability of FCC stacking sequence. The nano-twin generation and interactions during deformation are also explored preliminarily with the EAM potential.

**2:45 PM PM04.03.05**

**Multiscale Modeling of Mechanical Behavior of Al$_{0.1}$CrCoFeNi High-Entropy Alloy**

Yu-Chia Yang, Cuixia Liu, Chu-Nan Liu, Jeffrey Lloyd and Zhenhai Xu.

University of North Texas, Denton, Texas, United States; 2University of Texas at Dallas, Richardson, Texas, United States; 3Xian Technological University, Xi'an, China; 4Impact Physics, U.S. Army Research Laboratory, Aberdeen, Maryland, United States; 5Northwestern Polytechnical University, Xi'an, China.

High-entropy alloys (HEAs) have shown exceptional properties, including remarkable fracture toughness, high strength, and excellent resistance to fatigue. These properties of the HEAs result from their five-or more equiatomic components that lead to relatively high configurational entropy, relatively large lattice strains, and unique deformation mechanisms. However, the atomic-scale complexity presents challenges to explore the underlying mechanisms through computer simulations due to a lack of effective potentials. In this work, we have developed a multiscale modeling approach for the simulations of mechanical behavior of HEAs. In the first step, the vacancy energy and stacking fault energy are calculated with density functional theory (DFT) methods. Based on the DFT calculations, we have developed an accurate embedded atom model (EAM) potential for large-scale molecular dynamics simulation of Al$_{0.1}$CrCoFeNi HEAs. The DFT calculation results for Al$_{0.1}$CrCoFeNi HEAs show that there is a large variation in stacking fault energy in a range of -79 to 46 m/Å$^2$, depending on the local atomic environments. The origin of the negative stacking fault energy is discussed from the thermodynamic metastability of FCC stacking sequence. The nano-twin generation and interactions during deformation are also explored preliminarily with the EAM potential.

3:00 PM BREAK

**SESSION PM04.04: Microstructure Control for Mechanical Properties**

**3:30 PM *PM04.04.01**

**Microstructure Control and Resultant Change in Mechanical Properties in High Entropy Alloys**

Nobuhiro Tsuji, Tilak Bhattacharjee, Yu Bai, Nokeun Park, Shu Kurokawa, Pinaki Bhattacharjee, Rajeshwar R. Eleti and Shuhei Yoshida; 1Department Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Elements Strategy Initiative for Structural Materials, ESISM, Kyoto University, Kyoto, Japan; 3School of Materials Science and Engineering, Yeungnam University, Gyeongsan, Korea (the Republic of); 4Department Metallurgical and Materials Engineering, Indian Institute of Technology Hyderabad, Hyderabad, India.

High entropy alloys (HEAs) have a large capability for microstructure control through thermo-mechanical processing, since they are mainly composed of solid solution phases that are stable and deformable at wide range of temperatures. However, HEAs have been mostly studied in their as-cast or even as-homogenized states. In this presentation, some examples of microstructure controls in several kinds of HEAs are introduced. For example, fully-recrystallized ultrafine-grained microstructures with mean grain sizes of 200–400 nm could be obtained in CoCrFeMnNi and CoCrNi alloys. Such fine grain sizes are interesting from a viewpoint of nucleation of recrystallization. The ultrafine-grained HEAs showed very high yield strength compared with their coarse-grained counterpart, still maintaining excellent strain-hardening ability after yielding, which led to nice combinations of high strength and large tensile ductility. We have also succeeded in microstructure control in a eutectic HEA, AlCoCrFeNi2:1, through various thermo-mechanical processes and in enhancing the strength keeping adequate ductility.

**4:00 PM PM04.04.02**

**Design of Non-Equiatomic FeNiCoAl-Based High Entropy Alloys with Heterogeneous Lamella Structure Towards Strength-Ductility Synergy**

Cheng Zhang, Chaoyi Zhu, Tyler Harrington and Kenneth Vecchio; 1Materials Science and Engineering Program, University of California San Diego, La Jolla, California, United States; 2Department of NanoEngineering, University of California San Diego, La Jolla, California, United States.

Two non-equiatomic FeNiCoAl-based high entropy alloys (HEA) with heterogeneous lamella (HL) structures are fabricated through conventional thermomechanical processing. In the HL microstructure, fine-grain regions result from inhibited grain growth due to Zener pinning of boundaries by NiAl (B2) precipitates, while of coarse grained regions originate from grain growth within large deformation bands in the absence of precipitates. A back-stress strengthening mechanism, unique to deformation of heterogeneous microstructures, is verified through electron backscatter diffraction enabled geometrically necessary dislocation (GND) density analysis. Macroscopically, back-stresses in the current two HEAs with HL structures are measured from the loading-unloading-reloading experiment. This mechanism gives rise to the combination of both high strength and high ductility in HL-HEAs.

**4:15 PM PM04.04.03**

**Microstructural Design to Improve the Mechanical Properties of an Interstitial TRIP-TWIP High-Entropy Alloy**

Jing Su, Z. Li and Dierk R. Raabe; Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany.

High-entropy alloys (HEAs) have drawn considerable attention nowadays not only due to their massive solid solution structures and partly good mechanical properties but also for the reason that the concept uncovers a vast compositional space for future alloy development. Here we present a novel strategy of employing deformation-driven hierarchical microstructure design to enhance the mechanical properties of an interstitial carbon doped HEA. This is to combine the benefits of designing specific microstructure features with the compositional advantages of HEAs. The as-cast alloy was subjected to a sequence of thermo-mechanical processing including hot-rolling, homogenization, cold-rolling and tempering/annealing. A single FCC phase bimodal grain structure was obtained in the tempered specimen containing nano-grains (~50 nm) and large parent grains (10-35 μm) with pre-existing nano-twins.
Trinodal microstructures were produced upon annealing characterized by small recrystallized grains (<1 μm) associated with shear bands, medium-sized grains (1-6 μm) recrystallized through subgrain rotation or coalescence of parent grains, and retained large subgrain or plastic grains. A superior yield strength of 1.3 GPa with an acceptable ductility (~14%) was achieved in the bimodal microstructure owing to the presence of nano-sized grains and nano-twins. In the trinodal microstructures, the ductility was dramatically improved (~60%) compared to the bimodal structures due to the appearance of a multi-stage work hardening behavior. This important strain hardening sequence was attributed to the sequential activation of transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) effects as a result of the wide variation in phase stability promoted by the grain size hierarchy.

4:30 PM PM04.04.04 Pressure-Induced Phase Modifications in Al-Based High-Entropy Alloys Al_{x}CoCrFeNi (x=0.1, 0.3, 0.75, 1.5) Chenzhu Wang1, Cameron L. Tracy1, Suliye Park1, Chien-Hung Chen1, Tengfei Yang2, Congyi Li2, Yuguang Wang1, Yong Zhang1, Wendy L. Mao1 and Rodney C. Ewing1; 1Stanford University, Stanford, California, United States; 2The University of Tennessee, Knoxville, Tennessee, United States; 1Peking University, Beijing, China; 4University of Science and Technology Beijing, Beijing, China.

Pressure-induced structural modifications in high-entropy alloys with varying Al content, Al_{x}CoCrFeNi (x=0.1, 0.3, 0.75, 1.5), have been investigated at pressures up to ~50 GPa by synchrotron X-ray diffraction and transmission electron microscopy (TEM). In Al_{x}CoCrFeNi compounds with x<0.3, all of which exhibit initial pure fcc structures, the proportionality between the Al content and the transformation pressure is observed. This is attributed to the large size of Al atoms relative to those of the other constituent elements, which leads to more structural distortion in Al_{x}CoCrFeNi and subsequently an increase in the formation energy of the stacking faults. High-resolution TEM results show the variation of the stacking sequence from ABCABC (fcc) to ABABAB (hcp) in Al_{x}CoCrFeNi following exposure to high pressure. In Al_{x}CoCrFeNi, which exhibits an initial dual-phase structure, the result again shows the transformation to an hcp phase despite its higher Al content, which might be due to the presence of the bcc phase that is more amenable to the pressure-induced phase modification. However, the trend of transformation inhibition by increasing Al content is again observed, with Al_{x}CoCrFeNi retaining its initial structures up to the highest pressure achieved. High-pressure processing of this class of high-entropy alloys might allow for improvement and producing phases that are otherwise inaccessible.

4:45 PM PM04.04.05 Structural Screening of FCC and BCC Thin-Film HEAs Using Compositional Gradient Samples Azin Akbari, Artashes N. Ter-Ishahkayan and John Balk; University of Kentucky, Lexington, Kentucky, United States.

Combinatorial thin film samples of CrMnFeCoNiCu and TiVNbMoW were prepared by simultaneous magnetron sputtering of the alloying elements onto silicon wafer substrates. This arrangement yielded a wide composition gradient in the films and resulted in the formation of multiple phases. Some film regions exhibited the desired single-phase high-entropy alloy (HEA), albeit with non-stoichiometric compositions. In order to determine the extent of phase stability for these potential HEAs, multiple characterization techniques were utilized. Microstructure and composition of thin film samples were characterized via scanning electron microscopy and x-ray energy dispersive spectroscopy. Single-phase FCC and BCC regions were detected in the samples by x-ray diffraction and electron backscattered diffraction analysis. Mechanical properties of these alloys were screened across the composition range as well, using nanoindentation. Based on the results of this combinatorial approach, potential single-phase FCC and BCC HEAs were determined. Additionally, these alloys were cast in bulk form via arc-melting followed by thermomechanical processing, which yielded a homogeneous HEA in the FCC CrMnFeCoNiCu system.

PM04.05.01 Microstructure, Mechanical Properties and Wear Performance of Ultrafine-Grained CrFeNi-Based Medium Entropy Alloys Fuzeng Ren, Dingshan Liang, Weiwei Zhu and Canzan Zhao; Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China.

Distinct from traditional alloy design strategy, metallic alloys with nearly equiatomic multi-principle elements, frequently referred to high-entropy alloys (HEAs), have attracted considerable interests in the materials science community as a new class of engineering materials with the unique mechanical properties. However, most of the present HEAs consist of coarse grained microstructure. Here, we have fabricated an ultrafine-grained (UFG) equiatomic medium entropy alloy (MEA) CrFeNi by a combination of mechanical alloying and spark plasma sintering. The obtained bulk CrFeNi consists of 98% FCC-based solid solution phase with an average grain size of ~740 nm and 2% BCC Cr-rich precipitates with the grain size of ~450 nm located at the grain boundaries. A close examination further reveals that the FCC-matrix consists of a Ni-rich zone and a Cr-rich zone. Such UFG CrFeNi alloy has tensile yield strength of ~650 MPa with elongation to ~30%. To further enhance its mechanical properties, 5 at% Nb was added to the CrFeNi matrix after which the strength was significantly increased to ~800 MPa and the hardness was increased from 390 HV to 540 HV. We then systematically investigated the tribological performance of the two alloys at elevated temperatures. The fabricated CrFeNi based MEAs have shown a comparable high temperature wear performance to that of the Inconel 718 superalloy. Based on an in-depth characterization on the worn surface morphology, wear debris and subsurface microstructures formed during wear, the wear mechanism was discussed. Due to an excellent combination of strength, plasticity and high temperature wear performance, the fabricated UFG CrFeNi-based MEAs are promising candidates as a new class of high temperature alloys.

PM04.05.02 Bicontinuous BCC HEA/Cu Nanocomposite Made by Liquid Metal Dealloying Process Kooknoh Yoon, Ilhwan Kim and Eun Soo Park; Seoul National University, Seoul, Korea (the Republic of). Due to its high melting point, high sputtering resistance, low deuterium/tritium retention, and high thermal conductivity, tungsten has been recognized as the most promising candidate of plasma facing materials (PFMs) for fusion reactors. Meanwhile, copper based alloys have been proposed as the heat sink materials behind the plasma facing material due to its excellent thermo-mechanical properties. The joining of W to copper based heat-sink (CuCrZr) remain a main problem in the development of plasma facing component (PFC) due to the large difference in the coefficient of thermal expansion (CTE) between these two materials.
On the other hand, refractory high entropy alloys (RHEA) containing W, Nb, Mo, Ta etc. is reported recently. This multi-component system exhibits higher strength and vice versa due to solid solution strengthening and lower ductility against neutron irradiation damage. In this research, therefore, we fabricated composites of RHEA and Cu by liquid metal dealloying (LMD) process. To utilize this technique, we prepared a precursor material which contains elements having positive and negative enthalpy of mixing with Cu simultaneously, and we immersed it into high-temperature liquid copper to form bi-continuous composite material. Finally, we analyze strength and thermal conductivity of the composite systematically.

**PM04.05.03**

Spacegroup Monte Carlo Method Applied on Configurational Entropy of High Entropy Alloys

Yu Cheng Chen, Guan-Rong Huang, J.P. Chou, Peter K. Liao, J.W. Yeh and Alice Hu;
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; Physics Division, National Center for Theoretical Sciences, Hsinchu, Taiwan; Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Hong Kong, Hong Kong; *The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; *Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Researchers have calculated alloy configurational entropy with ideal gas mixing formula regardless of the intrinsic structure symmetry. How to define configurational entropy precisely for multi-component crystalline system is a tough question. The commonest topic related to such problem is using model which has only two kind of states (spin up/down) in the system. However, it becomes much more difficult to solve if we have more states in a system such as complicated compositions in high entropy alloys (HEAs). How can we deal with it? Here we develop an innovative method to solve this troublesome problem. By using the concepts in group theory and discrete mathematics, we can simplify the problem into Pólya counting problem. We also implement Monte Carlo method which speeds up computation time with just a little deviation from exact solution. And we will demonstrate how to apply this method to distinguish the configurational entropy for different structures of HEAs.

**PM04.05.04**

Tailoring Strength and Ductility of Non-Equiatomic Ti-V-Nb-Ta-Mo High Entropy Alloys

SangJun Kim, Hyunseok Oh and Eun Soo Park; Seoul National Univ, Seoul, Korea (the Republic of).

Recently, high entropy alloys (HEAs) with BCC structure composed of group-4 to group-6 elements (Ti, Zr, Hf, Y, Nb, Ta, Cr, Mo and W) were reported exhibit superior mechanical properties at high temperature above 1000 °C comparing Ni-based superalloy. However, it is known that the HEAs containing group-6 refractory elements (Mo and W) suffer from poor ductility at room temperature, while HEAs without group-6 refractory elements have high ductility at room temperature but show poor strength at high temperature. In this study, we investigated mechanical behavior of HEAs depending on the composition to develop HEA with high strength at high temperature and favorable ductility at room temperature. It is known that valence electron concentration (VEC) of BCC alloys has negative relationship with ductility, but elements with high valence electron (Mo and W) are responsible for high strength of the alloy. To balance the strength and ductility, Ti-V-Nb-Ta-Mo system, whose VEC is 5.0 in equiatomic composition, was selected. HEAs in equiatomic and non-equiatomic composition in the system were predicted to form single BCC phase by CALPHAD (calculation of phase diagram) approach, and experimentally confirmed to have single BCC phase. Mechanical properties of the HEAs were quantitatively analyzed in terms of VEC and solid solution hardening. The results could provide an effective guideline for tailoring mechanical properties of high entropy alloy with bcc structure, and developing promising HEAs for high temperature structural materials.

**PM04.05.05**

In Situ Grown Nanocrystalline High Entropy Alloy Oxide Particles on Reduced Graphene Oxide as Hybrid Electrode Material for Supercapacitor

S. Ramanruthu and Manita Sham Lal; Department of Physics, Indian Institute of Technology Madras, Chennai, India.

Supercapacitors are considered as one of the most promising electrochemical energy storage due to their high power density, large charge/discharge rates and long cycle life. A Hybrid electrode material is mainly a nanocomposite of carbon based nanomaterials and metal oxide nanoparticles. Reduced graphene oxide with high surface area and high conductivity shows electrical double layer capacitance behaviour whereas high entropy alloy oxides (HEAO) constructed with of five or more metal with equal or nearly equal quantities, shows pseudocapacitive behaviour. In this work, we successfully synthesized a novel hybrid electrode material, (CoCrCuNiAl) oxide nanoparticles uniformly embedded on reduced graphene oxide sheets (rGO) by simple in-situ sol-gel auto combustion method. The mixed (bcc and fcc) phase of the HEAO nanoparticles is confirmed from X-Ray Diffraction pattern while microstructure is studied using Transmission electron microscopy (TEM) wherein the average size of CCCNOA nanoparticle is ~20 nm. A solid-state supercapacitor with CCCNOA nanoparticle as electrode material is fabricated and the electrochemical energy storage performance is discussed.

**PM04.05.06**

Microstructure of a New Type of Co and Ni Based High Entropy Alloys

Daniel Laipple, Andreas Stark, Marcus W. Rackel and Florian Pyczak; Helmholtz-Zentrum Geesthacht, Geesthacht, Germany.

One frequent definition for High Entropy Alloys (HEA) is a material of single phase, this single phase being a solid solution of four or more alloying elements which are mixed in nearly equal content. Probably, partly due to the difficulty of generating such single phase materials this concept is often not followed strictly, by allowing certain amounts of a second phase which is often of an ordered intermetallic type. Along similar lines as for the single phase HEAs consisting of ordered phases can be designed. Instead of the whole single phase being of equiatomic composition of all alloying elements in the ordered phase, the principle can be applied on the sublattices of the ordered phase. Then all alloying elements occupying one sublattice have to be present on this sublattice in nearly equiatomic content. The resulting alloys are termed MOCCA standing for Multiphase and/or Ordered Constitutionally Complex Alloy. For their design pre-knowledge about the partitioning behavior of alloying elements between the different phases but also between the different sublattices is necessary. We studied initially the characteristics of six different such MOCCA high entropy alloys: (1) 77Co-8Al-8W-7Ta, (2) 77Co-6Al-6W-6Ta-6Ti, (3) 38.5Co-38.5Ni-6Al-6W-6Ta-5Ti, (4) 77Co-10Al-13W, (5) 38.5Co-38.5Ni-10Al-13W and (6) 77Co-8Al-8W-7Ti which were all based on the L12-Co3(Al,W) ordered phase. Information about partitioning between phases and sublattices is available from experimental and theoretical investigations and was used to design the alloys. The samples are manufactured by arc melting and were annealed at 1300°C for 12 h under Ar atmosphere respectively. Due to the results of the SEM investigations including EDX analysis, the compositions (3) and (6) were refined in a second step by (7) 36Co-39Ni-6.5Al-6W-6Ta-6Ti and (8) 77Co-9.5Al-9.5W-7Ti in order to achieve a single phase constitution. Again by evaluating the SEM results composition No (7) was refined in a third step by (9) 39Ni-37Co-7Al-7Ti-7Ta-3W.

**PM04.05.07**

High-Entropy Ceramics of Five-Component, Equimolar, Rare-Earth (RE) Oxides

Kuo-Pin Tseng and Waltraud M. Kriven; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.
To investigate the influence of cation radii on synthesizing high-entropy ceramics, a new system of five-component high-entropy oxides are reported here. Much research has been conducted in defining high-entropy alloys. However, the cation selection rules for high-entropy ceramics are still unclear. In this research, four rare-earth (RE) cations were selected and fixed. The fifth cation with larger radius was chosen from another set of eight different rare-earth (RE) cations. According to the rules of thermodynamics, each group of five cations were mixed in equimolar ratios to maximize the mixing entropy. Using the concept of atomic size difference (6) in high-entropy alloys, the cation radii difference in this system ranges from 1.25 to 3.71. Synchrotron-sourced X-ray powder diffraction patterns were measured here. The results show that all of these eight rare-earth (RE) candidates change into simple disordered high-entropy oxides after heat treatment. This indicates that the well-distributed cations in cubic-bixbyite structure are established in each group of candidates. Even though the radius of the largest cation is 1.16 times larger than that of the smallest one, all these cations still uniformly share the same lattice sites. Meanwhile, high-entropy oxides have the ability to keep all the cations in the same oxidation states. As we all know in oxides, some of cations tend to transform between trivalent states and tetravalent states under different conditions of temperature and pressure. Surprisingly, the high-entropy configuration can prevent the same type of cation from moving and aggregating. As a result, the valence states of all the trivalent cations are retained. This research provides a preliminary guideline of cation selection for synthesizing high-entropy ceramics in order to explore the next generation of structure-stabilized ceramics.

PM04.05.09
Ordering in a Series of Al-Containing Refractory High Entropy Alloys Ta-Nb-Mo-Cr-Ti-Al Alexander Kauffmann1, Hans Chen4, Sascha Seils4, Torben Böll1, Sandra Kaufmann-Weiss2, Ian Harding1, Sharan Kumar1, Dorothée Vinga Szabo31, Sabine Schlachetski1, Christian H Liebscher1, Franz Müller1, Bronislava Gorč1, Hans-Jürgen Christ1 and Martin Heinmaier3, 1Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; 2Institute for Technical Physics (ITEP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; 3School of Engineering, Brown University, Providence, Rhode Island, United States; 4Institute for Applied Materials (IAM-WK), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; 1Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; 2Institut für Werkstofftechnik, Universität Siegen, Siegen, Germany.

High entropy alloys (HEAs) based on the Ta-Nb-Mo-Cr-Ti-Al system are expected to possess high creep and oxidation resistance as well as outstanding specific mechanical properties due to comparably low density. However, we recently reported that these arc-melted and subsequently homogenized alloys exhibited a lack of ductility up to 600 °C depending on the specific alloy composition [H. Chen et al. in Metall. Mater. Trans. A 49 (2018) 772-781 and J. Alloys Compd. 661 (2016) 206-215]. In this presentation, we provide the results of comprehensive microstructural characterization of a series of Ta-Nb-Mo-Cr-Ti-Al derivatives for assessing ordering as potential origin for the observed lack of ductility. Backscatter electron imaging (BSE), energy dispersive X-ray spectroscopy (SEM-EDX and STEM-EDX) and atom probe tomography (APT) were used to prove uniform element distribution after homogenization in these alloys. X-ray diffraction patterns (XRD) of the Ta-free derivatives indicated W prototype crystal structure without the presence of significant superlattice peaks, whereas TEM diffraction experiments confirmed B2 order. The presence of thermal antiphase domain boundaries (APDBs) suggested that order resulted from a disorder-order solid-state phase transformation during cooling from the homogenization temperature. In MoCrTiAl, these APDBs were enriched in Cr and depleted in Ti as confirmed by STEM-EDX line scans as well as APT analyses. Based on these results, we present an experimental approach to determine the site occupation factors in order to refine the experimental XRD patterns of these alloys. These refinements provide the basis for a critical discussion of the conflicting absorption factors in XRD patterns in some HEAs while order is revealed by other techniques.

PM04.05.10
Possible Correlation Between Strength and Mean Square Atomic Displacement in Cr-Mn-Fe-Co-Ni High Entropy Alloys Makoto Asakura1, Kodai Niitsu1, Norihiko L. Okamoto1, Koretaka Yuge1, Kyosuke Kishida1, Haruyuki Inui1, Takashi Fukuda4 and Tomoyuki Kakeshita1, 1Center for Elements Strategy Initiative for Structural Materials (ESISIM), Kyoto University, Kyoto, Japan; 2Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 3Institute for Materials Research, Tohoku University, Sendai, Japan; 4Division of Materials and Manufacturing Science, Osaka University, Osaka, Japan.

High entropy alloys (HEAs) are equiatomic or nearly equiatomic solid solution alloys consisting of at least five elements, which crystallize into a single phase presumably due to the large contribution of configurational entropy to the Gibbs free energy. The equiatomic Cr-Mn-Fe-Co-Ni HEA with the face-centered cubic (FCC) structure has been reported to exhibit excellent ductility and exceptional fracture toughness at cryogenic temperatures. To date, these properties in HEAs have been explained within the framework of the classical theories of solid solution strengthening. However, the classical derivations for binary dilute alloys, such as Fleischer’s and Labusch’s models, are not applicable to HEAs because solute atoms in HEAs are no longer discernible. Very recently, Mean-Square Atomic Displacement (MSAD) is suggested to be a new parameter scaling the degree of solid solution strengthening. This is a value of lattice distortion averaged across whole crystal, and is evaluated by ab initio calculation with Special Quasi-random Structure (SQS) models. For polycrystalline equiatomic HEA and its derivatives, the positive correlation between their yield strength and MSAD0.5 values was reported [1]. However, since the yield strength in the form of polycrystals is anticipated to be perturbed by the grain boundaries and textures, critical resolved shear stress (CRSS) of the HEA crystal should be assessed with single crystals. In the present study, we fabricated single crystals of Cr-Mn-Fe-Co-Ni HEAs and its derivatives with which the composition of only one element is changed and the other four elements’ compositions are equiatomic by the Bridgeman method. Compression tests were performed on rectangular parallelepiped single crystals with the size of 2×2×5 mm3 with the [−123] loading axis at an engineering strain rate of 1.0×10−5 s−1 and at temperatures from 13K to 298K. MSAD values were calculated by ab initio method with SQS models. Bulk single crystals are successfully grown for all compositions. Positive linear relationship between CRSS and MSAD0.5 is elucidated as is previously reported for the relationship between yield stress and MSAD0.5 in the HEA polycrystals. In addition, this relationship is found to be even for non-equiatomic HEA derivatives; MSAD is anticipated to be an essential parameter scaling the degree of solid solution strengthening of broader class of FCC multi-component alloys.


PM04.05.11
Anomalous X-Ray Scattering Study of the Local Structure of Mo Atoms in FeCoCrNiMox (x = 0.11 and 0.23) High Entropy Alloys Haiyan He1, Bang Wang1, Si Lan2, Jacob Ruff1, Chen Tian Lin1 and Xin-Li Wang4, 1Physics, City University of Hong Kong, Hong Kong; 2Hong Kong University of Science and Technology, Hong Kong; 3Herbert Glieiter Institute of Nanoscience, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, China; 4Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York, United States; 5Mechanical and Biomedical Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

High entropy alloys which contain 5 or more elements often have a rather simple structure like body-centered-cubic (BCC) or face-centered-cubic(FCC). In spite of the simple average crystalline structure, the local atomic order of individual atomic species has remained an open question. In this study,
anomalous X-ray scattering was applied to determine the local structure of Mo in FeCoCrNiMox (x = 0.11 and 0.23), a high entropy alloy with FCC lattice. At the Mo absorption edge, the intensity of all diffraction peaks decreased, by nearly identical amount. Detailed analysis of the experimental data confirms that Mo atoms are randomly distributed instead of locally segregated in the FCC lattice.

The work was supported by the grant from the Research Grants Council of the Hong Kong Special Administrative Region [CityU 11215917]. Anomalous X-ray scattering was conducted at station A2, Cornell University, Cornell High Energy Synchrotron Source.

PM04.05.12
Plastic Deformation of Single Crystals of a Cr-Co-Ni Equiatomic Medium Entropy Alloy Kazuaki Fujihara1, Makoto Asakura1, Kodai Niitsu1, Haruyuki Inui1

Medium/high entropy alloys are a class of multi-component solid solution alloys with (nearly) equiatomic compositions, which are considered to be stabilized because of the large contribution of configurational entropy to the Gibbs free energy. Some of these alloys exhibit exceptional mechanical properties that their tensile elongation and fracture toughness increase with decreasing temperature simultaneously. Among various medium/high entropy solid solution alloys discovered so far, the Cr-Co-Ni equiatomic solid solution alloy with the face-centered cubic (FCC) structure has been reported to exhibit both the highest strength and highest elongation in a polycrystalline form. However, the detailed mechanisms endowing the excellent mechanical properties to the Cr-Co-Ni equiatomic alloy remain unclear in many aspects mainly because of the lack of fundamental studies using single crystals. In the present study, we prepared single crystals of the Cr-Co-Ni equiatomic solid solution alloy by directional solidification in an optical floating zone furnace and investigated the deformation behavior of the [-123]-oriented single crystals under uniaxial tensile and compressive loading as a function of temperature (13K to 1073K). Temperature dependence of the activation volume were investigated by strain rate change compression tests (1×10\(^{-5}\) to 5×10\(^{-3}\) s\(^{-1}\)). Stress-strain curves obtained from tensile tests at low temperatures exhibit a widely extended easy-gliding region (stage I) when it is compared to that for the Cr-Mn-Fe-Co-Ni equiatomic solid solution alloy. This is considered to reflect a relatively low stacking fault energy for the Cr-Co-Ni equiatomic alloy. The critical resolved shear stress (CRSS) of the Cr-Co-Ni equiatomic alloy is higher than that of the Cr-Mn-Fe-Co-Ni equiatomic alloy. The CRSS value increases significantly with decreasing temperature below room temperature and with increasing temperature above 873K. Activation volume of the Cr-Co-Ni equiatomic alloy is found to be much lower than those of binary FCC solid solution alloys.

PM04.05.13
Effect of Impurity Solute Atoms on Strength of α-Al (fcc) Single-Crystal Micropillars Soichiro Takeyasu, Naoki Takata, Asuka Suzuki and Makoto Kobashi; Department of Materials Process Engineering, Nagoya University, Nagoya-shi, Japan.

High-entropy alloys (HEAs) exhibit high ductility and strength and toughness with decreasing temperature, and it is widely known that CrMnFeCoNi is the fcc structure and maintains its single-phase, solid solution state at elevated temperatures. N. I. Okamoto et al. have recently demonstrated that single-crystal micropillars prepared from the HEA exhibit the size dependence of shear stress for the initial slip, which corresponds to pure fcc metals (Ni, Cu and Al). The study indicates the size dependence of strength would be independent of solid-solution atoms in fcc metals. In contrast, the size dependence of strength was scarcely reported in fcc solid-solution phases, whereby the influence of solid-solution atoms on the size dependence has not yet been elucidated even in fcc metals. In the present study, focusing on the commercial purity aluminum (2N purity) containing Fe and Si elements as impurity solute atoms, we have attempted to clarify the influence of trace solute atoms on the measured strength of microscale-sized pure aluminum. We have fundamentally examined the compression response of α-Al (fcc) single-crystal cylindrical micropillars with different diameters (approximately ranging from 1 to 10 μm) prepared on the sample surface of 4N and 2N purity Al sheets with the recrystallized microstructure. Micropillars were fabricated by FIB and compressed by the nanoindentation systems attached the flat punch (ϕ=20 μm). Slip systems were identified by crystal orientation analysis using electron back-scattering diffraction (EBSD) and scanning electron microscopy (SEM) observation. The compression tests for micropillars with various sizes demonstrated the flow stress of micropillars increases with decreasing pillar diameter. In the case of 4N purity Al, the observed size dependence of resolved shear stress for slip corresponds well to the previous studies on micropillars prepared from 5N and 3N purity Al sheets. The measured shear stress resolved onto a primary slip system (s) scaled by shear modulus (G) and the pillar diameter (d) scaled by Burgers vector (b) show the following correlation: \(\tau_s/G = 0.33d/b^{0.06}\). In the case of 2N purity Al, the size dependence of resolved shear stress is smaller than that observed in higher purity Al (5N, 4N and 3N). The resolved shear stress shows the following correlation with the normalized pillar diameter: \(\tau_s/G = 0.0062d/b^{0.19}\). These results indicate that the impurity solute atoms in pure Al would reduce the size dependence of strength. In the presentation, we will present the dislocations inside the micropillars observed by transmission electron microscopy (TEM) and discussed on the observed size dependence utilizing the single-arm dislocation source model. Furthermore, we will report the compression response of single-crystal micropillars of α-Al (Mg) solid-solution phases.

PM04.05.14
Micropillar Compression Deformation of Single-Crystal in CrMnFeCoNi High-Entropy Alloy Norihiko I, Okamoto1,5, Shu Fujimoto1, Yuki Kambara1,2,3,4,5, Hirokata Matunoshita1, Katsumi Tanaka1, Haruyuki Inui1,2 and Easo P. George2; 1Department of Materials Process Engineering, Nagoya University, Nagoya-shi, Japan; 2Center for Elements Strategy Initiative for Structural Materials, Kyoto University, Kyoto, Japan; 3Kobe University, Kobe, Japan; 4Center for Elements Strategy Initiative for Structure Materials, Kyoto, Japan; 5Ruhu University Bochum, Bochum, Germany.

High-entropy alloys (HEAs) comprise a novel class of scientifically and technologically interesting materials. Among these, equiatomic CrMnFeCoNi with the face-centered cubic (FCC) structure is noteworthy because its ductility and strength increase with decreasing temperature while maintaining outstanding fracture toughness at cryogenic temperatures. However, plastic deformation behavior has not been fully characterized, due to the difficulty of obtaining large single crystals of the HEA. Recent years, a method for micro-compression testing of single-crystal pillars prepared by focused ion beam (FIB) machining, making further investigation of plastic deformation behavior in HEA possible, has been developed. In the present study, we investigate the plastic deformation behavior of single crystals of the CrMnFeCoNi HEA by performing compression tests on micropillars at room temperature as a function of specimen size and crystal orientation, in order to deduce its bulk CRSS value and orientation dependence. We also characterize deformation mechanisms at low homologous temperatures by investigating the deformation behavior of bulk polycrystals at room temperature and 77K. Dislocation structure in a specimen deformed at 77K is investigated with Transmission electron microscopy (TEM). Stacking fault energy is thus deduced from the separation distance between the Shockley partials. The critical resolved shear stress (CRSS) in room temperature with bulk size is estimated to be ~33–43 MPa, ~10 times higher than that of pure nickel. CRSS depends on pillar size with an inverse power-law exponent of ~0.63, which is within the range reported in FCC metals (~0.5 to ~1.0) but close to the lower bound, and independent of orientation. The relatively low exponent of power-law in HEA corresponds to the high CRSS value, compared to those of the FCC metals. No orientation dependent is confirmed. Dislocations are smoothly curved without any preferred line orientation indicating no significant anisotropy in mobilities of edge and screw segments. Planar \(\frac{\pi}{2} < 111\) dislocations dissociate into Shockley partials whose separations range from ~3.5–4.5 nm near the screw rotation to ~5–8 nm near the edge, yielding a stacking fault energy of 30 ± 5 mJ/m². Although the stacking fault energy in HEA is not particularly low, compared to certain FCC alloys (e.g. Cu-Al binaries), the separations can be relatively large, due to its relatively high shear modulus. The large separation distance may account for the difficulty in cross slip and for the occurrence of deformation twinning at low
The shear-modulus-normalized CRSS of the HEA is not exceptionally high compared to those of certain concentrated binary FCC solid solutions. Its rough magnitude calculated using the Fleischer/Labusch models corresponds to that of a hypothetical binary with the elastic constants of our HEA, solute concentrations of 20–50 at.%, and atomic size misfit of ~4%.

**PM04.05.15**

Irradiation Behaviour and Response of High Entropy Alloys

Hongjun Fu1, Maak K. Patel1, Anna Kareer1, Karl Dawson1 and Karl R. Whittle1; 1University of Liverpool, Liverpool, United Kingdom; 2Materials, University of Oxford, Oxford, United Kingdom.

High Entropy Alloys (HEAs) have attracted interest within the nuclear context due to their predicted properties, and potential for tolerating radiation damage to high levels. The continued revolution of nuclear energy, coupled with increased utilisation of fuel, and reactor materials requires continued development of materials capable of tolerating high levels of induced damage within the core. Such increased utilisation of reactor materials, whether it be as cladding or as componentry within the core, can lead to enhanced operations of the reactor, with the potential for lifetime extensions of LWRs.

To this end we have studied four model HEAs Co1.5CrFeNi1.5Ti0.5Mo0.1, TaNbHfZrTi, AlCoCrFeNiSi0.1, and CoCrCuFeNi, for use within reactor cores. The impacts of radiation damage have been examined using ions as proxies for neutron damage. After irradiation with Au, Ni and He, the degree of damage has been examined by electron microscopy (SEM, TEM and EDX) to elucidate the microstructural changes, and grazing incidence X-ray diffraction (GIXRD).

**SESSION PM04.06: Fundamental Aspects of Entropy**

**Session Chair:** Jun Ding

Tuesday Morning, November 27, 2018

Hynes, Level 1, Room 105

8:30 AM **PM04.06.01**

High Entropy Alloys Beyond Configurational Entropy

Jorg U. Neugebauer, Fritz Koermann, Blazej Grabowski, Yuji Ikeda and Tilmann Hickel; Max-Planck-Institut fuer Eisenforschung, Duesseldorf, Germany.

The name-giving entropy contribution in high entropy alloys is configurational entropy. However, configurational entropy is only one out of several entropic contributions. In a real alloy electronic, magnetic, vibrational entropy, as well as local chemical order or defects can also play a role. Presently, the relevance of these contributions for the phase stability of bulk alloys, but also for deformation mechanisms such as the formation of stacking faults or twins, remains largely unknown. Combining ab initio calculations with advanced thermodynamic methods and statistical sampling approaches we are able to accurately determine the various contributions. A detailed analysis of the results shows that the conventionally assumed dominance of the configurational entropy is in general not valid. Thus, for a realistic description of the bulk phase stability, but also to identify suitable process conditions or alloy compositions - e.g. by adding interstitial atoms such as C - the various entropic contributions have to be included. Examples of quinary magnetic high entropy alloys where this approach has been successfully employed will be given.

9:00 AM **PM04.06.02**

From Symmetry to Entropy—An Inconvenient Truth of Crystal Configurational Entropy

C.H. Hu1, Yu Cheng Chen1, K.Y. Fung1, Peijun Yu1, Peter K. Liaw2, J.W. Yeh3 and Alice Hu4; 1City University of Hong Kong, Kowloon, Hong Kong; 2National Taiwan University, Taipei, Taiwan; 3National Chiao Tong University, HsinChu, Taiwan; 4The University of Tennessee, Knoxville, Tennessee, United States; 5National Tsing Hua University, HsinChu, Taiwan.

All along, researchers calculated configurational entropy with ideal gas mixing formula regardless which structure they are considering. However it is obvious that crystalline has symmetry while ideal gas does not. Therefore the very same ideal gas mixing value should not be assigned for all the other structures, such as body-centered-cubic (BCC), face-centered-cubic (FCC), hexagonal-close-packed (HCP), and others. Here we will show a precise definition how to determine configurational entropy for crystalline. Based on Burnside’s lemma in combinatorial mathematics and crystalline rotation-point-group, we successfully present the configurational entropy difference between FCC and HCP. This is the first time in thermodynamic science that we know how to distinguish configurational entropy differences, which cannot be known from density functional theory, molecular dynamics, or any other computational method. Therefore this result will initiate a whole new revision of all the entropy related theorem in all kinds of disciplines including calculations of phase stability in thermodynamic physics, diffusion in material science, molecule symmetry in chemistry, DNA entropy in biology, and even statistical mechanics. Included this research, we apply our result to explain a crucial example that how high entropy alloy phase transformation starts at cryogenic temperature from nanoscale region. This also indicates conventional physical metalurgy theorem may require serious modification efforts before appropriate application on HEAs.

9:15 AM **PM04.06.03**

Entropy Contributions to Phase Stability in Random Solid Solutions

Anus Manzoor1, Shubham Pandey2, Simon R. Phillpot2 and Dilipaneet S. Aidhy2; 1University of Wyoming, Laramie, Wyoming, United States; 2University of Florida, Gainesville, Florida, United States.

High entropy alloys (HEAs) contain multiple elements in large proportions that make them prone to phase separation. In the overall vision of designing HEAs for structural applications, in this work, using density functional theory (DFT) calculations, we elucidate the contributions of various entropies, i.e., vibrational, electronic and configurational towards the phase stability of random alloys. Taking examples of various alloy systems, we show that the entropy contributions could be quantitatively comparable to the mixing enthalpy; as a result including the entropy contributions is critically important in correctly predicting the alloy phase stability. We also show that while the configurational entropy always favors phase stability by reducing the Gibbs free energy, the role of vibrational entropy is not predictable. The configurational and vibrational entropies can either compete to destabilize or can collectively contribute to stabilize the solid solutions. As a result, even those systems that have negative mixing entropy can show phase instability revealed as a miscibility gap; conversely, systems with positive mixing entropy can have stable phases due to the entropic contributions. Finally, we show that the contribution of electronic entropy is minor compared to the other two entropies. This work contributes towards the computational framework necessary for predicting the correct phase stability of HEAs.

9:30 AM BREAK
10:00 AM *PM04.07.01
Deformation by Dislocations, Twinning, and Phase Transformations in Compositionaly Concentrated FCC Solid Solutions C. E. Slone, J. Miao, M. Ghazisaeidi and Michael J. Mills; Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio, United States.

The equiatomic NiCoCrFeMn alloy is an fcc solid solution that exhibits intriguing characteristics including very large strain hardening rates, large fracture toughness, and strong dependence of the yield strength at low temperature. These characteristics are closely linked to dislocation-mediated plasticity, yet little experimental work has explored dislocation dissociation, stacking fault energy, or core structures in these alloys. In this study, these dislocation characteristics have been determined in the NiCoCrFeMn alloy using scanning transmission electron microscopy techniques. In addition, substructure development at larger strain has been explored as a function of strain, and compared with the ternary NiCoCr equiatomic alloy. While twinning is prevalent at larger strains in NiCoCrFeMn, a transformation from the FCC structure to a fine-scale microtwin and hcp lath structure occurs in NiCoCr during large-strain deformation at room and cryogenic temperatures. In addition, first principles calculations using density function theory has been used to explore the relative phase stabilities and energy pathways for twinning and hcp phase formation. These modeling results are compared directly with atomic resolution scanning transmission electron microscopy evidence for these structures, and possible mechanisms by which they form are presented. In addition, the relationship of this phase transformation to the strength and work hardening behavior in these two alloys will be explored.

10:30 AM *PM04.07.02
Elastic Properties of Low, Medium and High Entropy Alloys with the FCC Structure Katsushi Tanaka, Takeshi Teramoto and Kazuki Yamada; Kobe University, Kobe, Japan.

Monocrystalline elastic constants of low, medium and high entropy alloys with the fcc structure have been analyzed systematically. According to our previous result, monocrystalline elastic constants of equiatomic quinary CrMnFeCoNi alloy show characteristic features indicating a relatively large elastic anisotropy and the existance of a strong directional interatomic interaction in the alloy. On the other hand, elastic constants of pure-Ni and FeNi low entropy alloy are analyzed as more metallic, that is a weaker directional interatomic interaction. In this study monocrystals of equiatomic low, medium and high entropy alloys with the fcc structure were grown by a modified Bridgeman method and the elastic constants were determined from liquid helium temperature to 1200 K using a ultrasound spectroscopy. The results show a systematic transition of the elastic properties from pure-metal to a high entropy alloy, though some scattering are observed depending on the alloying elements especially for midium entropy alloys.

10:45 AM *PM04.07.03
Study of Pseudo-Binary Diffusion in Single-Phase High-Entropy CrFeCoNi Alloys Adeline Durand1, Guillaume Laplanche1, Ying Yang2, Gunther Eggeler2 and Easo P. George2; 1Ruhr-Universität Bochum (RUB), Bochum, Germany; 2Materials Science and Technology Div, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

High-Entropy Alloys (HEAs) are single-phase alloys composed of multiple principal elements in relatively high concentrations. Consequently, traditional notions of solvent and solute do not apply, and it is not clear how this affects diffusion kinetics of the constituent elements. Sluggish diffusion is said to be an important characteristic of HEAs; however, it has been increasingly contested in recent years. The goal of this study is to investigate and better understand interdiffusion processes in HEAs.

We adopted the pseudo-binary model introduced by Tsai et al. [1] in which only two elements are diffusing against each other while the others are kept at a constant concentration. According to Tsai, in this situation, the interdiffusion, intrinsic and self-diffusion coefficients are assumed to be equal. In our experiments, all the constituent pseudo-binaries were studied at the same time with the help of suitable diffusion multiples. The following are our major results and conclusions:

(1) Up-hill diffusion was observed, proving that interactions between all constituent elements exist and should not be totally ignored in contrast to what was claimed in the model of Tsai et al. [1]

(2) No significant Kirkendall effect (voids or shift of initial interface) was noted, confirming that interdiffusion and intrinsic diffusion coefficients are indeed equal.

(3) The systematic study of all pseudo-binaries showed substantial differences between the diffusion speeds of a given element in different pseudo-binaries, which invalidates the assumption that intrinsic and self-diffusion coefficients are equal.

(4) Thermodynamic simulations are currently under way to rationalize our experimental observations.

In conclusion, even though some aspects of Tsai’s model have been disproven here and in the literature [2], the model still provides an efficient way to compare diffusion of elements in different conditions and can easily show the different interactions among them (e.g. whether certain elements enhance or slow down diffusion of others).


11:00 AM OPEN DISCUSSION

11:15 AM *PM04.07.05

High-temperature strength, toughness and oxidation resistance are exhibited by Ni-based superalloys. However, increasing the application temperatures for such alloys become problematic due to melting temperatures of around 1350°C. New class of materials that can withstand harsher conditions at elevated temperatures are therefore desirable.

High entropy alloys (HEA) based on refractory elements may achieve higher temperature operations with superior creep strength. At elevated temperatures, Mo based HEAs have been observed to exhibit good thermal and mechanical properties. Recently, a refractory Mo-W-Ta-Ti-Zr HEA was observed to exhibit greatly enhanced modulus of elasticity (3x at 300K) over near atomic cases and with higher moduli above 500K over commercial alloys (2.3x at 2000K).

In this study, periodic DFT and atomistic thermodynamic modelling is used to study the oxidation mechanisms in the Mo-W-Ta-Ti-Zr HEA. The special quasi-random structures (SQS) model was used to generate random structures in combination with the VASP DFT package. A Monte Carlo algorithm implemented in the ATAT package is used to match the correlation functions in the random structures for pairs up to the seventh nearest neighbor shells, triplets up to the fourth nearest neighbor shells and quadruplets up to the third nearest neighbor shells. The best representative random structure as shown in the figure below is used to create different surfaces and the most stable surface selected based on the calculated surface energy. The stable facets are subsequently reacted with oxygen to gain a detailed understanding of the surface oxidation process. A link between theoretical and experimental conditions are established by using a thermodynamic approach to establish different temperature and pressure regimes on the oxidized surfaces at different oxygen coverages.

11:30 AM PM04.07.06
High-Temperature Nanomechanical Behavior of HEAs for Service Under Extreme Conditions Youxing Chen¹, Eric D. Hintsala², Nan Li³, Douglas Stauffer⁴, Bartosz Nowakowski⁵ and Nathan Mara⁶; ¹University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; ²Bruker Nano Surfaces, Eden Prairie, Minnesota, United States; ³Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The potential good high-temperature mechanical performance of high entropy alloys (HEAs) has attracted significant attention for demanding nuclear applications. Although abundant high-temperature mechanical behavior data exists for bulk HEAs, high-temperature correlation of microstructure and mechanical properties, especially after exposure to ion irradiation, requires more investigation in order to continue optimizing performance. In this talk, we investigate two types of HEAs with different microstructures: fcc FeCoNiMn and dual-phase FeCrNiMnAl HEAs with a mixed fcc/bcc structure. The mechanical properties of both materials were studied before and after Fe ion irradiation at 500°C with a peak damage level of ~50 dpa. High-temperature (up to 500°C) mechanical maps of HEA alloys achieved by elevated temperature nanoindentation under a vacuum atmosphere clearly demonstrate mechanical contrast from different grains and phases. With increasing test temperature, both fcc and bcc phases soften to different extents, and radiation hardening for the fcc and bcc phases exhibit marked differences. The combined effect of temperature and radiation damage on mechanical behavior will be discussed in terms of dislocation-based hardening models and resulting defect populations at elevated temperatures.

11:45 AM PM04.07.07
FeMnNiAlCr High Entropy Alloys (HEAs) and Their Native Oxide Solar Absorbers for Concentrated Solar Power Systems Eldred Lee, Margaret Wu, Sheppard Somers, Ian Baker and Jifeng Liu; Dartmouth College, Hanover, New Hampshire, United States.

Concentrated solar power (CSP) systems enable efficient solar energy harvesting and large-scale storage in the form of heat, allowing to supply solar electricity even when the sun does not shine. This capability can mitigate the intermittency issue of solar electricity. Carnot’s Theorem dictates that a higher operation temperature of a CSP system lead to higher energy conversion efficiency. However, the maximal operation temperature of commercial CSP system is limited to 873K as common materials used for the tubing systems (e.g. stainless steel) cannot operate at higher temperatures due to challenges in mechanical & chemical stability. One challenge is the subpar creep resistance and excessive oxidation of currently used CSP tubing materials at high temperatures, leading to crack formation. Ni- & Ti-based and oxide-dispersion strengthened alloys can overcome the problems, but they are expensive. Another challenge is the receivers of CSP systems, where the sunlight is focused on solar selective absorber coatings. The receiver should absorb maximum solar radiation and convert it to heat with low thermal emittance loss at the IR regime. The conversion efficiency should ideally be >90% and stable at high temperatures (>973K). Yet the current coatings (e.g. Pyromark 2500) [1] have high emittance loss (~70%) & conversion efficiency below 90% under long-term at ~973K with a likely degradation in the thermal cycles of CSP systems. To address these challenges, we grow native oxides on two- & three-phase FeMnNiAlCr HEAs to lower the thermal emittance loss (<50%), increase the solar absorptance (>92%), and enhance the conversion efficiency (~91% at 973K). The formation of Fe-Mn oxides and surface microstructures contribute to the drastic enhancement of optical performances at high temperatures, as previously found with externally applied Fe-Mn oxide nanoparticle-based coatings [2]. The native oxides also act as protective layers via diffusion limited oxide growth, thereby enhancing the corrosion-resistance of the HEAs. Furthermore, these HEAs have a yield strength twice that of 304 stainless steel at 973K and a good balance between strength and ductility. When annealed at 1173K, the Vickers microhardness increases considerably due to the fine NiAl-enriched precipitates. The precipitates are stable at 973-1073K, further enhancing the creep resistance of the HEA tubing materials for CSP applications. Because low-cost Fe & Mn constitute ~70 at.% of our HEAs, they are inexpensive compared to Ni- & Ti-based alloys. Therefore, the unique synergy between the mechanical & optical properties of surface-oxidized FeMnNiAlCr HEAs provides a promising solution to cost-effective tubing materials for high-efficiency generation of CSP systems.


SESSION PM04.08: Mechanical Properties of FCC Alloys
Session Chair: Louis Santodonato
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 105

1:30 PM *PM04.08.01
Elementary Deformation Mechanisms in High- and Medium-Entropy Alloys Guillaume Laplanche¹, Joël Bonneville², Céline Varvenne³, Aleksander Kostka¹, William A. Curtin¹ and Easo P. George¹; ¹Institute for Materials, Ruhr-Universität Bochum, Bochum, Germany; ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Institute of Mechanical Engineering, EPFL, Lausanne, Switzerland; ⁴CNAM, Aix-Marseille University, Marseille, France; ⁵Physics and Mechanics of Materials, Institut PPRIME, University of Poitiers,
Recent progress in understanding the fundamentals of deformation in high- and medium-entropy alloys is reviewed. This presentation focuses on one of the most thoroughly investigated material systems, the fcc CrMnFeCoNi alloys. They have been shown to exhibit fascinating mechanical properties, including increasing strength and tensile ductility with decreasing temperature, with composition having a strong effect. Here, two model alloys from the CrMnFeCoNi alloy system are used to highlight key microstructural aspects responsible for strength, work-hardening rate, and ductility. Since the alloys deform by dislocation plasticity initially and mechanical twinning at higher strains, quantitative evolution of dislocation and twin densities, together with the magnitude and strain-dependence of activation volumes, are used to identify the elementary deformation mechanisms responsible for macroscopic mechanical behaviors. The activation volume at initial yielding is found to reflect the interaction of dislocations with solutes, in agreement with recent theoretical predictions, while its strong decrease upon straining is associated with forest hardening. The role of stacking fault energy on twinning is discussed and related to deformation twinning, which enhances work hardening capability and ultimate tensile strength.

2:00 PM PM04.08.02
Phase Stability and Deformation Behaviors of High-Entropy Alloys Bing Wang1, Muhammad Naeem1-2, Haiyan He1, Si Lan1-2 and Xun-Li Wang1, 2City University of Hong Kong, Kowloon, Hong Kong; 3Herbert Gleiter Institute, Nanjing University of Science and Technology, Nanjing, China.

It is rather amazing that high-entropy alloys consisting of multiple alloying elements in equal molar ratios can form a single phase solid-solution with an incredibly simple lattice, e.g., face-centered cubic (FCC). We have conducted a systematic study of the phase stability and deformation behaviors of CrFeCoNiMox (x=0 – 0.3) FCC high entropy alloys, using in-situ neutron scattering techniques and electron microscopy. For x=0.3, measurements by small angle scattering show that high-entropy alloys are stable up to 800 C, beyond which significant growth of precipitates were observed, which is responsible for the reduced strength at high temperatures. At room temperature, the deformation of CrFeCoNi alloys are dominated by dislocation activities, from dislocation slip at small strains to dislocation entanglement at large strains (up to 40%). Analysis of the diffraction peak widths demonstrates that the dislocation substructures are responsible for the unusual three-stage hardening behavior observed in this alloy. At low temperatures, the alloys deform by serration, with a complicated deformation path which is fully captured by in-situ neutron diffraction measurements.

2:15 PM PM04.08.03
Investigation of the Microstructure Evolution in Al0.1CoCrFeNi High-Entropy Alloy Liu Zhichao and Chengwen Tan; Beijing Institute of Technology, Beijing, China.

The quantitative characterization of the microstructure evolution in high-entropy alloy (HEA) during deformation is of great importance to understanding its strain-hardening behavior. In the current study, in-situ high-energy synchrotron X-ray diffraction was employed to characterize the microstructure evolution in a Al0.1CoCrFeNi HEA during a tensile test. The stacking fault probability and twin probability at different strain levels were analyzed by the Rietveld refinement method. Al0.1CoCrFeNi HEA exhibits a high ultimate tensile strength with a superior uniform elongation and a high strain-hardening rate. The stacking fault energy (SFE) of the Al0.1CoCrFeNi HEA by the synchrotron measurements was estimated to be 35MJ/m2. The increased volume faction of nano-twins and twin-twin intersections, formed during deformation, has been confirmed by transmission electron microscopy analysis. The high strain-hardening rate can be attributed to the increased density of dislocations and nano-twins.

2:30 PM BREAK

SESSION PM04.09: Phase Stability
Session Chair: Alexander Kauffmann
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 105

3:00 PM *PM04.09.01
Solid Solution Limit in High-Entropy Alloys—Quantitative Prediction and Experimental Verification Ming-Hung Tsai1, 2, Jian-Hong Li1 and Ting Chang1; 1National Chung Hsing University, Taichung, Taiwan; 2National Tsing Hua University, Hsinchu, Taiwan.

The criterion for the formation of simple solid solution phases has been an important issue in the HEA community. Most of the existing criteria are semi-empirical, with the threshold values obtained from experimental data. Some of criteria are theoretical, the tendency of phase formation is obtained by the comparing different hypothetical thermodynamic states. In this work, a new thermodynamic-based theory is proposed to predict the solid solution limit (SSL) in simple solid solution HEAs. Then, the solid solution limits of various elements in a model FCC base alloy are experimentally measured. These experimental values are used to verify the accuracy of existing models and our model. The results show that existing models evidently overestimate the SSL in HEAs. Our model has significantly higher accuracy than existing models, which provides new insights to the behavior of these multi-component solid solutions.

3:30 PM PM04.09.02
Predictive Multiphase Evolution in Al-Containing High-Entropy Alloys Louis J. Santodonato1, 2, Peter K. Liaw3, Raymond R. Unocic1, Hongbin Bei1 and James R. Morris1, 3; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Advanced Research Systems, Macungie, Pennsylvania, United States; 3Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

The mixing of five or more elements, in near equimolar concentrations, to form disordered substitutional solid solutions is a central feature of the class of materials known as high-entropy alloys (HEAs). It is now becoming clear that the most promising HEAs for practical applications may actually be those which undergo phase transformations and separations during cooling. The present talk describes an approach to guide the development of multi-phase HEAs, using a simple Monte Carlo model with parameters derived from first-principles calculations. These high-throughput simulations are compared with neutron scattering, in situ microscopy, and calorimetry measurements. We demonstrate that the present technique captures not only the qualitative features, but also gives accurate quantitative results for the intermetallic phase formation and microstructure evolution of the Al-containing HEAs. Work is underway to generalize the approach and study a wider range of compositions.

3:45 PM PM04.09.03
Quantification of Solid-Solution Phase Stability and Short-Range Ordering in High Entropy Alloy from Atomistic Simulations Zhenyu Liu and
High entropy alloy (HEA, also known as compositionally complex alloy) refers to simple-phase solid solution alloy that contains multiple principal components in equimolar or near-equimolar ratios. To computationally address the complexities of this type of high-order alloy systems, we have performed atomistic simulations to predict the solid-solution stability as well as the short-range ordering in CoCrFeNi and AlCoCrFeNi bulk alloys and CoNiRuRh nanoparticles. In our simulations, the interatomic interactions were described using a set of modified embedded atom method (MEAM) interatomic potentials for these alloy systems. First, we used atomic simulation methods to examine solid-solution phase formation rules for CoCrFeNi high entropy alloy. Using the Monte Carlo (MC) simulations based on the developed MEAM potentials, we sampled the thermodynamically equilibrium structures of the CoCrFeNi alloy and further predicted that the CoCrFeNi alloy could form a solid solution phase with high configurational entropy of 1.329 at 1373 K. Then, we examined the stability of this solid solution phase of the CoCrFeNi alloy against the well-recognized solid-solution phase formation rules by varying the MEAM potentials and thus tuning the atom size and mixing enthalpy in the alloy. Our simulation results revealed that it required atom size difference effect $\Delta a/a = 0.05$ and mixing enthalpy effect $-10$ kJ/mol $< \Delta H < 0$ kJ/mol for the modeled CoCrFeNi alloy to remain a single solid solution phase. Furthermore, we studied the stability of solid-solution phase of AlCoCrFeNi HEAs using the developed MEAM potentials and the atomistic MC simulation method. In our MC simulations, different constituent elements were allowed to exchange their positions and thus the modelled HEAs were relaxed to their thermodynamic equilibrium states after several millions MC steps at 1300 K. The mixing Gibbs free energy of the HEAs was calculated using adiabatic switching thermodynamic integration method. We predicted that the AlCoCrFeNi HEAs would form a single fcc solid-solution phase when $x < 0.21$, a single bcc solid solution phase when $x > 1.08$, whereas a mixture of fcc and bcc phases when $0.21 < x < 1.08$. Our theoretical results are quite consistent with experimental observation. Moreover, we investigated the formation of solid solution phase in Co$_{12}$Ni$_{20}$Ru$_{40}$Rh$_{20}$ nanoparticles with size ranging from 2 to 5 nm through a combined molecular dynamics (MD) and MC approach. Our simulation results indicated that the local severe lattice distortion could block the diffusion of atoms and hence lead to a stable solid solution phase during a carbothermal shock synthesis procedure. Consequently, we have demonstrated that atomistic simulation techniques as useful methods for understanding the composition-structure-property relation of novel high entropy alloys.

4:00 PM PM04.09.04

Accelerated Atomic-Scale Exploration of Phase Evolution in Compositionally Complex Alloys Alfred Ludwig$^{1, 2}$, Yujiao Li$^3$, Aleksander Kostka$^3$, Alan Savan$^4$ and Helge S. Stein$^1$; $^1$Institute for Materials, Ruhr-University Bochum, Bochum, Germany; $^2$ZGH, Ruhr-Universität Bochum, Bochum, Germany.

Single-phase compositionally complex alloys (CCA) may decompose into multiple phases at elevated temperatures or reactive environments. We present a new methodology to investigate their phase stability in an accelerated way using a combinatorial processing platform which enables: simultaneous synthesis of 36 identical atomic-scale-mixed films by combinatorial co-deposition of 5 elements on an array of 10 mm-diameter Si wafers; rapid phase evolution in the formed nanoscale reactors upon processing; direct atomic-scale analysis of phase evolution after each processing step by atom probe tomography, complemented by transmission electron microscopy. Using this approach, we efficiently elucidate phase evolution by monitoring the redistribution of individual atoms upon annealing. Exemplaric results from nanocrystalline CrMnFeCoNi show that this alloy is unstable and already decomposes after 1 hour at low temperatures of around 300°C. The combinatorial processing platform was also used to explore the oxidation of this CCA. This concept will accelerate the design of novel structural and functional nanocrystalline multinary materials with superior properties, as the phase space of multiple principal element alloys can be more quickly and efficiently explored, resulting in the knowledge of which phases form or decompose at different processing conditions.


4:15 PM PM04.09.05

Combinatorial Exploration of High Entropy Alloys Sebastian A. Kube$^1$, David Uhl$^2$, Amit Dutye$^3$, Aparva Mehta$^4$ and Jan Schroers$^4$; $^1$Yale University, New Haven, Connecticut, United States; $^2$Southern Connecticut State University, New Haven, Connecticut, United States; $^3$SLAC National Accelerator Laboratory, Menlo Park, California, United States.

High Entropy Alloys (HEAs) are compositionally complex and span a vast composition space with many compositions potentially forming single-phase solid solutions. The quantitative prediction of solid solution structure requires a basis of consistent experimental data covering a significant portion of the alloy space. Here, we create the basis for such predictions by fabricating and characterizing 2,478 quinary HEAs based on the elements Al, Cr, Mn, Fe, Co, Ni, and Cu through combinatorial co-sputtering and high-throughput EDX and synchrotron XRD. By mining the data, we show that the solid solution structure can be predicted through the atomic size difference and the content of BCC/FCC elements in the alloy. Also, we find that the BCC structure becomes increasingly favorable with increasing atomic size difference, because it accommodates atoms of various sizes more efficiently than FCC.

4:30 PM PM04.09.06

Electrochemical and Mechanical Properties of Al-Cr-Nb-Y-Zr Based Nitride Thin Films Kristina M. Johansson$^1$, Pavel Soucek$^2$, Ajshwarya Srinath$^1$ and Erik Lewin$^1$; $^1$Uppsala University, Uppsala, Sweden; $^2$Masaryk University, Brno, Czechia.

Recently multicomponent nitrides with five or more elements have attracted a lot of attention due to their excellent material properties such as high hardness, thermal stability as well as corrosion and oxidation resistance. These nitrides are based on the high entropy concept where the high entropy of mixing will favor the formation of a solid solution. In many cases, it has been shown that such nitrides can outperform their respective binary nitrides [1].

In this study, Al-Cr-Nb-Y-Zr-N thin films were synthesized to investigate the effect of nitrogen content on mechanical and electrochemical properties. The Al-Cr-Nb-Y-Zr-N system was chosen since binary and ternary nitrides based on Al, Cr, Nb and Zr have been extensively studied for their corrosion resistance and high hardness. Also, by addition of yttrium corrosion and oxidation resistance can be improved as previously studied for the Cr-Al-Y-N and Ti-Cr-Al-N systems [2-3]. The films were synthesized by reactive dc magnetron sputtering using elemental targets of the respective elements and an Ar/N$_2$ gas mix. The ratio of gases was varied in order to obtain films with varying nitrogen content, from pure alloy to nitride material. The films with no nitrogen was amorphous. For high nitrogen contents only one crystalline phase with NaCl-type structure is observed, indicating a solid solution material in analogy with the high entropy materials. The hardness increased up to 32 GPa for the films with highest nitrogen content, about 40 at.%. Corrosion resistance, studied by polarization measurements between -0.2 V to +1.5 V in a 1.0 M HCl aqueous electrolyte, showed improved corrosion resistance for all the studied samples, i.e. increased corrosion potential and lower current densities, compared to an industrial stainless steel reference sample (hyper-duplex stainless steel). Furthermore, the films with highest nitrogen content showed higher corrosion resistance compared to the metallic films. Thus, this material
system shows a potential for the use as protective coatings in harsh environments.

References

4:45 PM PM04.09.07
Pseudo High Entropy Alloys
Yonghua Meng, Jie Pan and Yi Li; Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China.

High-entropy alloys (HEAs) are defined as an alloy with at least five principal elements and equiatomic or near-equatomic composition. However, some so-called HEAs should be considered as pseudo-binary or ternary system due to similar properties of the constituent elements. Here we report our investigation of HEAs based on RE-Al-Co (RE = La, Ce, Pr, Nd Sm and Dy) elements with more than five principal elements. Our study shows that the microstructure changes from amorphous phase to multi-phases when the number of elements increases from 5 to 8. In addition, ZrTiHfTM (TM = Cu, Ni, Co and Fe) alloys exhibit the similar B2 structure with binary Zr6Cu38 alloy. These were attributed to possible decrease rather than increase in entropy because of mixing enthalpy of some elements (e.g. rare elements) is almost zero. In this regards, many of the HEAs should be considered as pseudo-HEAs.

SESSION PM04.10: Mechanical Properties of BCC Alloys
Session Chair: Katsushi Tanaka
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 105

8:30 AM *PM04.10.01
Theory of Strengthening in BCC High Entropy Alloys
William A. Curtin and Francesco Maresca; Ecole Polytechnique Federale, Lausanne, Switzerland.

The refractory BCC High Entropy Alloys (HEAs) in the class of Mo-Nb-Ta-V-W are very strong (1-1.5 GPa) at room temperature and have exceptional retained strengths of 400-500 MPa at 1600°C. The mechanistic origin of these outstanding properties is not yet understood, in spite of extensive experimental studies of these and related alloys. Here, we present a parameter-free theory for the strength versus temperature in this class of BCC HEAs based on the motion of edge dislocations through the random energy landscape created by the solute fluctuations. Excellent agreement with results from direct large-scale atomistic simulations at T=0K is achieved for a range of alloys. Moreover, very good agreement with experiments is achieved for the same alloys at T=300°C, and for the two alloys MoNbTaW and MoNbTaVW that have been studied up T=1600°C. The fundamental origins of the high retained strength are achieved because of large barriers to edge motion. The motion of screw dislocations is also considered, and are also strengthened but by different physical emerging from the high randomness in the alloy. The edge theory enables computationally-guided design of new alloy compositions aiming for the highest retained strengths and strength-to-weight ratios in this family of alloys, and several compositions are proposed.

9:00 AM *PM04.10.02
Body-Centered Cubic High-Entropy Alloys—Understanding of the Mechanical Properties and Associated Underlying Deformation
Mechanisms
Jean-Philippe Cousseau1, Guy Dirras2, Frederic Mompiou3, Daniel Caillard3 and Ivan Guillot1; 1ICMPE CNRS-UPEC, Université Paris Est, Thiais, France; 2LSPM CNRS, Sorbonne Paris Cité, Université Paris, Villetaneuse, France; 3CEMES-CNRS, Toulouse, France.

Thanks to an attractive concept, high entropy alloys are actually among the most studied materials in the metallurgical field. In addition to the exploration of new materials, they also provide the opportunity to revisit the basic concepts of metallurgy. Among the most studied high entropy materials, those with body-centered cubic system are particularly interesting as they mainly retain high mechanical properties and are candidates for structural applications under extreme conditions. The present talk provides an overview on the properties of single phase body-centered cubic high-entropy alloys. Analysis of the existing data from the available literature will be performed and trends relative to the mechanical behavior and underlying deformation mechanisms will be proposed. The emphasis will be put on recent experimental results aimed at bringing basic knowledge on the mobility of dislocations in such complex disordered solid solutions.

9:30 AM PM04.10.03
Development of Precipitation Strengthened CCAs in the AlCrFeNiTi System for High Temperature Structural Applications
Silas Wolff-Goodrich, Thorsten Meiners, Christian H Liebscher and Gerhard Dehm; Max Planck Institute, Düsseldorf, Germany.

The need to make energy generation and conversion more sustainable and to reduce the emission of harmful gases requires the development of novel high temperature stable materials. Several of the so-called compositionally complex alloys (CCAs) have been shown to possess unique property combinations and, in some cases, exceptional mechanical properties. There is much promise in the development of cost-effective CCAs with the necessary properties for use in high temperature applications. In particular, alloys with high degrees of both solid solution strengthening and precipitation of creep resistant ordered phases, such as the L2₁-Heusler phase, can be realised under this alloy development strategy.

In the present study we are exploring the AlCrFeNiTi system for alloys exhibiting a BCC solid solution matrix and hierarchically arranged B2-NiAl and L2₁-Ni₃TiAl precipitate phases. The goal is to obtain novel high temperature alloys with densities of approximately 6 g/cm³ and mechanical stability up to 900 °C. Using arc melted samples containing 5-35 at.% of each component, we have begun screening the composition space in this system. More than 15 unique alloy compositions have been produced and characterised in the as-cast state using XRD, DSC, SEM, and micro-hardness measurements. One particularly promising alloy with a composition of 25Al-15Cr-30Fe-20Ni-10Ti (in at.%) has been further investigated using high resolution TEM and STEM. We have observed a wide compositional range of stability for the L2₁ and BCC phases, with a strong trend to form higher L2₁ phase fractions up to ~70 vol.% for increasing Al content. Alloys with Ti concentrations of ~15 at.% tend to form large fractions of the Laves phase and for ~25 at.% Ti are almost entirely comprised of the Laves phase.

The trends thus far observed have guided us to the most promising region of the composition space in this system for the target application area, this region being (20-25)Al-(10-15)Cr-(30-35)Fe-(10-20)Ni-(5-10)Ti (in at.%). Upcoming work will include a comparison of results for arc melted compositions to results for thin film composition libraries, characterisation of vacuum-induction-cast (VIC) samples in both as-cast and heat treated conditions, as well as

*PM04.10.01

PM04.10.02

PM04.10.03

SESSION PM04.10: Mechanical Properties of BCC Alloys
High-entropy alloys (HEAs) with a vast alloy-design space have offered new avenues to explore novel low-cost, high strength-to-weight ratio structural materials. However, to date, no satisfactory light-weight HEAs (LWHEAs) have been developed, due to the difficulty in balancing strength, ductility, and density. In this study, we investigate the phase stability and transformation behavior of a newly-designed light-weight Al1.5CrFeMnTi HEA. The coherent precipitation of the nano-sized L21 phase within the body-centered-cubic (BCC) matrix at intermediate temperatures was observed, and their size, shape, coherency, and spatial distribution can be tuned through selected annealing treatments. Moreover, the CALculation of PHase Diagrams (CALPHAD) and first-principles calculations successfully optimize the compositions of light-weight HEAs with a coherent nano-sized L21 precipitate-strengthened BCC two-phase structure. With the support of the optimized CALPHAD database, first-principles calculations and experimental efforts, novel light-weight HEAs, featuring lower density and lower cost, have been designed for high-temperature and cost-effective light-weight applications.

Acknowledgments: We very much appreciate the support of the U.S. Army Research Office project (W911NF-13-1-0438) with the program managers, Drs. M. P. Bakas and D. M. Stepp and the National Science Foundation (DMR-1611180) with the program directors, Drs. G. Shiflet and D. Farkas. The present research used resources at the Nanophase Materials Sciences (CNMS) and Spallation Neutron Source (SNS), a DOE Office of Science User Facility operated by ORNL. Also, the present research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

10:00 AM BREAK

SESSION PM04.11: Refractory HEAs and Multiphase Alloys
Session Chair: Ian Mellor
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 105

10:30 AM *PM04.11.01
Solving the Strength-Ductility Trade-Off Dilemma of High-Entropy Alloys via Interstitial Hardening
Zhifeng Lei, Xiongjun Liu, Yuan Wu, Hui Wang and Zhaoping Lu; University of Science and Technology Beijing, Beijing, China.

Oxygen, one of the most earth-abundant elements, often appears as an undesired interstitial impurity in metallic materials. Even when providing strengthening it renders metals brittle, causing the strength-ductility trade-off dilemma, i.e., increasing the strength leads to decreasing ductility. Here, we report an anomalous interstitial strengthening effect of oxygen in a family of single-phase refractory high-entropy alloys (HEAs) at ambient temperature. In contrast to conventional interstitial strengthening, strength and ductility are both substantially improved when doping a model Ti2ZrHfNb HEA with 2.0 at.% oxygen, breaking the paradigm of the strength-ductility trade-off with an inexpensive and ubiquitous element. Alloying with oxygen leads to the formation of ordered oxygen complexes (OOCs) which pin dislocations and subsequently promote their cross slip and multiplication. This novel strain hardening mechanism improves work-hardening capability and thus ductility. This finding revises our current understanding of the effect of oxygen on the mechanical behavior of metallic materials and provides new pathways for the development of high-performing alloys which have the capability to access new performance regimes.

11:00 AM PM04.11.02
Development of Refractory High Entropy Alloys with Enhancing High Temperature Strength and Room Temperature Ductility
Ilhwan Kim, Hyunseok Oh and Eun Soo Park; Seoul National University, Seoul, Korea (the Republic of).

As science and technology has evolved, there exists an extreme environment where conventional materials are difficult to use. Refractory metals are one of the most promising candidates for extreme environment especially in high temperature condition. Tungsten is a widely used structural material exhibiting excellent physical properties in high temperature environment, with high melting point, high resistance against mechanical wear. For these properties, tungsten is currently being considered as structural materials in fusion power plants for plasma facing components (PFCs). However, refractory metals, including tungsten, have some drawbacks for using as structural materials. The first is a dramatic softening phenomenon in high temperature range. Their high strength and hardness in low temperature range cannot be maintained in high temperature range due to its softening phenomenon. The other is brittle behaviour below room temperature. Operating temperature of structural materials is determined above the ductile-to-brittle transition temperature (DBTT) below the recrystallization temperature. Therefore brittle behaviour at room temperature limits the application of refractory alloys because refractory alloy should be used above room temperature. In particular, the DBTT of refractory alloy is increased by small amount of adding elements. It means orthodox alloying concept cannot be answer to increasing strength and ductility of refractory alloys. Thus, it is required to develop a new-type refractory alloy to tailor these mechanical properties. In the present study, maintaining good properties of tungsten, we developed novel refractory alloys to enhance mechanical properties by utilizing design concept of high entropy alloys (HEAs). To design materials having high temperature strength and room temperature ductility, we use two parameters, atomic size misfit parameter for solid solution hardening and valence electron concentration. Because of mixing effects among the elements, tungsten based HEAs had enhanced mechanical properties than pure tungsten. To evaluate the high temperature mechanical properties, we conducted compression test and thermal conductivity measurement at high temperatures. As a result, tungsten based HEAs were improved to strength and ductility simultaneously. This study offers an explanation of the tendency between physical properties and configurational entropy. Moreover, the mechanical and thermal properties database provides us a better understanding of refractory alloys, which can suggest guidelines for tailoring refractory alloys.

11:15 AM PM04.11.03
Boundary Micro-Cracking in a Metastable High-Entropy Alloy Shaolou Wei, Jinwoo Kim and C. Cem Tasan; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.
Mechanically-induced martensitic transformation can be a double-edged sword: depending on composition and processing it can either lead to various beneficial mechanical effects (e.g. transformation-induced plasticity, transformation-toughening), or cause local brittleness and damage nucleation. While several corresponding guidelines are present in steels research, controlling microstructure metastability has not been drawing attention in the fast-growing field of high-entropy alloys. In the present work, we investigated the damage mechanisms of a mechanically metastable Fe₄₅Mn₃₅Co₁₀Cr₁₀ high-entropy alloy under uniaxial tensile loading. Our integrated in-situ scanning electron microscopy / electron backscatter diffraction experiments revealed a twofold effect of the highly localized strain, induced by asynchronously transformed martensite, leading to boundary damage nucleation and dissimilarly oriented martensitic variant formation. The latter suppresses slip transfer between adjacent grains, further expediting the growth of the nucleated damage incidents. Based on these experimental observations and corresponding theoretical calculations, we discuss the underlying mechanisms and propose a sequence of micro-events that create the observed phenomena.

11:30 AM PM04.11.04
Carbon Supersaturated Refractory Multicomponent Nanostructured Coatings Stefan Fritz, Paulius Malinovskis, Lars Riskehr, Linus von Fieandt, Erik Lewin and Ulf Janson; Uppsala University, Uppsala, Sweden.

The combination of ceramic hardness with high ductility is a major challenge in the design of protective thin films and high entropy alloys (HEAs) are a promising pathway to achieve new high-performance materials. While HEA thin films have been studied to some extent by experimental and computational materials science, there is only limited information available about the influence of carbon on HEA thin films, especially when prepared with physical vapor deposition techniques. In this study, we report on the influence of carbon on the structure and properties of two different HEA alloys in the Cr,Nb,Ta,Ti,W system. The metal composition of these alloys includes a near-equimolar alloy and a Ta,W-rich composition.

We have deposited Cr,Nb,Ta,Ti,W-C thin films by non-reactive magnetron sputtering. The material properties were strongly depending on the composition and the best results were observed for Ta,W-rich films which crystallise in a bcc structure with a strong (110) texture. TEM analysis revealed that the films exhibit coherent grain boundaries with specific crystallographic directions. The addition of 8 at.% led to the formation of a meta-stable bcc supersaturated solid-solution without the formation of carbide precipitates. The main effect of the carbon addition was a significant grain refinement reducing the column width from 35 to 10 nm, which resulted in an increase in hardness from 14 to 19 GPa while the reduced E-modulus was unaffected. The enhanced hardness will be discussed in terms of solid solution hardening and grain refinement strengthening. Nanoindentation deformation studies revealed that the addition of carbon significantly reduces the plastic deformation around the indents without showing any signs of crack formation which is explained by the special arrangement of the grain boundaries. Finally, the effect of carbon addition on the corrosion properties was likewise investigated in 0.6 M NaCl environment. High pitting corrosion resistance was found for the Cr,Nb,Ta,Ti,W-C thin film composition, with a corrosion potential of 0.23 V (vs. Ag/AgCl) and a transpassive region equal to hyper-duplex stainless steel (i.e. SAF3207HD).

11:45 AM PM04.11.05
Mechanical Behavior and Oxidation Resistance of a Particle-Reinforced Fe-Al-Cu-Ni-Ti Alloy Manja Krueger, Volodymyr Bolbut, Georg Hasemann, Katja Wollgarten and Dmitry Naumenko; 1University of Magdeburg, Magdeburg, Germany; 2IK-2, Research Center Jülich, Jülich, Germany.

We introduce the compositionally complex alloy (CCA) Fe₂₅Al₂₅Cu₁₁:Ni₁₀,5Ti₄,5 which provides attractive mechanical properties and a density of 5.6 g/cm³, which is lower compared to well-investigated alloys of the Al-Co-Cr-Fe-Ni-Ta-W family. This novel material has a bcc matrix phase and is reinforced by finely dispersed intermetallic particles, which are stable up to about 1100 °C. Hardness measurements and compressive tests in a temperature range between room temperature and 1100 °C show the advanced mechanical performance of this novel CCA compared to high entropy alloys (HEAs). These first results demonstrate the high potential of this alloy as structural engineering material for high temperature applications. During oxidation tests at 900 °C the material shows a slight mass gain which is due to the formation of an alumina layer at the surface. This layer has a thickness of ~1 µm after 100 h of thermal treatment, which again grows during further thermal cycling. Cyclic oxidation experiments at 1000 °C and 1100 °C resulted in spallation of this oxide layer, which leads to a mass loss of the samples. An approach to overcome this problem by the addition of a sixth alloy component will be discussed.

1:30 PM PM04.12.01
Applying Combinatorial and High-Throughput Methods to Develop Compositionally Complex Alloys Alfred Ludwig, Jan Alters, Janine Pfetzing-Mücklich, Jan Alters and Sigurd Thielenhaus; 1Institute for Materials, Ruhr-University Bochum, Bochum, Germany; 2ZGH, Ruhr-Universität Bochum, Bochum, Germany.

Compositionally complex alloys (CCAs) offer an almost unlimited composition space for new materials, which cannot be explored efficiently by conventional methods. Therefore, the combinatorial fabrication of CCA thin-film materials libraries and their high-throughput characterization is discussed. Materials libraries consist of well-defined composition spreads fabricated by co-deposition from up to five magnetron sputter sources. Chemical (composition), structural (phase, microstructure), electrical (resistivity) and mechanical properties (Young’s modulus, hardness) are measured using high-throughput characterization systems. The aims are to find the compositional limits of the single-phase solid solution existence range and to identify the multiphase constitution beyond these limits. Results for different CCA systems (transition metals, refractory metals) are shown and the visualization of multidimensional datasets is discussed.

1:45 PM OPEN DISCUSSION

2:00 PM PM04.12.02
High entropy alloys (HEAs) are a class of alloys that contain multiple principle elements and display interesting mechanical properties such as increasing ductility with decreasing temperature and resistance to softening at elevated temperatures. Details of the dominant atomistic deformation mechanisms as a function of temperature are key to understanding these unique mechanical trends. Small-scale mechanical testing is well-suited to investigate deformation mechanisms and isolated microstructural features such as grain or phase boundaries. Here we present molecular dynamics simulations of compression of single-crystalline FCC and BCC HEA nanowires and HEA nanowires that contain a single FCC/BCC axially-aligned phase boundary. In single-crystalline HEAs, we identify dominant deformation mechanisms from 50 K to room temperature and investigate the role of heterogeneity in defected crystal structures. In phase boundary-containing nanowires, we also discuss dislocation-boundary interactions and the role of the FCC/BCC interface as a source, barrier, or sink for dislocations. We supplement these results with calculations of stacking fault energy and also compare observed deformation mechanisms to experimental results of compression of single-crystalline and FCC/BCC phase boundary containing HEA nano-pillars.

2:15 PM PM04.12.03
Laser Processing as a High-Throughput Method to Investigate Microstructure-Processing Relationships in a High Entropy Alloy Mu Li and Katharine Flores; Washington University in St. Louis, Saint Louis, Missouri, United States.

The compositional complexity of multiprincipal element alloys, consisting of 4 or more elements without a dominant solvent, presents a challenge for studying their microstructural development and stability. In the present work, we apply a direct laser deposition processing method to construct compositional and microstructural libraries in an efficient and high-throughput manner. Phase formation in an AlCoCrFeNi high entropy alloy was first examined over a wide composition range. As the Al content increased from x = 0.15-1.32, the crystal structure was observed to transition from FCC to BCC/B2. While the onset of BCC/B2 formation was consistent with previously reported results based on cast materials, the FCC structure was observed at larger Al contents in the laser-deposited materials, resulting in a wider two-phase regime. In addition to the presence of the expected phases, the laser-processed microstructure was surprisingly consistent with that produced by casting. The 2-3 orders of magnitude faster cooling rates inherent to laser processing resulted in feature sizes 2-3 times smaller than cast materials, however the morphology of the phases was similar. At low-to-intermediate Al contents, the two-phase alloy exhibited a cellular structure, while at higher Al content, the FCC structure was isolated and confined to the BCC/B2 grain boundaries. The BCC/B2 morphology was also similar to that observed in cast materials. Ongoing work continues to investigate the sensitivity of the microstructure to the laser processing conditions, and will be discussed. This study suggests that the high-throughput laser processing method is an ideal method for rapidly and efficiently evaluating multiprincipal element alloys.

2:30 PM BREAK

SESSION PM04.13: Novel Synthesis and Mechanical Properties
Session Chair: Alfred Ludwig
Wednesday Afternoon, November 28, 2018
Hynes, Level 1, Room 105

3:30 PM PM04.13.01
Solid State Manufacture of High Entropy Alloys via the Metalysis Process Ian Mellor, Lyndsey Benson, Mike Ellis and Nader Khan; Metalysis Ltd, Rotherham, United Kingdom.

Historically Metalysis have produced tantalum, titanium and titanium alloy powders for high performance applications using their solid state electrochemical process. The route for alloy production involves initial preparation of a mixed metal oxide feedstock, followed by electro-deoxidation, to generate an intimately mixed alloy on a microscopic scale. This low energy intensive and environmentally friendly technology, has been used to demonstrate a number of High Entropy Alloys (HEA’s), with complex compositions and microstructures.

In most conventional cases, the manufacture of HEA’s involves high temperature melting, which puts all of the alloying elements into the liquid phase. This can lead to numerous problems and restrict the number of combinations, which can be reliably made. In particularly those where one needs to combine low melting and/or boiling point with refractory elements, and also where there are significant liquid density differences between the constituents causing melt segregation.

The aim is to present the preliminary work carried out by Metalysis, and to show how the solid state process, based on molten salt electrolysis, lends itself to the manufacture of the next generation of HEA’s. This study will focus on some examples whose constituent elements have large differences in both their melting points and liquid densities, for example, but not limited to, chromium, niobium, tantalum, titanium and aluminium.

3:45 PM PM04.13.02
Growth and Mechanical Characterisation of Single-Phase Single-Crystalline FCC and BCC High-Entropy Alloys Tim Lienig, Michael Feuerbacher and Carsten Thomas; Forschungszentrum Jülich GmbH, Jülich, Germany.

High-entropy alloys (HEAs) represent a novel class of metallic materials. Composed of at least five elements in equiatomic or near-equiatomic proportion they show crystalline long-range order while maintaining chemical disorder throughout their lattice. The simultaneous presence of topological order and chemical disorder is unique in metals and poses fundamental questions in basic materials science. Various alloy systems have been reported to form HEAs, crystallising in face-centred cubic, body-centred cubic, and hexagonal structure.

In-depth investigation of structure-property relations of HEAs requires high-quality single-phase, preferably single-crystalline samples. Single-crystalline samples allow the determination of intrinsic materials properties without the influence of secondary phases or grain boundaries.

We report on the mechanical characterisation of single-crystalline equiatomic fcc CrMnFeCoNi and our advancements in the production of single-crystalline bcc TiVZnNbHf HEAs. Single-crystals are grown by means of the Bridgman technique from master-alloys synthesised from high-purity elements by arc-melting and in an inductively-coupled levitation crucible. Mechanical characterisation was performed on a modified Zwick Z050 compression deformation rig.
CrMnFeCoNi single-crystals successfully produced by the Bridgman technique have a volume of several cubic centimetres and a maximum diameter of 20 mm, making the high-quality material accessible to most physical-property measurements. X-ray Laue back-scattering images taken across the surface are sharp and mutually consistent. SEM and light microscope images reveal a grain-free microstructure, with EDS measurements confirming the equiatomic composition of the crystal. Macroscopic specimens (2.5x2.5x5 mm³) prepared from the large single crystals are used to perform mechanical compression testing along different crystallographic directions. By incremental testing, e.g. stress relaxations and strain-rate changes, thermodynamic activation parameters of the plastic deformation mechanism are determined.

A growth route for equiatomic TiVZnNbHf single crystals is currently under development and will be presented additionally. Our previously published results reveal that this material is a homogeneous single-phase HEA with bcc structure that has a significantly lower melting temperature than TiZnNbHfTa bcc HEAs. Therefore single-crystal growth of TiVZnNbHf HEAs can be addressed by means of the Bridgman technique, and we expect to grow crystals of the same volume as CrMnFeCoNi single-crystals.

4:00 PM PM04.13.03
Microstructure and Phase Transformation in Al-Containing Refractory High Entropy Alloys SangJun Kim, Hyunseok Oh and Eun Soo Park; Seoul National University, Seoul, Korea (the Republic of).

Refractory high entropy alloys with BCC structure composed of group-4 to group-6 refractory elements (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W) were reported to exhibit superior mechanical properties at high temperature above 1000 C comparing Ni-based superalloys. Recently, Al-containing refractory high entropy alloys were reported to have unique structure in which disordered BCC phase (A2) are precipitated in ordered BCC matrix (B2). In spite of exceptional high strength at high temperature, however, they showed low ductility due to the ordered matrix and Zr-based precipitates in grain boundaries. Here, we investigated the phase transformation behavior of Al-containing refractory high entropy alloys to control the microstructure for balancing strength at high temperature and ductility at room temperature. Microstructural evolutions of various alloys in (Ti,Zr,Hf)-(Nb,Mo)-Al system during heat treatment were analyzed in terms of phase equilibrium and decomposition of disordered and ordered BCC phase. Through systematic studies of thermal processing condition, refractory high entropy alloy in which ordered B2 phase are precipitated in disordered A2 matrix was developed. This result could provide an effective guideline for tailoring microstructure of Al-containing refractory high entropy alloys, and developing promising HEAs for high temperature structural materials.

4:15 PM PM04.13.04
Two Modes of Screw Dislocation Motion in an Equiatomic Alloy Yuri Osetsky1, James R. Morris1,2 and George M. Pharr1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 3Texas A&M University, College Station, Texas, United States.

Molecular dynamics simulations show two distinct mechanisms of \(\frac{\pi}{2}\times110\rightarrow\{\{111\} screw dislocation glide in an equiatomic Ni-Fe solid solution face centered cubic crystal structure (fcc). At high stresses (above ~130 MPa), it glides under "typical" friction-controlled conditions. At lower stresses, the dislocation moves in a very rough manner that cannot be described as continuous glide but rather a motion through a set of obstacles. We demonstrate that these obstacles are localized and can produce large pinning, yet the dislocation does not exhibit significant bowing as normally expected for strong, localized pinning. The threshold stress for transition between modes depends on the dislocation segment length and ambient temperature. At 300 K the flow stress saturates at ~130 MPa for length above ~140 \(\ell\) (\(\ell\) is the Burgers vector). We demonstrate that the statistical behavior is important, with rare events dominating the behavior. The nature of internal obstacles to dislocation glide is likely due to the low stacking fault energy and composition effects in the core energy: dislocation accommodates its width and shape for its Shockley partials contain more Ni atoms. Energy barriers between minimum energy configurations define the flow stress. The observations are discussed in terms of their potential relevance to the mechanisms of plastic deformation in single-phase high entropy alloys.

This work was supported by the US Department of Energy Office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

4:30 PM PM04.13.05
Effect of Ti and C Additions on Microstructural Refinement and Mechanical Properties of Cast AlCoCrFeNi Compositionally Complex Alloys Alex Asabre1, Ulrich F. Volkert1, Oleg Stryzhyboroda2, Janine Pfetzing-Micklich1, Ulrike Hecht1 and Guillaume Laplanche1; 1Ruhr University Bochum, Bochum, Germany; 2ACCESS e.V., Aachen, Germany.

Hot forming tools need to exhibit good strength, high hardness and wear resistance at high temperatures, combined with an adequate ductility at high and low temperatures. Currently boron doped steels are used for such applications, however there is a growing demand of new materials with improved properties. In the present study, the influence of Ti and C additions on microstructure and mechanical properties of an as-cast multi-phase A12(C2O12C2F2F2N2) composition in at. % compositionally complex alloys is investigated. The alloys with various additions were arc melted and subsequently drop cast. The as-cast microstructures were characterized using scanning and transmission electron microscopy. Microstructural analyses revealed a Widmanstätten microstructure in all cast alloys consisting of face-centered-cubic (fcc) plates which formed upon cooling in a disordered body-centered-cubic (BCC) matrix containing ordered B2 precipitates. The additions of Ti and C resulted in microstructural refinement with the presence of titanium carbides at grain boundaries and inside the grains of the high temperature BCC matrix. This result in combination with thermodynamic calculations suggest that titanium carbides formed in the melt and acted as nucleation sites for heterogeneous nucleation during solidification. The volume fraction of the BCC phase slightly increases with increasing Ti and C additions while the Cr-, Fe-, Co-, and Ni-concentrations are decreased accordingly.

We present a high entropy alloy (HEA) from the system Al-Co-Cr-Fe-Ni-W:Mo-Si-C which was designed to allow for precipitation hardening by annealing in the temperature range from 600 to 900°C. The alloy development was performed using centrifugally casted specimens and supported by thermodynamic computations using ThermoCalc software and the TCFE9 database. The microstructure of two selected samples in as-cast and annealed
conditions was analysed using XRD, SEM, EBSD, EDX and TEM measurements. The as-cast microstructure consists of spinodally decomposed BCC dendrites enveloped by FCC/M23C6 eutectic. Upon annealing at 700°C for 24h nanoscale intermetallic phase precipitates form within the spinodal BCC as well as from FCC. Furthermore, the L12 phase precipitates within the FCC phase below 600°C. Precipitation is exquisitely uniform leading to an increase in microhardness from 415 HV0.5 in the as-cast state to 560 HV0.5 after annealing, making the material suitable for tooling applications. We investigated the stability and coarsening of this microstructure using (i) varying annealing temperatures and (ii) varying time for a constant temperature of 700°C. We will present the microstructure evolution during coarsening and the corresponding mechanical properties obtained from instrumented indentation experiments.

SYMPOSIUM PM05

TUTORIAL: Field-Assisted Sintering—Microwaves, SPS and Flash Sintering
November 25 - November 25, 2018

* Invited Paper

TUTORIAL
Field-Assisted Sintering—Microwaves, SPS and Flash Sintering
Sunday Afternoon, November 25, 2018
Hynes, Level 2, Room 208

1:30 PM
Field Assisted Processing of Advanced Materials Eugene Olevsky; Sand Diego State University

Sintering of powder materials is a widely used technological process, and, on the other hand, it is one of the most basic physical phenomena. The success of the industry in the development of computer-aided manufacturing made it possible to create a significant number of various devices for the processing of materials by the simultaneous action of heat, applied pressure, as well as electric current or electromagnetic field. These devices and processes belong to the area of so-called field-assisted sintering which offers fundamentally new materials processing conditions. Field-assisted sintering, which includes also the impact of electromagnetic factors, is, accordingly, a vivid example of a fundamental and multi-physics process. These sintering techniques enable materials and components with unique properties. Field-assisted sintering technologies thus represent an excellent experimental base for technologists engaged in the discovery of new materials. Simultaneously, field-assisted sintering opens up wide opportunities for modeling the processes of materials consolidation and synthesis taking into account numerous physical phenomena. The ninety minute tutorial will provide an introduction to sintering fundamentals as well as basics of field-assisted sintering techniques, including microwave and spark plasma sintering.

3:00 PM BREAK

Flash Sintering Rishi Raj; University of Colorado Boulder

In a 2010 paper it was shown that yttria-stabilized zirconia can be sintered in ~5 s at a temperature of 850oC. (Conventional sintering requires several hours above 1400 oC – flash sintering is about four orders of magnitude faster.) Since then many different ceramics, including those that are semiconductors, electronic conductors, ionic conductors and high insulators, have been processed in this way. The flash phenomenon occurs in powder pressed samples, polycrystals and single crystals. An abnormal increase in electrical conductivity, and electroluminescence (in addition to rapid sintering) are characteristics of flash. Results from in-situ experiments at Synchrotrons are starting to provide fundamental insights. Molecular dynamics models are showing the significance of phonon-electron interactions. A roadmap for flash manufacturing is starting to develop. This emerging new field cuts across, materials science, ceramics science, engineering and solid state physics.

4:30 PM
Open Discussion
Invited Paper

Superplastic Flow at Relatively Low Furnace Temperature can be attained in Dense Polycrystalline Oxide Ceramics such as Tetragonal ZrO2 Polycrystal (TZP). For the first time, by taking into account the explicit influence of the electric current effect on the SPS densification mechanism, the constitutive equations describing the electric current-assisted hot pressing of conductive powders are developed. The densification mechanism is determined by the inverse regression of the new SPS constitutive equations and by utilizing the experimental results on a conductive powder consolidation with and without the participation of the electric current effect. The developed model provides the theoretical basis of the new method of controllable interfaces which allows extending flash sintering/SPS to nearly all materials, controlling sample shape, and an energy efficient mass production of small and intermediate size objects.

Controllable Interface Approach in Field-Assisted Sintering

Voltage-Dependent Electronic Conductivity in Yttria-Stabilised Zirconia Ceramics

Reactive Flash Sintering

Potential Flash Sintering and Related Field-Enhanced Processing for Oxide Ceramics

Electric field enhanced sintering is gaining interest in recent years owing to the accelerated consolidation compared to conventional, pressure-less sintering. In particular, flash sintering, where densification occurs almost immediately (typically <10 seconds) under high electric field, has attracted extensive attention as an innovative sintering technique. The flash sintering has been demonstrated in various ceramics, and almost full density has been achieved at relatively low furnace temperature for very short time. The non-equilibrium, drastic densification under strong electric field results from accelerated diffusional mass transport triggered by flash event; electric conductivity of material is highly increased, and excess anion vacancies are generated beyond threshold field strength and temperature. We should note that the flash event is rather a common phenomenon in oxide ceramics; it has been reported that flash event takes place not only in powder compact but also in dense, polycrystals even in single crystal. By employing flash event, for instance, superplastic flow at relatively furnace temperature can be attained in dense polycrystalline oxide ceramics such as tetragonal ZrO2; polycrystal (TZP). For example, elongation to failure of more than 150% of nominal strain can be achieved in TZP at a furnace temperature of less than 1000°C and a strain rate of faster than 1×10⁻³ s⁻¹. Flash sintering and field-enhanced sintering-related phenomena can be innovative processing techniques, i.e. consolidation and near-net shaping, of ceramic materials.
Understanding and Controlling Flash Sintering—from a Case Study of ZnO to Other Ceramic Materials

This presentation will discuss a series of our recent studies of flash sintering. ZnO was used as our primary model system; TiO$_2$ and 8YSZ have also been studied. The effects of various doping, grain sizes (including single crystals) and sintering atmosphere have been systematically examined. A coupled thermal and electric runaway model has been developed to forecast the onset flash temperatures for ~20 cases with different materials, doping, particle sizes, and atmospheres [Acta Mater. 125:465 (2017)]. Using this new two-step flash sintering (TSFS) technology, fast densification with suppressed grain growth was achieved [Scripta Mater. 141: 6 (2017)]. Furthermore, various electric field/current effects on microstructural developments have been discovered and investigated. Interestingly, we recently demonstrated the feasibility of flashing ZnO at room temperature (without any furnace/external heating) to subsequently achieve ~98% densities in ~30 seconds with the adsorption of water vapor [Scripta Mater. 142: 79-82 (2018)]. This new water-assisted flash sintering (WAFS) technology represents an exciting opportunity for significant economic and cost savings.

The scientific questions and technological opportunities of flash sintering were discussed in a most recent Viewpoint article [Scripta Mater. 146: 260-266 (2018)].

11:00 AM *PM05.01.06
Insight into the Flash Sintering Process Mechanisms in Ceramics

Thomas Tsikalakos; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Flash Sintering (FS) utilizes the non-equilibrium rise in current under applied electric field to densify ceramic green body compacts in seconds. A new method, EDXRD Temperature Calibration, utilizes white energy dispersive x-ray diffraction (EDXRD) from a synchrotron source to track the lattice expansion of the ceramic during FS compared to the lattice expansion during conventional sintering (CS). The materials used in this study were ZnO, TiO$_2$, CeO$_2$ and BiFeO$_3$ oxides and BiC, TiB$_2$, ZrB$_2$, and BN nonoxides. This investigation analyzes the proposed mechanisms for the onset of the flash, the cause of the enhanced sintering kinetics during FS, and the temperature for each theory. The temperature has been measured directly as it causes a proportional thickening of the bonds, which increases the unit cell volume. For all materials the temperature during FS is close to that of CS. The new ways of performing FS experiments on ZnO by ramping the current linearly and by AC power supply, microstructural inhomogeneity, grain growth, and other physical properties will be also shown.

The FS of BiFeO$_3$ is a homogeneous process and since the FS takes place at quite low temperatures (350°C < T$_c$) it explains excellent dielectric properties. However, for CeO$_2$ and TiO$_2$, exhibited inhomogeneous lattice expansion from anode to cathode.

Acknowledgements

Thanks to my current group Harry Charalambous, Mary Anne Wassel, Dr. Shikhar Krishn Jha, & to ONR Dr. Antti Makinen ONR N00014-15-1-2492 & from Purdue ONR 4104-7892-820133 & to our collaborators: Dr. John Okasinski at Argonne N.L, Prof. Luis Perez Maqueda of University of Saville, Spain and his group, Dr. Haiyan Wang, Dr. Xinghang Zhang, Dr. R. Edwin Garcia, Xin Li Phuah, Han Wang, Jadhun Cho, Jin Li, and KSN Vikrant, at Purdue University, Dr. Amiyah Mukherjee at UC Davis, Dr. Steve Hellberg and Dr. Noam Bernstein at Naval RL.

SESSION PM05.02: Field-Assisted Processing Techniques II
Session Chairs: Woohong (Rick) Kim and Eugene Olevsky
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 101

1:30 PM *PM05.02.01
Energy Coupled to Matter for Field-Enhanced Processing

Raymond Brennan, Victoria Blair, Michael Kornecki, Nicholas Ku, Selva V. Raju, Franklyn Kelllogg, Michael Golt; Aubrey Fry and Carli Moorehead; U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

Energy Coupled to Matter (ECM) research at the U.S. Army Research Laboratory is focused on the study of material interactions with external fields to produce outcomes that are unattainable through conventional means, expanding materials-by-design and processing science capabilities beyond the current state-of-the-art. Research has been conducted to utilize these innovative technologies and material solutions for exploring structure-property relationships of ceramic materials based on their interactions with applied external fields (i.e. magnetic, electric, microwave, etc.). ECM research is focused on manipulation of microstructures, phase formation, and the overall behavior of materials subjected to controlled fields, which can enable rapid densification at reduced temperatures, grain and grain boundary modification, and crystallographic texturing. The ability to rapidly densify materials under less extreme processing conditions can allow for preservation of the nanoscale grain structure, providing the opportunity to improve mechanical properties including strength, hardness, and fracture toughness, which are vital to Army protection applications. Techniques for manipulating materials to make them more responsive to specific fields have also been investigated (ferromagnetic additives for magnetic fields, conductive second phases for electric fields, susceptor materials for microwave fields) to amplify these effects during processing. These strategies have combined experimental design, computational modeling, and in-situ characterization for development of unique ECM processes to enable field-enhanced production of improved components for protection, lethality, and energy-related (i.e. laser host, battery) Army applications.

2:00 PM PM05.02.02
Low Temperature Ceramics Processing Under Electromagnetic Fields—Decoupling Thermal and Field Effects

B. Reeta Jayan; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Understanding the coupling between electromagnetic (EM) fields and matter can advance low temperature processing of several materials including ceramics. It is hypothesized that the EM field depending on frequency and polarization modifies energy barriers for chemical reactions. This talk will demonstrate experiments that use thin conducting films to selectively localize EM field interactions. We aim to delineate processing-structure relationships by creating and probing instances where there can be specific field driven effects that can be distinguished from conventional thermal phenomena.

Specifically, our experiments will couple synthesis and characterization of binary ceramic oxide (e.g., ZrO$_2$) films on conducting (metal) layers under 2.4-2.5 GHz microwave radiation. The solution bath in which the growth happens remains below 250°C even during field exposure. We utilize synchrotron x-ray pair distribution function (PDF) analysis along with transmission electron microscopy (TEM) and Raman spectroscopy to study the crystallization and local atomic order in these thin films. By analyzing how EM field conditions (power, final temperature) influence the local atomic structure, we unlock the potential mechanisms underlying field-assisted phase transformations and the role of defects in these field-induced structural changes.
Defects from Two Perspectives—Microstructure and Impedance Spectroscopy Comparison of Flash Sintered 8YSZ Al2O3 and B4C tapes at room temperature using an electrical potential of 100 - 1500V/cm and a 100W 975nm CW laser to heat the sample. No additional Flash sintering is an energy efficient sintering technique, which has been extensively researched, in recent years. Most of the work reported is on joule bulk TiO2. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry curing/sintering methods leading to energy-efficient manufacturing processes; even for materials like ceramics that conventionally requires high temperatures exceeding 500-2500 oC. Lower temperature processing can further be expanded to other delicate materials such as polymers and can even realize novel polymer-ceramic and metal-ceramic composites for biomedical use.

Open questions remain, however, which may be greatly elucidated by considering these material-specific defect behaviors. For example, in samples processed under DC fields, inhomogeneous grain growth has been observed, with its relation to polarity changing based on the material processed. Furthermore, while the thermal runaway model explains the onset conditions of flash, no work has fully or conclusively proven a mechanism responsible for the rapid mass transport evidenced. Meanwhile, it is clear that the high electric fields in the process must simultaneously interact with the defects present in the material as well as add to the defect populations.

In the interest of exploring these defect contributions, we present a study comparing the final properties of flash sintered 8 mol% yttria-stabilized zirconia (YSZ) pellets using DC and AC fields. Microstructure is examined using scanning electron microscopy (SEM), and the final electrical characteristics are considered using impedance spectroscopy. While SEM gives direct microstructural observation, impedance spectroscopy fills in the picture with smaller scale defect and impurity implications specific to the grain boundary and bulk. A comparison between the two forms of characterization as well as conventionally sintered 8YSZ lends insight into fundamental reorganization and creation of defects produced in ion conductors during flash sintering.

Defects from Two Perspectives—Microstructure and Impedance Spectroscopy Comparison of Flash Sintered 8YSZ Carolyn Grimley1, Andre Prette2 and Elizabeth C. Dickey1; 1North Carolina State University, Raleigh, North Carolina, United States; 2Lucideon Limited, Stoke-on-Trent, United Kingdom.

Field assisted sintering (FAST) has been demonstrated for multiple ceramic materials as a promising sintering technique in shortening consolidation time and lowering sintering temperatures. Mechanistically the interplay between electric field and the polycrystalline material is a complicated process and the governing factor for rapid densification during FAST is still under debate. In this work, we approached this problem from computational modeling in the model system of rutile TiO2. We separately quantified the effect of Joule heating and non-contact electric field on ion diffusion both in bulk and at grain boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry phase calculation with electric field up to 8 MV/cm shows that electric field has negligible effect on both defect formation energy and migration barrier in bulk TiO2. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close to the grain boundary. We also demonstrated the defect concentration change in space charge layer formed at grain boundaries with external bias. These results indicate that the local atomic structure and space charge layer profile of grain boundaries are important in understanding electric field effect on polycrystalline materials.

Computational Insight for Field Assisted Sintering of TiO2: Jing Yang, Minh A. Dinh and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Field assisted sintering (FAST) has been demonstrated for multiple ceramic materials as a promising sintering technique in shortening consolidation time and lowering sintering temperatures. Mechanistically the interplay between electric field and the polycrystalline material is a complicated process and the governing factor for rapid densification during FAST is still under debate. In this work, we approached this problem from computational modeling in the model system of rutile TiO2. We separately quantified the effect of Joule heating and non-contact electric field on ion diffusion both in bulk and at grain boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry phase calculation with electric field up to 8 MV/cm shows that electric field has negligible effect on both defect formation energy and migration barrier in bulk TiO2. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close to the grain boundary. We also demonstrated the defect concentration change in space charge layer formed at grain boundaries with external bias. These results indicate that the local atomic structure and space charge layer profile of grain boundaries are important in understanding electric field effect on polycrystalline materials.

Computational Insight for Field Assisted Sintering of TiO2: Jing Yang, Minh A. Dinh and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Field assisted sintering (FAST) has been demonstrated for multiple ceramic materials as a promising sintering technique in shortening consolidation time and lowering sintering temperatures. Mechanistically the interplay between electric field and the polycrystalline material is a complicated process and the governing factor for rapid densification during FAST is still under debate. In this work, we approached this problem from computational modeling in the model system of rutile TiO2. We separately quantified the effect of Joule heating and non-contact electric field on ion diffusion both in bulk and at grain boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry phase calculation with electric field up to 8 MV/cm shows that electric field has negligible effect on both defect formation energy and migration barrier in bulk TiO2. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close to the grain boundary. We also demonstrated the defect concentration change in space charge layer formed at grain boundaries with external bias. These results indicate that the local atomic structure and space charge layer profile of grain boundaries are important in understanding electric field effect on polycrystalline materials.

Field assisted sintering (FAST) has been demonstrated for multiple ceramic materials as a promising sintering technique in shortening consolidation time and lowering sintering temperatures. Mechanistically the interplay between electric field and the polycrystalline material is a complicated process and the governing factor for rapid densification during FAST is still under debate. In this work, we approached this problem from computational modeling in the model system of rutile TiO2. We separately quantified the effect of Joule heating and non-contact electric field on ion diffusion both in bulk and at grain boundaries. In bulk, we predicted the equilibrium defect concentrations at various pressures and temperatures from first-principles calculations. Berry phase calculation with electric field up to 8 MV/cm shows that electric field has negligible effect on both defect formation energy and migration barrier in bulk TiO2. For grain boundaries, we studied titanium diffusion by classical force field molecular dynamics. Ti diffusion is orders-of-magnitude faster close to the grain boundary. We also demonstrated the defect concentration change in space charge layer formed at grain boundaries with external bias. These results indicate that the local atomic structure and space charge layer profile of grain boundaries are important in understanding electric field effect on polycrystalline materials.
into a steady state cycle with respect to its dynamic response. In this work, we explore the ability of coupled electric and magnetic field processing to develop a range of micro-architectures within a composite smart material system. The system consists of micron-sized barium hexaferrite (BHF) particles, which have strong magnetic anisotropy, embedded in various polymers including a relaxor ferroelectric (RFE) polymer having nano-crystalline domains. Externally applied electric and magnetic fields act orthogonally on the embedded barium hexaferite particles within the uncured composite due to the particles' planar shape and crystallographic c-axis magnetization, allowing multi-axis control of particle alignments. Furthermore, externally induced dielectrophoretic and magnetophoretic particle-particle interactions allow control of the arrangement of aggregates of particles, providing a second hierarchical level of control. Both levels have an inherent time dependence as well. The combination of BHF and the RFE polymer gives us, to varying degrees, the electrostatic response of traditional electroactive polymers coupled with the magnetostriuctive and magnetic-torque based response of magnetoactive elastomers. The microarchitectures formed, visualized using optical microscopy and SEM techniques, range from traditional chains of particles, to aligned clusters, to segregated agglomerations and are achieved within specific regimes of the processing parameter – constituent design space. The ability to tailor varying architectures is seen as a pathway to developing localized multi-material response, from a single set of constituents, through processing alone.

4:15 PM *PM05.02.07
Non-Thermal Microwave Effects and the Role of Spin Entropy Configurations Darvoosh Vashae, Amin Nozariabzarnaz and Kelvin Dosouza; North Carolina State University, Raleigh, North Carolina, United States.

Today microwave radiation is quite often used to derive chemical reactions. Rapid and convenient heating, product selectivity, and better control over the product properties are some of the main advantages of using the microwave synthesis. In some cases, the reactions happened at rates several thousand times faster than what is achievable with conventional heating at similar average temperature. The observation of such extraordinary effects has been the subject of a fundamental question that whether there exist additional microwave specific effects. One of the main reasons that contradict the direct interaction of the microwave field is the significantly smaller energy of the microwave photons than the energy of the chemical bonds. Therefore, microwave excitations have been believed cannot dissociate the bonds and can merely heat the material by exciting the rotation or torsion of the dipoles a.k.a. dielectric absorption. As we will discuss this is not covering the whole story, and a fundamental study at the molecular level offers a better understanding of the energy transfers and the interaction of the material with the electromagnetic field.

In recent years, remarkable studies have been focused on understanding the microwave effects that cannot be explained by equilibrium thermodynamics. We will group some of these effects based on our experiments and the literature into (a) field-induced deccrystalization, (b) enhanced solid-state reaction, (c) densification, (d) solid solution alloy decomposition, and (e) field-induced reduction. After a brief discussion of the existing theories or hypothesis associated with each group, we will present a detailed study that due to its molecular approach permits application to numerous experiments. In particular, we solved the master equation to describe the time evolution of the system under microwave radiation. Gillespie’s exact stochastic method was used to model the chemical reactions occurring within the system considering the collisional energy transfers, spin degeneracy, microwave absorption/emission, and the chemical reaction. The vibrational and rotational states were evaluated while counting the densities of states. Notably, the energy split due to the Jahn-teller spin crossover lead to a change in the density of states and amplified absorption/emission of microwave radiation, which could not be explained otherwise. The outcomes demonstrated a noteworthy increment in the number of trajectories experiencing chemical dissociation contrasted with the system without the microwave. The resonance absorption and emission of the microwave photons inducing a transition between the states of different spin configurations increased especially the dissociation rate. These outcomes can clarify at least partially a number of the non-thermal influences of the electromagnetic interactions with materials.
required for complicated experimentation with processes of different physical nature. In this paper, we present a 2D multiphysics model mimicking the steady-state temperature solution as a function of incident power. We show that an EMHE with particular thickness and dielectric properties of the layers is built for a triple-layered (fluid-ceramic-fluid) EMHE and is capable of capturing the S- and SS-profiles of power response curve which determines the principle of the EMHE.

The complex dielectric properties of Aluminum Nitride-Molybdenum ceramic matrix composites around the percolation threshold (5-25% Mo by weight) are measured using free-space transmission methods in the W-Band frequency range (75-110 GHz) and temperatures between 20-1000 degrees C. These investigations of the high-temperature electromagnetic properties of ceramic composites at millimeter-wave frequencies enable predictions of the absorption properties of these materials under millimeter-wave irradiation. The ceramics are fabricated with hot pressing to obtain a range of composite samples having compositions ranging from 5-25% Molybdenum (by weight) in an Aluminum Nitride matrix. The relationship between the DC conductivity, grain boundary, and grain bulk conductivity of a ceramic matrix with distributed metal particles is compared with the measured complex dielectric constant to determine millimeter-wave absorption properties near the percolation threshold for electrical conductivity. In addition, thermal conductivity data is presented using differential scanning calorimetry to determine the heat capacity and laser flash method to determine the thermal diffusivity of each composition up to 1000 degrees C. Chemical and microstructural analyses are performed to identify mechanisms giving rise to millimeter-wave absorption and dielectric losses, and including scan electron microscopy, energy dispersive spectroscopy, x-ray diffraction, tomography, mass spectroscopy, temperature-dependent AC impedance (1 Hz-1 MHz) using a Solartron furnace, and DC conductivity measurements using a high temperature four-point probe up to 1000 degrees C. Millimeter-wave heating and interactions based on complex dielectric properties are investigated using a 100 Watt klystron source operating at 95 GHz to study the millimeter-wave interactions, including measurements of the throughput and reflected power, with temperature, for refractory ceramics at high temperature under free-space irradiation.

Electromagnetic fields are used constantly in industry and research to order or disorder a material’s crystal lattice on very short timescales, however the fundamental mechanisms that underlie these processes are still unknown. Primarily the existence of non-thermal effects (when the field couples directly with the lattice) and how they can be distinguished from thermal effects (when the field’s energy is first converted to thermal energy before inducing lattice changes) is still an open question. In an effort to identify these effects we have been studying the phase formation and coverage of zirconia (ZrO₂) thin films grown using microwave radiation. Formation of cubic and tetragonal zirconia (c-ZrO₂, t-ZrO₂), metastable phases that usually use yttria (Y₂O₃) doping to become stable, suggest non-thermal effects. These phases were identified using glancing incidence X-Ray diffraction. This suggests existence of a non-thermal effect, as our syntheses don’t exceed 250 °C and these phases are not stable below 1,170 °C. Our films are grown in the microwave by selectively heating a conductive layer via ohmic heating. Upon changing the pattern of this conductive layer (while maintaining the same area) the phase that formed as well as the coverage of this pattern by the thin film was changed. We hope to continue exploring this relationship by using a design of experiments approach. We are also in the process of modeling the scattering by the conductive layer to observe how its geometry influences heating and hope to use finite element modeling in future to expand on this model. Dielectric properties of ZrO₂ will also help describe how the films are growing, which we are obtaining using W-band free space characterization methods.

An electromagnetic heat exchanger (EMHE) is a device which converts electromagnetic (EM) energy into usable form of heat energy. The working principle of the EMHE is based on a collective effect of EM wave propagation, heat transfer and fluid flow, so the development of an efficient device requires complicated experimentation with processes of different physical nature. In this paper, we present a 2D multiphysics model mimicking operation of a layered EMHE that simulates the nonlinear interaction between EM, thermal, and fluid flow phenomena involved in the operation of the EMHE. The model is built for a triple layered (fluid-ceramic-fluid) EMHE and is capable of capturing the S- and SS-profiles of power response curve which determines steady-state temperature solution as a function of incident power. We show that a EMHE with particular thickness and dielectric properties of the layers can operate efficiently by keeping temperatures during thermal runaway under control. Overall temperatures increase rapidly as soon as the local maximum temperature reaches a critical value. This condition is held true both in absence and in presence of fluid flow. It is demonstrated that the efficiency of the EMHE dramatically increases when thermal runaway is achieved. It is also shown that, with appropriate length of the layered EMHE, thermal runaway can be achieved at a lower power level.
Flash sintering has attracted significant attention lately as its remarkable rapid densification process at low sintering temperature leads to the retention of fine grains and enhanced dielectric properties. However, the underlying mechanism of flash sintering and mechanical behaviors of flash-sintered ceramics remain poorly understood. Here, we report the microstructure of flash-sintered yttria-stabilized zirconia (YSZ) and TiO2 by transmission electron microscope (TEM) and their high temperature in-situ micropillar compression studies inside a scanning electron microscope (SEM). Our studies on flash-sintered YSZ show that YSZ exhibits high inelastic strain (~8%) primarily due to phase transformation toughening below 400°C. At higher temperatures, crack nucleation and propagation are significantly retarded and prominent plasticity arises mainly from dislocation activities. The holding time and current density limit after the onset of flash for flash-sintered TiO2 significantly affect the microstructure and mechanical behavior. High dislocation density and stacking faults have been observed in the flash-sintered TiO2 under TEM. The presence of high-density defects generated during flash sintering plays a major role in the overall microstructure and mechanical behavior of ceramics.

9:00 AM PM05.04.02
Low-Temperature Phase Transitions in Microwave-Assisted Synthesis---The Role of Oxygen Defects and Non-Thermal Effects
Nathan Nakamura1, Elizabeth Culbertson2, Han Wang3, Haiyan Wang4, Simon J. Billinge2,4 and B. Reega Jayant5; 1Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Columbia University, New York, New York, United States; 3Purdue University, West Lafayette, Indiana, United States; 4Brookhaven National Laboratory, Islip, New York, United States.

Electromagnetic (EM) radiation can significantly affect ceramic synthesis and processing, inducing rapid, low-temperature crystallization, non-equilibrium phase formation, and altered material properties. In particular, microwave radiation (MWR)-assisted synthesis has demonstrated the ability to crystallize high-temperature ceramic phases at significantly lower temperatures than conventionally required and impact local atomic ordering relative to furnace-based techniques. However, the mechanisms underlying these effects are not well understood. To understand these mechanisms, it is necessary to characterize EM field effects not only on crystalline phase formation, but also on non-crystalline local atomic order due to defects or amorphous components. It has been theorized that defect generation and transport may play an important role in promoting the effects seen under EM field exposure. Therefore, the relationship between synthesis and processing parameters (e.g., temperature, pressure) and the type, concentration, and response of defects is critical to the efficient design of these materials. An increased understanding of the potential mechanisms underlying EM field-assisted techniques will create the opportunity to utilize these methods to stabilize non-equilibrium phases or phase mixtures with desirable material properties.

To better analyze how EM fields influence phase formation and transitions, we utilize X-ray pair distribution function (PDF) analysis complimented by transmission electron microscopy (TEM) and Raman spectroscopy to study the crystallization and local atomic order in ZrO2, TiO2, and ZnO thin films. We demonstrate that the low-temperature crystallization and phase transitions observed during MWR-assisted synthesis are not a result of purely thermal effects. In all materials studied, we find that MWR helps to crystallize phases at much lower temperatures than conventionally required, and that the local order differs in MWR and furnace-grown films. This indicates a clear effect of MWR exposure on phase formation. By analyzing the local atomic order across various synthesis conditions, we find that thermal effects (e.g., reaction temperature, heating rate) do not fully explain the phase transitions observed. From our results, we are able to gain insight into the importance of defects and potential mechanisms underlying field-assisted phase formation.

9:15 AM PM05.04.03
In Situ Pair Distribution Function Analysis of Atomic Displacement in TiO2 During Flash Sintering
Bola Yoon1, Devinder Yadav1, Rishi Raj1, Emanuele Sortino1, Sanjít Ghose1, Pankaj Sarin4 and Daniel Shoemaker1; 1Materials Science and Engineering Program, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado, United States; 2Energy Sciences Directorate/Photon Science Division, NSLS II, Brookhaven National Laboratory, Upton, New York, United States; 4Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; School of Materials Science & Engineering, Oklahoma State University, Tulsa, Oklahoma, United States.

Flash sintering is a novel field assisted sintering technique, whereby ceramics can be sintered in just a few seconds. For example, 3 mol% yttria stabilized zirconia (YSZ) was shown to sinter in < 5 seconds at a furnace temperature of 850°C under electric field of 120 V/cm. Recently, flash sintering has been extended to synthesize unusual materials which are far from equilibrium. However, the mechanism of flash sintering is still controversial. Several mechanisms have been proposed for flash sintering, such as joule heating and defect avalanche. Here, we study atomicistic understanding of flash sintering on TiO2 to elucidate its underlying mechanism. For this purpose, in-situ experiments of total X-ray scattering has been conducted at the National Synchrotron Light Source II at the Brookhaven National Laboratory. We have measured atomic displacement of O and Ti atoms within a unit cell, and found the unusual displacements in O atoms which are far greater than that from thermal expansion. It might imply that these atoms movements are the precursors to the generation of Frenkel pairs.

9:30 AM *PM05.04.04
Developing the Underlying Principles for Electric Field Assisted Sintering for Improved Ceramic Manufacturability
Clement Nicollet, Jing Yang, Minh A. Dinh, Harry L. Tuller and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Field assisted sintering (FAST) has demonstrated great potential in reducing temperature constraints imposed on ceramic materials during sintering. While there have been many phenomenological observations of FAST processes, mechanistic understanding of the effect of electric field has been understudied and remains open. In particular, quantifying cation diffusion at different temperatures and polarizations both in bulk and at grain boundary is important for resolving the densification process under electric field. To that end, we studied the effect of defect chemistry on the field assisted sintering of TiO2 by both sintering experiments and first-principles based modeling. Sintering experiments under electrical field were conducted inside a dilatometer to control the shrinkage of the material in real time. To separate out the Joule heating effect, we used controlled doping concentration and oxygen partial pressure to controllably vary the electronic conductivity of TiO2, thereby controlling the extent of the Joule heating contribution. By varying the main cationic defects between Ti vacancies and interstitials, as well as their concentrations, we studied their effect on the FAST process. In parallel, the equilibrium defect concentrations under relevant conditions were predicted utilizing a first-principles based computational framework. By combining equilibrium defect concentration with defect diffusivities obtained from force field molecular dynamics, we constructed Ti self-diffusion profiles as a function of temperature, oxygen partial pressure and electric polarization. The predicted Ti self-diffusion coefficient agrees reasonably well with experimental measurements and in both cases Ti interstitials contribute dominantly. Moving from bulk to grain boundary, we found a very weak space-charge effect and a three-order-of-magnitude increase in the diffusion coefficient due to decreased Ti migration barrier. This result implies that Ti diffusion is greatly accelerated at the grain boundary. Identifying these factors advances our understanding of the individual effects of Joule heating, bulk cation diffusion, grain boundary mobility and electric polarization on flash behavior, and thereby, guide better control of ceramic materials manufacturing by FAST technology.
Processes that utilize DC or low-frequency electric fields provide a driving force for ion migration in ionic materials. This is particularly true in electric-field-assisted sintering where both high fields and high temperatures are involved, which enhance the kinetics of ion migration. This talk will discuss the effects of sample and electrode boundary conditions on electric-field-induced ion migration and resulting stoichiometry gradients in the context of field-assisted sintering. The implications for conductivity evolution and microstructure development will be illuminated, with examples from field-assisted sintering of yttria-stabilized ZrO2 (YSZ) and BaTiO3. Lateral and axial microstructural gradients will be discussed with respect to the electrochemical, thermal and mechanical boundary conditions of the ceramic body during sintering. In addition, more complex composite systems, such as layered systems of YSZ and Al2O3, which exhibit interesting asymmetrical sintering behaviors, will be discussed.

Nanostructured ceramic materials have various structural and functional applications. Flash sintering has attracted significant attention as one of its remarkably rapid densification process at low sintering furnace temperature leads to the retention of nanograins. However, high-temperature mechanical behaviors of flash-sintered ceramics remain poorly understood. Here, we present the high temperature in-situ microcompression studies on ultrafine grained yttria-stabilized zirconia (YSZ) processed by flash sintering technique. At room temperature, the flash-sintered YSZ sustains a large strain before fracture due to the local temperature during this process. It is disputed whether the observed phenomena are thermal or non-thermal in nature. It is possible that coupling of microwave and matter can lead to localized heating, which would also result in rapid reaction/diffusion kinetics at preferential sites. But, this temperature inhomogeneity still does not explain the nucleation of meta stable phases under microwave. In this work, microwave radiation-assisted synthesis of TiO2 is performed with three different materials as substrate. In situ x-ray diffraction (XRD) is used to track the change in lattice parameters of both the substrate and the synthesized TiO2 powder during growth and crystallization. The lattice expansion was correlated with the actual temperature at the ceramic/substrate interface and within the ceramic itself. The temperature distribution and change in crystal structure is used to differentiate the thermal from the non-thermal contribution of externally applied fields during the process.

Microwave radiation-assisted synthesis reduces the reaction temperature and improves the yields compared to a conventional furnace synthesis. Additionally, it has been shown to alter the material properties of final product by incubating new phases, changing crystallinity, or modifying particle size distributions. For example, during an experiment involving synthesis of TiO2 on an indium tin oxide (ITO) layer under microwave radiation, a mixed phase structure consisting of a long-range anatase phase and a short-range amorphous phase was obtained. The results were linked to the formation of an oxygen-deficient meta stable phase under microwave irradiation. The exact mechanism, however, remains undetermined, as there is no direct method to measure the local temperature during this process. It is disputed whether the observed phenomena are thermal or non-thermal in nature. It is possible that coupling between microwave and matter can lead to localized heating, which would also lead to rapid reaction/diffusion kinetics at preferential sites. But, this temperature inhomogeneity still does not explain the nucleation of meta stable phases under microwave.

Microwave radiation-assisted synthesis of TiO2 is performed with three different materials as substrate. In situ x-ray diffraction (XRD) is used to track the change in lattice parameters of both the substrate and the synthesized TiO2 powder during growth and crystallization. The lattice expansion was correlated with the actual temperature at the ceramic/substrate interface and within the ceramic itself. The temperature distribution and change in crystal structure is used to differentiate the thermal from the non-thermal contribution of externally applied fields during the process.

In some wireless power transfer systems utilizing thermo-mechanical conversion methodologies, bulk susceptor materials are required to convert microwave or millimeter wave radiation to thermal power which is, in turn, converted to electrical power. These bulk susceptor materials may take the form of composites formed from a high thermal conductivity ceramic matrix in combination with a radiation-absorbing additive, such as lossy ceramic or metal particles. For ease of design, the effective dielectric loss of the susceptor composite should be dominated by the additive material. Additionally, the temperature-dependent dielectric loss of the composite should be as weakly exponential as achievable to limit the likelihood of thermal runaway effects and to better enable optimization over a wide range of operating temperatures. Ceramic composites present under investigation for use as mm-wave susceptors include aluminum nitride composed with molybdenum powder (AlN:Mo) and aluminum nitride composed with titanium diboride (AlN:Tib). Thermal properties, compositional and structural analysis, and high-temperature complex permittivity data will be presented for AlN:Mo compositions ranging from 0.25% to 4% Mo (by weight). Preliminary complex permittivity measurement data will also be presented for selected AlN:Tib formulations. Data presented on these AlN-based ceramic composites will be discussed in the context of suitability of these materials for use in future wireless power transfer experiments.

B. W. Hoff, M. S. Hilario, and A. E. Baros were funded by the Air Force Office of Scientific Research under FA9550-17-RD40449 and by the Operational Energy Capability Improvement Fund (OECIF). S. C. Hayden and R. O. Grudt were funded by Aramco Services Company. F. W. Dynys was supported by funding provided by the Air Force Research Laboratory.
Dielectric Breakdown in Ceramics—Conduction Mechanisms, Conducting Filaments and Breakdown Toughness

Gerold A. Schneider and Pia-Kristina Fischer; Hamburg University of Technology, Hamburg, Germany.

Even though dielectric breakdown in ceramics is a limiting factor for the reliability of electronic devices and components and despite almost 100 years of research there is no commonly accepted understanding of this phenomenon. In this talk a Griffith-type dielectric breakdown model is presented. The difference to previous models is that it is based on space charge limited conduction (SCLC) and not on Ohmic conduction. It is shown that in a lot of ceramics SCLC is most likely the dominating conduction mechanism at very high electric fields. As the origin of dielectric breakdown it is assumed that tiny electrically conducting filaments get unstable at the breakdown field and grow to the well known breakdown channels. To investigate this hypothesis artificial conducting channels were prepared in borosilicate glass using a Focused Ion Beam. It will be shown that the breakdown strength is linearly dependent on the inverse square root of the lengths of these filamentations, which is in agreement with the prediction of the model. From these results a breakdown toughness for borosilicate glass can be determined. In summary it is possible to describe the size dependence and scattering of the breakdown strength with this approach.

Electrochemistry and Electro-Kinetics in Zirconia Ceramics


Field assisted sintering such as flash sintering and spark plasma sintering attracts much attention in the ceramic community. It is of particular interest to clearly identify non-thermal effects, to understand diffusion/phase-transformation kinetics and to control microstructural evolution, aided by an electric field and maybe enhanced by far-from-equilibrium defects. To echo and argue on such non-equilibrium effects, we shall present our recent work on how electric field influences zirconia’s microstructure and how we can understand it within equilibrium. We emphasize applied electric field can greatly change local thermodynamics, hence influencing kinetics indirectly.

Phenomenological correlation: By grain growth experiments, we show hydrogen and electrochemical reduction enhances grain boundary mobility and cation diffusion in zirconia and ceria. [1-2]

Electrochemistry: Anions and electrons set up local equilibrium. Zirconia is a fast oxygen ion conductor with little electronic conductivity. So electrode reactions at metal/zirconia interface are necessary to convert electron flow in outer circuit to oxygen ion flow inside zirconia electrolyte. Yet it must in the end become sluggish, creating huge overpotentials and shift equilibrated defect concentrations. Through continuum-level simulations, we obtain a step-like oxygen potential profile responsible for observed grain-size transition inside electrically loaded zirconia, and a flux discontinuity at grain boundary responsible for observed cavitation.

Electro-kinetics: Cation diffusion determines global microstructure evolution. Cation diffusion in zirconia and ceria takes place via a vacancy mechanism [3-4], yet it is enhanced by reduction, which according to defect chemistry decreases the concentration of cation vacancy. This conundrum has been resolved by our recent first-principles calculations. We found reduction-created electrons can greatly lower cation’s migration barrier. It suggests a critical role of minor electronic defects in determining mass transport for oxides (even as ionic as zirconia), which had been totally overlooked by classical nonstoichiometric defect chemistry.

References
Polymer Patterning Via Electrohydrodynamic Instabilities
Neutron Diffraction—A Useful Tool to Study Structures of Polycrystalline Compounds

4:00 PM
the path towards the manufacturing of novel bulk iron oxide materials with superparamagnetic behavior.

minima and maxima of those waves experience slightly different electric field strengths. In a sufficiently strong electric field, the capillary wave maxima, a mismatch in their dielectric constants. This stress, along with thermal fluctuations, induces small magnitude capillary waves in the polymer film, and the stiffness and toughness. The interrelationships between supercrystalline structure and overall magnetic and mechanical features are explored, together with controlled development of bulk nanocrystalline ceramic materials with tunable magnetic properties and a unique combination of strength, hardness, stiffness and toughness. The green samples consist of organically-covered magnetite nanoparticles, with diameter below 18 nm and monomodal size distribution, self-organized into an extended tightly-packed supercrystalline lattice. The application of relatively low-temperature spark plasma sintering regimes leads to the controlled development of bulk nanocrystalline ceramic materials with tunable magnetic properties and a unique combination of strength, hardness, stiffness and toughness. The interrelationships between supercrystalline structure and overall magnetic and mechanical features are explored, together with the path towards the manufacturing of novel bulk iron oxide materials with superparamagnetic behavior.

3:00 PM BREAK

3:30 PM *PM05.05.04 Advanced Iron Oxide-Based Nanostructured Ceramics with Tailored Magnetic and Mechanical Properties Diletta Giuntini1, Elisa Torresani2, Kyle Chan2, Buesa Bor1, Berta Domenech1, Javier Garay1, Eugene A. Olevsky1 and Gerold A. Schneider1; 1Hamburg University of Technology (TUHH), Hamburg, Germany; 2San Diego State University, San Diego, California, United States; 3University of California, San Diego, California, United States.

Nano-structured and nano-grained materials are among the most promising applications of field-assisted sintering techniques, thanks to their characteristic ability to enhance densification and hamper grain growth through high heating rates and the aid of electric fields and current. The introduction of multifunctionality is also often made possible by combining tailored nano-architectures with such ultra-rapid processing methods. This study addresses the potential of spark plasma sintering for the production of advanced iron oxide-based ceramics with an enhanced combination of magnetic and mechanical properties. The green samples consist of organically-covered magnetite nanoparticles, with diameter below 18 nm and monomodal size distribution, self-organized into an extended tightly-packed supercrystalline lattice. The application of relatively low-temperature spark plasma sintering regimes leads to the controlled development of bulk nanocrystalline ceramic materials with tunable magnetic properties and a unique combination of strength, hardness, stiffness and toughness. The interrelationships between supercrystalline structure and overall magnetic and mechanical features are explored, together with the path towards the manufacturing of novel bulk iron oxide materials with superparamagnetic behavior.

4:00 PM PM05.05.06 Polymer Patterning Via Electrohydrodynamic Instabilities Katherine E. Copenhaver and Jason H. Nadler; Georgia Institute of Technology, Atlanta, Georgia, United States.

Patterned polymer surfaces can provide high-index contrast over a periodic matrix with 3-dimensional element shapes. The dielectric contrast and array pitch and height can be tuned to control specular reflection and achieve specific scattering characteristics. Surfaces with tailored scattering characteristics in the aforementioned ranges could be useful in producing frequency-selective windows for glare reduction, anti-reflective solar cells with enhanced efficiency, surface waveguides and whispering gallery-mode resonator arrays for integrated photonics and sensors, and surfaces with controlled emissivity for direct heat dissipation. Electrohydrodynamic (EHD) instabilities can be induced in polymers by placing a polymer film above its Tg in a strong electric field between two capacitor plates or electrodes. The polymer experiences an electrostatic stress at the interface between the polymer and air due to a mismatch in their dielectric constants. This stress, along with thermal fluctuations, induces small magnitude capillary waves in the polymer film, and the minima and maxima of those waves experience slightly different electric field strengths. In a sufficiently strong electric field, the capillary wave maxima, where the distances between the polymer film and the top electrode(s) are the smallest, are eventually drawn up to the top electrode. The wavelength of the instabilities in the film and the ability of the polymer to be drawn upward is a dependent on the competition between surface tension forces and the electrostatic stress imparted on the polymer. While EHD instabilities are typically used to pattern polymer surfaces on a nanometer-scale, instabilities have been induced in polymer films with air gaps up to 500 μm. Upper electrodes with non-planar structures have also been used to induce instabilities in polymer films, resulting in patterned polymer surfaces without contact. Size, shape, arrangement, and placement of the upper electrode relative to the polymer film and lower electrode, as well as the processing conditions such as temperature and applied voltage, can all be modified to produce a desired array of structures with tailored performance characteristics.

4:15 PM PM05.05.07 Controlling Catalytic Reaction Pathways via Magnetic Heating Natalia da Silva Moura, Pragathi Darapaneni, Kerry Dooley and James A. Dorman; Louisiana State University, Baton Rouge, Louisiana, United States.

The catalysis market is responsible for more than 35% of the world’s GDP, and it is involved in the most successful industrial sectors: energy generation, chemicals, and pharmaceuticals. Despite the remarkable advances in catalytic technologies, the industry still faces thermal management issues and accumulation of heat on reactor walls. Alternatively, it is possible to overcome the activation barrier using in situ methods via iron oxide (Fe3O4) exposed to an alternating magnetic field. In this work, Fe3O4 nanoparticles will be used to convert alternating magnetic fields to heat to study the effects of localized energy on the chemical transformation in a reference alcohol condensation reaction. 20 nm iron oxide nanoparticle spheres, cubes, and truncated octahedrons of tunable sizes are exposed to RF fields to drive an alcohol dehydration reaction. The size and shape of these particles are controlled by varying surfactant to precursor ratio in thermal decomposition reactions. These facets allow for the tuning of surface activity and heat generation, key parameters for selectivity and activity engineering. The heat generated is dependent on the spin configuration on the surface, with minimum heating rates at least 34% higher than commercially available particles. Surface functionalization with hydroxyl groups is performed to increase the interaction of Fe3O4 with alcohols in dehydrogenation reactions. This localized heat generation can be used to control surface functionalization for dispersion in aqueous solutions and conversion of alcohols. For spherical particles, the GC-MS data shows production of aldehydes and esters via thermal routes while RF induced reactions result in longer alkenes, such as decene, which is dependent on the applied magnetic field. These results indicate changes in the reaction mechanism associated with RF activation. Furthermore, to investigate the role of the surface of iron oxide without any surfactants on the mechanism of the reaction, spherical nanoparticles are also synthesized via co-precipitation routes. The catalyst is characterized before and after functionalization and reaction steps to probe the crystal structure, oxidation states of iron and morphology of the particles, using XRD, XPS, and HRTEM respectively. The reaction products are characterized via GC-MS to elucidate the reaction mechanism.
The macroscopic properties of polycrystalline ionic ceramics are determined by the doping levels, point defects, and their interaction with the microstructure, as they are specified via processing and the target application. Here, the starting powders react, densify, and coarsen into microstructurally tailored grain topologies that are aimed to enhance (but sometimes limit) the performance of the device that are part of. The extent of these interactions varies with grain size, crystallographic orientation, and misorientation distribution, as well as applied fields, such as stress or electric fields. In order to understand the grain boundary characteristics, including their electrochemical properties and the driving forces that control grain coarsening, a thermodynamically consistent diffuse interface theory is being developed. The theory naturally incorporates the effects of drag as they are imposed by the interfacially accumulated charged defects on the grain growth of polycrystalline ceramics. Applications to materials such as YSZ, GCO, and STO (and comparisons against experimental results) are presented.

Electromagnetic (EM) heat exchangers are devices which absorb EM radiation converting it into thermal energy to do work, such as run a turbine. Applications involving both solar and microwave energy have garnered increasing attention but have yet to utilize the potential benefits of short-wave interactions when the wavelength is comparable to a material’s microstructure. It has been shown for a three-layer laminate the Bragg resonance that occurs at this scale can be used to control steady state temperature and thermal runaway effects. We investigate these effects in a mathematical model approximating a porous medium for use in a heat exchanger. Classical homogenization methods average over the microscale to obtain a macroscopic description of the material, however they are incapable of describing short-wave behavior. High-frequency homogenization methods have been developed but are restricted to cases incompatible with modeling heat exchangers, such as assuming a lossless medium, spatially uniform dielectric constants, and reducing Maxwell’s equations to the Helmholtz equation. We develop a high-frequency homogenization technique that relax these assumptions, considering a laminate geometry composed of alternating layers of lossy dielectric material and lossless fluid channels in the homogenization limit. This model advances the designing of porous materials for efficient collection of energy in electromagnetic heat exchangers.

Nucleation of metastable vaterite CaCO₃ is mediated by electric fields. Wenhao Sun and Gerbrand Ceder; Lawrence Berkeley National Labs, Berkeley, California, United States.

Vaterite is a transient metastable polymorph of calcium carbonate that often appears during the multistage crystallization of CaCO₃. Nucleation of vaterite prior to the equilibrium phase calcite should, according to classical nucleation theory, be facilitated by a lower surface energy of vaterite than calcite. We perform a thorough density functional theory investigation of calcite and vaterite surface energies, and find, contrary to expectations, that vaterite unequivocally has the higher surface energy of the two phases. Here, we present a novel mechanism to rationalize the preferential nucleation of vaterite. Because the vaterite crystal structure is composed of alternating Ca²⁺/CO₃⁻ planes in the [001] direction, nanoparticles of vaterite possess a permanent electrostatic dipole moment. We show that nuclei of vaterite can be stabilized relative to calcite under electric fields that are consistent with charge inhomogeneities on mineral surfaces, in biogenic macromolecules, and in aqueous electrolyte solutions. The role of electric fields in nucleating the polar polymorph of CaCO₃ can be more generally leveraged to synthesize metastable polar phases of other materials, potentially opening the door to materials with novel or superior functionality.

During "flash sintering," the application of an external electric field results in rapid densification at significantly reduced temperatures in many materials. The flash event is accompanied by a dramatic increase in the conductivity of the sample and an expansion of the lattice constants. I will discuss the microscopic processes contributing to flash sintering. In particular, I will discuss the coupling between a non-equilibrium carrier distribution and defects within the grains. I will present examples of density functional calculations of defects in yttria-stabilized zirconia and titania. This work was performed in collaboration with Noam Bernstein and Steven C. Erwin at the Naval Research Laboratory.

Additive manufacturing enables production of complex shapes and customizable designs, using a wide variety of materials. Direct layer-wise sintering of ceramics using additive manufacturing techniques, however, has been an elusive goal due in part to the rapid kinetics required to sinter ceramic powders together one layer at a time. Flash sintering research using conventional furnace heating has demonstrated that application of an electric field during furnace sintering results in very rapid densification of ceramics, in most cases decreasing over an hour of sintering time to seconds. The simultaneous application of an electric field with laser scanning of ceramic powders is investigated as a method of enabling the processing of ceramic powder using selective laser sintering.
Electrochemical Effects on the Microstructural Evolution of STO

Suryanarayana V. Karra, Rheinheimer Wolfgang and R. Edwin Garcia; Purdue University, West Lafayette, Indiana, United States.

Grain growth experimental studies on perovskites exhibit unimodal or bimodal microstructures as a function of temperature and dopant concentrations, as a result of the underlying point defects and their interaction with the grain boundaries. The extent of these interactions varies with grain size, orientation and misorientation distribution, as well as processing temperature and amount of doping. A theoretical formulation based on a thermodynamically consistent diffuse interface model has been developed to understand the effects of dopants on the grain coarsening of polycrystalline ionic solids. The theory is applied to Fe-doped Strontium Titanate (STO). At small Fe amounts and low temperatures the microstructures exhibit unimodal and coarse microstructures. An increase in Fe concentration or temperature results in a bimodal grain size distribution that affects the overall grain growth dynamics. In agreement with experimental results, the developed theory provides a starting point to understand the effects of the structural and electrochemical state of the grain boundary properties and its impact on the microstructural evolution of STO, including the possibility of abnormal grain growth.

10:45 AM *PM05.06.07

Electric Field-Induced Softening (EFIS) of Alkali Silicate Glasses

Charles McLaren², William Heffner¹, Surapong Panyata¹, Bernhard Roling³, Rishi Raj¹, Nicholas Smith² and Himanshu Jain¹; ¹Lehigh University, Bethlehem, Pennsylvania, United States; ²Corning Incorporated, Corning, New York, United States; ³University of Marburg, Marburg, Germany; ⁴University of Colorado Boulder, Boulder, Colorado, United States.

Inspired by the observations of dramatic effects of electric field on sintering of ceramic powders, we investigated the effect of electric field on the softening of alkali silicate glasses that were heated at a constant rate under static load and fixed voltage. We observed abrupt softening and viscous flow at furnace temperatures well below the glass transition temperature, resulting in a new phenomenon, termed electric field induced softening (EFIS) of glass. The strain, the specimen temperature (obtained with a pyrometer), and the optical emission spectrum have been measured simultaneously as a function of time. Preceding the overall softening, localized hot spots are observed near the anode, which may meander before leading to an abrupt increase in electrical conductivity as well as photoemission. The effect is more pronounced (that is, it occurs at a lower temperature) with AC field of ~1 kHz than with DC electric field. Unusual events at the metal-glass interface, resembling dielectric breakdown are observed, which, however, are less localized in AC than in DC experiments. These observations suggest the following sequence of events: polarization of the sample from ion displacement under the application of electric field as in electro-thermal poling, formation of an alkali ion depletion layer, development of large internal electric fields across this layer, electrolysis and charge injection followed by dielectric breakdown, and very high localized heating near the anode, ultimately leading to thermal runaway and softening throughout the sample. The results suggest that AC electric field assisted softening may be better suited to practical applications of this phenomenon. The magnitude of EFIS is significantly larger in single alkali than in relatively lower conductivity mixed-alkali glass of same mole fraction of silica, raising the possibility that EFIS can be induced in highly conductive glasses even at ambient furnace temperature. Potential applications of EFIS will be presented.

11:15 AM *PM05.06.08

Laser Fabrication of Single Crystal within Glass—Influence of Polarization

Volkmar Dierolf¹, Keith Veenhuizen², Courtney Au-Yeung¹, Sean McAnany¹, Lejla Hoxha¹, Khalil Tafiti², Bruce Atkén¹, Dan Nolan¹, Dmytro Savitskyy³ and Himanshu Jain¹; ¹Lehigh University, Bethlehem, Pennsylvania, United States; ²Lebanon Valley College, Annville, Pennsylvania, United States; ³Corning Incorporated, Corning, New York, United States.

Spatially selective heating of a glass using lasers allows to precisely control the conversion of a glass into a single crystal. In particular, we have shown that it is possible to perform this conversion without ever melting the glass. In such a solid-solid conversion, the growth conditions are highly constrained, which produce unusual crystallization characteristics. In this presentation, we will give an overview of the most unique features which include preferred orientation of seed crystals and controlled rotation of the crystal lattice orientation both along and perpendicular to the growth axis. These concepts will be introduced for crystallization on the surface of a chalcogenide glass using a cw-laser as well as for 3D-crystallization inside a lithium niobosilicate glass. The dependence of these phenomena on the properties of the laser irradiation, in particular the laser polarization will be discussed. We will report on how the polarization determines the orientation of the seed crystal as well as how it determines the crystal growth. Interpretations of these phenomena will be presented.

11:45 AM ANNOUNCEMENT PRESENTATION/POSTER AWARDS
Part of this study was carried under the research of SIP in JST (Japan Science and Technology Agency). Multi-component systems of the alloys, including both substitutional and interstitial elements. In case of Ti-Al-M1-M2 quaternary systems, for example, we develop novel heat treatments to optimize the interaction parameters to calculate the phase diagram in good agreement with experimentally determined phase diagram, by taking into account the influence of deformation and kinetic aspects.

Intermetallic Titanium Aluminid based alloys are considered for high-temperature aero and automotive engine applications. The advantage of this class of innovative high-temperature materials is their low density in combination with good strength and creep properties up to 850°C. A drawback, however, is their limited damage tolerance at room temperature, which is reflected in a low plastic fracture strain and fracture toughness. Advanced engineering Titanium Aluminid alloys are complex multi-phase materials which can be processed by ingot or powder metallurgy. Engine components can be manufactured by casting as well as additive manufacturing, e.g. electron beam melting. Each ingot production process leads to specific microstructures which can be optimized by thermo-mechanical processing, e.g. isothermal or hot die forging and subsequent heat treatments. Thermo-mechanical processing can provide balanced mechanical properties, i.e. a minimum ductility at room temperature as well as sufficient creep strength at elevated temperature. In order to achieve this goal, the knowledge of the occurring solidification processes and phase transformation sequences is essential. Therefore, thermodynamic calculations were conducted to predict the phase diagram of engineering TiAl alloys. After experimental verification, these phase diagrams provided the basis for the development of heat-treatments. To account the influence of deformation and kinetic aspects sophisticated ex- and in-situ methods have been employed to investigate the evolution of the microstructure during thermo-mechanical processing. For example, in-situ high-energy X-ray diffraction was conducted to study dynamic recovery and recrystallization processes during hot-deformation tests. Novel high-strength Titanium Aluminid based alloys, such as TNM alloys have been developed in the last decade to meet the advanced requirements of aero engines. These alloys are characterized by a high content of β-stabilizing alloying elements, such as Nb and Mo. Because Nb and Mo represent the decisive alloying elements, this alloy family, based on the γ-TiAl phase, has been named “TNM alloys” in order to distinguish them from the well-known and even stronger “TNB alloys” which rely on a high Nb concentration and small additions of B and C. At room temperature, strength levels > 1000 MPa can be achieved in advanced TiAl alloys by appropriate thermo-mechanical processing and subsequent heat treatments. It is important to note that also high temperature properties, such as creep resistance, were considerably improved, e.g. by implementation of precipitation hardening, which further extend the application range of Titanium Aluminid based alloys.

Advanced this talk, we present achievements and design approaches for the development of wrought TiAl alloys to be used for LPT and HPC blades. First, we built up a new database for phase diagram calculations in advanced TiAl alloys by appropriate thermo-mechanical processing and subsequent heat treatments. It is important to note that also high temperature properties, such as creep resistance, were considerably improved, e.g. by implementation of precipitation hardening, which further extend the application range of Titanium Aluminid based alloys.

Innovation of structural materials is urgently being required for contribution to worldwide issues on energy, environment, and high performance jet engine development with larger thrust-to-weight ratio is one of them, since more than 30,000 new airplanes are to be produced by 2030. A five-year National project of “Structural Materials for Innovation (SM4I)” in Cross-ministerial Strategic Innovation Promotion Program (SIP) starting from 2014 is currently going on in Japan. In this project of SM4I, a focus is placed on innovative structural materials applicable for jet engines, where author at Tokyo Tech is committed to as a technical leader and take responsibility for alloy design and development of TiAl alloys in collaboration with other universities (Hokkaido Univ., Osaka Univ.) and industries (Kobe Steel, Ltd and IHI Co.). In this talk, design approaches and achievements for the development of wrought TiAl alloys to be used for LPT and HPC blades are presented. First, we built up a new database for phase diagram calculations in multi-component systems of the alloys, including both substitutional and interstitial elements. In case of Ti-Al-M1-M2 quaternary systems, for example, we optimize the interaction parameters to calculate the phase diagram in good agreement with experimentally determined phase diagram, by taking into considerations of temperature, aluminum and M1/M2 concentration dependencies in the four phases of β-Ti, α2-TiAl, α-Ti and γ-TiAl phases. Based on the phase diagram calculations, we successfully proposed model alloys with excellent hot workability even at higher strain rate and room temperature ductility of more than 1%. It should be noted that an introduction of bcc b-Ti phase and microstructure design using a unique phase transformation pathway of β→α→γ→β'γ in the multi-component systems makes it possible to have excellent properties in both process and service temperatures. We revealed the alloy with lamellar microstructure decorated by β'/γ duplex microstructure at the lamellar colony boundaries show better crack initiation and propagation resistance than that with fully lamellar microstructure. The detailed microstructure control method using the phase transformations and toughening mechanism will be presented.

Part of this study was carried under the research of SIP in JST (Japan Science and Technology Agency).

Phase Transformation and Microstructure Evolution during Continuous Heating of an Intermetallic β-homogenized Ti-43Al-7Mo (at.%) Alloy Petra Fedel1, Peter Staron1, Andreas Stark2, Thomas Klein1, 2, Helmut Clemens1 and Svea Mayer2; 1Department of Physical Metallurgy and Materials Testing, Montanuniversitaet Leoben, Leoben, Austria; 2Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Germany. Cross-ministerial Strategic Innovation Promotion Program (SIP) starting from 2014 is currently going on in Japan. In this project of SM4I, a focus is placed on innovative structural materials applicable for jet engines, where author at Tokyo Tech is committed to as a technical leader and take responsibility for alloy design and development of TiAl alloys in collaboration with other universities (Hokkaido Univ., Osaka Univ.) and industries (Kobe Steel, Ltd and IHI Co.). In this talk, design approaches and achievements for the development of wrought TiAl alloys to be used for LPT and HPC blades are presented. First, we built up a new database for phase diagram calculations in multi-component systems of the alloys, including both substitutional and interstitial elements. In case of Ti-Al-M1-M2 quaternary systems, for example, we optimize the interaction parameters to calculate the phase diagram in good agreement with experimentally determined phase diagram, by taking into considerations of temperature, aluminum and M1/M2 concentration dependencies in the four phases of β-Ti, α2-TiAl, α-Ti and γ-TiAl phases. Based on the phase diagram calculations, we successfully proposed model alloys with excellent hot workability even at higher strain rate and room temperature ductility of more than 1%. It should be noted that an introduction of bcc b-Ti phase and microstructure design using a unique phase transformation pathway of β→α→γ→β'γ in the multi-component systems makes it possible to have excellent properties in both process and service temperatures. We revealed the alloy with lamellar microstructure decorated by β'/γ duplex microstructure at the lamellar colony boundaries show better crack initiation and propagation resistance than that with fully lamellar microstructure. The detailed microstructure control method using the phase transformations and toughening mechanism will be presented.

Part of this study was carried under the research of SIP in JST (Japan Science and Technology Agency).
Improvement of Mechanical Properties of TiAl Alloys Fabricated by Electron Beam Melting though Microstructure Control

Ken Cho1, Masahiro Sakata1, Takumi Fukuoka1, Jong Yeong Oh2, Hiroyuki Yasuda3, Mitsuharu Todai2, Takayoshi Nakano1, Ayako Ikeda2, Minoru Ueda4 and Masao Takeyama2
1Osaka University, Suita, Japan; 2Institute of Nihon University National College of Technology, Nihon University, Japan; 3National Institute for Materials Science, Tsukuba, Japan; 4Metal Technology Co. Ltd., Tokyo, Japan; 5Tokyo Institute of Technology, Tokyo, Japan.

Improvement of Mechanical Properties of TiAl Alloys Fabricated by Electron Beam Melting through Microstructure Control

Ken Cho1, Masahiro Sakata1, Takumi Fukuoka1, Jong Yeong Oh2, Hiroyuki Yasuda3, Mitsuharu Todai2, Takayoshi Nakano1, Ayako Ikeda2, Minoru Ueda4 and Masao Takeyama2
1Osaka University, Suita, Japan; 2Institute of Nihon University National College of Technology, Nihon University, Japan; 3National Institute for Materials Science, Tsukuba, Japan; 4Metal Technology Co. Ltd., Tokyo, Japan; 5Tokyo Institute of Technology, Tokyo, Japan.

The present study applies a strategy of grain refinement on a γ-based Ti-45Al-7.5Nb intermetallic compound through high-pressure torsion (HPT) processing for 5 and 10 turns under a compressive pressure of 6.0 GPa at room temperature. Successful grain refinement was introduced in the duplex microstructure to have ultrafine lathes with thicknesses of 40-100 nm after 10 HPT turns. Exceptional hardness is recorded after the severe plastic deformation and the X-ray diffraction analysis confirmed the occurrence of phase transformation from γ-TiAl to α2-Ti3Al in the alloy. The close investigation demonstrated that hardness and texture evolution vary gradually from the sample surfaces to the core, thereby exhibiting a heterogeneous microstructure. Macroscopic plastic flow is estimated thorough the micro-mechanical responses by the nanoindentation technique for the TiAl alloy. This study demonstrates the promising feasibility of HPT processing for improving essential mechanical properties in the TiAl.

Low Pressure Turbine blades made of TiAl alloys are being used in three civil aircraft engine families (GEx, PW1000GTF, LEAP). The production process of TiAl semi-finished parts is based on three technological pathways: VAR ingot metallurgy, VAR Skull Melter homogenization and subsequent investment casting to oversized components followed by mechanical machining VAR ingot metallurgy, VAR Skull Melter homogenization and subsequent centrifugal casting in permanent moulds to small sized feed stocks for either forging or mechanical machining or direct mechanical machining:

- Plasma Arc Cold Hearth Melting to small sized ingots for direct mechanical machining
- In both processing routes b) and c), a substantial amount of valuable TiAl revert is being generated during the different processing steps. An industrial recycling process based on Vacuum Induction Skull Melting with subsequent centrifugal casting according to the technological pathway b) has been developed and commissioned at GfE. Appropriate revert preparation technologies prevent a detectable impurity pick-up from previous processing steps even for multiple use of revert. The corresponding revert preparation and revert conversion technology is approved and validated for the production of pre-materials for components for aircraft engines. The presentation addresses the origin of revert and the appropriate revert preparation technology. The recycling process via Induction Skull Melting is being introduced. Resulting products are indistinguishable from products resulting from the virgin production route via VAR Skull Melting with regard to chemical composition and microstructure.

Introduction of YSK-TiAl, Novel Wrought Alloy with High Strength and Advanced Producibility

Keiji Kubushiro, Yutaro Ota, Yohei Sakakibara, Shin Usui, Satoshi Takahashi, Kotaaro Tagawa and Masanobu Baba; IHI Corp, Yokohama, Japan.

The present study applies a strategy of grain refinement on a γ-based Ti-45Al-7.5Nb intermetallic compound through high-pressure torsion (HPT) processing for 5 and 10 turns under a compressive pressure of 6.0 GPa at room temperature. Successful grain refinement was introduced in the duplex microstructure to have ultrafine lathes with thicknesses of 40-100 nm after 10 HPT turns. Exceptional hardness is recorded after the severe plastic deformation and the X-ray diffraction analysis confirmed the occurrence of phase transformation from γ-TiAl to α2-Ti3Al in the alloy. The close investigation demonstrated that hardness and texture evolution vary gradually from the sample surfaces to the core, thereby exhibiting a heterogeneous microstructure. Macroscopic plastic flow is estimated thorough the micro-mechanical responses by the nanoindentation technique for the TiAl alloy. This study demonstrates the promising feasibility of HPT processing for improving essential mechanical properties in the TiAl.
the present work we study at high temperature the mobility of defects controlling the mechanisms responsible for creep. However, the study is approached through mechanical spectroscopy by measuring the internal friction (IF) spectra between 300 and 1350°C. On one hand, the high temperature background (HTB) of the IF is closely related to creep behavior [1], and on the other hand, the relaxation peaks of the IF spectra offer valuable information about the atomic diffusion mechanisms involved in creep [2,3]. In particular, the developed nano-lamellar microstructure allow us to discover and analyze a new relaxation peak, which remains hidden in between the IF peak associated to Ti diffusion in α2-Ti3Al phase [2] and the HTB. We have measured the IF spectra at different frequencies and performed a deep analysis to decompose the IF spectra into the different contributions and isolate the relaxation corresponding to each individual atomic mechanism. This way we measured the activation energy of the hidden relaxation, E_a=3.7 eV, which is attributed to the Aluminum diffusion in γ-TiAl phase. Moreover, a new atomic relaxation mechanism is proposed to explain the characteristic of the observed IF peak. Finally, the importance of the discovered relaxation is discussed in terms of its relationship with the atomic diffusion processes involved in creep.

11:30 AM PM06.01.09

Density Functional-Based Kinetic Monte Carlo Approach to Ni Pipe Diffusion

Luke Wirth1, Amir A. Farajian1 and Christopher Woodward2; 1Mechanical and Materials Engineering, Wright State University, Dayton, Ohio, United States; 2Air Force Research Laboratory, Dayton, Ohio, United States.

Pipe diffusion along dislocations in metals can occur at faster rates than in bulk regions, expediting creep and contributing to device failure. We use density functional theory methods to calculate the vacancy-mediated diffusion coefficient along a <1-1 0-> screw dislocation in FCC nickel. A lattice Green’s function technique is used to accurately configure the atomic structure surrounding the dislocation core. Vacancy hop rates within this region are calculated using principles of transition state theory with activation energy barriers and vibrational properties obtained from our ab initio framework. A kinetic Monte Carlo model then uses these rates to describe mass transport within the region on representative timescales at various temperatures.

SESSION PM06.02: Silicides and Ultra-High Temperature Alloys

Monday Afternoon, November 26, 2018

Hynes, Level 1, Room 104

1:30 PM PM06.02.01

Alloy Design of Refractory BCC-T2 Silicide-B2 Aluminide Multicomponent-Multiphase Alloys

Seiji Miura, Satoshi Takizawa and Ken-ichi Ikeda; Hokkaido University, Sapporo, Japan.

Refractory-metal based materials have attracted attentions for many years because of the increasing demand for high temperature components. In order to obtain such materials having superior properties for high temperature use, multicomponent-multiphase alloys are required. Authors have conducted studies on the mechanical and physical properties of BCC solid-solution phase, MoSi2-T2 silicide phase and B2 aluminide phase, together with phase equilibrium among these constituent phases. Authors have conducted the investigation on the effects of various additive elements on the strength and deformability of BCC solid solution. As (Nb, Mo)(Si, B), phase dispersion in Nb-Mo BCC solid-solution matrix has been studied by various researchers, we also try to understand the phase stability of T2 phase in alloys. Although silicide phases including (Nb, Mo)(Si, B) show superior oxidation resistance, we have focused on B2-aluminide coating because B2-NiAl coatings have been used for commercial Ni-based superalloys. To realize a three-phase alloys composed of refractory BCC, T2 silicide and B2 aluminide, phase equilibrium in ternary, quaternary and higher-order phase diagrams are experimentally investigated. Among them, brittle compounds such as Nb(Ni, Al)2 Laves phase form at the interphase boundary between NiAl and Nb-based alloys during high temperature heat-treatment. To avoid the formation of Laves phase, both the B2 phase composition and the BCC alloy composition were optimized based on the phase diagrams such as Nb-Al-Pd and Nb-Mo-NiAl, then a composition area at which BCC solid-solution phase equilibrates with B2 aluminide was found in Nb-Mo-Ni-Al-Pd quinary system. By the systematic investigation, it was found that the atomic size ratio of constituent elements is still an important key to understand the stability of ternary Laves phases including Al. For a further understanding of the substitutes behavior of elements in the Laves phase, electronic structure calculations based on the density functional theory (DFT) was performed on the alloy system including Si. This work was supported by the Advanced Low Carbon Technology R&D (ALCA) program of the Japan Science and Technology Agency (JST).

2:00 PM PM06.02.02

Role of Mo Solid Solution on Ultrahigh-Temperature Tensile Creep Deformation of MoSiBtic Alloy

KyoSuke Yoshimi1, Shihito Y. Kamata1, Shunichi Nakayama1, Sojirou Uemura2, Sadahiro Tsukerawa2, Gunther Egelier1 and Kouichi Maruyama1; 1Tohoku University, Sendai, Japan; 2Kumamoto University, Kumamoto, Japan; 3Ruhr-University Bochum, Bochum, Germany.

A Mo-Si-B-based alloy reinforced by TiC (65Mo-10Ti-5Si-10B (at.%)) shows high creep resistance estimated over the rupture time of 1000 h under 137 MPa at 1350°C and relatively good room-temperature fracture toughness over 15 MPa(m)1/2. The excellent mechanical properties arise from the high strength of Mo-Si-B (T2) and TiC, the good ductility of Mo solid solution, and the microstructural configuration of these phases. Under creep deformation, the resistance of Mo solid solution would be one of key factors controlling the overall strength of the material and the interfacial sliding between these phases would be the other factor. In this paper, the role of Mo solid solution on ultrahigh-temperature tensile creep deformation is addressed for the MoSiBtic alloy. The microstructural continuity of Mo solid solution was analyzed in terms of the percolation probability. It was clarified by the percolation probability analysis that both the Mo solid solution and brittle phases (T2 and TiC) were not 100%-continuous in the microstructure. EBSD and TEM observations for ruptured specimens presented dynamic recrystallization in Mo solid solution due to heavy plastic deformation during creep but much less plastic deformation in the brittle phases. These results represent that the creep strain was given by the dislocation creep of Mo solid solution and the interfacial sliding between the phases. The apparent activation energy of creep was estimated to be about 560 kJ/mol from the Arrhenius plot of the logarithm of the minimum creep rate against inverse temperature. The value is much higher than the activation energy of the self-diffusion of Mo. This strongly suggests that the rate-controlling process of this creep is governed by the bulk diffusion in Mo solid solution rather than interfacial diffusion. However, it is unlikely to be caused by Mo self-diffusion because of its lower activation energy, but it might be caused by impurity diffusion, for example, of interstitial (I)-substitutional (S) pairs. The role of Mo solid solution on ultrahigh-temperature tensile creep deformation of the MoSiBtic alloy will be further discussed with experimental data.

2:15 PM PM06.02.03
Density Reduced Mo\textsubscript{x}-(Mo,V)\textsubscript{y}Si\textsubscript{z}-(Mo,V)\textsubscript{y}SiB\textsubscript{z} Alloys Julia Becker\textsuperscript{1}, Ulf Betke\textsuperscript{1} and Manja Krüger\textsuperscript{2}; 1Otto von Guericke University, Magdeburg, Germany; 2IEK-2, Forschungszentrum Jülich GmbH, Jülich, Germany.

In terms of preserving resources and reducing environmental impacts, improving the efficiency of turbines for power plants and aircraft engines is an increasingly important research subject. Potential high performance materials are Mo-Si-B alloys. Consisting of a molybdenum solid solution (Mo\textsubscript{90}) phase and two intermetallic phases Mo\textsubscript{5}Si\textsubscript{3} (T\textsubscript{2}) and Mo\textsubscript{5}Si\textsubscript{3} those alloys present balanced room temperature fracture toughness, high temperature creep strength and oxidation performance. In this work vanadium as a lightweight element with a density of 6.1 g/cm\textsuperscript{3} has been identified as a potential alloying partner which can entirely be solved in the Mo\textsubscript{5}Si\textsubscript{3} phase as well as in the Mo\textsubscript{5}Si\textsubscript{3} and MoB\textsubscript{5} phase. To identify the role of vanadium in terms of strengthening the solid solution phase different Mo-XV (X = 5...50 at.%) alloy compositions were produced and evaluated by means of microhardness measurements. Additionally, quantitative values for solid solution hardening were determined by the approach of Labusch. Compared to other alloying concepts, e.g. Mo-Ti, vanadium affects a more balanced strength – ductility relation at room temperature, i.e. a slightly reduced strength but increased plastic deformability. In the next step, potential Mo-V-Si-B materials which provide a reduced density by about 20% as compared to reference alloy Mo-9Si-8B were investigated. Different alloy compositions were obtained by powder metallurgy to observe the effects of V as a solvent in the respective phases. The microstructure of the bulk Mo-40V-9Si-8B was characterized via SEM and XRD. From Rietveld refinements the preferred V sites in the lattices of the present phases were derived. The mechanical behavior was determined by microhardness measurements as well as constant displacement tests in the compressive mode between room temperature and 1100 °C. Three point-bending with notched samples as well as compressive creep tests reveal a high fracture toughness and acceptable creep strength of this new type of alloys. Therefore, the first results show a high potential as a lightweight version of Mo-Si-B alloys for structural applications.

2:30 PM PM06.02.04
A Phase Field Study on Script Lamellar Pattern of MoSi\textsubscript{2}/Mo\textsubscript{5}Si\textsubscript{3} Eutectic Chuanzi Zhu\textsuperscript{1}, Yuichiro Koizumi\textsuperscript{2}, Chuanqi Zhu\textsuperscript{1}, Akihiko Chiba\textsuperscript{1}, Kyosuke Kishida\textsuperscript{1} and Haruyuki Inui\textsuperscript{2}; 1Institute for Materials Research, Tohoku University, Sendai, Japan; 2Department of Materials Science and Engineering, Osaka University, Osaka, Japan; 3Center for Elements Strategy Initiative for Structure Materials (ESISIM), Kyoto University, Kyoto, Japan.

MoSi\textsubscript{2}-based alloys and composites have been considered as promising candidates for high temperature structural application. Directionally solidified (DS) Mo\textsubscript{5}Si\textsubscript{3}/Mo\textsubscript{5}Si\textsubscript{3} composites have a script pattern in which discontinuous Mo\textsubscript{5}Si\textsubscript{3} rods inclined to the growth direction are embedded within Mo\textsubscript{5}Si\textsubscript{3} matrix. Since a deeper understanding of pattern formation is crucial to the microstructure design for property optimization, a phase field model based on Multiphase-Field framework has been constructed to elucidate the responsibility of continuous nucleation on solid-liquid interface for the discontinuity of this pattern, which has a close relation to material toughness. Under solidification conditions with various growth rates, three dimensional computation results of microstructures reproduced the characteristics of script pattern observed by scanning electron micrography (SEM). In addition, the simulation results show good agreement in length scale of lamellar spacing with experimental images and analytical solutions obtained by Jackson-Hunt approach.

2:45 PM PM06.02.05
Printability of Mo-Si-B Alloys via Additive Manufacturing Janett Schmelzer\textsuperscript{1}, Silja-Katharina Rittinghaus\textsuperscript{2}, Andreas Weisheit\textsuperscript{2}, Martin Stobik\textsuperscript{3}, Jörg Paulus\textsuperscript{4}, Karl Gruber\textsuperscript{4}, Egbert Wessel\textsuperscript{4}, Manja Krüger\textsuperscript{2} and Christoph Heinze\textsuperscript{2}; 1Otto-von-Guericke-University Magdeburg, Magdeburg, Germany; 2Fraunhofer – Institut für Lasertechnologie, Aachen, Germany; 3NANOVAL GmbH & Co.KG, Berlin, Germany; 4Dr. Kochanek Entwicklungsgesellschaft, Neustadt a. d. Weinstraße, Germany; 5Institut für Energie- und Klimaforschung (IEK-2), Jülich, Germany; 6Siemens AG, Berlin, Germany.

Current research on high temperature metallic materials focuses on Mo-Si-B alloys which are candidates for novel turbine materials. For structural applications, an important phase field in the ternary Mo-Si-B system is located between the Mo solid solution phase (Mo\textsubscript{90}) and the silicides Mo\textsubscript{5}Si\textsubscript{3} (T\textsubscript{2}) and Mo\textsubscript{5}Si\textsubscript{3} (A\textsubscript{15}), which is known as the so-called “Berezik-triangle”. Near-eutectic Mo-Si-B alloys from this three-phase region exhibit outstanding creep properties, even above temperatures of 1100 °C, as well as a good oxidation resistance. However, ingot processing (IM) of this class of materials is challenging due to the high melting point of Mo-Si-B materials being typically > 2000 °C (eutectic Mo\textsubscript{90},Mo\textsubscript{5}Si\textsubscript{3},Mo\textsubscript{5}Si\textsubscript{3} alloys - 2000 °C). Different multi-step powder metallurgical processes (PM) were typically used in the past to produce dense Mo-Si-B samples under laboratory conditions. The introduction of a one-step processing route for this type of material via additive manufacturing (AM) or 3D printing represents an important innovation that will allow the production of complex bulk materials with net shape geometries (e.g. turbine blades). This work shows the feasibility of printing pre-alloyed near-eutectic Mo-Si-B powder materials via laser metal deposition (LMD). Therefore, Mo-Si-B powder was manufactured via gas atomization (GA) process out of solid raw materials meeting the requirements for AM regarding fluidability and particle size. The specific challenge is the ultra-high melting point of this type of alloys, accompanied by problems of interlayer bonding and defects that may occur during cooling. Compact multiphase Mo\textsubscript{90}Mo\textsubscript{5}Si\textsubscript{3}Mo\textsubscript{5}Si\textsubscript{3} builds containing low porosity could be manufactured. For further understanding of the microstructural evolution powder particles after GA were investigated and detailed analyses of the resulting microstructure were carried out. For purpose of comparison with PM and IM Mo-Si-B alloys first results of mechanical tests, e.g. hardness, compressive strength and creep response, are presented.

3:00 PM BREAK

3:30 PM PM06.02.06
Room Temperature Deformation of Transition-Metal Silicides Investigated by Micropillar Compression Method Kyosuke Kishida\textsuperscript{1,2} and Haruyuki Inui\textsuperscript{1}; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISIM), Kyoto University, Kyoto, Japan.

Transition-metal (TM) silicides have received considerable attention as promising structural materials for ultra-high temperature applications that can replace the currently used Ni-based superalloys because of their very high melting temperature above 2000 °C, good mechanical properties and good oxidation resistance. Extensive studies using bulk single- and poly-crystals have revealed that most TM silicides can plastically deform only at high temperatures above 1000 °C. The activation of various deformation modes has been reported so far, however, some ambiguity in the identification of operative deformation modes still remains mostly because of severe oxide formation on the specimen surface as well as dislocation climb, which is inevitable in the case of high temperature experiments. Recently, the micropillar compression method first introduced by Uchic et al. has been widely recognized as an attractive technique to investigate the mechanical response of not only pure metals but also various hard andbrittle materials at sizescales of tens of micrometers or less. Recently, we have applied the micropillar compression method to single crystals of various TM silicides such as TiM5Si2 (TM=Mo, Nb, Ta, V, Cr), TiM5Si3 (TM=Mo, Nb, Ti) and T2-Mo5SiB2 as a function of specimen size and loading axis orientation. For most of the TM silicides tested, plastic flow was observed if the specimen size is reduced to micron meter size. For T2-Mo5SiB2 phase, three different slip systems were identified to be operative at room temperature. The values of critical resolved shear stress (CRSS) for the three slip systems in T2-Mo5SiB2 are extremely high all exceeding 2 GPa. The CRSS value for each slip system increases with the decrease in the specimen size, following the inverse power-law relationship with an exponent much smaller than those reported for FCC and BCC metals. The dissociation scheme and glide plane (actual atomic
The microstructures are compared with respect to the nature and morphology of the phases, the chemical homogeneity and the porosity. The main detected temperatures; (4) bulk SPS samples with additional heat treatment (1500°C, 100 h). Quasi-static compression tests as well as creep tests, at 800°C and 1000°C, are presented.

This communication reports the study of an alloy with composition 43Nb-25Ti-3Mo-3Cr-6Al-20Si (at.%). The microstructure of this alloy has been investigated both experimentally through atomic-resolution scanning transmission electron microscopy imaging of their core structures and theoretically by first-principles calculations of the relevant generalized stacking fault energy curves.

Application of the single-crystal Ni base superalloys for turbine blades at temperatures of up to 90 % of their melting point already reached the limit of their development. Because of the beneficial physical and mechanical properties at high temperatures, Mo base alloys are very promising to substitute Ni base alloys. These materials possess high temperature strength and excellent creep resistance as well as acceptable fracture toughness. Nevertheless, the replacing of Ni base superalloys in turbine applications is still a difficult problem. This study is focused on FE calculations of the deformation of a simple turbine blade made of Mo based alloys under the typical loading conditions in comparison to conventional turbine blade materials, aimed to evaluate the feasibility of Mo base alloys.

The investigations of Mo base alloys displayed the best combination of the high temperature properties for alloys containing Si and B, specifically for the alloy family with a three-phase microstructure: ductile molybdenum solid solution phase and the two intermetallic phases Mo3Si and Mo5SiB2. However, an extensive knowledge about the physical and mechanical properties of each phase is not achieved yet. In this study, the creep properties of the individual phases are determined and applied for the estimation of the creep properties of the alloy in general. This provides a possibility for the advanced alloy design.

Phase Field Simulation of Spontaneous C11b-MoSi2/D8m-Mo5Si3 Eutectic Reaction in Directional Solidification Yuichiro Koizumi1, Chuanqi Zhu1, Toshihiro Yamazaki1, Akihiko Chiba1, Kurotaka Yuge2, Kyosuke Kishida1, Haruyuki Imai2; 1Tohoku University, Sendai, Japan; 2Osaka University, Suita, Japan. This model can take into account the elastic strain energy and the relaxation of strain by structural ledges. It is also possible to include interfacial segregation of ternary elements to the model. When spontaneous decomposition from liquid to C11b-phase and D8m-phase was assumed, inclined lamellar structures were formed under limited conditions, and the lamellar spacing decreased with increasing cooling rate as expected. It is suggested that the nucleation of DB6-Mo5Si3 is important for more quantitatively precise reproduction of script lamellar structure. The effects of nucleation will be presented by Zhu et al. elsewhere. Reference: [1] K. Fujiwara et al. Intermetallics 52 (2014) 72-85. [2] T. Yamazaki et al. Intermetallics 54 (2014) 232-241, [3] T. Yamazaki et al. Comp. Mat. Sci. 108 (2015) 358–366.

Microstructural Study of a Nb-Si Based Alloy Through the Different Steps of a Powder Metallurgy Route Virgil Malard1, 2, Stefan Drawin1, David Neumeyer3, Jean-Philippe Monchoux3, Anne Denquin1 and Alain Courtet1; 1ONERA, Châtillon, France; 2Paris-Saclay University, Saclay, France; 3CEMES/CNRS, Toulouse, France.

Niobium silicide intermetallic alloys are good candidates for applications as low-pressure turbine blades in aircraft engines for service temperatures between 800°C and 1000°C. The Nb-Si based alloys are multiphase materials constituted by a niobium solid solution Nbss, silicide phases of the NbSi3-α and / or Nb5Si3-β (tetragonal structure) and / or NbSi3-γ (hexagonal), sometimes NbSi type, depending on the heat treatments applied or the alloying elements added. The solidification structure is generally dendritic with more or less complex eutectic cells. Microstructure control during solidification and processing steps is essential to obtain good mechanical properties. This is difficult by conventional casting, knowing that forming processes (forging, etc.) require high temperatures for these materials which contain more than 50 vol.% of intermetallic phases. Powder Metallurgy (PM), thanks to the microstructural homogeneity it offers, and to easier shaping processes, is a manufacturing process that deserves to be studied.

Characterization Crystal Phase and Thermolectric Properties of Thin Film SrSi2 Kodai Aoyama1, Takao Shimizu1, Hideto Kuramochi2, Masami Mesuda1, Ryo Aikio2, Yoshiyuki Kimura1 and Hiroshi Funakubo1; 1School of Materials and Chemical Technology Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; 2Advanced Materials Research Laboratory, Tosoh Corporation, Ayase, Japan.

This work has benefited from State support managed by the ANR under the "Investissements d'Avenir" program through the MATEMCA project (reference ANR-10-EQPX-37) and from ANR funding through the SYNOPSIS project (reference ANR-15-CE08-0042).

Characterization Crystal Phase and Thermolectric Properties of Thin Film SrSi2 Kodai Aoyama1, Takao Shimizu1, Hideto Kuramochi2, Masami Mesuda1, Ryo Aikio2, Yoshiyuki Kimura1 and Hiroshi Funakubo1; 1School of Materials and Chemical Technology Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; 2Advanced Materials Research Laboratory, Tosoh Corporation, Ayase, Japan.

Silicon based alloys with good thermoelectric property such SiGe, MgSi and Mn-Si system have been widely investigated not only bulk form but also thin film form. α-SrSi2 is also a promising candidate as a thermoelectric material because it consists of abundant nontoxic elements and a good thermoelectric power factor near the room temperature was reported by Hashimoto et al. [1]. However, the number of researches is limited compared with former widely
investigated silicide and there are no reports in film form. In this study, we firstly prepared α-SrSi2 thin films on insulating substrates and measured their thermoelectric properties. Thin films of Sr-Si system were deposited on c-Al2O3 substrate by using RF magnetron sputtering method at various deposition temperature and total pressure. Constituent phases strongly depend on the deposition temperature. The films deposited below 400°C consisted of amorphous phase. Metastable SrSi2 phase with CaSi2 structure was obtained between 500 and 600°C and finally stable α-SrSi2 above 700°C. Metastable SrSi2 phase with CaSi2 structure showed low power factor below 10 μW/(m K2) for the temperature range of 100-400°C. On the other hand, α-SrSi2 show good thermoelectric power factor beyond 700 μW(m K2) at room temperature. This much value is larger than observed value of Mg2Si (111) one-axis-oriented films prepared by the same deposition process, maximum 130 μW/(m K2) at 300°C. The present result shows that α-SrSi2 is one of the promising candidates as thin film thermoelectric materials. [1]K. Hashimoto et al., J. Appl.Phys. 102 (2017) 063703.

Microstructure Design for Enhancement of Room-Temperature Ductility in Multi-Component TiAl Alloys Ryosuke Yamagata, Yotaro Okada, Hirotoyo Nakashima and Masao Takeyama; Materials Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Japan.

TiAl alloys are required high toughness and ductility for jet-engine applications. In previous studies, we clarified that introduction of the β-Ti / γ-TiAl duplex (DP) microstructure at the α2-Ti3Al / γ lamellar colony boundaries improves the stress intensity factor range threshold AK and decreases the Paris exponent m. Microstructure analysis revealed many slip lines exist in γ phase in DP region. This suggested that it is possible to enhance room-temperature ductility through controlling DP microstructure. Therefore, in this study, microstructure factors to enhance room-temperature ductility was investigated in multi-component TiAl alloys.

Multi-component TiAl alloys were used in this study. The microstructure was controlled by phase transformation of α → β + γ based on our phase diagram studies. Room-temperature tensile tests were conducted with a strain rate of 3 × 10^-4 s^-1 using an Instron-type universal testing machine. In order to removed surface strain that was introduced during machining, tensile test specimens were firstly electrical-polished. Microstructures observation was carried out using field-emission scanning electron microscopy. The room-temperature ductility changes from 0.1 % to 1.4 % with increasing of volume fraction of γ phase from 5 % to 80 %. However, γ single phase alloy did not show any ductility, less than 0.1 %. Microstructure analysis revealed that the key of factors for enhancement of room-temperature ductility are the large amount of γ phase (>70%) in DP region and the existence of β phase. The other techniques and mechanisms will be discussed in presentation. This study was supported by Strategic Innovation promotion Program (SIP) in Japan.

Microstructural Evolution in Mo-Alloyed Al-Rich Titanium Aluminides Reinhold Warthichler1, Frank Stein2, Martin Palm2, Helmut Clemens2 and Svea Mayer1;1 Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria; 2Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany.

Titanium aluminides based on the intermetallic γ-TiAl phase are well-established lightweight structural materials within the temperature range from 600 to 800°C due to their high specific (creep) strength, low density and sufficient oxidation resistance. Increasing the aluminum content lowers the density even further while improving the oxidation behavior and leads to the formation of Al-rich intermetallic phases, such as γ-TiAl2. Although for an alloy with a...
The microstructural evolution and transformation behavior of titanium aluminides is a complex interplay in alloy design, process development and under due to their peerless combination of material properties at high temperatures, intermetallic titanium aluminides have already started to be implemented as a turbine blade material in the low pressure section of the turbine engine.

As turbine blades are attached to the turbine disk by a specific dovetail connection, metallic surfaces are inevitably in direct contact under harsh mechanical loads as well as thermal conditions. In this regard, friction and wear issues always occur and can strongly affect the overall lifetime of the components. Within the scope of this study a basic analysis of the friction and wear properties of two γ-based TiAl alloys, namely TNM-B1 and GE 48-2-2, has been conducted using a high temperature pin-on-disk apparatus. Hereby, tests were performed covering a wide temperature range (up to 800°C) under variation of the counterpart material to simulate conditions that are relevant for today’s turbine engines.

As oxidation plays a vital role in terms of high temperature sliding wear conditions being the decisive factor for the specific wear mechanism and rate, the basic oxidation behavior of the chosen TiAl alloys has to be additionally investigated. Isothermal exposures in air were conducted to determine the respective influence of the exposure time (up to 1000h) as well as the temperature. Conclusively, wear losses/rates were calculated and changes in the occurring wear mechanisms were identified using a profilometer as well as different metallographic techniques to depict differences in the overall tribological performance of both substrates.

Gamma TiAl alloys are gaining acceptance as a lighter weight alternative to nickel-based superalloys in certain high temperature applications. Further successful adoption of these alloys into new aero-engine components requires additional improvements to temperature capability and property balances. Comprehensive understanding of composition-processing-microstructure-property correlation is essential in aiding the selection of suitable alloy composition and the control of processing conditions. Although simulations tools have been developed for such a purpose, trial-and-error approaches are still widely used in alloy design and process optimization.

In this work, we will present our work in the development of a simulation tool that can be used to accelerate the development of gamma TiAl alloys. In particular, we developed a thermodynamic database for TiAl-based alloys using the CALPHAD (CALculation of PHAse Diagram) approach. This database contains 16 components which covers most of the major and minor alloying elements for TiAl-based alloys. We have also developed a high throughput calculation (HTC) in Pandat software through which calculations at numerous alloy compositions can be performed and alloy compositions that satisfy user-defined criteria can be searched through data mining of the simulated results. In this presentation, we will demonstrate how we can use HTC function and the thermodynamic database we have developed for TiAl alloys to understand the effect of various alloying elements on the properties of TiAl alloys and therefore identify the alloy compositions with good potentials for certain applications.

The microstructural evolution and transformation behavior of titanium aluminides is a complex interplay in alloy design, process development and under...
operating conditions. In-situ neutron and synchrotron X-ray diffraction deliver unique and complementary insight into the material’s response to high temperature, deformation and extreme conditions. Neutrons illuminate a larger bulk volume and reveal quantitative phase abundance, bulk texture, lattice parameter changes and other ensemble averaged quantities. In contrast, fine-bundled high-energy X-rays deliver reflections from a number of individual grains. For each constituting phase, their statistics and behavior in time reveal information about grain growth or refinement, subgrain formation, static and dynamic recovery and recrystallization, slip systems, twinning, etc. Features will be presented on selected examinations on titanium aluminides, especially to characterize phase evolution and crystallographic changes upon heating and during plastic deformation, and severe conditions.

11:30 AM PM06.03.09
Formation of Orthorhombic Intermediate Temperature Phases in Different Commercial and Experimental γ-TiAl Alloys Marcus W. Rackel¹, Heike Gabrisch1, Uwe Lorenz1, Andreas Stark¹ and Florian Pyczak1, 2; 1Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; 2Brandenburgisch Technische Universität Cottbus-Senftenberg, Cottbus, Germany.

γ-TiAl alloys for aero engine blades can be produced by forging but the inherent brittleness of TiAl makes this difficult. A means to facilitate forging of γ-TiAl alloys is to stabilise the ductile soft disordered β phase at forging temperature. This is achieved by the addition of β stabilising elements as for example Nb, Mo or V and was successfully implemented in the TNM alloy. In the ideal case the β phase may be present at forging temperature but can be dissolved fully at service temperature where its presence is unwanted. Unfortunately, often not only the two phases γ and α2 are found at service temperature but additional stable or metastable phases are present. In an experimental Ti-42Al-8.5Nb alloy an orthorhombic phase constituent was identified which had the crystal structure of the O-phase and is a transformation product of α2-phase at temperatures below 650 °C. To unambiguously identify the phase and its transformation path high-energy X-ray diffraction (HEXRD) measurements at varying temperatures using in-situ specimen environments were performed. Based on literature knowledge the occurrence of O-phase is only expected for significantly higher niobium and lower aluminium contents.

Initially it was supposed that this O-phase is a feature of this very special experimental alloy composition. Nevertheless, screening tests over a wide variety of alloy compositions proofed that the O-phase can be found in a number of commercial as well as experimental alloys depending on composition and heat treatment history. In general it can be stated that alloy compositions with a combined content of β stabilising elements of 6 at.% or more and Al contents of 46 at.% or lower form O-phase to a greater or lesser extent. Minor alloying elements, such as boron or carbon exhibited no measureable effect on O-phase formation. The results can be valuable for the development of β stabilised TiAl alloys and the understanding of the long term behaviour of TiAl parts as the possibility of O-phase formation in the medium temperature range was until now disregarded for such alloys.

SESSION PM06.04: Titanium Aluminides III and Superalloys
Session Chairs: Alain Couret and Rui Yang
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.04.01
Influence of Solidification Condition on Boride Morphology in Cast TiAl Alloys Rui Yang; Institute of Metal Research CAS, Shenyang, China.

Boron additions are indispensable in gamma TiAl alloys designed for cast applications because borides of different structures, shape, and size or their mixtures limit grain growth during solidification, subsequent solid state phase transformation, and during hot isostatic pressing. Some forms of borides, such as very long ribbons, especially when concentrated and entangled, may degrade mechanical properties. In this talk, we attempt to classify the conditions for the formation of such borides according to alloy composition, cooling rate and solidification sequence. Experimental evidence will be presented from both cast turbine blades and wedge-shape samples with step thickness. Corresponding tensile test data will be discussed.

2:00 PM PM06.04.02
Phase Equilibria among β/α2/α/γ Phases and Phase Transformations in Ti-Al-Cr System at Elevated Temperatures Ali Shaaban¹, 2, Hideki Wakabayashi¹, Hiroyo Nakashima¹ and Masao Takeyama¹; ¹Department of Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan; ²Surface Protection and Corrosion Control Lab, Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt.

Designing of wrought TiAl alloys opens the window for a wide range of applications and it will not be exclusive to be applied as low-pressure turbine materials but also as high-pressure compressor materials. β-Ti phase in TiAl alloys allows excellent workability during processing and excellent mechanical properties in service temperatures. In other words, microstructure control using β-phase is a key to develop high-toughness wrought γ TiAl alloys. This can be accomplished by understanding the phase transformations involving β-phase. Effects of group V⁰ (V, Nb) and V⁰ (Cr, Mo) elements as β-stabilizers on phase equilibria of TiAl alloys above 1473 K were extensively studied by our group. It was found that V and Nb stabilize α2 against α. Also, the change in three-phase coexisting region β+α2+γ that exists above 1473 K to that of β+α2+γ occurs not just by the ordering transformation α→α2 (2⁰ order phase transformation) but by a transition peritectoid reaction β+α→α2+γ (1⁰ order phase transformation) at a temperature between 1453 K (the congruent temperature of α→α2) and 1400 K (the eutectoid reaction temperature of α→α2+γ) in Ti-Al binary system with decreasing temperature. Thus this phase transformation allows a unique transformation pathway for α→α2+γ in the ternary systems. However, it has not been clarified yet that the addition of group V⁰ elements (Cr, Mo) stabilizes either α or α2. Thus, in this study, the effect of Cr addition to TiAl alloy on the phase equilibria among the four phases and phase transformation pathways within the temperature range of 1473 K–1073 K were investigated using several alloys in the composition of interest. In between 1473 K–1373 K, the slope of β/a tie-line in the three-phase coexisting region of β+α2+γ remains basically unchanged where the Al content in β-phase is much lower than that in α-phase. However, this slope drastically rotates in a clockwise direction and the Al content between the two phases becomes nearly equal, in between 1373 K and 1273 K and below the eutectoid reaction temperature in the binary system (1400 K). This is a strong indication that thermodynamically α-phase exists even below the 1400 K, i.e. addition of Cr stabilizes α against α2 and the three-phase coexisting region of β+α2+γ at lower temperatures is formed through a ternary eutectoid reaction α→β+α2+γ with decreasing temperature. This three-phase tie-triangle moves towards lower Al content in alloys with lower Al content. In between 1173 K and 1073 K, no further shift was observed in the tie-triangle meanwhile it expands towards high Cr content in β-phase. Based on these information, a novel technique for developing a new wrought γ-TiAl with excellent workability during processing at elevated temperatures and excellent toughness in service conditions, could be proposed.

2:15 PM PM06.04.03
A Dislocation-Scale Characterization of the Evolution of Deformation Microstructures on a Bulk TiAl Alloy Antoine Guitton¹, 2, Hana Kriaa¹, 2,
Developing new materials and understanding how they deform is the main challenge of engineers in order to follow and predict the fast evolutions of our society. For instance, in a framework of energetic cost reductions, titanium aluminide (TiAl) alloys have attracted considerable attention due to their unique combination of properties such as high specific strength and stiffness, good creep properties and resistance against oxidation and corrosion, which make them suitable candidate materials for high temperature applications [1]. However, TiAl alloys are brittle at Room Temperature (RT), i.e. below their brittle-to-ductile transition temperature, which lies between 800°C and 1000°C [2]. Furthermore, their complex microstructures (multiphase, different types of microstructures, specific dislocation mechanisms…) with several impacts at different scales are puzzling the materials science community. Despite intense research, literature suffers from a lack of understanding of their elementary deformation mechanisms and the precise role of microstructures [2].

In order to address these questions, we report here, an original and an innovative approach bringing the necessary information, thus allowing linking the multiscale aspects of the mechanical behavior of TiAl alloys at RT. Particularly, we bring new breakthrough on the evolution of deformation microstructures at RT in the vicinity of interfaces in γ phase of a dual-phase bulk TiAl alloy. Plastic deformation is induced locally by μN-nanindentation. The evolution of the microstructures is characterized comprehensively by accurate Electron Channeling Contrast Imaging (αECCI) before and after deformation [3]. αECCI is a non-destructive groundbreakings procedure offering the ability to provide, inside a SEM, TEM-like diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [4]. Defects, such as dislocations, can be characterized by applying the TEM extinction criteria [5]. All features help to explain the poor ductility of the TiAl-based alloys at RT. Accommodation of the deformation is reported and a scenario is proposed [3].

References

2:30 PM PM106.04.04
Relationship Between the Microstructure and Atomic Relaxation Processes in the Last Generation of TiAl Intermetallics

Maria L. No1, Leire Uategui2, Thomas Klein3, Svea Mayer4, Helmut Clemens5 and Jose San Juan; 1Física Aplicada II, Universidad del País Vasco (UPV/EHU), Bilbao, Spain; 2Física de la Materia Condensada, Universidad del País Vasco, Bilbao, Spain; 3Materials Center Leoben, Leoben, Austria; 4Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria.

Engineering structural intermetallics exhibit outstanding stability at high temperature. Among the different families of intermetallics, γ-TiAl alloys are good candidates for propulsion systems in aero and automotive industries. Recently a third and a fourth generation bearing Nb and Mo in well-balanced quantities and small amounts of C and Si (TNM and TNM+ alloys) have been developed. Adequate thermal treatments of these alloys give a lamellar arrangement of α2/γ colonies that exhibits a good creep resistance at high temperatures, which has been studied by tensile creep experiments and mechanical spectroscopy /1,2/. A microstructural analysis before and after the mechanical spectroscopy experiments should give important information about the mechanisms responsible for the observed behaviour and this is the approach used along this study. In the present work two lamellar alloys were studied: Ti-43Al-4Nb-1Mo-0.1B (aT%) (TNM alloy) and Ti–43Al–4Nb–1Mo–0.1B–0.3C–0.3Si (aT+%) (TNM+ alloy) with a final aging thermal treatment at 1123K and 1173K respectively. Mechanical spectroscopy measurements between 850K and 1225K show the diffusion of several solute atoms at different temperatures. The activation parameters were determined by tensile creep and mechanical spectroscopy experiments. The regions of discontinuous precipitation surrounding the lamellar colonies were characterized by scanning electron microscopy (BSE, EDX, EBSD) technique. The lamellar α2/γ colonies and the small precipitates observed inside the lamellae were characterized by transmission electron microscopy (BF, DF, microdiffraction, nanodiffraction, STEM-HAADF, EDX) with a Titan Cubed 80-300KV working a 200KV. A good correlation between the mechanical spectroscopy results and the small precipitates characterized by TEM-STEM-EDX has been established through the corresponding models of precipitation and mechanical properties.

Acknowledgements:
This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO), CONSOLIDER-INGENIO 2010 CSD2009-00013 project, as well as by the Consolidated Research Group GIU17/071 from UPV/EHU. This work made use of the FIB and the TITAN Cubed microscope facilities of SGIKER from the UPV/EHU.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM PM106.04.06
The Effect of Oxidation on Microstructure and Phase Stability in the Subsurface Zone of Titanium Aluminides Exposed at High Temperatures

Mathias C. Galletz, Anke S. Ulrich, Lukas Menigs, Alexander Donchev, Ceyhun Oskay and Diana Fähßing; DEHEMA Research Institute, Frankfurt am Main, Germany.

Titaniumaluminides had been in the focus of research for more than three decades before they finally took off as part of modern aircraft engines in 2011. Due to their density of about 4 g cm⁻³ they offer a high specific strength since they weigh only the about half in comparison to nickel-based alloys. Thus, a favorable advantage in efficiency, noise reduction and fuel consumption is achieved. Because of their properties they gained interest also for application temperatures beyond the present range of ~750°C. This limit is defined by the strong degradation of their oxidation resistance above that temperature. Best oxidation resistance and the mechanical properties are also affect, however, the origin of this phenomenon is still under debate. In addition, several authors reported an increase in oxygen and nitrogen concentration in the surface region of TiAl-alloys. It was shown that the loss of ductility can be restored by removal of the surface and subsurface layer following high temperature exposure. One issue related to that is, that the oxygen and nitrogen uptake within the alloy are not easy accessible. Recently developed TiAl alloys and applications such as TMB® and TMB®+ aim for even higher application temperatures and improved hotworkability. Beside γ-TiAl and α₂-Ti₃Al, such alloys additionally contain the β₂ phase, whose impact on the high temperature oxidation and mechanical properties after exposure is hardly investigated and shows the requirement of a deeper understanding of the subsurface changes in such alloys due to dissolved
Due to the low density in combination with a high melting point, vanadium demonstrates a great lightweight potential for turbines in aircrafts or energy industry. Since vanadium as a structural material is in focus of research only recently, the effects of several alloying elements on the materials properties are not or insufficiently examined yet. Therefore, various binary V-X and ternary V-Si-X-systems, that frequently contain intermetallic phases, have been studied. By means of ingot metallurgy, vanadium samples with different concentrations of alloying elements were manufactured. Resulting from this, single phase vanadium solid solutions (V₃ₓ), two-phase and three-phase alloys were produced. Microhardness measurements and compression tests were carried out to determine the mechanical properties in dependence on the alloying components. The combination between mechanical characteristics and microstructural investigations enables conclusions concerning the materials behavior and the efficiency of solid solution strengthening and second phase strengthening. Therefore, SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction) methods were used to examine the microstructure, to identify phases and to measure elements concentration in the respective phases. Results achieved within this study may help to assess the potential of novel vanadium-based structural materials regarding to high temperature applications.

An Attempt to Design a New Class of Co-Based Superalloy with Improved Oxidation Resistance and Creep Property 
Zhenghao M. Chen1, Norihiko L. Okamoto1 and Haruyuki Imai1; 1Kyoto University, Kyoto, Japan; 2Tohoku University, Sendai, Japan.

Recently, a new ternary L1₂ (γ′) phase Co₃(Al,W), coexisting with a fcc solid-solution phase (γ) based on Co, has been discovered. With precipitation strengthening by the γ′ phase, this class of Co-base superalloys exhibits an improved high-temperature strength, compared to that of conventional Co-based superalloys. However, the creep property in ternary alloy is still insufficient, due to the insufficient high-temperature strength and the lack of γ′ in volume fraction. Besides, the oxidation resistance is also an unresolved problem. In previous studies, the effect of some alloying elements on Co-base superalloys has been investigated. Ni, Ta and Ti are effective in improving the creep property by either increasing the γ′ high-temperature strength or the γ′ volume fraction. On the other hand, Cr and Si are proved to be effective in improving oxidation resistance, but providing a negative effect on creep property, by decreasing the γ′ solvus temperature, unfortunately. Thus, in the present study, we investigate the effect of co-addition of alloying elements Ni, Ta, Ti, Cr, Si on Co-base superalloys, attempting to find out a composition exhibiting both excellent creep property and sufficient oxidation resistance, simultaneously.

Ingots of (Co₀.₈, Ni₀.₂)ₐAlₐₜ₉Taₐₜ₉Tiₐₜ₉Crₐₜ₉Siₐₜ₉ (at.%; a, b, x, y≥0) were prepared by arc melting. These ingots were homogenized at 1200 °C for 24 h in vacuum, followed by heat treatment at a sub-solvus temperature for 96 h. The γ′ solvus temperatures were determined by differential scanning calorimetry (DSC), and the microstructures were examined by scanning electron microscope (SEM). Single crystals with selected compositions exhibiting exclusive γ′/γ two-phase cuboidal structure and reasonable γ′ solvus temperature were prepared by modified Bridgman technique, followed by heat treatment at 900 °C for 96 h. Creep tests were performed in tension under the conditions of 137 MPa/1000 °C and 428 MPa/900 °C. Oxidation resistance behavior at 1000 °C were investigated with cyclic oxidation test for 200 h (20 cycles).

Although Cr and Si alloying decrease γ′ solvus temperature drastically, substituting W (and Al) with Ta (or Ti) is an effective way to increase γ′ solvus temperature without precipitating any secondary phases (such as D₀₁₉). Oxidation resistance in multicomponent alloys are indeed to be improved, compared to non-Cr, Si alloyed Co-7Al-8W-Ta-4Ti. However, Rupture time of tensile creep at the condition of 900 °C /428 MPa in 4Ta and 8Ti are extremely short, only few hours. 2Ta6Ti6 exhibits relatively high creep property at the condition of 1000 °C/137 MPa (103h in rupture), but still not sufficient (approximately one-third to Co-7Al-8W-Ta-4Ti). It seems that, unfortunately, improving oxidation resistance and creep property simultaneously in Co-based superalloy to a utility-level may come out to be difficult, unless new type of alloying elements that increase γ′ solvus temperature more effective than Ta would be discovered.

Alloying of Cr-Base Alloys by Ternary and Quaternary Elements and Their Effect on Oxidation and Nitridation Resistance at High Temperatures
Anke S. Ulrich1, Ali Solimani1, Petra Pfizenmaier2, Uwe Glatzel2 and Mathias C. Galetz1; 1High Temperature Materials, DECHEMA-Forschungsinstitut, Frankfurt a.M., Germany; 2Lehrstuhl Metallische Werkstoffe, University Bayreuth, Bayreuth, Germany.

Due to the high melting points Cr-base alloys are future candidates for materials for high temperature applications beyond Ni-base superalloys. In addition, high Cr content alloys offer lower densities compared to the commonly used Ni-base superalloys. However, for a future successful application still an optimal alloy composition has to be defined with respect to the improvement of nitridation, oxidation, and mechanical properties at high temperatures. In this work, the influence of Si, Ge, Mo, and Pt alloying on the oxidation and nitridation resistance of Cr-rich Cr₉ₓ–Cr₉Si alloys was investigated using thermogravimetric analysis at temperatures from 1050°C – 1350°C. The samples were additionally analyzed using EPMA, SEM, and XRD analysis. Based on the binary Cr₉ₓSiₓ alloy [at.%] around 2 at.% Si were substituted by ternary elements (Ge, Mo, Pt). Before oxidation, all investigated alloys had a two phase microstructure consisting of Cr₉ and Cr₉Si₁₅ phase. During oxidation an oxide scale of Cr₂O₃ and SiO₂ formed and nitrides were found underneath the scale. However, alloying showed a significant influence on the oxide scale formation, nitridation, and oxidation kinetics. Ge substitution decreased the spallation of the oxide scale, reduced the parabolic weight gain (by oxidation and nitridation), and interestingly, also the linear weight loss induced by the formation of volatile species. In the ternary Cr-Si-X (X = alloying element) systems, Ge and Mo alloying were both enriched at the subsurface zone during oxidation and remarkably decreased nitridation and the formation of brittle Cr₇N compared to the binary Cr-Si system. Their combination in a quaternary alloy, in turn, neutralizes these positive effects. Pt acted as nitrogen getter in a ternary Cr-Si-Pt alloy by forming an antiperowskite phase which simultaneously led to increased nitrogen uptake by the sample when Pt is present at the substrate surface. In order to further optimize the alloy composition, the mechanisms of the respective elements on oxidation and nitridation behavior are proposed for the ternary and quaternary alloys.

A Combinatorial Study on Phase Formation and Oxidation in the Thin-Film Superalloy Subsystems Co-Al-Cr and Co-Al-Cr-W
Alfred Ludwig1, Wim Biekert2, Martin Weiser3, Steffen Salomon1, Helge S. Steinh 1 and Sannakaisa Virtanen2; 1Institute for Materials, Ruhr-University Bochum, Bochum, Germany; 2Materials Science, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany.

In this work, the impact of high temperature exposure on the microstructure of TMB as well as the resulting effect on the mechanical properties at room temperature are investigated. For the latter, 4-point bending tests are conducted on samples before and after oxidation. Oxidation tests are carried out at 900 °C for varying times (24 h – 1000 h) in air. The evolution of the microstructural change (based on changes in phase fractions) in the subsurface zone is investigated over time. Based on EPMA and SEM the change of the microstructure in dependence of the distance from the surface is shown, quantified, and could be correlated to oxygen uptake. A mechanism for phase transition phenomena is proposed.
Two Co-based superalloy subsystems, Co-Al-Cr and the quasi-ternary system Co-Al-Cr-W with a constant amount of 10 at. % W, were deposited as thin-film materials libraries and analyzed in terms of phase formation an oxidation behavior at 500 °C in air. By combining energy-dispersive X-ray analysis and X-ray photoelectron spectroscopy high-throughput composition measurements, a detailed evaluation of the dependence between the initial multinary metal composition and the oxide scale composition which is forming upon oxidation on the surface of the thin film is established. Phase maps for both materials libraries are provided by high-throughput X-ray diffraction. In addition, the oxidation of a Co-Al-Cr-W bulk sample was analyzed and compared to a corresponding film in the library.

PM06.05.01
Micropillar Compression of Single Crystals of the Stoichiometric Ti₃Al and hcp-Ti
Kim Jingeum¹, Atsushi Matsumoto¹, Kyoosuke Kishida¹,² and Haruyuki Inui¹,²;¹ Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; ²Center for Elements Strategy Initiative for Structural Materials, Kyoto University, Kyoto, Japan.

Micropillar compression method has received a considerable amount of attention as a new method to investigate plastic deformation behavior of various crystalline materials in sub-micron scale. Previous studies mainly on single crystals of conventional FCC or BCC metals have revealed that various interesting features in micropillar compression experiments such as strain-burst behavior and size-dependent strength with a trend of “smaller is stronger”, which is generally described with an inverse power-law relationship between the strength and specimen size. Although various models to describe the size-dependent strength have been proposed, the validity of the proposed models and their applicability to other crystalline materials with low symmetry are still controversial. In order to understand the characteristic deformation behavior of single crystalline micropillars, systematic studies on various crystalline materials including those with lower crystal symmetry are considered to be important. In the present study, we focused on an intermetallic phase Ti₃Al with the hcp-based ordered structure of the D₀₁₉ type and its parent hcp-Ti in order to investigate how the size-dependent strength varies depending on the operative deformation modes and atomic ordering. Single crystal rods of the stoichiometric Ti₃Al and hcp-Ti were grown by directional solidification using an optical floating zone furnace. Micropillar compression tests of Ti₃Al and hcp-Ti single crystals were carried out as a function of loading axis orientation and specimen size. When the loading axis is parallel to a-axis, [1-100]<11-20> prism slip was confirmed to be activated in micropillars of both Ti₃Al and hcp-Ti. The values of critical resolved shear stress (CRSS) of the prism slip for both Ti₃Al and hcp-Ti. The power-law exponent for Ti₃Al was found to be much lower than that of hcp-Ti. Possible influences of the ordered structure on the difference in the size-dependent strength for the prism slip will be discussed based on the TEM observations of dislocations.

PM06.05.02
High-Resolution Electron Transmission Microscopy Study of Orthorhombic Phase in High Nb-Containing Lamellar γ-TiAl Alloy
Jian Sun; Shanghai Jiaotong University, Shanghai, China.

Recently, the formation of nano-scale modulated microstructure, consisting of orthorhombic phase and γₐ has been reported by several authors in high Nb-containing lamellar γ-TiAl alloys. However, the occurrence of such a unique modulated microstructure in high Nb-containing lamellar γ-TiAl alloys cannot be expected from the Al-Nb-Ti ternary phase diagram in the literature. Moreover, the formation mechanism and evolution of the modulated microstructure in high Nb-containing lamellar γ-TiAl alloys remain unclear and need to be investigated. In this work, we have proved that the orthorhombic phase is thermodynamically stable in the γₐ phase in high Nb-containing γ-TiAl alloys at high temperatures from the first-principles calculations. Transmission electron microscopy (TEM) studies showed that the formation of modulated microstructure takes place at temperature at and below 650 °C. The orthorhombic phase as a constituent of the modulated structure has the O₁ structure with a random occupancy of Ti and Nb atoms on the Wyckoff sites 8g and 4c2. The O₁ phase has a thin plate-like morphology with orientation relationships of [001]O//[0001]γ and <110>γ//[110]<110>α₂ at an initial precipitating stage. The habit plane for the O₁ phase lies at ⟨350⟩O//[130]α₂. TEM results further exhibited a remarkable enrichment of Nb in O₁ phase, indicating that the formation of the O₁ phase arises from a phase separation reaction in the γ₂ matrix, dominated by a diffusion mechanism. With an extension of annealing time up to 500 hours at 600 °C, the volume fraction of the O₁ phase increases remarkably, and the O₁ variants interact with each other and eventually develop into rectangle shape with perpendicular interfaces from the thin plate-like morphology. The retransformed α₂ phase at intersection points has been found to rotate by ~3.4 ° to the original α₂, leading to the formation of orthogonal habit planes for the single O₁ variant. The nano-indentation tests showed that the precipitation hardening effect of the O₁ phase is significant in the difference in the size-dependent strength for the prism slip will be discussed based on the TEM observations of dislocations.

PM06.05.03
Ordering and Disordering of β Phase in TiAl Alloys in Dependence of Alloy Composition
Victoria Kononikhina¹, Andreas Stark¹, Weimin Gan¹, Andreas Schreyer² and Florian Pyczk¹;² Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; ³European Spallation Source ERIC, Lund, Sweden.

γ-TiAl based alloys recently have started to replace Ni-based superalloys as a material for turbine blades in the low pressure turbine section of aircraft engines. γ-TiAl based alloys are characterized by low density (4 g per cm³), good oxidation and corrosion resistance, and high specific tensile and creep strength. The presence of the γ and α₂ lamellar colonies is desirable for good mechanical properties. Cubic phase being in its disordered state (A₂ structure) improves the forging properties of the alloys because it increases the alloys brittleness at the working temperatures of about 700-800 °C and has bad creep strength. Therefore, knowledge about the presence of β phase and of its ordering/disordering temperature is of high importance for the development of alloys with improved processing properties and for a prolongation of the turbine blades working time. Currently the presence of ordered βₐ phase in the binary phase diagram is still under discussion and the influence of the different β stabilizing elements on the ordering/disordering temperature is not systematically investigated. We studied ordering/disordering transformation with in-situ synchrotron and neutron diffraction techniques. A good contrast of neutron diffraction between ordered and disordered βₐ/β phases was used to confidently determine the presence of ordered βₐ. Three binary TiAl alloys (Ti-xAl with x = 39, 42 and 45) and five alloys with additional alloying elements (Ti-42Al-2Y with Y = Nb, Mo, Ta, Cr and Fe) were investigated. Three ternary alloys with 2 at.% of Fe, Cr, and Mo contain correspondingly 12, 8, and 18 vol.% of the ordered βₐ phase. By synchrotron investigations we determined the degree of ordering
Effects of Ta and Nb Addition on the Microstructure and Mechanical Properties of MoSi2/Mo5Si3/Mo5Si3C Eutectic Composites

Kosei Takeda1, Yuki Kambara1, Hirokata Matunoshita1, Kyoysuke Kishida1,2 and Haruyuki Imu1,2,3, 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

MoSi2, with the tetragonal C112 structure, has been considered as a promising material for ultra-high temperature structural applications because of its high melting point (2020 °C), excellent oxidation resistance, and relatively low density. However, poor fracture toughness at room temperature and insufficient high-temperature strength are still drawbacks to be improved for its practical applications. One possible way to solve these drawbacks is to form an in-situ composite with one or two strengthening phases. Among various candidates, we have recently focused on MoSi2/Mo5Si3 eutectic composites because of their high eutectic temperature (1900 °C for the binary alloy) and fine microstructures of the so-called script lamellar type formed simply by directional solidification (DS) and have studied the influences of ternary additions on the microstructure and mechanical properties of DS MoSi2/Mo5Si3 eutectic composites. Our previous studies have revealed that their high-temperature mechanical properties and fracture toughness values can be improved through refining the lamellar structure and controlling interfacial properties such as interfacial segregation of ternary elements and lattice misfits. We also have found that the DS ternary alloys with a small addition of C possess a homogeneous three-phase script lamellar structure composed of MoSi2, Mo5Si3, and Mo5Si3C and exhibit higher yield strength than the binary two-phase counterpart. In the present study, effects of Ta and Nb addition on the microstructure and mechanical properties of MoSi2/Mo5Si3/Mo5Si3C eutectic composites were investigated in order to establish a way to further improve the mechanical properties of MoSi2/Mo5Si3-based eutectic alloys. When part of Mo was substituted with Ta or Nb, a relatively homogeneous three-phase eutectic lamellar structure was obtained only at growth rates lower than 10mm/h during the DS process using an optical floating zone furnace, while a heterogenous eutectic microstructure with a cellular morphology was developed at higher growth rates. Nb atoms were partitioned mostly into Mo5Si3, while Ta atoms were partitioned into both Mo5Si3 and Mo5Si3C. Both volume fraction and average thickness of Mo5Si3 lamellae decreased in the Nb alloyed eutectic composites compared to those in the non-alloyed counterpart, which resulted in higher yield strength and better creep property of the Nb alloyed eutectic composites.

Phase Diagrams and Solidification Paths of MoSiBTiC Alloys

Kyoysuke Sawada1, Makoto Ohtsuka1, Haruki Nakashima1, Kyoysuke Yoshimi2 and Hiroyuki Fukuyma1, 1IMRAM, Tohoku University, Sendai, Japan; 2Graduate School of Engineering, Tohoku University, Sendai, Japan.

MoSiBTiC alloys are expected to be used for next generation high-pressure turbine blades. However, the phase diagrams of the alloys are still deficient. Our group has developed an ultra-high-temperature thermal analysis using blackbody radiation, which can be used above 2000 °C. In this study, MoSiBTiC alloys with several different compositions were thermally analyzed with this equipment to evaluate their phase transformation temperatures. In addition, the alloys were levitated and melted by electromagnatic levitation (EML) technique in a static magnetic field to observe solidification phenomena, and to obtain rapidly-solidified sample. The solidification paths of the alloys were studied from the thermal analysis and microstructures, and the partial phase diagrams of the alloys were constructed.

Each alloy powder was filled in a CaO-stabilized ZrO2 crucible having a blackbody cavity, and then heated and cooled in a radio-frequency furnace under Ar atmosphere. The heating and cooling rates were fixed at 10 °C / min. The sample was kept above 2000 °C for over 30 min to ensure homogenous melt, and then cooled. Temperature change during cooling was measured by a pyrometer, through the radiance from the blackbody cavity. The phase transformation temperatures were obtained from the cooling curves. On the other hand, each alloy was levitated and melted by EML technique in a static magnetic field of 10 T. The static magnetic field was applied to suppress convection in the melts. The temperature of the melts was measured by a pyrometer and controlled by adjusting the power of a heating laser. Multi-recalcescence was observed at the surface of the alloys during cooling. The phase diagrams of the alloys were constructed from the thermal analysis and microstructures, and the partial phase diagrams of the alloys were constructed.

Phase Equilibrium and Mechanical Properties of Cr-Mo-Nb-Si-B Alloys Composed of BCC and T-silicide Phase

Daisuke Goto1, Ken-ichi Kyogo Sawada1, Makoto Ohtsuka1, Haruki Nakashima1, Kyoysuke Yoshimi2 and Hiroyuki Fukuyma1, 1IMRAM, Tohoku University, Sendai, Japan; 2Graduate School of Engineering, Tohoku University, Sendai, Japan.

Cr-Mo-Nb-Si-B based alloys are promising materials for high temperature applications up to 800°C because of their light weight and high creep strength. However, the application of this material to jet engines is limited to the last stages of low pressure turbine blades due to low ductility and toughness for now. In order to apply this material to other parts such as high pressure compressor, toughening is essential. We performed fatigue crack growth tests on wrought TiAl alloys and revealed that introduction of β-Ti/γ duplex (DP) along α2-TiAl/γ lamellar colony boundaries increased the fatigue threshold, ΔKf, and decreased the Paris exponent, m. We proposed that the improvement of ΔKf is partly caused by the deformation of the DP microstructure. In order to verify this proposed mechanism, the quantification of deformation in each phase is important. In the present study, in-situ observation of tensile deformation in TiAl based alloys under an SEM at room and high temperatures is performed, and strain localization is measured by digital image correlation (DIC) technique. Three dimensional observation of the un-deformed and deformed materials is also conducted to observe the morphology of the microstructure and the crack stop points. The alloy with nearly lamellar (NL) microstructure, in which the volume fraction of DP is 7%, shows elongation of 0.14% at room temperature. Deformation is observed in both lamellar colonies and DP region in NL microstructure as a result of the strain localization measurement by DIC technique. In some favorably oriented lamellar colonies, strain localization along lamellae is more than five times as much as the macroscopic strain. The amount of deformation in each phase and the crack initiation and growth behavior during tensile will be discussed. This study was supported by Strategic Innovation Program Promotion (SIP) in Japan.

Phase Equilibrium and Mechanical Properties of Cr-Mo-Nb-Si-B Alloys Composed of BCC and T-silicide Phase

Daisuke Goto1, Ken-ichi

Effects of Ta and Nb Addition on the Microstructure and Mechanical Properties of MoSi2/Mo5Si3/Mo5Si3C Eutectic Composites

Kosei Takeda1, Yuki Kambara1, Hirokata Matunoshita1, Kyoysuke Kishida1,2 and Haruyuki Imu1,2,3, 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

γ-TiAl based alloys are promising materials for high temperature applications up to 800°C because of their light weight and high creep strength. However, the application of this material to jet engines is limited to the last stages of low pressure turbine blades due to low ductility and toughness for now. In order to apply this material to other parts such as high pressure compressor, toughening is essential. We performed fatigue crack growth tests on wrought TiAl alloys and revealed that introduction of β-Ti/γ duplex (DP) along α2-TiAl/γ lamellar colony boundaries increased the fatigue threshold, ΔKf, and decreased the Paris exponent, m. We proposed that the improvement of ΔKf is partly caused by the deformation of the DP microstructure. In order to verify this proposed mechanism, the quantification of deformation in each phase is important. In the present study, in-situ observation of tensile deformation in TiAl based alloys under an SEM at room and high temperatures is performed, and strain localization is measured by digital image correlation (DIC) technique. Three dimensional observation of the un-deformed and deformed materials is also conducted to observe the morphology of the microstructure and the crack stop points. The alloy with nearly lamellar (NL) microstructure, in which the volume fraction of DP is 7%, shows elongation of 0.14% at room temperature. Deformation is observed in both lamellar colonies and DP region in NL microstructure as a result of the strain localization measurement by DIC technique. In some favorably oriented lamellar colonies, strain localization along lamellae is more than five times as much as the macroscopic strain. The amount of deformation in each phase and the crack initiation and growth behavior during tensile will be discussed. This study was supported by Strategic Innovation Program Promotion (SIP) in Japan.
MoSiBTiC alloy is systematically investigated at various temperatures, aiming to clarify the effect of Ti5Si3. The alloy was prepared by arc-melting and superior high-temperature strength and a high fracture toughness. The alloys have complicated microstructures consisting of molybdenum solid solution. The SEM observation and EPMA analysis revealed that the area fraction of constituent phases and their compositions in those Mo-Si-B-TiC alloys were measured to be in the range of 14.6~15.6 MPa (m) 1/2. There appeared no clear relation between the fractal dimension of dispersion [2] for almost no B solubility was found in BCC solid solution. With increasing Si in alloys, A15 silicide phase ((Cr, Mo, Nb)Si) and/or Laves phase are stabilized. This work was supported by the Advanced Low Carbon Technology R&D (ALCA) program of the Japan Science and Technology Agency (JST).

PM06.05.08
High-Temperature Oxidation Behavior of a Ti5Si3-Containing Multiphase MoSiBTiC Alloy
Xi Nan, Mi Zhao and Kyosuke Yoshimi; Tohoku University, Sendai, Japan.

The 1st-generation MoSiBTiC alloy (65Mo-5Si-10B-10TiC, mol.%) has great potential in high temperature structure application because of its comparable density with Ni-based superalloys (~8.8 g/cm³) and excellent high-temperature strength. However, its poor oxidation resistance, especially at intermediate temperatures (700-900°C) prevents them from practical uses. A recent work by Zhao et al. showed that the introduction of Ti5Si3 into MoSiBTiC alloy was able to improve the oxidation resistance, but without detailed oxidation mechanisms provided. In this study, the oxidation behavior of a Ti5Si3-containing MoSiBTiC alloy is systematically investigated at various temperatures, aiming to clarify the effect of Ti5Si3. The alloy was prepared by arc-melting and then annealed at 1700°C for 24 hours. Oxidation tests were carried out in a thermon-gravimetric analyzer (TGA) for different time periods. Microstructures before and after oxidation tests were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The heat-treated 38Mo-20Ti-17Si-5B-10TiC alloy was composed of MoSS, Mo3Si, Mo5SiB2, Ti5Si3 and TiC phases. During oxidation test at 700°C, the alloy exhibited an initial transient stage of weight gain followed by an initial stage of weight loss. An initial transient stage, a steady state and an acceleration stage leading to catastrophic failure were observed at 800°C. The oxidation kinetic curves obtained at 900-1200°C showed continuous weight loss, including an initial transient stage and a steady state.

PM06.05.09
Topological Approach to Quantification of Microstructure in Mo-Si-B-TiC Alloys and Their Fracture Toughness
Sojirou Uemura1, Takateru Yamamura2, Kyosuke Yoshimi3 and Sadahiro Tsurekawa4; 1Department of Materials Science and Engineering, Kumamoto University, Kumamoto, Japan; 2Technical Division, Kumamoto University, Kumamoto, Japan; 3Department of Materials Science, Tohoku University, Sendai, Japan; 4Division of Materials Science and Chemistry, Kumamoto University, Kumamoto, Japan.

Mo-Si-B-TiC alloys are expected as a candidate for ultrahigh-temperature materials to replace Ni-base superalloys, because they have a low density, a superior high-temperature strength and a high fracture toughness. The alloys have complicated microstructures consisting of molybdenum solid solution (Mo3Si, Mo5SiB2, Ti5Si3, (Ti, Mo)C, and (Mo, Ti)2C phases and their eutectic phases. However, it has been still unclear how the microstructure affects mechanical properties of these alloys. It was reported so far that the topology like fractal analysis and percolation analysis were useful to correlate the microstructure with mechanical properties such as intergranular fracture. Accordingly, we applied the topological approach to evaluate microstructure in Mo-Si-B-TiC alloys and examined the correlation between topological parameters and the fracture toughness. For four distinct Mo-Si-B-TiC alloy ingots with the same composition (65Mo-5Si-10B-10TiC (at%)) were produced via conventional arc-melting (20g and 90g), drop-casting and plasma arc-melting techniques in an Ar atmosphere, followed by heat-treatment at 2073 K for 24 hours. Microstructure in those samples was observed by SEM, and then percolation and fractal analyses were performed on the binarized SEM-BSE images. The EPMA was used to evaluate the chemical composition of constituent phases. The fracture toughness, KIC, was evaluated using a three-point bending test based on the Irwin’s similarity relationship [1]. Three-points bending tests were conducted at a displacement rate of 5 µm/s. The specimens with the Chevron-notch had final dimensions of 2.5 mm (w) ×2.5 mm (h) ×12.5 mm (l). The Chevrons-notches were machined by electro-discharge machining with a brass wire of 0.1 mm in diameter. The SEM observation and EPMA analysis revealed that the area fraction of constituent phases and their compositions in those Mo-Si-B-TiC alloys were almost the same, but microstructures were different. The percolation probability of hard phases: Mo5SiB2, (Ti, Mo)Cx and (Mo, Ti)2C, was found to be more than 85%, whereas that of Mo5SiB2 was less than 20%. Accordingly, the microstructural feature of those alloys that the Mo5SiB2 clusters were distributed around the continuous hard phases, and then the fractal dimension of dispersion [2] of Mo5SiB2 phase was determined. The fracture-toughness of those alloys were measured to be in the range of 14.6~15.6 MPa (m) 1/2. There appeared no clear relation between the fractal dimension of dispersion [2] for Mo5SiB2 clusters and the fracture-toughness of those alloys. However, of particular importance is finding that the fracture-toughness monotonously increased with increasing a new parameter that was multiplied the fractal dimension of dispersion by the average perimeter of Moss clusters.

PM06.05.10
Oxidation Resistance and High-Temperature Strength of Cr-Added Novel MoSiBTiC Alloy
Tomonaka Hatakeyama and Kyosuke Yoshimi; Tohoku University, Sendai, Japan.

1st generation MoSiBTiC alloy, which mainly consists of Mo5SiB2, TiC and TiSi2-TiC four-phase alloy is expected to be a possible candidate for novel ultra-high temperature material because of its outstanding mechanical properties. However, its insufficient oxidation resistance at elevated temperature has caused barriers in practical application. In this study, we attempted to improve the oxidation resistance by two steps. First, by increasing Si with Ti content, a Mo5SiB2-TiSi2-TiC four-phase alloy was developed. The introduction of TiSi2 phase is aimed to increase a Si resource in the microstructure. Secondly, Cr was added on the four-phase alloy to reinforce its oxidation resistance especially at intermediate temperature around 800°C. The Cr addition maintains the constituent phases of the alloy in a compositional range, and thus a Cr-added four-phase MoSiBTiC alloy was successfully developed at a composition of Mo-10Cr-28Ti-14Si-6C-6B (mol%). As expected, newly developed MoSiBTiC alloy exhibited a much better oxidation resistance at 800°C than 1st generation one. The alloy composition modification led to the formation of protective Cr oxide below an outermost Ti oxide layer. In addition, this alloy has a much smaller density of about 7.1 g/cm³, resulting in about 20% improvement in the high-temperature specific strength at 1400°C compared with that of 1st generation alloy.
Effect of Ni, Ta Alloying on Yield Stress Anomaly in Co3(Al,W) Strengthening Phase with L12 Structure

Zhenzhao M. Chen1, Norihiko L. Okamoto2 and Haruyuki Imul1; Kyoto University, Kyoto, Japan; 1Tohoku University, Sendai, Japan.

Recently, a new ternary L12 (γ) phase Co3(Al,W), which can coexist with a fcc solid-solution phase (γ) based on Co, has been discovered. We have investigated the compression deformation behavior in polycrystals of the L12-Co3(Al,W) and found that Co3(Al,W) exhibits a positive yield stress-temperature dependence (yield stress anomaly: YSA) as in the case of Ni3Al and many other L12 compounds. However, our previous study of micropillar single crystals of L12-Co3(Al,W) has demonstrated that, the high-temperature strength of Co3(Al,W) is considerably lower than that of NiAl-based L12 compounds, due to a narrow temperature range of YSA in Co3(Al,W) (900-1100 K). Another study indicates that complex stacking fault (CSF) energy as well as γ' solvus temperature might be the key of improving the high-temperature strength of Co3(Al,W).

In the present study, we investigate the effect of Ni, Ta alloying on the anomalous temperature range in Co3(Al,W). Compression tests were conducted from 298 to 1423 K in vacuum. The onset as well as peak temperatures of YSA were thus determined from yield stress-temperature curves. Dislocations in specimen deformed at high temperatures were investigated with TEM. While, γ' solvus temperature was determined by differential scanning calorimeter (DSC). Slip trace formed at high temperatures was investigated by electron back-scatter diffraction. The result indicates that, with Ni, Ta alloying, reported to be effective to increase the CSF energy, the onset temperature of YSA shifts to the low temperature side. TEM observation reveals that dislocations introduced above onset temperature exhibit strong tendency to along in its screw orientation while that below onset temperature are curved and no special orientation preferred, indicating that YSA in alloyed Co3(Al,W) is also corresponding to the stress orientation lock. Thus, it is evident that alloying increasing CSF energy is effective in widening the YSA region by shifting onset temperature to the low temperature side. On the other hand, alloyed Co3(Al,W), possessing higher γ' solvus temperature, exhibits also higher peak temperature, compared to ternary Co3(Al,W). However, the correspondence between peak temperature and γ' solvus temperature is not strong among the alloyed Co3(Al,W), indicating that other effects, such as diffusion, may also influence on the mechanical properties at high temperature. Nevertheless, the slip trace analyses indicates that (111) slip plane makes the peak temperature range slightly above the temperature range and no slip plane transition occurs in the vicinities of peak temperature, unlike NiAl, in which the peak temperature corresponds to the (111)=[001] transition.

We confirmed that CSF energy is a dominant parameter of determining the onset temperature of YSA in both ternary and alloyed Co3(Al,W). On the other hand, γ' solvus temperature is a very important parameter, although may not be the only one, on peak temperature.

Effect of Multi-Elements Substitution on the Mechanical Properties of Intermetallic Compound

Suvi Yaramaka1, Ken-ichi Ikeda2 and Seiji Miura2; Department of Materials Science and Engineering, Hokkaido University, Sapporo, Japan, 2‘Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

It is well known that various elements substitute for a certain sub-lattice of intermetallic compounds. There are various experimental investigations on the effect of substitution elements on the mechanical properties, however, there are few reports on the effect of multi-elements substitution. In the present study, L12 type compound Ni3Al is selected as a model compound because of its substitution behavior is established. It was reported that various elements such as Co, Cu, Pt and Pr substitute for Ni-site, while Pt, Cu, Ga, Ge, Ti, V, Nb, Ta, Mo, W substitute for Al-site. These elements are expected to introduce local lattice distortion which may have effects on the motion of dislocations not only at room temperature but also at lower temperature region or higher temperature region. Several alloys composed of 5 or more elements including Ni, Co, Al, Mo, W are prepared using arc-melting machine and heat-treated at 900 ℃ for 168 h. Microstructures are investigated using FE-SEM (JEOL, JXA-8530F). Constituent phases are identified using XRD (PHILIPS, X’Pert Pro) and FE-EPMA (JEOL, JXA-8530F). Mechanical properties of phases are investigated using nano-indentor (Hysitron, Ti-950 Triboindenter) with a load of 10000 micro-N. Several alloys are found to include (Ni, Co)(Al, Mo, W, …) - L12 compound as one of the constituent phases. The hardness of these L12 phase investigated using nano-indentor are almost the same or higher than that of high strength Co3(Al,W) - L12 compound, and it is confirmed that multi-elements substitution is an effective way to improve mechanical properties of Intermetallic compound.

Effect of Ta Addition on Microstructure and Mechanical Properties of Dual Two-Phase NiAl-Ni3V Intermetallic Alloy

Kazushige Iorioi, Yasuyuki Kaneno and Takayuki Takasugi; Osaka Prefecture University, Sakai, Japan.

A dual two-phase intermetallic alloy exhibits microstructure composed of primary NiAl (L12) phase surrounded by a eutectoid microstructure comprised of Ni3Al and Ni3V (D022) phases which is formed by a eutectoid reaction from Al (fcc) phase. The intermetallic alloy with the dual two-phase microstructure shows attractive mechanical properties as high-temperature structural materials [1]. However, further increasing in mechanical properties is required to be used as advanced high-temperature structural materials. It has been reported that Ti and Nb not only stabilize the two constituent phases [2] but also play a role in effective solid solution strengtheners [3]. In this study, the effect of Ta addition which is other potential solid solution strengtheners in the dual two-phase intermetallic alloy is investigated. Ta was added to a base alloy with a composition 75Ni10Al15V (in at.%)+50 wt.% Ta by three substitution methods for Ni, Al and V. Alloy button ingots prepared by arc-melting were solution-treated at 1553 K for 5 h in a vacuum, followed by furnace cooling at a rate of 10 K/min. Microstructure observation was carried out by scanning electron microscopy (SEM) and electron probe micro analyzer (EPMA). Lattice parameters of the constituent phases were calculated from X-ray diffraction (XRD). Mechanical properties were evaluated by Vickers hardness test at room temperature.

The dual two-phase microstructure was especially fine in the 2Ta(Al) alloy among three substitution methods where the alphabet between the parentheses indicates the constituent element substituted by Ta. The hardness was observed to be ranked in order, the Base < 2Ta(V) < 2Ta(Ni) < 2Ta(Al) alloys. The solid solution hardening predicted from the unit cell volume increment rate |dV/dC|, where V is unit cell volume and C is Ta content dissolving in the
constituent phases, is ranked in order, \( \text{TaAl} \) – \( \text{TaV} \) < \( \text{TaNi} \). Based on the observed results of microstructure and hardness, and the calculation on lattice expansion in the constituent phases, it is suggested that the additional hardening operating on the \( \text{TaV} \) and \( \text{TaNi} \) alloys is dominated by the solid solution hardening while that operating on the \( \text{TaAl} \) alloy is dominated by the hardening due to fine microstructure in addition to the solid solution hardening, consequently resulting in the largest hardness.


\[ S. \text{ Kobayashi, K. Sato, E. Hayashi, T. Osaka, T.J. Konno, Y. Kaneno, T. Takasugi, Internmetallics, 23 (2012) 68-75.} \]


**PM06.05.15**

A New Ni-Based Superalloy for Parts of Advanced Engineering Plastics Injection Molding Machines

Takahiro Nakano, Hiroshi Nakamoto and Nobuyuki Funahira, Nachi-Fujikoshi Corp., Toyama-shi, Japan.

Use of engineering plastics has been steadily increasing in advanced industry hardware; automobiles, trains, aerospace, electronic parts, and electricity production/storage, where always demand materials with lighter, stronger, and more heat resistant properties, which has been persistent to attain their better performances, as called “high performance plastics”. A recent example is a group of fluorocarbon polymers (PFA) gradually replacing currently popular engineering thermoplastics or metals. PFA, however, stays elastic at low temperatures and shows its plasticity only above a transition temperature (~400 °C).

Engineering plastics have been made into many product shapes of complex geometries through injection molding machines with critical parts made of many conventional tool (high strength, high carbon) steels. However, for advanced engineering plastics, like PFA, we need wrought metals with more heat resistant strength. Another inevitable property required for those parts is resistance against hot corrosion, as those parts' surfaces are continuously exposed to high temperature corrosive gas during the PFA plasticization process. In this study we developed a new Ni-based wrought superalloy, (hereinafter called “F-alloy”) to be used for critical parts of advanced engineering plastics injection molding machines.

F-alloy has a characteristic as follows: the composition of this alloy was determined according to the L18 table of the design of experiment (DOE), which commonly practiced by a quality engineering method and enabled us not only reduce a number of experiments for new alloy developments but grasp quantitatively influence of each elements to the target properties; hardness and corrosion-resistance to PFA.

Experiment procedure is as follows; 18 melts of ingots, 10kg each, with 18 different composition were made by a laboratory induction melting furnace. The major alloy elements and composition were selected according to the L18 table of "DOE". The mechanical and metallurgical test samples were machined out from bars and plates made through press forging the 18 ingots, followed by heat treatments (solution and aging) at the temperatures predetermined by thermal and metallurgical analyses.

Hardness of F-alloy was measured at room temperature up to at 900 °C and the results were compared to the data of a conventional corrosion-resistant alloy (UNS N10276), a tool steel (UNS T30402), which has been commonly used for the parts of present injection molding machines. Hot corrosion tests were performed for F-alloy and two reference materials, the said corrosion-resistant alloy, and the said tool steel, being exposed composed with PFA at 400 °C.

The results of those experiments show that this alloy has both hardness (HV600 at 400 °C) and good hot corrosion-resistance to PFA at 400 °C, which is an outstanding characteristic compared to conventional materials for the parts of PFA injection molding machines.

**PM06.05.16**

Crystallographic Anisotropy of FeCr Sigma Phase (τP30) Caused from Site Occupation Behaviors in Fe-Cr-M Ternary Systems

Sota Maruyama, Satoru Kobayashi and Masao Takeyama; Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan.

To clarify the nature of FeCr-\( \sigma \) phase (τP30), the structural features of \( \sigma \) phase in Fe-Cr-binary and Fe-Cr-M ternary systems were investigated in this study. All of the alloys have a composition of \((Fe_{50})(Cr_{50-X}, MX), (Fe_{50-X}, MX)(Cr_{50})\) or \((Fe_{50-X}, MX)(Cr_{50-X}, MX)\), and were produced in arc melting furnace. The as-cast alloys were cold rolled by the height reduction of 50 % and equilibrated at 973 K and 1073 K for up to 1000 h to obtain \( \sigma \) single phase structure, with and without prior homogenization treatment at from 1273 K to 1523 K. Phase compositions analysis and identifications in annealed alloys were conducted by EPMA and powder XRD technique respectively. Obtained XRD profiles were further analyzed by means of Rietveld method. During the analysis, crystallographic parameters of lattice constants and site occupancies in non-equivalent five sub-lattice sites \((M1, M2, M3, M4 \text{ and } M5)\) were refined. It was found that lattice expansion and shrinkage of \( \sigma \) phase with changing composition were reasonably explained only by considering relative size difference between constituting and solute elements. i.e. larger elements like Mo expand lattice uniformly and smaller elements like Co or Ni do in opposite manner. On the other hand, when the specific type of the elements such as Fe or Si coming into the \( \sigma \) phase, lattice parameter ration \( c/a \) shows increase with increasing \( c \) axis and decreasing \( a \) axis. The nonuniformity cannot be explained only by consideration of atomic size, and other factors such as magnetic or interatomic interaction could be involved. Combined with \( X \)-ray profile analysis, it implied that the origin of crystallographic anisotropy is a characteristic site occupation behavior of the specific elements. The relations between preferential site occupation and its crystallographic features will be discussed in detail.

**PM06.05.17**

Refinement of Crystal Structure of Highly Ordered \( \eta^* \)-derivative Phase

Ryutaro Sakai1, Masaya Higashi2, Kodai Nishii1,2 and Haruyuki Inui1,2; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Strategic Materials (ESISM), Kyoto University, Kyoto, Japan.

Hot dip aluminized steels are practically used as automotive exhaust system parts because of their good heat resistance, corrosion resistance and designability. The coating layers have been believed to mainly consist of a thick \( \eta^* \)-FeAl phase and a thin \( \eta \)-FeAl13 phase. The orthorhombic \( \eta^* \)-FeAl13 (space group \( Cnmm \)) comprises chains of atoms with partial occupancies along the \( c \)-axis. Recent studies report that these sites are ordered in a different manner in relation to compositions, and that there are variations of ordered phases such as the \( \eta \) and \( \eta^* \) phases, which possess the framework structure of the \( \eta \) phase. Furthermore, another derivative of the \( \eta \) phase (the \( \eta^* \) phase) is suggested to exist by means of powder X-ray diffraction (XRD) analysis. However, the reported structure does not seem to be consistent in terms of the hierarchical ordering of the \( \eta \) phase. In this study, crystal structure of the \( \eta^* \) phase is assessed by means of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and XRD analysis. Ingot with Al-rich composition Fe-73.7 at.%Al was prepared by arc-melting method. After solution treatment at 1073 K for 8 hours, the ingot was encapsulated in vacuum-sealed quartz ampoules and heat-treated at 523 K for 60 days followed by water quenching. Thin foils for TEM and STEM observations were prepared by electro-polishing.

In the selected-area electron diffraction (SAED) patterns obtained from various incidence azimuth, there are superlattice diffraction spots in addition to fundamental ones of the \( \eta \) structure. For example, the superlattice diffraction spots are located at the positions that divide the distance between the 000 and 1-1-11 fundamental spots by two. From STEM observations, it is clarified that the \( \eta^* \) phase accompanies orderings of the atom sites with partial occupancies as those of the \( \eta \) and \( \eta^* \) phases. Furthermore, the \( \eta^* \) phase contains periodic anti-phase boundaries (APBs) normal to the \( c \) axis. According to the analysis of XRD pattern, APBs are presumably introduced to compensate for the \( c \)-axis lattice incompatibility among adjacent \( \eta \), \( \eta^* \) and/or \( \eta \) phases.
PM06.05.18
Plastic Deformation Behavior of Single-Crystalline Micropillars of the Fe-Cr Sigma Phase Masaoiti Kudaka1, Nobuyuki Kadota1, Kyoink Ishida1-2 and Haruyuki Inui1-2; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

The so-called sigma phase has long been considered to cause detrimental influences on the mechanical properties of stainless and heat-resistant steels mainly because of its high hardness and brittleness at room temperature that stem from its complex crystal structure (D8, structure, fP30, space group: P4/mnm, c/a ~ 0.52). Recently, it has been reported that the creep strength, ductility, yield strength and tensile strength of stainless steels can be improved if the distribution and morphology of the sigma phase are properly controlled. These results have caused a growing demand for fundamental understanding of plastic deformation behavior of the sigma phase itself. However, the deformation behavior of the sigma phase is largely unknown because of its brittleness at room temperature. Recently, micropillar compression tests of single crystals have been proved to be useful for studying fundamental deformation behavior of hard and brittle materials such as high temperature intermetallics, semiconductors and ceramics. In the present study, we have prepared single crystalline micropillars of the Fe-Cr sigma phase and compression-tested at room temperature as a function of loading axis orientation and specimen size. Plastic flow was observed at room temperature for all tested micropillars mostly exhibiting a smooth transition from elastic to plastic deformation similar to those observed for ductile materials. Four different slip systems were identified to be operative depending on the loading axis orientations. The values of critical resolved shear stress (CRSS) for the four slip systems identified are extremely high about 1.2 – 2.5 GPa. However, it should be noted that very good ductility more than 5% compressive strain was achieved for most loading axis orientations tested, which clearly indicates that the Fe-Cr sigma phase is not inherently brittle at least under compressive loading.

PM06.05.19
Structural Control of Porous Nickel Aluminides Fabricated by Reactive Synthesis with Space Holder Powder Ayaka Suzuki, Yumiao Shu, Naoki Takada and Makoto Kobashi; Nagaoka University of Technology, Nagaoka, Japan.

Porous metals have unique properties like ultra-low density, energy absorption, thermal insulation, sound absorption, fluid permeability, and so on. For example, the thermal conductivity of the porous metals with 80% porosity is about one tenth of the bulk metals. Transition metal aluminides, which have all of these properties, are expected as a high-strength energy absorber and a heat-resistant thermal insulator, and so on. Our group has developed a powder metallurgical process to synthesize porous titanium aluminides such as TiAl, Ti3Al, and Ti5Al by combining reactive synthesis and a spacer method, and revealed the high strength of porous TiAl. In the present study, we attempted to synthesize porous nickel aluminides like NiAl and Ni3Al through the reactive process and control their porous structure. Al powder with 2 μm in size and 99.99% in purity, Ni powder with 1 μm in size and 99% in purity, and sodium chloride (NaCl) particles with 30-50 μm in size and 99.99% in purity were used as starting powders. These powders were blended with various molar ratio of Al/Ni (3, 1, and 1/3). The volume fraction of NaCl was varied within the range of 0-80%. The blended powder was cold compacted at 25 MPa to obtain cylindrical precursors with 10 mm in diameter and height. An electric current sintering was performed under applying a pressure of 5 MPa. Temperature was raised in a rate of 0.5 K/s and held at 923 K for 10.8 ks. The sintered samples were soaked in water for 86.4 ks to leach out NaCl completely. For comparison, porous Al specimens were also fabricated by powder sintering and spacer method. X-ray diffraction measurements were performed operating at 40 kV and 20 mA with a Cu-Kα radiation in order to confirm the constituent phase. The porous structures of fabricated samples were observed with a scanning electron microscopy. Synthesized porous nickel aluminides had bi-modal pore size distribution. Large pore replicated the shape of NaCl particles. Small pore (0.5~4.0 μm in diameter) derived from reactive synthesis are formed where Al particles existed before the reaction. As the size of Al particles was larger, the size of small pores increased. Porosity of small pores increased with increasing the Al/Ni molar ratio. The porous structure can be controlled by the size and the composition of the starting powders.

PM06.05.20
Micropillar Compression Deformation of Single-Crystals of Cementite Fe3C Nobuyuki Kadota1, Kyoink Ishida1-2 and Wei Chen1-2; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan; 3School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, China.

Pearlitic steels with a lamellar structure composed of alternating ferrite and cementite (Fe3C) layers are widely used as high-strength steel wires and rails because of their high strength. The strength of pearlitic steel wires has been known to be improved further by drawing, which makes their lamellar structure much finer. These attractive mechanical properties related to their microstructure evolution during drawing have been considered to be strongly influenced by the mechanical properties of cementite. Cementite has the orthorhombic D012 structure (oP16, space group: Pnma, a = 5.08, b = 6.73, c = 4.52A), which is composed of corner- and edge-sharing carbon-centered trigonal prisms. Cementite has been considered to be brittle mainly because of its complex crystal structure with low symmetry. However, inherent deformation mechanisms of the cementite Fe3C are still largely unknown, except for some implications of plastic deformation observed as slip band propagation across very thin Fe3C lamella in pearlite grains and the thickness reduction of Fe3C lamella during the drawing process of pearlitic steel wires. This is mostly because of the lack of systematical studies using single crystals. Recently, micropillar compression tests have been proved to be useful in studying deformation behavior of various crystalline materials including those with serious difficulty in preparing bulk single crystals. In this study, single crystalline micropillars of cementite were fabricated by focused ion beam technique, and tested in compression at room temperature as a function of loading axis orientation and specimen size. Plastic deformation was observed at room temperature for all tested specimens. Five different slip systems were identified experimentally for the first time. The values of critical resolved shear stress for the five slip systems were confirmed to be very high about 1.0 ~ 2.0 GPa. Characteristics of identified slip systems such as actual glide plane and dislocation dissociation scheme were investigated by both experimentally through TEM analysis and theoretically by first-principles DFT calculations of generalized stacking fault energy.

PM06.05.21
Intermetallic Formation at Deeply Supercooled Ni/Al Multilayer Interfaces—A Molecular Dynamics Study Peng Yi, Michael L. Falk and Timothy P. Weihs; Johns Hopkins University, Baltimore, Maryland, United States.

Reactions at interfaces between different solid phases are critical processing steps for a variety of applications including microelectronics, superconducting magnet wires, coatings on turbine blades, and reactive materials. Due to the highly non-equilibrium nature of interfaces between metastable solid phases, phase formation at these interfaces is complicated and difficult to predict. It is well established experimentally that the first phase to form through an interfacial reaction need not be the most stable phase predicted by the phase diagram. As an example, DSC and TEM experiments in the Ni/Al multilayer system have suggested that the formation of intermetallic phases can be suppressed by a high heating rate, or by reducing the interspacing between the layers.1, 2 Two possible mechanisms were proposed to explain phase selection for interfacial reactions: a growth-controlled mechanism[3], and a nucleation-controlled mechanism[4].
Here we use molecular dynamics simulations to study the formation of the non-stoichiometric intermetallic compound, NiAl(B2), in the Ni-Al multilayer system, focusing on how composition gradients at the Ni/Al interfaces impact the intermetallic formation [5]. Simulations were designed to test the intermetallic formation under isothermal conditions within a constant composition gradient (10^{-7}-10^{-9} m⁻³) that mimics those found in nature, where Al and Ni layers inter-diffuse. Simulation temperatures of 800K and 650K were chosen so as to be above and below the compositionally-dependent melting point of Al-Ni solid solution. We observed melting or amorphization at the interface region due to intermixing at 800K or 650K, respectively. The intermetallic phase then forms at the interface from the melted or amorphous region through heterogeneous nucleation, followed by growth in both lateral and normal directions. Kinetics of the transformation follows the Johnson-Mehl-Avrami model and an Avrami exponent of 0.5 was extracted from the data obtained at 800K, and 0.1 for 650K. The NiAl formation is growth-controlled and the growth rate is found to increase with decreasing composition gradient. Our findings support a growth-competition mechanism of phase selection for interfacial reactions, which might be favored at high undercooling.


PM06.05.22

Atomistic Kinetic Monte Carlo Modeling of the Formation of G.P. Zone in Al-Cu Alloy

Hirosi Miyoshi1, Akio Ishii2, Hajime Kinizuka2 and Shigenobu Ogata3, 4; 1Graduate School of Engineering Science, Osaka University, Osaka, Japan; 2Kyoto University, Kyoto, Japan; 3Osaka University, Osaka, Japan.

Al alloys are widely used as key structural materials especially in aerospace and automobile industries owing to their high weight, high strength, and good workability. In Al alloys, nanosized clusters of solute atoms called Guinier-Preston (G.P.) zones play a significant role in the precipitation hardening effect, in which the Cu nanoclusters impede the movement of dislocations in the Al matrix while maintaining balanced strength and ductility. Thus, it is important to control the size, orientation, and shape of the nanoclusters for the adequate design of Al alloys. The observations with high-resolution transmission electron microscopy revealed that the structures of G.P. zones consist of disk-shaped, monoatomic layered precipitates of Cu atoms along the [100] planes. However, the detailed mechanism of the formation of the zones has not been clarified yet. Understanding of the atomistic mechanism may serve as relevant information for the design and exploitation of advanced Al alloys with excellent mechanical performance. In this study, to elucidate the atomistic behavior of solute atoms and vacancies in the process of the formation of G.P. zones, a framework of atomistic kinetic Monte Carlo modeling for Al-Cu alloys was developed based on density functional theory (DFT). An on-lattice potential model for a dilute Al-Cu-vacancy system was constructed using the DFT-calculated binding energies for the pairs and triplets of Cu atoms and a vacancy in the Al matrix, and then applied to atomistic kinetic Monte Carlo calculations. The DFT results revealed that the Cu-Cu pairs in the first-nearest neighbor (1NN) position and the Cu triplets with a 1NN bond angle of approximately 90 degree exhibit significant attractive interactions whereas a vacancy does not prefer to occupy sites neighboring to these Cu pairs and triplets. This suggested that a vacancy can diffuse rather randomly without strong bindings to Cu atoms and that Cu atoms gradually form clusters via a vacancy-assisted diffusion mechanism with a lowering of the energy of the system. Indeed, the results of atomistic kinetic Monte Carlo calculations supported this view and reproduced the planar segregation of Cu atoms along the [100] planes in a manner consistent with experimental measurements. Also, the effects of temperature and vacancy concentration on the formation of G.P. zone were investigated. The nucleation behavior of G.P. zone obtained from the kinetic Monte Carlo analysis was compared with the counterpart based on classical nucleation theory. The critical nucleus size for the formation of G.P. zone was estimated from the formation free energy of Cu clusters with considering a competition between the enthalpic and entropic contributions to the free energy at finite temperatures.
low microstructural stability of the Al alloys significantly reduces their strength at elevated temperatures. On the other hand, the commercial refractory metals and alloys (e.g. Ni-based superalloys) contain stable intermetallic phases with a high volume ratio of 50% or more as a strengthening phase, resulting in maintaining high strength even at high temperature. In this study, we designed two Al-based cast alloys strengthened by thermodynamically stable intermetallic phases with a high volume fraction.

We focused on eutectic reactions in order to have high volume fractions of intermetallic phases. We selected two commonly used metals, Zn and Mg, as alloying elements, and attempted to fabricate two types of α-Al (fct) matrix reinforced by η-ZnMg (hexagonal) and T-AlMgZn (cubic) intermetallic phases. Thermodynamic assessments revealed two alloy compositions of Al-36Zn-18Mg and Al-23.5Zn-22.5Mg (at%) with the α-Al (fct) phase reinforced with high fractions (>50%) of the η and T phases. The morphology of the α-Al phase in the eutectic colonies varied upon changing the neighboring intermetallic phase. The lamellar structure consisting of α-Al and η phases appeared in a large part of the cast Al-36Zn-18Mg alloy. In the cast Al-23.5Zn-22.5Mg (at%) alloy, rod-shaped α-Al phase was observed within T-phase matrix in the eutectic microstructure. These eutectic microstructures exhibit high stability at an elevated temperature of 300 °C. It was found that the solidification segregation of Zn component was observed around the eutectic cell boundaries in the Al-36Zn-18Mg alloy. The microstructural observation of the alloy exposed at 300 °C confirmed that the Zn-enriched regions would enhance the local microstructural change at elevated temperatures. This result demonstrates that the Al-23.5Zn-22.5Mg (at%) alloy is superior to the Al-36Zn-18Mg alloy in terms of microstructural stability at elevated temperatures. The fabricated alloys exhibited high hardness values exceeding 220 HV, which were much superior to those of conventional Al alloys. These alloys exhibited high hardness values exceeding 200 HV even after the exposure at 300 °C for 1000 h. In this presentation, crystallographic features of these eutectic microstructures will be presented in conjunction with transmission electron microscopy.

**PM06.05.25**

**Effect of Intermetallic Compound YAl2 Particles on the Corrosion Behavior of Mg-Li Matrix Composite**

Zihan Chen and Chonggao Bao; Xi'an Jiaotong University, Xi'an, China.

Mg-Li based alloys are currently the lightest among the metallic structural materials, and they have many excellent properties such as high values specific strength, mechanical casting properties, good damping capacity, good thermal conductivity and electromagnetic shielding performance. The strength of Mg-Li alloy is greatly improved by the composite strengthening of intermetallic compound YAl2 particles, but the low corrosion resistance of Mg-Li alloy is still the main factor that restricts the application of the alloy and its composites. The effect of intermetallic compounds YAl2 particles on corrosion behavior of Mg-Li matrix composite (YAl2/LA143) in 3.5 wt.% NaCl solution was systematically investigated. Microstructure was examined by Electron microscope, X-ray diffraction, and 3D laser scanning microscope. Corrosion performance was evaluated by immersion tests, electrochemical measurements, and direct visual observation. The results showed that the corrosion resistance of YAl2/LA143 composite improved significantly as the formation of a transitional interface layer by adding YAl2 particles. The diffusion of yttrium and aluminum atoms from YAl2 particles improved the stability of the surface film and enhanced the adhesion between the corrosion products and the substrate, which hindered the further expansion of pitting.

**PM06.05.26**

**Thermodynamics and Kinetics of Bimetalllic Nanoparticles from First Principles Calculations**

Shubham Pandey1, Robert Kochl1, Guangfang Li1, Hui Wang1, Scott Mixture2 and Simon R. Phillpot1, 1Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States; 2Inamori School of Engineering, Alfred University, Alfred, New York, United States.

We use Density Functional Theory (DFT) to characterize the energetics of Cu-Au and Ni-Au ordered alloys and the effects of epitaxial strain on their relative stabilities. We find that epitaxy on a Au substrate tends to destabilize Cu-rich alloy structures, while having little effect on Au-rich alloys. Work of adhesion is used to characterize the interfacial stability and we find higher works of adhesion for alloys grown epitaxially on Au, than on Cu or Ni. Diffusion in bulk intermetallics, random alloys and at epitaxial interfaces is analysed. Diffusion across the Cu-Au [111] interface is modeled for Au substrate where we find that, there is a barrier for Cu diffusion while Au diffusion is barrierless. Random alloys give identical migration barriers for both Cu and Au, and follow a Gaussian distribution. The computational results are correlated with experimental analysis of phase stability and kinetics in the corresponding nanoparticles.

This work was supported by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC) funded by the United States Department of Energy Office of Basic Energy Sciences through Award DESC0016574.

**PM06.05.27**

**Phase-Field Modeling of Evolution of Compact Ordered Precipitates in Ternary Alloy Systems**

Sandeep Sugathan and Saswata Bhattacharya; Department of Materials Science and Metallurgical Engineering, Indian Institute of Technology, Hyderabad, Hyderabad, India.

Several technologically important alloys exhibit compact precipitates in their microstructure. For example, tertiary Al-Sc-Li alloys form coherent L12 precipitates of Al-Li and Al(Sc,Li) during a two-step ageing process [Radmilovic et al., Nature Materials 10, 710 (2011)]. Al-Li phase envelopes the Al(Sc,Li) phase giving rise to a compact core-shell morphology with strong monodispersity. Modified Inconel 718 also exhibits a compact morphology where three orientational variants of γ envelop cuboidal γ′ precipitates [Cozar, R. and Pineau, A., Metall. Trans. 4, 47 (1973)]. Factors affecting the formation of such precipitates include alloy chemistry, relative interfacial energies between the coexisting phases, elastic misfit and solute diffusivities. We present a phase-field model in two dimensions to study the effects of alloy chemistry, interfacial energy and elastic stress (arising due to coherency) on the morphological evolution of compact precipitates. The model employs a modified regular solution description of the bulk free energy of the disordered matrix phase and ordered precipitates with coefficients obtained from the thermodynamic data for the relevant systems. Elastic strain energy of the three-phase system is described using Khachaturyan’s micromechanics theory. The temporal evolution of the spatially dependent field variables is determined by numerically solving coupled Cahn-Hilliard and Allen-Cahn equations for composition and order parameter fields, respectively. We use a semi-implicit Fourier spectral scheme to integrate the governing equations. We systematically vary the gradient energy coefficients and misfit strains to study their effect on the development of compact precipitates. Further, we vary the mobilities of diffusing species in order to understand their effect on the stability of compact morphology. The sign and degree of misfit as well as the relative interfacial energies between the phases affect solute partitioning, thereby influencing the formation of compact morphology. Our simulations show the development of stable core-shell morphology when the misfit between the ordered precipitate phases is lower than those with the matrix phase although the interfacial energies between the coexisting phases do not satisfy the criteria proposed by Cahn J. W. and Cahn, J. Chem. Phys. 65, 6245 (1976). Thus, the elastic interactions between the phases is a crucial factor affecting the stability of “monodisperse” core-shell microstructures. We further conclude from our simulations that low mobility of solute atoms forming the core lead to sluggish coarsening of compact core-shell structures.

**PM06.05.28**

**Superelasticity in Micro/Nano Pillars of Cu-Al-Be Shape Memory Alloys**

Valeria Fuster1, Jose F. Gómez-Cortés1, Maria L. No2 and Jose San Juan3; 1Fisica Materia Condensada, Universidad del País Vasco, Bilbao, Spain; 2Fisica Aplicada II, Universidad del País Vasco, Bilbao, Spain; 3Instituto de...
Shape memory alloys are functional intermetallics which undergo a reversible martensitic transformation responsible for the shape memory and superelastic effects. In addition, shape memory alloys offer the highest work output density, in comparison with other smart materials, and consequently are firm candidates to be incorporated as sensors and actuators into MEMS and NEMS because of their ability to undergo the thermal or stress-induced martensitic transformation (superelastic) with a high-displacement actuation. A good shape memory behaviour and superelasticity were recently reported in Cu-Al-Ni SMA [1, 2, 3]. However, among the different explored alloy families, up to now Cu-Al-Ni is the only SMA system exhibiting good properties at nano-scale.

The aim of the present work is to explore a novel Cu-Al-Ni SMA system and to this purpose [001] oriented D03 single-crystals grown from a Cu-12.0Al-0.47Be (wt.%) shape memory alloy were synthesized in our laboratory. This alloy has the martensitic transformation temperatures below room temperature, showing excellent superelastic properties at macroscopic scale. Then, in the present study we carried out a quantitative characterization and analysis of the superelastic behaviour at the micro and nano scale. A series of pillars covering a broad-range of size diameters, between 265 nm and 1.800 μm, were milled by Focused Ion Beam (FIB) from single crystal slides. These pillars were studied by hundreds of nano-compression cycles at room temperature using instrumented nanoindentation. Our results show that this alloy also exhibits an excellent superelastic behaviour at small scale, as well as a size effect on the critical stress to induce the transformation. In addition, the analysis of such size effect shows that the critical stress follows a power-law type as a function of the pillar diameter, in agreement with recent reports in the Cu-Al-Ni system [3]. These results seem to confirm the universality of the power law found in Cu-based SMA, and open the door for future small-scale applications.


PM06.05.29
Isomteric Martensitic Transformation Behavior of NiCoMnIn Metamagnetic Shape Memory Alloy Yosuke Yano1, Kodai Nishi2, Ryosuke Kainuma1 and Haruyuki Inui1; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyotou University, Kyoto, Japan; 3Department of Metallurgy, Materials Science and Materials Processing, Tohoku University, Sendai, Japan.

Dynamics of thermo-elastic martensitic transformations (MTs) is described by the nucleation and growth processes, and in particular the former is associated with only the forward transformation. In relation to this, isothermal forward MT behavior with a C-shaped curve in TTT (Time-Temperature Transformation) diagram has been discussed in terms of the thermal activation process of nucleation, but not studied for the reverse MT. Considering the dominance of nucleation process is different with respect to the direction of MTs, isothermal dynamics of the reverse MT is expected not to be the same as that of the forward one.

In the present study, we investigated the isothermal and non-isothermal behaviors of magnetic-field-induced martensitic transformation in Ni$_{40}$Co$_{30}$Mn$_{2}$In$_{13.2}$ magnetic shape memory alloy. Non-isothermal MT was performed for various scanning routes of temperature and magnetic field to figure the phase diagram. Isothermal MT was examined by settling magnetic field and temperature at various stages of forwarding/reversing MTs. Isothermal holdings showed logarithmic evolutions of transforming fraction both in the forward/reverse MTs. However, its temperature and time dependences were in contrast with respect to transforming directions; while isothermal forward MT showed iso-fraction C-shaped curves in the TTT diagram as reported elsewhere, isothermal reverse MT showed only lower half of C-shaped curve that terminates at the reverse MT finishing temperature.

This alloy is shown to know an increasing MT hysteresis upon cooling due to the development of thermal activation nature of MT. By decomposing the hysteresis into thermal activation and non-thermal activation components, the origin of different isothermal MT behaviors between forward/reverse MTs was discussed. We propose a new formula that can describe the dynamics of forward/reverse isothermal MTs simultaneously by taking into account the thermal and non-thermal activation processes of nucleation and growth.

PM06.05.30
Influence of NiAl Precipitation on the Martensitic Transformation of Cu-Al-Ni Shape Memory Alloys Nora Egido1, Jose San Juan2, Isabel Ruiz-Larrea1, Mariano Barrado1, Tomasz Breziewski1 and Maria L. No1; 1Facultad de Ciencias, Universidad de Guadalajara, Guadalajara, Mexico; 2Física Aplicada II, Universidad del País Vasco (UPV/EHU), Bilbao, Spain.

Shape memory alloys (SMAs) exhibit a diffusionless martensitic transformation (MT) between the high-temperature phase (austenite) and the low temperature phase (martensite). SMAs have recently attracted renewed interest from the scientific community as a result of their behavior and properties at micro and nano scales [1,2]. At present the technological applications of SMA are based on superelastic, pseudoelastic and shape memory thermomechanical properties and in particular the CuAlNi SMAs with small amounts of Ni show their best properties as single crystals without α and γ1 precipitates. The CuAlNi is a disordered L21 phase that transform during cooling to an ordered β, monoclinic martensite or to an ordered γ',orthorhombic martensite or to both of them.

With the idea that NiAl B2 precipitates could improve the mechanical properties of the CuAlNi SMAs, by hardening the austenite phase, in the present research work the influence on the thermal martensitic transformation of larger amounts of Ni and their precipitation as NiAl, has been studied. The best temperature, thermal treatment and quenching process has been determined in order to avoid the precipitation of the other non desirable stable phases γ', α and α. Oriented [001] single crystals with 26.26Al-5.05Ni-68.69Cu (At.%) were used in the present work. Internal friction (IF) experiments were employed to optimize the thermal treatments and temperatures in order to obtain and control the NiAl precipitation. The microstructure of the as-quenched samples from 1173K, without precipitates, and the thermally treated samples, with precipitates, were determined by different techniques of scanning electron microscopy (SE, BSE, EBSD) focus ion beam (slice mode) and transmission electron microscopy (BF, DF, STEM-HAADF, EDX) with a philips CM-200 and a TitanCubed 80-300KV with the super-X detector ChemiSTEM. The results show us that it is possible to control the density and the size of NiAl precipitates avoiding the α and γ1 stable phases and preserving the martensitic transformation.


PM06.05.31
Mechanical Properties of Au–Cu–Al Biomedical Shape Memory Alloys Containing Ag Ayano Toriyabe1, Kenji Goto1, Akira Umise1, Hiroyasu Kanetaka4 and Hideki Hosoda2; 1Institute of Innovative Research (IIR), Tokyo Institute of Technology, Yokohama, Japan; 2Tanaka Kikinzoku Kogyo K.K.,
AuCuAl alloy is a promising shape memory alloy which is suitable to X-ray radiography and magnetic resonance imaging. In order to enhance biocompatibility and antibacterial activity of AuCuAl alloy, Ag addition to AuCuAl alloy was focused in this study. Because Ag ions released from material bring strong antibacterial effect in human body. However, the effect of Ag addition to AuCuAl of phase constitution, transformation behavior and mechanical properties has not been reported in the literature. Several AuCuAl alloys containing Ag in which Ag is expected to substitute for the Au sites and Cu sites were fabricated by Ar arc-melting method. They were hot-forged at 873K and solution-treated at 773K for 3.6ks followed by ice water quenching. Phase constitution, transformation temperatures, microstructure and chemical compositions were evaluated by θ-2θ X-ray diffractometry (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy, respectively. Mechanical properties were evaluated by micro Vickers hardness tests and tensile tests, compression tests at room temperature.

The phase constitution of 45Au-25Cu-25Al-5Ag and 50Au-25Cu-25Al-5Ag alloys was L21, parent single phase at RT by XRD. However, 45Au-25Cu-25Al-5Ag alloy contained small amount of second phase by SEM. Reverse martensitic transformation finish temperature by DSC was 240K in 45Au-25Cu-25Al-5Ag and 243K in 50Au-25Cu-25Al-5Ag, which were approximately 50K lower that of the stoichiometric AuCuAl. Then, martensitic transformation temperature was decreased by Ag addition but the substitution site seems little influence. Micro Vickers hardness of 50Au-25Cu-25Al-5Ag and 45Au-25Cu-25Al-5Ag alloys was HV272 and HV236, respectively. These values were higher than HV170 of AuCuAl. By tensile tests at RT, both Ag-added alloys exhibited no plastic deformation due to the intergranular fracture, similar to the AuCuAl. The ultimate tensile strength of both alloys was 182 and 177 MPa, which was higher than that of AuCuAl. Then, Ag addition is found to enhance hardness and fracture strength of Au-Cu-Al alloys. This work was supported by Grant-in-Aid for Scientific Research Kiban S 26220907 from Japan Society for the Promotion of Science (JSPS).

Ductility Enhancement of AuCuAl Biomedical Shape Memory Alloys by Introducing FCC α Phase
Akira Umise1,2, Koki Yamaji1, Hayato Gunji1, Kenji Goto1,3, Masaki Tahara1, Takao Hanawa2 and Hideki Hosoda1; 1Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Japan; 2Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda, Japan; 3Tanaka Kikinzoku Kogyo K.K., Isehara, Japan.

Au-based shape memory alloys exhibiting good biocompatibility and excellent X-ray radiography have a large potential to exceed Ti-Ni SMAs in the field of biomedical implant devices. Especially AuCuAl alloys have attracted attention. However, on the present available data, ternary polycrystalline AuCuAl alloys which are often brittle due to intergranular fracture. In this study, we focused on introduction of second phase at grain boundaries that must enhance grain boundary cohesive strength, and mechanical properties were investigated. The second phase selected is α phase that is the fcc terminal solid solution of (AuCu) in the Au-Cu-Al system.

Au-37Cu-15Al (AuCuAl single phase) and Au-37Cu-15Al (AuCuAl+α two phases) alloys (hereafter, in at%) were prepared by Ar-arc melting method using a non-consumable W electrode. Both electrodes were expected to have a similar chemical composition of AuCuAl phase. The ingots were hot-pressed at 873K for 21.6ks and solution-treated at 773K for 3.6ks followed by water quenching. Microstructural observation and chemical analysis were done by scanning electron microscopy equipped with energy dispersive X-ray spectrometry (SEM-EDX). Phase constituent and phase transformation were characterized by θ-2θ X-ray diffractometry and differential scanning calorimetry, respectively. A cyclic loading-unloading tensile test with a constant strain increment of 1% was performed at RT.

SEM and XRD analysis revealed that Au-37Cu-15Al alloy contains α phase. The chemical composition of the matrix AuCuAl and fcc phase in Au-37Cu-15Al alloy were 48.3Au-35.3Cu-15.8Al and 45.6u-40.6Cu-13.8Al, respectively. Then, the chemical composition of matrix in Au-37Cu-15Al is close to that of Au-33Cu-Al. Then, the difference of phase is in comparison with Au-33Cu-15Al single-phase alloy. The tensile tests revealed that the elongation of Au-37Cu-15Al alloy containing α phase was much lower than that of Au-37Cu-15Al alloy.

Ductility Improvement of Ni-Mn-Sn Magnetic Shape Memory Alloys by Co and Cu Addition
Kun Zhang and Changlong Tong; Harbin University of Science and Technology, Harbin, China.
Compared to the traditional shape memory alloys (SMAs), ferromagnetic shape memory alloys (FSMAs) show a strong coupling between structure and magnetism. Except for thermal drive, FSMAs can produce force and deformations in response to a magnetic field. Recently, the applications of Ni-Mn-Sn FSMAs in actuator, sensor, and solid-state refrigerator can be expected due to their unique phase transition mechanism and rich physical properties. The low working temperature and the poor mechanical properties are the crucial problems limiting the application and development of Ni-Mn-Sn FSMAs. Moreover, to increase the working temperature, it is necessary to elevate the martensitic transformation temperature (Ms) while keeping the Curie temperature (Tc) unchanged. How to solve all the problems mentioned above at the same time is the key. In this paper, the new idea for increasing the working temperature and enhancing the mechanical properties is proposed by doping two elements simultaneously. Owing to the performance of different roles in Ni-Mn-Sn alloys, adding Co and Cu at the same time may elevate Tc while keeping the Ms high, and improve the mechanical properties of Ni-Mn-Sn alloys. The results of the DSC and TGA curves show that martensitic transformation is observed in Ni$_{53}$Co$_{12}$Mn$_{26}$Sn$_{11}$Cu$_{10}$ alloy.

Fabrication of Thermoelectric Power Generator Using Solely N-Type Mg$_2$Si for Automotive Application

Intermetallic silicide of magnesium silicide (Mg$_2$Si) is a promising candidate for practical thermoelectric (TE) power generation, because it has several promising features, such as the abundance of its constituent elements, its non-toxicity, and the facts that it is light weight and has the capability of generating power. For automotive applications, lighter and tougher thermoelectric power generators are advantageous; however, these applications are sometimes demanding on the devices. Mg$_2$Si has already achieved a ZT value greater than unity. In order to realize its practical use as a TE generator (TEG), both low fabrication cost and a significant lifetime at an elevated operating temperature are important. We have developed n-type Mg$_2$Si TE elements as parts of a feasible TE device. There are economic advantages to using Mg$_2$Si in thermoelectric devices. Basically, the p-type conductivity of Mg$_2$Si is possible but the thermoelectric properties of p-type material are not equivalent to those of n-type Mg$_2$Si one. Therefore, a so-called “unileg” device structure, incorporating only a n-type Mg$_2$Si TE leg, is one possible solution to realizing practical Mg$_2$Si TEGs. Compared with the conventional p-structure TE module, which comprises both p- and n-type TE elements, the uni-leg structure alleviates the problems associated with the difference in thermal expansion between p- and n-type TE elements at high temperature. To reduce the electrical and thermal contact resistance of the module, each part of the module was joined using new soldering intermetallic alloys. We are currently tuning the TE chip power generation ability by modifying the type of dopant and the contents of the matrix and the TE chip dimensions. The elemental n-type Mg$_2$Si TE chip, which is doped by donor impurities with dimension of 5x5x5 mm$^3$, exhibits power generation density of 4.1 W/cm$^2$ over a temperature difference between 737 K and 373 K (DT~ 500 K). Using this TE chip, a prospective unileg structure module TE device consisting of the arrangement of 6 TE chips in a line as a basic TEG structure. The thermal distribution and p-power generation characteristics for the fabricated unileg TEG was analyzed using finite element modeling using the ANSYS code, and the heat transfer analysis to understand the thermal impedance characteristics using the Flow Designer code. A making a consistency between the calculation parameters of the ANSYS and the Flow Designer and the fabricated TEG, precise measurements of the temperature, heat flow, and power generation at various probe points on the module were made. Fabricated TE module were examined for vibration test corresponding to automotive test procedures. Moreover, results obtained from automotive engine simulation using GT-POWER will be also discussed in terms of power generation ability and adaptability for attaching to automotive exhaust line.

Synthesis of N-Type Mg$_2$Si Using Conventional Vertical Bridgman Method for Thermoelectric Power Generation Application

Magnesium silicide (Mg$_2$Si) has been identified as a promising advanced thermoelectric (TE) material and it has some important attributes in that it is lightweight, there is a worldwide abundance of its constituent elements, and it is non-toxic. Moreover, since it has good power generation performance in the mid-temperature (~900K) range, it is expected that it can be applied in the automotive industry or in industrial furnaces. The current status for Mg$_2$Si is aimed toward TE module fabrication and appropriate system integration techniques for electric vehicle (EV) range-extender waste-heat recovery applications. For the industrialization, thermal stability under the practical operation temperatures is needed to ensure the power generation durability. Mg$_2$Si is its capability for being doped in order to modify its electrical conductivity, thermal conductivity and durability at elevated operating temperatures. Typically, impurity elements were introduced into a congruent melt of Mg$_2$Si using the “All Molten Synthesis” method. Then, the resultant polycrystalline Mg$_2$Si was pulverized and then sintered using a “Plasma Activated Sintering” (PAS) technique to form a TE power generation chip. However, we have been trying to establish a TE chip fabrication directly from melt synthesis Mg$_2$Si, so polycrystalline Mg$_2$Si by all-molten synthesis using Bridgman method is performed. For the industrialization of Mg$_2$Si TE chip for generator, thermal stability at the practical operation temperatures is predominant requirement, thus a synthesis possessing with a thermodynamically stable grain boundary were made with less process contaminant. Because the instrument of oxidation of residual Mg during synthesis process is seen to be closely associated with an onset of degradation. Typically, degradation of the Mg$_2$Si TE chip begins from MgO located at grain boundaries and proliferate to the periphery, when the TE chip is elevated up to mid-operation temperature. Thus, we are interested in an elimination of residual metallic Mg or MgO at grain boundary, namely, an obtaining thermally stable grain boundary of polycrystalline Mg$_2$Si by all-molten growth method. The examined Mg$_2$Si grown specimens were heavily doped with donor impurities of Sn and isoelectric impurity of Zn to enhance their power generation characteristics. In this report, we discuss about crystalline quality, doping behavior and corresponding TE properties (Seebeck coefficient, electrical conductivity, thermal conductivity, power factor and figure-of-merit), thermal durability of all-molten synthesized polycrystalline Mg$_2$Si.

Nanocrystallization and Recoilless Fraction Determination of Fe$_{68.5}$Co$_{10}$Nb$_{3}$Cu$_{1}$Si$_{15.5}$B$_{7}$ Ferromagnetic Alloy

Amorphous alloy Fe$_{68.5}$Co$_{10}$Nb$_{3}$Cu$_{1}$Si$_{15.5}$B$_{7}$ was obtained by melt spinning. Samples cut from the foil were annealed at 450, 550, 650 and 750 C in a vacuum furnace. 57Fe Mossbauer spectroscopy was used to identify the crystalline phases formed and the orientation of the magnetic moments based on the refined values of the hyperfine parameters. The as-quenched sample was analyzed with a hyperfine magnetic field distribution and corresponded to an in-plane orientation of the magnetic moment directions. Similar field orientation and orientation were obtained for the specimen annealed at 450 C, while for Fe$_{68.5}$Co$_{10}$Nb$_{3}$Cu$_{1}$Si$_{15.5}$B$_{7}$ system analyzed previously we obtained the onset of nanocrystallization at this annealing temperature.

Fabrication of Thermoelectric Power Generator Using Solely N-Type Mg$_2$Si for Automotive Application

Hiroto Hamba,
Takuya Kodama, Daishi Shiojiri and Tsutomu Iida; Material Science of Technology, Tokyo University of Science, Tokyo, Japan.

Synthesis of N-Type Mg$_2$Si Using Conventional Vertical Bridgman Method for Thermoelectric Power Generation Application

Hiroto Hamba,
Takuya Kodama, Daishi Shiojiri and Tsutomu Iida; Material Science and Technology, Tokyo University of Science, Tokyo, Japan.

Nanocrystallization and Recoilless Fraction Determination of Fe$_{68.5}$Co$_{10}$Nb$_{3}$Cu$_{1}$Si$_{15.5}$B$_{7}$ Ferromagnetic Alloy

Monica Soreasa and Kevin Byerly2, 1Duquesne University, Pittsburgh, Pennsylvania, United States; 2NETL, Pittsburgh, Pennsylvania, United States.
sample annealed at 550 C exhibited the nanocrystalline state formation due to the observation of the DO3 structure of the Fe-Si alloy with small amounts of Co replacing Fe in the composition. Five distinct sextets in the Mossbauer spectra could be assigned to $^{57}$Fe$^{57}$$\text{Ni}$-$\text{Al}$, $^{57}$Fe-$\text{Al}$, $^{57}$Fe-$\text{Al}$ and $^{57}$Fe-$\text{Al}$ and a metalloid enriched amorphous grain boundary phase. The relative line intensities showed that the magnetic moments were distributed at random. The spectra of the samples annealed at 650 and 750 C were also indicative of nanocrystallization, with the magnetic moments reoriented out-of-plane for the last sample. This behaviour is in contradistinction with that of the Co-rich system, which was totally crystallized at these annealing temperatures. Our results show that small Co additions can lead to the formation of nanostructures over a wide range of annealing temperatures. A new series of Mossbauer spectra was obtained by recording simultaneously the intensity transmitted by a superposition of the sample with the stainless steel etalon, based on the dual absorber method recently introduced by us. The values of the recoilless fraction could be derived from the relative spectral areas. The $f$ factor maintained values close to 0.7 for all samples measured, but dropped to 0.37 for the sample annealed at 750 C. This behavior could be related to the presence of elastic stresses in the system, which caused the out-of-plane reorientation of the magnetic moment directions.

PM06.05.38
Fabrication and Mechanical Thermoelectric Properties of Mg$_2$Si Reinforced with Intragranular SiC Nano Particles

Junko Nakano, Ryo Inoue, Tsutomu Iida and Yasuo Kogo; Tokyo University of Science, Tokyo, Japan.

Thermoelectric (TE) materials could play an important role in a global sustainable energy solution. Magnesium silicide (Mg$_2$Si) is a promising TE material because of light weight, high abundance of its constituent elements and high thermoelectric properties around 873 K (figure of merit, $ZT = 0.96$). For these reasons, Mg$_2$Si is expected to apply the component of automobile. However, Mg$_2$Si presents brittle failure behavior and its fracture toughness is quite low ($\sim 0.64$ MPa m$^{1/2}$, which is smaller than that of typical structural material). Therefore, it is necessary to improve fracture toughness. Particle dispersed strengthening is a prospective way to improve fracture toughness of brittle materials because the secondary phase dispersed intergranular or intergranular restrain crack propagation. However, the reinforcement dispersed matrix grain boundaries has negative influence on thermoelectric properties. In this study, intragranular-composites prepared by melting process to improve fracture toughness without reducing thermoelectric properties.

Pre-synthesized all-molten commercially available polycrystalline Mg$_2$Si-Sb 0.5 at. % - Zn 1.0 at. % was used as a starting material. Mg$_2$Si ingots were pulverized to powder with sizes of less than 25 μm. In addition, the powders were mixed with silicon carbide (SiC) nanoparticles. The volume fraction of SiC was set to be 1-10 vol%. The powder mixtures were pressed under uniaxial pressure and packed by Mo foil. Then, the pressed samples were sealed in a quartz tube which was filled with argon gas. In addition, the compacted samples were heated at 1358 K for 5 min. Melted samples were pulverized to powder with sizes of less than 25 μm. Then, the powders were sintered by plasma activated sintering (PAS). Young’s modulus and fracture toughness of the sintered pellets were measured by ultrasonic pulse method and indentation fracture (IF) method. Electrical conductivity, Seebeck coefficient and Thermal conductivity were also measured by four-terminal sensing, thermo-electromotive force method and laser flash method. Dimensionless figure of merit ($ZT$) was determined using those values. We successfully incorporate SiC nanoparticles within Mg$_2$Si grains through melting treatment. Fracture toughness of intragranular-composites increases about 80% compared with pure Mg$_2$Si-Sb 0.5 at. % - Zn 1.0 at. %. In contrast, TE properties are decreased with increasing volume fraction of SiC nanoparticles. However, we could confirm the effect of SiC nanoparticles dispersed within Mg$_2$Si grains, because electrical conductivity of intragranular-composites is higher than that of intergranular composites. In this presentation, the influence of SiC nanoparticles dispersed Mg$_2$Si grains on mechanical thermoelectric properties will be discussed.

PM06.05.39
The Effect of Vibration on Mechanical and Electrical Properties of Magnesium Silicide Based Thermoelectric Modules

Tetsuro Takagi, Keisuke Nagayoshi, Takashi Nakamura, Ryo Inoue, Tsutomu Iida and Yasuo Kogo; Tokyo University of Science, Tokyo, Japan.

Magnesium-based silicide (Mg$_2$Si) is one of the most attractive materials for application in thermoelectric generators (TEG) because this material has high power generation efficiency at 300-600 °C. TE modules are typically composed of n-type and p-type TE leg, however difference of thermal expansion between p-type and n-type TE leg becomes critical problem. For fabrication of the Uni-leg TE modules composed of Mg$_2$Si, silver-alloy braze was used for bonding between legs and the metal terminals. In this case, nucleation of crack owing to thermal expansion mismatch of constituent materials is inevitable. Recent studies used aluminum as a bonding layer instead of silver-alloy braze because of its low melting point. These TE modules are usually subjected to thermal cycling and continuous vibration during operation, however, effects of vibration on mechanical, and electrical properties of TE modules have not been sufficiently investigated. For designing reliable TE module, it is necessary to understand mechanical properties of the interface and degradation of interface properties by vibration. The objective of this study is to develop TE modules fabricated by Al foil. Furthermore, evaluation of interface properties was done before and after vibration tests.

Polycrystalline Mg$_2$Si-Sb 0.5 at. % - Zn 1.0 at. % with particle size 25-75 μm was used as raw material. The Mg$_2$Si powder was sintered by plasma activated sintering (PAS). The Ni foils and the Mg$_2$Si pellet were bonded by PAS at 923 K under a pressure of 10 MPa in Ar atmosphere for 10 min. The Ni/Mg$_2$Si TE leg and the Ni terminal were bonded by hot pressing using the aluminum foil. The microstructure and phase composition of the prepared samples were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The shear strength of the interface between Al/Ni before and after vibration test was measured by bonding tester PRT1101 with a displacement rate of 0.1 mm/min. The vibration test was also performed under the condition of 33, 200, 400 Hz frequency for 4 h by simple harmonic motion parallel to the interface using electrodynamic vibration test system al210/SA1M. Finite element (FE) analysis was also done to calculate natural frequencies and stress/strain distribution in TE modules during vibration.

Mg$_2$Si/Ni$_3$Al ($\eta$-phase) is formed between Ni electrode and Mg$_2$Si after hot pressing. Two phases were formed at the Ni/Al interface. Based on the results of microstructural analysis, evaluation of mechanical properties, and numerical simulation, the effect of simple harmonic motion parallel to the interface on performance of TE modules will be discussed.
We explore deformation structures arising from room temperature compressive deformation of polycrystalline Pt modified RuAl alloy. Intermetallics such as NiAl and CoTi that possess high melting points deform by \(< 100\) slip at room temperature while B2 phases such as CuZn and FeAl with relatively lower melting points or order-disorder temperatures deform by \(< 111\> slip. RuAl, although it has relatively high melting point, occupies a unique position in this hierarchy in that slip occurs by both \(< 100\> and \(< 111\> dislocations with debris of sessile \(< 110\> dislocations and complex dipole structures. \(< 100\> dislocations are cusped and cross slip frequently. \(< 111\> dislocations trail dipoles and also decompose into sessile configurations of \(< 110\> or \(< 100\> dislocations in near screw orientations. An analysis of gamma surfaces in RuAl and the energetics of dislocation dissociations provides insight into its deformation behaviour.

9:00 AM PM06.06.02  
Diversity and Phase Equilibria in Highly-Ordered \(\eta\)-Fe\(_2\)Al\(_5\) Derivative Phases  
Kodai Niitsu\(^1\), Rytaro Sakai\(^2\), Masaya Higashi\(^1\) and Haruyuki Inui\(^1\); \(^1\)Kyoto University, Kyoto City, Japan; \(^2\)ESISM, Kyoto, Japan.

While being one of the most fundamental and practically important binary systems, Fe-Al binary system still has intriguing issues on its constituting phases and phase equilibria. The orthorhombic \(\eta\)-Fe\(_2\)Al\(_5\) (space group \textit{Cmcm}) is such an intermetallic compound, raising inconsistencies in its crystal structure and ordering tendency. To date, several derivatives with highly-ordered crystal structures such as \(\eta'\), \(\eta''\), \(\eta'''\) and \(\eta\)\(_m\) phases have been reported to exist with slightly deviated stoichiometry from that of the \(\eta\)-Fe\(_2\)Al\(_5\) phase. While various attempts have been demonstrated by means of transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and differential scanning calorimetry, some controversial remains on their crystal structures and the phase equilibria among these phases.

In this study, we fabricated various Fe-Al alloy ingots with Al content of \(68\%\)–\(74\%\) and homogenized at various temperatures. TEM and scanning transmission electron microscopy (STEM) observations were performed on the thin foils prepared by electro-polishing. To refine the crystal structures, XRD was alternatively performed on the single crystals of some homogenized alloys. As a result of systematic TEM and STEM observations, four kinds of highly-ordered intermetallic compounds (termed as \(\eta'\), \(\eta''\), \(\eta'''\) and \(\eta\)\(_m\) in line with previous reports) are observed in addition to the \(\eta\) phase. These compounds have different ordering tendencies with maintaining the framework of the \(\eta\) phase, thus that their stoichiometry is slightly different from each other. In addition, periodic anti-phase boundaries (APBs) are observed in some of the compounds, which are presumably introduced to compensate for the lattice mismatch among the adjacent compounds. In spite of strong similarity in crystal structures, their phase stabilities show a remarkable contrast; the \(\eta''\) and \(\eta'''\) phases seem to be stable up to \(\approx 1300\) K with the solubility range of \(\approx 1\) at.\% but the \(\eta'\) and \(\eta\)\(_m\) phases exist only below \(-650\) K with little solubility range. This contrast may be attributed to the hierarchical ordering among these structures. The conclusive phase diagram will be also shown in the presentation.

9:15 AM PM06.06.03  
Creep Mechanism of Lamellar Fe-Al Alloys  
Anke Schmitt\(^1\), Sharvan Kumar\(^2\), Alexander Kauffmann\(^3\) and Martin Heilmair\(^4\); \(^1\)Karlsruhe Institute of Technology, Karlsruhe, Germany; \(^2\)Brown University, Providence, Rhode Island, United States.

Iron aluminides are possible alternatives for steels in warm-temperature application due to their low-density and oxidation-resistance. However, their frequent use is limited mainly due to a low ductility at room temperature and rather poor creep resistance at elevated temperatures beyond \(600^\circ\)C. In order to improve the creep resistance of B2-ordered FeAl classical physical metallurgy approaches are used, such as solution strengthening, precipitation strengthening and dispersion strengthening. As previously demonstrated for TiAl, a lamellar microstructure can enhance the creep resistance as well. In the Fe-Al system, a lamellar microstructure can be obtained by an eutectoid transformation in the composition range of \(55\%\)–\(65\%\) Al. Particularly, the high-temperature \(\varepsilon\)-phase, Fe\(_2\)Al\(_5\) decomposes into B2-ordered FeAl and triclinic FeAl\(_2\). The creep resistance of such a lamellar alloy was previously studied in a constant true stress of 100 MPa and \(700^\circ\)C in compression. It exhibits a characteristic minimum after achieving a strain of roughly 0.5\%, which is followed by an increase of the creep rate with increasing time and strain. The absence of a pronounced steady-state regime is attributed to a deterioration of the lamellar structure in the vicinity of colony boundaries. The determined stress exponent indicates a creep based on dislocations motion. Nevertheless, the presence of the two phases combined with a high interphase density due to the lamellar morphology precluded final understanding of the individual contributions to the observed creep response -- both, in the early stages as well as at and just beyond the minimum creep rate. Thus, TEM investigations of creep eutectoid FeAl material were performed on samples that were isothermally creeping under above conditions and interrupted for microstructure analysis at characteristic strains. In this presentation we will discuss the following situations determining the strain rate response of the lamellar materials: a) Both phases contribute to the creep deformation from the beginning and the degradation of the lamellar morphology is responsible for the increase of the strain rate beyond the minimum. b) Only one of the two phases deforms and the second phase does not contribute directly to creep throughout the entire experiment, and the degradation of the lamellae causes the increase of the strain rate beyond the minimum. c) The second phase starts to creep-deform beyond the minimum causing the increase in the strain rate and subsequently, lamellae degradation enters the picture as well.

9:30 AM PM06.06.04  
Understanding Structural Phase Transitions Between the Simpler Structures and Topologically Close-Packed Phases  
Anirudh Rau Natarajan and Anton Van der Ven; University of California, Santa Barbara, Santa Barbara, California, United States.

Structural phase transitions between vastly different crystal structures are often exploited to enhance the properties of structural and functional materials. Understanding the transformation mechanism in applications such as shape-memory, magnetocaloric, high-entropy and precipitation strengthened alloys is thus critical to developing better alloy chemistries. However, very few links between disparate structure classes are known. Further, such phase transitions typically involve several length-scales, making it difficult to develop rigorous ab-initio mesoscale models. In this talk, we will describe a new facile pathway connecting the simpler structures to a hierarchy of topological close-packed phases consisting of Kagomé nets and triangular layers. Several typical intermetallic compounds such as the Laves phases are specific members of this family of structures. First-principles calculations reveal that the pathway connecting the simpler structures to a hierarchy of topological close-packed phases consisting of Kagomé nets and triangular layers. While various attempts have been demonstrated by means of transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and differential scanning calorimetry, some controversial remains on their crystal structures and the phase equilibria among these phases.

In this study, we fabricated various Fe-Al alloy ingots with Al content of \(68\%\)–\(74\%\) and homogenized at various temperatures. TEM and scanning transmission electron microscopy (STEM) observations were performed on the thin foils prepared by electro-polishing. To refine the crystal structures, XRD was alternatively performed on the single crystals of some homogenized alloys. As a result of systematic TEM and STEM observations, four kinds of highly-ordered intermetallic compounds (termed as \(\eta'\), \(\eta''\), \(\eta'''\) and \(\eta\)\(_m\) in line with previous reports) are observed in addition to the \(\eta\) phase. These compounds have different ordering tendencies with maintaining the framework of the \(\eta\) phase, thus that their stoichiometry is slightly different from each other. In addition, periodic anti-phase boundaries (APBs) are observed in some of the compounds, which are presumably introduced to compensate for the lattice mismatch among the adjacent compounds. In spite of strong similarity in crystal structures, their phase stabilities show a remarkable contrast; the \(\eta''\) and \(\eta'''\) phases seem to be stable up to \(\approx 1300\) K with the solubility range of \(\approx 1\) at.\% but the \(\eta'\) and \(\eta\)\(_m\) phases exist only below \(-650\) K with little solubility range. This contrast may be attributed to the hierarchical ordering among these structures. The conclusive phase diagram will be also shown in the presentation.

9:45 AM PM06.06.05  
Ultrahigh Elastically Compressible Intermetallic Compound, CaKFe\(_{4}\)As\(_{4}\)  
Gyhuo Song\(^1\), Vladislav Borisov\(^2\), William Meier\(^1\), Keith Dusoe\(^1\), John T. Sypic\(^1\), Roser Valenti\(^2\), Paul Canfield\(^3\) and Seok-Woo Lee\(^1\); \(^1\)University of Connecticut, Storrs, Connecticut, United States; \(^2\)Theoretical Physics, Goethe University, Frankfurt am Main, Germany; \(^3\)Physics and Astronomy, Iowa State University, Ames, Iowa, United States.

Intermetallic compounds often exhibit superior physical and chemical properties due to their unique atomic arrangements and crystal structures, but their practical applications have been significantly limited because most intermetallic compounds are extremely brittle and are not able to absorb strain energy
high enough to sustain its structure. The nature of strong covalent bonds and complexity of crystal structures usually do not permit the plastic deformation, so brittle failure occurs at the elastic limit even less than 0.5% except a few limited materials such as shape memory intermetallic compounds. Therefore, it is extremely rare to obtain a large amount of elastic deformation over 10% in intermetallic compounds.

However, CaKFe₄As₄ recently began to receive great attention due to its superelasticity and potential usage of high temperature superconductivity. These two super-properties do not typically get along because superconductors, which are brittle oxides or intermetallic compounds in many cases, shatter easily particularly under non-hydrostatic stress state. Here, by synthesizing a single crystalline CaKFe₄As₄ through Sn-flux solution growth and performing in-situ micromechanical experiments, we report that the giant compressible strain, 13~17%, is possible under uni-axial compression along c-axis. Notably, this material is able to absorb the strain energy orders of magnitude higher than advanced engineering materials. The density functional theory shows that this unusually large elastic axial compressibility results from the half-collapsed tetragonal phase transition, which is induced by As-As atomic bond formation and magnetic moment collapse, and significant local compliance. All these processes are fully reversible upon unloading. Also, we performed in-situ cryogenic micromechanical test with liquid nitrogen cooling capability, and confirmed that superconductivity could be suppressed by inducing the half collapsed tetragonal around 1 GPa. This huge uni-axial reversible deformation mechanism is differentiated from the conventional shear mechanism, martensite-austenite phase transformation of shape memory intermetallic compounds and can be extended to over 1000 AX₂Y₂- and ABX₄Y₄-structured intermetallic compounds. Furthermore, this giant elastic strain could make strain engineering possible, leading to the development of mechanically-switchable functional materials, for instance, superconductivity switching even under uni-axial mechanical loading, which is significantly desirable for device applications.

10:00 AM BREAK

10:30 AM PM06.06.06 Predicting Defect Behavior in Intermetallic Compounds by Merging Ab Initio Modeling and Machine Learning Mark Ates1,2, Bharat Medasani1, Hong Ding1, Wei Chen3, Kristin Persson1,2, Andrew Canning1, Maciej Hanaszczyl and Anthony Gamsu1, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 3Pacific Northwest National Laboratory, Richard, Washington, United States; 4Illinois Institute of Technology, Chicago, Illinois, United States; 5University of California, San Diego, California, United States.

We present a combination of machine learning and high throughput calculations to predict point defect behavior in binary intermetallic (A–B) compounds, using as an example systems with the cube B2 crystal structure (with equatomic AB stoichiometry). High throughput first principles density functional calculations have been employed to compute intrinsic point defect energies in 100 B2 intermetallic compounds. The systems are classified into two groups: (i) those for which the intrinsic defects are antisites for both A and B rich compositions, and (ii) those for which vacancies are the dominant defect for either or both composition ranges. The data was analyzed by machine learning-techniques using decision tree, and full and reduced multiple additive regression tree (MART) models. Among these three schemes, a reduced MART (r-MART) model using six descriptors presents the highest fit and predictive accuracy. This model is used to predict the defect behavior of other B2 compounds, and we find that 45 % of the compounds considered feature vacancies as dominant defects for either A or B rich compositions (or both). The ability to predict dominant defect types is important for the modeling of thermodynamic and kinetic properties of intermetallic compounds, and the present results illustrate how this information can be derived using modern tools combining high throughput calculations and data analytics. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231: Materials Project program KC23MP.

11:00 AM PM06.06.07 Design of a Hardenable Cu-Cr-Nb Alloy by Laser Metal Deposition Amoon R. Kim1, Dora Maischner2, Andreas Weisheit2, Eric Jagle2 and Dierk R. Raabe1, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; 2Fraunhofer Institute für Laserotechnik, Aachen, Germany.

Dilute copper alloys are of high interest, uniquely at the intersection of the property combination, specifically conductivity (thermal/electrical) and mechanical strength (hardness). We propose the design of a dilute Cu-Cr-Nb alloy focusing on achievement of greater hardening (146 VHN), compared to respective established ternary alloys. We achieve this goal, by processing the alloy by laser metal deposition (LMD). Importantly, we utilize a lower alloying solute amount (4 at.%; lower by at least ~ 33%) compared to previous alloys. Careful alloy compositional choice results in introduction of novel hardening contribution in this ternary system, by coherence of precipitates enriched in chromium. The precipitate hardening, size and chemical composition has been investigated by transmission electron microscopy and atom probe tomography. The coherency hardening operates in conjunction with dispersed Laves phase particle hardening. Each of the contributions has been modelled, which adds up to match the measured hardness of 146 VHN. Spatial homogeneity of hardening has been established by means of nano-indentations across the alloy sample. The hardening attained is in the as-produced condition itself i.e. after LMD. This is because of favorable LMD processing conditions for in-situ precipitation (intrinsic heat treatment).

11:15 AM PM06.06.08 A New Ab Initio Modeling Scheme for Ion Self-Diffusion Coefficient Applied to ε-Cu₃Sn Phase of Cu-Sn Alloy Tom Ichihara1, Genki Prayogo2, Kenta Hongo3, 4 and Ryo Maezono3, 4, School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; 3School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; 4Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; 5PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Japan; 6Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan.

Ion diffusion via vacancy relates to various properties such as corrosion, monotectoid, fracture, and degradation in material solids. To reveal the microscopic processes of ion diffusion, ab initio simulations have been used commonly. On the other hand, when evaluating self-diffusion coefficient, its application has been limited in just simplest systems, because it is difficult to model diffusion coefficients based on predictable quantities especially for complicated structures such as long-range periodic crystals.

We tackled this issue with our own idea in order to simplify the complicated connection of ion sites based on the calculated barrier energies. We established a modeling scheme, introducing a couple of novel concepts, "domain division" and "coarse graining" of the diffusion network. The first concept is expected to be useful for long-lange periodic structures: We classify the diffusion routes into three groups 1–3, according to their barrier energies, $E_1 < E_2 < E_3$. The diffusion routes in group III can be excluded from the diffusion network, because an ion jump affects the diffusion coefficient by the Boltzmann factor of barrier energy. Then, if the diffusion network is (fortunately) separated into a few types of disjunct domains, the problem is reduced into multiple modelings for each domain. These modeling are further simplified with the second concept. Since vacancies can move along the diffusion routes in group 1 more frequently than those in group 2, ion sites connected by these routes can be replaced with just a single site. Then, the diffusion networks of each domain are course-grained with the representative sites to be simplified.
We applied the modeling scheme to evaluate the diffusion coefficient of Cu ion in ε-Cu5Sn alloy, which is a typical system having long-range periodicity. The predicted diffusion coefficients agree with experimental values, and it is better than those reported by a classical molecular dynamics by a digit. Furthermore, we justified the constructed model by comparing the correlation factor with that of two-dimensional hexagonal lattice at high temperature limit.

11:30 AM PM06.06.09
Solidification Microstructure of Ti-Ag and Ti-Ag-Nb Immiscible Alloys Focusing on the Formation of Intermetallic Compounds Takeshi Nagase; Osaka University, Ibaraki, Japan.

Ti-Ag alloy system is characterized by a flat liquidus line and the existence of two intermetallic compounds (TiAg and Ti2Ag) in the binary phase diagram. The solidification microstructure of binary Ti-Ag alloys and ternary Ti-Ag-Nb alloys were investigated focusing on the formation of intermetallic compounds. In binary Ti66.7Ag33.3 alloy, the conventionally cast ingots obtained by arc melting technique showed a dendritic structure that included Ti-Ag-based intermetallic compounds; on the other hand, the rapidly solidified melt-spun ribbons showed a particulate microstructure comprising Ag-rich globules and a Ti-rich matrix phase without Ti-Ag-based intermetallic compounds. The formation of emulsion-like structures in the rapidly solidified specimens can be explained in terms of liquid phase separation [1]. The occurrence of the liquid phase separation also can be seen in Ti-Nb-Ag alloy [2].

References

11:45 AM PM06.06.10
Microstructure-Corrosion Property Correlation in Graphene Oxide Containing SnZn and SnNi Composite Coatings Rekha Mahendrakar; Indian Institute of Science, Bangalore, India.

Coatings have been traditionally used for protecting the underlying substrate against corrosion. Recently, it has been demonstrated that chemical inertness and impermeability of graphene/graphene oxide (GO) makes them excellent coating material for corrosion protection. Use of only graphene/GO as coating material is however impractical due to challenges associated with large scale production of graphene/GO sheet with minimal defects at low cost. One other way to employ these materials for corrosion protection is by incorporating them into the matrix of conventional coatings. Researchers have shown that composite metallic coatings containing graphene/GO exhibit higher corrosion resistant than corresponding pristine metallic coatings. This work explores the correlation between microstructure and electrochemical behaviour of SnZn-GO and SnNi-GO composite coatings electrodeposited on mild steel substrate. Amount of GO in the composite coatings was varied by changing the concentration of the chemically synthesized GO in the electrolyte bath. Corrosion behaviour of the SnZn and SnNi coatings were examined through potentiodynamic polarization and electrochemical impedance spectroscopy methods. Transmission electron microscopy technique was used to investigate the coating microstructure. In the case of SnZn-GO composite coating, relative compactness of the coatings increased with increase in the concentration of GO. Texture and the crystallite size, however, did not show any significant variation with the concentration of GO in the coatings. Microstructural investigation of the coating cross-section revealed large scale segregation of Zn-rich and Sn-rich phases in pure SnZn coating. However, in the case of SnZn-GO composite coatings uniform distribution of Zn phase in Sn-rich matrix was observed. This distribution caused early and uniform formation of ZnO, which is the corrosion product, yielding better corrosion resistance for the SnZn-GO composite coatings as compared to pure SnZn coating. In the case of SnNi-GO composite coating, morphological characterization revealed the presence of rod shaped features in a flat matrix. Structural characterization showed presence of Sn-rich phase along with Ni3Sn4, Ni3S2 and Ni5Sn intermetallics. Crystallite size of the Sn-rich phase decreased significantly due to the addition of GO. Microstructural investigation revealed that the SnNi coating without GO contained Sn and Sn-Ni solid solution grains. Whereas, SnNi coatings with GO contained Sn grains with Ni present at the grain boundaries. With increase in the GO content in the SnNi-GO composite coatings, size of the Sn sub-grains within the larger Sn grains reduced. Smaller Sn sub-grains and presence of Ni at the grain boundaries facilitated formation of the oxide corrosion products which provided protective cover and enhanced the corrosion resistance behaviour for the composite coating.

SESSION PM06.07: Intermetallic Precipitates
Session Chairs: Anne Denquin and Dierk Raabe
Wednesday Afternoon, November 28, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.07.01

We report about recent findings which reveal the close connection and interdependence among Fowler-Guggenheim-type equilibrium segregation, local spinodal decomposition and phase transformation phenomena at lattice defects. We show that several types of phase formation effects at grain boundaries and dislocations can be jointly understood in terms of preceding equilibrium segregation and decomposition precursor states. Random high angle grain boundary structure features seem to be of secondary relevance for these phenomena owing to prevalence of the local chemical driving forces. Corresponding examples which have been documented by applying site-specific correlating atom probe tomography and electron microscopy probing are given for Fe-Mn model steels [1-3], superalloys and high entropy alloys [4].

References
Effects of Si on Phase Stability and Precipitation Behavior of C14 Laves Phase (Fe, Cr)\(_2\) (Nb, Mo) in High Cr αFe-base Alloys Yoshisato Kimura, Ko Kato and Yaw Wang Chai; Tokyo Institute of Technology, Yokohama, Japan.

Ferritic stainless steels with high Cr contents around 20 at% can be used not only for heat resistant alloys such as exhaust manifolds of automobile engines but also for functional alloys such as separator or/and interconnector of fuel cells. It is important to control microstructure of ferritic stainless steels focusing on morphology of C14 Laves phase precipitates depending on applications. Structural applications tend to require fine and homogeneous distribution of C14 Laves phase, while gradient distribution with rather large volume fraction would be desirable for functional applications mentioned above. The objectives of the present work are to understand effects of the Si addition on phase stability and precipitation behavior of C14 Laves phase (Fe,Cr stoichiometric ratio) in the Fe-Cr-Nb-Mo quaternary αFe-base model alloys, and to determine the growth mechanism of C14 Laves phase in the bcc αFe matrix.

It is interesting that the addition of Si remarkably enhances the precipitation of C14 Laves phase cooperatively with Mo. For instance, the volume fraction of C14 Laves phase increases about twice as large in an Fe-20Cr-0.5Nb-2Mo alloy (in at%) by the addition of 2 at% Si compared with Si-free counterpart under the same aging condition at 1073 K for 24 hours. Contrary to this, the addition of Si is not effective to increase the volume fraction of C14 Laves phase on a Mo-free Fe-20Cr-0.5Nb alloy. It is suggested that the addition of Si improves the phase stability of C14 Laves phase while the partitioning of Mo into C14 Laves phase would be promoted due to the attractive interaction between Mo and Si. It is noteworthy that the site preference of Si in binary C14 Laves phase, Fe\(_2\) Nb and Fe\(_2\) Mo, was examined using the electron probe microanalysis. It was found that Si substitutes for the both-site in Fe\(_2\) Nb, and for the Fe-site in Fe\(_2\) Mo. The lattice mismatch between the bcc αFe matrix and C14 Laves phase decreases as the Mo content increases, which may lead to the uniform distribution of fine Laves phase precipitates. We have also determined that the growth mechanism of C14 Laves phase in the bcc αFe matrix is the ledge mechanism in an Fe-20Cr-0.5Nb-1Mo alloy annealed at 1073 K for 24 hours, using the transmission electron microscopy. The terrace is formed on the close-packed basal plane of hcp C14 structure as we predicted. Precipitation particles tend to grow in a needle-like shape depending on the anisotropic difference of lattice mismatch. The addition of Si up to 2 at% on Fe-20Cr-0.5Nb-1Mo alloys seems not to have appreciable effect on the ledge mechanism of C14 Laves phase precipitates.

Role of Cr-rich Carbide Precipitates in the Intergranular Oxidation of Ni-Cr Alloys Maria Sushko, Daniel Schreiber, Kevin Rosso and Stephen Bruemmer; Pacific Northwest National Laboratory, Richland, Washington, United States.

The influence of grain boundary Cr carbides on the intergranular (IG) oxidation behavior of a Ni-16Cr alloy is considered using a novel atomistic-to-mesoscale model and three-dimensional atom probe tomography (APT). The results show that Cr carbide strongly perturbs the collective reactive dynamics of oxidizing species and alloy elements in the IG region. Strong attractive interactions between oxygen and carbide create a driving force for Cr and Ni accumulation in the grain boundary adjacent to the carbide, and for the depletion of Cr and Ni ahead of the oxidation front beyond the carbide. High local Cr chemical potentials from Cr carbide and Cr in the alloy dictate preferential oxidation of Cr and the formation of Cr\(_2\)O\(_3\) in the region adjacent to the carbide 1-2 nm away from the carbide surface. APT observations also reveal Ni accumulation at the interphase between the carbide and Cr\(_2\)O\(_3\), possibly indicating emergence of a distinct interfacial phase. The results inform a mechanistic model underlying the thermodynamics of IG oxidation of a Ni-Cr alloy in the presence of Cr carbide, and shed light on the mechanism of carbide-assisted protection of the alloy against grain boundary corrosion/oxidation. Our findings can be used for the development of new alloys that are more stable under extreme conditions.

Microstructure and Strength of Heat-Resistant Aluminum Alloy Strengthened by T-Al\(_6\)Mg\(_{11}\)Zn\(_{11}\) Intermetallic Phase Naoki Takata, Masato Ishihara, Satoshi Nakatsuka, Asuka Suzuki and Makoto Kobashi; Nagoya University, Nagoya, Japan.

Wrought aluminum (Al) alloys with relatively high specific strength are widely used for radial compressor impellers in vehicle turbochargers. The limited high-temperature strength determines the service temperature of compressor impellers for turbochargers. One of the common wrought Al alloys used for radial compressors is alloy 2618. However, its strength is significantly reduced at temperatures above 200°C. Thus, further improving the combustion efficiency at elevated temperatures is necessary to increase the service temperature of the Al alloys applied for the radial compressor impellers. In the present study, we designed an aluminum (Al)-based alloy with α-Al (fcc) matrix strengthened by T-Al\(_6\)Mg\(_{11}\)Zn\(_{11}\) (cubic) intermetallic phases using a large two-phase region of α and T phases in the Al-Mg-Zn ternary system for the possible application of the radial compressor impellers operating at elevated temperatures above 200°C. Thermodynamic assessments revealed a composition of Al-5Mg-3.5Zn (at%) with the α-Al phase reinforced with high fractions (approximately 10%) of T phase. We attempted to control microstructure of the Al-5Mg-3.5Zn alloy by the solution treatment and subsequent aging. T phase preferentially precipitates on grain boundaries in the α-Al matrix, which increases the area fraction of T phase on grain boundaries during the aging. The granular precipitates of T phase were dispersed rather homogeneously in the α-Al matrix with a particular orientation relationship of (1-11), (1-21) and [011], // [111] at elevated temperatures above 300°C. During the aging at 200°C there were numerous fine precipitates with a mean size of approximately 20 nm in grain interior, which is likely the metastable phase associated with T phase. The present alloy aged at 200°C for 1 h exhibits high yield strength of approximately 260 MPa at 200°C, which is much superior to those of the conventional Al alloys at an
Elevated temperature corresponding to possible service temperatures for the compressor impellers in turbochargers.

4:15 PM PM106.07.06
The Role of Intermetallic Particles on the Bendability of AA6xxx Alloys  Sin Ting Cynthia Chang1, Miroslav Smid1, Samy Hocine1,2 and Helena Van Swygenhoven-Moens1,2; 1Photons for Engineering and Manufacturing Group, Paul Scherrer Institut, Villigen, Switzerland; 2Neutrons and X-rays for Mechanics of Materials, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The role of intermetallic particles on the bendability of Al 6xxx alloys is investigated during in-situ bending tests in a scanning electron microscope (SEM). High resolution digital image correlation (HR-DIC) analysis is undertaken to investigate the role of microstructural features on the strain partitioning and the role of pre-existing voids and precipitates on early stages of the crack initiation and fracture. Aluminum alloys AA6014 and AA6016 after T4 temper, i.e. after solution heat treatment and quenching are investigated in as-received and pre-strained (10% strain) conditions. The in-situ bending setup was developed in-house and is based on a Kammrath & Weiss tensile module suitable for a scanning electron microscope (SEM) chamber. The experiments are performed with constant displacement rate and with several interruptions for SEM imaging at selected displacement values. DIC with high spatial resolution is performed using colloidal silica (OPS) particles. Full-field strain maps are complemented with Electron Backscatter Diffraction (EBSD) maps before and after the bending. The crystal orientation data enables the identification of activated slip planes observed by HR-DIC. Furthermore, EBSD data document the different texture evolution in the compression and tension parts of the specimen.

It is observed that the pre-existing voids and cracks along the intermetallics play an important role in the strain localization. At small bending, intermetallics can deform and become elongated in the tension direction. With further bending, strain localization is observed around intermetallics leading to cracking of intermetallics and producing additional voids in-between the intermetallics. Failure mechanisms are often related to the presence of fine precipitates along grain boundaries. The final crack leading to sample failure propagates along the cracked intermetallics. The results are discussed in terms of the different type of intermetallics present in AA6014 and AA6016.

4:30 PM PM106.07.07
Superior Mechanical Properties Induced by Extrusion in Mg-Based Long-Period Stacking Ordered (LPSO) Phase Alloys Koji Hagiwara1, Zixuan Li1, Michiaki Yamasaki2, Yoshito Kawamura2 and Takayoshi Nakano3; 1Osaka University, Osaka, Japan; 2Kumamoto University, Kumamoto, Japan.

The recent hot topic found in Mg-alloys containing large amount of long-period stacking ordered (LPSO) phase is the unusual increase in the strength by the extrusion. In this study, the detailed mechanisms which induce the drastic strengthening of the LPSO-phase alloys by extrusion was first elucidated on the basis of the quantitative analysis. To achieve this, the temperature and loading orientation dependence of the deformation behavior of the Mg0.9Zn0.1 extruded alloy which contains a ~86 vol.% of LPSO-phase were examined. Using several extruded alloys with different extrusion ratio, the influence of extrusion ratio to the microstructure formation and the following mechanical properties were examined. Rectangular specimens were cut by electro-discharge machining from the as-cast ingot and extruded alloys, and the mechanical properties of them were examined by compression tests. The tests were conducted in a temperature range between the room temperature and 400 degree C in a vacuum. Two loading orientations were selected for the compression test; one is parallel to the extrusion direction (0 orientation), and the other is inclined at an angle of 45 degree from the extrusion direction (45 orientation), to clarify the anisotropic mechanical properties of the extruded alloys. As a result, the yield stress of the LPSO phase alloy was found to exhibit a strong orientation dependence varied with the extrusion ratio. Especially, the yield stress of the extruded alloy with the reduction ratio of 10 showed an extremely high value more than 450MPa when loaded at 0 orientation, while it was largely reduced when loading at 45 orientation. This strong anisotropy of the plastic deformation behavior was considered to be derived from the variation in the deformation mechanisms depending on the loading orientation because of the development of strong (10-10) fiber texture along the extrusion direction. Basal slip was found to govern the deformation behavior at 45 orientation, while the predominant deformation mechanism varied from basal slip to the formation of deformation kink band at 0 orientation, as increasing in the extrusion ratio. In addition, it was found that the introduction the deformation kink band boundary during the extrusion process effectively act as strong obstacles against the motion of basal slip. This contributes to the drastic increase in the yield stress and work-hardening rate of the LPSO-phase alloys in the wide temperature range investigated.

4:45 PM PM106.07.08
Atomistic Simulation and Modeling of γ-Precipitate Nucleation in Mg-Al Alloys Peng Yi and Michael L. Falk; Johns Hopkins University, Baltimore, Maryland, United States.

Magnesium alloys have drawn increasing interest as a lightweight material for applications in transportation and aerospace industries. Some Mg-Rare earth alloys have shown significant precipitation hardening properties. These hardening properties are determined by the morphology and distribution of the precipitate particles, which strongly depend on the processing conditions during aging treatment, for example, temperature, applied strain, and the presence of defects like dislocations. It is important to understand how these processing conditions affect the precipitation process, particularly during the initial nucleation stage. This understanding is crucial for processing condition optimization, property prediction, and materials design for performance improvement and cost reduction.

We studied the nucleation of γ-Mg17Al12 precipitates in Mg-Al alloys with various solute Al concentrations, using atomistic simulation and modeling methods. The critical nucleus size at 277°C (550K) was determined using molecular dynamics simulations with a survival probability method. The critical nucleus size is very sensitive to the solute concentration; and is compared with calculations based on the chemical driving force and interfacial energy. The external pressure plays an important role in affecting the critical nucleus size as well. The external pressure not only changes the misfit strain energy, but also significantly changes the interfacial energy. As a result, although γ precipitate is denser than the a matrix, counter-intuitively nucleation is favored under tension conditions rather than compression conditions.

We also calculated the effect of dislocations on the nucleation of γ precipitate. The theoretical framework detailed in a number of [1, 2] and first-principle calculation database were used for our thermodynamic modeling in calculating the nucleation rate of dislocation facilitated precipitation. The calculation results were used to compare with recent equal channel angular extrusion (ECAE) experiments of γ precipitation at 150°C (423K), where the dislocations are found to be preferable forming sites for the precipitates.

NiTi shape memory alloys (SMA) are used in the medical device industry for fabricating self-expandable stents, stent grafts and heart valve frames that can be implanted with minimally invasive techniques. This material experiences a reversible stress-induced martensitic phase transformation from its parent austenite form (B2 austenite ↔ B19’ martensite) that is accompanied by 6-8% recoverable strain. The stress for the reverse transformation (martensite to austenite) is lower than that for the forward transformation, resulting in a stress-strain hysteresis. The combination of device geometry, deployment practice and conditions that prevail in service makes evaluating and isolating factors that control the cyclic deformation response and fatigue failure as well as predicting high cycle fatigue life of these biomedical implants particularly challenging. In uniaxial tension, the austenite-to-martensite transformation progresses heterogeneously, leading to a complex distribution of strain whose local magnitudes differ from what is globally imposed. Thus, mechanistically interpreting the cyclic response of ultrafine ligaments that compose the stent construct in bending poses a significant scientific challenge. To address some of these issues, we have used a mildly center-tapered flat dog-bone specimen geometry that has been subjected to uniaxial tensile cyclic loading from the lower stress plateau where the material is in a mixed-phase state to mimic device service conditions. We apply controlled displacement amplitudes and obtain local strains experienced by the co-existing phases in the specimen gauge section using digital image correlation; we use a high-speed camera to monitor the specimen surface to track phase transformation and fracture initiation and propagation. We have examined the consequence of imposed cyclic frequency and testing medium on cyclic response. Additional experiments have been conducted to obtain fatigue life as a function of imposed displacement amplitude. The results from these experiments will be presented and their implications will be discussed.
Deformation Behavior of Stoichiometric Au2CuAl resonance imaging are drawbacks. Then, in order to overcome these problems, we have proposed AuCuAl shape memory alloy especially for endovascular application. The high ductility and the excellent SE in the CAM SMA is reviewed and the microstructural control to obtain the ultra-large single crystal is introduced. New route to obtain an extremely large single crystal using abnormal grain growth only by cyclic heat treatment was examined. In this presentation, the alloy design for obtaining high interfacial energy is preferentially formed in the initial stage of martensitic transformation. Group A and C show relatively low interfacial energy. This is one of the reasons that group C is preferentially formed in the initial stage of martensitic transformation.

CuAlMn (CAM) alloy is one of the attractive shape memory alloys for practical applications because of high superelastic (SE) performance, high cold-workability and low cost. The SE properties of CAM alloy are known to be affected by relative grain size and the single-crystalline specimens show excellent properties [1]. Recently, our group has established the method for obtaining extremely large single-crystals in this alloy by cyclic heat treatment (CHT) without deformation process [2], and to achieve fabricated ultra-large single-crystalline rods of about 700 mm in length [3]. On the other hand, the most critical drawback for the practical use in this alloy is the low cyclic properties. Actually, in Cu17Al11.4Mn (at.%) alloy, the residual strain suddenly increases at about 100th cycle [4], while keeping a low value until 10^5 cycles in NiTi [5]. In this work, for the CuAlMnNi (CAMN) alloys, in which precipitation hardening by NiAl B2 phase is expected, the microstructures and the cyclic SE properties were examined. CAMN single-crystalline sheets with dimension of 1×5×60 mm^3 were obtained by the CHT process as well as in the CAM alloys. In the CAMN sheet, excellent cyclic properties in SE with the residual strain smaller than 0.5% at 2000th cycle for applied strain of about 5% were obtained. This dramatic improvement in cyclic properties is due to coherent precipitation of the NiAl phase.

References

Ultra-Large Single Crystals by Abnormal Grain Growth in Cu-Al-Mn Heusler-Type Shape Memory Alloy

Intermetallic compounds are generally brittle, which is one of the main reasons to impede practical use. In 1996, we reported Cu-Al-Mn (CAM) shape memory alloy (SMA) with high ductility by decrease of degree of order in the parent phase with L21 ordered structure [1]. The superelastic (SE) property in SMA is affected by grain size [2] and single-crystalline sample is known to show SE property better than polycrystalline one. Recently, we discovered a new route to obtain an extremely large single crystal using abnormal grain growth only by cyclic heat treatment [3]. In this presentation, the alloy design for the high ductility and the excellent SE in the CAM SMA is reviewed and the microstructural control to obtain the ultra-large single crystal is introduced.

(References)

Deformation Behavior of Stoichiometric AuCuAl

Although TiNi becomes widely applied for biomedical applications, the possibility of Ni-hypersensitivity, weak X-ray radiography and artifact in magnetic resonance imaging are drawbacks. Then, in order to overcome these problems, we have proposed AuCuAl shape memory alloy especially for endovascular intervention. In the present study, the deformation behavior of the stoichiometric Au25Cu25Al (at.%) alloy is comprehensively summarized in addition to recent achievements by micro compression tests. It should be noted that the stoichiometric composition of B2 AuCuAl (Spangold) is recognized to be Au2CuAl, but in this study, we regard the stoichiometry as AuCuAl due to L21 Heusler of the parent phase. Mechanical tests used were indentation test, tensile test, compression test for polycrystal material as well as micro compression test for micro pillars. Micro Vickers hardness of AuCuAl is around 170HV. By tensile tests at room temperature, the polycrystalline alloy specimens generally exhibit intergranular failure during elastic deformation. This brittleness is partially due to large grain size. The ultimate tensile strength is less than 100MPa. On the other hand by compression tests, the specimens show relatively good plastic deformation around 10% and the maximum stress is around 700MPa. By the micro compression tests, the single crystal specimens show clear shape memory and superelastic behavior. The stress for inducing martensite linearly increases with increasing test temperature and obeys the Clausius-Clapeyron type relationship. By taking into account of the observed slip planes during plastic deformation and the deformability of polycrystal, the dislocation slip is judged to be <111> type, instead of <100> and <101> types. This implies the polycrystalline materials must exhibit room temperature tensile deformability when the intergranular failure is suppressed, similar to B-added Ni3Al. This work is supported by Grant-in-Aid for Scientific Research Kiban S 25220907 from Japan Society for the Promotion of Science.
11:15 AM *PM06.08.08
The Effects of Defects and Microstructure on the Superelasticity of 1:2:2 Ternary Intermetallic Compounds Jan N. Baker1, Keith Duseo2, John Sypek3, Seok-Woo Lee4 and Christopher Weinerberger1; 1Colorado State University, Fort Collins, Colorado, United States; 2University of Connecticut, Storrs, Connecticut, United States.

1:2:2-intermetallic compounds with the ThCr2Si2-type crystal structure have recently been shown to exhibit superelastic responses to hydrostatic, and ε-axial uniaxial compression. It has been shown that the nature of this response can be altered through processing which is associated with the formation of point defects. In this talk, we combine materials theory and DFT to examine the role defects have on the mechanical response and phase stability of two compounds: CaFe2As2 and LaRu2P2. First, we explore the nature of isolated point defects in these materials. Then, we investigate the stability of high densities of these defects. We further investigate the responses of these defected structures using DFT, as well as how these structures, when combined with the pure compounds, alter the responses of these composites. These results are then compared against recent experiments, explaining the processing-microstructure-property relations of differently-fabricated samples. We are able to gain insight into the similarities and differences between two specific 1:2:2-intermetallics.

11:30 AM *PM06.08.09
Utilizing Shape Memory Alloys for Novel, Non-Pneumatic Tire Design Santo Padula and Colin Creager; NASA Glenn Research Center, Cleveland, Ohio, United States.

Conventional mobility elements, such as pneumatic tires, suffer from a number of issues related to reliability. Two of the more prevalent problems are the high likelihood of single point failure owing to puncture (i.e. flat tire), and loss of efficiency due to reduction in tire pressure over time. In order to overcome these limitations, alternative compliant tire designs not requiring pneumatics are being widely investigated. Although current designs have addressed some of the aforementioned issues, many of the designs tend to have their own set of limitations. First, most of the non-pneumatic tires designed for high load applications often have restricted envelopment capability, making their performance less than optimal, especially on uneven terrain. Second, many of the designs that can achieve larger envelopment capability tend to still suffer from large amounts of plasticity (permanent deformation) or failure (rupture). Both of these limitations are the direct result of the choice of material being used for the design; conventional metals undergo plastic deformation at low strain while elastomer-based designs are often too rigid for the localized deformations needed for high envelopment.

Recent advancements at the NASA Glenn research center in a unique class of metals know as shape memory alloys (SMAs) has opened the design space for non-pneumatic compliant tire technologies allowing designs to incorporate orders of magnitude more deformation without damage. The work presented herein highlights the advantages of using SMAs as compared to conventional metals. Additionally, the development of a unique SMA compliant tire design capable of carrying up to 13.2 kN (3000 lbf) with reversible, local deformations on the order of the side wall height will be presented.

SESSION PM06.09: Other Functional Intermetallics
Session Chairs: Yoshisato Kimura and Matthew Willard
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.09.01
Microstructure and Magnetic Properties of τ – MnAl Jan Baker; Dartmouth College, Hanover, New Hampshire, United States.

τ–MnAl adopts an ordered tetragonal L12 crystal structure with two atoms per unit cell. It has a theoretical maximum energy product, (BH)max, of ~100 kJ/m3, which is twice that of AlNiCo magnets, and a density-compensated (BH)max that is almost two-thirds the value for SmCo magnets. It has a magnetocrystalline anisotropy constant, K1, of ~2 MJ/m3, and thus it is of great interest as a permanent magnet. Fortuitously, it is composed of relatively inexpensive elements. It can be made by heating to above 870°C to produce the high-temperature hexagonal ε-phase and then either quenching to room temperature and re-annealing at temperatures up to ~500°C or by simply slow cooling. The transformation introduces anti-phase boundaries, microtwins, stacking faults and dislocations. During the transformation to τ – MnAl it is difficult to avoid some conversion to the equilibrium trigonal γ2 (Al8Mn5) and complex cubic β-Mn phases.

In this presentation, we will outline a variety of MnAl processing routes including gas atomization, rapid solidification processing using the Pratt and Whitney RSR process, and casting followed by pulverization to produce MnAl powders. The resulting particulates were mechanically milled to produce MnAl powders. The results will be compared with the magnetic properties obtained after various bulk and powder processing techniques.

2:00 PM *PM06.09.02
First-Principles Assessment of Nd-Fe-B Thermodynamic Properties for Application in CALPHAD Adrie Tri Hanindrino1, Soumya Sridar2, K.C. Hari Kumar2, Kenta Hongo3 and Ryo Maazono2; 1Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, Nomi, Japan; 2School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; 3Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; 4Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, India.

The Nd-Fe-B system is of great interest in the field of magnetic materials. Currently commercially available, powerful permanent magnets use the ternary phase Nd2Fe14B as a base due to its high degree of magnetisation and relatively robust coercivity. The knowledge of phase equilibria and thermochemical properties of Nd-Fe-B system is therefore of great value in the context of optimization of alloy chemistry, manufacturing and application of magnetic materials based on this system.

The CALPHAD method of computational thermodynamics provides a framework to obtain phase equilibria information and thermochemical properties of materials in a cost-effective and efficient manner. The method relies on Gibbs energy functions of constituent phases, which are generated using thermodynamic modeling. Here first-principles calculations of thermodynamic properties can play an important role by means of providing crucial input data required for thermodynamic modeling. These data include formation enthalpy and heat capacity at constant pressure (Cv) for selected phases.
Contribution of localized 3d/4f orbitals, which is very important for the system in question, presents a challenge for the \textit{ab initio} framework stemming from exchange-correlation approximation. Mott insulators are also a well-known example of this issue, of the ‘strongly correlated’ class of materials. To address this challenge, we implement a simplified Hubbard correction under the Density Functional Theory (DFT) framework. We show that this DFT+U method results in relatively reliable values of formation enthalpy, certainly more so than classical exchange-correlation approximation (non-corrected). In order to obtain the phonon frequencies, the forces acting on the atoms in the perturbed supercell are calculated using DFT. \( C_\text{p} \) is then evaluated under the quasi-harmonic approximation (QHA) to account for volume dependence of phonon frequencies. In contrast to the available data, we find that the computed values deviate considerably from Neumann-Kopp rule. These computational results are expected to improve the reliability of Gibbs energy functions obtained by CALPHAD approach.

2:15 PM PM06.09.03
Influence of Thermo-Mechanical History on Disorder \textendash Order Transformation in 18 Carat Red Gold Alloys Marina Garcia Gonzalez1, 2, Nadine Baluc1, Steven Van Petegem1 and Helena Van Swygenhoven-Moens1, 2; 1Paul Scherrer Institute, VILLIGEN, Switzerland; 2IMX - NXMM, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; 3SPH-ENS, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Residual stress management is a major concern during the processing of 18 carat Au-Cu-Ag red gold alloys. Depending on the thermo-mechanical history and chemical composition of these precious alloys, residual stresses cause reduced workability, shape distortions and eventually fracture. The solid state disorder/order phase transformation forming \( \text{Au}_2\text{Cu}_3\text{Sn}_5 \) nano-precipitates lies at the origin of the problems.

18 carat red gold is an age-hardenable alloy which hardens via chemical ordering. Above the critical temperature (~350°C) the alloy shows a chemically disordered FCC structure. However, below this temperature, chemical ordering takes place and a dispersion of harder nano-precipitates of \( \text{Au}_2\text{Cu}_3\text{Sn}_5 \) phase starts to form. This causes a tetragonal distortion of the initial cubic lattice and induces strong misfit strains. Order/disorder phase transformations are diffusional; therefore, any industrial process that affects the vacancy density and its distribution (such as thermal treatments and plastic deformation) may influence the kinetics of precipitation. This implies that the final microstructure and volume fraction of the ordered precipitates will depend on the history of thermo-mechanical operations.

Our study investigates how thermal parameters and plastic deformation affect the ordering kinetics and the microstructure of the precipitates, with the aim of understanding the link between precipitation and residual stress. \textit{In-situ} x-ray diffraction experiments during cooling are performed at the P07 beam line in PETRA III (DESY, Germany). Diffraction patterns were recorded during cooling, using cooling rates between 100 and 800 K/min. Subsequently, the samples were isothermally aged with and without prior plastic deformation. Rietveld refinement is performed to derive the volume fraction of precipitates. By applying the isothermal JMAEK model, the reaction rates and activation energies are obtained. The results are discussed in terms of the thermo-mechanical history.

2:30 PM PM06.09.04
Microstructure Characterisation of Ni-75 at.% Al Raney Type Alloy as a Result of Cooling Rate and Chromium Doping Naveed Hussain1 and Andrew M. Nullis; University of Leeds, Leeds, United Kingdom.

The effect of cooling rate on the phase composition of gas atomized Raney type catalysts was studied using the Ni-75 at.% Al composition. The resulting particles were sieved into 3 standard size fractions and analysed using XRD with Rietveld refinement: as expected the three phases, \( \text{Al}_2\text{Ni}, \text{Al}_3\text{Ni}, \) and \( \text{Al}-\text{Al}_3\text{Ni} \) eutectic were identified. Differing phase compositions in the 3 size ranges were identified which offer a possible explanation for varying catalytic activity with cooling rate. With increasing particle size, there is more \( \text{Al}_3\text{Ni} \) and less \( \text{Al}_2\text{Ni} \). The amount of \( \text{Al} \) eutectic also decreases as the particle size increases. This agrees with the expectation that the higher cooling rates experienced by the smaller droplets allow less time for the peritectic conversion of \( \text{Al}_2\text{Ni} \) to \( \text{Al}_3\text{Ni} \) to proceed. This in turn results in a more \( \text{Al} \)-rich residual liquid, increasing the volume fraction of eutectic. This was further confirmed when analysing the microstructure using SEM backscatter imaging. \( \text{Al}_2\text{Ni} \) was found to be encased in a shell of \( \text{Al}_3\text{Ni} \) characteristic of peritectic reactions. The remainder of the alloy was found to consist of \( \text{Al}_3\text{Ni} \) eutectic. The SEM backscatter imaging also indicated that the larger particles, experiencing slower cooling rate, had a less dendritic and a more globular structure than the smaller particles. Similar Raney type Ni-75 at.% Al doped with 1.5 at.% Cr were synthesised using the same method and sieved into the three standard size fractions. It was found that the Cr doped alloys exhibited a more dendritic character than the undoped samples in the corresponding size fraction, although the material still displayed an increasingly dendritic character with increasing cooling rate. The phase composition found by Rietveld refinement also followed a similar trend to the undoped samples with decreasing amounts of \( \text{Al}_2\text{Ni} \) formed at the higher cooling rates. However, significant amounts of an additional phase, \( \text{Al}_3\text{Cr}_2 \), were also observed. Rietveld refinement found that a larger amount of \( \text{Al}_3\text{Cr}_2 \) was present than could be accounted for by the addition of 1.5 at.% Cr. This can be explained by the substitution of Ni onto the Cr lattice, as confirmed by Rietveld refinement. \( \text{Al}_3\text{Cr}_2 \) was found to be located mostly at the boundary of the \( \text{Al}_3\text{Ni} \) and \( \text{Al}-\text{Al}_3\text{Ni} \) eutectic phases during elemental mapping and quantitative image analysis of backscattered electron micrographs. This indicates that precipitation of \( \text{Al}_3\text{Cr}_2 \) is towards the end of the solidification process. The relatively large amounts of the \( \text{Al} \)-rich \( \text{Al}_3\text{Cr}_2 \) may explain the enhanced catalytic activity observed following leaching of Cr-doped Raney catalysts.

2:45 PM PM06.09.05
Nb/Sn Coatings for Next Generation Particle Accelerators Michael J. Kelley1, Uttar Pudasaini1, James Tuggle2, Grigory Eremeev3 and Charles Reece4; 1College of William & Mary, Williamsburg, Virginia, United States; 2Virginia Tech, Blacksburg, Virginia, United States; 3Thomas Jefferson Laboratory, Newport News, Virginia, United States.

Nb/Sn has the potential to achieve superior performance in terms of quality factor, accelerating gradient and operating temperature (4.2 K vs 2 K) resulting in significant reduction in both capital and operating costs compared to traditional niobium SRF accelerator cavities. Tin vapor diffusion coating of Nb/Sn on niobium appears to be a simple, yet most efficient technique so far to fabricate such cavities. Here, cavity interior surface coatings are obtained by a process of nucleation followed by deposition. The first step is normally accomplished with Sn/SnCl4 at a constant low temperature (~500 °C) for several hours. To elucidate the role of this step, we systematically studied the niobium surface nucleated under varying process conditions. The surfaces obtained in typical tin/tin chloride processes were characterized using SEM/EDS, AFM, XPS, SAM and TEM. Examination of the surfaces nucleated under the standard conditions revealed not only tin particles, but also tin film on the surfaces All the nucleation attempted with SnCl2 yielded better uniformity of Nb/Sn coating compared to coating obtained without nucleation, which often included random patchy regions with irregular grain structure. Even though the variation of nucleation parameters was able to produce different surfaces following nucleation, no evidence was found for any significant impact on the final coating. Coatings cross-sectioned by FIB and examined by EBSD showed columnar structure. Composition measurement by XPS sputter profile showed constant Nb/Sn composition except adjacent to the interface. Examination of overcoated samples by FIB/EBSD showed growth by formation of new grains at the interface.

3:00 PM BREAK
Phase Evolution of Nanostructured Fe-Si-Al-Based Intermetallic Phases in Soft Magnetic Alloys Matthew A. Willard, Maria Danil, Rajesh Jha, David Grimmer, Aaron Stehner and Cristian Ciobanu; Case Western Reserve University, Cleveland, Ohio, United States; 2Colorado School of Mines, Golden, Colorado, United States; 3Bard High School Early College, Cleveland, Ohio, United States.

Nano crystalline soft magnetic materials are the latest and most promising of the soft magnetic materials that were developed at the end of the 20th century. They have since been studied extensively, and various alloy compositions have been developed and optimized for ambient and extreme (cryogenic and elevated temperature) applications. Their advantage lies in the unique combination of fine microstructure, crystal structure and composition, which can be achieved by rapid solidification and subsequent controlled annealing. In this article, we discuss the requirements and the characteristics of the designing these alloys and how it affects the crystal structure, microstructure and eventually the magnetic performance of new alloys designed for use at temperatures below 150K in applications such as cryo-power electronics and magnetic shielding. Efforts to use computational materials science to accelerate the alloy design process will be discussed.

Composition Dependency of Thermoelectric Properties in Ca-Mg-Si System Using Thin Films Prepared by RF Magnetron Sputtering Method Hiroshi Funakubo, Mutsuo Uehara, Mao Kurokawa, Atsuo Katagiri, Kensuke Akiyama, Takao Shimizu, Masaaki Matsuume, Hiroshi Uchiwa and Yoshisato Kimura; 1Tokyo Institute of Technology, Yokohama, Japan; 2Kanagawa Institute of Industrial Science and Technology, Ebina, Japan; 3Sophia University, Tokyo, Japan.

Ca-Mg-Si ternary system consists of abundant and non-toxic elements. This system includes MgSi that reported to show good thermoelectric properties and realize both p- and n-type conduction. CaMgSi is expected to show good thermoelectric properties. However, the investigation of the thermoelectric property in Ca-Mg-Si system is limited to the narrow composition region. Investigation for wide composition region, possibility of the composition dependency in the sinterability remains a problem to evaluate the thermoelectric property in case of the sintered body. To overcome this problem, we selected thin films that can make dense samples for wide range of composition. In the present study, films of Ca-Mg-Si system were prepared by RF magnetron sputtering system and thermoelectric properties were investigated for wide composition region. Films with wide composition range were successfully obtained on (001)Al2O3 substrates at the deposition temperature of 260-340 °C using Mg target with various numbers of Ca and Si chips. Obtained films were post heat treated at 500-700 °C under the 5% hydrogen included argon atmosphere. Conductivity type of the films mainly changed by the Ca/(Ca+Mg+Si) ratio of the films and p-type and n-type conduction were observed below 0.6 and above 0.7, respectively. Single phases of CaMgSi and CaMg22Si were successfully obtained and showed p-type. Maximum power factor of 0.15 mW/(mk2) at 400 °C was obtained for the films with Ca:Mg:Si = 0.2:0.2:0.6. In our presentation, we show the systematic data of the crystal structure and thermoelectric properties as a function of film composition.

Enhancing Thermoelectric Properties through Control of Nickel Interstitials and Phase Separation in Heusler/Half-Heusler TiNi1.1Sn Composites Emily E. Levin, Francesca Long, Jason Douglas, Malinda Buffon, Leo Lamontagne, Tresa Pollock and Ram Seshadri; University of California, Santa Barbara, California, United States.

Heusler intermetallics, including compounds crystallizing in the F–43m half-Heusler and Fm–3m full-Heusler crystal structures, are known for their diverse functional properties, a consequence of their wide chemical tunability. At intermediate compositions between the half-Heusler and full-Heusler, some systems appear to phase separate while others form complete solid solutions. This differing behavior constitutes an additional tuning parameter in the development of these compounds as functional materials. Here we discuss the half-Heusler/Heusler system Ti(1−x)NiSn (0 ≤ x ≤ 1) where a driving force for phase separation exists. However, we have found that appropriate heat treatment can trap Ni interstitials by design, in order to strongly accentuate the thermoelectric properties.[1] Rietveld analysis of synchrotron X-ray diffraction confirms the incorporation of Ni interstitials into the half-Heusler, and electron microscopy illustrates the evolution of microstructure with heat treatments. Half-Heusler samples with Ni interstitials display an enhanced Seebeck coefficient due to potential in-gap states and modification of the carrier concentration,[2] leading to an improved power factor. Furthermore, Ni interstitials act as point defects, scattering phonons and reducing thermal conductivity, leading to over fivefold increase in room temperature figure of merit compared to homogenized TiNi1Sn. Further annealing at low temperature allows the excess Ni to diffuse, forming full-Heusler nanocrystallites which also act to scatter phonons and lead to over 2× increase in the figure of merit as compared to homogenized TiNi1Sn.


Kinetic Analysis of Crystallization Reaction Within Co-Sn Alloy Muna S. Khushaim, Fatimah Alahmary, Ahmad Al-Joraid and Torben Boll; 1Taihahu University, Ahmedabad, India; 2King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 3Karlsruhe Institute of Technology–Institute for Applied Materials, Karlsruhe, Germany.

Co-Sn alloy is an important system for Sn-based anode materials of lithium ions batteries due to the different interesting intermetallic compounds nucleate and grow during crystallization reaction. These compounds are: CoSn, CoSn2 and CoSn3. These intermetallic compounds, which are containing Sn, are important as anode materials in order to provide a means for efficient Li storage. Co–Sn alloys are applied in specific high-tech applications; and hence study the kinetics of the crystallization reaction of this system and the dependency of the activation energy for crystallization of different intermetallic phases on the temperature might provide a method to control the reaction and the synthesized products. Moreover, a critical knowledge about the growth mechanism will assist in the understanding of the of the melting – solidification region within Co-Sn system. In this study, Co–Sn alloy with ratio of approximately 1:3 were prepared by using metal flux method using arc-melter technique. Microstructure characterizations of the samples have been done by using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The alloy was heated under a non-isothermal condition by using differential scanning calorimetry (DSC) at different heating rates. After observing the exothermic changes which indicate to the crystallization of different intermetallic phases during the DCS scanning, different isoconversional methods were applied in order to determine the variation of the activation energy of crystallization with temperature. In order to shed light on a segregation of atoms at the interface between the metal flux and different intermetallic phases, and hence understanding the growth mechanism of the observed intermetallic phases, atom probe tomography (APT) is used. Using APT as a sophisticated tool allowed us to obtain a critical knowledge of nano scale evolution of the microstructure and investigate the intermediate steps in the mechanism of flux-grown intermetallic phases. The results obtain from APT analysis in combination with the calculation of the variation of activation energies of different
intermetallic phases with the temperature provide new combined methods to investigate the kinetic of crystallization reaction within Co-Sn alloy.

4:45 PM PM06.09.10
Room Temperature High Pressure Hydrogen Storage in Mg2Ni Nanoparticles Decorated Frustule-Nitrogen Doped Graphene
S. Ramaprabhu and Sai Smruti Samantaray; Indian Institute of Technology Madras, Chennai, India.

Hydrogen as an alternative energy carrier is a promising solution for reducing CO2 emissions and its related adverse effects on the environment. However, lack of an economically viable, safe and efficient storage method is a significant barrier between its production and use. This problem arises mainly due to the low energy per unit volume of hydrogen under ambient conditions. Hydrogen storage in metal hydrides is a better option in comparison to the conventional hydrogen storage methods in terms of safety, but the requirement of high temperatures for the dissolution of the adsorbed hydrogen is disadvantageous. Magnesium based materials have the potential as good hydrogen storage materials and have been widely investigated. But, their practical utilization is hindered by poor thermodynamics and sluggish dehydrogenation kinetics. With the aim of overcoming this barrier, we have synthesized low cost Mg based alloy nanoparticles decorated frustule –nitrogen doped graphene (Mg2Ni-N-D-G) and investigated its hydrogen storage properties. The underlying hydrogen storage mechanism in the synthesized nanocomposite is the spillover effect. Mg2Ni decorated nitrogen doped graphene (Mg2Ni-N-G) systems have been previously studied in our laboratory and a hydrogen storage capacity of ~4 wt% at room temperature and moderate hydrogen equilibrium pressures has been obtained. Combining this with the unique physical and chemical properties of diatom frustules such as large surface area, chemical inertness and good porosity has proved to be fruitful for hydrogen storage. Hence, the synthesized nanocomposite Mg2Ni-N-D-G is explored as a potential hydrogen storage material to obtain a gravimetric density of ~ 5wt% at room temperature and moderate hydrogen pressure.

SYMPOSIUM PM07

Plasma-Based Synthesis, Processing and Characterization of Novel Materials for Advanced Applications
November 26 - November 28, 2018

Symposium Organizers
Davide Mariotti, Ulster University
Tomohiro Nozaki, Tokyo Institute of Technology
Mohan Sankaran, Case Western Reserve University
Chi-Chin Wu, U.S. Army Research Laboratory

* Invited Paper

SESSION PM07.01: Carbon and Organic Materials
Session Chairs: Sumit Agarwal and Mariadriana Creatore
Monday Morning, November 26, 2018
Hynes, Level 1, Room 107

8:30 AM *PM07.01.01
Mass-Production of CNT Materials from Gas Phase Chemical Vapour Deposition and Microwave Plasma
Brian Graves, Fiona Smail and Adam Boies; Engineering, University of Cambridge, Cambridge, United Kingdom.

The exceptional mechanical, thermal, and electrical performance of carbon nanotubes (CNTs) makes them ideal for a wide range of applications, however they are costly to produce and difficult to integrate effectively with other materials. We have developed several continuous gas phase CVD processes that can synthesize novel CNT bulk-produced materials at high mass-throughput.

The presentation will demonstrate how CNTs can be grown and synthesized into macroscopic materials using continuous gas phase processes. In a tube furnace, CNTs are grown with gas phase CVD from catalyst particles comprised of a transition metal and sulphur. As the CNTs increase in length and number concentration, they agglomerate to form an aerogel which can be extracted continuously from the reactor. The self-assembled CNT structure can be wound to form fibres and mats which can be easily integrated into composites, wires, and heat pipes, among many other applications. New developments of this process will be discussed along with the properties and applications of the resulting CNT materials.

We are also currently working towards replicating this aerogelation process with a microwave plasma reactor, in which we have previously synthesized a metal oxide – CNT composite material for the anodes of lithium ion batteries. This plasma-based process exhibits several key advantages over other techniques. The extremely high temperature of the plasma permits vaporization of a wide range of precursor materials, including those in powdered, elemental form which are ideal for an industrial process since they are cheap and readily available. The plasma also has a high energy density, meaning that a large mass throughput can be achieved with a small system. Large-scale production of these materials with this method could contribute to significant advances in materials for an array of engineering fields.

9:00 AM PM07.01.02
Plasma Activation of Carbon Fiber Reinforced Thermoplastics
Trey Oldham1, Daniel R. Ferriell2, Marcus A. (Tony) Belcher2, Alexander Rubin2 and Elijah Thimsen1; 1Washington University in St. Louis, Saint Louis, Missouri, United States; 2The Boeing Company, St. Louis, Mississippi, United States.
Carbon fiber reinforced thermoplastic (CFRTP) composites are a platform material for structural applications due to their high fracture toughness, lightweight, and chemical resistance. However, the chemical inertness of the thermoplastic hinders the material’s ability to robustly bond to form structural assemblies. Non-thermal plasma treatments of CFRTP composites have been shown to overcome this limitation by producing an activated surface. The highly reactive surface comprised of ions and radicals is intrinsically unstable, resulting in the deterioration of the activation state over time. The ability to characterize the activation state is of significant importance in terms of quality control of bonded structural assemblies. In this work, a novel, non-destructive method of determining the activation state of plasma-treated surfaces was discovered using Kelvin probe force microscopy (KPFM) surface potential measurements. Activated surfaces are characterized by a sharp, well-defined surface potential distribution. The sharp peak is hypothesized to be due to the presence of quasi-stable radical-ion complexes. Plasma-treated CFRTP surfaces being uniformly comprised of anionic and radicalic species is supported by KPFM, contact angle, magnetic force microscopy (MFM), and radical scavenger experiments. Radical-anion complexes are only stabilized when both species are present (i.e., radicals readily react in the absence of anions and vice versa). Evidence in support of radical-anion stabilized complexes was observed by a decrease in radical scavenging activity of a plasma-treated sample which had been charge-neutralized compared to non-neutralized plasma-treated sample. MFM measurements provide an independent verification of this result.

9:15 AM OPEN DISCUSSION

9:30 AM PM07.01.04
Effect of Airborne Contaminants on Plasma-Induced N-Doping of Graphene Films Germain Robert Bigras, Xavier Glad, Richard Martel and Luc Stafford; Université de Montréal, Montréal, Quebec, Canada.

Graphene has been extensively studied thanks to its promises for the next generation of electronic and optoelectronic devices [1]. The availability of versatile post-processing techniques of graphene is mandatory for applications in which properties of pristine graphene are insufficient. In recent years, various methods, including plasma-based approaches, have been explored to tune the doping with nitrogen atoms of graphene films as a means of either increasing the electron density or inducing a band gap [2]. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. Studies often blindly aim at increasing the nitrogen content while minimizing defect generation. In addition, very few measures are taken into account to control the gas phase impurities. Even for freshly grown graphene, Li et al. [3] showed that the graphene receive a strong variation of its hydrophobicity within days due to the deposition of hydrocarbons on the surface. Analysis of the N-doping dynamics must therefore discriminate if N- incorporation occurs in the airborne contaminants or in the graphene lattice itself.

In this work, we explore the potential of the late afterglow of a microwave N₂ plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils. The low ion density (< 10⁴ cm⁻³) and the high density of reactive neutrals (> 10¹⁴ cm⁻³) and metastable species (> 10¹⁰ cm⁻³) of the nitrogen late-afterglow [4] are believed to enhance chemically driven surface reactions over purely physical ion bombardment. Therefore, enhanced functionalization at the surface is expected due to interactions between nitrogen and the hydrocarbons. In addition, the tunable nature of the nitrogen afterglow allows the exposition of the sample to a continuum of environments; from damaging conditions (Early afterglow - EA) to a milder region (Late Afterglow - LA).

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/(N+C+O) = 19% for LA and 49% for EA) while RS assessed an uncommonly low damage generation (D:G ≈ 0.4 for LA and D:G ≈ 1.3 for EA) for such incorporation. Transfer towards SiO₂ substrate reveals the loss of a strong proportion (80%) of weakly bonded nitrogen moieties for LA-treated graphene. This can be explained by a significant incorporation of N atoms within the hydrocarbon layer.


9:45 AM PM07.01.05
Roll-to-Roll Vacuum Deposition of Polymers with In-Line Curing—A Comparison of Two Curing Sources (Plasma and Electron Beam) Carmen Alonso Herr and Hazel Assender; 1University of Oxford, Oxford, United Kingdom.

The high-speed roll-to-roll deposition of smooth, thin layers of polymer in vacuum, by flash evaporation of the monomer followed by radiation curing, is useful for smoothing and topcoat layers (e.g. for high performance gas barrier films) as well as dielectric for capacitors and OTFTs. The properties of a diacrylate (TPGDA), deposited using different curing sources (plasma and electron beam, both which are used commercially for in-vacuum polymer layer deposition) have been studied, both with the layer attached to the polymer substrate, and by removing the thin film from the substrate to study the properties of free-standing films. The degree of cure, which determines mechanical, adhesion and stability properties for example, has been measured by FTIR-ATR and by Soxhlet extraction to reveal the relative contributions of free monomer and ‘dangling ends’ in the network. This degree of cure, and the film thickness (by ellipsometry), mechanical properties (by dynamic mechanical thermal analysis) and surface topography (by AFM) have been characterized as a function of process parameters, and a comparison has been made between the two curing sources. A model is proposed to describe the differences: for plasma curing density of reactive species created is independent of the layer thickness, and hence the degree of cure depends primarily upon the flux of radiation. In contrast for E-Beam cured samples, the number of reaction centres created depends primarily on the thickness of the coating. Such an understanding of the curing leads us to link the process parameters with other polymer’s properties, which is relevant especially when creating multilayers such as barrier coatings or devices for organic electronics.

10:00 AM BREAK
The ever-increasing demand for high-quality nanosized materials coming from many industrial and research fields has spurred the research on viable methods for their synthesis. In the first part of the talk, RF inductively coupled plasmas for nanoparticle synthesis will be introduced as an effective tool for the continuous production of nanoparticles at high throughput. This technology has encountered the interest of many industrial nanoparticle producers thanks to its distinctive features such as high energy density, high chemical reactivity, high process purity, large plasma volume and long residence time; also, RF synthesis of nanoparticles benefits from the large number of available process variables (e.g. power, frequency, process gases, phase of the precursor and system geometry) that ensure the versatility of the process and from the high cooling rate ($10^{-3}$--$10^{-5}$ K/s) in the tail of the plasma, that allows to produce tailored nanoparticles with a narrow particle size distribution (PSD). During the talk, advantages and disadvantages of the technology will be introduced, focusing, in particular, on the challenges posed by up-scaling. The use of modeling instruments as supporting tools for the design and engineering of industrial-scale high-throughput thermal plasma systems for nanoparticle synthesis will be discussed [1, 2]. The second part of the talk will deal with Cold Atmospheric Plasmas (CAPs) as the centerpiece of a family of simple and environmentally friendly methods for the synthesis and modification of nanostructures in liquid environments [3]. Results highlighting the role of the chemical composition of the liquid environment (either NaCl + NaOH or NaCl only, dissolved in distilled water) on the characteristics of the produced nanoparticles will be presented. Furthermore, the possibility of synthesizing nanoparticles from a nebulized solution containing metallic salts will be discussed; an applicable example, where this process is employed to produce an antibacterial coating composed of a layer of antibacterial silver nanoparticles embedded within two polymeric thin films, will also be provided. A similar approach, simultaneously depositing silver nanoparticles and a polymeric matrix, will be presented as well [4].

References

Work partially supported by European Union’s Horizon 2020 research and innovation program under grant agreement No 646155 (INSPIRED project)

11:00 AM PM07.02.02
Ultra-Small Metallic Nanocrystals Synthesis from Solid Wire Precursors via an Atmospheric Pressure Microplasma Bruno Alessi, Atta ul Haq, Dilli Babu Padmanaban, Paul Maguire and Davide Mariotti; University of Ulster, Newtownabbey, United Kingdom.

Metal nanoparticles are interesting for a wide range of scientific fields. Particles with diameters ranging from 10 nm up to hundreds of nanometers exhibit attractive properties for various applications (e.g. catalysis, chemical sensors etc.). Some of the most studied characteristics are for instance related to the possibility of tuning localized surface plasmon resonance, which depends on the nanoparticle size, shape and surrounding environment. Meanwhile, particles with diameters below 10 nm down to and below 1 nm, approach a new regime and can in some cases associated to large molecular clusters, with properties of interest to electronics and semiconductor science. Model calculations for such metallic quantum dots predict, depending on the composition, the opening of the energy bandgap and the consequent appearance of photoluminescence effects. However, most of the synthesis methods that yield narrow size distributions employ high vacuum methods or use surfactants to sterically control particle size during their synthesis. Atmospheric pressure microplasmas recently revealed their value for nanomaterial synthesis. Microplasmas simultaneously offer a cheap alternative to low pressure plasmas and some unique peculiarities. For example, the high ratio of energetic electrons allows activating chemical reactions which are otherwise hard to achieve. These plasmas at atmospheric pressure typically show also high electron densities and enhanced rate of ion-neutral interactions, which are mainly responsible for charging and selective heating of particles inside a plasma. The former preventing agglomeration of particles and the latter allowing to achieve higher particle temperatures compared to the gas background. A clear advantage of microplasmas for nanomaterial synthesis is the small residence time of nucleating particles inside the active plasma region, which can be reached with a flow-through type reactor. Moreover, samples can be easily prepared either as evenly dispersed colloids or as solid films of stacked particles.

In the current work, ultra-small metallic nanocrystals, or quantum dots (below 5 nm) of different elements such as tin, copper, bismuth and others have been produced with a gas phase atmospheric pressure microplasma using the corresponding solid bulk form as precursor; we discuss material characterization as well as the potential underlying mechanism of formation supported by a few different experimental plasma diagnostics.

References

11:15 AM PM07.02.03
Low Temperature Plasma Synthesis of III-V Stibnide and Nitride Nanocrystals from Bulk Metals Necip B. Uner and Elijah Thimsen; Washington University in St. Louis, Saint Louis, Missouri, United States.

Low temperature plasma (LTP) is a unique gas-phase synthesis tool for various forms of nanomaterials. The nonequilibrium environment in the LTPs has been utilized to synthesize many semiconductor nanocrystals in tubular flow-through reactors by using suitable vapor precursors. These materials mostly comprise Si, Ge, various sulfides and oxides. III-V semiconductors, which constitute an important family of materials for optoelectronic applications, haven’t been explored as well. Although reports on the synthesis of InP and GaN have been reported, stibnides and nitrides currently don’t have an established method of synthesis that yields high quality nanocrystals. In this work, we present a general plasma synthesis route for bare nanocrystals of GaSb and GaN. The method diverges from the previously reported syntheses of semiconductor nanocrystals, since use of vapor precursors is avoided. Instead, aerosols of constituent metals are generated in evaporation and condensation sources. These aerosols of Ga, Sb and gaseous nitrogen bearing species were used as precursors. Produced aerosols are mixed and then sent into a flow-through Ar LTP reactor. Aerosols vaporize inside the LTP and the generated vapor re-forms the compound semiconductor by way of nucleation and condensation [1]. Since particles obtain unipolar negative charge inside the LTP, Coulombic repulsion prevented the formation of agglomerates. Synthesized particles were verified to be free-standing and crystalline via transmission electron microscopy. Furthermore, particles were mixed on atomic scale. Stoichiometry was found to be adjustable by manipulating the input aerosol concentrations and input plasma power. In addition to results on reactor operation and on extensive ex-situ characterization of materials by means of electron microscopy and x-ray diffraction, functionalization of the produced nanocrystals by surfactants and the resulting photoluminescent properties of the materials will be presented.

References
At the present stage of nanotechnology development nanoparticles are considered as important building blocks for the construction of nanodevices with working parameters exceeding those of the bulk analogs. Therefore, to reach the distinctive properties of nanoparticles the development of the controlled synthesis procedures that enable tuning the particles parameters during the preparation is now considered to be crucial. Among the nanoparticles fabrication methods plasma-assisted techniques that imply the combination of top-down and bottom-up approaches, are considered to be promising for controlled fabrication and targeted modification of nanoparticles parameters such as size distribution, phase composition, inner structure and surface chemistry. The present paper summarizes the developed plasma and laser-assisted approaches focusing on the controlled fabrication and modification of nanoparticles of different composition and morphology.

Several plasma-assisted techniques were used in the experiments: electrical discharge in liquids, plasma generated in contact with liquid, laser ablation in liquid and laser irradiation of colloidal solutions. Studying the influence of liquid composition on the particles properties it has been found that electrical discharge and laser ablation in non-reactive liquids can be used for effective fabrication of metallic and semiconductor (Si, Ge) nanoparticles. In contrast, plasma generation in reactive liquids by electrical discharge or laser ablation can be simple but effective route for binary nanoparticles synthesis.

For the effective fabrication of composite nanoparticles the combined laser-plasma approaches have been developed. One of them is based on the sequential laser ablation of targets in liquids that can be used as a tool to prepare binary or ternary nanocomposites as well as for the doping of nanocrystals. Another route of the compound nanoparticles preparation is based on the laser treatment of the nanoparticles mixtures. Special attention has been paid to the production of metastable alloys as their formation is favorable under the conditions of dense plasma with high temperature and pressure.

For this, the combined plasma-laser approach based on electrical discharge treatment of the micropowders suspension in liquids with subsequent laser irradiation of the formed colloids has been developed that has been shown to be suitable for fabrication of Cu-Zn, Ag-Cu, Ge-Sn and Si-Sn alloys as well as binary and ternary compounds, such as GdSi2, GdSi2Ge and CuInSe2. The surface chemistry of the prepared nanoparticles can be additionally adjusted by treatment of the prepared colloid by plasma in contact with liquid. This method was demonstrated to be effective for the improvement of the luminescent efficiency of the carbon and silicon quantum dots promising for photovoltaic and biomedical applications.
number of 4-fold coordinated dopant atoms are located within the core of the nanoparticle to explain their plasmonic resonance. Furthermore, we find that low-temperature annealing of these nanocrystals produces an apparent increase in the concentrations of dopant atoms within the nanocrystal core. K. Hunter acknowledges support by the National Science Foundation Graduate Research Fellowship Program under Grant No. 00039202. This work was supported primarily by the U.S. National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program. The use of beamline 11-ID-B of the Advanced Photon Source, a U.S. Department of Energy (DOE), Office of Science User Facility, operated for the DOE Office of Science by Argonne National Laboratory was facilitated under Contract No. DE-AC02-06CH11357.

2:15 PM PM07.03.03
Synthesis of Silicon Nanoparticles in a Low Pressure Microwave Plasma Reactor on a Pilot Plant Scale—Characterization of Particle Growth and Influence of Different Process Conditions on Particle Characteristics

Fredrik Künze, Stefan Kuns, Mathias Spree, Tim Huesler, Hartmut Wiggers and Sophie M. Schnurri, IUTA, Institut für Energie- und Umwelttechnik e.V., Duisburg, Germany; JIV, Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, Duisburg, Germany; CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany.

Within the last years, numerous research results have indicated that nano-sized silicon can be used for a multitude of different applications. Especially its size-dependent properties such as limited phonon transport (in thermoelectric devices), structural flexibility (for battery applications) or quantum-confined optical properties (for optical applications) are of high interest. Gas-phase synthesis is a suitable method for the continuous production of high amounts of specific nanoparticles, which enables applications based on highly-pure nanostructured materials. Up to now, microwave plasma reactor processes have mainly been investigated on the laboratory scale and only a few very approaches were dealing with scaling to higher production rates. Therefore, microwave supported plasma reactors are not yet regarded as a competitive manufacturing method to produce high amounts of nanoparticles with consistent high quality.

In this work, a microwave plasma reactor is used for the generation of silicon nanoparticles from gaseous monosilane (SiH4) at the pilot scale. The reactor uses a microwave frequency of 915 MHz and a microwave power up to 50 kW in contrast to 2.45 GHz and 6 kW on the laboratory scale. It will be shown that this reactor enables the formation of highly crystalline and either soft-agglomerated or hard-agglomerated silicon nanoparticles depending on the process conditions. In order to characterize the growth process of the particles within the plasma reactor, samples of particles were extracted directly from the gas phase at different distances from the plasma utilizing high-speed thermophoretic sampling. Furthermore, the systematic investigation of process conditions reveals that the particle size and aggregation can be independently controlled by a selective adjustment of the process conditions. It was identified that a higher gas outlet velocity of the nozzle results in a reduced residence time, thus leading to shorter growth time and smaller particles. In contrast, an increase in SiH4 concentration up to 48 vol.% does not lead to further growth of isolated primary particles but promotes aggregate formation from smaller primary particles. In addition, it is shown that we are able to run a production process with consistently good quality of the silicon nanoparticles at high production rates of up to 200 g/h. Therefore, a full-day synthesis of silicon nanoparticles was performed. Nanoparticles were collected at fixed time intervals during the synthesis period and characterized via BET measurements and TEM images. This continuous sampling allows to detect unwanted changes of the particle characteristics during the synthesis and gives an indication of the long-term stability of the plasma process. The results indicate a stable process for many hours.

The authors gratefully acknowledge the support by the German research foundation (DFG) in scope of the research group 2284 “Model-based scalable gas-phase synthesis of complex nanoparticles”.

2:30 PM *PM07.03.04
Boron and Phosphorus Co-Doped Colloidal Silicon Quantum Dots

Minoru Fujii, Hiroshi Sugimoto and Shinya Kano, Kobe University, Kobe, Japan.

A colloidal solution of Si quantum dots (QDs) is a versatile material for electronics, optoelectronics and biophotonics. Recently, we have developed a new type of all-inorganic Si QDs that can be dispersed in alcohol and water almost perfectly without organic ligands, and exhibit size-dependent luminescence in the near-infrared range in water. The unique property of the QDs arises from the unique structure. The QD has a core-shell structure; the core is heavily B and P codoped crystalline Si and the shell is an amorphous layer composed of B, Si and P. The shell induces negative potential on the surface and prevents agglomeration of Si QDs in polar solvents. Furthermore, isolation of an exciton in a crystalline core from environment by the shell makes the luminescence insensitive to the change of the environment and robust for chemical treatments. To the liquid-free surface of codoped Si QDs, molecules in a solution can access easily, and thus a variety of charge-transfer-induced processes such as a photocatalytic effect and chemical doping are expected. In this presentation, we first discuss the structure of codoped Si QDs based on the data obtained by atom probe tomography and transmission electron microscopy. We then discuss the size dependence of the energy state structure, especially that of the donor and acceptor levels, based on the data obtained by scanning tunneling spectroscopy, photoemission yield spectroscopy and photoluminescence spectroscopy. We then discuss charge transfer interaction between Si QDs and adsorbed molecules, including the photocatalytic activity and chemical doping. We show the formation of a variety of nanocomposites composed of codoped Si QDs and noble metal nanostructures, and discuss the enhanced optical responses due to the coupling with the localized surface plasmon resonances of metal nanostructures. Finally, we discuss the electrical transport property of a Si QDs film produced from the colloidal solution and demonstrate the possible application as electronic devices.

3:00 PM BREAK

SESSION PM07.04: Thin Films, Coatings and ALD I
Session Chairs: David Graves and Chi-Chin Wu
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 107

3:30 PM *PM07.04.01
Low Resistivity HfN Layers by Plasma-Assisted ALD with External rf Substrate Biasing

Mariadriana Creatore; Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands.

In this contribution I will discuss the deposition of HfN by means of plasma-assisted ALD. The process adopts tris(dimethylamino)cyclopentadienylhafnium [CpHf[NMe2]3] as Hf precursor and H2 or Ar/H2 plasmas as reducing co-reactant. Films are found to exhibit...
an electrical resistivity of 9.0 × 10³ Ω cm, in the absence of external substrate biasing [1]. The latter is attributed to the presence of oxygen in the film up to 20 at%, which is responsible for a limited Hf²⁺ fraction of 0.65. First-principles DFT calculations are adopted to explore the underlying mechanisms of O incorporation: chemisorption of H₂O from the reactor background on the bare HfN surface is kinetically and thermodynamically highly feasible, and leads to Hf-OH surface groups. A steady decrease in electrical resistivity down to 3.3 × 10³ Ω cm is observed upon increasing the substrate potential up to -130 V by externally biasing the substrate [2]. The variations in electrical resistivity with the potential correlate with the extent of grain boundary scattering in the films, which significantly decreased upon increasing the potential up to -130 V. The latter is primarily due to major changes in the film chemical composition, namely the decrease in O content to less than 2 at% for a potential of -130 V and an associated increase in the Hf³⁺ fraction up to 0.82. In parallel, DFT calculations reveal that cationic species present in Hf plasma are highly reactive towards the surface – OH groups. An increase in the energy of bombarding cations promotes the dissociation of Hf-OH surface bonds, followed by H₂O formation and desorption. When heavier and more energetic ion bombardment (as generated in an Ar/H₂ plasma) is applied, the electrical resistivity goes down to 4.1 × 10³ Ω cm. It is worth noting that such low resistivity is achieved for films as thin as ~35 nm. Next to a high Hf(III) oxidation state fraction of 0.86±0.02, the key towards the very low resistivity is the suppression of in-grain defect density and nano-porosity in HIN films. Overall, the application of a substrate potential is shown to highly affect the chemical composition, microstructure and the associated electrical properties of the HIN layers.


4:00 PM PM07.04.02
Synthesis of Layered Sulfide Heterostructures via RF Sputtering
Dennise M. Roberto1,2, Sage Bayers2 and Andriy Zakutayev2; University of Colorado-Boulder, Boulder, Colorado, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Deposition of layered chalcogenide materials allows for generation of novel material systems with tunable optical and electronic properties sensitive to changes in both dimensionality and the stacking sequence of constituent compounds. Synthesis of kinetically-controlled products can be achieved by the deposition of an amorphous “initial state” in which thickness and composition are precisely controlled, thus enabling rational study of structure-property relationships as a given material progresses from a monolayer to a more bulk-like state. To date, only selenide and telluride thin films have been demonstrated in this vein. We show the first synthesis of sulfide materials assembled under this framework and generate heterostructures comprised of alternating layers of crystalline MoS₂ and SnS. RF sputtering is utilized to generate thin films of amorphous material in which layer-by-layer control of phase relationships is a given material progressively from a monolayer to a more bulk-like state.

4:15 PM PM07.04.03
AIN Etching Under ICP Cl/BCl3/Ar Plasma Mixture—Experimental Characterization and Plasma Kinetic Modeling
Mohammad Rammal1,2, Ahmed Rifaihi1, Delphine Néel1, Dahlia Make1, Alexandre Shen3 and Abdou Djouadi1,2; 1Institut des Materiaux Jean Rouxel, Nantes, France; 2University of Nantes, Nantes, France; 3III-V Lab, Palaiseau, France.

AlN is one of the III-V materials used in a new generation of electronic and optoelectronic devices especially in high power devices. Indeed, thanks to its good conductivity, it is well qualified to evacuate heat from the devices and thus improves their performance and reliability. One of the challenges is to succeed in the pattern transferring from the mask to AlN material using plasma etching process. Chlorinated plasmas are well tested to etch AlN material. Some studies show that chlorinated plasmas containing only molecular chlorine or with argon is not efficient to properly succeed the etching step in terms of selectivity, anisotropy and surface roughness. The addition of BCl₃ seems to improve the performance of the AlN etching. However, it remains difficult to find the optimal operating conditions that improve the morphological properties of etched AlN structures. In this context, we present experimental results of AlN etching using ICP BCl₃/Cl₂/Ar plasma mixture. The AIN is deposited on Si and InP substrate using DC magnetron sputtering. Then, a SiO₂ patterned hard mask is used to have a selective etching. The etch rate reached is 200 nm/min; with a small problem of microtrenching and a sidewall angle of 75°. This problem can be overcome using simulation in which the optimum etching conditions can be found. In parallel, plasma kinetic model of BCl₃/Cl₂/Ar is developed to study the effects of the reactor parameters such as RF power, pressure and gas flow rates on the neutral and charged species evolution as well as the electron temperature and density. The model is based on the 0D global kinetic model. Mass balance equations of 34 neutrals, negative and positive ions coupled to the charge neutrality equation and power balance equation are established to quantify the species densities and their fluxes onto the substrate surface. Particular attention is given to the analysis of the percentage of BCl₃ gas effect on the reactive species densities involved in the etching processes such as the positive ion and atomic chlorine densities.

4:30 PM PM07.04.04
Surface Reactions During Plasma-Assisted Atomic Layer Deposition of SiN₃
Sumit Agarwal; Colorado School of Mines, Golden, Colorado, United States.

The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for novel atomic layer deposition (ALD) processes for a variety of materials including Si-based dielectrics such as SiN₃. Development of new ALD techniques that can meet the demands for semiconductor manufacturing requires an atomic level understanding of the surface reaction processes. In our lab, we use in situ optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALD.

In this presentation, I will discuss the low-temperature plasma-assisted ALD of SiN₃ films where one of the key challenges has been to grow conformal films in high-aspect-ratio nanostructures such that the sidewall structure and composition is the same as the top surface. I will discuss the surface reactions that occur during ALD of SiN₃ using chlorosilanes and aminosilanes as the Si precursors with an NH₃ and N₂ plasma, respectively, as the nitrogen source. The NH₃ plasma based processes show >95% conformity, but the wet-etch rate in dilute HF is much higher for the sidewalls compared to the planar surface. While N₂ plasma based processes show a low wet-etch rate for both the sidewalls and the planar surface, the conformity is ~50%. Based on these observations, we have developed a new three-step ALD process for SiN₃ growth using Si₂Cl₆ followed by CH₃CN, and then an N₂ plasma. I will show that in this three-step ALD process because nitrogen is supplied to the surface partially in a thermal step followed by an N₂ plasma, the films are more conformal with a sidewall wet etch rate that is intermediate between NH₃ and N₂ plasma based ALD processes.
Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. However, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-4] for directly fabricating narrow GNR arrays with a clear transport gap [5]. Since the establishment of our novel GNR fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98%) is realized [6]. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The improvement of thermal stability of Ni nanobar can be a key to realize the GNR nucleation in our method, which can be given by supplying higher density of carbon plasma to liquid-phase Ni nanobar. The wettability of liquid-phase Ni nanobar against to the SiO2 substrate is also found to be an important factor forming the suspended structure of GNR. It is also revealed that the minimum length of GNR can be decided by the wavelength of Plateau-Rayleigh instability known as a traditional instability of fluid flow. Furthermore, unique optoelectrical property, known as persistent photoconductivity (PPC), is also observed in our suspended GNR devices. By using the PPC, GNR-based non-volatile memory operation is demonstrated. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [7-9] in industrial scale.

References

8:30 AM *PM07.05.01
Bottom up Synthesis and Optoelectrical Application of Suspended Graphene Nanoribbon Arrays in Wafer Scale Toshiaki Kato and Toshiro Kaneko; Tohoku University, Sendai, Japan.

9:00 AM PM07.05.02
Optical-Erasable TiO2 Non-Volatile Memory Using Deep Trap Charges Taewoon Kim1,2, Jung Wook Lim1,3, Seong Hyun Lee1, Jeho Na1, Jiwoon Jeong1, Kwang Hoon Jung1,2, Gayoung Kim1,2 and Sun Jin Yai1,2. 1ICT Materials Research Group, Materials & Components Basic Research Division, Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); 2Advanced Device Engineering, University of Science and Technology, Daejeon, Korea; 3Company of Korea.

Recently, oxide-based metal-oxide-semiconductor field-effect transistors (MOSFETs) have been actively studied for the applications of non-volatile memory devices in transparent and flexible electronic products. Oxide-MOSFETs have much lower off-state leakage current than Si-MOSFETs, allowing low-power memory operation, and further advantages such as good uniformity, low process temperature, and high transmittance in the visible wavelength range. Conventional oxide-based non-volatile memory generally uses positive and negative gate voltage (Vg) pulses to achieve the program and erase states, respectively. However, the n-type nature of most oxide semiconductors makes it difficult to conduct sufficient amounts of holes in the channel oxides, leading to a high power consumption and long erase times; thus input power sources (e.g. light) in addition to voltage are required. In a memory device, the difference between the programming and erasing voltages is known as the “memory window”. In a non-volatile memory, the memory window should be set to secure a sufficient margin of read voltage (V(read)) for stable device operation; wider memory windows can be achieved with more defect sites trapping more charges. However, shallow traps among the defect sites adversely affect device stability. Therefore, it is necessary to selectively exclude shallow trap sites to satisfy both a wide memory window and high device stability.

In this work, we propose TiO2 MOSFET-based non-volatile memory device, employing the deep trap interface (DI) sites as a simple floating gate without tunneling oxide. For the fabrication of TiO2 MOSFET, 80 nm-thick Al2O3 gate dielectric layer on 30 nm-thick TiO2 films were deposited by plasma enhanced atomic layer deposition on a n+ Si wafer which plays a role of back gate. In order to demonstrate performance of TiO2 MOSFET, we measured electrical characteristics of the fabricated devices in the dark and violet light (VL)-irradiated conditions at 25 ºC. For VL irradiation, we used standard LEDs (center wavelength of 400 nm) as a light source with an incident power of 0.13 W/cm². This device demonstrated a high on/off ratio of 103 and a sizable memory window due to deep traps at the interface between Al2O3 and TiO2. Interestingly, irradiation with 400 nm VL could completely restore the program state to the initial state (performing an erasing process) owing to the visible light-sensitive TiO2 channel. Device reproducibility was greatly enhanced by selectively passivating shallow traps using an in-situ H2-plasma treatment. The passivated memory device showed a highly reproducible memory window and on-state current even during a retention bake test at 85 ºC. We expect that our simple-structured TiO2-based non-volatile memory device, which is completely erasable only by light irradiation and shows reproducible and stable operation, will usefully employed in a wide range of future electronic devices.

9:15 AM PM07.05.03
Impact of CMOS TiN Metal Gate Process on Microstructure and Its Correlation with Electrical Properties Pushpendra Kumar1,2,3, Florian Domenge1, Charles Leroux2, Patrice Gergaud2 and Gerard Ghibaudo3; 1STMicroelectronics, Crolles, France; 2CEA-LETI, Grenoble, France; 3Université Grenoble Alpes, Grenoble, France.

TiN metal gate has been introduced in advanced CMOS devices for its advantages such as eliminating Fermi level pinning and phonon scattering, but it also introduces the metal gate granularity due to multiple crystal orientations. This may impact device electrical and physical properties, such as effective
workfunction WF_eff, threshold voltage local variability σV_TH, mechanical stress and sheet resistance. σV_TH might be reduced by reducing the TiN grain size or by obtaining a unique crystal orientation and so we have focused on identifying TiN metal gate process conditions that can achieve this goal. Hence, the impact of RF Physical Vapor Deposition (RF-PVD) parameters, Ar pressure and RF power, on the preferred orientations and size of the TiN crystallites is investigated.

28nm CMOS FDSOI HKMG stack was deposited, consisting of 1 nm SiO2 interfacial layer, 1.8 nm HfSiON High-k layer and 5 nm TiN gate deposited by RF-PVD with combined DC and RF generators. TiN is formed by reactive sputtering of a pure Ti target in a nitrogen-containing ambient of Ar:N2. Ar pressure and RF power were varied over a wide range. The preferred orientations and grain size are determined by X-Ray Diffraction (XRD), in out of plane (0-20) and in-plane configurations respectively. Sheet resistance is measured by 4 probe method and thickness by X-ray-reflectometry (XRR) to calculate TiN deposition rates. Mechanical stress was calculated by applying Stoney’s equation and Ti/N ratio is measured by X-ray fluorescence (XRF).

It is observed that as Ar pressure decreases and RF power increases, average grain size, σTiN <200/>TiN <111>, deposition rate and film mechanical stress increases. For 3 conditions a unique TiN grain orientation is obtained. As the RF power increase and pressure decrease, the number of Ar+ ions and number and energy of sputtered Ti atoms increase. Increased Ti atoms energy enhances crystal growth and favors the preferred orientation <200>, having the lowest energy. Increased Ar+ ions, due to channeling effect, enhances crystal orientation and will re-sputter TiN <111> crystals more than <200>. Increase in Ar+ and Ti number and energy will result in denser films due to peening effect, thus increasing the stress. TiN sheet resistance follows an inverse power law as the grain size is decreased due to an increase in grain boundaries.

EOT and WF_eff were extracted by fitting CV measurements with Poisson Schrödinger simulations for devices with varying EOT. Extrapolation of WF_eff to EOT=0 gives intrinsic TiN workfunction (WF_m) + dipole at SiO2/high-k interface (δ). WF_m change is expected to depend on the % of <200>/(WF_m=4.6eV) or <111> (WF_m=4.4eV). The electrical extraction of WF_m = δ evidences an opposite trend. Our results strongly suggest that WF_m expected shift is hidden by an opposite effect at the SiO2/high-k interface due to the sensitivity of its dipole to TiN process. The Ti/N ratio is playing a major role with a suppression of dipole δ for Ti rich gates.

9:30 AM PM07.05.04

Advanced packaging requires ever-increasing I/O counts which calls for shrinkage in the Cu interconnect dimension while meeting device performance and reliability. In Applied Materials, we are enabling fine line/spacing (L/S) Cu redistribution line (RDL) by scaling the barrier thickness, controlling amount of wet etch critical dimension (CD) loss and controlling undercut, developing plasma surface treatment to meet electrical performance specs, and exploring new material with better barrier property. We demonstrated end-pointed Ti etch process with 10nm Ti barrier thickness to reduce undercut from >300nm to <20nm and extend RDL scaling to sub-2um regime. Step coverage is not compromised with such thin barrier as demonstrated by successful plating on topography features. With end-pointed Cu etch process, we were also able to reduce Cu CD loss from >0.3um to <0.1um and reduce line resistance non-uniformity from >1mOhm to <0.5mOhm. We established the importance of plasma treatment to lower RDL electrical leakage from >1mA to <1nA. Low leakage is critical to minimize device power dissipation.

9:45 AM PM07.05.05

The fabrication of hybridised silicon nanospheres by simplified plasma-enhanced chemical vapour deposition (PECVD) without the need for seed particle injection or microwave plasma has been improved upon by applying a modified multi-layer deposition technique (ML-PECVD). In this, we have incorporated our method for fabricating the hybridised nanospheres with the topical advantage presented by the ML-PECVD method for active functionalisation of the particles within the plasma itself. Additionally, we have improved the active control of nanospheres during plasma formation utilising our proprietary spectroscopic imaging system.

As the physiochemical properties of nanoparticles depend on their size and shape, isolation within a suitable matrix permits single-particle analysis and experimentation, overcoming averaging effects. Following suspension in ethyl acetate, analysis of the multiasblattice ordering was observed by SEM, µRAMAN and plasmonic nanospectroscopy on both crystalline silicon (c-Si) and semiconductor polymer substrates. While c-Si acts as a suitable measurement surface, our interest is aimed at the inclusion of the hybridised nanospheres to flexible opto-electronic devices. To this extent, suitable pairing between the nanosphere and polymer functionalisation states are desired. Typically, this must be done ex-situ of the deposition process, however, our method utilised exchange bias effects with suitable semiconductor polymer substrates within the deposition chamber during deposition. This presents a promising methodology for the rapid fabrication of active opto-electronic materials while removing extensive chemical processing between fabrication layers.

10:00 AM BREAK

SESSION PM07.06: Energy, Catalysis and Interfaces I
Session Chairs: Bruce Koebl and Mohan Sankaran
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 107

10:30 AM *PM07.06.01
Gas-Surface Reactivity of Vibrationally Excited Molecules—Energetics, Dynamics, and Their Significance in Interfacial Reactivity Arthur Utz;
Tufts University, Medford, Massachusetts, United States.

Vibrationally excited molecules exhibit enhanced reactivity in the gas phase and on surfaces. In high temperature or plasma processing environments where they are abundant, they are potentially important, or even dominant contributors to chemical reactivity. This talk will highlight state-resolved gas-surface scattering experiments that use infrared laser excitation of molecules in a supersonic molecular beam to quantify a molecule's reaction probability as a function of its incident kinetic, vibrational and rotational energy and quantum state. The experiments quantify how effectively vibrational energy promotes a molecule's dissociative chemisorption probability on the surface, and how that efficacy varies with the energy and the character (e.g. bend vs. stretch) of the molecule's vibrational motion. We find that the reactivity of individual molecules is strongly influenced by the dynamics of the molecule-surface collision. Vibrationally mode-selective chemistry, in which reaction probability, S0, depends on the molecule's vibrational motion, and not just its energy, and bond selective reactivity, in which a localized vibrational excitation dictates which bond breaks, are the rule, rather than the exception in our studies of
methylene dissociation on Ni and Ir surfaces. These markedly non-statistical reactivity patterns result from the limited duration of the methane molecule-surface collision, and the resulting constraint on the time available for significant energy redistribution within the reaction complex. A consideration of the rates and pathways for vibrational energy flow within the reaction complex provides a qualitative picture for predicting the extent of non-statistical behavior that might be expected in more complex reactive systems.

The ability to control precisely and independently how energy is partitioned among translational, rotational, and vibrational motion of the gas-phase molecule and surface atom excitation allows to explore chemical reactivity over a wide range of strongly non-thermal conditions. These measurements have proven to be invaluable benchmarks for testing and validating the absolute accuracy of DFT-based electronic structure calculations. Varying surface temperature for a fixed energetic configuration of the gas-phase reagent reveals a dramatic surface temperature enhancement that is most pronounced near the energy threshold for reaction. Coverage-dependent measurements of reactivity show how the surface-bound carbon products of methane's dissociation can initially enhance, and then inhibit further methane activation on Ni(111).

Nonthermal plasma-assisted reaction enhancement mechanism in porous Ni/Al2O3 catalysts (3-mm spherical pellets) in CH4/CO2 conversion was investigated. Dielectric Barrier Discharge (DBD) was employed for this purpose. In the plasma catalysis, carbon filaments were deposited only on the external surface of catalyst pellets, providing the clear evidence that the DBD and catalyst interaction is possible only in the external surface of the pellets: neither generation of DBD nor the diffusion of excited species in the internal micropores is possible. Meanwhile, coke distribution over the pellet cross-section revealed the coke formation in the internal micropores was diminished dramatically by DBD, although plasma and catalyst interaction is limited only in the external surface. We also found that the external surface of catalyst pellets was oxidized exclusively by DBD, forming NiO shell with thickness of ca. 20 micrometers. Ni catalyst was not oxidized in the thermal catalysis regime. Such unique reaction behavior was explained by the catalyst effectiveness factor. The reactivity of plasma generated species is so high that the surface reaction of those species completed at the external surface of pellets: Carbon deposition and oxidation cycle is accelerated by the plasma generated reactive species at the external surface of pellets, while those species do not diffuse towards internal micropores.

According to the molecular beam experiments, vibrationally excited CH4 is known to promote dissociative chemisorption over the metal surface. Although vibrationally excited species have yet to be identified experimentally in the high-pressure nonthermal plasma system, the numerical simulation of one-dimensional streamer type discharge plasma (typical in DBD) predicted that the vibrationally excited CH4 is the most abundant and long-lived species produced by low energy electron impact. Likewise, vibrationally excited CO2 and H2O are expected to promote catalytic surface reactions; nonthermal plasma is the viable and economical approach to generate copious amount of vibrational species at low temperature. Based on these ideas, nonthermal plasma enabled greenhouse gas conversion was diagnosed by temperature programmed reaction spectrometry as well as materials characterization by XRD and Raman spectroscopy. Moreover, carbon deposition and Ni catalyst oxidation behavior was correlated in the plasma- and thermal-catalysis regime, enabling clear insight into the reaction enhancement mechanism induced by nonthermal plasma. The reaction enhancement mechanism were further discussed in relation to vibrationally excited species.

Due to their higher specific surface area, nanoscale structured materials possess excellent optoelectronic properties [De Mello Donegá C, 2014]. Here in our work, we demonstrate the synthesis of nanoscale zinc oxide tetrapods (ZnO-TPs) from zinc metal wire in ambient air using an atmospheric pressure microplasma technique. The ZnO-TPs were characterised for crystal structure (scanning electron microscopy, transmission electron microscopy and x-ray diffraction), chemical composition (x-ray photoelectron spectroscopy) and optical properties (ultraviolet-visible spectroscopy, photoluminescence). The ZnO-TPs consist of tetragonally placed arms each of about 65 nm length and 11 nm diameter; these particles are further classified as wurtzite phase with each arm particularly grown along the (0002) plane containing polar surfaces. The lattice parameters of the crystals were evaluated using Rietveld refinement procedure [Luca Lutterotti, 1999]. The analysis of optical properties shows that the ZnO-TPs exhibit sharp absorption near the ultraviolet region of the electromagnetic spectrum due to direct band electronic transition. Photoluminescence shows a strong ultraviolet emission due to band to band transition and with a weak visible-violet emission due to interface traps or interstitial Zn metals. Phase purity is confirmed by XPS and x-ray crystal diffraction measurements. Overall, the characterization shows that ZnO-TPs crystals are free from its oxygen vacancies. The formation mechanism of ZnO-TPs in the plasma is initially characterized by sputtering of metal atoms from the Zn solid wire precursor. The interaction of the plasma afterglow with the surrounding air contributes to reacting of the plasma product with air oxygen and fast quenching. While nitrogen does not contribute to the chemistry of the ZnO-TPs, there is evidence that it plays a crucial role in determining the quality of nanocrystals produced. We finally demonstrate the applicability of the plasma process in the fabrication of solar cells, where ZnO-TPs were used as the electron transport layer for devices with methyl ammonium lead iodide perovskite as the absorber.

Reference

Plasma chemistry has been the subject of considerable studies due to the intrinsic characteristics brought by highly non-equilibrium state and high reactivity of chemical species. These characteristic properties include ultra-fast reaction time (~10^-4 s), mild reaction condition (ambient pressure and temperature), and rapid start-up/ shutoff. Plasma-catalysis, which combines nonthermal plasma with various catalysts, is based on the bilateral interaction. The potential applications of plasma-catalysis include hazardous VOCs removal, NOx removal, ammonia synthesis, CO2 conversion, and fuel reforming. Many of synergistic effects have been reported by many researcher groups in the past 10 years. However, the degree of enhancements seems to be dependent on the type of combinations (i.e. reactor configuration, power supply, type of catalysts, and operating conditions). In this regard, fundamental studies are necessary to accelerate the broad use of plasma-catalysis in many industrial fields. Our recent study on the time-resolved ICCD imaging of surface streamer provided different nature of streamer depending on the polarity of applied voltage. Especially, a counter-propagating cathode-directed streamer initiated from ground electrode (anode) was appeared. This presentation will cover from the current understanding the interaction of plasma and catalyst to the possible applications in various chemical reactions.

11:00 AM *PM07.06.02
Nonthermal Plasma Enabled Catalysis of Greenhouse Gas Zunrong Shen, Seigo Kameshima, Kenta Sakata and Tomohiro Nozaki; Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Understanding of Plasma Catalysis form Surface Streamer Propagation Hyun-Ha Kim; AIST, Tsukuba, Japan.

PM07.06.03
Microplasmas Synthesis of Nanoscale Zinc Oxide Tetrapods – Crystal Growth and Optical Properties Dilli Babu Padmanaban, Darragh Carolan, Bruno Alessi, Conor Rocks, Paul Maguire and Davide Mariotti; Plasma Science and Nanoscale Engineering group, NIBEC, Ulster University, Belfast, United Kingdom.
The authors would like to acknowledge financial support from the JSPS KAKENHI Grant Number 18H01208.

metal-free substrates which eliminates the need for transfer. Additionally, the approach is additive, producing materials wastage and producing materials at the point-of-need including patterned structures.

Two examples of thin film materials will be presented that demonstrate the capabilities of this synthesis approach: hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS2), both of which are layered materials and can be produced atomically thin. To synthesize h-BN, a single-molecular precursor, ammonia borane, is initially prepared as a thin film by spray deposition, spin coating, or ink-jet printing, and subsequently converted in a cold-wall reactor with a planar, atmospheric-pressure dielectric barrier discharge. We performed a systematic study of h-BN growth with plasma-assisted heating and heating alone. Micro Raman spectroscopy shows that the minimum nucleation temperature is lowered from 800 to 500 °C by the addition of a plasma. From the full-width-half-maximum (FWHM) of the E2g Raman scattering peak characteristic of h-BN, we also find that the crystal domain size is larger with a plasma. From capacitor devices, the dielectric properties of the synthesized h-BN are found to be improved with a plasma from a relative permittivity of 2.8 to the near-maximum value of 3.7. To synthesize MoS2, a similar approach of converting its corresponding single-molecule precursor, ammonium tetrathiomolybdate with a plasma has been studied. In this case, a single-step conversion leads to a rough, nanostructured film. Adding a second thermal annealing produces a very smooth (RMS < 0.5 nm) and continuous film. We will discuss potential superior properties of these films over exfoliated and CVD-grown films, as well as preliminary studies of their applications as electrocatalysts and transistor elements.


2:30 PM BREAK

SESSION PM07.08: Nanostructured Materials
Session Chairs: Toshiaki Kato and Davide Mariotti
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 107

3:00 PM *PM07.08.01
Microplasma Jet Spray Deposition of Nanostructured Materials for Energy Applications Michael Gordon; Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

The ability to synthesize a wide range of nanostructured materials, as well as integrate them into larger systems, is fundamental to the development of next-generation micro- and optoelectronic devices, sensors, and energy harvesting and storage technologies. Toward this goal, we have developed a versatile, plasma spray-like deposition technique, based on flow-through hollow cathode discharges at 10-100 Torr (microplasma jets), that can deposit nanoparticles, dense layers, and structured thin films of crystalline materials on virtually any surface (e.g., conductors, insulators, polymers, fibers, and lithographic patterns). A superionic microplasma jet is seeded with organometallic precursors under reducing or oxidizing conditions to create a directed flux of growth species (e.g., atoms, ions, clusters, and/or nanoparticles) that are subsequently 'spray-deposited' onto the surface of interest at room temperature. A diverse range of nanostructured materials, e.g., metals (Cu, Ni, Pd), oxides (CuO, ZnO, MnOx, RuOx, NiOx, FeOx, CoOx), doped oxides (Fe3Ni, Ni3), and spinels (NiFe2O4), with different morphologies (nanoparticles, dense columnar films, or hierarchical nanostructures, etc.) can be realized with the technique. Applications to be discussed include Fe-doped NiO and Fe3Ni2O for electrocatalysis (OER); NiO and CoOx for supercapacitors; and combining microplasma spray deposition with photolithography and lift-off to create MnOx and RuOx-based microsupercapacitors for on-chip energy storage.

3:30 PM PM07.08.02
One-Pot Synthesis of Boron Nitride Nanotube/Metal-Ceramic Hybrids by Thermal Plasma Keun Su Kim1, 2, Homin Shin1, Martin Couillard3, Mark Plunkett1, Dean Ruth1, Christopher Kingston1 and Benoit Simard2; 1 National Research Council Canada, Ottawa, Ontario, Canada; 2Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada.

Boron nitride nanotubes (BNNTs) are nano-sized rolled-up cylinders of single- or few-layered hexagonal BN sheets. Thanks to their ultra-strong impact resistance and lightweight, BNNT-metal or ceramic nanocomposites are highly promising in the development of advanced hard armours such as anti-ballistic body armours or armoured vehicles1; however, developments of such composites have been significantly hampered by the low reactivity of pristine BNNTs towards metal or ceramic matrices, as well as by the complexity and inefficiency of BNNT functionalization via multistep post-processing. To address this issue, we have developed a new plasma process in which growth of BNNTs and their subsequent surface modification (e.g., doping or decoration) with metal or ceramic nanoparticles occur in a same reactor. The density functional theory (DFT) study was performed first to gain insights into stable structures of BNNT-metal/ceramic hybrids and their reaction stoichiometry. Based on the theoretical predictions, synthesis experiments were conducted with different additive materials such as AlN, TiN, and Cu in order to provide different reactivity to BNNTs. The morphological properties and chemical compositions of the products were assessed by various characterization techniques including SEM, TEM, TGA, FT-IR, UV-Vis, and XRD. The results of optical emission spectroscopy (OES) and 2D thermo-fluid modelling studies will be also presented to discuss the growth mechanism of those hybrid materials in this plasma process.


3:45 PM PM07.08.03
Growth and Characterization of Nano-Platelet IrOx Films Milena B. Graziano1, Brendan Hanrahan1, Thomas C. Parker2, David Baker1, Bradley Sanchez1, 3; Manuel Rivas1, 3 and Paul Sunal1; 1University of Maryland, College Park, Maryland, United States; 2Aberdeen Proving Ground, Aberdeen, Maryland, United States; 3U.S. Army Research Laboratory, Adelphi, Maryland, United States; 4University of Connecticut, Storrs, Connecticut, United States; 5General Technical Services, LLC, Wall, New Jersey, United States.

Iridium oxide (IrOx) is a well investigated compound with superb physical and electrical properties that have proven advantageous to numerous medical, electrochemical, and microelectronic systems. Its vast applicability is attributed to its electrical and ease of fabrication using common deposition
Cold plasma consists of electrons, ions, excited atoms and molecules, neutral gas species, and UV radiation that occur at low temperatures and can be used to initiate chemical reactions. Often plasma treatment is carried out in high vacuum, low-pressure devices. Vacuum plasma treatment allows plasma particles to achieve large mean free paths and results in very energetic ions and electrons capable of rapid and extreme surface modification and highly successful chemical grafting. However, low-pressure devices are most suitable for batch processing of substrates. They require long pump down times and have a limited volume per batch. Therefore, the integration of these devices into a continuous industrial manufacturing process is not readily achievable. Atmospheric-pressure plasma, as used in this research, allows for the continuous treatment and curing of substrates and transforms an otherwise costly and small-batch technology into a commercially viable approach for high-volume processing. Despite the lower mean free paths of atmospheric plasma systems, proper selection of processing parameters and working gas can be used to successfully induce chemical reactions. These chemical reactions include the polymerization of monomers and their attachment to material substrates. The use of cold atmospheric-pressure plasma to induce chemical reactions eliminates the need for heat, allowing for heat-sensitive materials to be processed and coated with desired functional finishes. These high-performance coatings can add attributes to the finished goods such as high levels of water and oil repellency, photoresistive, and antireflective properties. As such, the use of plasma treatments in various industries, including automotive, electronics, and building materials, is growing rapidly. Efficient plasma polymerization systems are designed to provide a versatile, environmentally friendly, and cost-effective method of surface modification.
**PM07.09.01**

**Surface Treatment Against Process Oxidation of Ultra-Thin Silver Films**  
Soroush Hafezian1, Rodolphe Béain1, Ludvik Martinu2 and Stéphane Kéna-Cohen1,  
1École Polytechnique de Montréal, Montréal, Quebec, Canada.

Metallic transparent conductors play an important role in modern optoelectronic devices and as heat-reflectors in energy saving applications. Their high conductivity and high transparency for thicknesses below a few nanometers are crucial for device functionality. In particular, silver thin films demonstrate high sheet conductivity shortly after percolating as well as a neutral transmitted color. Moreover, silver can easily be scaled to coat large surfaces with the help of physical vapour deposition techniques such as magnetron sputtering, providing nanoscale uniformity over a few square meters. Silver, however, is extremely sensitive to reactive oxygen and requires special precautions in reactive plasma-based processes. One strategy for protecting silver thin films is to have a thinner (~3 nm) metallic film (here Ti) as protective layer. As the silver/barrier double-layer is exposed to the O2 plasma, reactive species diffuse through the Ti barrier layer which gradually transforms into a film of TiOx. This metal-oxide layer eventually self-passivates and blocks oxygen diffusion. However, in the presence of oxygen and ultraviolet radiation, if the barrier thickness is not adequate or if the oxidation process is too severe, reactive species can diffuse through the barrier and lead to film failure.

In this work, we characterize the degradation mechanism of silver at the interface with the barrier and present a solution to reduce and prevent the process oxidation of silver in a reactive environment. We first compare the growth of silver films deposited by magnetron sputtering on glass, ZnO and (3-Mercaptopropyl)trimethoxysilane (MPTMS) treated glass. The bare glass and ZnO film represent a case of physisorption with low and high surface energy, respectively. Higher surface energies tend to reduce the mobility of sputtered silver atoms and lead to early coalescence. The MPTMS-treated glass, thanks to the thiol bond formation, represents a case of chemisorption process where the incoming silver atoms are attached to the sulfur available on the surface. Samples are covered with a 2-nm barrier titanium film and exposed to reactive O2 plasma. XPS and TOF-SIMS analysis on the samples reveal that the degradation process starts with the migration of silver through the top titanium barrier. We quantify the degradation by comparing the atomic content of silver present at the very top of the degraded samples. We find that in the case of the ZnO and glass substrates there is a much higher amount of silver migrating through the top barrier to the surface compared to the MPTMS-treated glass. We attribute this difference of migration to the sulfur-silver bonds provided by the MPTMS monolayer.

**PM07.09.02**

**Universal High-Resolution Surface-Structuring Technique for Fabricating Complex 3D Nanopatterns by Plasma Process and Its Application in Display Devices**  
Hwan-Jin Jeon1, Department of Chemical Engineering and Biotechnology, Korea Polytechnic University, Siheung-si, Korea (the Republic of).

High-resolution, high-aspect-ratio nanostructure patterning technology has the potential to be of significant value in various fields such as nanoelectronics, optics, biosensors, energy devices, and display devices owing to the optical and electric peculiarities of nanostructured materials. Lots of approaches, which include nanosprint, photo-, interference-soft-edge, colloidal lithography and electron-beam assisted deposition, have been studied to achieve 3D 10-nm-scale features.

Recently, we introduced a new surface nanostructuring technique termed “secondary sputtering lithography (SSL)”, which enables the fabrication of 10 nm-scale ultrahigh-resolution 3D patterned structures of substrate surface with high aspect ratios over large areas by utilizing secondary sputtering phenomena during plasma ion etching process. This new technique utilizes the secondary sputtering phenomenon, wherein target material particles are emitted by accelerated Ar+ ions over a large angular distribution, leading to the fabrication of 10nm scale high-resolution patterns without complicated equipment. We have successfully created various nanostructures on a 10 nm-scale, including ultrathin lines, hole-cylinders, and honeycomb structure. We have also applied ~10nm-scale line patterns with a high aspect ratio to align liquid crystal molecules. High-resolution patterning (~20 nm) of indium-tin-oxide (ITO) surface layers with a high aspect ratio (~10) was successfully carried out without damage to the electrical/optical properties of the ITO, and the patterned ITO could function as a bifunctional conductive alignment layer for liquid crystal devices without a conventional polymer alignment layer fabrication process.

**PM07.09.03**

**VHF Plasma CVD Synthesis of Photochromic ZnO Nanocrystal**  
Hiroshi Kaijyama1, Shin Kuboyama2, Hiroki Uyama3, Atsushi Otomo4, Shuhei Inoue5, Yukihiko Matsusaka1, Keiji Takata2 and Kichiho Uchinoto2, 1Tokushima Bunri University, Sanuki-shi, Japan; 2Tokushima Bunri University, Sanuki-shi, Japan; 3Kyushu University, Kasuga-shi, Japan; 4Hiroshima University, Higashi-Hiroshima-shi, Japan; 5Kansai University, Suita-shi, Japan.

Zinc oxide (ZnO) is a promising material for ultraviolet optical devices, especially in light emitting diodes and lasers. In this study, it is shown that ZnO nanocrystal synthesized by a VHF plasma CVD process is a photochromic material. The structural and electronic properties of PC states are investigated.

We developed a VHF (80MHz) plasma CVD apparatus, which could hold stable plasma with a high electron density and low electron energy at the pressures up to 100 Pa. Because of this, the growth of nanocrystals in a vapor phase is greatly promoted. For the ZnO synthesis, a vapor of Zn(C2H5)2 was introduced to a VHF plasma of a gas mixture of argon (Ar) and oxygen (O2). The ZnO film was formed on an unheated substrate. The film was exposed to UV lights and annealed at various temperatures. An x-ray absorption fine structure (XAFS) measurement was done to analyze the changes of local structures.

The as grown films were transparent. An AFM observation showed that the films consisted of ball-like nanocrystal with a diameter of 60-120 nm. The gas pressure during the plasma synthesis was a few hundred Pa. A substrate was not heated. Therefore, it is plausible to consider that crystal growth completed in a vapor phase.

The transparent film (as grown) changed to dark color by UV (254 nm) irradiation in an ambient air at 300 K. This is the PC transition of ZnO nanocrystal. The PC states were quite stable at the temperatures up to 500 K. At 550 K, however, the color gradually changed back to transparent like as grown films. The transparent film once experienced PC transition again changed to PC states by UV irradiation. However, the PC films annealed at 600 K never
Here we present a facile synthesis of Au@Ag bimetallic nanoparticles using a novel atmospheric-pressure microplasma-assisted electrochemistry. Most widely used method. However, this conventional approach is usually time-consuming and laborious. In our experiments, microplasmas are defined as gaseous discharges formed in electrode geometries where at least one dimension is less than 1mm. Due to surface volume ratio of the core and the shell can produce strong excitation and scattering spectra than pure Ag and Au nanoparticles. Therefore, Au@Ag have attracted considerable attention because of the embedded Ge nanocrystals that results from RF-PECVD growth. In the context of these findings the produced “virtual” Ge substrates for mitigating the problem of polar/nonpolar low-mismatch GaAs–Ge interface, Ge surface baking at 400 C and 700 C for 5min and 10min, respectively has been carried out. The growth of GaAs is based on two-step method. The structural properties of the GaAs layer are studied using HRSEM with EDX and cross sectional TEM. High-Resolution TEM images show high-quality Ge/GaAs interface where no anti domain interfaces are seen. This might be attributed to the embedded Ge nanocrystals that results from RF-PECVD growth. In the context of these findings the produced “virtual” Ge substrates for GaAs growth can provide a robust method for scaleable integration of high performance III-V photovoltaics devices with large area Si wafers.

PM07.09.05
Plasma Enhanced Processing of Ge Films on Silicon as a Virtual Substrate for Lattice Matched GaAs Growth
Ghada H. Dushaq, Ammar Navafleh and Mahmoud Rasras; 1Engineering, New York University, Abu Dhabi, Abu Dhabi, United Arab Emirates; 2Electrical Engineering and Computer Science, Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates.

Direct growth of germanium (Ge) on silicon (Si) substrate is a key approach for the development of future high-speed photonics and electronic devices. Germanium is an ideal template for growing GaAs due to the lattice mismatch. This will enable the fabrication of tandem solar cell and GaAs based photodetectors on low cost Si platform. While the lattice mismatch between GaAs material and Ge is significantly low compared to GaAs directly on Si, the considerable lattice mismatch of ~4.2% between Si and Ge must be considered to grow high quality Ge layers on Si and enable its use for high quality GaAs growth. Several research groups have reported high quality Ge layers on Si, however, temperatures as high as 650 C were used in performing the epitaxial deposition, also post annealing process is required. Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) has an advantage of depositing Ge at 400 C. The plasma power in RF-PECVD system acts as another energy source that stimulates energetic ions and free radicals to be deposited on the surface of the wafer at lower temperature. In this work, we present a direct growth mechanism of thin Ge-on-Si films at low temperature using RF-PECVD. These films will be used as a template to initiate GaAs growth for heterojunction solar cells. A two-step temperature technique and different GeH4 flow rates have been employed during the deposition process as the following: step one (low temperature (LT), high rate (HR)) the deposition was performed at 350 °C with 3 sccm flow of GeH4. In step two (high temperature (HT), low rate (LR)) of the Ge deposition the growth is carried out at 500 °C with 1 sccm of GeH4. The results show that this optimized growth limits the defect nucleation or dislocation misfit to 50 nm at the Si/Ge interface. Moreover, the measured threading dislocation density (TDD) of 700 nm thick Ge films is ~1x10^6 cm^-2 which paves the way to achieve high quality growth of GaAs for solar cells. After this, the RF-PECVD grown Ge film on Si is used as a virtual substrate to initiate GaAs growth.

PM07.09.06
Microplasma-Assisted Synthesis of Core-Shell Au@Ag Bimetallic Nanoparticles for SERS Applications
Guan-Jun Chen and Wei-Hung Chiang; National Taiwan University of Science and Technology, Taipei, Taiwan.

Surface enhanced Raman scattering (SERS) is a promising technology for various applications including plasmonic devices. Photo energy generation and conversion, biomedicinal detection and chemical sensing. Gold-Silver core-shell bimetallic nanoparticles are extensively used in SERS, due to the unique localized surface plasmon resonance (LSPR) property [1]. Au@Ag allow tuning the physical and chemical properties through the composition and radius ratio of the core and the shell can produce strong excitation and scattering spectra than pure Ag and Au nanoparticles. Therefore, Au@Ag have attracted great attention in material science, surface science, and biological analysis by SERS. To synthesize this attracted material, seed-mediated growth is the most widely used method. However, this conventional approach is usually time-consuming and laborious. Here we present a facile synthesis of Au@Ag bimetallic nanoparticles using a novel atmospheric-pressure microplasma-assisted electrochemistry. Microplasmas are defined as gaseous discharges formed in electrode geometries where at least one dimension is less than 1mm. Due to surface volume change, microplasmas can be operated stably with an aqueous solution as an electrode at atmospheric pressure. Energetic species formed in the microplasma is capable of initiating electrochemical reactions and nucleating particles in solution without chemical reducing agents [2]. In our experiments
result, we found Au@Ag bimetallic NPs can be a synthesis in a minute time scale. The as-produced samples were extensively characterized by TEM, XRD, Raman, XPS and UV-Vis spectroscopy. We further systematically studied the Raman and XPS spectra to verify the molar ratio of the Au-Ag bimetallic nanoparticle using Rhodamine 6G (R6G) as the Raman probe molecules. The result indicates that the special ratio of Au@Ag bimetallic nanostructure gives significant enhancement of SERS signal than pure Au, Ag nanoparticle in similar size and verify ratio of Au/Ag will induce different SERS performance.

References


PM07.09.07 Effects of Nitrogen Impurity on Sputtering Growth of ZnO Films on Si(111) Substrates Soichiro Muraoka, Jiahao Lyu, Daisuke Yamashita, Kunihiro Kamatoki, Kazunori Koga, Masaharu Shiratani and Naho Itagaki; Kyushu University, Fukuoka-shi, Japan.

ZnO is a multi-functional material with a distinctive property set and a wide range of existing and emerging applications. We have recently developed a fabrication method of high-quality ZnO films employing magnetron sputtering, “nitrogen-mediated crystallization (NMC)”, where crystal nucleation and the growth are controlled via absorption-desorption behavior of nitrogen “impurities” [1-4]. By utilizing the films grown via NMC as buffer layers, single crystalline ZnO films with atomically flat surface have been successfully fabricated on 18%-lattice mismatched sapphire substrates. Here, we employ 15% lattice mismatched Si(111) substrates, which offer significant advantages in terms of cost, wafer size, and electrical and thermal conductivity, for NMC growth of ZnO and see what happens if nitrogen impurity is added into the growth atmosphere. First, 10-nm-thick NMC buffer layers were deposited on Si(111) substrates by RF magnetron sputtering in Ar/N2 atmosphere. The substrate temperature was 750°C, and the total gas pressure was 0.35 Pa. Next, 1-um-thick ZnO films were fabricated on NMC buffer layers by RF magnetron sputtering in Ar/O2 atmosphere. The substrate temperature was 700°C, and the total gas pressure was 0.70 Pa. We observed NMC method leads to significant change in the grain size of buffer layers. The average grain size derived from AFM images jumps from 9.2 to 24 nm by adding N2 gas into sputtering atmosphere. The analysis on height-height correlation function (HHCF) indicates that N2 addition causes an increase in the lateral correlation length \(\xi\), a measure of migration length of adatoms, from 15 to 29 nm. Such enhanced migration allows adatoms to reach the thermodynamically favored lattice positions, and thus leads to the large grain size as well as to high crystal quality of the films deposited on them. In fact, we observed high quality of ZnO film on NMC-ZnO buffer layer, where the full width at half maximum (FWHM) of (002) rocking curve is 0.67°, one-fourth of that for the films fabricated without buffer layers. The crystal quality has been further improved by introducing 1-nm-thick AlN layers prior to NMC-buffer layer deposition. The FWHM of ZnO film on AlN/NMC-ZnO double-layer is significantly small of 0.50°, attributed to AlN layer protecting Si surface against oxidation and thus promoting epitaxial growth of ZnO on the surface. We believe that the high-quality ZnO films obtained in this study will open up a new avenue for ZnO-based devices on Si substrates that would have a great impact on Si integrated circuit technology.

This work was supported by JSPS KAKENHI Grant Number 18H01206P, Sumco Science and Technology Foundation, and NTT collaborative research.

PM07.09.08 Electrical Property Change of Transparent Doped ZnO by Zn Addition and Desorption Yasuyuki Yamada1, Shuhei Funaki1, Orkut Sancakoglu1,2 and Rei Sugihara1; Shimane University, Matsue, Japan; 1Dokuz Eylul University, Izmir, Turkey.

Doped ZnO films show low electrical resistivity comparable to indium-tin oxide films and is suitable for transparent electrodes. To obtain a high performance in opto-electrical properties, many deposition studies have been conducted. However, optimum conditions have not been revealed because electrical properties vary with deposition method, equipment and even position in a deposited film. This is because crystalline defects that deteriorate electrical properties are not revealed and controlled completely. In a planner magnetron sputtering method, suppression of electrical conductivity happens to the deposition position facing the erosion area on the target. This suppression is caused by the positional distribution of crystalline defects induced by the incidence of high-energy particles coming from the erosion area.

To reveal the critical defect types to affect electrical properties of doped ZnO film, we have studied the property change of the films with different structures that provide different state and amount of Zn vacancy in the crystal after high temperature annealing. Three types of film structures of Ga-doped ZnO (GZO) were prepared by RF magnetron sputtering method at room temperature. One of the types is a simple monolayer of GZO on a glass substrate. Second one is SiO2/GZO layered structure. Third one is a zinc inserted GZO film, SiO2/GZO/Zn/GZO. For the GZO layer deposition, the substrates were placed on a substrate holder parallel to the target. Typical GZO thickness was 200 nm. SiO2 capping layers were deposited also by RF magnetron sputtering with the thickness of 70 nm. Zn metal layers were deposited 6 nm in thickness between two 100 nm-thick GZO layers. GZO monolayer films showed resistivity about 1X104 Ωcm after deposition. As the films annealed at 500°C for 30 min in vacuum, the resistivity decreased due to the improvement of crystalline perfection. However, annealing for longer times and at higher temperatures caused apparent increase of resistivity and decrease of carrier density. On the other hand, SiO2 capped GZO films showed no significant increase in carrier density after long and high temperature annealing. These behaviors indicate that Zn desorption from GZO lattice creates defects that reduce carrier density. Zn inserted GZO films showed slightly decreased resistivity after the deposition and as they were annealed resistivity was further reduced to 3X102 Ωcm. In addition, Zn inserted films exhibited no difference in resistivity between films deposited at center and erosion positions. Increase in carrier density and homogenization in resistivity by the enrichment of Zn atoms in GZO lattice can be explained by Zn vacancy. Inhomogeneous distribution of Zn vacancies existed in the as-deposited films trap electron carriers and decrease of Zn vacancies improves electrical properties. The results obtained in this study contain revealing information on crystalline defects that control properties of doped ZnO films.

PM07.09.09 Catalyst-Free Growth of C-Axis Aligned (ZnO)x(InN)1-x Nanorods by RF Magnetron Sputtering Nanoka Miyahara, Daisuke Yamashita, Daisuke Nakamura, Kazunori Koga, Masaharu Shiratani and Naho Itagaki; Kyushu University, Fukuoka, Japan.

We present catalyst-free growth of (ZnO)x(InN)1-x nanorods on c-plane sapphire substrate by RF magnetron sputtering. (ZnO)x(InN)1-x (called ZION hereafter) is a new semiconducting material, a pseudo-binary alloy of wurtzite ZnO and wurtzite InN [1-3]. This ZION has a tunable band gap over the entire visible spectrum and a high optical absorption coefficient of 105 cm-1, making ZION a promising material for solar cells and light emitting devices. Here, we report for the first time c-axis aligned ZION nanorods where the one-dimensional structures should bring about superior electronic/photonic properties.

ZION films were deposited at 450°C by RF magnetron sputtering on c-plane sapphire substrates. O2, N2 and Ar gases were used and the total pressure was
than 6% O₂ in sputtering atmosphere display resistivity of (7-13) × 10⁻⁴ Ω-cm, carrier concentration of (7.1-11.5) × 10²⁰ cm⁻³ and Hall mobility of (5.5-8.7) cm²V⁻¹s⁻¹, and show marginally superior electrical parameters, just below the critical threshold value of 6% O₂ in sputtering atmosphere. With increase of substrate temperatures display a minimum in reflectance in the range of (1250–1800) nm due to plasma resonance, depends on the carrier concentration. This work was supported by JSPS KAKENHI Grant Number 18H01206, Samco Science and Technology Foundation, and NTT collaborative research.


PM07.09.10
Investigation on Photovoltaic Properties of Nb-Doped MoS₂ Thin Films Grown by Magnetron Sputtering Seyed A. Shahahmadi1,2, Siti Z. Othman2, Puvaneswaran Chevathanth1, Halina Misran1, Md. Akhtaranuzaman1 and Noowish Amji3,2; 1Institute of Sustainable Energy, Universiti Tenaga Nasional, Kajang, Malaysia; 2Electrical Electronic and Systems Engineering, Universiti Kebangsaan Malaysia, Bangi, Malaysia; 3Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi, Malaysia.

In this study, the effect of niobium (Nb) on properties of molybdenum disulfide (MoS₂) thin film absorber layer is investigated. So far, MoS₂ (0.6-20 nm) monolayers have got the most interest for nanoscale electronic devices. However, properties of MoS₂ thin films (> 50 nm) have not been explored in details for photovoltaic (PV) applications. Hence, various films (up to 150 nm) such as undoped MoS₂, MoS₂:Nb (0.05%), and MoS₂:Nb (0.5%) are deposited by radio frequency magnetron sputtering to investigate the usage as PV materials. These films are also subjected to dynamic sulfurization process at 550°C for 90 min to improve the crystallinity and optical properties. Results from field emission scanning electron microscope (FESEM) show similar surface morphology in all samples and the tendency for vertical lamellae growth that represents type-I layered structure. Moreover, it is found that the thickness of the as-deposited samples increased about 50 nm after sulfurization probably due to the volumetric expansion. Structural properties are characterized by grazing incidence X-ray diffraction and it is found that the films exhibit dominant diffraction peak corresponding to (101) plane at 2θ = 33.7 degree, which also points to the lamellae structure as observed earlier in FESEM images. Transmittance and absorbance are obtained by UV-VIS-IR spectrometer in the range of 300–2500 nm. It is found that sulfurization leads to the emergence of a peak at 1062 nm in the transmittance spectra, besides the increase of average transmittance (300-1300 nm) from 30% to 44% for as-deposited MoS₂. The peak position shifts to higher energies (up to 794 nm) as the Nb increases, which is correlated to the changes in band structure. Carrier concentration, mobility, and resistivity are obtained from Hall measurement and n-type semiconducting properties are detected in all samples. Hole concentration drops from 10¹⁴ cm⁻³ to 10¹⁵ cm⁻³ after sulfurization while mobility increases from 0.035 to 22.6 cm²/Vs for as-deposited MoS₂. The increase of Nb reduces the resistivity of the as-grown films from 6.78 to 4.9 Ω.cm and similar trend is also attained for sulfurized MoS₂ films.

PM07.09.11
Electrical and Optical Studies of Ga-Doped ZnO Films Grown by Reactive Co-Sputtering of Zn and GaAs Shrvan Kumar Appani, Samanth V Rayapati and S.S. Major, Indian Institute of Technology Bombay, Mumbai, India.

Ga-doped ZnO (GZO) films were deposited by reactive co-magnetron co-sputtering of zinc and GaAs (~ 3% of the area of erosion track) in Ar-O₂ mixture. This work focuses on the role of oxygen percentage (4–10%) in sputtering atmosphere and substrate temperature (350 °C to 500 °C) in controlling the electrical and optical properties and investigating free carrier effects in heavily doped GZO films. XRD studies show in all the films display single wurtzite phase of ZnO with nearly complete c-axis orientation and practically negligible strain. The conducting GZO films deposited at 375 °C with less mono-layers have got the most interest for nanoscale electronic devices. However, properties of MoS₂ thin films (> 50 nm) have not been explored in details for photovoltaic (PV) applications. Hence, various films (up to 150 nm) such as undoped MoS₂, MoS₂:Nb (0.05%), and MoS₂:Nb (0.5%) are deposited by radio frequency magnetron sputtering to investigate the usage as PV materials. These films are also subjected to dynamic sulfurization process at 550°C for 90 min to improve the crystallinity and optical properties. Results from field emission scanning electron microscope (FESEM) show similar surface morphology in all samples and the tendency for vertical lamellae growth that represents type-I layered structure. Moreover, it is found that the thickness of the as-deposited samples increased about 50 nm after sulfurization probably due to the volumetric expansion. Structural properties are characterized by grazing incidence X-ray diffraction and it is found that the films exhibit dominant diffraction peak corresponding to (101) plane at 2θ = 33.7 degree, which also points to the lamellae structure as observed earlier in FESEM images. Transmittance and absorbance are obtained by UV-VIS-IR spectrometer in the range of 300–2500 nm. It is found that sulfurization leads to the emergence of a peak at 1062 nm in the transmittance spectra, besides the increase of average transmittance (300-1300 nm) from 30% to 44% for as-deposited MoS₂. The peak position shifts to higher energies (up to 794 nm) as the Nb increases, which is correlated to the changes in band structure. Carrier concentration, mobility, and resistivity are obtained from Hall measurement and n-type semiconducting properties are detected in all samples. Hole concentration drops from 10¹⁴ cm⁻³ to 10¹⁵ cm⁻³ after sulfurization while mobility increases from 0.035 to 22.6 cm²/Vs for as-deposited MoS₂. The increase of Nb reduces the resistivity of the as-grown films from 6.78 to 4.9 Ω.cm and similar trend is also attained for sulfurized MoS₂ films.

PM07.09.12
Influence of Flash Lamp Annealing on Ga-Doped ZnO Films Reis Susiriya, Yasuji Yamada, Arisa Sakaguchi and Shuei Funki; Shimane University, Matsue, Japan.

Zinc oxide (ZnO) attracts many attentions to be studied as an oxide semiconductor. Resistivity of ZnO semiconductor added with Ga or Al is almost equal to Sn doped In₂O₃ (ITO). Recently, we have been studying electrical properties of Ga doped ZnO (GZO) films deposited by radio frequency (RF) magnetron sputtering at room temperature and revealed that annealing at high temperatures for 30 min improves electrical properties. As annealing temperature increases, mobility of GZO films were increases gradually. Carrier concentration increases as annealing temperature increases up to 350°C,
however, it decreases at higher temperatures than 400°C. While longer annealing time reduces carrier density, shortening the annealing time in the order of a minute at a high temperature increases carrier density, resulting in electrical resistivity lower than the 350°C annealing for 30 min. From these behaviors of carrier density, we have concluded that the reduction of carrier density is caused due to zinc atom desorption from the GZO lattice. Therefore, it is very curious to know the effect of extremely short time annealing on carrier density and resistivity. Flash lamp annealing technique is used for very short time of annealing, as short as milliseconds, often used in Si semiconductor industry. We applied this technique to the annealing of transparent GZO films as a post-annealing. GZO films with thickness of 200 nm were deposited on quartz glass substrates at room temperature by RF magnetron sputtering. These films were annealed by using a xenon lamp with the pulse width from 1 to 5 milliseconds in the ambient atmosphere. Electrical properties and crystallinity were measured by van-der-Pauw method and XRD measurement. By the flash lamp annealing in appropriate pulse width and power, carrier density of the films increased and mobility was unchanged, resulting in decrease of resistivity. The change of properties of the GZO film by flash lamp annealing is different from conventional furnace annealing. The carrier density of GZO film decreases at higher temperatures than 400°C by a conventional furnace. On the other hand, it does not decrease by the flash lamp annealing as the power increases until the films are caused fatal damage. In conclusion, short time is slightly higher than those annealed for typical annealing time using conventional heating equipment.

PM07.09.13

Structural and Mechanical Characterization of Amorphous Carbon-Silica Thin Films Deposited on Stainless Steel Substrates by PECVD Neithoth J. Stand Figueurete1, Erika Abigail Ochoa Becerra1, Leonardo Mathias Leidens2, Carlos Alejandro Figuereot2, Fernando Lazaro Freire J3 and Marcelo Eduardo Huguenin Maia da Costa41; 1Physics, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil; 2Universidade de Caxias do Sul, Caxias do sul, Brazil.

Nowadays, various materials are being studied, for instance, diamond like carbon (DLC) which has properties such as low friction coefficient, high hardness, mechanical wear resistance, optical transparency and high electrical resistivity, these properties can be modified used other elements such as Si, N, O, etc. The DLC thin film is very useful as a protective coating on metallic pieces such as stainless steel, but there is an issue: the low adhesion of the DLC on this type of substrate, caused by its high internal stress and low thermal stability.

Our work is about the study an amorphous carbon-silica thin films used an organosilicon, this precursor was deposited using a rf-PECVD (radio frequency plasma enhanced chemical vapor deposition) on steel surface (ISO316L). The precursor was hexamethyldisiloxane (HMDSO) in its liquid state at room temperature and atmospheric pressure.

Those films were deposited in several self-bias and two different substrate temperatures (200°C, 300°C, at room temperature there was no deposition). The deposition pressure was 2.6 Pa and they were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, profilometer measurements and nanoindentation.

Our results indicate that the temperature plays an important role in the adhesion of the amorphous carbon-silica thin film with the steel surface, although at temperatures lower than 150°C the adhesion is poor. The films deposited at 200°C and 300°C with different self-bias had an excellent adhesion, the spectra Raman showed that this films are amorphous and with X-ray photoelectron spectroscopy we noticed, that the percentage of Si-C and C-C binding increase as the self-bias. The hardness of these films were of the order of 20GPa.

PM07.09.14

Role of Organosilicon Films Deposited by PECVD Protecting Polypropylene Against Photodegradation Walter R. Waldman1, Amanda d. de Freitas7, Felipe Fernandes8, Elidiane C. Rangel9, Nilson C. Cruz10, Adriana O. Silva11 and Joyce Araujo12; 1Federal University of São Carlos, Sorocaba, Brazil; 2University of São Paulo State—UNESP, Sorocaba, Brazil; 3Materials Metrology Division, National Institute of Metrology, Quality and Technology, Duque de Caxias, Brazil.

The sensitivity of polymers to photodegradation when exposed to the weather limits their options for outdoor use and reduces their shelf life. The deposition of thin films of organosilicon by plasma on polymers can influence its resistance to photodegradation without interfering in aspects such as color or brightness in bulk properties due to the transparency and nanometric dimension of these films. Polypropylene samples were coated with organosilicon films by plasma-enhanced chemical vapor deposition (PECVD). First, a five-minute pre-treatment with oxygen gas, pressure 9 Pa, radiofrequency 13.56 MHz and power of 50 W. Subsequently the organosilicon films were deposited for 30 or 60 minutes at a pressure of 6 Pa, an atmosphere of 50 % of O2 and 50% of HMDSO, radio frequency 13.56 MHz and power 80W. We exposed the samples to a UV-C light of fluorescent, germicidal, 15W power, maximum emission at 254 nm wavelengths, at 48, 96, 144 and 192 hours. We characterized the samples by MEV, FTIR, UV-Vis, XPS, profilometry and contact angle goniometry.

FILMS were homogeneous and continuous with a thickness between 300 and 550 nm and roughness between 20 and 30 nm. FTIR and XPS measurements after degradation showed that there was no difference between pure polypropylene and polypropylene coated with organosilicon films in the formation of indicators for polypropylene photodegradation, such as hydroxyls and carbonyls. It is clear that the organosilicon film did not offer photoprotection against the auto-oxidation cycle, so we expected the decrease of molar mass by the chain scission, consequent increase of the surface crystalline domains and formation of cracks, which compromise the mechanical properties making the material fragile. However, Scanning Electron Microscopy (SEM) results show that while fissures of virgin polypropylene have a width of 3.5 to 5 micrometers and a length of several millimeters, the polypropylene coated with organosilicon films had cracks with a width of 0.5 to 1 micrometer and length of 2 to 5 micrometers. Along to the fact that the organosilicon film keeps adhered to polypropylene during the photodegradation period, we conclude that the organosilicon film mechanically held the surface cohesion of the polymer material, limiting the crack propagation, despite the oxidation reactions of the polymer. This is, to our knowledge, the first observation of mechanical stabilization of polymers by thin films deposited in plasma. This role of the organosilicon thin film deposited on polypropylene can allow the development of protections for polymers exposed to the weather with benefits as the increase of the useful life and a smaller detachment of photodegraded layers, diminishing the environmental impact by the minor production of secondary microplastics.

PM07.09.16

Plasma Surface Treatment as an Important Tool for Polymer Applications Pericles L. Santana, José Roberto R. Bortoleto, Elidiane C. Rangel, Nilson C. Cruz and Steven F. Durrant; State University of Sao Paulo, Sorocaba, Brazil.

We demonstrated in this work, the use of plasma immersion techniques as an important tool for polymer surface modification. The treated polymers found out a lot of applications, one it is possible to change a thin layer of its surface keeping the bulk properties. Among the properties changed by plasma immersion techniques, it was analyzed the surface topography by contact angle measurements, surface morphology evaluated by Atomic Force Microscopy, the transparency at visible range using a UV-Visible-nxt Infrared Spectrometry and the barrier properties against water vapor measured by gravimetric method. The major results shows a selective surface physico-chemical properties being possible to obtain, hydrophobic or hydrophilic behavior, appearing smooth or rough surfaces, increase or loss of transmitted light, presenting an increase of barrier properties, depending on the plasma composition and technique used, when the temperature can be controlled during the processes. The quantitative measurements exhibit low or high values of contact angle, (Wettability), Surface roughness (Morphology), and Optical transmittance (Transparency) in the visible range. In most cases, the increase of barrier properties measured by gravimetric method is important for food packaging applications and optical devices, for example. Other applications can be
considered for the treated polymers such as: biocompatibility, adhesion and medical applications.

PM07.09.17
Ammonia (NH₃) Gas Detection Based on Tin-Nitride Chemi-Resistive Sensor Teena Jangid and G. M. Rao; Indian Institute of Science, Bangalore, India.

Tin-nitride has not received the experimental attention given to similar IV-Nitrides such as Si₃N₄ and Ge₃N₄. Although Sn nitride has semiconducting properties, suitable for micro-electronic and optoelectronic devices, large disparity in the atomic radii of N and Sn poses a challenge in obtaining good quality tin-nitride films. In this study tin-nitride thin films were prepared on glass and Si substrates, by reactive radio frequency magnetron sputtering of metallic tin target (3" diameter and 3 mm thick) in nitrogen gas ambient. Process parameters such as substrate temperature, target-substrate distance, N₂ gas pressure and RF power were varied in a systematic way, to find-out best suitable combination of these parameters for growth of pure poly-crystalline tin-nitride films. Deposited films were characterized for their crystalline structure and surface morphology by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) and results revealed that pure tin-nitride films can be grown at 600°C substrate temperature, 15 W RF power in pure nitrogen gas ambient, if target-substrate distance is fixed at 10 Cm.

To date, no work has been carried out on gas sensors, using tin-nitride as the sensing material for NH₃ gas. Chemi-resistive gas sensing characteristics of tin-nitride film (~60 nm thickness) deposited at optimized process parameters, were investigated for NH₃ in air at room temperature, as a function of gas concentration (10–70 ppm). Upon exposure to NH₃, the electrical resistance of the tin-nitride film was found to decrease. The sensor exhibited low base line drift and high sensitivity to NH₃ gas at concentrations as low as 10 ppm with fast response and recovery time at lower concentrations. The sensor exhibited a sensitivity of 0.065 (at 10 ppm) to 0.3 (at 70 ppm), recovery of 4 sec (at 10 ppm) to 23 sec (at 70 ppm), and recovery of 6 sec (at 10 ppm) to 23 sec (at 70 ppm) for NH₃. The NH₃ sensing mechanism can be explained on the basis of the depletion of chemisorbed oxygen at the film surface.

PM07.09.18
Dielectric and Ferroelectric Behaviors of Modified PZT Thin Films Synthesized by Pulse Laser Deposition Mohan K. Bhattacharji¹, Alvaro Instan¹, Sita Dugù¹, Pawan Kumar² and Ram Katiyar¹; ¹Physics, University of Puerto Rico, Rio Piedras, San Juan, Puerto Rico, United States; ²Physics, Gurukula Kangri University, Haridwar, India.

We synthesized highly oriented 0.90[Pt(Zr₀.₅₃Ti₀.₄₇)₀.₁₀LaₓSc₁₋ₓ]O₃-δ, where 0 ≤ x ≤ 0.6 thin films on La₀.₆₇Sr₀.₃₃MnO₃ (LSMO) coated MgO (100) substrates utilizing laser ablation process in oxygen atmosphere. We optimized thin films deposited at a substrate temperature of 650°C using KrF excimer laser of wavelength, λ = 248 nm, f = 5 Hz and energy/pulse 270 mJ, and annealed at 700°C for half an hour in an oxygen atmosphere. The orientation of the thin films was examined by x-ray diffractometry. We carried out elemental analysis of thin films by high resolution X-ray photoemission spectroscopy (XPS). The morphology and surface roughness of thin films were analyzed by Atomic force microscopy (AFM). The dielectric measurements were conducted on LSMO/PLZTS/Pt metal-ferroelectric-metal capacitors using impedance analyzer as a function of temperature (100-600 K) and frequency (10-10³ Hz). The ferroelectricity of thin films was probed by hysteresis measurements. High dielectric constant, low losses and high remnant polarization of thin film capacitors are suitable characteristics for applications in electronic devices.

In Situ Stress Measurements of W and Nanocrystalline Nanotwinned Cu Deposited by HiPIMS Alison Foregall, Swannee J. Shin and Yinnmin Wang; Lawrence Livermore National Laboratory, Livermore, California, United States.

High power impulse magnetron sputtering (HiPIMS) is an emerging method for the deposition of thin films. Pulsed power applied to a sputtering target at a low duty cycle and high power density generates a dense plasma with a high percentage of sputtered ions. The resulting films have improved properties of adhesion, hardness, density, and uniformity compared to films deposited with traditional magnetron sputtering. The technique also shows potential in synthesizing advanced microstructures such as nanocrystalline nanotwinned films. In-situ stress measurements have been performed on HiPIMS W and nanocrystalline nanotwinned Cu and contrasted with DC sputtered films under similar processing conditions, followed by characterization and microstructure analysis of the resulting films.

LLNL-ABS-753116. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors acknowledge the support of LDRD program (17-ERD-048) at LLNL.

PM07.09.20
Laser Ablation of Molybdenum foil Immersed in Precursor Solution Mostafa Mozael, Bernard Kear and Stephen D. Tse; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Titanium dioxide belongs to the transition-metal oxide family and forms several polymorphs, including anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). In comparison with other polymorphs, anatase-TiO₂ is preferable for solar cell applications because of its high electron mobility, low dielectric constant, and low density. The main drawback is that it does not absorb well visible light. In this work, a novel method is used to synthesize amorphous molybdenum-doped-TiO₂ nanoparticles, which upon subsequent post-annealing, transform into nanocrystalline structures. The resulting nanoparticles display photocatalytic activity, which is improved after doping, in comparison to that for undoped nanoparticles. Amorphous Mo-doped-TiO₂ nanoparticles are synthesized using pulsed-laser decomposition of a molybdenum foil immersed in liquid titanium tetraisopropoxide (TTIP). Interaction between the focused laser beam and the Mo substrate generates a submerged-plasma, where vaporization of the Mo substrate along with decomposition of the liquid precursor combine to produce Mo-doped TiO₂ nanoparticles upon quenching by the surrounding unreacted liquid precursor. The as-synthesized nanoparticles have non-crystalline or amorphous structures, primarily because of rapid condensation and quenching of vaporized species from the plasma-reaction zone. Interestingly, upon subsequent heat treatment in air or oxygen, starting at ~400°C, transformation to the more stable anatase-TiO₂ phase occurs, but doped with molybdenum. Initial results show that Mo-doped anatase TiO₂ exhibits a higher UV and visible photochemical activity than that for undoped anatase-TiO₂. Heat treating the nanopowders were investigated in this work to study the effect on crystal structure of TiO₂ after doping with molybdenum ions. It is notable that the phase transformation from anatase to rutile of Mo-doped TiO₂ samples is delayed a certain temperatures, implying that the molybdenum may help to stabilize the anatase phase.

PM07.09.21
Micro-Plasma Based Enhancement in Dielectric and Piezoelectric Properties of ZrO₂ and BaTiO₃ Based Multifunctional Composite Thin Films by Surface Modification—Comparison of Plasma Regimes and Materials Characterization Using Corona Discharge Harlavnreet Brar¹, Walker Tuff², Saquib Ahmed³, Edbertho Leal-Quiroz³ and Sankha Banerjee¹; ¹California State University, Fresno, Fresno, California, United States; ²Mechanical Engineering, Buffalo State College, Buffalo, New York, United States; ³Mechanical Engineering, University of California, Merced, Merced, California,
Atmospheric pressure and ambient temperature based micro-plasmas have been used in polarization and alignment of dipoles in ferroelectrics. The same phenomenon can be used to enhance the surface energy and surface characteristics of composite multifunctional thin films by means of surface modification. The current work involves the use of dielectric barrier and corona discharge based atmospheric micro-plasmas to treat ZnO-Epoxy-BaTiO3 nano-composite flexible thin films towards enhancement in electrical, dielectric and piezoelectric properties of these composites. The ZnO volume fraction is varied from 1-10%, while the BaTiO3 volume fraction is held constant at 40%. Both voltage driven (stable) and current driven (pulsed) corona discharge regimes are identified and used to process the thin films. The voltages in the stable regimes are varied from 8 – 11 kV, while the current is held constant around 0.01 mA. The current in the pulsed regime is varied from 0.05 – 0.1 mA and the voltage is held constant around 9 kV. The surface properties are characterized by multi-point probe measurements to map and analyze the effect of the different plasma regimes. The composite thin films are also tested for their bulk dielectric, impedance, electrical and piezoelectric properties. The effects of the different plasma regimes on the surface micro-structure are analyzed using a scanning electron micrographs and energy-dispersive x-ray spectroscopy.

PM07.09.22
Synthesis of Nanoscale Optical Multilayer Coatings via Reactive Magnetron Sputtering Chelsea D. Appleget and Andrea Hodge; Aerospace and Mechanical Engineering Department, University of Southern California, Los Angeles, California, United States.

Optical multilayers are comprised of nanoscale layers, where the layers are arranged to alter the way the material reflects and transmits light. The interplay of these nanolayers increases the potential for novel combinations of properties, including transparency and strength. These characteristics are important for applications that require light penetration for function but a robust barrier for protection. For these reasons, optically transparent multilayers are promising materials because they offer extraordinary strength, hardness, heat resistance, and most importantly, transparency in both the UV/Vis/NIR wavelengths.

A series of optical nanomultilayers were synthesized using sequential DC and RF reactive magnetron sputtering. The nanomultilayers were designed using predictive methods for maximized optical transmittance, and the experimental results were compared with calculated transmittance values. The effects of deposition parameters were examined in order to understand their influence on the interface, microstructure, mechanical deformation and light propagation of the films. As-sputtered layer roughness, interfaces, and texture were characterized using SEM, TEM, and XRD. Overall, this work focuses on reactive magnetron sputtering of multifunctional nanoscale multilayers, and the effect of the as-deposited microstructure on resulting mechanical and optical properties is discussed.

PM07.09.23
Iron Oxide-Hydroxide Photovoltaic Nanomaterials Synthesized by Atmospheric Micro-Plasma Ayasha Shanmuki, Marieme Ndaw, Sz-Chian Liou, Sabir Pokharel, Mobolaji Zondode, Saroj Pramanik, Jiang Li, Abdellah Lisfi, Yongle Pan and Yucheng Lan; 1Department of Physics and Engineering Physics, Morgan State University, Baltimore, Maryland, United States; 2Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 3Department of Biology, Morgan State University, Baltimore, Maryland, United States; 4Department of Civil Engineering, Morgan State University, Baltimore, Maryland, United States; 5\( ^{\oplus} \) U.S. Army Research Laboratory, Adelphia, Maryland, United States.

With the increasing global energy demand and diminishing fossil fuel reservation, renewable and environmental-friendly sustainable energy is interested in the past years. Solar photovoltaic technology is a promising way to collect solar energy into electricity directly. Iron oxides and hydroxides are one kind of candidate materials for photovoltaic materials because of their abundance on earth and chemical stability in aqueous media. Here, iron oxide-hydroxide was synthesized in aqueous solutions by the atmospheric micro-plasma. The hydroxide powders were characterized by X-ray powder diffraction, transmission electron microscopy, Raman scattering, and UV-vis spectroscopy. The effects of pH values, electric fields, and synthesis temperatures etc were systematically studied to understand the morphology, crystallinity, magnetic property, band-gap, and UV-visible light absorptions. The plasma reaction mechanism was discussed. The as-synthesized nanomaterials were further fabricated into dye-sensitized solar cells and their photovoltaic properties were investigated.

PM07.09.24
Controllable Plasma Based Synthesis of MoS2 for Optoelectronic Applications Dipanjan Nandi, Dhvanini Gudi, Xinsong Lin, Andrea Sedgwick, Manisha Gupta and Jianin Fan; 1Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada; 2Centre for Oil Sands Sustainability, Northern Alberta Institute of Technology, Edmonton, Alberta, Canada; 3Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Recent advancement of two dimensional (2D) materials paves new avenues for potential optoelectronic and nanotechnology applications. Advancement in molecular biology, atomic and molecular physics demands new techniques to explore the atomic level features of different 2D materials as these materials have exciting optoelectronic properties [1, 2]. Mechanical exfoliation and chemical vapor deposition (CVD) are two well-known techniques for MoS2 synthesis. Monolayers of MoS2 are attached with van der Walls forces and can hence be exfoliated easily. However, it is difficult to control the structural parameters such as size, shape, and thickness of the exfoliated MoS2 flakes. CVD technique used for synthesis of good quality MoS2 crystals lacks in in-situ thickness control. Pulsed laser deposition (PLD) is a well-established laser plasma based material growth technique to maintain good stoichiometry for complex compound materials with good control in thickness and repeatability.

In this work, PLD technique is used for growing large area homogeneous MoS2 thin films for nanoscale optoelectronic applications. This study focuses on the optimization of the PLD growth parameters for obtaining high-quality uniform large area MoS2 thin films on quartz, sapphire and SiO2/Si substrates and characterizing the physical properties. In this work, a pulsed KrF (248 nm, 15 ns, 10 Hz) laser is used for ablation of the 99.9% pure MoS2 target. Major parameters influencing the quality of MoS2 thin film like the laser fluence, target-substrate distance, substrate material and temperature along with the ambient gas pressure will be optimized to obtain thin films with high crystallinity and mobility.

Initial growths at different temperatures (room temperature to 850°C) indicate higher crystallinity at higher temperatures like 700°C to 850°C. Also, we have been able to control the growth time to obtain 2-3 monolayer MoS2 thin films, which have been confirmed by the Raman peaks at 382.1 cm\(^{-1}\) and 404.9 cm\(^{-1}\). Initial measurement at room temperature shows electron mobility of 0.19 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for ~30 monolayers. Metal-oxide-semiconductor capacitor will be fabricated to calculate the doping concentrations and Hall measurements will be performed to calculate the carrier mobility. Material, optical and electrical characterization of the optimized MoS2 thin films grown using PLD will be presented. Future prospects of this work is to fabricate nanoscale field effect transistors on flexible substrates for flexible electronic applications.

Reference:

1. Yan Chen et al., ACS Appl. Mater. Interfaces, 8, 47, 32083-32088 (2016).
Methods are widely used to synthesize ATO nanocrystals. However, to meet the electronic conductivity requirements, post-synthesis anneal treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and size distribution of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO powders with respect to size and core-shell structure formation will be discussed in details in conjunction with TEM, S/TEM, VSM and XRD results.

Non-equilibrium atmospheric pressure plasma has emerged as a new platform technology for the synthesis/surface engineering of various nanomaterials. When interacting with water, a high density of gas phase plasma electrons become solvated in the liquid, creating a rapid cascade of transient non-linear chemical reactions and highly reactive radicals. As plasma induced species and reactions propagate through the liquid, they are interrupted at solid surfaces, leading to energetic final reactions. In this work, we deployed a direct current (DC) room temperature atmospheric pressure plasma (APP) for the in situ synthesis of gold nanoparticle/nanocarbon (AuNP/NC) hybrid structures in aqueous solutions. More specifically, carboxyl functionalized multi-wall carbon nanotubes and graphene oxide nanosheets have been decorated with different sized AuNPs through manipulating the gold salt (HAuCl4) precursor concentration in the aqueous mixture. UV-vis spectroscopy and zeta potential analysis suggested that the bonding between the [AuCl4] complex and nanocarbons carboxyl functional group took place prior to the APP processing. These binding sites facilitated the preferential nucleation and growth of AuNPs through the APP induced liquid chemistry. The AuNP/nanocarbon hybrids also demonstrate enhanced Raman scattering and greater photothermal conversion efficiency under the irradiation of NIR laser, hence may hold great potential in future multi-modal cancer treatment involving bio-imaging and hyperthermia therapy.

For electrochemical applications, metal-oxide materials have attracted research interest as alternative electrode materials for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area and uniform distribution of the particles. Among thermodynamically stable metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high electrical conductivity by incorporation of suitable Sb doping, 2) high chemical stability over a wide range of pH values and reduction potentials, and 3) abundant constituent elements. In liquid phase, sol-gel and colloidal methods are widely used to synthesize ATO nanocrystals. However, to meet the electronic conductivity requirements, post-synthesis anneal treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and size distribution of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. ATO nanocrystals were formed in plasma by reacted precursor vapors. Thin films comprised of ATO nanocrystals were then immediately deposited by inertial impact deposition of the aerosol resulting from plasma synthesis. A variety of methods were utilized to characterize the resulting materials, and determine properties such as film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were investigated by Fourier-transform infrared (FTIR) absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the thin film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation, and the effects of nanocrystal size on the transport properties of ATO thin films will be presented in this work.


For electrochemical applications, metal-oxide materials have attracted research interest as alternative electrode materials for reactions occurring at positive potentials in the presence of water. Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area and uniform distribution of the particles. Among thermodynamically stable metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high electrical conductivity by incorporation of suitable Sb doping, 2) high chemical stability over a wide range of pH values and reduction potentials, and 3) abundant constituent elements. In liquid phase, sol-gel and colloidal methods are widely used to synthesize ATO nanocrystals. However, to meet the electronic conductivity requirements, post-synthesis anneal treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and size distribution of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. ATO nanocrystals were formed in plasma by reacted precursor vapors. Thin films comprised of ATO nanocrystals were then immediately deposited by inertial impact deposition of the aerosol resulting from plasma synthesis. A variety of methods were utilized to characterize the resulting materials, and determine properties such as film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were investigated by Fourier-transform infrared (FTIR) absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the thin film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation, and the effects of nanocrystal size on the transport properties of ATO thin films will be presented in this work.


Directed Plasma Synthesis of TiO2 Nanopatterning for Templated Growth and Alignment of Au and Alloyed Nanoparticles Ming Kit Cheng, Brandon J. Holybee, Akshath R. Shetty and Jean Paul Allain; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.
TiO₂ has been an important semiconductor for optical applications including: photovoltaics and photocatalysis, due to favorable properties such as wide band gap, chemical stability and low cost. Recently the incorporation of photonic crystal (PC) structures and noble metal nanoparticles (NPs) on the free surfaces have been carried out to exploit the photonic and plasmonic resonance in enhancing absorption of a broader sunlight spectrum. The optical performance can be further improved if they can be coupled. A versatile processing synthesis approach that can control the shape, size and alignment of NPs to scale is needed to maximize the coupling. Directed low-energy plasma and ion-beam synthesis is a promising technique to induce complex nanopatterns such as ripples on various material surfaces. These nanopatterns can then act as a template for the growth and alignment of NPs with high areal density at nanometer scales. Ions extracted from plasma can also modify the surface chemistry and wettability, which mediates NP growth kinetics and adhesion onto the surface. However, few research focuses on plasma-based nanosynthesis on TiO₂ despite its wide usage, unlike other widely-used materials such as Si. Therefore, it is necessary to first examine the parameters necessary to nanopattern TiO₂ via plasma nanosynthesis. Moreover, when dealing with a non-flat surface with PC structures, additional factors such as non-uniform sputtering rate across the surface and shadowing effects by the structures have to be examined.

We were able to induce periodic ripples with wavelengths and amplitude varying between 14-57 nm and 0.9-3.0 nm respectively on a 100 nm thick TiO₂ film coated on a polymer substrate with 1D diffraction gratings via Ar⁺ and O₂⁺ irradiation at an oblique angle and varying fluence. The photonic resonance peak of the substrate was blue-shifted from 860 nm to as low as 838 nm. In a particular case in which the beam orientation is oblique relative to the gratings, an additional peak about 40 nm higher than the primary one appeared. Moreover, while both Ar⁺ and O₂⁺ can nanopattern TiO₂, Ar⁺ created oxygen vacancies and reduced the oxide while O₂⁺ suppressed its formation. Ordered ripples also appeared at a lower fluence with less defects when using O₂⁺. Our goal is to utilize these ripples for a templated NP growth by glancing angle PVD, by exploiting the shadowing effect by the ripples to facilitate nucleation and NP alignment. We will investigate the ability to tune the NP size, shape and spacing and its plasmonic properties by varying the ripple dimensions and deposition parameters, in order to achieve broadband absorption and coupling with photonic resonance. We will also examine whether creating or suppressing oxygen vacancies is more beneficial to NP growth. For the composition of the NPs, we will not only examine conventional Au NPs, but also novel metallic alloy NPs that is cheaper, more sustainable and absorbs light more efficiently.

9:30 AM PM07.10.04
Nanocomposite Thin Films Obtained with Cold Atmospheric Pressure Plasma Processes
Jacopo Profili and Luc Stafford; Université de Montréal, Montreal, Quebec, Canada.

In the last decade, many efforts have been made for the understanding and the analysis of nanocomposite thin films. The new properties created by these materials open a wide range of possibilities for new industrial applications. Different physical and chemical advanced processes are used to develop these products. Among them, low plasma pressure processes have been studied since Philips’s work in 1982. Today, the desire to reduce production costs and environmental impacts of the manufacturing process allowed the study of new plasma approaches at atmospheric pressure. These systems offer the possibility to reduce the amount of precursor and favor the process scale-up in a production line. Recently, some researchers have demonstrated the possibility to use colloidal suspensions as precursors for the synthesis of nanocomposite thin films in atmospheric pressure dielectric barrier discharge (DBD). This approach broadens the chemical range of obtainable nanocomposites because of the large variety of commercially available suspensions. Through this work, we aim to highlight the current understanding of the process and the remaining scientific challenges for the synthesis of a homogeneous distribution of chemical phases with plasma treatment. The DBD is obtained between two parallel alumina plates separated with 1 mm gas gap. An AC high voltage in the kV frequency range is used to sustain a homogeneous Townsend discharge in N2-N2O gas mixtures. Titanium dioxide nanoparticles (TiO₂ NPs, anatase phase, 20 nm in diameter) are functionalized and mixed with Hexamethyldisiloxane (HMDSO) to get a stable colloidal solution. This suspension is injected in the gas mixture using a pneumatic injector coupled to a nebulizer. The obtained colloidal aerosol is then evaporated before reaching the discharge chamber. Plasma-deposited coatings were then characterized by SEM, FTIR and XPS. The hydrodynamic radius of particles (and agglomerates) in the colloidal solution was determined using Dynamic Light Scattering analysis (DLS). The electrical analysis of the process shows that the discharge remains stable and homogeneous during the injection of the suspension, indicating that nanoparticles do not affect the physical regime of the discharge. The SEM analysis indicates that spherical agglomerates remain included in a dense matrix or stuck on the surface. The size distribution of these structures can be larger than 1 micrometer, i.e. bigger than the coating thickness. The Raman peak at 143 cm⁻¹, associated with the anatase structure, shows no structural change of NPs during their interaction with the discharge. Our results show that the observed agglomeration can take place at different steps of the process, including in the initial suspension, during the atomization process and as a result of plasma interactions. Finally, our results reveal that the transport dynamics of NPs can judiciously be controlled using custom-designed voltage waveform.

9:45 AM PM07.10.05
Additive Manufacturing of Nanomaterials Using Plasmas
Kyle O’Shea, Alexander Ha and Rebecca J. Anthony; Michigan State University, East Lansing, Michigan, United States.

Plasma reactors have been used for synthesis of many types of nanomaterials with great success, from a range of materials including semiconductors and metals. These reactors feature versatile operation across pressure, power, and size regimes. While low-pressure plasmas typically lead to nanoparticle ensembles with the narrowest size distributions, atmospheric pressure plasmas can produce high-quality and tunable nanocrystals particularly when the reactor size is miniaturized. Both the small reactor size and atmospheric pressure operation contribute to the potential to use these reactors in roll-to-roll manufacturing and other large-scale deposition schemes, removing batch post-processing steps and enhancing the ability to incorporate the nanoparticles into the manufacturing stream.

Here we present our work on additive manufacturing of silicon nanoparticles using an atmospheric pressure glow discharge. The reactor consists of a quartz tube encircled by a powered coil electrode (one end floating) supplied with RF power at 13.56 MHz, together with a coaxial central ground electrode. We supply silane and argon gas (total gas flowrate ~ 200 sccm) for silicon nanoparticle production. Silicon nanoparticles are produced in the plasma and spray out of the tube onto the substrate beneath. The nanoparticles are crystalline with a relatively wide size distribution (5-40nm) as verified using transmission electron microscopy and the ensembles exhibit photoluminescence near 600 nm. The reaction is performed in air, and the nanoparticle surfaces are coated in an oxynitride layer as determined using Fourier-transform infrared spectroscopy. The reactor is mounted to a computer-controlled 3D manipulator which allows the nanoparticles to be deposited in pre-programmed patterns in all three coordinates directly out of the reactor. Our current work focuses on characterizing the deposition properties including porosity, mechanical properties, and yield while simultaneously engineering the reactor to enable narrower linewidth and a smaller size distribution of nanoparticles, along with controlled shell composition and thickness using additional gas flows. This work could lead to directly printable nanocrystal layers and coatings for in-situ fabrication of devices and other technologies.

10:00 AM BREAK
Effect of Zr Target Power on Structure Property Relations of Ni-Zr Alloy Thin Films Processed by DC Magnetron Co-Sputtering

The application of strong electric fields in water and organic liquids has been studied for many years, because of its importance in electrical transmission processes and its practical applications in biology, chemistry, and electrochemistry. More recently, liquid-phase electrical discharges have been investigated, and are being developed. Recent advances in pulsed power technology permitted application of much faster voltage rise times (including the subnanosecond range) and revealed that plasma-like phenomena can, in fact, occur in fluid phase quasi-homogeneously without any bubbles and voids. Very sharp rise times leads to overvoltage and development of a non-thermal discharge (direct ionization of liquid phase) before fluid moves forming bubbles or gas voids. Here we present the first results on characterization and diagnostics of nanosecond-pulsed discharge in liquid nitrogen and characterization of produced materials.

* This work is supported by the Army Research Office (grant # W911NF-17-1-0597, PI: Dobrynin).

11:00 AM PM07.11.02
Synthesis, Processing, and Characterization of Materials Processed by Spark Plasma Sintering

Spark Plasma Sintering (SPS) has been employed as a very effective method for consolidation of powders into dense polycrystalline materials. We have employed SPS as a unique approach for material synthesis, including crystal growth. Moreover, due to the internal localized heating during SPS processing, the rapid, low temperature densification of fine-grain powders can be realized. Since only the surface temperature of the sample powders rises rapidly by self-heating, grain growth is minimized, thus high density, bulk polycrystalline semiconductors with nano-scale grains can be achieved. This technique is important in obtaining thermoelastic materials whereby grain-boundary scattering is realized thus allowing for materials with enhanced thermoelectric performance, as compared to the same polycrystalline material with micro-scale grains. A variety of examples, including synthesis and, in particular, the crystal growth of materials with complex crystal structures that have not been previously synthesized even in microcrystalline form, will be presented. In addition, our consolidation technique for nanostructured materials will be discussed, with specific emphasis on an understanding of specific processing conditions and their effect on the morphology of different semiconductors and the resulting grain size and product density.

11:15 AM PM07.11.03
Effect of Zr Target Power on Structure Property Relations of Ni-Zr Alloy Thin Films Processed by DC Magnetron Co-Sputtering

A comparative study has been carried out on microstructural evolution, surface roughness, nanoindentation and scratch behavior, electrical resistivity, and corrosion resistance of Ni1-xZrx (0.13≤x≤0.40) thin films deposited on Si-(100) substrate by DC magnetron co-sputtering of high purity elemental targets in argon atmosphere. The Zr target power has been changed from 75 watt to 175 watt by keeping the Ni power constant at 200 watt. The film compositions have been examined by energy dispersive X-ray. Grazing incidence X-ray diffraction (GIXRD) studies have shown presence of Ni-rich solid solution, Ni3Zr and amorphous phase in all the films, with Ni3Zr being additionally observed in the Ni5Zr13 film. Analysis of GIXRD data along with transmission electron microscopic studies have shown that volume fractions of both amorphous phase and Ni3Zr are increased, whereas the average crystallite size is decreased with increase in Zr concentration. Nanoindentation hardness and Young’s modulus as well as electrical resistivity measured by Van-der Pauw four-probe method are influenced by volume fractions of both Ni3Zr and amorphous phase. Surface roughness and coefficient of friction obtained from atomic force microscopy and nano-scratch experiments, respectively decrease, whereas corrosion resistance in 3.5 wt% NaCl solution increase with Zr concentration primarily due to increase in amorphous phase content. Resistance to pitting corrosion is facilitated by formation of ZrO2-rich passive film, as confirmed by X-ray photoelectron spectroscopy.

11:30 AM PM07.11.04
Atmospheric Pressure High Power Impulse Plasma Source (HiPIPS) for Deposition of Metallic Coatings

Southwest Research Institute (swRI) is developing a novel atmospheric pressure, non-thermal High Power Impulse Plasma Source (HiPIPS) technique for field applicable deposition of metallic protective coatings. The HiPIPS technology is an advanced variation of atmospheric pressure plasma process that uses high power pulsed DC generators. Power is applied in microsecond pulses at low duty factor (< 10%) and low frequency (< 1 kHz) leading to high peak power densities (tens of kWatts) and high peak currents (hundreds of Amps) while keeping low overall power (< 50 W) and low processing temperatures (< 50 °C). These conditions result in the generation of a highly dense plasma discharge, with increased ionization for surface modification and deposition of coatings. SwRI has conducted a systematic experimental study on the HiPIPS process parameters and resultant coating properties towards proof-of-concept development of HiPIPS deposition of CoCr, Ti-6Al-4V and TiN coatings. Plasma properties were characterized using current-voltage probes and optical emission spectroscopy (OES). The microstructure and elemental composition of resulting deposited were examined using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD).
Tailoring the Magnetocaloric Potential of AlFe₂B₂ Using Conventional and Additive Manufacturing Processing Schemes 

Radhika Barua¹, Brian Lejune², Brandt Jensen³, Ryan Ott⁴, Matthew J. Kramer⁴; ¹Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; ²Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; ³Division of Materials Science & Engineering, Ames Laboratory, Ames, Iowa, United States; ⁴Department of Mechanical Engineering, Northeastern University, Boston, Massachusetts, United States.

Material processing schemes play a critical role in guiding the development of emerging magnetocaloric materials for energy-related applications such as magnetic refrigeration and thermomagnetic energy conversion. To this end, the intermetallic boride AlFe₂B₂ has attracted considerable attention due to its low cost, promising thermal properties that promote effective heat transfer (specific heat capacity \( C_p = 120 \text{ J mole}^{-1} \text{K}^{-1} \)), thermal conductivity \( \kappa = 5.6 \text{ W m}^{-1} \text{K}^{-1} \), and moderate magnetocaloric response near room temperature (adiabatic temperature change \( \Delta T_{\text{ad}} = 1 \text{ K} \) and magnetic entropy change \( \Delta S = 2.6 \text{ J kg}^{-1} \text{K}^{-1} \) at \( \mu_0 H = 2 \text{ T} \)). In this work, a number of synthesis methods to form single-phase AlFe₂B₂ alloys were investigated. Further, the feasibility of 3D-printing honeycomb shaped samples was explored. It is surmised that AlFe₂B₂ is amenable for construction of magnetocaloric heat exchangers where the working material may be shaped as channel structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid. Overall, this study provides strategies for maximizing the magnetofunctional potential of AlFe₂B₂.

* Invited Paper

8:30 AM *TP01.01.01
Exploiting First and Second Order Phase Transitions in Magnetocaloric NiMn-Based Heusler Compounds Francisco Alberini¹, Cecilia Bennati², Simone Fabbrici², Riccardo Cabussi¹, Francesco Cugini¹, Nicola Sarzi Annadi², Massimo Solzi², Antonio Pepicelli² and Ciro Visone²; ¹IMEM-CNR, Parma, Italy; ²Università di Parma, Parma, Italy; ³Università del Sannio, Benevento, Italy.

Room temperature magnetic refrigeration requires materials with large isothermal entropy and adiabatic temperature changes at around 293 K and negligible thermo-magnetic hysteresis, when cycled in magnetic fields below 2T. Ferromagnetic shape memory Heusler compounds with metamagnetic martensitic transformations are among the most studied materials for magnetocaloric applications thanks to their high adiabatic temperature changes \( \Delta T_{\text{ad}} \) related to their inverse magnetocaloric effect [1]. These materials are rare earth free, easy-to-prepare and offer large tailoring possibilities. Remarkably, thanks to the strong discontinuities of the physical properties at the martensitic transformation (e.g. magnetization, volume), caloric effects can be obtained not only by applying magnetic fields but also stress and pressure, enabling multicaloric applications [2,3]. Although very high values of adiabatic temperature change have been reported, metamagnetic Heuslers show poor reversibility due to hysteresis and spreading of the transition. By taking advantage of suitable substitutions, in NiMn-based Heusler alloys it is possible to tune the order and the number of transitions that can be exploited for magnetocaloric applications. In the present talk we will report some particular cases in the phase diagram of NiMnGa and NiMnIn compounds and discuss the reversible and irreversible contributions to the magnetocaloric effects, based on in-field calorimetry and direct \( \Delta T_{\text{ad}} \) measurements. Interesting effects occurs when the first order magnetostructural and second order Curie transition are almost coincident. In In-based compounds, for example, the coexistence of direct and inverse magneto calorific effects can be obtained [4]. The possible exploitation of direct and inverse MCEs in alternative refrigeration cycles will be discussed.


9:00 AM TP01.01.02
Tailoring the Magnetocaloric Potential of AlFe₂B₂ Using Conventional and Additive Manufacturing Processing Schemes Radhika Barua¹, Brian Lejune², Brandt Jensen³, Ryan Ott⁴, Matthew J. Kramer⁴; ¹Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; ²Department of Chemical Engineering, Northeastern University, Boston, Massachusetts, United States; ³Division of Materials Science & Engineering, Ames Laboratory, Ames, Iowa, United States; ⁴Department of Mechanical Engineering, Northeastern University, Boston, Massachusetts, United States.

Suction-casting allows fabrication of samples of various composition, including Al₁₋ₓMₓFe₂B₂ (M=Ga and/or Ge, x<0.1). Experimental data obtained using structural and magnetic probes indicate that the unit cell volume, saturation magnetization (Mₛ), Curie temperature (Tₘ) and specific heat capacity (Cₚ) of the samples increase with increased Ga and Ge content (x). Relative to the unmodified parent AlFe₂B₂ sample, a larger than two-fold improvement in the magnetocaloric effect (MCE) was observed in the Al₁₋ₓGaₓFe₂B₂ specimen (\( \Delta S = 6.5 \text{ J kg}^{-1} \text{K}^{-1} \), \( \Delta T_{\text{ad}} = 2.2 \text{ K} \) at \( \mu_0 H = 2 \text{ T} \)). Intriguingly, the solid solubility of Ga and Ge in AlFe₂B₂ was determined to be negligible and it is deduced from calorimetric data that additions of these substituent elements alter the solidification route for formation of the AlFe₂B₂ phase. The enhanced MCE of the Al₁₋ₓ(Ga/Ge)ₓFe₂B₂ samples is ascribed to a combination of chemical bonding and electronic effects arising from a hypothesized enrichment of Fe atoms on the Al sites within the (ac) plane of the AlFe₂B₂ lattice. These results provide fundamental insights regarding the phase stability of the Al-Fe-B ternary system, and guide development of AlFe₂B₂ samples of complex geometries using laser engineered net shaping (LENS). The MCE of cylindrical LENS samples (5 mm dia; 30 mm length) was found to be comparable to that of corresponding undoped suction-cast samples (\( \Delta S_{\text{LENS}} = 2.8 \text{ J kg}^{-1} \text{K}^{-1} \), \( \Delta T_{\text{ad,LENS}} = 1.1 \text{ K} \) at \( \mu_0 H = 2 \text{ T} \)). Further, the feasibility of 3D-printing honeycomb shaped samples was explored. It is surmised that AlFe₂B₂ is amenable for construction of magnetocaloric heat exchangers where the working material may be shaped as channel structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid. Overall, this study provides strategies for maximizing the magnetofunctional potential of AlFe₂B₂.
9:15 AM **TP01.01.03**

**Disorder and Electron Correlation Effects in the Ground State of Ni-Co-Mn-Sn Alloys with Heusler Structures**

Bernardo G. Barbiellini, 1, 4, Aki Pulkkinen, 2, Johannes Nokelainen, 1, Vladimir Sokolovskiy, 3, Vasiliy Buchelnikov, 3, Mikhail Zagrebin, 3, Katariina Pussi, 3, Erkki Lähderanta, 2 and Alexander Granovsky, 3

1Physics, LUT, Lappeenranta, Finland; 2Chelyabinsk State University, Chelyabinsk, Russian Federation; 3Physics, Moscow State University, Moscow, Russian Federation; 4Department of Physics, Northeastern University, Boston, Massachusetts, United States.

We consider ab-initio calculations of Co-doped Ni-Mn-Sn shape memory alloy. The Co doping leads to a decrease in both the martensitic transformation temperature and the Curie temperature of martensite and to an increase in the Curie temperature of austenite. Besides, large magnetisation changes occur in the vicinity of structural transformation. As a result, the tuning of Co and Mn contents can lead to favorable magnetocaloric properties [1]. In this work, we focus on the effect of atomic disorder and electron correlation on the structural, magnetic and electronic properties of Ni-Co-Mn-Sn systems by using the Density Functional Theory (DFT) implemented in the VASP and SPR-KKR packages [2, 3] within a 32-atom supercell and the coherent potential approximation, respectively. The optimized atomic positions for compositions studied are obtained by the USPEX package [4]. To study the effect of exchange-correlation, a series of ground state calculations were performed using both the GGA-PBE functional and Meta-GGA with SCAN functional of DFT [5].

[1] Huang et al., APL. 104 (2014)132407

9:30 AM **TP01.01.04**

**Magnetic and MagnetoCaloric Properties of Fe-(W)Ta Thin Films**

Surabhi Shaji, Nikhil R. Mucha, Prakash Giri and Dhananjay Kumar

1 North Carolina A&T State University, Greensboro, North Carolina, United States; 2University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

A first hand magnetocaloric effect (MCE) in rare-earth free Fe-W (Ta) thin film systems, induced by simultaneous transformation in structural and ordered magnetic phases, is reported. The MCE has been realized by varying the levels and types of dopants in the Fe-host. These materials systems in thin film form have shown a crystallographic phase transition from a regular body center cubic (BCC) crystal structure to a distorted BCC. Applying the Maxwell relation to the magnetization (M) versus magnetic field (H) curves at various temperatures, we have calculated dM/dT vs H the integration of which provides a quantitative information about isothermal entropy change. We have observed positive a MCE with a maximum entropy value of 6.9 J/K-m³ for the magnetic field changing from 0.05 – 0.5 T. The mass specific entropy changes are small in comparison with existing magnetocaloric material. A peak in dM/dT versus H has shown that maximum entropy change takes place around 0.15 T, which is more than an order of magnitude lower than the magnetic fields generally used to realize a large MCE effect.

9:45 AM **TP01.01.05**

**Thickness Dependent Size Effects on Hysteresis in Electrochemically Deposited Thick Film NiMnSn Heusler Alloys**

Yijia Zhang, Julia Billman and Patrick Shamberger

Texas A&M University, College Station, Texas, United States.

Characteristic length scales of Heusler alloy films, including film thickness and grain size, affect the transformation hysteresis by altering internal energy barriers to interphase boundary motion. Previous studies have illustrated strong film thickness effects on transformation temperatures of nanoscale TiNiCu thin film with film thickness < 100 nm, and that stress hysteresis and temperature hysteresis of CuAlNi microwires increased with decreasing wire diameter with diameter < 100 μm. However, length-scale dependent hysteresis has yet to be determined for other classes of caloric materials, including Heusler alloys. Understanding such transformation behavior at small length scales is critical for microelectronic and micromechanical applications, for promoting rapid heat transfer through caloric alloy thin films and thin wires, in strain-coupled magnetoelectric composites, and in microstructured multifunctional composites and foams.

By annealing electrochemically deposited multi-layer monatomic (Ni, Mn, Sn) films, Ni0.5Mn0.386Sn0.114 Heusler alloy films with decreasing thicknesses, 14.5, 8.7, and 2.9 μm, were synthesized. Phase transformation temperatures and sizes of nearly four hundred grains on each film were collected optically while the samples were heated or cooled. These data showed that the average grain areas/volumes decrease with decreasing film thicknesses. For grains within a single film (constant thickness), there is no statistically significant correlation between grain area or volume and hysteresis width. At the same time, film hysteresis increases with decreasing film thicknesses (from 4.9°C at 14.5 μm to 15.7°C at 2.9 μm). Previously, Chen and Schuh (2011) attributed the size effect in the hysteresis of small CuAlNi alloy microwires to the enhanced internal frictional work during transformation, associated with an increase in surface area and volume ratio. Our thickness dependent size effects could be similarly explained by internal friction-induced energy dissipation, whereby the thinner the film is, the stronger the interactions between interphase boundaries and the film-substrate interface, and the more energy is dissipated by frictional work. A power law model is fit to hysteresis width-film thickness data, and is used to elucidate scaling relationships which govern size dependence of hysteresis in Heusler alloy thin films, which are compared against previously observed size-dependent hysteresis in other thermoelastic martensitic transformations.

10:00 AM BREAK

10:30 AM OPEN DISCUSSION

11:00 AM **TP01.01.07**

**Orientation Relationships and Lattice Matching Effects on Hysteresis in (Mn,Fe)2(P,Si) Phase Transitions**

Timothy D. Brown and Patrick Shamberger

Texas A&M University, College Station, Texas, United States.

Hysteresis associated with the non-diffusive phase transformation in magnetocaloric (Mn,Fe)2(P,Si) alloys creates substantial energy dissipation.
undesirable for cooling applications. Although reduced hysteresis has been achieved in this system through tuning of Mn/Fe and P/Si site occupancies, a deeper understanding of the underlying mechanisms necessary for designing low-hysteresis materials across a wide range of critical temperatures has proved elusive. A successful and general mechanistic theory relating hysteresis to lattice matching has been developed for similar transformations in thermoelastic martensites, dependent on both the change in lattice parameters and the orientation relationships between the parent and daughter crystal lattices. Despite the theory’s success and generality, the parent-daughter orientation relationships in (Mn,Fe)(P,Si) have not yet been established, and the lattice matching theory has not yet been tested against hysteresis in this system. In this work, we establish the orientation relationships for basal and prismatic planes in hexagonal (Mn,Fe)(P,Si) alloys through two independent experiments: (1) comparison of temperature-dependent x-ray diffraction pole figures below and above the phase transition and (2) electron backscatter diffraction orientation mapping of adjacent grains of coexisting magnetic parent and non-magnetic daughter phases. Afterwards, we combine these orientation relationships with experimental measurements of lattice parameter discontinuities in order to calculate the lattice mismatch parameter \( \lambda_2 \) for several representative alloys in the (Mn,Fe)(P,Si) system. Finally, the calculated mismatch is correlated with the samples’ hysteresis as measured from calorimetry experiments and compared with the predictions of the theory, thereby establishing whether lattice matching effects may also be used to control hysteresis in (Mn,Fe)(P,Si) alloys’ phase transitions.

11:15 AM TP01.01.08
Effect of Phase Segregation on Phase Transformation Behavior in (Mn,Fe)(P,Si) Alloys

Timothy D. Brown, Jonathan S. Van Buskirk, Daniel Galvan and Patrick Shamberger; Texas A&M University, College Station, Texas, United States.

Alloying in quaternary (Mn,Fe)(P,Si) allows for highly tunable phase transformation temperatures and hystereses, potentially enabling high-efficiency magnetocaloric cooling over a wide range of temperatures. However, compositional control of the alloy is also subject to complex thermodynamic constraints, as evidenced by segregation of multiple transforming hexagonal phases, as well as precipitation of a non-transforming cubic P-poor (Mn,Fe)Si phase. In either case, the composition, and therefore hysteresis and transformation temperature, of the transforming phases are modified significantly from the nominal bulk composition, thereby obscuring direct causal relationships between composition and transformation behavior. Thus, in order to recover these relationships, as well as to control the expression of transforming phases of interest for cooling applications, it is critical to map out the thermodynamic phase coexistence of the alloy system. In this work, we investigate thermodynamically driven phase segregation behavior in (Mn,Fe)(P,Si) by measuring the compositions and mass fractions of coexistent transforming and non-transforming phases for a range of nominal alloy compositions \((1.20 < \text{Mn} < 1.25; 0.35 < \text{P} < 0.50)\) through quantitative wavelength dispersive spectroscopy and backscatter electron imaging. It is found that oxygen preferentially segregates to the cubic phase over the hexagonal phase (5 at. % vs. <1 at. %), suggesting oxygen plays some role in mediating the stabilization of the cubic phase. Measured compositions of the expressed transforming hexagonal phases are then combined with critical transformation temperatures and thermal hystereses from calorimetry experiments to map out the underlying dependence of the transformation behavior on the phase compositions. The analysis suggests Mn/Fe site occupancy plays a much larger role than P/Si in controlling hysteresis of the phase transition, providing insight into the nature of the energy barriers that fundamentally control hysteresis in this alloy system.

11:30 AM TP01.01.09
Spatially and Temporally Resolved Temperature Measurements of Magnetocaloric Materials Under Varying Applied Magnetic Field


We present an experiment where magnetocaloric samples are spatially and temporally resolved using infra-red (IR) thermography. The spatial resolution is approximately 10x10 microns, while the temporal resolution is 170 Hz. The magnetic field applied to the sample is varied in a controlled way and thus the dynamics of the first order phase transition are observed on the sample surface. We also present complimentary differential scanning calorimetric (DSC) measurements and are therefore able to relate the specific heat peaks of a single sample with the temperature distribution as observed by IR. This work presents our preliminary results for the first order phase transition of La(Fe,Si,Mn)13Hz compounds and describes the challenges of bringing the device into operation. Moreover, an outlook for comparing the results with a time-dependent numerical model, which can predict the material behaviour by finding its internal magnetic field and including finite heat transfer calculations, is given.

11:45 AM OPEN DISCUSSION

1:30 PM TP01.02.01
Optimizing the Electrocaloric Effect by Molecular Dynamics Simulations

Anna Grünebohm; University of Duisburg Essen, Duisburg, Germany.

In this talk I will discuss the benefits of ab initio based molecular dynamics simulations [1] for the optimization of the electrocaloric effect (ECE). The basic principles of the ECE are now well understood [2]. A further optimization asks for a detailed understanding of the impact of phase transitions as well as atomic, defect and domain structures on the ECE and its reversibility. Simulations allow to isolate these factors and predict design rules for ferroelectric materials and composites with superior cooling responses.

I will focus on the factors giving rise to a large inverse caloric response [3], in particular phase transitions [4] and internal bias fields [5].

[3] A. Grünebohm et al., Energy Technol. 10.1002ente.201800166, ‘18,
M. Marathe et al., Phys. Status Solidi (b) 225, 1700308, ’18,

2:00 PM TP01.02.02
Electrocaloric Studies on Epitaxial BaTiO3-Based Thin Films

Stefan Engelhardt1,2, Pengfei Song1,2, Christian Molin2, Sylvia Gebhardt3, Sebastian Faehler4, Kornelius Nielsch4, and Ruben Huehne1; IFW Dresden, Dresden, Germany; 2TU Dresden, Dresden, Germany; 3Fraunhofer IRTS, Dresden, Germany.

Electrocaloric (EC) materials show reversible thermal changes in response to the variation of an applied electric field. This EC effect got a renewed interest within the last decade due to the quest for energy-efficient cooling technologies and recent discoveries of large adiabatic temperature changes \( \Delta T \) in various ferroelectric thin films during the application or removal of an electric field. Among them, lead-containing oxides exhibit strong caloric effects but contain hazardous elements. BaTiO3 (BT) based materials might be a more environment-friendly alternative to these compounds. Therefore, we have chosen BaZr0.1Ti1-xO3 (BZT) and BaHf0.1Ti1-xO3 (BHT) as model systems for our studies in order to investigate the correlation between the composition dependent phase transitions, the dielectric and ferroelectric properties as well as the EC effect of such BT based thin films. Moreover, we use epitaxial films, which additionally enable a detailed microstructural analysis as well as a study of orientation dependent properties.

Accordingly, epitaxial BZT and BHT films were grown by pulsed laser deposition on single crystalline substrates utilizing a conducting oxide buffer layer and additional top electrodes to obtain capacitor like structures. The grown films were studied by X-ray diffraction as well as scanning electron and atomic force microscopy. Depending on the specific growth parameters, a twin-free epitaxial growth and a smooth surface morphology is observed. Temperature dependent measurements of the relative permittivity suggest diffuse phase transitions, where the transition temperature clearly varies with the film composition. The EC properties of the thin films were determined by an indirect method from temperature dependent polarization measurements showing values of up to 0.3 K for a \( \Delta E \) of 170 kV/cm. We assume that the clamping of the thin films to the rigid substrate reduces the magnitude of the EC effect significantly compared to the respective bulk materials. Finally, we will present our approaches for the direct measurement of the EC effect in our epitaxial thin films.

This work is supported by DFG priority program 1599 “Ferroic cooling”.

2:15 PM TP01.02.03

Epitaxial Na0.5Bi0.5TiO3 Based Thin Films for Electrocaloric Studies

Bruno M. Magalhães1, Stefan Engelhardt1, Sebastian Faehler4, Christian Molin2, Sylvia Gebhardt3, Kornelius Nielsch4, and Ruben Huehne1; IFW Dresden, Dresden, Germany; 2Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany; 3Technische Universität Dresden, Dresden, Germany.

Substantial efforts are being employed to the search and development of efficient and environmentally friendly materials with potential for solid state cooling. Motivated by recent discoveries, electrocaloric cooling might be a promising solution as an innovative refrigeration technique, as it shows a significant variation in temperature by adiabatically switching an applied electric field. Among them, lead-free thin films have raised an increased interest in research as they avoid the harmful effects of lead-containing materials. The purpose of our study is to investigate the electrocaloric effect in such lead-free epitaxial thin films. In particular, we are focusing on microstructural changes close to the phase transition of Na0.5Bi0.5TiO3 (NBT) in order to understand the basic mechanisms of the caloric effects, which might enable a further optimization of the electrocaloric properties for specific applications. Accordingly, the growth of NBT thin films with BaTiO3 and SrTiO3 additions is targeted to study the influence of the deposition parameters on the microstructural and the electrocaloric properties in this material system.

Therefore, NBT-based epitaxial thin films were grown by pulsed laser deposition on a variety of single crystalline substrates using LaSr1-xCoO3 as a bottom electrode for a subsequent ferroelectric characterization. The structural characterization displays an epitaxial growth of NBT on the different substrates. Temperature and frequency dependence of the dielectric properties were assessed to measure the temperature of maximum permittivity \( T_m \). Simultaneously, the electrocaloric temperature change was determined indirectly by the dependence of polarization on temperature and electric field strength. Finally, we will discuss the impact of the deposition parameters on the structural and functional properties of the grown films.

This work is supported by the DFG priority program 1599 “Ferroic cooling”.

2:30 PM TP01.02.04

Large Electrocaloric Effects in PST Multilayer Capacitors Over a Wide Range of Useful Temperatures

Bhavi Nair1, Tomoyasu Usui1, Sam Crossley1, Xavier Moya1, Sakyo Hirose1 and Neil D. Mathur2; 1Murata Manufacturing Co., Ltd., Nagaokakyo-shi, Japan; 2Applied Physics, Stanford University, Palo Alto, California, United States; 3Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Using both thermocouples and infrared imaging, we report large electrocaloric effects in PbSc0.5Ta0.5O3 multilayer capacitors near room temperature. For field changes of 29.0 V \( \mu \text{m}^{-1} \), we find changes of temperature that peak at 5.5 K, and exceed 3 K for starting temperatures that span 176 K. This directly measured performance in a macroscopic body improves upon the magnetocaloric response of gadolinium when driven by expensive permanent magnets, suggesting the possibility of a straight swap in prototype cooling devices.

2:45 PM TP01.02.05

A New Class of Electrocaloric Materials—Exhibiting Large Electrocaloric Response at Low Electric Field

Xin Chen, Wenhan Xu, Biao Lu, Tian Zhang, Qing Wang and Qiming Zhang; The Pennsylvania State University, University Park, Pennsylvania, United States.

Electrocaloric effect (EC) is the temperature and change in a dielectric material as the applied field changes. ECE occurs due to electrical field induced dipole-entropy change in dielectrics, which is an extremely efficient form of energy conversion exhibiting minimum losses, e.g., polarization-electric field coupling approaching 100% efficiency. The past decade has witnessed the discovery and advancement in electrocaloric polymers, which display large electric field induced temperature and entropy changes.

In contrast with a burgeoning literature on large ECE in various ferroelectric materials, there are no EC devices employing these materials, demonstrating a meaningful cooling power. The critical barrier for the transition from high performance EC materials to practical EC devices is the dielectric breakdown. Hence, EC devices have to work under electric fields far below their dielectric breakdown. On the other hand, EC devices to achieve sufficient cooling power require large size EC films, which can further reduce their dielectric breakdown. To address these issues, high performance EC materials should possess a large EC response at large fields far below dielectric breakdown. However, the EC response of the state-of-art EC polymer P(VDF-TrFE-CFE) at these practical field range is not high even though it possesses a large ECE at high electric fields (\( > 100 \text{MV/m} \)).

In this work, inspired by the materials concept of high entropy alloys, in which the presence of a large number of elements increases the entropy of the alloys, we developed a new class of EC polymer, tetrapolymer, which possesses a large dipolar entropy. Moreover, the tetrapolymer exhibits a critical end point behavior at low electric fields, thus leading to a giant EC response at low electric fields, which have the promise for high performance and highly reliable EC coolers.
Elastocaloric cooling is currently under extensive study owing to its great potential to replace the conventional vapor-compression technique. In the first part, I will present a Ni$_{50}$Fe$_{19.0}$Ga$_{27.1}$Co$_{3.9}$ ferromagnetic shape memory single crystal, which exhibits giant elastocaloric effect of 11 K and ultralow fatigue behavior during above 12,000 mechanical cycles. The numerical simulation shows that this unique alloy offers 18% energy saving potential and 70% cooling capacity enhancement potential than the conventional shape memory nitinol alloy in a single-stage elastocaloric cooling system, making it as a great candidate for the energy-efficient air conditioner application. Second, I will introduce a Ni$_{50}$Mn$_{11.1}$In$_{16}$Cu$_{2.5}$ metamagnetic shape memory alloy exhibiting giant adiabatic temperature changes of 13 K upon loading. Simultaneously, a small thermal hysteresis of 3 K and an exceptional phase transformation stability over 10$^7$ magnetic field cycles have been achieved by ensuring the compatible kinematic conditions of specific lattice interface. Moreover, we proposed an approach to reduce hysteretic losses and improve the reversibility of magnetoelastic effect by manipulating transformation paths evoked by magnetic field and stress, and therefore such a multicaloric approach is attractively beneficial for reaching high energetic utilization efficiency.

4:00 PM TP01.03.02
Stability of Additive Manufactured NiTi for Compressive Elastocaloric Properties Beyond One Million Cycles
Huilioug Hou$^1$, Emrah Simsek$^2$, Tao Ma$^2$, Suxin Qian$^3$, Drew Stasak$^1$, Naila Al Hasan$^1$, Lin Zhou$^2$, Yunho Hwang$^1$, Reinhard Radermacher$^1$, Matthew J. Kramer$^2$, Ryan Ott$^2$, Jun Stasak$^1$, Ji Hidaka$^1$ and Ichiro Takeuchi$^1$; $^1$University of Maryland, College Park, College Park, Maryland, United States; $^2$Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota, United States; $^3$Iowa State University of Science and Technology, Ames, Iowa, United States.

We report on properties of additive manufactured Ni–Ti alloys in the geometries of solid rods and hollow tubes. We have characterized their room-temperature superelastic and elastocaloric properties after one million cycles. Alloy compositions are flexibly and quickly adjusted by controlling the flow rate of elemental powders during synthesis. Unique microstructure in the material results from rapid solidification and thermomechanical processing with the phase transformation occurring near room temperature. A quasi-linear superelasticity and elastocaloric cooling temperature changes up to 4.1 K are observed in the additive-manufactured alloys under uniaxial compressions at room temperature. We perform extended cycling tests of the alloys while in-situ monitoring their stress-strain properties. Elastocaloric properties are monitored after every 200,000 cycles. After 1,000,000 cycles, the alloys exhibit superelasticity and the stability of alloys after a large number of cycles.

4:15 PM TP01.03.03
Fatigue Influencing Factors in NiTi Based Shape Memory Alloys for Elastocaloric Cooling
Lars Bunke$^1$, Hanlin Gu$^2$, Florian Bruederlin$^2$, Christoph Chluba$^1$, Manfred Kohl$^1$, Richard James$^2$ and Eckhard Quandt$^1$; $^1$Institute for Materials Science, Kiel University, Kiel, Germany; $^2$Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota, United States; $^3$Istitute of Microstructure Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany.

Caloric cooling is an emerging technology with the potential to replace traditional technologies like environmentally harmful vapor compression systems, which already operate close to their theoretical efficiency limit or rather inefficient thermoelectric devices. Within the field of caloric, elastocaloric materials show high latent heats larger than 20 J g$^{-1}$. The elastocaloric effect in shape memory alloys (SMAs) is based on the reversible stress induced martensitic phase transformation. Binary NiTi is a benchmark material for elastocaloric materials, since it shows a high effect size > 15 K and is widely accessible. On the other hand NiTi shows a poor fatigue life resulting in an early breakdown of the device. It is assumed that the material has to withstand at least 10$^7$ cycles. Recently it was demonstrated that magnetron sputtered TiNiCu based SMAs show negligible fatigue for 10 million cycles, an effect size > 10 K and tuneable transformation temperatures below RT [1,2]. These materials possess a unique microstructure with coherent precipitates, acting as nucleation centres for the phase transformation and a grain size in the sub µm range. In addition they show a nearly perfect compatibility of the austenite and martensite phase, which can be expressed by the cofactor conditions [3]. If fulfilled an unstressed transition layer between the corresponding phases is created, leading to a phase transformation without slip, reduced hysteresis and an increased fatigue life. First demonstrators using a solid to solid heat transfer show a maximum temperature span of 14 K [4]. Within this talk several NiTi based shape memory alloys will be discussed in terms of microstructure, compatibility and fatigue life to determine critical parameters for the design of SMAs with a sufficient fatigue life.

Acknowledgements: Funding by the DFG priority program SPP1599 ferroic cooling is gratefully acknowledged.

References
materials, several demonstrators of cooling systems have been developed and characterized by various groups. In general, for an energy- and cost-efficient system, the heat transfer between elastocaloric material and heat sink and source is essential. While most published systems use either thermal conduction or forced convection, here an elastocaloric system using latent heat transfer in combination with thermal diodes is presented. Similar to gravity-assisted heatpipes, thermal energy is efficiently transported by condensation and evaporation processes leading to heat transfer rates which are several orders of magnitude larger than in conventional systems. Furthermore, no additional pumps are required for transporting the heat exchange fluids, enabling systems with large temperature spans and competitive COPs at the same time.

In this work, an experimental setup based on this system approach is shown, using an extender wheel for providing compressive force on Nitinol tubes and showing the proof of concept of heat transfer in combination with elastocaloric materials.

SESSION TP01.04: Poster Session: Caloric Materials for Highly Efficient Cooling Applications
Session Chairs: Sakyo Hirose, Lluis Manosa, Vitalij Pecharsky and Anja Waske
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

TP01.04.01
Mechanochemical Synthesis and Magnetocaloric Properties of Nanostructured Equi-Atomic FeRh with the Ordered B2 Structure Shalabh Gupta1, Yaroslav Mudryk1, Biswas Anis1, Jacob Rabe1 and Vitalij Pecharsky1, 2; 1Ames Laboratory, Ames, Iowa, United States; 2Material Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

The equiaxed, sub-micron sized particles of Fe50Rh50 were synthesized by solvent-free mechanochemical co-reduction (MCR) of iron chloride (FeCl3) and rhodium chloride (RhCl3) followed by annealing between 600–1000 °C under argon. Typically, nearly equiatomic, ordered FeRh alloys exhibiting first-order transition are synthesized from the elements by arc-melting and annealing. The resulting large grains are difficult to scale-down because of the high ductility of the alloy. The bottom-up syntheses, such as MCR, inherently produce materials with grain-size in sub-micron to nano regime, allowing greater flexibility in tailoring the properties. In a typical MCR synthesis, the chloride (or fluoride) metal precursors are mixed in a 1:1 molar ratio in an agate mortar followed by high-energy milling along with a stoichiometric amount of Li-metal under argon. After about 2 h of milling, the reaction product contains no trace of halide salts. Prior to annealing, the LiCl (LiF) by-product is washed out with water-ethanol mixture. The cleaned sample is then heated under Ar at 600°C for 24 h and quenched in ice-cold water at which point the ordered B2 structure is obtained in high-purity. The temperature dependence of magnetization, M(T), was measured in field cooled protocol between 5 K and 400 K at different magnetic fields, and the magnetic entropy change, DSM, was calculated from the M(T) curves using Maxwell’s equation. In contrast to regular magnetocaloric effect (MCE), in case of inverse MCE (I-MCE), magnetic field induced enhancement in magnetic configuration entropy is observed. The as-synthesized particles of Fe50Rh50 alloy exhibit maximum I-MCE around ~340 K, which is attributed to a first-order antiferromagnetic to ferromagnetic transition. The maximum value of DSM near the transition is ~9 J Kg⁻¹K⁻¹ at 2 T, which is about 25 % smaller than that of bulk Fe50Rh50 but is larger than that of Gd, the benchmark material for the room-temperature magnetocaloric applications. In a fine particle system, grain boundaries play a vital role in determining magnetic and magnetocaloric properties. Grain boundaries are sources of crystalline disorder, which can affect the magnetic correlations. In some cases, disorder effects can suppress the first order transition. It is noteworthy that fine particles of Fe50Rh50 (average size <1 μm) retain a first order transition with large DSM despite the large concentration of disordered grain boundaries.

This work is performed under auspices of the caloric materials consortium, CaloriCool®, which is a member of the Energy Materials Network and is supported by the Advanced Manufacturing Office of the Office of Energy Efficiency & Renewable Energy and managed jointly through the Advanced Manufacturing and Building Technologies Office of the U.S. Department of Energy. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University of Science and Technology under Contract No. DE-AC02-07CH11358.

TP01.04.02
X-Ray Magnetic Circular Dichroism Study on Ni Based Thermoseeds for Self-Controlled Hyperthermia Applications Sudin Pandey1, Alpha T. N'Diaye2, Igor Dubenko1, Anil Aryal1, Dipanjan Mazumdar1, Shane Stadler1 and Naushad Ali1; 1Department of Physics, Southern Illinois University Carbondale, Carbondale, Illinois, United States; 2Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Ni-Cu alloys are potential magnetocaloric thermoseeded materials for application in self-controlled magnetic hyperthermia methods. The magnetic ordering temperatures and magnetic properties of Ni-Cu alloys can be tailored to fit within a range suitable for hyperthermia applications. To understand the details of the electronic and magnetic structures of these alloys, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements were done at the L2,3 absorption edges of Ni in ferromagnetic Ni-Cu. In this case, the XMCD technique has provided valuable information on how doping affects the relative magnetic moment on the Ni site. XMCD measurements employing the total electron yield method (i.e., surface sensitive to the depth of few nm) show that the collective of surface Ni atoms has a lower Curie temperature than that of the bulk. The influences of small compositional changes through the substitution of Cu for Ni on the electronic and crystal structures and thermomagnetic properties was studied to determine the optimized composition suitable for functional magnetic hyperthermia applications.

SESSION TP01.05: Magnetocaloric Materials and Systems II
Session Chairs: Franca Albertini and Julia Lyubina
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

8:30 AM *TP01.05.01
Topology of Thermomagnetic Generators for the Conversion of Low Temperature Waste Heat to Electricity Anja Waske1, 2, Daniel Dzekan1, Kai Seilschopf3, Alexander Stork4, Kornelius Nielsch1 and Sebastian Faehler4; 1IFW Dresden, Dresden, Germany; 2Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany.
9:00 AM TP01.05.02

Effect of Al and Fe Solubility on Magnetostructural Properties of AlFe₂B₂
Brian Lejeune¹, Deborah Schlage², Brandt Jensen¹, Thomas Lograsso², Matthew J. Kramer¹ and Laura Lewis¹; ¹Northeastern University, Boston, Massachusetts, United States; ²Materials Science and Engineering, The Ames Laboratory, Ames, Iowa, United States.

One of the main design criteria for caloric materials is the ferroic phase transition temperature, magnetism, and antislattice occupancy in the magnetostructural AlFe₂B₂ system. This orthorhombic system is comprised of abundant elements, possesses a near-room-temperature magnetostructural phase transition temperature Tt and exhibits good magnetic cooling potential (ΔS = 4.4 J/kg-K @ μB/M = 2 T) [1,2]. Preliminary results suggest that the magnetic phase transition temperature is highly sensitive to Fe and Al solubility within the AlFe₂B₂ phase, allowing for tuning of the transition temperature through control of processing conditions.

A drop-cast ingot of composition Al₂Fe₂B₂ was used as the initial charge for Bridgman single crystal growth of the AlFe₂B₂ phase, allowing for Al-Fe composition regulation down the pathway of solidification. The influence of Al and Fe antisite defects within the AlFe₂B₂ crystal structure was assessed with X-ray diffraction, temperature-dependent magnetometry and compositional assessment from energy dispersive spectroscopy. Clear trends in composition are confirmed as a function of the Fe:Al at% ratios (1.94-2.06). In particular an Fe-rich AlFe₂B₂ phase due to Fe residing on the Al site results in an enhanced Tt relative to the stoichiometric composition. These findings quantify the sensitivity of the magnetic transition temperature in AlFe₂B₂ to antisite defects, where a 2 at% difference in Fe and Al content leads to a large change in Tt spanning 280-315 K. The interplay between Al and Fe site occupancy and the resultant structural and magnetic responses provides flexibility to tailor the magnetic phase transition temperature of the AlFe₂B₂ system.


9:15 AM TP01.05.03

Magnetocaloric Properties of the Magnetically Frustrated Mineral, Gaudefroyite
Colin Greaves¹, Rukang Li² and Guangjing Li¹; ¹University of Birmingham, Birmingham, United Kingdom; ²Beijing Center for Crystal Research & Development, Beijing, China.

New materials for refrigeration devices are needed for efficient, clean operation at a variety of temperatures. In adiabatic magnetic refrigeration using the magnetocaloric (MC) effect, cooling is related to the entropy change that occurs when a magnetic field is removed from a magnetic material. Efficient MC refrigeration requires stable materials that give a large change in magnetic entropy and has traditionally been achieved using expensive rare earth cations with large moments. In this presentation we will describe how mineral structures can point the way to new types of magnetic materials with excellent MC properties in the absence of rare earth cations. The mineral schafarzikite, Fe₁₉₁₉₂O₉₂, has a tetragonal structure comprising chains of edge-linked FeO₆ octahedra running along [001]. Following our studies of how the magnetic order of this structural family can be controlled, we then sought new materials with similar chains of linked octahedra, but frustrated interchain interactions, since enhanced MC behaviour has been predicted for frustrated magnetic materials. The mineral gaudefroyite, Ca₆Mn₆O₆(BO₃)₃CO₃, was particularly attractive because its chains of edge-linked Mn₆⁺ octahedra are located on a Kagome lattice perpendicular to the chains, and introduce inherent magnetic frustration between the chains. The low temperature magnetic properties of gaudefroyite were therefore investigated: extremely high MC effects were observed at temperatures suitable for liquefying hydrogen, ca. 20 K. The properties, which will be summarized, are better than those of existing optimized oxide materials at this temperature, but no rare earth element is present; the temperature changes are also exceptionally rapid because of the magnetic frustration. We now have low temperature neutron powder diffraction data collected in fields of 0-3 T within the temperature range 0.1-15 K, and the presentation will focus on these results. We will report an ordered antiferromagnetic structure (q=0, 120⁰ alignment) below 11 K, which transforms to a ferromagnetic ground state in fields greater than 1.5 T; ferromagnetism was also found at these fields for temperatures above 15 K. The results will be discussed in relation to the observed MC properties. The concept demonstrated could be of value for sustainable materials for liquefying hydrogen for transport/storage in a future hydrogen energy economy and could possibly be extended to materials operating at other temperatures.


9:30 AM TP01.05.04

XAS and XMCD Studies of Ni-Mn-In-B Thin Films
Sudip Pandey¹, Alpha T. V'Diaye², Anil Aryal³, Igor Dubenko³, Sujey Roy⁴, Shane Stadler⁵ and Nahed Alfi⁶; ¹Department of Physics, Southern Illinois University Carbondale, Carbondale, Illinois, United States; ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Ni-Mn-In-B thin films were synthesized on Si substrate using ultra high vacuum magnetron sputtering. Metamagnetic transition with thermal hysteresis has been observed on 30 nm Ni₈₆Mn₂₅In₈₂-₉₂H₃₅ thin film from the magnetization measurements. The temperature dependences of magnetization curves are found to be similar with those of bulk counterpart with the shift in transition temperatures. Electronic and magnetic properties of Ni₈₆Mn₂₅In₈₂-₉₂H₃₅ thin
The thermomagnetic generator (TMG) is a promising device to convert low temperature heat to electricity by using the change in magnetization with temperature of a ferromagnetic material placed in a magnetic circuit. Thus the magnetic flux, provided by permanent magnets, also changes and induces a voltage in a pick-up coil according to Faraday’s law of induction. This principle of energy harvesting is known for more than a century but no prototypes and only few proof of concepts have been realized. However theoretical consideration predicted the efficiency of such a device approach the thermodynamic limit. Here we present a TMG with a new topology of the magnetic circuit. This topology allows the magnetic flux to change its direction, resulting in a doubled magnetic flux amplitude. Thus the electrical power of the generator is increased by a factor of four. The topology of the magnetic circuit within the generator is optimized with FEM simulations. An additional advance of the realized topology is avoiding hysteresis as well as magnetic stray fields, which results in further improvement in electrical power output. A La-Fe-Co-Si alloy, developed for magnetocaloric refrigeration, is used as thermomagnetic material, since it exhibits a large and sharp change of magnetization in a small temperature range. Thereby low temperature heat can be thermally switched the thermomagnetic material, are experimental parameters as well. With these measurements and with the electrical power output, the efficiency of the energy conversion is determined. In the experiments the parameters are adjusted for an optimum in electrical power output and efficiency. These values of this TMG are significant higher in comparison to previously published proof of concepts. The experimental evaluation of this prototype allows to suggest further improvements of TMGs and paves the way for these devises to become competitive with thermoelectric generators for low temperature waste heat recovery.

10:30 AM OPEN DISCUSSION

SESSION TP01.06: Electrocaloric Materials and Systems II
Session Chairs: Anna Grünebohm and David Schwartz
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

10:45 AM *TP01.06.01
Phase Transitions in Elastic Media and the Enhancement of Caloric Effects Peter B Littlewood1, Gian Guzman-Verri2 and Xavier Moya3; 1James Franck Institute, University of Chicago, Chicago, Illinois, United States; 2Materials Research Science and Engineering Center (CICIMA), University of Costa Rica, San José, Costa Rica; 3University of Cambridge, Cambridge, United Kingdom.

The metal-insulator transition driven by strong electronic correlations – generically called the “Mott” transition – is usually described entirely by electronic Hamiltonians, with models designed to exhibit emergent phenomena such as magnetism and superconductivity. In real solids, the electronic localization also couples to the crystal lattice, and it turns out that these elastic degrees of freedom insert important new entropic phenomena more familiar in soft matter physics.

The coupling to the lattice induces elastic strain fields, which have intrinsic long-range interactions that cannot be screened. When strain fields are produced as a secondary order parameter in phase transitions - as for example in ferroelectrics - this produces unexpected consequences for the dynamics of order parameter fluctuations, including the generation of a gap in what would otherwise have been expected to be Goldstone modes. A very important class of transition metal oxides – the perovskites – can be thought of as an array of tethered octahedra where the Mott transition produces a shape-change in the unit cell. Coupling of the fundamental order parameter to octahedral rotations gives rise to large entropic effects that can shift the transition temperature by hundreds of degrees K,[1], essentially by exploiting the physics of jammed solids. The insight might offer ways to make better refrigerators by enhancing electro-caloric and magneto-electric effects.[2]


11:15 AM TP01.06.02
A Regenerative Electrocaloric Cooling Device—Numerical Modelling and Experimental Validation Uros Plaznik1, Marko Vrablj2, Zdravko Kutnjak1, Barbara Malic2, Brígida Rozic2, Jaka Tusek1, Alojz Poredos1 and Andrej Kitanovski1; 1Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia; 2Jozef Stefan Institute, Ljubljana, Slovenia.

A research and development on a cooling device based on an active electrocaloric regenerator (AER) made of bulk ceramic material (1-x)Pb(Mg1/3Nb2/3)O3-xPbTiO3 (PMN-100xPT) will be presented. For that purpose, a new, 2D transient numerical model of the AER based on the energy equation for the solid electrocaloric material and the heat transfer fluid was developed and implemented in Matlab software. The model allows to investigate the cooling characteristics (temperature span, cooling power and efficiency) of an AER at different operating conditions (mass-flow rate, operating frequency, applied electric field change, etc). In addition, the model includes the impacts of the electrocaloric material’s hysteresis and the...
electric-energy recovery released during the depolarization (discharging) of the electrocaloric material on the AER performance. The results of the numerical analysis show that the degree of electric energy recovery has a crucial impact on the efficiency of the electrocaloric device. By comparing an idealized electric-energy recovery system, the energy efficiency (expressed by the coefficient of performance - COP) of the device could be increased by up to ten times compared to the case of without the energy recovery. A validation of the numerical model was performed through the design, construction and experiments on a new AER cooling device (without electric-energy recovery system). The experimental results revealed a maximum specific cooling power of 16 W kg⁻¹ and a maximum temperature span of 3.1 K. A comparison between the numerical and experimental results shows that model can correctly predicts the trends of cooling characteristics with respect to various operating parameters. On the other hand, there is some deviation between the absolute values of the cooling characteristics calculated with the numerical model and the experimental results. These deviations are mainly due to some effects not included in the numerical model, for example flow maldistribution.

11:30 AM *TP01.06.03

It has been more than two decades since electrocaloric-based temperature lifts on the order of 20°C were first reported in the ceramic materials and more than a decade since equivalent lifts were observed in polymeric thin films. Yet, since that time, the demonstration of even a single high performance electrocaloric-based cooling module has not been realized. Indeed, only modest performance (<5°C total lift) has been achieved when such modules have been challenged against a temperature incline. Coefficients of performance (COP) have been either unreported or inconsequential. Conversely, theoretical models predict the potential for regenerative cooling with lifts in excess of 10°C at COPs of ~6. In this talk we examine the cause of the shortfall in module performance from a material perspective. We discuss: (1) The impact of performance parasitics. (2) Active area loss due to dielectric breakdown and local arcing. (3) Degraded performance due to stress concentration, clamping from the electrode metallization and cyclic fatigue. Solutions to film and electrode failures can potentially be found by using material engineering to improve electrical, mechanical, and thermal-caloric properties.

SESSION TP01.07: Mechanocaloric Materials and Systems II
Session Chairs: Kilian Bartholome and Jian Liu
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

1:30 PM *TP01.07.01
Active Elastocaloric Regenerators—Tension vs Compression Loading Jaka Tusek; Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia.

The elastocaloric effect (eCE) associated with a stress-induced martensitic transformation in shape memory alloys (SMA) has recently shown a promising route for high-efficiency, solid-stated cooling and heat-pumping applications. It was already demonstrated that the most effective way of utilizing the caloric effects (magnetocaloric, electrocaloric, elastocaloric) in a practical cooling device is so-called active caloric regenerator, which is a porous structure made of caloric material. It has a double function in a caloric cooling device; it works as a refrigerant as it contains active caloric material as well as a regenerator and enables an enhancement of the temperature span between heat sink and heat source.

In this talk different possibilities of active elastocaloric regenerator geometries to be loaded in tension and compression will be reviewed and discussed. Both tension and compression loading has some important pros and cons for elastocaloric cooling. The main advantage of tension loading is the ability to apply thin elements and small channels for the fluid-flow that allows for fast and efficient heat transfer, while its main disadvantage is reduced fatigue life when compared to compression loading. However, thin elements which would enhance heat transfer characteristics are difficult to compress without buckling. It is therefore a big challenge to design an active elastocaloric regenerator that is geometrically stable during compression loading, while maintaining high eCE and highly efficient heat transfer.

The fatigue strain limits and the associated eCE for durable operation (~10⁶ cycles) of Ni-Ti plates to be applied in efficient active elastocaloric regenerator loaded in tension will be presented. In addition, different potential geometries of an active elastocaloric regenerator to be loaded in compression, such as block with holes, set of tubes in a holder, shell-and-tube-like regenerator, etc., will be discussed together with the main challenges associated with those geometries.

2:00 PM TP01.07.02
Comparison of Electrocaloric Materials on Basis of Material Related Cooling Power Florian Weyland¹ and Nikola Novak²; ¹TU Darmstadt, Darmstadt, Germany; ²Institute Jozef Stefan, Ljubljana, Slovenia.

The centerpiece of solid state coolers using caloric effects, i.e. electrocaloric, magnetocaloric or mechanocaloric, is the caloric material. In the search of a refrigerant for electrocaloric cooling devices a large number of ferroelectric materials, with their respective adiabatic temperature change, have been identified. To find the most suitable material not solely the electrocaloric but also the thermophysical properties need to be accounted for. To compare materials with each other a useful figure of merit is the material related cooling power, as it considers the material properties, i.e. electrocaloric effect and thermophysical behavior, without including device specifications. The performance characteristics of ferroelectric materials are determined to a large degree by the nature of the paraelectric to ferroelectric phase change. Here, the electrocaloric and thermophysical properties of BaTiO₃ (BT) and 0.72PbMg₁/₃Nb₂/₃O₃-0.28PbTiO₃ (PMN-28PT) single crystals and polycrystalline BaZr₀.₃Ti₀.₇O₃ (BZ₃T) ceramics are compared. BT and PMN-28PT are typical representatives of first order and relaxor-like ferroelectrics, respectively. Furthermore, they both show a dielectric permittivity peak around ~400 K. The BZ₃T ceramics are BT derived compositions with Zr-ions substituted on the Ti-ion site. By the amount of Zr-ion substitution the phase change characteristic and transition temperature is modified. The dependence of the material related cooling power of those materials on the dimensionless temperature, characteristic distance and holding time for heat transfer is determined on the basis of directly measured electrocaloric temperature changes, thermophysical properties and a simple model based on Newtonian cooling of a thin plate. It is shown, that a decrease in the holding time for heat transfer increases the cooling power. It is found that the higher thermal conductivity of BT contributes significantly to its large cooling power. At temperatures near the Curie point the electrocaloric temperature change of BT is large and hence, the cooling power is large. In contrast, the relaxor-like PMN-28PT exhibits a much broader range of peak cooling power, which can be useful for widening the temperature range of operation. The BZ₃T displays a broad peak of maximum cooling power near room-temperature. Although device-level factors, such as thermal resistances at electrode interfaces are ignored, the results suggest a simple basis of comparison for ferroelectric materials. In addition, the derived equation for the material related cooling power is used to compare the different caloric effects with each other.
Low Temperature Magnetocaloric Materials for Cryogenic Gas Liquefaction by Magnetic Cooling Technique

In this work we report on the results of investigation of low temperature magnetocaloric materials based on ReTm2 compounds (Re- rare earth's, Tm – transition metals) for magnetic refrigeration in cryogenic application. Special accent made for investigation an influence of severe plastic deformation on magnetocaloric properties of such alloys.

Copper Based Elastocaloric Materials

Elastocaloric cooling has high Coefficient of Performance and minimum environmental impact. In 2014, U.S. Department of Energy ranked it as the most promising new HVAC technology to replace vapor compression. While many alloys exhibit elastocaloric effect, few can simultaneously meet the criteria on delta T, biasing stress, and cost. To date, NiTi remains as the best material for elastocaloric cooling application. While NiTi alloy has high latent heat and long fatigue life under compression, it requires large stress (>600 MPa) and it is prohibitively expensive, which makes it difficult for wide spread industrial and consumer applications. This talk reviews the concept of elastocaloric cooling, the challenges and the progress of developing copper based elastocaloric materials using combinatorial materials development approach.

SESSION TP01.08: Magnetocaloric Materials and Systems III

Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Berkeley AB

3:00 PM TP01.08.01
Synchrotron and Neutron Diffraction Studies of Boron Doped Ni-Mn-In Heusler Alloys Sudin Pandey1, Tej Lamichhane1, Amal Al-Wahish2, Alpha T. N'Diaye2, Amil Aryan1, Pinaki Das1, Igor Dubenko1, Susjoy Roy1, Dipanjan Mazumdar1, Helmut Kaiser1, Shane Stadler1 and Naushad Ali1; 1Department of Physics, Southern Illinois University, Carbondale, Illinois, United States; 2Department of Physics & Astronomy, Iowa State University, Ames, Iowa, United States; 3University of Missouri Research Reactor, University of Missouri-Columbia, Columbia, Missouri, United States; 4Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 5Department of Physics & Astronomy, Louisiana State University, Baton Rouge, Louisiana, United States.

Natural gases are one of the main sources of energy nowadays and will be of increasing importance in the near future. Currently, there is an upward trend of the production and consumption of this type of energy including methane, hydrogen, oxygen etc. For its storage, liquefaction is needed, which requires complex energy-intensive compressor devices operating at cryogenic temperatures. The efficiency of traditional liquefaction methods is quite low at temperatures below 150 K. We propose here a fundamentally different approach to liquefy gases - the emerging magnetic cooling technology. With the recent progress in superconducting magnets with static magnetic fields of up to 15 – 22 T, cooling at cryogenic temperatures can enable a revolution in the technology of gas liquefaction. A review on recent scientific publications reveals the large variety of different magnetic materials showing a significant magnetocaloric effect in the relevant temperature region of 15 to 150 K [1]. Thus, the efficient liquefaction of almost any natural gas in the same type of magnetic cooling machine would be possible [2-5].

3:20 PM TP01.08.02
Low Temperature Magnetocaloric Materials for Cryogenic Gas Liquefaction by Magnetic Cooling Technique

Natural gases are one of the main sources of energy nowadays and will be of increasing importance in the near future. Currently, there is an upward trend of the production and consumption of this type of energy including methane, hydrogen, oxygen etc. For its storage, liquefaction is needed, which requires complex energy-intensive compressor devices operating at cryogenic temperatures. The efficiency of traditional liquefaction methods is quite low at temperatures below 150 K. We propose here a fundamentally different approach to liquefy gases - the emerging magnetic cooling technology. With the recent progress in superconducting magnets with static magnetic fields of up to 15 – 22 T, cooling at cryogenic temperatures can enable a revolution in the technology of gas liquefaction. A review on recent scientific publications reveals the large variety of different magnetic materials showing a significant magnetocaloric effect in the relevant temperature region of 15 to 150 K [1]. Thus, the efficient liquefaction of almost any natural gas in the same type of magnetic cooling machine would be possible [2-5].

In this work we report on the results of investigation of low temperature magnetocaloric materials based on ReTm2 compounds (Re- rare earth’s, Tm – transition metals) for magnetic refrigeration in cryogenic application. Special accent made for investigation an influence of severe plastic deformation on magnetocaloric properties of such alloys.


Getting the Most Out of Your Magnetocaloric Heat Pump

A magnetocaloric heat pump, dimensioned to the requirements of a domestic house in Northern Europe, has been designed, constructed and tested. The design has been optimised towards a heating power of 1500 W and a temperature span of about 20 K. The regenerator beds are packed with 10 layers of spherical La(Fe,Mn,Si)13H particles. The use of such magnetocaloric materials with a first order magnetic phase transition imposes constraints on how the temperature span of a magnetocaloric device may be controlled, which again imposes constraints
on the type of heating system the heat pump can be connected to. Different ways of dealing with this issue will be presented and discussed.

Part load conditions where less than the maximum heating power is required can be achieved by varying the flow rate or the frequency. However, by combining the control of the two parameters it is demonstrated how it is possible to increase the coefficient of performance (COP) for part load conditions. Finally, the experimental and modelling performance of the heat pump will be considered in the context of connection to a ground source and an underfloor heating system, for the heating of a model house.

4:30 PM TP01.08.04
Stability of Magnetocaloric La(Fe\textsubscript{x}Co\textsubscript{y}Si\textsubscript{1-x-y})\textsubscript{13} in Water and Air
Khushar Javed\textsuperscript{1}, Ravi L. Hadimani\textsuperscript{1}, Brent Williams\textsuperscript{1}, Shane Harstad\textsuperscript{1}, Vitalij Pecharsky\textsuperscript{2,3} and Shahab Abdolvand\textsuperscript{2,3}
\textsuperscript{1}Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; \textsuperscript{2}Division of Materials Science and Engineering, Ames Laboratory, US Dept. of Energy, Ames, Iowa, United States; \textsuperscript{3}Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

Lanthanum Iron Silicide with Cobalt substitution, LaFe\textsubscript{x}Co\textsubscript{y}Si\textsubscript{1-x-y}\textsubscript{13}, is a room temp magnetocaloric material and these particles exhibit different magnetic properties when stored in air and compared to the same stored in the sample. With the sample with a nominal composition of LaFe\textsubscript{x}Co\textsubscript{y}Si\textsubscript{1-x-y}\textsubscript{13}, was prepared by arc-melting and these Ingot pieces were annealed at 1050°C for 7 days followed by quenching in ice-cold water. The annealed pieces were crushed to particle size of 100μ and then ball-milled using a SPEX8000 mill for 10 min. PANalytical X'Pert Pro diffractometer shows that powder stored in water for 14 days appear to be missing some of the Bragg peaks and develop low-Bragg angle halos typical of non-crystalline components. It concludes that both types of powders; milled and course crushed samples react with water.

The course crushed powder stored in air and water show sharp transition at the Curie temp Tc = 300K without large magnetization above the Tc. The milled fine-particle sample stored in air shows significantly broadened transition at Tc, and that stored in deionized water for 14 days shows no obvious magnetic transition; both show large magnetizations above 300K. This is indicative of relatively fast hydrolysis and removal of some or all La, likely as hydroxide, from fine powders, leaving behind La-poor and, potentially, La-free Fe-Co-Si containing ferromagnetic residue with much higher Curie temp.

The milled sample stored in water also shows the highest saturation magnetization followed by both sample stored in air. The course crushed sample stored in water shows the maximum MCE of AS = 11 J Kg\textsuperscript{-1}K\textsuperscript{-1} near 300K with the change of 3T magnetic field and highest relative permeability while the milled sample stored in water has the lowest entropy change. The milling process has induced broadening of the transition. Course crushed sample stored in water and in air have similar magnetocaloric effect. It can be concluded that the course crushed samples contain larger particles and smaller surface area as compared to milled samples which have less than micron size particles. Water added to the milled sample leads to hydrolysis and removal of some of the La as hydroxide from fine powders, leaving behind La-poor Fe-Co-Si containing ferromagnetic residue of possibly Fe\textsubscript{3}O\textsubscript{4} or Co\textsubscript{3}O\textsubscript{4} with much higher Curie temp as follows from the absence of the obvious magnetic transition(s) and large magnetization beyond 300K. The course crushed samples show much greater stability and sharper magnetic transition when stored both in air and water. The course crushed sample stored in water has sharper magnetic transition and course crushed magnetization hence it shows the highest entropy change among all 4 types of samples.

Acknowledgement
Synthesis of material was supported by the Division of Materials Sciences at Ames Laboratory that is operated for the U.S. Department of Energy (DOE) by Iowa State University of Science and Technology under contract No. DE-AC02-07CH11358.

4:45 PM TP01.08.05
Electron-Phonon vs. Moment-Volume Coupling in Hydrogenated and Mn-Doped LaFe\textsubscript{13-Si\textsubscript{13}} Compounds
Markus E. Gruner\textsuperscript{1}, Alexandra Terwey\textsuperscript{1}, Joachim Landers\textsuperscript{1}, Soma Salamon\textsuperscript{1}, Werner Keune\textsuperscript{1}, Katharina Ollefs\textsuperscript{1}, Iliya Radulov\textsuperscript{2}, Valentin Brabänder\textsuperscript{2}, Jiyoung Zhao\textsuperscript{1}, Michael Y. Hu\textsuperscript{3}, Thomas S. Toellner\textsuperscript{3}, Eisen E. Alp\textsuperscript{3}, Oliver Gutflies\textsuperscript{3} and Heiko Wende\textsuperscript{3}
\textsuperscript{1}Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia, United States; \textsuperscript{2}Division of Materials Science and Engineering, Ames Laboratory, US Dept. of Energy, Ames, Iowa, United States; \textsuperscript{3}Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

Fully hydrogenated LaFe\textsubscript{13-Si\textsubscript{13}} is one of the most interesting candidates for room temperature magnetic refrigeration. The first order nature of the magnetic transition is connected to its itinerant electron magnetism, which gives rise to a peculiar coupling between all microscopic degrees of freedom. By combining first principles calculations in the framework of density functional theory (DFT) and nuclear resonant inelastic X-ray scattering (NRIXS) we investigate the interplay of electronic structure, magnetism and vibrational degrees of freedom in fully hydrogenated LaFe\textsubscript{13-Si\textsubscript{13}}. In the past, we could show that for the non-hydrogenated ternary compound, the itinerant nature of the Fe moments, which is responsible for the large volume change, gives rise to the adiabatic electron-phonon coupling [1,2]. This leads to a cooperative contribution of magnetic, electronic and vibrational degrees of freedom to the entropy change, which results in the excellent caloric properties [1,3]. By hydrogenation it is possible to shift the operating range to ambient conditions, which is required for mass market application. A common strategy is to fully load the material with hydrogen and fine-tune the transition temperature by adding other components, such as Mn.

In this contribution, we demonstrate that the same mechanism acting in LaFe\textsubscript{13-Si\textsubscript{13}} is also responsible for the superior magnetocaloric properties of the hydrogenated compound LaFe\textsubscript{13-Si\textsubscript{13}}H\textsubscript{13}. Again, the cooperative nature of the vibrational contribution to the entropy change is essentially determined by an anomalous softening of vibrational modes arising from the itinerant nature of the Fe moments, which is not destroyed by the hydrogenation. We find that hydrogen dominates the vibrational density of states at low energies, which one rather expects for heavy elements. Despite this, its contribution to the change in vibrational entropy remains rather small. Since full loading with hydrogen involves the occupation of only a part of the available (24d) lattice sites, we also discuss the site-occupation of hydrogen based on total energy calculations and by comparing vibrational density of states from DFT involving different distributions of hydrogen with the NRIXS measurements. Finally, we will give an outlook on the impact of a partial substitution of Fe with Mn on the vibrational properties and the coupling mechanism.

Financial support by the Deutsche Forschungsgemeinschaft via SPP1599 is gratefully acknowledged.

A new test system, CaloriSMART (Small-scale Modular Advanced Research Test station), is being developed to support new caloric materials
development efforts. This system is intended for rapid evaluation of performance of caloric materials in small quantities, 5-50 grams, over a wide range of
operating conditions (frequencies from 0.1 to 5 Hz, utilization from 0.2 to 1, and environment temperatures from -10 to 50 C) using magnetic, stress, and
electric fields, and combinations thereof as the driving fields. CaloriSMART is capable of measuring temperature spans at known cooling loads, zero span
cooling power, and passive heat transfer characteristics of regenerator beds.

The magnetocaloric system module can apply magnetic fields of 1.1 T or 1.4 T and exhibits very precise control over the flow profile and rotational speed.
Thorough characterization of the system using Gd as a baseline material demonstrated operation over the full range of operating conditions. It was found
that the no-load temperature span could be increased by as much as 10% using precise control and timing of the flow profile with respect to the field
application. Testing also revealed the importance of equal dwell time inside and outside the magnetic field in obtaining maximum performance. Test results
from several magnetocaloric materials will be presented.

The elastocaloric module design goals were to minimize forces needed to actuate materials while having the capability of testing samples in both tension
and compression. Unique regenerator designs based on composite structures of passive materials and active sections have been developed for both tension
and compression. While the compression arrangement limits access for heat transfer, it also allows for compression of a large sample without buckling. The
presentation includes initial test results based on these regenerator configurations using readily-available NiTi materials.

Future plans for module designs and regenerator testing will be discussed with particular focus on electrocaloric and multi-caloric capabilities. Initial ideas
for incorporating materials of different forms into useful and robust regenerator geometries are also presented.

This work has been carried out under the auspices of CaloriCool® – the caloric materials consortium – which is a part of the Energy Materials Network.
The consortium is funded by the Advanced Manufacturing Office and is managed jointly by the Advanced Manufacturing Office and Building
Technologies Office of the Office of Energy Efficiency and Renewable Energy of the United States Department of Energy. The research was performed at
the Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. DE-AC02-
07CH11358.

9:00 AM *TP01.09.02
Heat Conductivity and Energy Efficiency of Electrocaloric Materials Emmanuel Defay, Luxembourg Institute of Science and Technology, Belvaux,
Luxembourg.

The specificity of electrocaloric (EC) materials among the other caloric materials is that electric field is the stimulus required to trigger the EC effect. The
advantage is that it is rather straightforward to apply an electric field on an EC capacitor. The main drawback is that electrodes and electric threads have to
be systematically associated to EC materials. These specificities induce two dedicated answers to two recurrent questions posed by all caloric principles,
namely energy efficiency and effective thermal conductivity.

Regarding energy efficiency, one can address the challenge through intrinsic means, meaning finding the best materials able to provide the largest variation
of entropy for the lowest input electric energy. Thanks to the electric nature of the stimulus, one can also think of extrinsic means to enhance substantially
the overall effective efficiency of given EC heat exchangers, typically by recycling the electric energy used to trigger the EC effect.

Besides, the necessity of using electrodes to trigger the EC effect infers extra complications when it comes to exchange heat. Indeed, using electrically
insulating caloric fluids limits their nature to poorly thermally conductive ones. On the other hand, figuring out EC prototypes without fluid infers
complex engineering and raises specific issues about solid-solid heat exchange. Besides, EC materials are generally weak thermal conductors. This
nowadays stands probably for the main hurdle to make convincing heat exchanger prototypes.

In this talk, we will address efficiency and thermal exchange of EC materials by drawing first the state of the art and then by giving potential solutions to
envision future EC heat exchangers.

9:30 AM TP01.09.03
Predictive Modeling of Electrocaloric Heat Exchangers Alvar Torello Massana1, Romain Faye1, Tomoyasu Usui2, Sakyo Hirose2 and Emmanuel
Defay1, 1Luxembourg Institute of Science and Technology, Luxembourg, Luxembourg; 2Murata Manufacturing Co., Ltd., Nagaokakyo, Japan.

In recent years, several Electrocaloric (EC) heat exchangers have been proposed, covering different kinds of mechanisms and working principles. Despite
this fact, little has been told about the numerical modeling of these devices.

In this work, finite elements simulations carried out with COMSOL Multiphysics software are presented. These simulations consist of 2D-representations
of the lead scandium tantalate multilayers capacitors (PST MLC) 22mm x 10.4mm x 1mm parallel-plates based active regenerator that is currently being
developed in LIST, where a maximum temperature difference of 1K in the device has recently been measured. In the model, the EC effect is triggered by
applying equivalent heat power square pulses synchronically with the induced bidirectional laminar flow of a dielectric fluid. The model is proved to match
the experiment for the first two minutes of performance before experimental intrinsic losses make the data moderately diverge.

Within this transient regime, the model is able to predict the performance of our heat exchanger for new sets of parameters. The results obtained showed
that by enlarging the length of the parallel plates by a factor of three or by decreasing their thickness by a factor of two, the temperature difference in the
device could increase already up to 7 degrees. The performance of other working fluids, which at the moment are not experimentally feasible to implement,
was also attempted. In the case of water, with better thermal properties, the frequency of the cycle was increased up to three times, displaying very
encouraging results. In conclusion, the modeling investigated indicates plenty of scope for ongoing improvement, reporting more than 10 K when the
simulation parameters were optimized.

9:45 AM BREAK

10:15 AM *TP01.09.04
Solid-State Electrocaloric Heat Pump David E. Schwartz, Yunda Wang, Michael Benedict, Jamie Kalb, Joseph Lee and Ziyang Zhang; PARC, Palo
Alto, California, United States.

Electrocaloric materials have the potential to enable compact, high-efficiency cooling devices. One advantage of electrocaloric heat pumps is the capability
for fully solid-state designs that do not rely on pumped fluid to transfer heat to and from the cooling elements. The core of an electrocaloric heat pump is a set of capacitors based on a dielectric material with a large electrocaloric effect (ECE). ECE can be characterized by adiabatic temperature change with applied electric field. Both polymer and ceramic materials with large ECE have been developed. However, realizing multilayer capacitors with large heat capacity has remained elusive. To date, the demonstration of electrocaloric heat pump demonstrations have utilized commercially available capacitors based on barium titanate (BTO), which have a small ECE <1K at maximum field, or capacitors with only one or two layers of polymer materials. This talk will describe PARC’s approach to solid-state electrocaloric heat pump design capable of high temperature span with limited parasitic thermal mass. Recent results of a demonstration system utilizing high performance bulk ceramic multilayer capacitors will be presented.

SESSION TP01.10: Multicaloric Materials
Session Chair: Lluis Manosa
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Berkeley AB

10:45 AM *TP01.10.01
Multi-Field Modulated Hysteresis Loss and Multicaloric Effect Feng-Xia Hu1,2, Qing-zen Huang3, Ji-rong Sun4,5 and Bao-gen Shen1,2; 1Beijing National Laboratory for Condensed Matter Physics and State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, China; 2School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, China; 3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Solid state refrigeration based on magnetocaloric, electrocaloric, mechanocaloric effect (multicaloric effect) has attracted world-wide attention for its environmental-friendly and energy-saving superiority over the conventional vapor compression technique. Here, we report our recent progress on multi-field modulated hysteresis loss and multicaloric effect for the well-known La(Fe,Co,Si)13[1], FeRh [2], and NiIn-type MM’X [3] materials. For a room temperature La(Fe,Co,Si)13, magnetocaloric material, enhanced magnetocaloric effect (MCE) by hydrostatic pressure has been demonstrated as magnetic measurements under pressure. To understand the origin, we performed neutron powder diffraction studies on the crystal and magnetic structures as a function of temperature under different pressures [4]. The change of atomic local environments and 5 kinds of Fe-Fe bonds (B1-B5) with pressure were illustrated. Detailed analysis indicated that the sensitivity of intra-icosahedron Fe-Fe bonds (B1, B2, B3) to hydrostatic pressure is mainly responsible for the change of magnetic properties. Moreover, we found that the change of lattice volume AV/V across Curie temperature TC becomes significantly larger with increasing pressure. Accordingly, lattice entropy change was estimated by Debye approximate. The results indicate that the contribution of entropy change from lattice increases by ~40% as the pressure increases to 11.3 kbar. This result indicates that hydrostatic pressure is an effective way to dig the lattice contribution. Multicaloric effect and the contribution from interplay between spin and lattice are also discussed. On the other hand, hysteresis loss is a longstanding problem harming refrigeration efficiency, which exists in most of giant magnetocaloric materials. Here we report a new way to reduce hysteresis loss in the model FeRh materials. Utilizing strain memory effect to engineer the magnetization process of FeRh film, a large reduction of hysteresis loss was achieved, consequently effective refrigeration capacity and COP (coefficient-of-performance) remarkably increases in a designed refrigeration cycle [5]. We also studied the impact of film strain on the magnetostructural coupling of NiIn-type Mn-Co-Ge-In films grown on different substrates. Strain modulated phase transition and MCE has been demonstrated [6].

This work was supported by the National Key Research and Development Program of China (2017YFB0702702, 2014CB643700), and the National Natural Sciences Foundation of China (51531008, 51771223, 51590880).


11:15 AM TP01.10.02
Ultra-Low-Field Magneto-Elastocaloric Cooling in a Multiferroic Composite Device Huilong Houl, Peter Finkel2, Margo L. Starch2; Jan Cun3,4 and Ichiro Takenchi2; 1University of Maryland, College Park, College Park, Maryland, United States; 2U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 3Ames Laboratory, Ames, Iowa, United States; 4Iowa State University of Science and Technology, Ames, Iowa, United States.

Given that caloric materials are ferroic materials which undergo first (or second) order transitions near room temperature, they open up intriguing possibilities for novel multiferroic devices with hitherto unexplored functionalities coupling their thermal properties with different fields (magnetic, electric, and stress) through composite configurations. Here, we demonstrate a composite magneto-elastocaloric effect with ultra-low magnetic field (0.16 T) in a compact geometry to generate a cooling temperature change as large as 4 K using a magnetostiction/superelastic alloy composite. Such composite systems can be used to circumvent shortcomings of existing technologies such as the need for high-stress actuation mechanism for elastocaloric materials and the high magnetic-field requirement of magnetocaloric materials, while enabling new applications such as compact remote cooling devices.

11:30 AM *TP01.10.03
Multicaloric Effects—Materials and Modeling Antonio Planes1, Teresa Castan1, Lluis Manosa1 and Avadh Saxena2; 1Física de la Matèria Condensada, Universitat de Barcelona, Barcelona, Spain; 2Los Álamos National Lab, Los Alamos, New Mexico, United States.

Multicaloric materials thermally respond to changes in their properties induced by the application or removal of multiple external fields. Particularly interesting are a class of multiferroic materials which are characterized by a strong interplay between different ferroic properties in the region where these properties emerge via a phase transition. In this talk, we will discuss a general thermodynamic framework to describe multicaloric effects in this class of materials. We will show that multicaloric effects comprise the contributions from caloric effects associated with each ferroic property and the cross-contribution arising from their interplay. In these materials, the use of more than one driving field can induce larger thermal changes, with smaller field magnitudes, over wider ranges of operating temperature. In addition, this permits to reduce hysteresis in one driving field in a controlled manner by transferring it to another field. These results will be illustrated with available experimental data.
1:30 PM TP01.11.01
Giant Barocaloric Effects at Low Pressure in Organic Salts Xavier Moya; Department of Materials Science, University of Cambridge, Cambridge, United Kingdom.

Barocaloric materials driven by hydrostatic pressure are currently being considered for cooling applications, following the observation of giant barocaloric effects in a small number of magnetic materials and ferroelectric materials. Here I will present pressure-dependent calorimetry data to demonstrate giant barocaloric effects in two organic salts that are made of cheap abundant elements, and that operate under low pressure.

2:00 PM TP01.11.02
Design and Operation of a 100 W Elastocaloric Compression-Based Active Regenerator David Catalini1, Nehemiah Emaikwu1, Jan Muehlbauer1, Suxin Qian2, Yunho Hwang1, Reinhard Rademacher1 and Ichiro Takeuchi1; 1University of Maryland, College Park, Maryland, United States; 2Xi’an Jiaotong University, Xi’an, China.

We have constructed and operated a 100W single-stage elastocaloric active regenerator based on compression of a bundle of NiTi tubes. Commercially available NiTi tubes placed inside a metallic sleeve undergo stress-induced martensitic transformation via compression. We use water as the heat transfer fluid which flows through the tubes. A numerical model of the system was developed in the Matlab/Simulink environment to solve the dynamic heat transfer and accounting for the thermodynamics-based phase transformation kinetics model of NiTi. The numerical tool was used to evaluate the influence of the operating parameters in the system’s performance and to find the optimal conditions for maximum temperature lift across the active regenerator. For compressive stress of 4%, where materials DT is 8K, an initial run has given the temperature lift of 13.5K under no cooling load conditions. The design can be scalable by adding parallel beds to increase cooling capacity and to add a work recovery mechanism to increase efficiency.

SYMPOSIUM TP02

TUTORIAL: Thermal Characterization of Materials and Devices
November 25 - November 25, 2018

1:30 PM Thermal Characterization of Wide Bandgap Semiconductor Materials and Device Samuel Graham; Georgia Institute of Technology

The development of wide bandgap semiconductors have enabled new optoelectronic, RF, and power electronic devices and their performance and reliability are strongly coupled to their thermal behavior. In this tutorial, a number of optical and electrical methods will be reviewed which allow for the characterization of the thermal properties of wide bandgap materials including thermal conductivity and thermal interface resistance at contacts. In addition, metrology methods for mapping temperature under steady-state and high speed thermal transients relevant to RF operation will be discussed along with their limitations and areas which remain a challenge to researchers.

3:00 PM BREAK

3:30 PM Challenges in Measuring Nano- to Micro-gram Samples: Scanning Calorimetry and Thermoviscoelasticity Gregory B. McKenna; Texas Tech University
Novel developments in making ultra-stable glasses lead to measurement challenges because extremely small amounts (nano- to micro-grams) of material are produced. We will describe work using chip calorimetry to determine the thermal properties and the cooling rate dependence of the Tg. In addition, nano-scale rheology on these materials can be carried out to determine material dynamics using a novel bubble inflation measurement method developed in our labs.

SYMPOSIUM TP02

Thermal Analysis—Materials, Measurements and Devices
November 26 - November 30, 2018

Symposium Organizers
Leslie Allen, University of Illinois at Urbana
Martin Kuball, University of Bristol
Sindee Simon, Texas Tech University
Feng Yi, National Institute of Standards and Technology

Symposium Support
University of Illinois at Urbana-Champaign (Coordinated Science Lab and Material Science & Engineering)

SESSION TP02.01: Novel Thermal Methods and Applications
Session Chairs: Sindee Simon and Feng Yi
Monday Morning, November 26, 2018
Sheraton, 3rd Floor, Fairfax AB

8:00 AM *TP02.01.01
Heat Capacity Determination—Tricks of the Trade Mary Anne White; Dalhousie University, Halifax, Nova Scotia, Canada.

Sometimes very accurate heat capacity data are required; an example would be for the calculation of a thermodynamic cycle that involves small differences between large numbers. Sometimes less accurate data would still be useful, especially if they can be acquired quickly. In this talk, some instances of each situation will be presented, along with tips to attain high-accuracy data using relaxation calorimetry, moderate accuracy with using DSC, and quantitative estimates using other means.

8:30 AM *TP02.01.02
The Boiling Temperature of Ionic Liquids—An Experimental Approach Amir Abdelaziz1, Sergey P. Verevkin3 and Christoph Schick1,2; 1Institute of Physics & Competence Centre “CALOR, University of Rostock, Rostock, Germany; 2A. Butlerov Institute of Chemistry, Kazan Federal University, Kazan, Russian Federation; 3Institute of Chemistry & Competence Centre “CALOR, University of Rostock, Rostock, Germany.

The very low vapor pressure of ionic liquids is challenging to measure. At elevated temperatures the liquids might start to decompose, at relatively low temperatures the vapor pressure becomes extremely low to be measured by conventional methods. We developed a highly sensitive method for mass loss determination at temperatures starting from 350 K up to 800 K. The technique is based on fast scanning (10 000 K s⁻¹) and an alternating current (AC) calorimeter equipped with a chip sensor, that consists of a free-standing SiN₅ membrane (thickness < 1 μm) and a measuring area with lateral dimensions of the order of 100 μm. A small droplet (diameter ca. 300 μm) of an ionic liquid is vaporized isothermally from the chip sensor in a vacuum-chamber. The surface-to-volume-ratio of such a droplet is large and the relative mass loss due to evaporation is therefore easy to be monitored by the changing heat capacity (J K⁻¹) of the remaining liquid. The vapor pressure is determined from the measured mass loss rates using the Langmuir equation. The method was successfully tested with determination of vapor pressures and the vaporization enthalpy of the archetypical ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][NTf₂]). The created in this way data set in the extremely broad temperature range 358 K to 780 K has allowed estimation of the boiling temperature of [EMIm][NTf₂]. The value (1120 ± 50) K should be considered as the first reliable boiling point of this ionic liquid obtained from experimental vapor pressures measured in the most possible close proximity to the normal boiling temperature.

References:


9:00 AM TP02.01.03
Liquid to Glass/Crystal Transitions in Ionic Liquids Studied by Fast Thermal Conductivity Measurements

Carlos López-Bueno, David Bugallo Ferrón, Victor Leborán, M.C. Giménez-López and Francisco Rivadulla, Centro de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Santiago de Compostela, Spain.

We have developed an experimental setup for the simultaneous measurement of the thermal conductivity and heat capacity of liquids. This system is an extension of the 3ω method [1] capable to measure a sample volume of the order of ~500 nL, which is an important advantage for the characterization of nanofluids, in which having a large amount of sample is sometimes difficult to achieve [2]. The setup is designed for fast measurements during a thermal ramp, which along with the extremely small volume required allows the possibility of using it in a cryostat for analysing the temperature dependence of the thermal conductivity in a variety of fluids, across phase transitions, kinetic studies, etc.

Particularly, in this work we will present the study of the low temperature thermal and electrical conductivity of different ionic liquids around their liquid-to-solid transition. Using these methods we are able to identify a spinodal decomposition temperature in in 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM TFSI) around 150K. Below this temperature, the glassy phase is unstable against the formation of a crystalline phase in the whole system. This produces a 30% variation of the thermal conductivity of the system, depending on the thermal history. We discuss the possibility of using ionic liquids as configurable models to study the low temperature thermal conductivity of ionic solids.

References


Acknowledgements

This work was supported by the Ministry of Science of Spain (Projects No. MAT2016-80762-R), the Consellería de Cultura, Educación e Ordenación Universitaria (ED431F 2016/008, and Centro Singular de Investigación de Galicia accreditation 2016-2019, ED431G/09), the European Regional Development Fund (ERDF), the Xunta de Galicia and the European Union (European Social Fund- ESF).

9:30 AM TP02.01.05
Abrupt Size Effect Observed in Layered Materials Below Critical Size—Linking Thermal Analysis with Local Structural Analysis

Zichao Ye1, Lito De la Rama1, Mikhail Efremov2, Andre Sutrisno3 and Leslie Allen1; 1Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Materials often exhibit exotic properties because of “discrete regions”, regions that have different chemical environment from the remaining part of the system. Material at the first level is treated as a uniform “bulk” with single sets of intrinsic and extrinsic characteristics; the next level incorporates finer details of the system by segmenting it with discrete regions, including interfaces (e.g., lamella mating boundaries), surfaces (e.g. nanoparticle spheres) and defects (e.g., gauche kinks). The effect of these discrete regions is highlighted by material miniaturization. At extremely small scale lengths (<10 nm), properties of the “whole” object (e.g., melting, lattice structure, bandgap, conductivity, optical) are dominated by the nature of “local” discrete regions.

Regular thermal analysis using calorimetry has no depth perception – it only yields average thermodynamic values, whereas NMR has the unique capability to probe the local structure of each individual atom. Here we link calorimetry (NanodSC or DSC) thermal analysis with 31C NMR structural analysis to report an abrupt bulk-to-discrete transition in 2D layered silver alkanethiolate (AgSCn, n=1-16) with a critical chain length of ~7. None of the carbon group share identical chemical environment below the critical length, making AgSCn (n=2-6) uniquely different materials, even though the crystal structures of all AgSCn are preserved throughout. Extraordinary changes of thermodynamic properties, including ~500% increase of melting enthalpy and ~50°C increase of melting point, are also observed at the bulk-to-discrete transition. This transition is universal for aliphatic layers, including n-alkanes with a critical chain length of n=11. A new 3D spatial model is constructed to divide the aliphatic chains of AgSCn into three bulk or discrete segments: (a) tail segment that forms interlayer interfaces, which are never planar structures but have 3D depth; (b) head segment that is strongly affected by the metallic core; (c) bulk mid-chain segment which shows similar properties to the hydrocarbon chains in polyethylene. The presence (multilayer) or absence (1-layer) of odd/even effect is exclusively attributed to the nature of the localized tail segment. Bulk-to-discrete transition occurs when material properties are dominated by the discrete head and tail segments over the bulk segment at/below critical length. This work is seminal to the design of novel aliphatic lamellae with tailorable properties and has applications in molecular electronics and biophysics.

10:00 AM BREAK

10:30 AM TP02.01.06
Phase Transformations in CuZr-Based Shape Memory Thin Films Analyzed by Combinatorial Nanocalorimetry

Koost J. Vlaskak and Mark Miao; Harvard University, Cambridge, Massachusetts, United States.

We have investigated the phase transformations in sputtered CuZr-based shape memory thin films using a combinatorial nanocalorimetry technique that is capable of making differential calorimetric measurement on thin-film samples with a sensitivity as small as 12 pJ/K. We first investigate the crystallization kinetics of amorphous as-deposited equiatomic CuZr samples and demonstrate non-Arrhenius diffusion kinetics that is well described using a phenomenological model based on the fragility of super-cooled liquids. We then explore the conditions for the formation of the martensitic phase.
responsible for the shape memory properties of this alloy. We will show that fast, low-temperature cycling through the martensitic transformation increases the hysteresis, which we attribute to the accumulation of defects during the martensitic transformation. If, however, the austenitic phase is given sufficient time at elevated temperature to annihilate these defects, the transformation is stable under thermal cycling conditions. The addition of Ni to the CuZr alloy raises the martensite transformation temperature making it a potential high-temperature shape memory alloy. The microstructures of select CuZrNi samples have been analyzed using XRD and cross-sectional TEM. We will present the effects of composition, heat treatment, and grain size on the transformation temperature, hysteresis, and functional stability of the samples. We will also demonstrate that under certain conditions the martensitic transformation proceeds in an explosive fashion. The transformation behavior of these alloys will be discussed in light of ab initio simulations of the materials system.

11:00 AM - TP02.01.07
Physical Limits of Laser Gold Nanowarming

Kanav Khosla1, Li Zhan1, Aditya Bhati1, Aiden Carley-Clopton1, Mary Hagedorn2, and John Bischof1,2; 1Department of Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; 2Smithsonian Conservation Biology Institute, Smithsonian National Zoological Park, Washington, District of Columbia, United States.

In this work we explore the physical limits of a new technique to rewarm vitrified droplets and zebrafish embryos impregnated with 1064 nm resonant gold nanorods that are irradiated by a Nd:YAG ms pulsed laser. Importantly, the droplets and the embryos loaded with 2 M PG are first cooled by a modified cryostop at rates estimated to be 90,000 °C/min to a visually transparent state in liquid nitrogen. Numerical modeling demonstrates possible differences in warming depending on full mixing (droplets) vs. micro-injection into the yolk of the zebrafish. Experimental measurements based on optical transparency vs. cloudy behavior are then used to judge the physical success of the procedure. From this we present a map of the successful laser power, pulse length, CPA concentrations and gold concentrations that can yield physical success for laser gold nanowarming.

11:30 AM - TP02.01.08
Non-Contact Thermal Analysis with Fast and Micro-Scale Thermographical Imaging

Junko Morikawa; Tokyo Institute of Technology, Tokyo, Japan.

Non-contact quantitative thermal imaging in micro-scale is attractive to realize the non-contact thermal analysis. It visualizes not only the typical thermal analysis on phase transitions and thermal degradation, but also the heat transfer. We propose a system of infrared camera equipped with an original optics and temperature calibration algorithm, which enables to achieve the high-quality and fast-speed thermal imaging. The Infrared (IR) optical lens design has been optimized to each wavelength band of the photon type and the thermal type detectors of IR FPA. Typical applications to observe the freezing biological cells and the crystallization of organic molecular crystals are reviewed. Combined with the techniques of microscale flying spot laser and the superimpose processor, the method is applied to determine the heat transport properties. The recent instrumentation of thermospectroscopy and the high temperature imaging systems are also introduced.

11:45 AM - TP02.01.09
Time-Domain Transient Fluorescence Spectroscopy for Thermal Characterization of Polymers

Hao Wu1, Yanan Yu2, Yangheng Xiong2 and Xin Zhang2; 1School of Power and Mechanical Engineering, Wuhan University, Wuhan, China; 2Department of Mechanical Engineering, Boston University, Boston, Massachusetts, United States.

In this work, a time-domain fluorescence spectroscopy technique is developed to characterize thermophysical properties of polymers. The method is based on fluorescence thermometry of materials under periodic pulse heating. In the characterization, a continuous laser (405 nm) is modulated with adjustable periodic heating and fluorescence excitation. The temperature rise at sample surface due to laser heating is probed from simultaneous fluorescence spectrum. Thermal diffusivity can be determined from the relationship between normalized temperature rise and the duration of laser heating. To verify this technique, thermal diffusivity of a polymer material (PVC) is characterized as 1.031×10^-7 m^2/s, agreeing well with reference data. Meanwhile, thermal conductivity can be obtained by the hot plate method. Then, both steady and unsteady thermophysical properties are available. Quenching effect of fluorescence signal in our measurement can be ignored, as validated by longtime laser heating experiments. The uncertainty induced by uniformity of laser heating is negligible as analyzed through numerical simulations. This non-destructive fluorescence-based technique does not require exact value about laser absorption and calibration experiment for temperature coefficient of fluorescence signals. Considering that most polymers can excite sound fluorescence signal, this method can be well applied to thermal characterization of polymer-based film or bulk materials.

SESSION TP02.02: Thermal Properties of Polymers and Biomaterials

Session Chairs: John Bischof and Christoph Schick
Monday Afternoon, November 26, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM - TP02.02.01
Fast Scanning Calorimetry of Silk Protein

Peggy Cebe; Physics and Astronomy, Tufts University, Medford, Massachusetts, United States.

Silk is a naturally occurring biopolymer used in textiles for over 5000 years. The properties of the B. mori silk protein, fibroin, are related to its secondary structures, such as helices, random coils, turns, and beta pleated sheet crystals. We have prepared fibroin by extracting it from the native cocoons and use this as a starting material for our investigations into the polymorphic structure of the protein. Using infrared spectroscopy and heat capacity measurements, we quantify the amounts of the different secondary structures. By varying processing treatments, two crystalline polymorphs, Silk I and Silk II, can be formed and their structure and properties studied using X-ray diffraction and fast scanning calorimetry (FSC). Silk degrades before melting when heated at slow rates. With FSC, we heat silk at 2000 K/s, thereby minimizing effects of thermal degradation. We show that beta pleated sheet crystals melt to form unstructured non-crystalline fibroin protein, upon the input of heat energy alone. We show that Silk I crystals melt at (565 ± 14) K, while Silk II crystals melt at (624 ± 11) K. A general method for using FSC to estimate the thermodynamic heat of fusion is presented, and demonstrated for the beta pleated sheet crystals. The FSC methods developed here for the study of silk are readily transferable to studies of other crystalline materials, such as synthetic polymers, amino acids, and proteins.

2:00 PM - TP02.02.02
Thermal Transport and Flow in Polymeric Materials

David Venerus1,2, David Nieto Simavilla3, Andy Kiessling2 and Jay D. Schieber2; 1NJIT, Newark,

Minneapolis, Minnesota, United States; 2Conservation Biology Institute, Smithsonian National Zoological Park, Washington, District of Columbia, United States; 3Hawaii Institute of Marine Biology, University of Hawaii, Kaneohe, Hawaii, United States; 4Department of Biomedical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.
The strong coupling of mechanical and thermal effects in polymer processing flows has profound implications on both the processability and final properties of the material. Simple molecular arguments suggest that Fourier’s law must be generalized to allow for anisotropic thermal conductivity in deforming polymeric materials. In addition, theoretical results suggest a linear relationship between the thermal conductivity tensor and the stress tensor, or a stress-thermal rule. Using a novel optical method based on Forced Rayleigh Scattering (FRS) developed in our laboratory, we obtain quantitative measurements of all components of the thermal diffusivity tensor in polymers subjected to deformation. These data have been used to carry out the first (and only) tests of the stress-thermal rule, which we have found to be valid for several polymer chemistries in both shear and elongational deformations. More recently, we have developed a novel technique based on Infrared Thermography (IRT) that complements FRS and allows for the study of a wider range of polymeric materials. The IRT technique also allows us to investigate the dependence of heat capacity on deformation. These experiments are used to develop an understanding of the molecular mechanisms of thermal transport in polymers that are essential for the development of advanced materials.

2:15 PM *TP02.02.04 Utilizing Fast-Scan Calorimetry on Polymer Crystallization and Melting with Gibbs-Thomson, Hoffman-Weeks and Thermal Gibbs-Thomson Plots Akhiko Toda; Hiroshima University, Hiroshige-Hiroshima, Japan.

Crystallization and melting behaviors of chain-folded polymer crystals are examined by fast-scan calorimetry (FSC) combined with other various methods including small angle X-ray scattering (SAXS) with Gibbs-Thomson, Hoffman-Weeks, and thermal Gibbs-Thomson plots, which offer new insights on polymer crystallization mechanism. The melting point of lamellar crystals formed isothermally at \( T_M \) was measured by FSC and calibrated in terms of the heating rate dependence on the basis of the modeling of melting kinetics for the determination of the melting point at zero heating rate \( T_M^0 \). By combining \( T_M \) with the crystalline lamellar thickness \( d_c \) determined by SAXS, the Gibbs-Thomson (G-T) plots of \( T_M \) and \( T_M^0 \) are utilized for the determination of the equilibrium melting point of chain-extended infinite-size crystal \( T_M^L \). The Hoffman-Weeks (H-W) plot of \( T_M^0 \) against \( T_M \) is an alternative method of \( T_M^L \) determination. For many polymers, both of the plots, especially the G-T plots, are curved. In order to understand the meaning of the curved G-T and H-W plots, we propose a thermal Gibbs-Thomson plot in terms of the melting point \( T_M \) and the total heat of fusion \( \Delta H_f \) in the secondary stage of isothermal crystallization, during which thickening and perfecting of lamellar crystals undergo and bring the shift in both of \( T_M \) and \( \Delta H_f \) with longer annealing time.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM TP02.02.05 Thermal Properties and Structure of Electrospun Blends of PVDF and Fluorinated Copolymers Nelaka Govinna, Ilin Sadeghi, Ayse Asatekin and Peggy Cebe; Tufts University, Medford, Massachusetts, United States.

We report a study of the structure and thermal properties of blends comprising poly(vinylidene fluoride), PVDF, and a random copolymer of poly(methyl methacrylate) and 1H,1H,2H,2H-perfluorodecyl methacrylate, which are candidates for applications as superoleophobic membranes for oil-water separation. Blend composition was systematically varied by controlling the PVDF-to-copolymer ratio. The role of processing method and copolymer content on structure and properties was investigated for both fibers and films. Non-woven fibrous membranes were obtained by electrospinning (ES) solutions of PVDF and copolymer, at 20% w/v in a mixed solvent, N,N-dimethylacetamide/acetone (1/1 v/v). Scanning electron microscopy showed that bead-free fibers were obtained at all compositions. Fiber diameter ranged from 0.4 μm – 1.9 μm, and thinner fibers were obtained for PVDF content above 80 wt.%. As the copolymer content in the blends increased, the degree of crystallinity and the onset of degradation for each blend decreased while the glass transition fibers were obtained at all compositions. Fiber diameter ranged from 0.4 μm – 1.9 μm, and thinner fibers were obtained for PVDF content above 80 wt.%. Processing conditions had a greater impact on the crystallographic phase of PVDF than the copolymer content. For crystalline ES fibers, the blend composition was systematically varied by controlling the PVDF-to-copolymer ratio. The role of processing method and copolymer content on structure and properties was investigated for both fibers and films. Non-woven fibrous membranes were obtained by electrospinning (ES) solutions of PVDF and copolymer, at 20% w/v in a mixed solvent, N,N-dimethylacetamide/acetone (1/1 v/v). Scanning electron microscopy showed that bead-free fibers were obtained at all compositions. Fiber diameter ranged from 0.4 μm – 1.9 μm, and thinner fibers were obtained for PVDF content above 80 wt.%. As the copolymer content in the blends increased, the degree of crystallinity and the onset of degradation for each blend decreased while the glass transition temperature \( T_g \) increased, as evidenced by differential scanning calorimetry (DSC), Wide-angle X Ray Scattering (WAXS) and thermogravimetry (TG) experiments. The variation of \( T_g \) followed the Kwei model of \( T_g \) mixing in polymer blends and suggest strong intermolecular interactions between the PVDF and copolymer molecules when the copolymer is present in large quantities, and relatively weaker interaction when the copolymer fraction is smaller than 0.15. Processing conditions had a greater impact on the crystallographic phase of PVDF than the copolymer content. For crystalline ES fibers, WAXS and infrared spectroscopy indicated only polar phases were present, and beta was dominant over gamma phase at all compositions. In comparison, solution cast films also contained polar phases, with an increase of gamma phase PVDF. Melt crystallized films formed non-polar alpha phase exclusively.

3:45 PM *TP02.02.06 The Unfolding and Refolding Properties of Proteins—A Case Study on Lysozyme Zhiwu Yu; Department of Chemistry, Tsinghua University, Beijing, China.

Proteins, serving as the principal structural and functional units in living organisms, have highly ordered structures and conformations folded from peptide chains. When subjected to stress such as heat or chemicals, proteins may unfold. The unfolded peptide chains have the potential to refold when the stress factors are completely/partially removed. In this presentation, the unfolding/refolding behaviors of a model protein, lysozyme, are discussed in detail.

First, a method to differentiate the two-state and non-two-state unfolding of proteins is discussed. It is called an interruption-incubation protocol: protein solutions are incubated at different interrupting temperatures to allow the partial unfolding of the macro-molecules. Then the thermal behaviors of the proteins upon reheating are examined. Comparisons between lysozyme and a few other proteins including bovine serum albumin will be presented.

Second, the folding/unfolding behavior of lysozyme in the presence of micelles composed of the unstructured b-casein proteins will be presented. Depending on the b-casein/lysozyme molar ratio, the partially unfolded structure of lysozyme can occur. This partially unfolded state of lysozyme loses most of its tertiary structure and, after heating, the denatured lysozyme molecules are trapped in the charged coatings of b-casein micelles and cannot refold upon cooling. The thus obtained protein complex can be viewed as a kind of special polyelectrolyte complex micelle.

Third, the unfolding/refolding behavior of lysozyme in the presence of a negatively charged polyelectrolyte sodium poly(styrenesulfonate) or PSS will be presented. With elevated PSS concentration, a new state (state I) is first formed via a “two-state” conversion process and this state can further convert to a completely unfolded state (state II) via a “non-two-state” conversion mechanism.

Finally, the mutual influence of lysozyme and lipid liposomes consisting of neutral and negatively charged phospholipids on their thermal behaviors will be presented. Interestingly, the enrichment of the negatively charged lipids cannot be induced by the native and ex situ unfolded (unfolded in the absence of liposomes) lysozyme, but requires that lysozyme undergo an in situ unfolding process (unfolding in the presence of liposomes).

4:15 PM TP02.02.07
A Novel Approach to Evaluate Microorganism Viability and Microbial Growth Using the Highly Versatile Heat-Transfer Method (HTM) Kai Betlem, Mikhaljo Zubko, David Sawtell, Bart van Grinsven, Thomas Cleij, Peter Kelly and Marloes Peeters; 1Manchester Metropolitan University, Manchester, United Kingdom; 2Maastricht University, Maastricht, Netherlands.

The Heat Transfer Method (HTM) is a novel, versatile and low-cost thermal technique that has already shown its use in the analysis of (biological) targets ranging from small molecules, to DNA, to whole cells and bacteria. The surface can be functionalized with specific receptors (DNA, polymers) for measurements and is the central element through which the heat flux will pass. The internal temperature of the heat sink, $T_s$, is measured by a thermocouple and steered via a controller, which is connected to a power resistor. The front side of the chip is exposed to the liquid, where $T_2$ is measured at the solid–liquid interface. To extract the heat-transfer resistance $R_\text{HT} (\text{°C/W})$ quantitatively, the ratio of the temperature difference $\Delta T = T_1 - T_2$ and the input power $P$ according to $R_\text{HT} = \Delta T/P$, is analysed. Changes at the interface will reflect in a difference in the overall thermal resistance $R_\text{HT}$.

Here, we report a novel application for the HTM with the real-time viability study of microbes, using yeast (Saccharomyces cerevisiae) as a model organism. To accompany this study, the existing flow cell was redesigned, preventing the build-up of gases produced in the metabolic cycle yeasts, leading to an increase of the $R_\text{HT}$ signal corresponding with the increasing concentration of cells in the flow chamber. Therefore, it was possible to discriminate between a wild type strain (DLY640) and a temperature sensitive mutation (cdc13-1) based on the growth kinetics. At temperatures higher than 30 °C the mutant strain stops growing. This corresponds to a decrease in temperature of the optimal growth rate of the cells compared to wild type yeast cells.

The influence of factors inhibiting the replication process of yeast cells can be followed in real-time using this technique. Here, the signal increase in the thermal resistance under normal growth conditions ceased when changing to a growth medium depleted of nutrients, the introduction of a toxic component (CuSO4) or application of a thermal shock treatment. Upon restoring the normal conditions, only the nutrient depleted condition remained viable, in all other situations the yeast cells were permanently eliminated. These results were confirmed by classical plating experiments of yeasts that were exposed to the same conditions as during the HTM measurement.

Having the advantages of simplicity, signal processing and portability, the setup can be used on site without requiring a lab environment. The described methodology is versatile and can be adapted to study different antimicrobial properties, such as the response to antibiotics on a wide range of different microbes.


4:30 PM TP02.02.08 Determination of the Thermophysical Properties of Nucleobases with Fast Scanning Calorimetry Amir Abdelaziz, Dmitry Zaitsau, Sergey P. Verelkin and Christoph Schick; 1, 2, 3 ‘Competence Center ‘CALOR, Rostock University, Rostock, Germany; 2’Institute of Physics, Rostock University, Rostock, Germany; 3’Institute of Chemistry, Rostock University, Rostock, Germany; 4’Kazan Federal University, Kazan, Russian Federation.

The determination of the thermophysical properties, e.g. fusion temperature, fusion enthalpy, sublimation enthalpy and vapour pressure lay within focus of many scientific fields and industrial applications. These values are directly connected to the intermolecular forces in crystal state, provides the lattice energy, change in ordering by going from crystal to gas phase and the solubility properties of organic molecules.

In many cases investigation of thermally labile systems e.g. biomolecules at slow heating rates are accomplished with low thermal stability of them. The application of classic techniques to measure their thermophysical properties often fails, making the estimation of the corresponding thermodynamic parameters, like melting temperature, enthalpy of fusion, vapor pressure highly inaccurate or even impossible.

In the present study, fast scanning calorimetry was successfully applied for determination of the sublimation vapour pressure, enthalpies of sublimation and melting behaviour of the nucleobases cytosine, thymine, adenine, uracil and guanine, the building blocks of DNA and RNA, which are known to decompose at high temperature.
Electrospinning is a process used to create polymer fibers with diameters on the order of nanometers to microns. Blending polymers with nanomaterials, such as carbon nanotubes or graphene, to create nanocomposites can improve the thermal, mechanical and electrical properties of the host polymer. In this study, we investigate the effects of blending carbon-based fillers on the structural and thermal properties of electrospun fibers of poly(ethylene terephthalate). PET fiber solutions containing 1.0 wt.% multi-walled carbon nanotubes (MWCNTs) or graphene flakes were electrospun from hexafluoroisopropanol. The fibers were characterized structurally using wide angle X-ray scattering, infrared spectroscopy, and scanning electron microscopy. Thermal properties were studied using thermogravimetry and temperature modulated differential scanning calorimetry (TMDSC). Fiber diameters ranged from 670 to 900 nm. WAXS revealed that the as spun homopolymer as well as the composites containing 1.0 wt% of MWCNTs or graphene were amorphous. Prior to thermal analysis the fiber mats were dried at 85 °C for 20 minutes to evacuate any solvent, as well as minimize effects due to fiber shrinkage. Addition of the MWCNTs or graphene resulted in a modest decrease of the glass transition and cold crystallization temperatures. Quasi-isothermal TMDSC of the dried fiber mats reveals less mobile amorphous fraction in the blends. MWCNT-based composites had mobile amorphous fraction of 0.83 while graphene-based composites and neat PET fibers had 0.89 and 0.91, respectively. Cold crystallization during QI-TMDSC increased the solid fractions of the MWCNT composite, graphene composite and neat fibers to 0.53, 0.50 and 0.43 respectively. Future work will include investigation of the fiber composites using broadband dielectric spectroscopy.

**TP02.03.03**

Properties of Poly(Ethylene Terephthalate) Electrospun Fibers Containing Carbon Nanotubes or Graphene 
Andrew G. Clark and Peggy Cebe; Physics, Tufts University, Medford, Massachusetts, United States.

Shape memory polymers (SMPs) are materials considered to be intelligent due to the ability to be programmed to fix a temporary shape and subsequently regain their original shape after the application of an appropriate stimulus. They have been studied by researchers in different fields such as chemistry, materials engineering, mechanics, biomedical sciences, and microelectronics engineering. In addition to the benefits cited, they are low cost, easy to process and can have their properties easily modified through the combination with other chemical compounds, in order to expand the field of application, taking into account the needs of the market and favoring the technological advances. In this work, we analyze and compare the thermally induced shape-memory effect (SME) of two different polymer systems, one being a thermoplastic formed by a semi-interpenetrating network of poly (methyl methacrylate) and poly (ethylene glycol) (PMMA / PEG), and the other thermosetting based of the DGEBA epoxy resin (DER 331) using the aliphatic amine Jefamine D230 (DGEBA / D230). Each material was characterized according to its ability to deform, fix a temporary shape and recover, as well as response time and life cycle, which corresponds to the number of consecutive cycles that can be performed without failure. PMMA / PEG exhibited higher deformation rate and shape fixation, but DGEBA/D230 showed higher recovery rate and shorter response time. The differentiated behavior in the analyzed systems is directly associated to the molecular structure. The higher DGEBA / D230 cross-linking density allows for faster and more efficient response, but PMMA / PEG thermoplasticity is vulnerable to long-range molecular chain slippage.

**TP02.03.04**

Cyclic Phase Transformation Behavior in Shape Memory Zirconia—Single Crystals vs Polycrystals 
Isabel Crystal, Alan Lai and Christopher A. Schuh; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In shape memory materials, cyclic martensitic phase transformation can accumulate damage over many cycles due to the mismatch stresses developed amongst the phases and grains. Reducing such mismatches improves the cyclic performance, as known in brittle Cu-based shape memory alloys, where structures with relatively fewer grains (i.e. oligocrystalline or single crystalline specimens) exhibit better cycling properties than conventional polycrystals. The purpose of the present work is to assess this approach in zirconia-based ceramic systems, which are attractive for their high temperature capabilities and higher transformation stresses than shape memory metals, yet are also known to be brittle and experience fracture during the martensitic transformation. Specifically, this work compares tetragonal-to-monoclinic transformation behavior of polycrystalline and single crystalline samples of yttria-doped zirconia compositions. The evolution of transformation enthalpies and strains as well as sample mass and integrity are measured to characterize thermal cyclic performance. Microscopic examination also provides insight into microstructural changes after repeated transformation.

**TP02.03.05**

The Shape Memory Effect in Polymer Systems Based on PMMA/PEG and Epoxy DGEBA / D230 
Katia Furlani and Ruben Rodriguez; State University of Northern Fluminense, Campos dos Goytacazes, Brazil.

Shape memory polymers (SMPs) are materials considered to be intelligent due to the ability to be programmed to fix a temporary shape and subsequently regain their original shape after the application of an appropriate stimulus. They have been studied by researchers in different fields such as chemistry, materials engineering, mechanics, biomedical sciences, and microelectronics engineering. In addition to the benefits cited, they are low cost, easy to process and can have their properties easily modified through the combination with other chemical compounds, in order to expand the field of application, taking into account the needs of the market and favoring the technological advances. In this work, we analyze and compare the thermally induced shape-memory effect (SME) of two different polymer systems, one being a thermoplastic formed by a semi-interpenetrating network of poly (methyl methacrylate) and poly (ethylene glycol) (PMMA / PEG), and the other thermosetting based of the DGEBA epoxy resin (DER 331) using the aliphatic amine Jefamine D230 (DGEBA / D230). Each material was characterized according to its ability to deform, fix a temporary shape and recover, as well as response time and life cycle, which corresponds to the number of consecutive cycles that can be performed without failure. PMMA / PEG exhibited higher deformation rate and shape fixation, but DGEBA/D230 showed higher recovery rate and shorter response time. The differentiated behavior in the analyzed systems is directly associated to the molecular structure. The higher DGEBA / D230 cross-linking density allows for faster and more efficient response, but PMMA / PEG thermoplasticity is vulnerable to long-range molecular chain slippage.
Iron oxide (Fe$_2$O$_3$) is one of the most abundant compounds in nature. This material has four well-known crystalline polymorphs, which exhibit different structural arrangements and physicochemical properties. These particular features have driven the use of this oxide for technological applications in water splitting, gas sensors, lithium-ion batteries, and magnetic storage devices. A fundamental concept is that controlling the thermal stability as well as final microstructure of Fe$_2$O$_3$ at nanoscale is possible to tailor its electric and magnetic properties. Hence, the aim of our study was focused on the thermal behavior of Fe$_2$O$_3$ nanoparticles previously grown via hydrothermal reactions at 160°C for 8 h. These nanoparticles were pressed and conformed as pellets (green compact), which were sintered in a dilatometer (DIL) by using a temperature range from 30 °C to 1300 °C under argon atmosphere. This analysis revealed a size-dependent sintering mechanism, since these nanoparticles presented a lower densification capability of a gel at a temperature gradient of 20 to 60 °C over 10 cm is raised up to 205% for 20 kbp DNA fragments. The enhanced separation is due to larger pore size of the gel at higher temperature, which will reduce diffusion resistance and increase migration rate. Theoretical analysis confirms that diffusion rate is proportional to temperature to the third power. Given the easiness and spatial flexibility of light modulation, the photothermally generated temperature gradient can be a powerful way to enhance separation capability of a given gel in electrophoresis.

Thermal Stability and Microstructural Behavior of Sintered Iron Oxide Nanoparticles
Josiane C. Souza, Edson R. Leite and Júlio César Szczancoski; Federal University of São Carlos, São Carlos, Brazil.

Iron oxide (Fe$_2$O$_3$) is one of the most abundant compounds in nature. This material has four well-known crystalline polymorphs, which exhibit different structural arrangements and physicochemical properties. These particular features have driven the use of this oxide for technological applications in water splitting, gas sensors, lithium-ion batteries, and magnetic storage devices. A fundamental concept is that controlling the thermal stability as well as final microstructure of Fe$_2$O$_3$ at nanoscale is possible to tailor its electric and magnetic properties. Hence, the aim of our study was focused on the thermal behavior of Fe$_2$O$_3$ nanoparticles previously grown via hydrothermal reactions at 160°C for 8 h. These nanoparticles were pressed and conformed as pellets (green compact), which were sintered in a dilatometer (DIL) by using a temperature range from 30 °C to 1300 °C under argon atmosphere. This analysis revealed a size-dependent sintering mechanism, since these nanoparticles presented a lower densification temperature (~750 °C) than Fe$_2$O$_3$ microparticles synthesized by other conventional routes (~1300 °C). In order to monitor the strengthening of the microstructure (neck growth between particles), densification (removal of porosity accompanied by shrinkage), and coarsening (grain growth and/or pore growth), other Fe$_2$O$_3$ pellets were sintered in a dilatometer (DIL) by using a temperature range from 30 °C to 1300 °C under argon atmosphere. This analysis revealed a size-dependent sintering mechanism, since these nanoparticles presented a lower densification temperature (~750 °C) than Fe$_2$O$_3$ microparticles synthesized by other conventional routes (~1300 °C). In order to monitor the strengthening of the microstructure (neck growth between particles), densification (removal of porosity accompanied by shrinkage), and coarsening (grain growth and/or pore growth), other Fe$_2$O$_3$ pellets were sintered in the DIL at 750 °C for 12 h and 900 °C for 1 min, respectively. In this case, both presented relative densities ranging from 50% to 80%. On the other hand, scanning electron microscopy (SEM) images indicated the presence of several grain grown containing interconnected porous. For pellets sintered at 900 °C for 1 min, X-ray diffraction patterns were indexed to α-Fe$_2$O$_3$ phase, while at 750 °C for 12 h was identified a mixture of α-Fe$_2$O$_3$ and Fe$_3$O$_4$. Magnetically cubic structure and hematite - rhombohedral structure. The existence of adsorbed water and organic compounds were detected by means of differential thermal analysis and thermogravimetry. These substances were able to affect the mass transport and densification process in Fe$_2$O$_3$ pellets.
obtaining an insulating oxide film from metal-ethylenediaminetetraacetic acid (EDTA) complex. We synthesized thick Er₂O₃ and Y₂O₃ films on aluminum alloy (A5052) from two types of metal-EDTA complexes (EDTA-Er-H and EDTA-Y-H) using a flame sprayer. The deposition of metal oxide in the proposed synthesis involves two mechanisms, namely, chemical reaction and physical collision. It begins with a chemical reaction in which metal-EDTA complex is decomposed and oxidized to form metal-oxide particles. Therefore, the properties of the deposited film depend on the temperature and velocity of the moving particles. It is the physical collision of the metal-oxide particles with the substrate happens, and forms a film as the accumulated layer of incident particles solidify. First, in order to optimize the fabrication conditions for TBCs, the adhesion between the A5052 and the oxide film was evaluated, and the splat morphology was investigated. Next, thick oxide films were synthesized on A5052 based on optimized synthesise conditions. Although the Y₂O₃ film synthesized on A5052 was annealed close to the melting point of the A5052 substrate, it showed strong adhesion without delaminations. As results, the obtained Er₂O₃ having porosities of 3.8 to 23.3% film with thickness of 105-125 μm, and the Y₂O₃ film having porosities of 8.1 to 21.8% with thickness of 85-163 μm were fabricated on A5052 substrate. These results indicated that thick metal oxide films with various microstructures were fabricated by chelate flame method.

TP02.03.12
Thermal and Spectral Analysis of Microencapsulated Leuco Dyes
Donovan R. Bassett, Danielle Hall, Alexis Corbett, Binit Shapati, Kannan Sivaprakasam and John E. Sinko; St. Cloud State University, Saint Cloud, Minnesota, United States.

Leuco dyes are phase-change materials that undergo characteristic thermal and spectral changes with temperature. These materials have the potential to contribute to energy savings by reducing the light absorption of structures at high temperatures. In this study, we characterized a set of microencapsulated leuco dyes with transitions at 20°C, 25°C, and 30°C. These materials were subjected to differential scanning calorimetry and thermogravimetric analysis to understand the thermodynamic behavior around the transition points. UV-Vis-NIR diffuse reflectance spectra were also collected under quasi-isothermal forced heating and cooling of coating samples. The thermal and spectrosopic results were compared as a function of temperature to establish the thermo-optical characteristics of the leuco dyes for application as energy capturing coating materials. Spectra of leuco dyes were also simulated and compared to the experimental data. The comparison of temperature-dependent optical and thermal data could provide the basis to diversify the use of leuco dyes as practical phase-change materials and in other applications.

TP02.03.13
Developing a Novel Platform for Characterizing Thermoelectric Materials for Uncooled Detectors for Land Imaging Applications
Riley A. Reid¹, Emily Barentz², Brendan Bramman¹, Ari D. Brown¹, Steven Cagiano², Nicholas P. Coster², Vilem Mikula¹ and Alicia T. Joseph¹; ¹North Carolina State University, Raleigh, North Carolina, United States; ²NASA-Goddard Space Flight Center, Greenbelt, Maryland, United States; ³University of Waterloo, Waterloo, Ontario, Canada.

Thermal land imaging (imaging at ~8-14 μm optical wavelength) is an essential tool for understanding and managing terrestrial freshwater resources. Current thermal imaging instruments employ low temperature detectors, which require cryocoolers. Consequently, cost-saving reductions in size, weight, and power can be achieved by employing uncooled detectors. One uncooled detector concept, which NASA is pursuing, is a thermopile detector with sub-micron thick doped-Si thermoelectric materials. In order to characterize the thermoelectric properties of the doped silicon, we designed and optimized a novel apparatus. This simple apparatus measures the Seebeck coefficient with thermally isolated stages and LABVIEW automation. We optimized thermal stability using PID tuning and optimized the thermal contact between the thin film samples and stages using electrically conductive springs. Utilizing our apparatus, we measured the Seebeck coefficient of 0.45 micron thick phosphorus-doped single crystal Si samples bonded to alumina substrates. Using these Seebeck coefficient measurements and four-wire electrical resistivity measurements, we determined the relationship between the thermoelectric figure of merit and dopant concentration. These characterization results for doped-Si will guide our thermopile detector design to provide an optimal and competitive detector alternative for future thermal imaging instruments.

TP02.03.14
Effect of Annealing Temperature and Oxygen Pressure on TiO₂ Films Grown on c-Cut Sapphire Substrates via Pulsed Laser Deposition
Alexandra Gordienko¹ and Anthony B. Kaye¹; ¹Texas Tech University, Lubbock, Texas, United States; ²United States Air Force Nuclear Weapons Center, Kirtland Air Force Base, New Mexico, United States.

Titanium dioxide (hereafter, titania or TiO₂) is a well-studied material, but despite of its 100 year history we still don't know everything about this material. It used to be thought that only one of the tetragonal phases of titania - rutile - can be grown on sapphire substrates. That is the reason why a comprehensive study of annealing effects on both phases of titania on c-cut sapphire doesn't exist. In previous works, we developed two pulsed-laser deposition protocols to grow both pure rutile and pure anatase films on this substrate, these protocols are used as the basis of this study. Titania has a number of properties that make it useful for a wide variety of applications; these include using titania as the basis for energy efficient solar cells, as photocatalytic materials to clean air and water, for self-cleaning coatings, as components of various sensor devices, and as a gate dielectric in MOSFET technologies. Further, because it is a wide bandgap semiconductor, titanium dioxide is becoming increasingly important for many next-generation optical and electronics applications, such as transparent electronics systems, transparent thin-film transistors, and see-through active matrix displays. The success of each of these applications depends critically upon the particular crystallographic state (anatase, rutile, or brookite) of the titania being utilized. This is why the annealing effects on the resulting phase of this material can be very important. Titania thin films were grown via pulsed-laser deposition technique on c-cut sapphire substrates using two pre-determined recipes: one leading to creating pure rutile, and one creating pure anatase films. Each of the resulting films was post-annealed in a vacuum furnace at different temperatures in 200 to 900 °C in 100 degree increments and at different oxygen pressures (5, 35 and 50 mTorr). The phase of the resulting films was later determined using x-ray diffractionmetry. Phase content of the films was later analyzed based on the fraction of each phase in overall peak intensity. The quality of each film was was studied using atomic force microscopy.

TP02.03.15
3D Printed Polypropylene Nanocomposites for Thermal and Electrical Conductivity Applications
Yuval Shmuely¹, Vedant Singh², Daniel Chao³, Ahmed Shata¹, Mustafa Zaidi¹ and Miriam Rafailovich¹; ¹Stony Brook University, Stony Brook, New York, United States; ²The Wheatley School, Westbury, New York, United States; ³Hunter College High School, New York, New York, United States.

Polypropylene (PP) is a common polymer being used in many products in all industrial fields. However, due to its relatively high crystallinity percentages it has difficulties in being produced in modern plastics production technology – 3D printing. In this work we show how crystallinity in the printed structure can be advantage due to its orientation that has great potential for conductance applications and also can increase the mechanical properties. We also show how incorporation of thermal conductive nano-fillers as Graphene nano platelets (GNPs) and hexagonal Boron Nitride (hBN) at 0, 5 and 10 wt% combined with the polymer orientation can lead to optimal thermal and electrical conductivity properties of the printed products. We modified the Gcode input to the printer and studied the printing process in order to study the printing conditions for optimal interfilaments fusion and printed product properties.
We used high resolution infra-red thermal camera to measure the thermal conductivity of the printed structure. We also used high voltage resistivity meter to measure the electrical properties. In addition, we used small angle X-ray scattering (SAXS) microbeam to study the macrostructure in the printed structure as function of the radial position from the filaments “skin” and interface to the “core” of the filaments. Our results show the significant improvement to the conductivity properties when the nano-fillers are being introduced to the matrix and in particular, the graphene nano platelets. We Acknowledge support from the National Science Foundation (Inspire Award No. 1344267) and The Morin Foundation Trust.

TP02.03.16
Evaluating the Coefficient of Thermal Expansion at Elevated Temperatures through Nanoindentation
Samuel Bacon, Kurt E. Johanss, Phil Webb, Rich Anthony and Warren Oliver; KLA-Tencor, Milpitas, California, United States.

The characteristics of thermal expansion for materials in low volumes is vital to effective manufacturing and service life. High temperature Nanoindentation is seen as a path to effectively evaluate the properties of the thermal expansion in significantly smaller volumes then what is conventionally measured by a thermomechanical analyzer. A series of experiments were run to explore the technique using coated and uncoated samples using molybdenum, aluminium and nickel plated copper to evaluate the potential for the technique to measure material expansion on the nanometer scale. A nanoindenter is found to be able to be replicate measurement on bulk materials and is found to be able to provide insight into underlying mechanisms in layered materials expansion.

TP02.03.17
High IR Transparency of Ultra-Thin Drawn UHMWPE/LDPE and UHMWPE/MDPE Blended Films via Solvent Casting
Yassine Ait-El-Aoud1, Seong Don Hong1, Richard Pang1, Svetlana V. Boriskina2, Michael Okamoto1, Alkim Akyurtlu3 and Richard M. Osgood1; 1Natick Soldier Research, Development and Engineering Ctr., Natick, Massachusetts, United States; 2Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Electrical Engineering Department, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Polyethylene (PE) is well known polymer and has an extremely large spectrum of applications, depending on the particular molecular weight, chain length, and density. The micro and nano-structure polyethylene fibers in arrays have recently attracted great attention mainly in textile fiber industry for wearable personal thermal management. Lately, researchers have shown theoretically [1] and experimentally [2] that a particular type of polyethylene, UHMWPE [3] and Nanoporous [4] respectively, is transparent to long wave-infrared body radiation but opaque to visible light. This new passive generation of fabrics could lead to a possible wearable technologies that release heat in hot climates. UHMWPE is a type of polyethylene with extremely long molecular chains that are highly entangled and resulting in a high viscosity after melting. Therefore, UHMWPE raw materials need to be adjusted to meet the melt-spinning processing requirements. It has been shown that the processibilty and flowability of UHMWPE could be improved by 1) adding nanocomposites and/or 2) blending at certain mass ratio with low-density polyethylene (LDPE) or medium density polyethylene (MDPE). Yet, the melt-spinning of ultra-thin drawn UHMWPE/LDPE and UHMWPE/MDPE blended fibers which is our main focus aim remains a challenge whereas the blended films are feasible.

In this study, we have firstly investigated the optical properties of highly oriented ultra-thin drawn UHMWPE/LDPE and UHMWPE/MDPE blended films in the infrared wavelength range (7mm-14mm) via solvent casting. The blended films were drawn at various draw ratio from 5 times to 100 times at 130 °C. Preliminary results showed that highly transparent films with a total transmittance surpassing 95% were obtained by a mass ratio of 8:2 w/w % at draw ratio of 60 times with high crystallinity. The solvent-cast blend films were prepared by pre-mixing polymer powders then adding the mixed powders into decalin solvent in a silicone oil bath. Gradually, the temperature of the oil was increased to 150 °C in three stages within 3 hrs and was stable within ± 0.5°C precision. Secondly, we have been working on developing a thermal model of blended fibers that predict the heat transfer. This thermal model takes into consideration all possible modes of non-radiative heat transfer (convection + conduction) and radiative interaction (total reflection +total transmission +absorption) between skin-fabric and fabric-environment. The temperature cross the fabric is assumed to be uniform and the ambient temperature is approximated large relative to the fabric surface. The air gap between the skin and the fabric is taken sufficiently small.


TP02.03.18
Fabrication of Shape Memory Polymer Composites Using MWNT and Their Applications to Deployable Antennas
Yong-sun An1, 2, Young-min Kim1, 2, Yeontae Kim3, Jong Kyoo Park1 and Woong-Ryeol Yu1, 2; 1Seoul National University, Seoul, Korea (the Republic of); 2Agency for Defense Development, Daejeon, Korea (the Republic of).

Deployable antennas have an advantage of good transportability due to their small volume when folded. A space vehicle is launched with folded antenna, which will conduct assigned jobs after unfolded in space. Existing deployable antennas have some drawbacks such as heavy weight and small deformability. Shape memory polymer (SMP), a smart material which can recover the original shape from temporary deformation by external stimuli (e.g., temperature), can be used to overcome these disadvantages. Deployable antennas made up of SMPs have excellent properties such as lightweight, large deformability, good processability, and self-transformation capability without any power devices. However, they are not proper for aerospace application due to limited recovery force and speed caused by low stresses at rubbery states and low thermal conductivity. To enhance the mechanical and thermal properties of SMPs, the shape memory polymer composites (SMPCs) were prepared using surface-modified multi-walled carbon nanotubes (MWNTs) and an epoxy-type of SMP matrix. Raman spectroscopy was used to investigate the increased disorders in the surface of MWNTs after functionalization, which was verified by the XPS analysis. The thermal conductivity of the SMPC was measured by laser flash method. The functional groups in the surface of MWNTs formed covalent bonds with the polymer matrix so that the thermal interfacial resistance of SMPC was reduced, resulting in higher thermal conductivity. Then, the thermomechanical and the shape memory properties of SMPCs were characterized. Finally, a miniature of SMPC antenna (reflector) was fabricated and its deployment test was quantitatively characterized. Improved modulus at the rubbery state and increased thermal conductivity resulted in the high recovery force and speed.

SESSION TP02.04: Thermal Properties of Glasses I
Session Chairs: Leslie Allen and Gregory McKenna
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Fairfax AB
Tailoring the Microstructure of Ce-Based Metallic Glass by Fast Scanning Calorimetry

Bingge Zhao, Manman Wu, Qiqie Zhai and Yalai Gao;
Shanghai University, Shanghai, China.

Differential fast scanning calorimetry (DFSC) is capable of heating and cooling a sample at ultrafast rates, allowing freezing the high-temperature structure down to ambient temperature. Additionally, the sensitivity of DFSC is in the order of nJ/K, making it possible to detect weak thermal signal and reveal phase transitions that are invisible by conventional differential scanning calorimetry (DSC). These two features permit the quantitative analysis on the formation of metallic glass. In this study, Ce$_{65}$Al$_{10}$Cu$_{20}$Co$_{5}$ (at. %) metallic glass was in situ prepared by DFSC, during which the nucleation and crystallization are quantitively determined. With the increase of cooling rate, the nucleation is suppressed, producing the amorphous structure free of nuclei. Based on that, an isothermal annealing was followed, which tailored the microstructure ranging from relaxed local configurations to nanocrystals. By the reheating after annealing, the role of structure tailoring on glass transition, crystallization is demonstrated according to the Johnson-Mehl-Avrami (JMA) equation.

Highly stable glasses prepared by vapour deposition at deposition temperatures around 0.85 of their glass transition temperature exhibit higher density, kinetic and thermodynamic stability with respect to their glassy counterparts obtained directly from the liquid [1]. In these vapor-deposited glasses molecular packing is so tight that the transformation into the supercooled liquid proceeds in time scales much longer than the alpha relaxation time and occurs, for sufficiently thin films, through an heterogenous mechanism starting at the free surface [2-4]. In-situ membrane-based nanocalorimetry is an ideal tool to explore the thermodynamic properties of the glass and its transformation into the supercooled liquid during temperature upscans [5]. By using appropriate capping layers the front mechanism can be suppressed and stable glasses without free surfaces transform through a ‘nucleation and growth’ like process. The transformed fraction follows a sigmoidal shape and can be explained using the KJMAE model, initially derived for crystallization studies. The isothermal kinetic stability increases by a factor of 50 with respect to the uncappped stable glass. We also identify, both in thin films and bulk materials, the existence of a rejuvenation process that is compatible with a cooperative mechanism.

10:45 AM *TP02.04.05
Tuning the Structure of Molecular Glasses through the Kinetic Arrest of Liquid-Liquid Phase Transitions
Lian Yu; Univ of Wisconsin-Madison, Madison, Wisconsin, United States.

The structure of a glass is usually considered just amorphous and not much different from the structure of its precursor liquid. There has been increasing evidence, however, that the structure of molecular glasses can be engineered to a great extent to achieve high density and high structural order – properties desired for many applications. These “new glasses” can be prepared by physical vapor deposition and by the kinetic arrest of first-order transitions in the liquid state. We discuss two examples in the latter category. In the case of D-mannitol (and the previously studied triphenyl phosphite), two glasses can be prepared with a large difference in enthalpy (60 J/g) and density (2 %), one by quenching the ordinary liquid and the other by annealing the ordinary liquid to induce a polyamorphic transition. In the case of itraconazole, the transition to layered liquid-crystalline structures can be bypassed partially or completely by varying the cooling rate, producing glasses with continuously tunable smectic order. For this rod-like molecule, kinetic arrest of the end-over-end rotation controls how much smectic order gets trapped in the glassy state. These two examples illustrate the potential to manipulate the structure of amorphous materials to improve their properties, and the role of FDSC in understanding liquid-liquid phase transitions. Ref.: Zhu, M.; Yu, L. J. Chem. Phys. 2017, 146, 244503. Teerakapibul, R.; Huang, C.; Gujral, A.; Ediger, M. D.; Yu, L. Phys. Rev. Lett. 2018, 120, 055502.

11:15 AM *TP02.04.06
Phase Transformation in Nano-Structured Materials Measured by Fast Differential Scanning Calorimetry
Juergen E. Schawe; Mettler Toledo GmbH, Schwerzenbach, Switzerland.

Fast differential scanning calorimetry (FDSC) is a non-adiabatically chip calorimetry technique. The commercial available Flash DSC 2+ enables typical heating and cooling rates in the order of 40,000 K/s in a temperature range between -100 °C up to 1000 °C. This technique is used to study the formation of differently structured glasses and non-isothermal nucleating processes in bulk metallic glass alloys. Depending on the thermal history and the heating conditions monomorphic polymorphic phases can be formed which can be transformed into the more stable phase on different pathways. Furthermore, we discuss a method to distinguish between heterogeneous and homogeneous nucleation processes.

11:45 AM TP02.04.07
Conjugated Polyelectrolytes are Feeling the Heat—A Ratiometric Nanothermometer for Solution, Hydrogels and Thin Polymer Films
Pierre Karan; Chemistry, American University of Beirut, Beirut, Lebanon.

Temperature is a fundamental variable that controls and drives many chemical, biological and physical processes. Nowadays, there is a tremendous drive to explore and understand processes at the nanoscale level in many fields of science and technology. We report a self-referencing ratiometric nanothermometer based on short conjugated polyelectrolytes (CPEs). The probe is prepared by complexing a phenylene-based polymer with polyvinylpyrrolidone (PVP), an amphiphilic macromolecule that destabilizes the CPE π-π stacking. This makes it possible to shift the equilibrium between the less emissive aggregated state of the CPE (520 nm) and its more emissive single chains (450 nm) within a useful temperature range (15.0–70.0 °C). The probe is used as a noninvasive fluorescent method for mapping thermal fluctuations in solution, hydrogel matrices and thin film polymers using an unmodified commercially available digital single-lens reflex camera (DSLR). We are currently exploring thermal processes in microwell structures. The reported temperature sensor has the potential to provide a wealth of information when thermal mapping is correlated with chemical or physical processes.

1:30 PM *TP02.05.01
Nano-Scale Dynamic Measurements—Flash DSC and Nanobuble Inflation of Ultra-Stable Amorphous Fluoropolymers
Gregory B. McKenna and Heedong Yoon; Texas Tech University, Lubbock, Texas, United States.

The advent of novel experimental techniques that make it possible to work with nanogram quantities of material has revolutionized the study of nanofluidic materials. Furthermore, the relevant techniques have also made it possible to investigate novel materials that are only made in extremely small quantities. It is this latter case that we address here. We have succeeded in making and characterizing ultra-stable amorphous fluorocarbon films made by vacuum pyrolysis deposition (VPD). The ultra-stable amorphous fluorocarbon is very deep in the energy landscape or deep glassy section of the “unexplored region” of glasses between the a very low fictive temperature Tf and the glass temperature Tg. By combining rapid chip scanning calorimetry (Flash DSC) with the Texas Tech nanobuble inflation method we not only determine that the deposition conditions lead to a value of Tg that is very near to the Kauzmann temperature Tk, but we are also able to measure the viscoelastic response in the temperature regime encompassing Tk to slightly above Tg and determine the temperature dependence of the dynamics in this regime. The question ultimately addressed is whether or not the relaxation time (or viscosity) diverges at a finite temperature above absolute zero and near to Tk as anticipated in theories in which an ideal glass transition is postulated. The measurements near to and above Tg give upper bounds to the equilibrium relaxation times because in the regime where T>Tg the material has a lower specific volume and lower enthalpy than the equilibrium glassy state. Furthermore, because the Tg is approximately equal to Tk, which is 56 K below the Tg in this case, the range of measurements is greater than previously achieved using a 20 million year old amber material. For the amber the glass had a fictive temperature some 43.6 K below Tg. Our results confirm the amber results and are consistent with the idea that the observed Vogel-Fulcher behavior of glass-forming liquids seen above the Tg does not persist into the deep glassy state where T>Tg. Rather the response deviates from the super-Arrhenius behavior of the Vogel-Fulcher function and tends towards an Arrhenius-like behavior, albeit with very high apparent activation energy. These results challenge theories that demand divergence of the relaxation times or viscosities at a finite temperature as well as the idea of an ideal glass transition. The studies were only possible because of our ability to make dynamic, both calorimetric and viscoelastic, measurements on nano- to micro-gram quantities of material.

2:00 PM TP02.05.02
Profiles in Local Glass Transition Temperature Near and Across Polymer Interfaces
Connie B. Roth; Emory University, Atlanta, Georgia, United States.

Local thermal analysis using fluorescence has made it possible to map out the profile in local glass transition temperature Tg(c) as a function of
position z across a glassy-rubbery polymer-polymer interface. Starting with the weakly immiscible system of polystyrene (PS) and poly[n-butyli
te] methacrylate] (PnBMA) whose bulk \( T_g \) values differ by 80 K, we observed a broad and asymmetric dynamical profile in \( T_g(z) \) spanning 350–400 nm from one bulk \( T_g \) value to another [J. Chem. Phys. 2015, 143, 111101]. We have since observed similar behavior in a number of weakly immiscible systems, consistently showing a longer-ranged \( T_g(z) \) perturbation for a lower \( T_g \) polymer next to a hard interface than a higher \( T_g \) polymer next to a soft interface [J. Chem. Phys. 2017, 146, 203307]. More recently we have explored this difference of hard vs. soft neighboring domain by investigating the \( T_g(z) \) profile in PS next to polydimethylsiloxane (PDMS) with varying crosslink density to systematically change the modulus of the neighboring domain without also changing the chemistry of the interface. We observe that the local \( T_g(z) \) in PS at a distance of \( z \approx 50 \) nm away from the PS/PDMS interface can vary by 45 K when the PDMS modulus changes from –1 to 3 MPa, supporting theoretical predictions that modulus is a controlling variable. Interestingly, the length scale \( z \approx 70–90 \) nm at which bulk \( T_g(z) \) of PS is recovered for this more strongly immiscible system is significantly shorter than what would be expected (\( z \approx 225–250 \) nm) for this soft neighboring domain based on our previous results. Our studies have also discovered that this strong coupling of the dynamics across dissimilar polymer-polymer interfaces only occurs if the interface has been well formed and annealed to equilibrium suggesting that some aspect during polymer interface formation (broadening of interface, chain interpenetration, or interfacial roughening) may be significant in controlling the observed behavior. Efforts to separate these different factors have led us to investigate rough interfaces and substrates with end-tethered chains finding that low grafting densities, coinciding with the “mushroom-to-brush” crossover regime, result in large increases in local \( T_g \) with \( T_g(z) \) profiles consistent with a hard polymer interface [ACS Macro Letters 2018, 7, 269-274].
Influence of Temperature on Microstructure and Mechanical Properties of Polymer Composites

We believe that cavity-optomechanics based probes are broadly-applicable and will benefit a wide range of AFM-based dynamic observations in conducting measurements in water. Finally, I will discuss our efforts to further increase the PTIR throughput by 200-fold, i.e. 500,000x with respect to conventional measurements and to conduct measurements in water.

We validate these new capabilities using polymer films and measure the intrinsic thermal conductivity (\(\eta\)) of metal-organic framework (MOF) individual microcrystals, a property not measurable by conventional techniques. MOFs are a class of nanoporous materials promising for catalysis, gas storage, sensing and thermoelectric applications where accurate knowledge of \(\eta\) is critically important. Additionally, the improved sensitivity enables measurement of nanoscale IR spectra of monolayer this sample with high signal to noise ratio (\(\approx 170\)).

Recently, new AFM modes, improved modeling, better calibration, and more optimal probe design have become available[5], expanding the possibilities for quantifying mechanical properties at the nanoscale. This presentation will demonstrate the use of this new capability in examining microscopic domains and interphase regions within a polymer composite over a wide range of frequencies and temperatures.

References


4:00 PM TP02.06.02

Influence of Temperature on Microstructure and Mechanical Properties of Polymer Composites

The relationship between the microstructure and mechanical properties of microscopic domains within polymer composites is important due to their influence on macroscopic material performance and function. Mechanical properties of polymers are time-dependent, so a full understanding requires measurements over a range of frequencies and temperatures. Ideally, one would like to observe the mechanical behavior of these domains while they pass through their glass transitions in order to better understand the influence of size effects and confinement.

Atomic Force Microscopy (AFM) has the nanometer level resolution and sensitivity needed to investigate these samples, but accurate comparisons with established rheological measurements have proven to be more elusive. Resonant methods like TappingMode[1] and contact resonance[2] provide mechanical property maps at discrete frequencies that are many orders of magnitude higher than bulk measurements. Non-resonant methods like force spectroscopy[3] and PeakForce Tapping[4] provide a better match in frequency, but face challenges in calculating intrinsic mechanical properties like loss tangent and storage modulus.

Recently, new AFM modes, improved modeling, better calibration, and more optimal probe design have become available[5], expanding the possibilities for quantifying mechanical properties at the nanoscale. This presentation will demonstrate the use of this new capability in examining microscopic domains and interphase regions within a polymer composite over a wide range of frequencies and temperatures.

References


4:15 PM TP02.06.03

Quantitative Thermometric Scanning Thermal Microscopy and Thermomechanical Nanoindentation from Room Temperature to >1,000°C

The functionality and performance of polymeric materials is largely determined by a complex interplay of chemical and mechanical properties, often at the nanoscale. In order to understand these complex material systems and further improve them, it is necessary to measure and map them at that same nanoscale. Macroscopic polymer behavior is often characterized with temperature dependent mechanical analysis measurements such as dynamic mechanical analysis (DMA). Previous approaches to making similar measurements on the nanoscale, while having some success at quantifying stress and...
strain as a function contact area and frequency have relied on indirect measurements of the tip-sample contact temperature. Using a combination of a laser heated tip with a unique, an integrated thermocouple combined with a scriptable DMA interface, we can quantitatively evaluate temperature and frequency dependent polymer properties with sub-100nm resolution. This approach has enabled three key advances we will cover in this presentation:

1. High temperature Scanning Thermal Microscopy. The probes discussed here, coupled with photothermal heating can routinely operate at temperatures in excess of 1,000°C.

2. Localized thermal analysis combined with quantitative nanomechanical imaging. The ability to quantitatively ramp the tip temperature (estimated at rates in excess of 10⁶°C/minute) allow quantitative and highly localized measurements of phase transitions, mechanical and other temperature dependent properties.

3. Fouled tip cleaning. A common problem in AFM, fouling of the tip with material from the sample, can be greatly mitigated with localized heating of the tip. We will demonstrate that repeatable quantitative modulus measurements[1] can be accomplished by cleaning the tip with a simple protocol.

The tip structure of the thermocouple integrated probe has been described elsewhere [2]. During the experiments the tip and the thermocouple materials were found to be stable in the excess of 1000°C, expanding the regime of the DMA of the polymeric material that were not possible with existing technologies.


4:30 PM TP02.06.04
Development of a Multimodal Imaging Platform Based on Photoinduced Thermal Desorption and Analysis by Atmospheric Pressure Chemical Ionization Mass Spectrometry Oleq Orcheminskyy,1, 2 Matthias Lorenz,2 Stephen Josse,2 Mario Viani,1 Aleksander Labuda3 and Roger Proksch1; 1 Asylum Research, Santa Barbara, California, United States; 2 Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The key to advancing materials is to understand and control their structure and chemistry. Thorough chemical characterization can be challenging since many existing techniques analyze only a few properties of the specimen, thereby requiring multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. We recently introduced the utilization of a photoinduced cantilever heating technology developed by Oxford Instruments for the localized thermal desorption and analysis and presented a closed cell design for sampling on an Oxford Instruments Cypher ES microscope to interface with a Thermo Orbitrap Velos Pro mass spectrometer using inline atmospheric pressure chemical ionization (APCI). The photoinduced cantilever heating technology works with standard AFM probes that are compatible with advanced AFM modes for the nanomechanical and electromechanical characterization of samples. We previously demonstrated below 500 nm spatial resolution for the spot-sampling by thermal desorption from thin layers and the chemical analysis of small organic molecules in full scan MS mode.

We demonstrate the application of multiple and advanced AFM measurement modes such as AMFM nanomechanical characterization on a single AFM cantilever, combined with photoinduced thermal desorption and analysis by mass spectrometry to link chemical composition with material functionality. We show the chemical analysis by mass spectrometry of gas phase species evolving from polymeric material in contact with a heated AFM probe, spatially resolved with nanometer resolution, and identify small organic molecules and characteristic fragments and pyrolysis products from the polymer. We present results from systematic studies of factors limiting the efficiency of transport and ionization of material evolving from the sample surface, with the objective to enhance the achievable spatial resolution and compound coverage of the multimodal imaging platform. Parameters studied include the timing of the photothermal cantilever heating and analysis by mass spectrometry, transport conditions for the gaseous material from the closed desorption cell to the mass spectrometer, and the operating conditions of the inline ionization stage. Computational fluid dynamics (CFD) simulations were used to study the uptake and transport of material. Experimental studies on prototype cell models prepared by additive manufacturing provide support for the modeling data.

4:45 PM TP02.06.05
Calibration Techniques for Robust Quantitative Scanning Thermal Microscopy—A Comparison of Strategies and Best Practices Adam A. Wilson1, 2; 1 US Army Research Laboratory, Adelphi, Maryland, United States; 2 National Research Council, Washington, District of Columbia, United States.

As we continue to improve our ability to miniaturize, manipulate and leverage materials and devices down to the nanoscale, the limit to advancement in many fields leveraging nanotechnology is accurate measurement of material properties at these scales. Scanning thermal microscopy (SThM) boasts the best available spatial resolution among thermal metrology techniques, leveraging the nanometer-scale resolution afforded by atomic force microscopy. However, SThM has suffered from a lack of consistent, reliable quantitative usage. This is largely due to tip-sample interaction, with the sample’s topography leading to artifacts in the observed signal. Several recent efforts have attempted to more robustly calibrate the probe-sample thermal interaction and account for topographically-induced artifacts. Among the most commonly used thermal exchange parameter calibration strategies are the implicit (curve fitting) method, the step method, and the intersection method, which each rely on at least two materials as reference samples, while recent advancements include single-sample calibration strategies. However, to date, there has not been a comparative study between calibration methods, or efforts to demonstrate the limits of each technique.

This work compares the performance and suitability of probe-sample thermal exchange calibration strategies, discusses the most frequent failure modes, and offers guidance for best practice in quantitative usage of SThM. As an example of determination of accuracy of calibration and best practices, we demonstrate that under conditions previously published using the intersection technique (kref = 1.1 Wm⁻¹K⁻¹ and kref = 1.5 Wm⁻¹K⁻¹), significant deviation (>50%) in measured sample thermal conductivity is observed when measuring samples with thermal conductivity values larger than those of the reference samples, but we demonstrate that by calibrating with reference samples having a wide range of sample thermal conductivity (kref = 0.5 Wm⁻¹K⁻¹ and kref = 50 Wm⁻¹K⁻¹), the measured values may be expected to be accurate to within 20% for the entire range. Similar analysis will be performed on data from both previously published studies and new experimental results using the step method, the implicit method, and the novel single-sample calibration strategies to demonstrate which method(s) provide the most accurate values for local thermal conductance measurement and in what ranges and experimental conditions the quantitative accuracy may hold. This work is poised to offer a timely comparison between several emerging and widely used calibration techniques for SThM, and aims to unify efforts for improved accuracy and reliability in future quantitative studies using SThM.
In this work, the indentation size effect (ISE) is studied for temperatures ranging from 300K to 475K using nanoindentation experiments and molecular dynamics simulations. CaF2 single crystals are indented using a high temperature nanoindenter and the pop-in load was observed to decrease with increasing temperature. Increasing the temperature of the material also led to a reduction in the material dependent plasticity length scale defined in the Nix-Gao relation as well as the hardness at infinite depths.

The experiment is supplemented with MD simulations of nanoindentation into a free surface of CaF2. A suitable CaF2 potential for high temperature was first selected via comparisons between simulated and experimental vacancy formation energy as well as melting point temperatures. Changes in dislocation structure with increasing indentation depth were then studied for various temperatures for the (111) planar direction. The study thus provides much insight into the relationship between temperature and dislocation mechanisms during nanoindentation and underscores the effect of temperature on dislocation structure and formation.

Reduction in thermal conductivity by phonon confinement effect of In0.53Ga0.47As nanofilms

Reduction in thermal conductivity of the nanostructured materials has been widely known for having the reduced phonon mean free path by its nano-size boundary scattering. At even smaller size, the phonon confinement effect from the decrease of the phonon group velocity can happen in nanostructured materials leading to further reduction in the thermal conductivity. We measured the thermal conductivity of In0.53Ga0.47As nanofilms with various thicknesses from 70 to 10 nm by the T-bridge method, and analyzed it by the Callaway’s thermal conductivity model. It is found that the calculated thermal conductivities of below 20-nm-thick nanofilms based on the bulk In0.53Ga0.47As group velocity cannot accurately predict the measured thermal conductivities. The group velocities of nanofilms are evaluated by the calculation of the phonon dispersion relation, and these show that there is a significant reduction in the group velocity along the decrease in the thickness. According to these reduced group velocities, the re-calculated thermal conductivities of below 20-nm-thick nanofilms are successfully agreed with the measured ones. The phonon confinement effect is found to be another key factor to explain the low thermal conductivities of below 20-nm-thick In0.53Ga0.47As nanofilms.

Extraordinary Electronic Contribution to Thermal Transport in Free-Standing Graphene Nanoribbons with Low-Disorder Edges

Previous research on thermal transport in graphene has focused on the lattice contribution while the electronic contribution is regarded as 0.1%-1%. Here, we report experimental evidence of extraordinary electronic contribution to heat conduction in graphene nanoribbons (GNRs) with low-disorder edges. By the electrical self-heating method, the thermal conductivity of a plasma-CVD-grown 43nm-wide suspended GNR with near-zigzag edges was measured to be below 5% of that of large pristine graphene and exhibits a temperature dependence that indicates width confinement. The electronic thermal conductivity, which is converted from the measured electrical conductivity by the Wiedemann-Franz law, reaches as high as ~20% of the total thermal conductivity at 120-360K. This finding is attributed to the different effects of edge scattering on phonons and electrons for the particular edge structure, as well as the cleanliness of the as-grown sample. Even the low level of edge disorder in the near-zigzag GNR can lead to strong phonon-edge scattering, but the superior electron transport is preserved, which agrees well with previous simulations. Our work highlights the importance of electronic thermal conductivity in GNRs, and suggests the edge manipulation as a promising way to independently control electron and phonon transport in GNRs for potential thermoelectric applications.

Non-Contact Temperature Difference Measurement of Cleavage Plane Nanogap Electrodes with Large Surface Area

Vacuum nanogap electrodes are expected to significantly improve thermal power generation efficiency, which is considered difficult with conventional thermoelectric materials. In order to apply the vacuum nanogap electrodes as a thermal power generation element, the properties of nanogap, especially heat transfer at the nanogap should be investigated because enhancement of the heat transport due to the near-field heat radiation effect cannot be ignored in the vacuum gap of nanometer order. However, the measurement is difficult because it needs high temperature and spatial resolution. In addition, it is difficult to create a spatial temperature difference in a nanometer scale region. Furthermore, it is also challenging to achieve both large area and uniform narrow gap by conventional fabrication methods such as electron beam lithography, metal plating, and focused ion beam processing, where the opposing surfaces of the gap are neither parallel nor flat. Also, the emission area achieved by the aforementioned methods are only of the order of several nm², which makes these vacuum nanogap electrodes impractical from the viewpoint of the power generation. In this research, we have proposed a method to make nanogap electrodes by exploiting the advantages of interplanar cleaving in single crystal silicon, choosing (111) as cleavage plane. In cleavage fracture, a smooth fracture surface parallel to the crystal plane is exposed, so it is expected that the opposing surface of the obtained nanogap electrodes will become parallel and smooth. We fabricated MEMS devices with silicon-on-insulator wafers with device layer thickness of 5 um, oxide sacrificial layer thickness of 2 um, handle layer thickness of 400 um, device layer surface orientation (110). Silicon beam in the device, oriented in <111> direction was cleaved by applying tensile stress using a micromanipulator. As a result, nanogap electrodes having a parallel and smooth surface area of several tens of um² were obtained, which makes the cross-sectional area several thousand times larger than conventional nanogap electrodes. Comb drive actuators and a gold wire for joule heating were integrated in the device, and the gap distance control and heating near the nanogap electrodes were carried out. For temperature measurement, micro-Raman spectroscopy was used. The temperature resolution in our measurement was about 1 K and the spatial resolution was 1 um or less. We were successful to produce and maintain a spatial temperature difference of up to 60 K in a 180 nm size distance. However, in order to evaluate the proximity effect of heat transfer in the vacuum nanogap, higher temperature resolution and accuracy is needed; therefore, we continue to
We have studied a conducting oxide CaCu4RuO8 as an alternative conducting material for Pt as various high temperature operating electrical devices such as solid oxide fuel cells and gas sensors. The resistivity of CaCu4RuO8 is lower than 1 mΩcm even at 500 °C, and the temperature dependence of resistivity is metallic. In our previous study, we have successfully formed CaCu4RuO8 thick film on alumina substrate by screen-printing process, which is one of the practical process, via mixing with CuO as a sintering additive [1]. Then, we have fabricated a SnO2 gas sensor using CuO-mixed CaCu4RuO8 thick film as both electrodes and a heater on an alumina substrate (3.0 × 2.5 × 0.3 mm). In this study, we investigated the heat generation property of the CuO-mixed CaCu4RuO8 thick film heater in the sensor in order to evaluate the potential of CaCu4RuO8 [2]. The temperature of the CuO-mixed CaCu4RuO8 thick film heater increases at least up to 600 °C without any problems such as thermal runaway and hot spots, and the temperature is linearly changed with applied voltage. The heater remains intact after long-term operation at high-temperature and a large temperature change of 500 °C within 10 s. We conclude that the CuO-mixed CaCu4RuO8 thick film heater is proven to be robust and reliable, and can replace Pt heaters in gas sensors.

crucible, homogeneous solidification behaviour with deep undercooling was observed. The microstructure was different between crucible solidified sample, and levitating solidified sample. Deep undercooling in homogeneous solidification induces fast growth of primary dendrite arm, on the other hand heterogeneous solidification induced thick and short primary dendrite arms. Finally, Microstructure was investigated to figure out solidification behaviour of each condition and to control mechanical and thermal properties of W-Ta alloys. Likewise to previous research, deep undercooling sample had long primary dendrite arms and low secondary dendrite arm spacing, which can induce higher yield strength than heterogeneous solidification sample. Ultimately, because the study of properties near melting temperature of W-Ta alloys is deficient for lack of systematic experiment, this study can be a touchstone to study measuring property of ultra-high temperature refractory alloys.

TP02.07.09
The Role of Molecular Chain Length and Side Group Weight on Thermal Transport In Electrosynlow Vinyl Polymer Nanofibers Xin Zhang1, Yin Zhang2, Lin Yang1, Qian Zhang1, Akara Ueda2, Matthew Fitzgerald3, Richard Mu2, Deyu Li4 and Leon Bellan1; 1Vanderbilt University, Nashville, Tennessee, United States; 2Southeast University, Nanjing, China; 3Fisk University, Nashville, Tennessee, United States; 4Tennessee State University, Nashville, Tennessee, United States.

Polymeric materials have found extensive use in a variety of applications due to their facile synthesis and processing, low-cost and tunable and attractive properties. Since a recent studying employing molecular dynamics techniques suggested that a single-chain polyethylene (PE) could possess extremely high thermal conductivity (≈300 Wm⁻¹K⁻¹) several research efforts have been devoted to investigating a variety of factors that may result in the enhanced thermal transport in polymer nanofibers. Recent experimental results have demonstrated that the thermal conductivity of an individual ultra-drawn polyethylene nanofiber can achieve ≈104 Wm⁻¹K⁻¹, which is three orders of magnitude larger than that of bulk PE. However, the dependence on several critical factors, such as molecular chain length and side group composition, is still not understood.

To explore the influence of molecular chain length, we prepared PE nanofibers with four different molecular weights (Mₚ) using the electrospinning process. The thermal conductivity of various electrosyn low PE nanofibers was determined using a well-established thermal bridge device composed of suspended microheaters/thermometers. Our results indicate that nanofibers composed of higher molecular weight polymers exhibit larger thermal conductivity, which is attributed to more efficient energy transport along the polymer chain direction compared to cross chain direction. It is noteworthy that PE fibers with lower Mₚ (35,000 and 125,000) exhibit monotonically increasing thermal conductivity versus temperature, typical for amorphous materials. However, for higher Mₚ PE fibers (420,000 and 3,000,000), a peak thermal conductivity appears as temperature increases, which is a signature of phonon Umklapp scattering in crystalline materials.

To investigate the impact of side group composition, we electrospun three types of vinyl polymer nanofibers, namely polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA) and polyvinyl chloride (PVC). These polymers have the same planar-zigzag carbon backbones as PE, but with one or two hydrogen atoms replaced by different heavier side groups (OH, CI or F) in each monomer unit. In order to examine the role of side groups, we purposely choose the molecular weight of all polymers such that their polymer chain lengths were as close as possible. The measured thermal conductivity of four different types of polymer fibers shows a clear trend indicating κ_PVDF > κ_PVA > κ_PVCL > κ_PE, which implies that thermal conductivity decreases as the side group becomes heavier. Additionally, it is believed that the enhanced thermal conductivity of electrosyn low nanofibers may correlate with their increases in Young’s modulus. As such, we measured the Young’s modulus of several individual electrosyn low PVA, PVC and PVDF nanofibers using an atomic force microscope. The measured Young’s modulus of PVA was larger than that of PC and PVDF, which agrees with the thermal conductivity trend.

TP02.07.10
Tuning Thermal and Electrical Properties of NiO Films by UV/O3 Treatment for Resistive Memory Applications Sanchit Deshmukh1, Raisul Islam1, Christopher Saltonstall2, Eilam Yalon3, Thomas Beecham4, Krishna Saraswat1 and Eric Pop1; 1Stanford University, Stanford, California, United States; 2Sandia National Laboratories, Albuquerque, New Mexico, United States.

Resistive random access memory (RRAM) devices store information by switching a sub-50 nm diameter, locally conductive filament (CF) in insulating materials such as oxides like NiOx [1]. Because switching an individual CF needs both high fields and elevated temperatures, sufficient Joule heating is necessary for device operation. In this context, the thermal interfaces of the CF with surrounding oxides and metal electrodes need to be properly understood, as they govern the operation of RRAM devices. The CF thermal physics is also complicated by vacancies, whose role is not adequately understood in such oxides [2,3].

Here we probe RRAM oxide interfaces by studying vacancy-dependent thermal properties of sub-stoichiometric NiOx for the first time. We demonstrate that tuning the vacancy concentration at such interfaces can aid in tuning the electrical contact resistivity (ρC) and thermal boundary conductance (TBC) to Ni-vacancy rich NiOx films. We deposit 400 nm thick NiOx films using sputtering in an Ar:O2 ambient from a NiO target, with stoichiometry close to 1:1. We tune the Ni vacancy concentration at the top surface by treating the films with O3 under UV light for different durations. Previous work [4] shows that we can tune the electronic properties of NiOx films using this technique. Circular transfer length measurements (C-TLM) on these treated films reveal a decreasing ρC from 3.8 × 10¹⁰ to 1.5 × 10¹⁰ Ω·μm² with increasing treatment time from 0 to 30 min, while NiOx film resistivity reduces from 15 to 1 kΩ·cm.

We use similarly treated films with 60 nm thick Pt blanket top deposition post-treatment for thermal measurements. We perform time-domain thermoreflectance (TDR) measurements to separate out the film thermal conductivity and the TBC at the top metal-film interface. With increasing UV/O3 treatment time from 0 to 30 min, we see an increase in the TBC from 175 to 420 MW/m²K, with a negligible change in the corresponding NiOx thermal conductivity ~7 W/mK. The contribution of the electronic component of NiOx thermal conductivity, calculated from the Wiedemann-Franz Law, remains negligible with treatment. With increased vacancy density at the interface, there is a decrease in the electrical and thermal contact resistance to the NiOx films. This suggests that increased vacancy concentration in an oxide, as observed in a CF, enhances electronic and thermal conduction across the metal-oxide interface, in general. These results show that electronic and thermal energy transport can be tuned across interfaces of RRAM oxides by controlling the vacancy concentration, an important step in designing energy-efficient RRAM devices.

TP02.07.11
Thermal Characterization of High-Al Composition AlGaN High Electron Mobility Transistors Samuel H. Kim and Samuel Graham; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

AlGaN-channel high electron mobility transistors (HEMTs) are promising candidates of ultra wide-bandgap transistors for power and RF applications. Their promise derives from the large breakdown field. The breakdown voltage of high-Al composition Al(x)Ga(1-x)N (x > 0.5) is expected to be about 3x higher than that of GaN. Also, thermal conductivity of AlN is 6x higher than sapphire, and 1.5x – 2x higher than GaN. These lead to significantly high power and RF figure of merit, especially at elevated temperatures, when Al(x)Ga(1-x)N (x > 0.5) channel layers are used instead of GaN in HEMTs. One study showed that, the 3 μm thick high quality AlN buffer layers over sapphire substrates provide excellent thermal conduction, enabling stable device operation.
operation with negligible drain-current degradation up to 250 °C. Unlike GaN/AlGaN HEMTs, however, there is no thermal characterization study reported for these ultra wide-bandgap transistors.

In this study, we investigate thermal response of high-Al composition AlGaN HEMTs. Thermal characterization techniques have been developed to evaluate the temperature distribution of wide band gap electronics that will be applied to these AlGaN HEMTs. We utilize Raman thermometry, IR thermal imaging, and transient thermoreflectance imaging to investigate the temperature distribution of these devices. Raman thermometry has been well established to be spatially and temperature accurate when monitoring the thermal response of devices under steady state DC biasing conditions. IR micro thermal imaging is a widely used tool to image temperature distributions of electronic devices. Lastly, transient thermoreflectance imaging will be used to not only monitor the formation of the hotspot under pulsed biasing, but also image temperature distribution across the channel.

SESSION TP02.08: Thermal Devices and Sensors
Session Chairs: Ming Su and Zichao Ye
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Fairfax AB

8:00 AM TP02.08.01
Development of In Situ High-Temperature High-Resolution Transmission Electron Microscopy Using a Picometer Scale Sample Manipulation System Manabu Tezura, Hideki Kobayashi, Takuya Okamoto, Koichi Murakami and Tokushi Kizuka; Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

Heath resistant materials, which are subjected to high temperatures up to ~1700 K at strong external force, are key advanced structural materials. Microstructural dynamics of materials in phase transformation, precipitation, behavior of point defects, grain-boundaries, and interfaces at actual using environments should be investigated to design and improve such materials. In situ high-temperature transmission electron microscopy (HTTEM) can be applied to the observations of texture and deformation process at high temperatures [1]. However, in most of previous HTTEM, the observation was performed at conventional magnifications. In this study, we developed a new type of HTTEM for the investigation of microstructural dynamics during mechanical deformation using a piezodriving system [2-4].

A molybdenum mesh heater was mounted on a sample holder for HTTEM. A direct current was applied to the heater to increase its temperature due to Joule heating. The heater temperature while applying bias voltages was measured using a pyrometer. The heater temperature successfully increased up to the maximum temperature, i.e., approximately 2000 K [2]. In situ HTTEM observation was carried out with an acceleration voltage of 200 kV in a vacuum of 1 x 10^{-8} Pa. The fracture and deformation processes of gold nanocontacts at 930 K could be observed at the atomic resolution.


8:15 AM TP02.08.02
A Study on the Thermal Coefficient of Resistance Dependency of Infrared Microbolometer Jun Kyo Jeong1, Byeong Jun Jeong1, Jaeseop Oh2, Hi Deok Lee1 and Ga Won Lee1; 1Chungnam National University, Daejeon, Korea (the Republic of); 2National Nanofab Center, Daejeon, Korea (the Republic of).

An uncooled infrared microbolometer is a principle that measures temperature changes due to infrared absorption as a change in resistance. Compared with the cooling type infrared microbolometer, the process is comparatively simple and can be manufactured with a high yield, and is advantageous in terms of packaging. This advantage is useful as a next-generation infrared sensor. The uncooled infrared microbolometer is fabricated as a focal plane arrays with high performance combined with the microbolometer and signal detection circuit fabricated using MEMS (Micro Electro Mechanical System) technology.

In order to produce a high-performance infrared microbolometer, sensitivity and response speed must be improved. The main issues of infrared microbolometer are good thermal isolation, high absorption, good sensitive layer and good stability structure thermal transfer. In order to solve these problems, the application of the shape of the floating structure and the optimization of the geometry of the support structure to reduce the heat loss, High thermal coefficient of resistance (TCR) performance sensing membrane research for high sensitivity sensing, and stability for physical structure and simulation for optimizing heat transfer. In this paper, we have studied the temperature dependence of TCR, which defines thermal properties using COMSOL simulation for the fabrication of high-performance uncooled infrared microbolometer. The structure of the uncooled infrared microbolometer designed in this study has an air-gap corresponding to λ/4 of the far-infrared wavelength, mainly 8 μm, that is to be detected. The structure consists of cantilever, absorption layer, resistance layer, and passivation layer. The uncooled infrared microbolometer measures the current change due to the joule heating caused by the driving voltage and the incident infrared energy. simulations were conducted in COMSOL Multiphysics 5.3a software to verify and optimize the device design. The device was simulated as a 3D model using Electric Currents module, Heat Transfer in Solids. To improve the accuracy of the simulation, the TCR of the resistive layer a-Si was set as a function of temperature. In addition, the heat generation of the device is set to be the same as that of the actual device in consideration of heat loss to the outside. Although the TCR has been widely known as a parameter that greatly affects the characteristics of the bolometer, the influence of temperature dependence of the TCR on the device performance has not been fully considered. Through this study, we tried to show that the characteristics of the device can be more efficiently optimized by simulating the physical properties (resistivity, TCR, etc.) of the absorption layer and resistance layer of the uncooled microbolometer.

8:30 AM *TP02.08.03
Phase Change Nanoparticles for Biosensing, Barcoding and Enhanced Cooling Ming Su; Northeastern University, Boston, Massachusetts, United States.

Nanomaterials have been widely studied for their electronic, magnetic, mechanical, and chemical properties. We have studied the unique thermal properties of a new type of nanomaterials, nanoscale phase change materials (i.e., nano-PCMs). This group of materials may have any chemical composition, as long as there is a solid-liquid phase transition when temperature is changed. We have made a number of nano-PCMs and explored their applications in biosensing, barcoding, and enhanced cooling. Metallic nano-PCMs and organic nano-PCMs have been made with precise thermodynamic properties (melting temperature and enthalpy) based on phase diagram knowledge. These nano-PCMs have been used to enhance heat transfer capability of a variety of fluids, to detect multiple molecular biomarkers of diseases, to create cover barcodes that can be added into objects, and to prevent catalytical reactors from thermal runaway.
Different semiconductor materials including amorphous Si, Ge and MoS2 flake are tested. As nanomaterials are blooming up in recent years, the properties of individual nanostructures have attracted a lot of interests, which were reported to be significantly distinct from their bulk counterparts in many cases [1-4]. Based on specific in-situ testing platforms, routine mechanical experiments [1,2], chemical/electrochemical reactions [3,4] can be carried out on micro/nanometer-scale specimens in SEM/TEM. Nevertheless, the thermal management of small specimens remains challenging. A few of solutions are available for nanothermometry. For instance, nano-thermometers, like Ga in CNT were developed to measure temperature in TEM [5]. Nanometer-sized particles with low melting point were employed to indicate the temperature distribution of specimens irradiated by electrons [6]: VO2 nanowires were used to estimate the temperature of nanomaterials [7]; Even the temperature distribution of Al foil was mapped directly by electron energy loss spectrum [8]. While to figure out heat transfer through nanostructures, MEMS devices have to be fabricated, and careful analysis of thermal circuit is necessary [9]. Recently, we developed a new method to investigate the thermal properties of nanostructures in TEM. In this study, we are introducing a new nanoscale heat flow meter based on an individual VO2 nanowire, which can be utilized to quantify the thermal conductivity of nanostructures. The thermal conductivity of SnSe was measured as 1.86±0.21 W.k-1.m-1. According to literature, our measurement is close to the calculated value in the first-principles study, 1.55 W.k-1.m-1 [10]. We believe that our platform will open an avenue to exploring thermal properties of nanostructures.

References:
develop a first-order one-dimensional heat-transfer model to establish the temperature response of ultra-long hot films in a fiber microfluidic channel. The improved flow sensing range in a multi-segment sensor, as predicted by the 1D analytical model, is corroborated by numerical simulations and experiments.

Record-setting flow-rate sensitivity was demonstrated in this work over an ultra-wide flow-rate range and unprecedentedly low pressure drop. The successful incorporation of high-TCR, high-resistance conductive polyethylene as the temperature-sensitive hot film yields a voltage response of 0.8 V/K and a flow-rate sensitivity of 384 mV/(uL/min) between 0 and 20 uL/min. This ultrahigh voltage response allows the fiber sensor to operate at a maximum temperature rise of merely 20 °C, 5–10x smaller than that in typical MEMS sensors and important for handling biomedical samples. In addition, this ultrahigh voltage response enables ultralow pressure drop of 8 Pa at 100 uL/min, orders of magnitude lower than conventional MEMS thermal flow sensors. More importantly, we have realized a high-pressure sensitivity measurement range of 5–200 uL/min through a multi-segment structure where each segment reaches its peak sensitivity at different flow rates.

Our work combines novel material systems and new device structures that deliver new functionality and significant improvements in performance. This unconventional form of flow sensors paves the way towards a complete functional overhaul of microfluidics feed lines needed in large-scale multi-chip integration in microfluidics and opens new possibilities in lab-on-fiber technologies.

9:45 AM TP02.08.07
Thermal Analysis of Nanophotonic Structures Using Noise Thermometry and the Thermoelectric Effect
Kelly W. Mauser1, Phillip Jahelka1, Rebecca Gladell1, Michael Kelzenberg1, Colton R. Bukovsky1, Seyoon Kim2, K. C. Schwab1 and Harry A. Atwater1; 1California Institute of Technology, Pasadena, California, United States; 2ICFO–The Institute of Photonic Sciences, Barcelona, Spain.

Generating localized, high electric field intensity in nanophotonic and plasmonic devices has many applications, including enhancing chemical reaction rates, thermal radiation steering, chemical sensing, and photovoltaics. Along with a strongly localized electric field comes a temperature rise in non-lossless photonic materials, which can affect reaction rate, photosynthetic efficiency, and other properties of the system. Measuring temperature rises in nanophotonic structures is difficult, and methods commonly employed suffer from various limitations, such as low spatial resolution (Fourier transform infrared microscopy), bulky and expensive setups (scanning thermal microscopy), intrusive methods that interfere with nanophotonic structures (Pt resistive thermometry), or the need for specialized materials (temperature-dependent photoluminescence). We overcome these limitations with the first-ever demonstration of temperature measurements of nanophotonic structures by employing both room temperature noise thermometry and the thermoelectric effect under ambient conditions without external probes, by utilizing the properties of the materials that make up the nanophotonic structure itself. We have previously estimated the ΔT in a nanophotonic device using the thermoelectric effect [1], but could not determine the absolute temperature of the system. In the application we will discuss, the absolute electron temperature of the nanophotonic material itself is measured. Because Johnson-Nyquist noise is material independent and is a fundamental measure of absolute temperature, there is theoretically no need for calibration as in the case of resistive thermometry. To measure the temperature rise of a nanophotonic resonant region remotely, the Seebeck coefficient of the material is first carefully measured using noise thermometry, then the thermoelectric voltage generated in the nanophotonic materials themselves is measured from electrical leads spanning the resonantly excited region. To accomplish this, we have developed a metrology technique capable of simultaneously measuring electrical noise at two locations on the nanophotonic structure as well as the electrical potential between the two points, under chopped laser illumination that heats the structure via nanophotonic absorption, thus providing drift-corrected light-on/off temperature information.

Furthermore, this method can be used to deduce thermal time constants of the system, which will be discussed. We have successfully measured temperature rises in a room-temperature guided mode resonant nanophotonic system using the described method from several degrees above ambient to 320 K with high fidelity and reproducibility, and these results show an excellent match to simulation.


10:00 AM BREAK

10:30 AM TP02.08.08
Environment Sensing with Porous Photonic Structures
Francisco Gallego-Gómez and Cefe López; Consejo Superior de Investigaciones Científicas, Madrid, Spain.

Photonic colloidal crystals, also referred to as artificial opals, for their photonic properties, have wide applicability in many fields such as sensing, light harvesting, etc. Understanding their ability to transduce fluids adsorption and confinement into a photonic response [1-3] allows to envisage new perspectives for integrated platforms for accurate control of liquid-solid interplay [4-5]. In particular, simple spectroscopic monitoring of the photonic bandgap allows to study vapor adsorption and condensation, wetting, inhibition and confined flow within their porous network. (Opals may offer a number of benefits compared to current devices. Beside the easy and versatile fabrication in different scales with diverse materials and post-manufacture treatments, the main advantage of artificial opals resides on the photonic nature of the output, which ensures high sensitivity and fast response, while no further sensors or imaging devices are required.)

Here we gather recent achievements that prove the potential of opals as photonic devices with extremely sensitive response to adsorption and condensation phenomena, both humidity and temperature dependent. On the one hand, water condensation in the nanoporous opal network under saturated vapor conditions was studied near the dew point [6]. As a particularly interesting feature, the photonic signal sharply changed at the onset of dew formation, and allowed in situ monitoring of the condensation process. As the dew point sensitively depends on both opal and atmosphere temperatures, the opal response can be employed for precise control of temperature in versatile situations. On the other hand, distinct opal response can be obtained from selective pore filling in a gaseous environment, as demonstrated in a hierarchically porous carbon opal [7]. Specifically, the photonic signal sharply reacts to the filling of microporosity, a fact that, for a given gas pressure, drastically depends on the thermal energy of the adsorbate molecules. Thus, we propose the unique photonic response of microporous opals as a novel, powerful means for thermal analysis.


10:45 AM TP02.08.09
Effect of Band Parameters on Generation-Transport-Recombination (GTR) of Minority Carriers
Sadid Muneer, Helena Silva and Ali Gokirmak;
For semiconductor devices under extreme electrical stress, substantial number of minority carriers are generated (G) at high temperature, are transported (T) under electric field, and recombine (R) at some place away from the generation location, creating an effective heat pump that adds to the symmetric Joule heating, leading to an asymmetric thermal profile [1]. Our electrothermal finite element model captures the impact of the GTR process and shows the general trend of the correct asymmetry. However, the asymmetry observed in the experiments with silicon microwires is much stronger than the modeling results [1]. An alternative to better model the non-equilibrium processes that give rise to GTR is to use a semiconductor modeling approach. However, the conventional semiconductor models’ transport and band parameters are not tailored for extremely high temperatures. As an example, the equilibrium carrier concentration for silicon near melting is predicted as ~10^20 cm^-3 with conventional semiconductor physics instead of the melt concentration of ~10^22 cm^-3 [2]. We have constructed a detailed non-equilibrium finite element semiconductor modeling platform, including electron and hole continuity equations, Poisson’s equation for local potential calculation, and associated recombination mechanisms (SRH, Auger), to quantify and better understand the carrier-carrier and carrier-lattice interactions that gives rise to the GTR process and the consequent asymmetry [3],[4]. In the present work we specifically investigated temperature dependence of intrinsic carrier concentration [5], screening of Auger recombination at high carrier density [6], and collapse of bandgap near melting [7]. The results show that careful calibration of these parameters is essential to model GTR phenomenon and capture the correct direction and extent of the asymmetry.

References

11:00 AM TP02.08.10
Morphology, Device Performance and Thermal Behavior of a Molecular Liquid Crystalline/Fullerene Blend Alexander J. Bourque1, Chad Snyder2, Sebastian Engmann2, Lee Richter2 and David Jones1; 1The University of Melbourne, Melbourne, Victoria, Australia; 2National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The morphology and performance of thin-film photovoltaic devices comprising an active layer blend of a molecular liquid crystalline material (BQR) and a fullerene derivative (PC$_7$BM) were investigated here to assess the impact of thermal processing. In-situ grazing incidence x-ray scattering (GI-SAXS, GI-WAXS), differential scanning calorimetry (DSC) and photoluminescence spectroscopy (PL) were applied to study the active layer across a range of blend compositions to correlate morphological changes, thermal behavior and photoactivity, respectively. Enhanced BQR crystallinity and phase purity was observed for increasing temperatures with optimal device performance peaking at 120°C; device performance suffered at progressively higher temperatures due to over-coarsening of acceptor/donor domains. DSC measurements were paired with in-situ GI-WAXS measurements subject to the same thermal history to identify multiple liquid crystal and crystalline transitions in the blend. Finally, melting point depression theory was applied to estimate the Flory-Huggins interaction parameter for the binary blend.

11:15 AM TP02.08.11
Micro-Thermocouples with Extreme Sensitivity Daniel R. Assumpcao1, Shailabh Kumar2, Vinayak Narasimhan2 and Hyuck Choo1, 2; 1Electrical Engineering, California Institute of Technology, Pasadena, California, United States; 2Medical Engineering, California Institute of Technology, Pasadena, California, United States.

High-resolution detection of temperature changes in small scales could open up a new scientific vista by, for example, providing valuable intuition for energy distribution in nanophotonic structures or revealing functional details of cell biology based on subtle temperature differences [1]. Thermocouples are temperature-sensing devices that have been widely used in many applications for their simple fabrication, ease of measurements, and accuracy [2]. Micro-scale thermocouples made of IC-process-compatible metals such as Ni, Cr, or Au layers have been demonstrated for various applications [2], but they suffer from small Seebeck coefficients and consequently poor sensitivity, yielding temperature-sensing resolutions larger than 2 °C. The use of rare and expensive alloys such as bismuth and antimony telluride with high Seebeck coefficients could improve the sensitivity but requires sophisticated fabrication processes [3].

By taking the advantage of the high Seebeck coefficient of silicon, we have demonstrated a new approach for designing metal-on-silicon thermocouples with a noticeably high Seebeck coefficient of 9.17×10^-4 V/°K and temperature-sensing resolution of 0.01 °K (theoretical limit: 0.00055 °K). We have also kept the device fabrication straightforward: it only involves photolithography and metal-lift-off on a silicon substrate because we chose materials with appropriate electronic properties and selectively formed Schottky barriers and Ohmic contacts to establish electrical isolations and conduction without adding fabrication steps. The Seebeck coefficient of our thermocouple is 30 times larger than values reported for standard thin metal-film thermocouples and comparable to Seebeck coefficients of rare alloy-based thin-film thermocouples that require sophisticated and costly fabrication processes. The temperature measurements were highly linear, with a linearity coefficient of 1. Our circuit analysis performed on the metal-on-silicon thermocouples shows that these devices can be further miniaturized down to a few micron size and arranged in a dense array format with an inter-device spacing of a micron without degrading the performance.

Furthermore, we applied this approach to demonstrate a highly flexible metal-on-silicon thermocouple with enhanced thermal sensitivity (bending radius: 1.51 cm). The outstanding performance of our thermocouples combined with an extremely thin profile, bending flexibility, and simple fabrication process will proliferate its use in diverse thermography applications in the micro- and nanoscales.

References
Understanding the Superior Temperature Stability of Iridium Light-Emitting Electrochemical Cells Melanie Bowler, Tianle Guo, Anton Malko and Jason D. Slakey; The University of Texas at Dallas, Richardson, Texas, United States.

Gallium nitride (GaN) and its alloy AlGaN are being increasingly pursued for power electronics as their low specific resistivity, high mobility, and ultrawide bandgaps provide a pathway to smaller devices, a “smarter” grid, and better utilization of renewable energy sources. Per their moniker, power devices must handle—and dissipate—tremendous energy loads. These loads, in turn, can lead to self-heating sufficient to dampen both performance and reliability. To minimize self-heating, it is necessary to assess how the thermal properties of GaN and AlGaN are modified from their “textbook” value during device processing. Here, using a combination of time domain thermal reflectance (TDTR) measurements with material modeling, significant size-induced reductions in thermal conductivity are found in both GaN and AlGaN for layer thicknesses typical of devices. These reductions emerge from the interaction with the EM wave is still poorly understood, but we have started to provide analytic explanation to the collected experimental results.

SESSION TP02.09: Thermal Conductivity of Semiconductors
Session Chairs: Sukwon Choi and Ali Shakouri
Wednesday Afternoon, November 28, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM *TP02.09.01
Size Dictated Thermal Conductivities of GaN and AlGaN Thomas Beechem1, Christopher B. Saltanstill1, Hamidreza Seyfi2, Asegun Henry2 and Andrew Allerman1; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

Gallium nitride (GaN) and its alloy AlGaN are being increasingly pursued for power electronics as their low specific resistivity, high mobility, and ultrawide bandgaps provide a pathway to smaller devices, a “smarter” grid, and better utilization of renewable energy sources. Per their moniker, power devices must handle—and dissipate—tremendous energy loads. These loads, in turn, can lead to self-heating sufficient to dampen both performance and reliability. To minimize self-heating, it is necessary to assess how the thermal properties of GaN and AlGaN are modified from their “textbook” value during device processing. Here, using a combination of time domain thermal reflectance (TDTR) measurements with material modeling, significant size-induced reductions in thermal conductivity are found in both GaN and AlGaN for layer thicknesses typical of devices. These reductions emerge from the interaction with the EM wave is still poorly understood, but we have started to provide analytic explanation to the collected experimental results.

SESSION TP02.08.13
Mechanics of Materials Interaction with Electromagnetic Wave Diana Gamzina, Emilio Nanni, Paul Welander and Sami Tantawi; Technology Innovation Directorate, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Advances in understanding RF breakdown have led to improvement in accelerator performance, but detailed knowledge of the temporal material changes due to its interaction with RF continues to be an unknown. It has been observed that an RF structure can be conditioned to handle significantly higher accelerating gradients by slowly ramping up RF power levels fed into the structure and that the RF breakdown rate can be reduced by utilizing copper with higher hardness numbers. While surface imaging post operation clearly show surface damage, the practical findings provide limited insight into material’s behavior under RF loading. We evaluate the mechanics of material during its interaction with an electromagnetic (EM) wave. This analysis impacts the development of advanced RF accelerators and sources; it also informs the development of materials resistant to EM radiation damage and of material synthesis techniques that utilize EM fields for achieving far-from-equilibrium material states.

During RF heating, a sub-micron thick material surface layer is heated instantaneously creating steep and non-linear thermal gradients, which eventually (on sub-ms scale) evolve into linear thermal gradients. The transient thermal gradients and the boundary conditions imposed on the material cause the state of stress to temporally evolve. Furthermore, even though cubic material like copper has an isotropic coefficient of thermal expansion, its elasticity is highly anisotropic. Polycrystalline copper that is used for the manufacturing of RF cavities undergoes multiple high temperature thermal cycles that fully anneal the material so that the resulting material grain size is on the order of a few millimeters. As a result, local material response to the EM heating then also depends on the orientation of the crystal structure with respect to the material surface. It has been observed that highly compliant (100) direction oriented grains show significantly less damage than stiff (111) direction oriented grains; similar results were reported for laser induced damage in copper. Significantly higher stress levels are induced in the (111) grain when compared to the (100) grain for the same thermal strain values because of the difference in the elastic moduli. Conditioning of the RF structures is analogous to a strain-hardening process, but with temporally varying strain rate conditions. Similar to other strain hardening methods, the dislocation density eventually saturates with increasing strain values and, as a result, the RF structure reaches its peak RF operation gradient. Starting with a harder material (high dislocation density) allows one to jump to higher gradient levels (strain values) without generating additional dislocations. The evolution of the material surface during the interaction with the EM wave is still poorly understood, but we have started to provide analytic explanation to the collected experimental results.
breakdown voltage. While much effort goes into the electrical characterization of these devices, complete thermal characterization is lacking. The diodes used in this study consisted of a 420 µm n-GaN substrate on which MOCVD was used to grow 15 µm n GaN (Si), 500 nm p-GaN (Mg), and 30 nm p'-GaN (Mg). The completed chips consist of diodes with diameters of 100 µm, 300 µm, 500 µm, and 1000 µm. One set of devices was subjected to passivation with a polyimide film, while the other set of devices was non-passivated. Electroluminescence (EL) was performed on both sets of devices, and it was found that non-passivated devices demonstrated increased EL intensity at the mesa edges, most likely due to enhanced surface recombination, and subsequently showed IV characteristics that outperformed the passivated devices in terms of power handling capabilities at high forward voltages. When a high-power operating point is set for a diode, there can be a significant increase in temperature, which leads to thermal expansion, and other reliability issues inherent in the cyclic operation of a power device. To investigate the thermal response, we used time domain thermoreflectance (TDTR) to evaluate the thermal conductivity of a vertical GaN p-n diode as a function of depth. Transient thermoreflectance imaging was used to observe variations in heating profiles across devices of different diameters when operated at the same power densities, and to observe the transient temperature rise and fall for each of the diodes.

2:15 PM TP02.09.03
Thermal Analysis of GaN HEMTs Using Near Bandgap Thermoreflectance Imaging
Georges Pavlidis1,2, Dustin Kendig2, Luke Yates3, Banafsheh Barabadi1, Brian Foley1 and Samuel Graham1; 1Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2CNST, National Institute of Standards and Technologies, Gaithersburg, Maryland, United States; 3Massachusetts Institute of Technology, Boston, Massachusetts, United States; *Microsanj LLC, Santa Clara, California, United States.

Transient thermoreflectance imaging (TTI) is a CCD based thermometry technique that can map the temperature distribution across a surface. For materials, such as gold, where the thermoreflectance signal has a strong linear temperature dependence, TTI has shown to have a high spatial (300 nm/pixel) and temporal resolution (50 ns). Consequently, the technique has been primarily used to monitor the gate metal temperature distribution in GaN High Electron Mobility Transistors (HEMTs) and enable characterization of the device's transient thermal dynamics. The origin of the extreme localized heating in GaN HEMTs, however, is known to be in the active GaN layer and thus accurate characterization of the temperature across the channel is necessary. Using a UV LED excitation source with a wavelength near the bandgap of GaN, TTI of the GaN channel in GaN HEMTs is presented and verified for the first time via the comparison of the gate metal temperature. A pixel by pixel calibration method is implemented to improve the spatial accuracy and account for any variability in the thermoreflectance coefficient across the device. Performing full transient scans, the time constants associated with the GaN region are found to be shorter than those measured via the gate metal. To ensure a strong thermoreflectance signal from the GaN surface, the importance of using an excitation wavelength near the bandgap of the GaN channel is highlighted. Through the analysis of HEMTs with different residual stresses in the GaN channel (engineered by using superlattice structures), the effect of the bandgap on the magnitude and the linearity of the thermoreflectance coefficient is presented and discussed. Overall, the improvements of TTI discussed in this study make the technique an accurate and effective method to measure the temperature distribution of both the gate metal and GaN.

2:30 PM BREAK

3:30 PM *TP02.09.04
Electro-Thermal Analysis of Ultra-Wide Bandgap Electronics
Sukwon Choi; The Pennsylvania State University, University Park, Pennsylvania, United States.

To extend further the electrical performance envelope of wide bandgap (WBG) power and radio frequency (RF) electronics based on gallium nitride (GaN) and silicon carbide (SiC), device engineers are actively pursuing the development of generation-after-next ultra-wide bandgap (UWBG) devices. At the time being, aluminum gallium nitride (AlGaN), β-gallium oxide (Ga2O3), and diamond are technologically relevant UWBG materials that have bandgaps larger than that for GaN (3.4 eV). While UWBG devices are built to operate under higher power densities compared to current state-of-the-art WBG counterparts, the thermal conductivities of AlGaN and Ga2O3 are lower than those for GaN and SiC by an order of magnitude. Therefore, self-heating is one major challenge for these UWBG devices. Electro-thermal interactions that lead to self-heating in AlGaN and Ga2O3 devices need to be accurately assessed and understood to accomplish the successful transition from WBG devices to the UWBG technology.

In this work, we will demonstrate the use of an integrated optical thermography scheme (Raman thermometry, thermoreflectance imaging, and infrared thermography) to study the steady-state and transient thermal characteristics of state-of-the-art AlGaN and Ga2O3 devices. These include AlGaN high electron mobility transistors (HEMT), Ga2O3 Schottky Barrier Diodes (SBD), and lateral Ga2O3 metal-oxide-semiconductor field-effect transistors (MOSFET). Results are validated through the use of coupled electro-thermal modeling. In addition, we will report our recent progress on the development of new optical temperature and stress metrology techniques suitable for UWBG electronics including “2-D transducer-assisted Raman thermography.”

4:00 PM TP02.09.05
Spectral Focusing of Thermal Conductivity in GaN—A First Principles Study
Jivtesh Garg; University of Oklahoma, Norman, Oklahoma, United States.

We find using first-principles analysis of thermal conductivity (k) in isotopically pure GaN that almost 60% of the heat is conducted by phonons in a very narrow frequency range of 5–7 THz (spanning only 9% of the frequencies in GaN). This spectral focusing of thermal conductivity is found to be due to a combination of two effects – large increase in lifetimes of phonons through suppression of anharmonic scattering in the 5–7 THz frequency range, coupled with a large phonon density of states at the same frequencies. Understanding of the effect is provided by solving the phonon Boltzmann transport equation in the single mode relaxation time approximation along with the use of harmonic and anharmonic force constants derived from density functional theory. The results can have important implications for engineering thermal performance of devices based on GaN.

4:15 PM TP02.09.06
Electron-Beam Probing of Vibrational Modes Across Semiconductor Interfaces with Nanometer Spatial Resolution
Zhe Cheng1, Juan Carlos Idrobo2 and Samuel Graham1; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

As the relentless miniaturization of microelectronics, thermal management becomes an integral challenge for sake of device reliability and safety. Due to the highly-scaled architecture of these electronic systems, heat dissipation can be significantly influenced or even dominated by interfaces. A fundamental understanding of vibrational modes near interfaces which contribute to interfacial heat transfer is still missing, especially at nanoscale spatial resolution. The development of a modern monochromated aberration-corrected scanning transmission electron microscopy (STEM) system makes it now possible to probe vibrational modes with a spatial resolution better than 1 nm and with an energy resolution better than 15 meV. In this work, a GaN+5 nm AlN+SiC...
interface sample was grown by molecular beam epitaxy and cut into a cross-section STEM sample (around 100 nm thick) using a Focused Ion Beam. Electron energy-loss spectroscopy (EELS) line profiles across the interfaces were collected. The spectra show vibrational peaks arising from SiC optical phonons (110 meV) across all data points. The detected SiC peaks in the AlN and GaN layers are long-range evanescent phonon fields (the beugrenzunf)gelfect). Acoustic phonons are also detected in the energy range between 30–40 meV, which originate from GaN, AlN and SiC. The most interesting feature of EELS results is the presence of an enhancement of the phonon intensity near the interface for both optical and acoustic phonon modes. For three positions near the two interfaces (GaN/AlN and AlN/SiC), the phonon intensities are larger than those measured in the GaN and SiC layers, which may be attributed to surface phonon resonance or interface modes. Here, we will discuss our experimental results and present a theoretical understanding of the observed features in light of improving thermal management at the nanoscale. [1]

[1] The electron microscopy part of this research was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy Office of Science User Facility (JCI). This research was conducted, in part, using instrumentation within ORNL’s Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

4:30 PM *TP02.09.07
Advances in Sub-Micron and Nanosecond Resolution Thermal Characterisation of Wide Bandgap Semiconductor Devices and Materials James W. Pomeroy, Martin Kuball and Babar Omer; University of Bristol, Bristol, United Kingdom.

GaN has transformed high-power, high-frequency RF amplifier and power switching technology, enabling more compact and efficient devices. Increasing the operating power density has enhanced device performance, although effective heat dissipation at the channel length scale becomes more critical. Concentrated Joule heating close to the gate generates large heat fluxes in GaN HEMTs: In extreme cases temperature gradients of 100°C/μm can be generated locally. Accurate temperature measurement in and around the transistor channel is essential to predict the meant time to failure (MTTF) and ensure reliability. Measuring the temperature distribution on this length scale also allows us to identify and improve any thermal resistance bottle-necks between the device channel and the heatsink. Conventional temperature measurement methods (e.g. IR thermography, Electrical) underestimate the channel temperature due to their limited spatial resolution, or in the case of pulsed operation, temporal resolution. The requirement for sub-micron spatial and nanosecond temporal resolution has driven the recent development of novel optical thermal characterisation techniques. We review a variety of techniques: Time resolved Raman thermography, including the application of solid immersion lenses for sub-micron resolution 3-D mapping; Raman nano-particle thermometry for surface temperature measurement on a variety of materials; UV transducer-less thermoreflectance. Hyperspectral Quantum-dot Thermal Imaging (HOTI) will be introduced – a very recently development. The application of these techniques to aid the development of next-generation devices and materials is discussed, including GaN-on-diamond and other wide bandgap semiconductors.

SESSION TP02.10: Thermal Properties of Reactive Materials
Session Chairs: Jeffery DeLisio and Karsten Woll
Thursday Morning, November 29, 2018
Sheraton, 3rd Floor, Fairfax AB

8:00 AM TP02.10.01
Sample Controlled Thermal Analysis for Studying Energetic Materials Pierre-Henry Esposito1, Renaud Denoyel1, Thomas Neisius2 and Marie-Vanessa Coulet1; 1MADIREL - UMR, CNRS and Aix Marseille University, Marseille, France; 2Féderation de Chimie, CNRS and Aix Marseille University, Marseille, France.

Among nanoenergetic materials, aluminum powders are at the center of numerous works since they remain an additive of choice in many energetic formulations [1]. In all those applications, it is the highly exothermic reaction of aluminum with an oxidant that confers to the powders their reactive and propulsive properties. The underlying idea of replacing micropowders by nanopowder is to take advantage of the enhanced reactivity that the nanoscale confers to the system. Whatever the scale under consideration, any aluminum particle is covered by a thin alumina layer whose thickness does not vary much with the size of the aluminum core [2]. At low heating rates, the oxidation is controlled by a diffusion mechanism in which this alumina layer plays an important role due to its various polymeric transitions [3,4]. The enhanced reactivity of aluminum nanopowders is thus linked to size reduction effects of the particles but also to structural changes of the alumina layer. Recently, morphology of the particles and grain nanostructureation of the aluminum core were also proposed as relevant parameters that could allow tuning the material properties [5].

In this contribution, we show that thermal analysis is a useful tool for understanding the oxidation mechanisms in aluminum powders. Powders with different morphology (sphere or flakes) and various sizes (from micro- to nano-scale) are compared. Firstly, it is shown that combined thermogravimetric (TG) and differential thermal analysis (DTA) performed up to 1500°C allows to establish reliable criteria of reactivity that can be extrapolated to realistic conditions. Secondly, the oxidation reaction is studied using kinetically controlled thermal analysis [6]. In this mode where the oxidation rate is constant, the kinetics equations are simplified which facilitates the modeling of the experimental data. This modeling, together with ex-situ oxidation studies [7], enables to predict the oxidation behavior as a function of structural parameters such as specific surface area and morphology.


The Direction Générale des Armées (DGA) is acknowledged for financial funding.

8:15 AM TP02.10.02
Characterization of Cure of Polymeric Materials by Dielectric Analysis (DEA) Yanxi Zhang; Netzsch Instruments North America, LLC, Burlington, Massachusetts, United States.
A variety of questions may arise during the curing process. For example, at which temperature, or after how much time, does the resin begin curing? How high is the reactivity? When is curing complete? How can the curing cycle be optimized? Is there any potential for post-curing? The answers to questions such as these can be investigated by using Dielectric Analysis (DEA), not only in the laboratory environment, but also in-process.

Dielectric Analysis (DEA) allows for the measurement of changes in the dielectric properties of a resin during curing. This technique can be used in studying the curing behavior of thermosetting resins, adhesives, paints, and coatings in nearly any application.

Various application examples about epoxy and other polymeric materials are included in the presentation, including heat cure and UV cure.

8:30 AM TP02.10.03
Time-Resolved Speciation and Calorimetry of Reactive Nanolaminates at High Heating Rates

Jeffery B. DeLisio1, Feng Yi2, David LaVan2 and Michael R. Zachariah3; 1Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States; 2National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Sputter deposited reactive nanolaminates are of great interest for “on chip” energetic applications, but standard analytical techniques lack the ability to characterize these materials on timescales representative of a combustion event. In addition, the simple geometry at the fuel/oxidizer interface of multilayered nanolaminates provides an ideal system to further study the oxygen transport in thermite based reactions, making it possible to probe factors such as the influence of interface-to-volume ratio and its effect on ignition and energy release. Previously, temperature jump (T-Jump) time-of-flight mass spectrometry (TOFMS) was employed to characterize ignition/decomposition temperatures and gas phase speciation of these systems at high heating rates, but this system lacks the ability to measure the energetics of a reaction. Recently developed chip-based nanocalorimeters are capable of making thermal measurements at sufficient frequencies to characterize the energetics of these reactions. In this work, a chip-based nanocalorimeter developed at NIST was integrated with a TOFMS system to enable simultaneous measurement of temporal thermal dynamics and detection of evolved gas species at heating rates up to ~10^6 K/s. This integrated system was first tested by analyzing the decomposition of electrospray deposited salts and metal oxide particles. Reactive nanolaminates were then directly sputtered onto the nanocalorimeter sensors and the effect of bilayer number and thickness was characterized. For an aluminum/copper oxide (Al/CuO) reactive nanolaminate system, one reaction step was observed for a sample with a bilayer thickness of 33 nm. However, a two-step reaction mechanism was observed as the bilayer thickness was increased to 66 nm and beyond: solid-state reaction occurring at the interfaces of Al and CuO before the melting of Al and a much faster liquid−solid reaction right after the melting of Al. In addition, analyzing the measured power from nanocalorimetry provides a more direct method, compared to optical emission and mass spectrometry based methods, for determining the ignition temperature while also being able to measure actual energy output from films with nanoscale thicknesses.

9:00 AM TP02.10.04
Tailoring the Microstructure of Metallic Thin Films Utilizing Heating Rate Effects on Phase Transformations in Reactive Al/Ru Nanolaminates

Karsten Woll1, Tobias Neuhauser1, Christoph Pauly2, Gemma Tinti3, Nicola Casati3 and Anna Bergamaschi3; 1Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; 2Materials Science & Engineering, Functional Materials, Saarland University, Saarbruecken, Germany; 3Paul Scherrer Institut, Villigen, Switzerland.

Reactive metallic nanolaminates or multilayers undergo exothermic runaway reactions when heated with rates larger than about 10^4 K/s. This behavior creates an interest of reactive nanolaminates for applications where local heat sources are required, e.g. in microscale-joining technology. The presented study considers another type of leveraging the reaction attributes. We address the question whether the exothermic phase transformations during ignition, that typically occur under high heating rates, can be utilized for microstructure tailoring of metallic thin films. From a fundamental point of view, the phase transformations occur at solid-solid or liquid-solid interfaces and are still an open field of research. As a model system, we chose Al/Ru nanolaminates and explore for subcritical heating how an increase in heating rate up to about 10^4 K/s affects the phase evolution and how this increase alters the properties of precipitating phases such as stoichiometry or morphology. In greater detail, we use conventional thermal analysis, namely differential scanning calorimetry, to reveal the phase transformations under slow heating and analyze the kinetics of the phase growth within a Johnson-Mehl-Avrami-type model. Complementary, in situ X-ray diffraction with synchrotron radiation enables us to determine the type of the growing phase and to corroborate the growth kinetics. In conjunction with the experiments, we apply classical nucleation theory combined with the diffusion kinetics to estimate the nucleation temperature observed during thermal analysis. The latter analysis protocol at low heating rates serves as reference for our high heating rate study. The advent of nanocalorimetry in the field of reactive materials enables us now to systematically analyze the transformational behavior under the rates of interest < 10^4 K/s. We perform experiments on Al-rich Al/Ru nanolaminates in the subcritical heating rate regime in combination with time-resolved X-ray diffraction using synchrotron radiation. In addition, we study the microstructure in the transmission electron microscope to correlate changes in the precipitating phase with the increase in heating rate. Eventually, we suggest pathways how the latter effects may help to tailor microstructures in thin films, e.g. to fabricate nanocomposites with optimized mechanical properties.

9:15 AM TP02.10.05
Frequency-Domain Thermal Conductivity Measurement for Reactive Solids and Melts at High Temperatures

Matthew Winger1, Andrew Z. Zhao1, Yasuhiko Kodera1, Hongwu Xu2, Stephen J. Obrey2 and Javier E. Garay1; 1University of California, San Diego, La Jolla, California, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

High temperature materials and melts are increasingly being investigated for next generation energy technologies such as batteries utilizing molten compounds, and high temperature heat transfer fluids (HTFs), and thermal energy storage (TES) materials. Such systems aim to take advantage of the chemical and transport properties of the melts or the higher intrinsic thermodynamic efficiencies that come with higher temperature. To utilize such compounds for melt-based systems and as HTFs in TES systems their thermal transport properties from the solid phase through the melt should be well characterized to understand how best to extract or retain heat and mitigate thermal design issues. Additionally, these materials can be highly corrosive or reactive at elevated operating temperatures and for specific material chemistries requiring that any thermal measurement technique can withstand harsh thermal and chemical sample environments in addition to being sensitive to the thermal properties under consideration. Here we describe a hot-wire geometry based thermal measurement system for accurate thermal conductivity measurements of solid compounds and melts. The chosen wire geometry is highly suitable for high temperature measurements of both solids and, particularly, liquids due to its relatively simple design and extensive working temperature range. Traditional hot-wire thermal measurement techniques pass a DC current through a thin resistive wire element suspended within a
Besides the influence of the choice of the halide, we will present the impact of a variation of the A-site cation (Cs vs. MA). An average thermal for the corresponding thin-film samples, which are treated by a planar hot pressing procedure to avoid topography artifacts (surface roughness <1 nm) [5].

crystals and thin films by means of dynamic Scanning Near-field Thermal Microscopy (SThM) [4]. The thermal conductivity of CH3NH3PbX3 single challenging, and only a few studies exist [2-4]. Recently, we reported on the thermal conductivity of methylammonium lead halide perovskite single importance for optimal performance and reliability [1]. As the thermal conductivity of perovskites is relatively low, it's experimental assessment is

Inkjet-Assisted Nanocalorimetry for Optimization of Trace Detection Feng Yi, Jeffrey Lawrence, Matthew Staymates, Greg Gillen and David LaVan; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Nanocalorimetry is capable of generating rapid and arbitrary heating profiles to gather thermal and thermodynamic measurements with high sensitivity. Here, we are studying the dynamics of the heating cycle to optimize trace detection. For the sample preparation, Inkjet printing is used to pattern samples on the active area of the nanocalorimeter and also allows for an estimate of the sample mass. Procedures have been developed to print exemplar trace materials onto nanocalorimeter sensors with precise control of position and sample mass. Nanocalorimetry results on several materials are shown to demonstrate the measurement capability.

Phase Evolution in Al/Ni Multilayer Thin Films Studied by Combined Nanocalorimetry and Sub-Millisecond X-Ray Diffraction Tobias Neuhäuser1, Gemma Tinti2, Harald Leiste1, Nicola Casati1, Anna Bergamaschi2, Michael Stüber1 and Karsten Woll1; 1IAM, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; 2OFLC/001, Paul Scherrer Institut, Villigen, Switzerland; 3WLGA/229, Paul Scherrer Institut, Villigen, Switzerland.

High strength typically compromise deformability in metallic materials. To overcome this conflict, we strive to develop thin film nanocomposites where hard intermetallic phases are embedded in a ductile metallic matrix. Our approach considers metallic nanolaminates or multilayers as starting materials. PVD sputter deposited Al/Ni multilayers serve as model materials. To generate hard phases at the nanoscale, we utilize phase separation where intermetallic phases precipitate predominantly at interfaces and/or grain boundaries upon annealing. Based on theoretical calculations, the chosen heating rate up to values of about 106 K/s have an impact on the phase formation. However, when heated with an overcritical rate to a specific ignition temperature, these materials exhibit uncontrolled runaway exothermal reactions. Up to now, the phase formations driving the ignition are not yet understood. The challenging task in terms of investigation is the highly dynamic character of the reaction, where transformations occur within microseconds. Traditional characterization tools operate at time scales that are too slow to reveal the individual transformations in detail. We developed an in situ technique where we combine chip-based nanocalorimetry and time-resolved X-ray diffraction with synchrotron radiation. Eventually, the achieved time resolutions of 50 μs enabling us to correlate the calorimetric information with the microstructure evolution during the reaction. In greater detail, we explore the role of interdiffusion, phase formation and melting for the runaway reaction initiation under high heating rates. Kinetic considerations are performed via nanocalorimetry with integrated pulse heating combined with ex situ X-ray diffraction. Effects of the high heating rates during ignition as well as the influence of the multilayer geometry on the early stages of phase formation are studied. Eventually, the elucidation of the transformations occurring at the threshold of ignition enables us to develop guidelines for microstructure development of nanocomposites.
conductivity $\lambda$ of 0.36 $\pm$ 0.08 W/(mK) is determined for cesium-lead-bromide perovskite thin films. These results fit very well with the data published for CsPbBr$_3$ single crystals [3]. We demonstrate that the observed standard deviations of $\lambda$ are attributed to high local variance of $\lambda$ within the measured area. In order to determine the low thermal conductivity in perovskite thin films with high spatial resolution using the 3w-technique, we employ a thermal conductivity mapping in the frequency domain, for the first time. This technique allows us to detect simultaneously the topography, the local thermal conductivity, and the thermal diffusivity. Hereby, we will demonstrate that thermal conductivity variations between 0.33 to 0.38 $\pm$ 0.01 W/(mK) can even be found within one single crystal grain. The differences in thermal conductivity, even between the individual grains, are explained by different dimensionalities of Ca-based perovskites (3D: CaPbBr$_3$, 2D: CaPb$_2$Br$_5$), which are evidenced by X-ray diffraction to be present. The local differences in the product of the density and specific heat capacity are examined and will be discussed. The setup and properties of this system will be presented from the engineering point of view taking different mixing techniques into account. The advantage of our advanced measurement technique will be discussed with respect to phase separation analyses.


11:00 AM TP02.11.03

Zirconium pentatelluride (ZrTe$_5$) has recently attracted renewed interest owing to its high anisotropy in its thermal properties, which may find applications in nanoscale electronic devices. In this work, we have measured the thermal conductivity and thermal diffusivity of ZrTe$_5$ single crystals using a 3w-technique. The results show that the thermal conductivity is strongly influenced by the crystal orientation, with a value of $\lambda = 0.31 \pm 0.01 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature for the [110] direction and $\lambda = 0.42 \pm 0.02 \text{ W m}^{-1}\text{K}^{-1}$ for the [001] direction. The anisotropy factor, $\eta = \lambda_{[110]} / \lambda_{[001]}$, is found to be 1.34, indicating a significant anisotropy in the thermal transport properties of ZrTe$_5$. These results are in agreement with previous studies on ZrTe$_5$ single crystals and suggest that ZrTe$_5$ is a promising material for applications requiring low thermal conductivity.

11:15 AM TP02.11.04
Impact of Ultrafine Nanostructuring on the Phonon Wave Transport of Si Phononic Crystals Kouhei Takahashi$^1$, Takashi Kawasaki$^2$, Naoki Tambo$^3$, Masaki Fujikane$^1$, Kunihiko Nakamura$^1$, Tatsuya Naito$^1$, Yuxuan Liao$^2$, Makoto Kashigawa$^2$ and Junichiro Shiomi$^1$; 1. Panasonic Corporation, Osaka, Japan; 2. Panasonic Corporation, Tokyo, Japan; 3. University of Tokyo, Tokyo, Japan.

Phonon engineering has attracted much attention for developing new thermal transport properties in solids. In phonon engineering, nanostructuring plays an essential role. The effect of nanostructuring on the thermal transport is mainly twofold: (i) enhance the phonon boundary scattering and (ii) change the dispersion relation of phonons. The former mechanism is traditional, while the latter mechanism is still under debate. In this work, we have investigated the impact of ultrafine phononic crystals on the thermal transport properties of silicon. We have fabricated silicon nanowires with different pitches using electron-beam lithography and subsequent dry etching. We have measured the thermal conductivity of these nanostructures using time-domain thermoreflectance (TDTR) and found that the thermal conductivity decreases significantly with decreasing the pitch size of the nanostructures. We have modeled the thermal transport using the effective-medium theory and found that the reduction in thermal conductivity is due to the increased boundary scattering at the interfaces of the nanostructures.
electrical conductivity. The RT through-plane lattice thermal conductivity analyzed by time-domain thermoreflectance (TDTR), however, is surprisingly found to be defect-insensitive, indicating phonon-phonon interaction dominates the thermal scattering. Furthermore, a strong correlation is observed between the lattice thermal conductivity and the out-of-plane lattice dimension such that the elongation of the out-of-plane lattice parameter can suppress the thermal conductivity from ~7.8 W/mK to ~1.2 W/mK. By engineering the lattice and defects, we successfully realized the selective and independent manipulation of the thermal conductivity (by ~7-fold) and the electrical conductivity (by ~5 orders of magnitude) in single-phase epitaxial WO3 thin films. It not only enriches the functionalities of WO3, but also sheds light on designing new thermoelectric and thermal interface materials.

11:45 AM TP02.11.06
Comprehensive T-Type Method for the Thermal and Thermoelectric Properties Measurement of Micro/Nano Wires and Ribbons Shaoyi Shi, Weigang Ma and Xing Zhang; Tsinghua University, Beijing, China.

Micro/nano wires and ribbons have large technological applications and new fundamental physical phenomena. Especially in nanoscale, the properties of nanowires and nano-ribbons may be significantly different from bulk, and the measurement method for bulk materials even cannot be applied. Development of the precise measurement method for micro/nano wires and ribbons is becoming the frontier research and has been attracting intense interest. We have developed an integrated T-type method for comprehensively measuring the thermal and thermoelectric properties of micro/nano wires and ribbons. In the T-type method, the dc heating-dc detecting, four probe, and ac heating-dc detecting modes are applied to measure the thermal conductivity, electrical conductivity and Seebeck coefficient, respectively. The thermal and thermoelectric properties can be comprehensively determined on the same sample in the same measurement configuration. By applying the T-type method, some typical micro/nano wires and ribbons, including graphene fiber and single bismuth sulfide nanowire, have been studied.

1:30 PM *TP02.12.01
Advances in Ultrafast and Nanoscale Thermoreflectance Thermal Imaging Ali Shakouri1, Kerry Maize1, Sami Alajlouni1, Amir K. Ziabari1 and Dustin Kendig2; 1Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States; 2Microsanj LLC, Santa Clara, California, United States.

Static and dynamic hot spots and temperature non-uniformities limit the performance and reliability of electronic devices and integrated circuits. Here we review recent advances in transient thermoreflectance imaging to characterize temperature distribution in active devices. Imaging de-blurring techniques have been used to increase spatial resolution down to 100nm and temporal resolution is down to sub-nanosecond levels for full-field imaging and 100fs for single point measurements. While the lock-in or boxcar averaging techniques measure the change in surface or interface reflection coefficient very accurately, calibrating the thermoreflectance coefficient is essential to obtain absolute temperature profiles. A key challenge in thermal imaging of power devices is the separation of temperature induced change in reflected light due to thermal expansion. Both effects scale with the power dissipation in the device. Auto-focus and digital alignment can alleviate many of the edge effects in the thermal image, and multi-spectral thermoreflectance imaging can provide one of the most robust calibration methods to accurately obtain absolute temperature rise in power devices. Calibration of the thermoreflectance coefficient in micron-sized regions is further complicated due to sample movements when the stage temperature is changed. Here, we show that the transient temperature distribution can be used to calibrate thermoreflectance coefficient of unknown surfaces. Finally, semi-transparent coatings can create optical interferences in the reflected light which leads to a non-linear thermoreflectance coefficient. Methods to accurately extract the temperature in the presence of a non-linearity are presented. Several examples, including power GaAs, SiC, and GaN devices as well as through-the-substrate thermoreflectance imaging in silicon flip-chip bonded chips are presented. Finally, we briefly discuss the issue of defining temperature and what is actually measured in submicron regions. For Si, GaN, and many other semiconductors, Fourier law fails when the diameter of the heat source or the thermal penetration depth is less than a micron at room temperature.

2:00 PM TP02.12.02
Direct Imaging of Suppressed Thermal Transport near Individual Grain Boundaries in Polycrystalline Diamond Aditya Sood1, Ramez Cheaito1, Tingyu Bai2, Heungdong Kwon1, Yekan Wang2, Chao Li2, Luke Yates3, Thomas Bougher3, Samuel Graham3, Luke Yates3, Thomas Bougher3, Samuel Graham3, Mehdi Ashleghi2, Mark S. Goorsky2 and Kenneth E. Goodson1; 1Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States; 2Microsanj LLC, Santa Clara, California, United States; 3Georgia Institute of Technology, Atlanta, Georgia, United States.

Understanding the impact of lattice imperfections on nanoscale thermal transport is crucial for diverse applications ranging from thermal management to energy conversion. Grain boundaries (GBs) are ubiquitous defects in polycrystalline materials, which scatter phonons and reduce thermal conductivity (κ). Historically, their impact on heat conduction has been studied indirectly through spatially-averaged measurements, that provide little information about phonon transport near a single GB. Here, using spatially-resolved time-domain thermoreflectance (TDTR) measurements in combination with electron backscatter diffraction (EBSD), we make the first localized measurements of κ within few μm of individual GBs in boron-doped polycrystalline diamond. We observe strongly suppressed thermal transport near GBs, a reduction in κ from ~1000 Wm⁻¹K⁻¹ at the center of large grains to ~400 Wm⁻¹K⁻¹ in the immediate vicinity of GBs. Furthermore, we show that this reduction in κ is measured up to ~10 μm away from a GB [1]. A theoretical model is proposed that captures the local reduction in phonon mean-free-paths due to strongly enhanced phonon scattering near the disorder-rich grain boundaries. Our results provide a new framework for understanding phonon-defect interactions in nanomaterials, with implications for the use of high κ polycrystalline materials as heat sinks in electronics thermal management.


2:15 PM TP02.12.03
Rethinking Phonons in Disordered Solids—Crystals with Defects/Impurities and Random Alloys Hamidreza Seyf and Asegun Henry; Georgia Institute of Technology, Atlanta, Georgia, United States.

Current understanding of phonons treats them as plane waves/quasi-particles of atomic vibration that propagate and scatter. The problem is that conceptually when any level of disorder is introduced, whether compositional or structural, the character of vibrational modes in solids changes, yet nearly
all theoretical treatments continue to assume phonons are still waves. For example, the phonon contributions to alloy thermal conductivity (TC) rely on this assumption and are most often computed from the virtual crystal approximation (VCA). Good agreement is obtained in some cases, but there are many instances where it fails—both quantitatively and qualitatively. Here, we show that the conventional theory and understanding of phonons requires revision because the critical assumption that all phonons-normal modes resemble plane waves with well-defined velocities is no longer valid when disorder is introduced. Here we show, surprisingly, that the character of phonons changes dramatically within the first few percent of impurity concentration, beyond which phonons more closely resemble the modes found in amorphous materials. We then utilize a different theory that can treat modes with any character and experimentally confirm its new insights.

2:30 PM TP02.12.04
Effect of Quenched-in Vacancies on Precipitation in Aluminium Alloys Measured by Differential Fast Scanning Calorimetry Bin Yan1,2, Benjamin Milkeret1,2, Olaf Kessler4,5 and Christoph Schick1,2,3,4,5; 1Institute of Physics, University of Rostock, Rostock, Germany; 2Competence Centre CALOR, University of Rostock, Rostock, Germany; 3Kazan Federal University, Kazan, Russian Federation; 4Faculty of Mechanical Engineering and Marine Technology, University of Rostock, Rostock, Germany.

Quenched-in vacancies are point defects that can be present in materials after quench from high temperature. Quenched-in vacancies increase the rate of solute diffusion and therefore the kinetics of phase transformations. In this study different concentrations of vacancies were froze-in by quenching from solution annealing temperature at different cooling rates up to 3×10^6 K/s by differential fast scanning calorimetry (DFSC). Then artificial aging at different temperatures and time followed by a differential reheating method (DRM) enables both time and temperature-dependent investigations of vacancy-induced precipitation in aluminium alloys. The method can potentially be transferred to similar systems or related solid-state phase transformation systems also beyond the particular system analysed in the present study.

2:45 PM TP02.12.05
Effect of Vacancies and Domain Walls on the Thermal Conductivity of PbTiO3 Thin Films David Bugallo-Ferrón1, Elias Ferreiro-Vila1, Eric Langenberg2,3, Gustau Catalán1, Neus Domingo1, Darrell G. Schronym2 and Francisco Rivadulla1; 1CiQUS-University of Santiago de Compostela, Santiago de Compostela, Spain; 2Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 3Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, Barcelona Institute of Science and Technology, Barcelona, Spain.

We report the effect of ferroelastic domain walls on the thermal conductivity of thin films of PbTiO3. We fabricated a series of films by Molecular Beam Epitaxy on SrTiO3 (001) substrates over a wide range of Pb/Ti ratio. X-ray diffraction and Piezoelectric Force Microscopy were used to correlate the thermal conductivity results with the distribution of ferroelastic domains as a function of Pb/Ti. Our results show that stoichiometric strained PbTiO3 films show an anomalously reduced thermal conductivity, comparable to that of highly defective samples. These results suggest that ferroelastic domain walls have a large effect on the thermal conductivity of this material, opening the possibility for reversible modulation of thermal conductivity by an external stimulus in ferroelastic oxides.

3:00 PM BREAK

3:30 PM TP02.12.06
Determining the Mechanical and Thermodynamic Properties of Iron Meteorites Below 300 K Matthew Bonidie1, Christopher Noyes1, Roy Forrestano1, Daniel Britt1, Robert Macke1, Guy Consolmagno3 and Cyril Opeil1; 1Boston College, Chestnut Hill, Massachusetts, United States; 2Physics, University of Central Florida, Orlando, Florida, United States; 3Spectola Vaticana, Vatican City, Italy.

Iron meteorites are primarily kamacite or taenite based Fe-Ni polycrystalline alloys that solidify from planetary cores over a timespan of 1×10^7 years via thermal radiation into the vacuum of space. Depending on their Ni composition and cooling rates, iron meteorites crystallize into either fine octahedrite, coarse octahedrite, or haxahedrite crystal structures.

Through the use of resonant ultrasound spectroscopy, the elastic constants and Young’s modulus were measured as a function of temperature from 10-300 K, allowing a comparison of how Ni percentage, crystallographic structure, and impact history effect the mechanical behavior of these meteorites. In addition, specific heat capacity, thermal conductivity, and thermal inertia of the iron meteorites will also be discussed.

This work is supported by NASA, SSERVI (Solar System Exploration Research Virtual Institute) and CLASS (Center for Lunar and Asteroid Surface Science) under grant No. NNA14AB05A.

3:45 PM TP02.12.07
Thermal and Phonon Spectral Transport Analysis for New High Thermal Conductivity Materials Joon Sang Kang, Man Li, Huuduy Nguyen, Huan Wu and Yoonjie Hu; University of California, Los Angeles, Los Angeles, California, United States.

Understanding the origins of high thermal conductivity is of great importance to thermal science and applications of thermal management and energy conversion, but remains a significant challenge in the field. Recent theoretical work including first-principles has predicted new class of thermal materials with high thermal conductivity beyond state-of-the-art materials and approaching that of diamond (>1000 W/mK). However, experimental demonstration and understanding have been limited by materials synthesis, measurement accuracy, and theoretical tools. Here, we describe our current progress in developing high conducting thermal materials using advanced chemical synthesis approach to achieve high quality single crystalline crystals and analyzing the spectral phonon mode contributions using density functional theory and Boltzmann transport equations[1]. The heat conduction and phonon transport with size dependence are carried out by thermal mapping spectroscopy technique[2]. We investigate the effects to thermal conductivity from defects, interfaces, and grains. Our work aims for systematic investigation and material improvement for ultrahigh thermal conductivity and brings the promise of rational material design to achieve its theoretical limit. The significant impacts of this research in improving the efficiency of thermal energy conversion and management will also be illustrated.

References:

4:00 PM OPEN DISCUSSION

4:15 PM TP02.12.09
**Thermal Conductivity Evaluation of Polymer Crystals—An Ab Initio Study**

Keishu Utimula1, Tom Ichihba2, Ryo Maezono2 and Kenta Hongo3, 4, 5; 1School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; 2School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; 3Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; 4PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Japan; 5Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan.

Lattice thermal conductivity (LTC) has been calculated mainly using linear lattice models or molecular dynamics simulations, but their theoretical reliability strongly depends on empirical parameters and choice of force field. With the advent of massively parallel computers, a more systematic and reliable approach to the evaluation of LTC has emerged, i.e., *ab initio* anharmonic lattice dynamics calculations, where the linearized phonon Boltzmann equation is used to approximate a LTC formula, Peierls- Boltzmann equation, at the cubic anharmonic level. This approach has successfully reproduced LTC for several inorganic semiconductors in a wide range of LTC from ~1 to ~10² W/mK. However, few works have ever applied this approach to polymer systems, although the LTC of polymers is one of the most important quantities for industrial purpose. It is well known that higher crystallinity in polymers increases LTC, indicating that polymer crystals are expected to have the highest LTC. Experimentally, however, perfect crystallizations are not realized for most polymers. Hence their upper limits of LTC are still unknown, though such values would provide useful guidelines for high-LTC polymer design. On the other hand, it is easy to model the polymer crystal structures and apply the simulations to calculate the LTC values, which are regarded as the theoretical upper limit of those of the polymers.

We have applied *ab initio* anharmonic lattice dynamics simulations to both chain and crystal polyethylene in order to evaluate their LTC values. It is established that their temperature dependences of LTC agree well with previous experiments. In addition, we found that polyethylene has comparatively long phonon lifetime, which mainly gives good LTC to the polymer. In this talk, we will report on not only these results but also several typical polymers such as polyethylene terephthalate and phenylene sulfide.

**An Inverse Problem Framework for Extracting Phonon Properties from Thermal Spectroscopy Measurements Including Systems Featuring Interfaces with Unknown Properties**

Mojtaba Forghani and Nicolas G. Hadjiconstantinou; Massachusetts Institute of Technology, CAMBRIDGE, Massachusetts, United States.

Thermal spectroscopy has been established as a promising experimental method for characterizing the transport behavior of materials and as a useful alternative to density functional theory (DFT) calculations which are expensive and not always in agreement with real experimental measurements. While there have been significant advances enhancing the reliability and accuracy of this experimental technique, the inverse problem of extracting material properties from the experimental observations remains an open problem. In particular, it was recently shown [Forghani et al., Phys. Rev. B 94, 155439 (2016)] that techniques based on assuming validity of Fourier's law are invalid, unless a set of rather restrictive conditions are met.

We have recently proposed an inverse problem framework [Forghani and Hadjiconstantinou, Phys. Rev. B 97, 195440, (2018), Forghani et al., Phys. Rev. B 94, 155439 (2016)] that can be employed to extract mode dependent material properties, such as relaxation times or interface transmissivities, from thermal spectroscopy measurements. The proposed technique solves the inverse problem by iterating between solutions of the forward (relaxation) problem and thus requires solutions that capture the mode-dependent physics; these solutions can be either analytical or numerical, including stochastic.

In this presentation we focus on applications of this technique to the extraction of phonon properties using *ab initio* anharmonic lattice dynamics calculations, where the linearized phonon Boltzmann equation is used to approximate a LTC formula, Peierls- Boltzmann equation, at the cubic anharmonic level. Specifically, we show that our method is able to reconstruct phonon free path distributions from experimental measurements obtained from a transient thermal grating setup. We also show that the proposed method can be used to extract phonon free-path distributions from systems featuring interfaces with unknown properties. We also discuss the extension of the method for reconstruction of the interface properties.

We expect that due to the generality of the proposed method, extension to other quantum mechanical particles, other material properties, and other numerically/analytically available algorithms for solving the forward problem, will be feasible.

**Thermal Characterization of Sodium-Sulfides at High Temperature**

Andrew Z. Zhao1, Matthew C. Wingert1, Yasuhiro Kodera1, Hongwu Xu2, Andrew Z. Zhao1, Matthew C. Wingert1, Yasuhiro Kodera1, Hongwu Xu2, Stephen J. Obrey3 and Javier E. Garay1; 1University of California, San Diego, San Diego, California, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Metal sulfides have a unique range of electronic and mechanical properties that has resulted in their exploration for next generation batteries, catalysts, semiconductors, and thermoelectrics. Many functional metal-sulfides must operate at high temperatures, but their thermal properties under extreme conditions have not been extensively studied and are not well understood. Measuring the thermal properties of highly reactive materials, such as metal-sulfides, has been challenging due to the corrosion and breakdown of sensor and containment materials at high temperatures. To advance the development of functional metal-sulfides, we seek to understand their structure and thermal properties at high temperatures. Here, we present a frequency-domain hotwire technique to measure the thermal conductivity of various sodium-sulfides at high temperatures. Unlike traditional hotwire measurement techniques, which apply a heat flux to a large sample volume to probe the temperature of the sample versus time, our custom system and sensor reduce the necessary sample volume to below 5 mL and probe the sample’s thermal response in the frequency domain. Our system and sensor have been designed to survive corrosive chemical environments at temperatures up to 750 degrees Celsius. The thermal conductivity of sodium-sulfides at high temperatures have been measured for the first time and are presented here. The structure of the sodium-sulfides is examined using x-ray/neutron diffraction and electron microscopy; this approach helps provide structural insights into the experimental and theoretical thermal transport properties of sodium-sulfides.
Lattice Dynamics Across the Temperature- or Pressure-Induced Structural Phase Transition in SnSe and SnS

Tyson Lanigan-Atkins1, Shan Yang1, Jennifer Niedziele2, Dipanshu Bansal1, Hao Hong2, Songxue Chi2, Andrew May2, Daniel Pajerowski2, Georg Ehlers1 and Olivier Delaire3; 1Duke University, Durham, North Carolina, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

SnSe and SnS are two promising thermoelectric materials, which have demonstrated outstanding figure-of-merits, but whose transport properties exhibit strong anisotropies tied to their layered crystal structure. At high temperature or high pressure, they undergo a continuous structural phase transition between a low-symmetry Pnma phase and a higher-symmetry Cmcm phase (SnSe: Tc ~ 805K and Pc ~10GPa, SnS: Tc ~880K). In order to rationalize the strong anharmonicity and anisotropy in thermal conductivity, we have used time-of-flight (TOF) and triple-axis inelastic neutron scattering (INS) to map the phonon dispersions and density of states (DOS) of both compounds at high temperature across the phase transition. Our results show a striking, extended softening and broadening of phonon excitations with temperature and the soft mode character of this transition is clearly revealed. We extracted the phonon scattering rates by deconvoluting instrumental resolution effects, for both time-of-flight and triple-axis measurements. Scattering rates calculated from the two methods agree remarkably well. We performed systematic first-principles simulations of the temperature-dependent phonon dynamical structure factor, S(Q,E), and scattering rates, which we compare with our experimental results. Furthermore, we have used TOF neutron diffraction, inelastic X-ray scattering and Raman spectroscopy to track the transition as a function of pressure finding good agreement with the previously reported transition pressure of ~10GPa. The projected DOS is tracked with pressure in order to follow the anisotropy of the lattice dynamics with pressure. We contrast some of the behaviors observed in our measurements and simulations with roskalt chalcogenides (SnTe, PbTe, PbSe).

Funding from US-DOE/BES/MSED, Office of Science Early-Career-Award, and as part of the S3TEC-EFRC.

8:45 AM TP02.13.02
Thermal Stability Enhancement of Alpha Tin Films by Strain Engineering Jinshin Yao1,2, Huanhuan Song1,2, Shunji Xia1,2, Yu Gu1,2, Yuanfeng Ding1,2 and Hong Lu1,2; 1College of engineering and Applied Sciences, Nanjing University, Nanjing, China; 2National Laboratory of Solid State Microstructures, Nanjing University, Nanjing, China.

Alpha tin (α-Sn, also known as gray tin), a metastable phase of tin, is a zero band gap semimetal with a diamond structure. Since Fu and Kane [1] predicted that alpha tin could be a topological insulator under certain strain, a lot of work have been done to study the topological properties of this material [2-4]. However, the growth of high quality alpha tin film remains challenging due to its low phase transition temperature and lack of appropriate substrates. We have successfully grown a series of alpha tin films on InSb (001) substrates by molecular beam epitaxy (MBE). The film thickness varies from 10 nm up to 400 nm. Atomic force microscope (AFM) shows a smooth surface morphology with roughness under a few nanometers. Transmission electron microscope (TEM) confirms the diamond structure of the alpha films.

It is known that bulk alpha tin is only stable up to 13.2 °C. Our interest is to utilize strain to enhance the thermal stability of alpha tin films, and the strain is tuned by varying the film thickness during the epitaxial growth process. The InSb substrate provides a compressive strain (0.14%). We have used temperature dependent XRD (T-XRD) and temperature dependent Raman for this study. The temperature range covers from -100°C to 250°C. The XRD results show the high crystalline quality of the alpha tin films. Clear thickness fringes are observed for all the samples, and reciprocal space mapping (RSM) shows that the alpha tin films can be strained up to 400 nm. Temperature dependent results show that the phase transition temperatures of our films can be increased to 120°C, and the transition temperature increases as the film thickness decreases. This enhancement is confirmed by both temperature-dependent XRD and Raman results. The linear thermal expansion coefficient of alpha tin film is extrapolated for the first time to be 7.14x10^-6/°C.

Our study shows that strain is an effective way to engineer the thermal stability of the alpha tin films. The thermal stability enhancement ensures the reliability of all the following electrical and thermal characterizations above room temperature. We have observed magnetoresistance and superconductivity in these films.

9:00 AM TP02.13.03
Anisotropic and Quasi-Ballistic Thermal Transport in Nanostructure Embedded GaSb Thin-Film Semiconductors Yee Rui Koh1,2, Hong Lu3, Arthur Gossard4 and Ali Shakouri1; 1Purdue University, West Lafayette, Indiana, United States; 2Birck Nanotechnology Center, West Lafayette, Indiana, United States; 3Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, United States; 4University of California, Santa Barbara, Santa Barbara, California, United States; 5Nanjing University, Nanjing, China.

Gallium antimonite (GaSb) is a promising candidate for the high speed electronic and long wavelength photonic devices, e.g. infrared detectors, photovoltaic, diode lasers, etc. Previous measurements and theoretical studies focused on the bulk thermal conductivity of the GaSb. [3][2] For submicron devices, or at high frequencies, it is important to study thermal transport in the GaSb thin films. Time-domain thermoreflectance (TDTTR) is used to study thermal transport in 2μm thick GaSb film with embedded semimetallic ErSb nanoparticles. [3] We show that GaSb is among few non-alloy semiconductors showing the phonon quasi-ballistic effects. The apparent cross-plane thermal conductivity of pure GaSb thin film sample drops by ~15% when the pump modulation frequency is increased from 0.8 MHz to 10 MHz at room temperature. The frequency dependence of the cross-plane thermal conductivity disappears with the presence of 3%-20% ErSb nanoparticles. We also employed the beam reduction TDTTR method [4] to study the anisotropic thermal transport in GaSb thin films. The ratio of cross- to in-plane thermal conductivity of the ErSb: GaSb samples vary from ~0.2 for pure GaSb to ~0.7 for GaSb with 20% ErSb nanoparticles volume concentration. Potential causes of the anisotropy from lattice mismatch with the substrate to self-organization of embedded nanoparticles in nanowire forms are discussed. Detailed temperature dependence measurements for both in-plane and cross-plane thermal conductivity of the ErSb:GaSb samples are also presented.


9:15 AM TP02.13.04
Thermal-Optical Readout of Multi-Level Thermal Emissivity Ge2Sb2Te5 Patterns Miao Wang, Sichao Hou and Ming Su; Northeastern University, Boston, Massachusetts, United States.

Ge2Sb2Te5 thin film (100 nm) can be patterned with multi-level crystalline and thermal emissivity states using laser in large scale. Various patterns can be fabricated by tuning laser power and speed. X-ray diffraction (XRD) and infrared analysis results show that Ge2Sb2Te5 thin film has different thermal emissivity at different crystalline states. In-situ repeated heating of the Ge2Sb2Te5 thin film confirms the tendency between crystalline and thermal emissivity change. Both the infrared image and thermal emissivity can be readout by infrared camera. The colorful infrared image enables easily identification of Ge2Sb2Te5 crystallite change. The multi-level emissivity states of patterns produce multi-level optical data storage for future phase-change devices.

9:30 AM TP02.13.05

Phase change memory (PCM) stores information in the phase (conductive crystalline or resistive amorphous) of glass forming materials, typically a chalcogenide. One of the largest hurdles for PCM is the tradeoff between data retention and switching speed. Wang et al. [1] demonstrated increased switching speed without decreased retention by reducing grain size in phase change materials. We propose grain boundary melting (GBM) as the mechanism behind this improvement. With nanocrystalline phase change materials, reset may be achieved with only partial amorphization of the active volume, leaving isolated crystalline nuclei. This decreases the volume of amorphization required for reset while providing multiple sites for simultaneous crystallization for set, reducing power and time requirements for both reset and set operations. Additionally, classical nucleation theory (CNT) predicts that the minimum stable grain size \( r_c \) increases with temperature, effectively lowering the melting temperature for smaller grains.

We model GBM based on thermodynamic properties of Ge\(_2\)Sb\(_2\)Te\(_5\) (GST). We obtain phase and temperature dependent specific heats \( C_p \) as explained in our previous work [2] with an additional constraint of the specific heat difference for the liquid and crystalline phases \( \Delta C_p \) at the glass transition extracted from the fragility [3] based on ultra-fast DSC measurements of GST [4]. We determine the temperature dependent \( r_c \) with CNT using free energy and entropy differences between phases \( \Delta G \) and \( \Delta S \) calculated from \( \Delta C_p \). Finally, we obtain temperature and size dependent GBM rates based on \( \Delta G \) and the kinetic growth velocity \( U_{\text{gb}} \) extracted from ultra-fast DSC measurements [4]. We incorporate GBM in our finite element phase change model [5]–[8] and simulate reset and set for reported device and grain sizes [1]. We show that GBM reduces set and reset times as grain sizes decrease and contributes to increased PCM variability due to device-to-device and cycle-to-cycle gain map changes.

High frequency RF, laser diodes and some silicon ASIC devices are a particular class of devices where power densities are pushing limits of kw/cm². Many of these devices are now reaching the limit of current heat spreading technologies. Consequently, there is a continual need to improve thermal performance while reducing the cost.

To date, the integration of SiC (400 W/mK) substrates with GaN has provided the best option for GaN HEMT and MMIC technology for high power applications. However, despite the use of SiC substrate, adequate heat spreading is still the limiting factor in determining the maximum power dissipation for GaN based electronics. As such, the path to long-term reliability is often achieved by de-rating the maximum power dissipation. A far better heat spreading solution incorporating CVD diamond (2000 W/mK) has the potential for a factor of 3× or higher increase in power density relative to current state-of-the-art GaN devices.

In this presentation we demonstrate success in integrating a thinner layer of very high thermal conductivity CVD diamond with lower thermal conductivity CVD diamond consistent with targeted thermal performance at lower cost. In the built of this hybrid material, the high thermal conductivity material will be the bonding interface to the RF/microwave device to enable immediate heat spreading. The lower thermal conductivity material will be the bonding interface to the heat sinking side, enabling cost effective heat transport. The integration of the layers is achieved through back to back deposition of the bi-layers. The challenge is to make the synthesis conditions conducive to achieving material quality and matching of the bi-layers mechanical properties to fabricate a robust final product.

The presentation will report on the analysis and results obtained by using Lee, S et al, to establish the limit of spreading layer thickness (layer 1). The model indicated that for a 100 mm x 100 mm hot spot, minimum thermal spreading resistance is achievable with minimum thickness of about 150-200 mm. The confirmation of a minimum spreading that would lead to minimum spreading resistance was verified for Biot numbers varying from <1 to >100.

Required layer 2 thickness (low thermal conductivity material) to maintain lowest thermal resistance and maintaining mechanical integrity and thickness specifications was established by classical heat transfer solutions. Additionally, an Abaqus model for typical multi-finger RF device with and without a diamond heat spreader was developed to compare the effect of graded concept where the thickness of high/low thermal conductivity is part of the sensitivity analysis and part of this presentation.

Three different techniques were used to judge the quality and success of the output material. These are through plane characterization using optical and thermal methods and in-plane measurement using heated bar and the results of those findings are a part of this presentation.

**SYMPOSIUM TP03**

Emerging Low-Temperature Thermal Energy Conversion Technologies  
November 26 - November 29, 2018

Symposium Organizers  
Michael Chabinyc, University of California, Santa Barbara  
Terry Hendricks, California Institute of Technology  
Kedar Hippalgaonkar, Institute of Materials Research and Engineering  
Shannon Yee, Georgia Institute of Technology

Symposium Support  
Linseis Inc.

* Invited Paper

SESSION TP03.01: Organic and Polymer Thermoelectrics I  
Session Chairs: Christian Muller and Shannon Yee  
Monday Morning, November 26, 2018  
Sheraton, 3rd Floor, Gardner AB

8:00 AM *TP03.01.01  
PEDOT-Based Thermoelectric Materials and Devices Qingshuo Wei; National Advanced Institute of Science and Technology, Tsukuba, Japan.

In this talk, we are going to focus on two topics. The first one is understanding of the doping mechanism of poly(3,4-ethylenedioxythiophene). We have shown that PEDOT was doped by protons. The doping and de-doping processes using protonic acid and base are fully reversible. We are going to demonstrate that the use of protonated EDOT moieties as an end group to prepare organic conductors is a promising approach toward highly conductive organic materials. In the second part, we are going to present proof-of-concept studies of organic thermoelectric devices fabricated by thermal lamination. With an air-cooled heat sink, the device exhibited a power output of ca. 100 microwatt, which is sufficient to power practical devices.

8:30 AM TP03.01.02  
Thermoelectric Polymer Films with High Power Factor Arising from the Significant Seebeck Coefficient Enhancement by Surface Energy Filtering Guan Xin, Zeng Fan and Jianyong Ouyang; Materials Science and Engineering, National University of Singapore, Singapore, Singapore.
Thermoelectric (TE) materials are important for sustainable development because they can be used to directly convert heat into electricity. Compared with inorganic TE materials, polymers have advantages of lower cost, high abundance, high mechanical flexibility and low or no toxicity. However, the Seebeck coefficient of the poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) can be enhanced by coating second layer materials. The Seebeck coefficient enhancement is ascribed to the surface energy filtering induced by these materials. The surface energy filtering can increase the mean electron energy and thus the Seebeck coefficient of the PEDOT:PSS films. After coating second layer on PEDOT:PSS films sequentially treated with acid and base can give rise to a power factor of 401.2 μW m⁻¹ K⁻² with the Seebeck coefficient of 47.2 μV K⁻¹ and electrical conductivity of 1801 S cm⁻¹.

8:45 AM TP03.01.03
Analyzing the Effect Preferred Orientation and Doping on the Transport Properties of Bi₂Te₃₋ₓSex Alloys for Thermoelectric Power Generation Applications

When attempting to find new alternative energy resources new technological developments must be made to bring society one step closer to a cleaner environment. Thermoelectric devices take thermal heat, either directly from solar energy or as a byproduct of fuel burn, and transform it to electricity. At its core is to prepare high performance TE nanocomposites, both p- and n-type, in a time and energy efficient way. The performance of thermoelectric devices is assessed by the dimensionless figure of merit ZT of the material, defined as $ZT = \frac{\alpha^2 \sigma}{k}$, where $\alpha$, $\sigma$, $k$ and $T$ are the Seebeck coefficient, the electrical and thermal conductivities, and the absolute temperature, respectively. The thermal conductivity is a combination of thermal conductivity via electrons, $\kappa_e$, and via phonons, $\kappa_l$. The main difficulty in improvement of the efficiency of a thermoelectric device is due to the complex relation between $\alpha$, $\sigma$ and $k$. Improving the performance of thermoelectric materials is usually done either by improving the power factor, $\alpha^2 \sigma$, or by applying phonon scattering methods in order to lower the thermal conductivity.

Bismuth-telluride-based alloys are of great importance not only as the best thermoelectric materials with the maximal ZT values close to unity near room temperature, but also due to the potential for further performance improvement. In this study Bi₂Te₃₋ₓSex compositions were electronically optimized by various CH₃ doping levels, preferred alignment of the crystallographic orientation, and its scaling performances. Finally, we will show a few examples, including porous materials and thin films. [1] www.openbte.org [2] G. Romano and J. McLachlan1 and Natalie Stingelin4, 1; 1Imperial College London, London, United Kingdom; 2SABIC, Riyadh, Saudi Arabia; 3Queen Mary University of London, London, United Kingdom; 4Georgia Institute of Technology, Atlanta, Georgia, United States.

9:00 AM TP03.01.04
OpenBTE—An Open-Source Solver for the Phonon Boltzmann Transport Equation in Multi-Dimensional Structures

Over the last decades, Fourier’s law has been challenged by measurements of heat transport at small length and time scales. In fact, when the mean free path (MFP) of heat carriers (i.e. phonons) becomes comparable to the characteristic length, heat travels quasi-ballistically, therefore deviating from standard diffusive theory. The Boltzmann transport equation (BTE) has been the mainstream model of non-diffusive heat transport and has been applied successfully to simple cases, such as thin films and nanowires. However, as complex geometries become increasingly accessible experimentally, a more flexible BTE solver is needed. In this talk, we will present OpenBTE [1], an open-source solver for the space-dependent phonon BTE in three-dimensional structures. The code is interfaced to first-principles calculations from which bulk-related data is collected, and to a Fourier’s solver to model low-MFP phonons, so that the framework is entirely parameter-free across all the scales. Furthermore, thanks to its finite-volume formulation, OpenBTE can easily handle complex-shaped geometries, offering a unique capability of thermal conductivity tuning. OpenBTE groups phonons based on their MFPs, an approach that boosts the computational efficiency, especially for complex-unit cell materials [2]. We will also describe the adopted parallelization scheme and its scaling performances. Finally, we will show a few examples, including porous materials and thin films. [1] www.openbte.org [2] G. Romano and J. C. Grossman. *Heat conduction in nanostructured materials predicted by phonon bulk mean free path distribution.* Journal of Heat Transfer137.7 (2015): 071302.

9:15 AM TP03.01.05
Chain Morphology Effect on Thermal Conductivity of Polymer-Based Materials

Polymers are an attractive alternative to inorganic thermoelectric materials as they are lightweight, generally of low cost to manufacture, offer freedom-of-design as well as having low thermal conductivity. However, our fundamental understanding of thermal transport in polymeric systems needs to be drastically improved to gain the capability to design systems for thermal applications from the outset. The abundance of variety of polymers systems renders this task highly challenging. For instance, while blending is a well-known route for the manipulation of polymer properties, little is known how various blending options affect the thermal conductivity of the blend components and the overall blend. Here, we use polymers with model functional groups and discuss the effect of blending on chain conformation and how, in turn, this changes the thermal transport of the overall material. We draw comparisons to other multicomponent systems such as organic/inorganic hybrid materials and present data that start allowing us to establish design rules and how structural features – both in blends and inorganic/organic hybrids – affect thermal conductivity. Ultimate goal is to provide a general understanding on a broad range of systems that can be used to tune the thermal conductivity of polymers to the final required properties.

9:30 AM TP03.01.06
Thiophene Polymers for Thermoelectric Blends and Composites

The ability to control the carrier energy levels, functional group polarity, and film morphology make organic and polymeric semiconductors (OSCs) especially attractive for various energy interconversions. Their mechanical flexibility, low temperature processing, potential printability, capability of blending to form composites, and use of common elements are additional attractive features. In this presentation, we focus on thiophene polymers blended with dopants and Fermi level-setting additives for thermoelectric applications. Two thiophene polymers, poly(bisdodecylthioquaterthiophene) and poly(bisdodecyl thioquaterthiophene) (PQT12 and PQTS12, respectively), were used in active layers. From measurements of cyclic voltammetry and the electronic characteristics, we found that the introduction of sulfars into the side characteristics traps found in films of the PQTS12. Doping the polymer with sulfur in side chains (PQT512) with the strong oxidant nitrosountemonium tetrafluoroborate (NBOF4), we obtained a very high conductivity up to 350 S cm⁻¹, which is the highest reported nonionic conductivity among films made from dopant-polymer solutions. We found the combination of efficient charge transfer, tighter π-π stacking and strong intermolecular coupling is responsible for the high conductivity. Furthermore, the high conductivity is stable in air without extrinsic ion contributions that are associated with the polymer most often used for high conductivity, poly(ethylenedioxythiophene) (PEDOT:PSS). The thermoelectric power factor compared favorably with prior reports for p-type polymers that were made by the alternative process of immersion of polymer films into dopant solutions, and fit the established models for thermoelectric polymers. Additional data obtained from thiophene
copolymers containing the ethylenedioxiithiophene subunit supported these conclusions. The applicability of these polymers in hybrid composites will also be considered.

10:00 AM BREAK

SESSION TP03.02: Organic and Polymer Thermoelectrics
Session Chair: Howard Katz
Monday Afternoon, November 26, 2018
Sheraton, 3rd Floor, Gardner AB

1:30 PM *TP03.02.01
Bulk Doping Strategies for Plastic Thermoelectrics Christian Muller; Chalmers University of Technology, Goteborg, Sweden.

Molecular doping of conjugated polymers is a widely explored tool for the preparation of highly conducting materials for organic thermoelectrics. While doping of thin films is well understood, there is a lack of doping strategies that can be applied to bulk materials. Hence, the up to millimeter thick architectures, which are needed to construct the legs of a thermoelectric generator, are more challenging to realize. In this talk two bulk doping strategies are presented. Foams of poly(3-hexylthiophene) can be sequentially doped without compromise in thermoelectric performance. Further, conjugated polymers with more polar oligo ethylene glycol side chains show improved compatibility with the dopant. As a result, thermally stable p-doped films with a high electrical conductivity of 100 S/cm can be prepared. The same concept is also applicable to n-type polymers, with conductivities reaching 0.3 S/cm.

2:00 PM TP03.02.02
Intrinsically Conductive Polymers with a Power Factor of >700 μW/(m K²) Jianyong Ouyang; National University of Singapore, Singapore, Singapore.

Organic thermoelectric materials have drawn great interest because of their advantages including mechanical flexibility, easy availability, non-toxicity and low thermal conductivity. Thermoelectric materials with high ZT are required for highly efficient thermoelectric conversion. But the electrical conductivity and Seebeck coefficient of thermoelectric materials are interdependent. Hence, the power factor of organic thermoelectric materials is remarkably lower than their inorganic counterpart.

Here, I will present some of our works in developing intrinsically conductive polymers with high thermoelectric power factors. We developed methods to enhance both the Seebeck coefficient and electrical conductivity of intrinsically conductive polymers. We observed an ultrahigh power factor of >700 μW/(m K²) on intrinsically conductive polymers.

2:15 PM TP03.02.03
Polymer Morphology Dominates Over Energy-Dependent Scattering in Organic-Inorganic Hybrid Thermoelectrics Pawan Kumar, Edmond Zaia, Erol Yildirim, D V M. Repaka, Shao-Wang Yang, Jeffrey Urban and Kedar Hippalgaonkar; 1IMRE, Singapore, Singapore; 2Chemical Engineering, University of California, Berkeley, California, United States; 3IHPC, Singapore, Singapore; 4Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Hybrid (organic-inorganic) materials have emerged as a promising class of thermoelectric materials, achieving power factors (S²σ) exceeding those of either constituent. The mechanism of this enhancement is still under debate, and pinpointing the underlying physics of transport has proven difficult. In this work, we combine transport measurements with extensive theoretical simulations and first principles calculations on a prototypical PEDOT:PSS-Te(Cux) nanowire hybrid material system to understand the effect of templating and charge transfer at inorganic-organic interface on the observed high thermoelectric performance. Further, we apply the framework of the recently developed Kang-Snyder universal charge transport model to show that scattering of holes in the hybrid system, defined by the energy-dependent scattering parameter (s), remains the same as in the host polymer matrix; performance is instead dictated by polymer morphology manifested in an energy-independent transport coefficient. We build upon this universal language to explain thermoelectric behavior in a variety of PEDOT and P3HT based hybrids.

2:30 PM TP03.02.04

New smart or electronic textiles cross conventional uses to include functionalities such as light emission, health monitoring, climate control, sensing, storage and conversion of energy, etc. Here, thermoelectric textiles not only hold great promise in becoming the power source of next generation wearable electronics, but also could become on-spot climate control devices. Further, thermoelectric textiles are also interesting from an industrial perspective since their flexibility and conformability make them suitable for energy recovery from curved surfaces in the mid to low temperature range. For example, a thermoelectric textile could be designed to be wrapped around a steam pipe to harvest waste heat.

Intrinsically conductive polymers have gained attention in the field of thermoelectric textiles because they are made of earth-abundant elements, they show, in general, good mechanical properties and flexibility, they can be processed using low cost large-scale methods such as solution processing and they have an intrinsically low thermal conductivity.

Aqueous dispersions of PEDOT:PSS can be processed into fibers using a traditional wet-spinning process where the polymer solution (dope) is coagulated using a non-solvent (Okuzaki et al. 2003). In this work, we study how the variation of typical wet-spinning parameters such as the dope concentration, composition of the coagulation bath, applied draw, flow rate, etc., affect the thermoelectric properties of PEDOT:PSS wet-spin fibers. Additionally, we also explore possible post-treatments to enhance further the thermoelectric properties of these fibers.

2:45 PM BREAK
Disordered Transport in Highly Doped Materials—Vapor Doping of a Model Small Molecule System

Experimental evidence of the effect of quantum interference on the room-temperature electrical conductance of single-molecules opens the possibility of exploiting quantum interference in single molecules and self-assembled molecular layers.

Groningen, Groningen, Netherlands.

The choice of dopant and the method used to introduce a dopant can greatly influence the resulting electronic and thermoelectric properties of conjugated polymers. In this work, we systematically examine the effects of the side chains of a series of fullerene derivatives by varying their polarity and length. By carefully controlling the doping level, we find an electrical conductivity of 2.3 S/cm with a power factor of 23.1 μW/mK² which leads to an estimated figure of merit of 0.12.

Electrostatic interactions. This is accomplished by tailoring their side chains. We find that both the miscibility and doping efficiency are improved by using polar side chains.

The fullerene derivative with a hydrophilic triethylene glycol side chain (PTEG-1) is used as the host and 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-ylphenyl) dimethyamine (n-DMB) as the dopant. It is found that PTEG-1 molecules readily form layered structures parallel to the substrate after solution processing. The fullerene cage plane is alternated by the triethylene glycol side chain plane; the n-DMB dopants are mainly incorporated in the side chain plane without disturbing the π-π packing of PTEG-1.

Since the polar side chains offer the space for accommodating dopant molecules and influence the molecular order, their length also plays a key role in the doping process. We systematically examine the effects of the side chains of a series of fullerene derivatives by varying their polarity and length. By optimizing the side chains, we find an electrical conductivity of 2.3 S/cm with a power factor of 23.1 μW/mK² which leads to an estimated ZT value of 0.1.

The effectiveness of polar side chains for n-doping conjugated polymers is also verified in the case of the poly[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl-alt-5,5'-4,2'-thiophene)] (N2200) system. Replacing the alkyl side chains of N2200 with polar side chains causes a 200 times enhancement in electrical conductivity. The underlying charge transport mechanism in molecularly doped fullerene derivatives and n-polymer is also explored. Our work offers insights into the roles of side chains in n-type organic thermoelectrics.
we investigate the influence of large molybdenum complexes as dopants vs. smaller iron complexes on the electrical conductivity and Seebeck coefficient of several conjugated polymers. For multiple polymers we find that the large molybdenum complexes lead to electrical conductivities that are over an order of magnitude higher than that of the iron complexes at low doping concentrations. With the same number of polarons present based on absorbance measurements, the larger molybdenum complexes lead to higher electrical conductivities than the smaller iron complexes. We attribute the greater electrical conductivity achieved with the molybdenum dopants to lower coulombic attraction energies that result in more delocalized polarons. However, the electrical conductivity of the polymers doped with the molybdenum complexes saturate at lower doping concentrations than the iron complexes. Thus, the iron complexes can lead to overall greater electrical conductivities and higher power factors than the molybdenum complexes. Surprisingly, ferric chloride can dope PDPP-4T efficiently and lead to higher electrical conductivities than with Mo(tfd)$_3$, despite the ionization energy of PDPP-4T being 0.4 eV higher than the electron affinity of ferric chloride.

8:00 AM *TP03.03.01
Can Polymer–Carbon Nanotube Composites Ever Be Better Thermoelectrics Than Pristine Materials? 
Mariano Campoy-Quiles; Institute of Materials Science of Barcelona, Bellaterra, Spain.

It has been recently suggested that once the polymer chains have done their role helping to disperse the nanotubes, the thermoelectric properties of a polymer-carbon nanotube (CNT) composite would be better if the polymer is removed altogether. This vision does not, however, consider that the polymer can offer other benefits, such as helping to dope the CNTs, varying the system thermal conductivity, changing the microstructure or serving as binder for the respiratory hazardous CNTs. In this talk I will describe different polymer-CNT combinations and fabrication protocols and show some cases examples in which composting is a good option.

First I will show the case of nanocellulose-CNTs films grown by bacteria. By introducing the CNT dispersions in the culture media, bacteria produce nanocellulose films in which the CNTs are finely dispersed. The resulting films are thermally stable at least until 500°C, can be bended completely, and even wrapped around heat sources of random shapes, greatly enhancing the thermal boundary conductance. Using Raman thermometry, we show a 20-fold reduction of the in-plane thermal conductivitiy of the composite with respect to the reference bulky paper. The ZT of the composites is similar to that of the reference, while saving about 90% of the expensive component, the CNTs.

Then, I will describe several cases of CNT doping by the polymer, including changing the character from p- to n-type. Finally, I will discuss the properties of polymer-CNT structures in which the polymer is on top of the CNTs.

8:30 AM TP03.03.02
Optimization of Potential Barrier for Enhanced Thermoelectric Performance of PEDOT: PSS/Bi$_2$Te$_3$ Composite Films via Polar Solvent Vapor Annealing
Wan Sik Kim$^1$, Gopinath Anoop$^1$, Hyejeong Lee$^2$, Hyun Bin Kim$^2$, Soo Hyeon Kim$^3$, Gi Won Goo$^3$, Hyeumyoung Lee$^3$, Hyeon Jun Lee$^3$, Bongjin S. Mun$^4$, Ji-Woong Park$^1$, Eunji Lee$^1$ and Ji Young Jo$^1$; $^1$Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); $^2$Korea Atomic Energy Research Institute (KAERI), Jeongeup, Korea (the Republic of); $^3$Korea Basic Science Institute (KBSI), Daejon, Korea (the Republic of).

The efficiency of TE materials can be evaluated by the dimensionless figure of merit $ZT = \sigma T / \kappa$ or power factor $P = \sigma^2 T / \kappa$, where $\sigma$ is the Seebeck coefficient, $\kappa$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is absolute temperature. The equations of $ZT$ and $P$ imply that high $\sigma$, high $\kappa$, and low $\kappa$ are required for achieving a high efficiency from the TE materials. High $\sigma$ and $\kappa$ reduce Joule heating as well as improve the energy conversion efficiency of heat to electricity, while a low $\kappa$ prevents thermal shorting between two ends. However, because of the conflicting relationship between $\sigma$ and $\kappa$, it is challenging to enhance the efficiency of a single TE material. For example, an enhancement of $\sigma$ is usually accompanied by a decrease of $\kappa$ and an increase of $\kappa$, which has restricted in achieving a maximized $ZT$.

To solve these problems, the energy filtering effect, which occurs at an interface between two different components in nanocomposites and superlattices, has been found to be successful in solving the conflicting relationship of TE factors via enhancement of $\kappa$ without significant reduction of $\sigma$. However, experimentally, an enhanced $P$ or $ZT$ has not been achieved in many composites. The reason is because, in reality, the $\sigma$ of the nanocomposites has been significantly reduced by the inappropriate potential barrier at the interface of the component materials. This implies that the introduction of any potential barrier is not the key, but an appropriate barrier to simultaneously enhance $\sigma$ and $\kappa$ so that to achieve a maximized $P$ or $ZT$.

Here, we synthesize the poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS)/Bi$_2$Te$_3$ nanowires (NWs) composites films treated by polar solvent vapor annealing (PSVA) to systematically investigate the TE factors and optimize potential barrier energy at their interface for enhanced TE performance. The PSVA treatment results in enhancement of $\sigma$ and variable work function of PEDOT:PSS due to changes in structure and PEDOT to PSS ratio. The composite films are annealed for 10, 30, 60, and 120 min using dimethyl sulfoxide to modulate work function of PEDOT:PSS for variable potential barrier energies of composite films. Enhanced $\sigma$ is attributed to two different (phase separation and PSS de-doping) structural changes of PEDOT:PSS as PSVA duration. The $\kappa$ is varied by different magnitude of energy filtering effect caused from various potential barrier energies. The highest $\sigma$, $\kappa$, and $\kappa$ at room temperature are 44.3 mV/K, 1015 S/cm, and 203 mW/mK$^2$, respectively in 120 min PSVA treatment of PEDOT:PSS/Bi$_2$Te$_3$ NWs composite film which exhibits 0.11 eV of potential barrier energy. This work highlights simultaneous enhancement of both $\sigma$ and $\kappa$ by the energy filtering effect, which is controlled through tuning the potential barrier energy at interface in organic-inorganic composite materials.

8:45 AM TP03.03.03
A New Approach for Enhanced Thermoelectric Performance of Polymer/Inorganic Bulk Composites
Kaya Wei$^1$ and George Nolas$^1$; $^1$University of South Florida, Tampa, Florida, United States; $^2$National High Magnetic Field Laboratory, Tallahassee, Florida, United States.

Polymers are currently of great interest for thermoelectric applications, primarily due to a specifically unique combination of properties that are atypical of inorganic material, including mechanical flexibility, low cost, low temperature and cost processing, and general non-toxicity. Moreover, for specific polymer/inorganic composite-enhanced thermoelectric performance, as compared to the conducting polymer alone, has been realized. Here we employ PEDOT:PSS/thermoelectric Bi$_x$Sb$_{1-x}$Te$_3$-alloy p-type composites as a model system to demonstrate a new approach to enhanced performance in polymer/inorganic composites: Ethylene Glycol (EG) treatment of PEDOT:PSS, to enhance conductivity in the polymer, and spark plasma sintering (SPS) processing, to consolidate the composites into dense, bulk materials with less distortion of the polymer chains therefore resulting in even higher electrical conductance. Together with a low thermal conductivity, we achieved greatly enhanced thermoelectric performance as compared to the EG treated polymer.
alone. Moreover, our approach allows for the preparation of polymer/inorganic thermoelectric composites to be processed in a form that allows these composites to be incorporated in existing applications of current refrigeration devices. In addition, we demonstrate that SPS processing is the only method that can provide such results, since hot pressing, cold pressing or mold forming results in extensive distortion of the polymer chains whereas SPS does not, in part due to the current flowing through the composite material during SPS processing.

9:00 AM *TP03.03.04
Less is More—Thermoelectric Performance Enhancements in Polymer-Free Semiconducting Single-Walled Carbon Nanotube Networks Andrew Ferguson and Jeffrey Blackburn; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

There is growing interest in carbon nanostructures for a variety of electronic and optoelectronic applications. We will present studies aimed at understanding and improving the thermoelectric (TE) performance of single-walled carbon nanotube (SWCNT) thin film networks, built upon polymer-based extraction of semiconducting SWCNTs that eliminates metallic SWCNTs and other impurities. Rational choice of the starting SWCNT material and polymer allows us to sensitively tune the semiconducting SWCNT diameter distributions within the composites. When employed in conjunction with a doping process that allows exquisite control over the charge carrier density, we demonstrate that the peak performance, as determined by the TE power factor, is dependent on the SWCNT diameter.2 Modification of the extraction process produces semiconducting SWCNT thin films where nanotube bundling is minimized during network formation and the polymer can be completely removed in the solid state, resulting in intimate tube-tube contacts. By controlling the bundle size and extent of polymer remaining in the semiconducting SWCNT network we demonstrate TE power factors that double the performance of semiconducting SWCNT networks previously demonstrated.2,3 We trace the improved performance to enhanced electrical conductivity, resulting from improved doping and strongly enhanced charge carrier mobility, and analyze our data within the framework of a recently developed TE transport model. We show that removal of the polymer from the semiconducting SWCNT network has negligible impact on the thermal conductivity, which appears to be limited by dopant-induced phonon scattering.


9:30 AM TP03.03.05
Optimization of the Thermoelectric Figure of Merit in the Conducting Polymer PEDOT:PSS Films Through Incorporating 1-d Nano-Structured BiTe Compound Junyoung Lim, Sangwon Jo and Yongsok Seo; Seoul National University, Seoul, Korea (the Republic of).

Thermoelectric materials can generate electricity from unused waste heat and natural heat sources. To fabricate efficient thermoelectric materials, novel nano-structuring approach of mixing inorganic semiconductors of BiTTe alloys with highly conducting polymer (PEDOT: PSS) was devised. This thermoelectric nanocomposite material was prepared through the alloy nanorods forming process in the PEDOT : PSS solution. Two step reduction process allows easy formation of the alloy. Uniform alloy nanorod-PEDOT:PSS composite suspension was obtained which spread well on the substrate with ease of controlling the thickness. High conductivity of PEDOT: PSS provides excellent passage of electrons with low thermal conductivity. The nano-composite has a Seebeck coefficient 48mVK−1 and an electrical conductivity of 1300 Scm−1 at room temperature. The corresponding power factor was 316 mWm−2K−2 to yield a figure of merit [ZT]=0.41, which makes this nano-composite materials useful for waste energy harvesting at low temperature.

9:45 AM TP03.03.06
Multifunctional Thermoelectric Yarn Based Smart Textiles for Energy Harvesting, Cooling and Tactile Sensing Yuanyuan Zheng, Xinzhi Hu and Kun Zhang; Donghua University, Shanghai, China.

In contrast to thin-film based thermoelectric generators (or 2D-TEGs), three-dimensional deformable textile-shaped thermoelectric generators (T-TEGs) show great appeal for smart textiles owing to their excellent structural compatibility with textiles and diverse capabilities of powering wearable electronics, microclimate controlling, adaptively temperature and tactile sensing. However, there have been no reported T-TEGs that can simultaneously accommodate the demands for practical application. In this work, we manufacture organic-based T-TEG with multifunctionality by assembling segmentally-doped carbon nanotube yarn (CNTY) with PEDOT: PSS (P-type) and polyetherimide (N-type) inks into a spacer fabric. As an electricity generator, the T-TEG shows superior voltage and power output of 51.5 V/m² and ~786 μW/m² at a temperature difference of 20 K, respectively. Interestingly, applying one-volt electrical input can lead to the surface temperature drop of approximately 2-5 kelvins, causing a typical sensation between cool and cold, showing exceptional potential for human thermoregulation in smart textiles. Moreover, we shows the excellent wearing performance of T-TEG and ultrahigh sensitivity to the tactile touch including pressure (1.388 KPa−1) and thermal (11.623 K°) stimuli. [q11] To our knowledge, all these results make the developed T-TEG outperforming all reported organic-based F-TEGs and T-TEGs. The developed strategy can inspire the manufacturing of cost-effective T-TEGs with the well-established industrial processes.

10:00 AM BREAK

SESSION TP03.04: N-Type Organic Thermoelectrics
Session Chairs: Michael Chabinyc and Shannon Yee
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Gardner AB

10:30 AM *TP03.04.01
Self-Dopant Design Principles in N-Type Organic Thermoelectrics Daniel Powell, Jonathan Ogle and Luisa L. Whittaker-Brooks; Chemistry, University of Utah, Salt Lake City, Utah, United States.
Small molecule n-type semiconductors are typically doped by blending the semiconductor with extrinsic compounds that readily generate radicals, necessitating that the semiconductor and dopant be co-soluble. In perylene diimides these solubilizing groups, and also the dopants themselves, tend to be sterically bulky and can disrupt the packing structure of organic films; decreasing the electronic coupling between adjacent molecules and hindering charge mobility. The dopants may also aggregate during film casting, decreasing the number of charge carriers available to the system and creating additional grain boundaries. Additionally, the introduction of dopants modifies the density of states near the Fermi-energy such that populated states now exist at some energy relative to the LUMO of the organic semiconductor. Upon charge transfer the energies of these states distort in ways that may be very difficult to predict, leading to a broader density of states. The molecular design of the semiconductor, and also the selection of the proper dopant is a difficult process with several convoluted considerations. These challenges may be mitigated by intrinsically doping the n-type organic semiconductor via a process dubbed self-doping. Herein, we have investigated the effects of self-dopant structure on the processability and doping efficiency in a variety of perylene diimide n-type organic semiconductors. We believe our findings provide fundamental design rules for the fabrication of effective self-dopants geared toward increasing the thermoelectric properties of n-type organic semiconductors.

11:00 AM TP03.04.02
Air-Stable Thermoelectric Materials Based on N-Type Nickel-Coordination Polymers for Energy Harvesting Akanksha K. Menon, Rylan Wolfe, Seth Marder, John R. Reynolds and Shannon Yee; Georgia Institute of Technology, Atlanta, Georgia, United States.

Over 60% of available waste heat is at temperatures below 250 °C. Low cost and large scale thermoelectric devices based on conducting polymers can capture this heat and convert it directly into electricity. Organic materials are suitable for low grade thermal energy harvesting as they can be synthesized from abundant elements and can be processed from solution using low cost fabrication techniques. Furthermore, their low thermal conductivity and flexible nature enable new device architectures and applications. Despite these advantages, polymer-based thermoelectric devices have not made an impact and this is largely attributed to the lack of high performance n-type polymers (power factor > 10 µW/m-K²). To address this, we investigate metallo-organic polymers (also known as coordination polymers) as a suitable class of n-type polymers that are electrically conducting and maintain their stability in air. First, we present the synthesis, characterization and thermoelectric properties of n-type poly(nickel-ethenetetrathiolate) or NiETT. By modifying the reaction conditions and film post-treatment by annealing, the thermoelectric properties can be simultaneously enhanced to obtain a high performing n-type polymer that maintains its stability under ambient conditions. Specifically, to address challenges with the reproducibility of air-oxidized NiETTs, a chemical oxidant is used to systematically tune the thermoelectric properties. Furthermore, the observations and insight gained from the ETT study are extended to other metallo-organic polymers such as the poly(nickel-tetrathioxalate) or NiTTO. This is another coordination polymer that is easier to control synthetically as it is polymerized electrochemically. Herein, we present for the first time the thermoelectric properties of NiTTO films in a PVDF matrix, as well as its thermoelectric properties with varying counterions. Finally, temperature-dependent thermoelectric property measurements reveal that these polymers show semiconducting behavior that is consistent with thermally-activated hopping transport. The development of these two high performance and air stable n-type materials enables their application in realistic devices for thermoelectric energy harvesting.

11:15 AM TP03.04.03
Organometallic Coordination Polymers for Thermoelectric Applications Bob C. Schroeder and Zilu Liu; Chemistry, University College London, London, United Kingdom.

Over the decades, scientific evidence has mounted that the emission of anthropogenic greenhouse gases is the main reason for the increase of surface temperatures observed on Earth. Abandoning fossil fuels in the short term, however, is both technologically difficult and economically risky. Therefore, it would be advantageous to use the produced energy more efficiently thereby curbing the overall energy production and ultimately the greenhouse gas emissions. Around 60% of the energy input is lost after conversion as waste heat, of which half is so-called low temperature (~<200°C) waste heat. A technology suitable to recover waste heat and transform it into usable electricity is thermoelectric generators. Due to the so-called Seebeck effect, applying a temperature differential across a suitable material will generate an electric voltage. Recovering the low-temperature waste heat however via thermoelectric generators is challenging, mainly because current technologies are based on rare, often toxic elements (i.e. tellurium, lead, …); and as a result, thermoelectric modules are rather expensive and can only be efficiently operated at elevated temperatures. It is therefore paramount to develop new thermoelectric materials, able to harvest low-temperature waste heat efficiently.

The ideal thermoelectric material possesses a high electrical conductivity, while at the same time being an excellent thermal insulator. Whereby it is relatively straightforward to find materials which fulfil one of these critical requirements, it is much more difficult to find a single material accomplishing both. Materials based on organometallic coordination polymers are attractive candidates for thermoelectric materials because they have shown promising electrical conductivities, while at the same time maintaining low thermal conductivities. This paper will discuss several synthetic approaches leading towards different organometallic coordination polymers with various geometries, and will investigate not only the effect of the molecular geometry on the thermoelectric properties, but also the effects of the coordinated metal cations.

11:30 AM TP03.04.04
Anisotropic Thermal Conductivity Measurements of Semiconducting and Thermoelectric Polymers Using a Suspended Film 3-Omega Technique Sampath Kommandur and Shannon Yee; Georgia Institute of Technology, Atlanta, Georgia, United States.

Anisotropic thermal conductivity can complicate the performance of semiconducting polymer thin-films in applications such as thermoelectrics. Anisotropic measurements of low thermal conductivity polymers are challenging and there are a limited number of appropriate measurement techniques. Suspended film 3-omega is an appropriate technique but has often required unfavorable microfabrication. Herein, we report on the utility of the suspended 3-omega technique that uses shadow masking, and no other microfabrication techniques, in performing anisotropic (in-plane and through-plane) thermal conductivity measurements of semiconducting polymers - P3HT and commercially available N2200, and n-type thermoelectric polymers - poly-nickel ethenetetraitolates (poly(Ni-ETT)) and poly-nickel tetrathioxalates (poly(Ni-TTO)).

The necessary conditions for the validity of a 1D heat transfer model and experimental guidelines for in-plane thermal conductivity measurements of polymer thin-films are developed. Measured thermal conductivities are compared with predictions from the conventional k-min model and a recent empirical model that more accurately predicts the temperature dependence.

11:45 AM TP03.04.05
Soluble Alkali-Metal CNT Salts for N-Type Thermoelectric Composites Bernhard Dorling and Mariano Campoy-Quiles; ICMAB-CSIC, Bellaterra, Spain.

We report on a promising method that allows to simultaneously disperse and n-dope carbon nanotubes (CNTs). This is achieved by reducing CNTs with Alkali metals like Potassium [1]. The resulting polyelectrolyte salts spontaneously dissolve in polar solvents like DMSO, without requiring any deleterious mechanical methods like sonication, which are known to reduce CNT length. We have explored a range of commercially available CNTs, and show that this method allows to disperse even very long CNT species, which are near-intractable to process without
introducing defects otherwise.

Apart from making them soluble, a pleasant side effect of the reduction is that after the solvent has evaporated, the Alkali metals remain in the film and dope the CNTs, resulting in buckypapers that exhibit a negative Seebeck coefficient. The obtained n-type power factors reach hundreds of μWm⁻¹K⁻², on par with the p-type power factors of the neat CNTs. Furthermore, inspired by previous art [2,3], we show that the CNT solubility can be strongly increased by adding crown ethers to the solution [2], which also improves the doping efficiency and air-stability of the formed films [3].

Finally, we will discuss our results on n-doped CNT-polymer composites prepared using this method.


SESSION TP03.05: Thermoelectrics and Organic Electronics
Session Chairs: Riccardo Di Pietro and Andrew Ferguson
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Gardner AB

1:30 PM *TP03.05.01
The Development and Use of Dopants to Modulate the Electrical Properties of Conjugated Polymers Seth R. Marder; School of Chemistry and Biochemistry, School of Materials Science and Engineering and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia, United States.

Conjugated polymers have attracted interest for thermoelectric applications due to their potential for use in low-cost, large-area, devices. In this talk I will discuss the development of n- and p- dopants and the role they can play in modulating the electronic properties of conjugated polymers.

2:00 PM TP03.05.02
Flexible, Multi-Functional Organic-Inorganic Composites for Passive Thermal Management via Conduction and Radiation Luis M. Lozano; 1, 2, Seong Don Hong; 1, 4, Hadi Zandavi; 1, Yi Huang; 1, Gang Chen; 1, Richard M. Osgood; 3 and Svetlana V. Boriskina; 1, 3, 4 and Galen D. Stucky; 3 and 4. 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Escuela de Ingeniería y Ciencias, Tecnológico de Monterrey, Monterrey, Mexico; 3U.S. Army Natick Soldier Research, Development and Engineering Center, Natick, Massachusetts, United States; 4Defense Agency for Technology and Quality, Seoul, Korea (the Republic of).

Thermal management is nowadays focused on overcoming several challenges for energy savings in buildings, as well as for improving reliability and preventing premature failure in electronic devices. Passive thermal management strategies that enable cooling without any electricity input could therefore have a significant impact on global energy consumption. Consequently, there are both needs and opportunities for novel materials to help address some of these thermal management challenges, which fuel the research progress on developing new materials with high thermal conductivity and tailored thermal emittance properties. In this regard, polymers continue to infiltrate modern technologies due to their unique combination of properties, such as light weight, durability, flexibility, corrosion resistance, low cost, and ease of processing. However, the application of polymers in thermal management has been largely hampered by their low thermal conductivities. Here we report the fabrication of ultra-drawn polyethylene-based thin films filled with inorganic nanoparticles that show both spectrally-tailored absorptance/emittance properties and lateral heat-spreading functionalities. The high thermal conductivity is achieved by the alignment of polyethylene chains, which have a backbone structure of carbon-carbon bonds, while the inorganic filler provides the means to engineer optical properties of films in the broad spectral range. Furthermore, the filler dispersion within the polymer matrix is improved after the drawing process, which even generates better mechanical properties in the composite film. These results provide a feasible route for large-scale fabrication of passively cooling surfaces for heat management in terrestrial and space-based applications.

This work was supported by the NSRDEC ‘Thermal Management of Fibers and Films’ program, through ARO sponsored ISN.

2:15 PM *TP03.05.03
Evidence for Low Disorder, Narrow-Band Charge Transport in the Thermoelectric Response of Semicrystalline Polymer Semiconductors Riccardo Di Pietro; Hitachi Cambridge Laboratory, Cambridge, United Kingdom.

Semiconducting polymers possess unique mechanical, thermal and electrical properties that make them interesting candidates for thermoelectric applications. However, the recent development of semicrystalline polymer semiconductors with field-effect mobilities comparable to and sometimes exceeding those of amorphous silicon has exposed the limitations of commonly used disorder-based charge transport models which were developed originally for more disordered, lower mobility materials. This is especially true when including in the picture the thermoelectric properties of this class of materials.

I will present our work on the structural, electric and thermoelectric characterisation of semicrystalline polymers for which we have recently shown a correlation between charge density dependence of mobility and the size of the crystalline domains in the polymer film [1]. We have characterised the temperature and charge carrier dependence of the Seebeck coefficient and found it in contradiction with charge transport models based on energetic and positional disorder. On the very contrary these measurements provide direct experimental evidence for narrow band conduction at the charge densities typically observed in thin film transistors. The comparison with the conductivity measurements highlights an additional aspect which is the need to include electron-electron interactions to consistently explain the measured properties.[2]

Based on these findings, we propose an alternative charge transport model that explicitly accounts for the presence of interspersed crystalline and amorphous regions within the polymer film and for local electron-electron interactions. This approach captures all the unique features observed experimentally and highlights new directions which can lead to a further improvement of both electric and thermoelectric performance of polymer semiconductors.

The flexible thermoelectric generator (f-TEG) is a very promising technology for energy harvesting to enable self-powered wireless sensors and wearable devices, an area of exponential growth. Here, we present a scalable and cost-effective additive manufacturing process to fabricate f-TEGs using colloidal nanocrystals, and an innovative and highly efficient photonic sintering method to sinter large areas of printed films using pulsed light. Flexible TE films and devices were printed using screen printing and aerosol jet printing, followed by pulsed photonic sintering process. The pulsed sintering confines the delivered thermal energy within the printed film region without over heating the substrate, enabling TE film sintering on flexible polymer based substrates with relatively low melting point. In addition, the pulsed sintering limits grain size growth due to an ultrafast heating and cooling process, and lower thermal conductivity can be achieved than films sintered by conventional thermal processing.

Until recently, research into thermoelectrochemical cells had primarily focused on aqueous electrolytes, predominantly with the ferri/ferrocyanide redox couple. The electrochemical potential of this redox couple depends on temperature, and therefore in a device with two electrodes held at different temperatures a potential difference is created. Thus, these cells allow direct thermal to electrical energy conversion with no carbon emissions. 

Until recently, research into thermoelectrochemical cells had primarily focused on aqueous electrolytes, predominantly with the ferri/ferrocyanide redox couple. The electrochemical potential of this redox couple depends on temperature, and therefore in a device with two electrodes held at different temperatures a potential difference is created. Thus, these cells allow direct thermal to electrical energy conversion with no carbon emissions. 

The highest power outputs to-date for thermoelectrochemical cells using IL electrolytes have been achieved through our use of a high entropy change CoII/IIIbpy3 redox couple. Here we discuss our research into the use of a range of Fe and Co-based complexes in different IL and IL/solvent mixtures for thermal energy harvesting. The Seebeck coefficient and thermoelectrochemical cell performance is shown to be strongly influenced by the nature of the redox couple and the IL. We also discuss our recent research into the development of quasi-solid state electrolytes using either water-based or IL-based electrolytes.

(p × n)-type transverse thermoelectrics are introduced as an alternative to conventional or “longitudinal” thermoelectrical materials for applications at room temperature and below. A microscopic theory for such materials is explained, based on a simple two-band anisotropic effective mass model for conduction and valence bands. Such materials are predicted to have performance advantages over standard thermoelectrics in small-scale devices as well as at cryogenic temperatures.

Transverse thermoelectrics drive heat orthogonal to an applied electric current. As such they have the geometric advantage that the heat-flow cross section is independent of the current-flow cross section. As the name suggests, this unique behavior of (p × n)-type transverse thermoelectrics results from having a Seebeck tensor with orthogonal p- and n-type Seebeck behaviors. One feature of such materials is that the bandgap should be of order several kT at the optimal operation temperature, and that the optimal performance occurs near intrinsic doping. Whereas conventional thermoelectrics must be extrinsically doped n-type or p-type to function, these intrinsic materials will not suffer from dopant freeze-out, opening a new cryogenic range of operation for solid state cooling.

Transverse thermoelectrics have the device advantage of having full thermoelectric performance in a single-leg. This single-leg structure makes it trivial to achieve “infinite stages” of Peltier cooling, for example, which can only be achieved with standard thermoelectrics in a cascaded multi-stage structure. Single-leg (p × n)-TTE’s can also be scaled down to microscale devices, giving them niche applications that cannot be addressed by conventional multi-leg thermoelectric coolers or heaters.

Compared earlier transverse thermoelectric paradigms, the transverse Seebeck response in (p × n)-type transverse thermoelectrics is due to structural asymmetry in the band structure of a single crystal. Thus a simple two-band anisotropic effective-mass model is shown to be adequate to explain experimental data on such materials. From such a model, ambipolar resistivity Seebeck and resistivity tensors can be calculated. The predicted transverse thermoelectric behavior is shown to be maximized with the Fermi energy near mid bandgap. A transverse power factor PF is introduced, and from the published literature, we propose the following materials as candidate materials for (p × n)-type TTE: Re₂Sr, Cs₂BuTe, PdCoO₂, Na₂CoO₃ (ρ = 0.45, 0.55) and Li₂xMoO₃/7.
Thermoelectric effect, which is voltage generation under a temperature gradient, can be induced by electron or/and ion transport. Here the two different transport mechanisms and their thermoelectric properties are discussed, and the transport behaviors in polymer only and polymeric composites are compared. While thermoelectric voltage induced mainly by electrons is typically smaller than that of ions, the voltage can be continuously generated. Recently reported thermally-induced ion transport needs to be utilized in a non-continuous manner, but it exhibits extremely large thermally induced voltage. Based on thermally induced ion transport, novel methods have been developed for simultaneously harvesting and storing electrical energy without losing the benefit of solid-state non-moving part devices like conventional thermoelectrics. We called the device thermally chargeable supercapacitor (TCSC), and arrays of TCSC have been batch-fabricated, and connected together to raise the output voltage up to 2.1 V, suggesting excellent suitability for roll-to-roll mass manufacturing and practical implementation of thermal energy harvesting. The outcomes suggest that it may be feasible to eliminate needs for battery replacement and wired connections to power lines for various distributed electronic systems whenever and wherever a temperature gradient is present.

Ab Initio Design of a Transparent Thermoelectric Oxide—ZnSb2O6

Adam J. Jackson, Alex M. Ganose, Winnie Leung, Benjamin A. Williamson, and David O. Scanlon; Chemistry, University College London, London, United Kingdom; Thomas Young Centre, University College London, London, United Kingdom; Diamond Light Source Ltd., Didcot, United Kingdom.

Thermoelectric devices have a range of applications for energy conversion and recovery. As renewable technology reaches more ambitious scales, new requirements and opportunities emerge. Primarily the drive has been to identify materials with a high thermoelectric figure of merit $ZT$. Metal oxides are appealing due to their high chemical and thermal stability and avoid dependence on the limited supply of heavy anions such as Te. Electrical conductivity has been achieved in many wide-bandgap metal oxides and carrier concentrations can be manipulated by extrinsic doping. These transparent conducting oxide (TCO) materials form a vital component of devices including solar cells and display screens. So far, their thermoelectric performance has been limited by the relatively high lattice thermal conductivity of crystalline oxides, leading to an interest in nanostructuring.

We have performed third-order lattice dynamics calculations to predict the intrinsic lattice thermal conductivity of ZnSb2O6, which is found to be less than half that of ZnO across the whole operating temperature range. We have also examined the defect chemistry of the system, identifying appropriate dopants for an n-type zinc antimonate device. Device modelling identifies an optimal carrier concentration which is found to be achievable based on the study of defect transition levels. The corresponding value of $ZT$ is over 0.5: greater than existing n-type thermoelectrics. We conclude that ZnSb2O6 has the potential to form the n-type component of a high-performance transparent thermoelectric device.

Session Chairs: Michael Chabinyc, Terry Hendricks, Kedar Hippalgaonkar and Shannon Yee
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

TP03.06.01
Sanju Gupta and Romneey Meek, Western Kentucky University, Bowling Green, Kentucky, United States.

Three-dimensional scaffolds comprising different ratio of graphene nanosheets and multi-walled carbon nanotubes (GA-CNT, hereon) macro-assemblies. The resulting hydrothermally synthesized hydrogels are freeze-dried and thermally reduced to yield graphene and graphene-carbon nanotube aerogels with ultralow densities and tunable mesoscopic pore sizes. These 'all carbon' aerogels prepared as monolithic solids from suspensions of few-layer graphene oxide nanosheets and small diameter multiwalled carbon nanotubes in which organic wet chemistry is used to cross-link the individual sheets and with carbon nanotubes. In contrast to methods that utilize physical cross-links between graphene oxide nanosheets, this approach with polymeric linkers and organic functionalization provides covalent carbon bonding among the graphene sheets and molecular attachment with carbon nanotubes, respectively, thus facilitating rapid and facile electron transport. As a result they are expected to exhibit improved electrical conductivities, moderate thermal conductivity, highly interconnected multiplexed topology with large internal surface areas thus promoting enhanced surface ion adsorption which makes these mesoporous materials viable candidates for use in harvesting thermo-electrochemical energy and energy storage technologies. Thermoelectric property measurements for both the carbon nanotube aerogels by themselves and for hybrids with graphene nanosheets revealed promising and unprecedented ($p$-type and $n$-type) thermopower values, especially with electrolyte with an upper bound to 3.2 mV/K. We used complementary analytical techniques including electron microscopy, temperature dependent electrical property, and Raman spectroscopy while evaluating performance to establish microstructure-processing-property-performance correlations. This work is supported in parts by KSEF-RDE Grant, KY NASA EPSCoR and KY NSF EPSCoR Grants.

TP03.06.02
Investigation for PEDOT:PSS Thermoelectric Properties Changes with Additive Process
Won-Tae Park, Marco Cassinelli, Peitro Pandolfini, Chanil Park, Mario Cairomi, Jung-Hyun Kim and Yong-Young Noh; Dongguk University, Seoul, Korea (the Republic of); Yonsei University, Seoul, Korea (the Republic of); Istituto Italiano di Tecnologia, Milano, Italy.

Printed electronics have been developed with various synthesized high performance conducting organic materials for flexible devices as display,
Continuous Thermal Tunability of VO2-SiO2 Nano-Composite Capacitors

Exploration of Organic Redox Couples for use in Thermogalvanic Devices
present thermogalvanic devices retain the drawback of coupled ionic and thermal conductivity which limits their conversion efficiency.

Here, we explore the use of organic active species in thermogalvanic devices. Organics are of interest due to their high entropy of reaction and heat capacity resulting in large Seebeck coefficients and open circuit potentials. Additionally, organics have tunable physical and electrochemical properties which expands the materials design space. To this end, we leverage recent technology developments in redox flow batteries (RFB) to improve performance of thermogalvanic generators. The proposed cell retains key advantages of RFBs, namely independent energy and power scaling, durability, and low cost while decoupling the conductive and thermal properties present in solid-state devices. We extend Tester’s results on an aqueous copper system [4] to organic active species with a novel reactor design. A range of organic active species are examined by cyclic voltammetry, bulk electrolysis, and other techniques at various temperatures and top-performers are transferred to the thermogalvanic cell for further performance analysis. In addition, we report a few engineering advances to the thermogalvanic cell to mitigate losses and improve cell potential.

References
1. Lawrence Livermore National Laboratory. Web: <https://flowcharts.llnl.gov/content/assets/images/charts/Energy/Energy_2017_United-States.png>
measurements. These transport properties were studied in the temperature range between 85 and 300K. The thermoelectric performance of La(Ca)CoO ceramics was improved as a consequence of the decreasing of its electrical resistivity with Ca doping and metallic LaSrCoO adding. The composite exhibits maximum values for the thermoelectric power factor, PF and the figure of merit ZT close to 28 μW/K² cm and 0.5, respectively. Thus, the behavior observed in the transport properties become these composites promising materials for use in thermoelectric devices for low-temperature applications.

TP03.06.11
Transport properties of CNT-PEDOT/PSSA Polymer Composites
Sebastian Forest1 and Kofi Adu1, 2; 1Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, United States; 2Physics, The Pennsylvania State University, Altoona, Altoona, Pennsylvania, United States.

Organic thermoelectric materials are receiving considerable attention due to the fact that they can be potentially used for fabricating flexible, printable, and low cost organic thermoelectric generators (OTEGs). Conjugated polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3-hexylthiophene) (P3HT) and polyaniline (PANI) are some examples of organic thermoelectric materials. However, for fabricating the OTEGs, the thermoelectric performance of the conjugated polymers needs to be improved further. Recently, carbon nanotubes (CNTs) have been used as effective additives for improving the thermoelectric performance of conjugated polymers. By adding CNTs to the conjugated polymer matrix, density of the electrical pathways in the nanocomposite increases; thereby, greatly enhancing the electrical conductivity. The enhanced electric conductivity results in enhanced thermoelectric performances of the CNT-conjugated polymer nanocomposite. We present our results on temperature dependence transport properties of CNT-PEDOT/PSS composite and boron doped composites of different CNT loading (0.1 wt%, 0.5 wt%, 1.0% 2.0% and 5.0 wt%) and correlate the CNT loading with the electrical conductivity.

TP03.06.12
Porous SnSe1-xSx Nanosheets as Promising Ternary Nanocrystals for Thermoelectric Applications
Hyun Ju Taeseob Oh, Dabin Park, Hyunwoo Oh and Joohoon Kim; Chung-Ang University, Seoul, Korea (the Republic of).

Herein we report a higher figure of merit (ZT) in SnSe based thermoelectric materials by markedly reducing the thermal conductivity, which is achieved via three promising strategies: substitution with isoelectric S atoms, exfoliation of nanosheets from a bulk ingot, and chemical transformation of the material into a porous structure. SnSe1-xSx nanosheets are prepared by hydrothermal Li-intercalation and subsequent exfoliation process from bulk SnSe1-xSx ingots. The substitution of S atoms into SnSe and the exfoliation of SnSe1-xSx nanosheets contribute to the scattering of phonons at numerous atomic disorders and nano-sized boundaries, resulting in effective reduction of the thermal conductivity and an enhanced ZT. The introduction of porosity into the SnSe1-xSx nanosheets through the chemical transformation process further reduces thermal conductivity, which leads to a higher ZT. Finally, the porous SnSe1-xSx nanosheets has an outstanding ZT of 0.12 at 310 K, significantly higher than that of pristine SnSe.

TP03.06.13
Thermal-Charging Electrochemical Cell for Converting Low Grade Heat in Isothermal Operation
Xun Wang and Shien Ping Feng; The University of Hong Kong, Hong Kong, Hong Kong.

A tremendous amount of energy is wasted in the form of low grade heat from source below 100 °C. Current thermoelectric or thermoelectrochemical technologies are still facing with low efficiency from limited temperature difference, balance between electric and thermal conduction, and construction on specific scenario such as thermal cycle. Here we proposed a new thermoelectrochemical system with graphene oxide(GO) as positive electrode and polyaniline(PANI) as negative electrode which can operated in isothermal condition to continuously converting low grade heat into electricity. We observed that GO had a high thermal response due to oxygen containing functional groups, and the electrochemical cell with GO as positive electrode and titanium foil as electrode could reach a high temperature coefficient of 3.5 mV/K. When heating up the cell, a heat induced voltage difference can be created and current can be generated by promoting the oxidation reaction of PANI if employing PANI as negative electrode. This system demonstrated a thermal-electricity energy conversion efficiency of 3.92% when operating in 90 °C. The findings show enormous potential to harvest low grade heat via thermoelectrochemical cell.

TP03.06.14
Synthesis of High Conducting and Thermoelectric PEDOT:PSS/Carbon Materials Aerogel for Dual-Sensors
Gyume Hyeon Yoon, Sang Woo Lee and O Ok Park; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Poly(3,4-ethylendioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is one of the promising conducting polymers which exhibit p-type thermoelectric property, having the various characteristics such as water solubility, flexibility, and commercial availability. In this paper, we fabricated thermoelectric nanocomposite aerogel, composed of PEDOT:PSS and carbon nanotube (CNT) via an easy and reproducible freeze-drying methods. CNT could be simply dispersed in PEDOT:PSS aqueous solution, due to the secondary interactions between them, for example, pi-pi interaction and van der Waals interaction. At 140 degrees celsius, crosslinker, glycidoxypropyl-trimethoxysilane (GOPS) reacted –OH groups and epoxy group in the solution and robust nanocomposite aerogels were successfully formed. These nanocomposite aerogels showed better electrical conductivity and thermoelectric effect than those of pristine PEDOT:PSS aerogels due to embedding CNTs into PEDOT:PSS matrix. As an application of the fabricated aerogel, we also demonstrated highly sensitive pressure/temperature(P/T) dual-sensor using PEDOT:PSS/CNT aerogel. By simply mixing CNT and cross-linking agent in PEDOT:PSS solution, electrical and thermoelectric properties were improved as well as the sensitivity of the P/T dual-sensor.

TP03.06.16
Photo-Seebeck Effects in Doped P3HT Composites
Harold O. Lee and Sam-Shaing Sun; Norfolk State University, Norfolk, Virginia, United States.

As the global energy and environmental preservation needs continue to grow, the demand for renewable and clean energy conversion materials and devices continues to rise as well. Thermoelectric (TE) materials and devices can convert waste heat into electricity and therefore it can be a potential renewable and clean energy source. TE materials research and development has been mostly focusing on inorganic semiconductors such as Bi-Te or Sb-Te alloys with thermoelectric figure-of-merits (ZT values) around one at room temperature. Inorganic TE materials generally exhibit high electrical conductivity but also high thermal conductivity that is inversely related to the thermoelectric figure of merit (ZT values). Organic and polymeric materials typically exhibit low electrical conductivities, high Seebeck coefficients, and orders of magnitude lower thermal conductivities as compared to their inorganic counterparts. However, the electrical conductivities of organic/polymeric materials are tunable via doping or molecular engineering. In this study, a series of carefully doped P3HT composites are systematically evaluated for heat as well as light modulated devices. Along with a high absorption coefficient, when the polymer film thickness is less than the penetration depth of the incoming photons, the photo effects are significant and could be very useful for light modulations of thermoelectric functions. With further systematic studies and a better understanding of the mechanisms behind the photo-Seebeck effect, the development of potential high-efficiency multi-function materials and devices appears feasible.
It is well known that temperature sensitivity is one of the main drawbacks of photovoltaics (PV). Especially in the case of optically concentrated systems, the solar cell working temperature is always much higher than ambient temperature. High working temperatures increase carrier recombination, therefore decreasing solar cell performance. In this context heat recovery strategies are in principle a solution to balance this loss increasing the overall system efficiency. Among these solutions thermoelectric hybridization has already been shown to be an effective candidate. However, the field of solar cell thermoelectric hybridization is still burgeoning. Often, works in literature are contradictory and in some case the work reports unphysically large efficiency improvements. It is thought that the false efficiency improvement observed is due to incorrect experimental procedures, such as the implementation of very optimistic cold side temperatures, and the lack of normalization to active area when combining PV and TEG output contributions.

In this communication we report the development and the rigorous characterization of Gallium Indium Phosphide (GaInP) solar cells hybridized with Bismuth Telluride (Bi2Te3) thermoelectric generators (TEGs).

The results showed an inversion of the solar cell temperature sensitivity with an absolute efficiency gain of 2% (~15% of the sole PV efficiency) corresponding to an optimal working temperature of around 400 K. We find that the key to this improvement is the use of a wide-gap solar cell and the implementation of thermal strategies that prevent heat dissipation to the environment. In addition, the variation of both gain and optimal temperature as a function of the optical concentration were studied, showing the applicability of this kind of hybridization in different contexts.

These results, which are in excellent accordance with a more general theoretical model already reported by the authors, demonstrate in an accurate fashion the real potential of thermoelectric hybridization of solar cells.

Influence of the Mobility Ratio and Density of States Width on the Thermoelectric Properties of Polymer Blends Ashkan Abtahi1, Yadong Zhang2, Xuyi Luo1, Jianguo Mei1, Seth R. Marder3 and Kenneth R. Graham3; 1University of Kentucky, Lexington, Kentucky, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States; 3Purdue University, West Lafayette, Indiana, United States.

Conjugated polymers can be used in mechanically flexible and low cost thermoelectric (TE) devices, but their thermoelectric performance must be improved to make them commercially viable. The performance of thermoelectric materials depends on the electrical conductivity, Seebeck coefficient and thermal conductivity. In polymer based TE materials the polymer needs to be doped to become electrically conducting. The higher the doping concentration, the more electrically conductive the material becomes, but generally at the cost of a decrease in the Seebeck coefficient. Blending of π-conjugated polymers has been proposed as a method to minimize the tradeoff between electrical conductivity and the Seebeck coefficient, thus potentially allowing higher power factors to be reached. By blending polymers, the total density of states (D.O.S.) in the material will be manipulated, which may be used to alter the energy dependence of charge transport in the TE material. Manipulating the D.O.S., particularly by introducing highly conductive states at higher energies with respect to the Fermi energy, allows the energy dependence of charge transport to be enhanced and the Seebeck coefficient increased.

The major parameters that we expect to impact the power factor in polymer blends are the mobility ratios between the pure polymer and the shape of D.O.S. Here, we use a model introduced by Bässler and Arkhipov to theoretically probe how the mobility ratio and the shape of the D.O.S. impact the Seebeck coefficient and thermoelectric performance. These calculations are then used to fit experimental data of various polymer blends with varying mobility ratios and D.O.S. distributions. We find that a narrower D.O.S. and higher mobility of the added polymer with respect to host polymer can lead to an enhancement in the Seebeck coefficient of the TE material, but we do not observe increases in the power factor.

Thermoelectric Properties of Unsorted and Sorted Single-Walled Carbon Nanotube Sh Tsuyohiko Fujigaya1, 2; 1Kyushu University, Fukuoka, Japan; 2JST, Saitama, Japan.

Single-walled carbon nanotubes (SWNTs) especially their semiconducting type are promising thermoelectric (TE) materials due to their high Seebeck coefficient. In this study, we measured the electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (κ) of sorted semiconducting SWNTs (s-SWNTs) and metallic SWNTs (m-SWNTs) together with their mixture and the unsorted SWNTs to study the effect of sorting for the conversion efficiency, which is often evaluated as the power factor (PF) and figure of merit (ZT = S²σT/κ). We found that as the s-SWNT purity increased, ZT increased, mainly due to the increasing of Seebeck Coefficient. Thermal conductivity on the other hand, remains the same with the increase of s-SWNT. Our group is the first to report thermal conductivity and ZT of SWNT sheet with different s-SWNT purity.

Dual-Beam Pulsed Laser Deposition of GaTe5/(Bi2Sb)2Te5 Nanocomposite Films for Thermoelectric Applications Bo-Yao Yu, Chih-Chuan Su, Po-Hung Chen and Chun-Hua Chen; Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Heterogenization of nanomaterials has become one of the most promising strategies for modifying thermoelectric materials. The introduction of heterogeneous dopants could not only selectively improve intrinsically-poor specific properties of the base materials, but potentially break the physically coupled thermoelectric properties due to the created various heterogeneous functional interfaces for further enhancing the overall thermoelectric figure of merit (ZT). In this work, a series of novel Ga2Te5/Bi2Sb2Te5 heterogeneous nanocomposite films with different compositional ratios were successfully deposited on SiO2/Si substrates using a dual pulse laser deposition system. The optimized electrical conductivity of 303 S/cm and Seebeck coefficient of 295 μV/K found with the composition of Ga2Te5/Bi2Sb2Te5 of 45% and 40% higher than those reported for Bi2Sb2Te5. In overall, the corresponding power factor of 26 μW/cmK2 is approximately two times higher than that found for Bi2Sb2Te5.

Improving the Thermoelectric Power Factor in 2D Materials Using Periodic Potential Barriers Adithya Komminni and Zlatan Aksamija; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

The conversion of waste heat to electricity using thermoelectric devices has the potential to improve our energy utilization efficiency. Significant research efforts over the past two decades have been devoted to increasing the efficiency of thermoelectric (TE) energy conversion via nanostructuring. One approach to improve the TE efficiency is electron filtering where "cold" (low energy) electrons are restricted from participating in transport by an energy barrier. However, the impact of electron tunneling through thin barriers and resonant states on TE properties, especially in two-dimensional (2D) mono- and few-layer materials, has been given significantly less attention. In our previous work, we simulated the effect of energy filtering and quantum-
mechanical (QM) tunneling through a series of potential barriers in silicon and found that tall, sharp barriers can significantly enhance the TE power factor. We extend our previous work to study the effect of energy filtering from a series of potential barriers in 2D materials, such as those arising from lateral or vertical van der Waals heterostructures, superlattices, or when a monolayer is exposed to a series of electrostatic gates. In this work, we develop a comprehensive transport model that includes electron-phonon coupling and electron-impurity scattering alongside with quantum effects arising from the potential barriers. Our model captures the carrier-potential interactions in the Wigner formalism as an additional force term called the “quantum evolution operator”, which is added to the semi-classical Boltzmann transport equation (BTE). The resulting Wigner-Boltzmann transport equation is solved using Rodeo’s iterative method, with the electronic structure data being pre-calculated from density functional theory (DFT). We then study the impact of height, width, and shape (smoothness) of the potential barriers on TE properties. Our simulations show a steady increase in TE efficiency with the height of the potential barrier in gated single layer (SL) molybdenum disulfide (MoS₂), reaching a maximum enhancement of approximately 25 percent. Further, we explore the impact of the barrier width and shape and find that, unlike 3D, sharp, narrow barriers are not always better. We attribute this to the unique step-like 2D electronic density of states. This study identifies ways to achieve high TE performance in nanoscale thermoelectric devices with periodic features, such as van der Waals heterostructures and superlattices. The improvement in TE efficiency helps in the development of energy-efficient devices ranging from wearables powered by scavenging body heat, to thermal sensors, and solid-state electronic cooling.

TP03.06.22
Tuning Band Structure and Electronic Transport in Multilayered Semiconductor Nanostructures Sanjumitha Neogi and Vitaly Proshchenko; University of Colorado Boulder, Boulder, Colorado, United States.

When the device size reaches the nanoscale, scattering at interfaces dictates the device functionality. Additionally, dimensional reduction significantly modifies the properties of carriers in the nanostucture. A complete treatment of transport in a multi-interface system requires solving the complex interplay between dimensional confinement and interface scattering. In this work, we investigate electron transport in layered Si/Ge superlattices with imperfect interfaces employing density functional theory in combination with semi-classical Boltzmann transport theory. We demonstrate tunability of electron transport in multilayered nanostructures by the introduction of compositional variability, engineered interface structures and external strain. The structural variability induces strain that strongly influences the bonding environment and therefore, the charge densities in these structures. The modified charge densities directly impact electronic band structures and subsequently, cross-plane electronic transport across the multilayered systems. Our work establishes a direct relationship between the introduction of local and global strain and cross-plane transport in multilayered semiconductor superlattice structures. One representative result from our study is that introduction of positive strain (tension) in the in-plane direction of Si/Ge superlattices leads to significant improvement of the Seebeck coefficient at higher carrier concentrations. Our work establishes strategies to attain a phonon-glass-electron-crystal regime in order to achieve a high ZT for thermoelectric applications. The project is funded by the DARPA (DSO) MATRIX program. This work used XSEDE, which is supported by NSF grant number ACI-1053575.

TP03.06.23
Thermoelectric Properties of MA P-Type BiSbTe-NFC Hydrogel Composite Films Under Applied Pressure Deepa Madan1, Eunhwa Jang1, Aswani Possapati1, Nathaniel Jang2 and Liangbing Hu3; 1University of Maryland Baltimore County, Baltimore, Maryland, United States; 2University of Maryland College Park, College Park, Maryland, United States.

Flexible Thermoelectric generators (TEGs) are attractive because they can potentially provide higher power density, can have higher aspect ratio elements, and are more scalable than conventional TEGs. Flexible TEG devices are printed on flexible substrates using thermoelectric (TE) inks consisting of TE particles, a suitable binder, and a solvent. Films printed using TE inks typically have much lower performance as compared to commercially available bulk TE pellets. A high amount of insulating binder present in inks deteriorates the electrical properties and overall performance of printed TE films. In this work, we explore a novel binder, synthesize efficient TE particles with suitable dopants, and perform cold-pressing to densify the films to improve the TE performance of p-type TE materials. We chose wood-based nanofoiber cellulose (NFC) hydrogel as a binder because a very small amount of hydrogel is sufficient to provide good adhesion strength and flexibility. We initially check the feasibility of use of NFC hydrogel as a binder with commercially available Sb₂Te₃ TE particles. Then, followed by synthesizing various mechanically alloyed (MA) particles using Te as a dopant with the objective of improving the TE performance. For optimizing thermoelectric inks we made films with different weight ratios of the binder and the TE powder (e.g., 1:100, 1:1000, and 1:10000). Unlike most other TE films with thermostet polymers that require high curing temperatures and long curing time, NFC hydrogel TE composite films are cured at the room temperature in a short time to achieve good properties. These films were then subjected to a range of uniaxial pressure (10 Mpa to 1000 Mpa) for 5 minutes to densify the films. A significant improvement in the electrical conductivity was achieved by varying the applied pressures. Optical microscope and SEM images showed that (1) the number of pores in the NFC hydrogel phase with particles decreased with an increase in the weight ratio of the TE powder, and (2) the NFC hydrogel phase and particles were compacted and densified. Because the particles aggregate with each other, the grain boundaries and scattering were reduced, helping improve the electrical conductivity. SEM cross-section images revealed that with higher TE particles concentration, the TE films have more uniform and denser surfaces. The best sample among various MA BiSbTe samples was 1:10000 binder to MA BiₓSb₁ₓTe₃ (which consists 8% extra Te) at 600 Mpa applied pressure. Its power factor of 1338.8 μW/mK² is approximately 15 times that of MA Bi₀.₅Sb₁.₅Te₃ sample for which no pressure was applied. Overall, the low mass loading of binder to particles ratio, the addition of extra Te to MA BiₓSb₁ₓTe₃ improved the power factor by approximately 130 times (1:10000, 600Mpa, MA BiₓSb₁ₓTe₃) as compared to Sb₂Te₃-NFC composite films without any external pressure.

TP03.06.24
The Transverse Seebeck Effect Oded Rubin1, Stuart Laurence2 and Nicholas Tiliakos3; 1University of Maryland, College Park, Maryland, United States; 2Innovercing LLC, Ronkonkoma, New York, United States.

In anisotropic single crystal materials the Seebeck coefficient tensor may contain non-zero off-diagonal elements. With proper crystal alignment, a unidirectional heat flux generates EMFs both parallel (normal Seebeck voltage) and perpendicular (transverse Seebeck voltage) to the temperature gradient. This presentation will highlight the theoretical and practical advantages and challenges in utilizing the transverse Seebeck effect in miniature high-speed heat flux sensors. Compatible with large scale microfabrication, this technology is suitable for microcalorimetry and fast thermal analysis of materials and processes.

TP03.06.25
Nanoporous V–VI Chalcogenides Nanoplates for Efficient Thermoelectrics with Preferential Interfacial Scattering Chaochao Dun4, Jian Wang5, Kirill Kovnir4, David L. Carroll3 and Yanliang Zhang1; 1Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana, United States; 2Department of Chemistry, Iowa State University, Ames, Iowa, United States; 3Physics Department, Wake Forest University, Winston Salem, North Carolina, United States.

Flexible Thermoelectric generators (TEGs) are attractive because they can potentially provide higher power density, can have higher aspect ratio elements, and are more scalable than conventional TEGs. Flexible TEG devices are printed on flexible substrates using thermoelectric (TE) inks consisting of TE particles, a suitable binder, and a solvent. Films printed using TE inks typically have much lower performance as compared to commercially available bulk TE pellets. A high amount of insulating binder present in inks deteriorates the electrical properties and overall performance of printed TE films. In this work, we explore a novel binder, synthesize efficient TE particles with suitable dopants, and perform cold-pressing to densify the films to improve the TE performance of p-type TE materials. We chose wood-based nanofoiber cellulose (NFC) hydrogel as a binder because a very small amount of hydrogel is sufficient to provide good adhesion strength and flexibility. We initially check the feasibility of use of NFC hydrogel as a binder with commercially available Sb₂Te₃ TE particles. Then, followed by synthesizing various mechanically alloyed (MA) particles using Te as a dopant with the objective of improving the TE performance. For optimizing thermoelectric inks we made films with different weight ratios of the binder and the TE powder (e.g., 1:100, 1:1000, and 1:10000). Unlike most other TE films with thermostet polymers that require high curing temperatures and long curing time, NFC hydrogel TE composite films are cured at the room temperature in a short time to achieve good properties. These films were then subjected to a range of uniaxial pressure (10 Mpa to 1000 Mpa) for 5 minutes to densify the films. A significant improvement in the electrical conductivity was achieved by varying the applied pressures. Optical microscope and SEM images showed that (1) the number of pores in the NFC hydrogel phase with particles decreased with an increase in the weight ratio of the TE powder, and (2) the NFC hydrogel phase and particles were compacted and densified. Because the particles aggregate with each other, the grain boundaries and scattering were reduced, helping improve the electrical conductivity. SEM cross-section images revealed that with higher TE particles concentration, the TE films have more uniform and denser surfaces. The best sample among various MA BiSbTe samples was 1:10000 binder to MA BiₓSb₁ₓTe₃ (which consists 8% extra Te) at 600 Mpa applied pressure. Its power factor of 1338.8 μW/mK² is approximately 15 times that of MA Bi₀.₅Sb₁.₅Te₃ sample for which no pressure was applied. Overall, the low mass loading of binder to particles ratio, the addition of extra Te to MA BiₓSb₁ₓTe₃ improved the power factor by approximately 130 times (1:10000, 600Mpa, MA BiₓSb₁ₓTe₃) as compared to Sb₂Te₃-NFC composite films without any external pressure.
Nanoporous architectures are known to have low thermal conductivities thanks to the enhanced phonon scattering at pore interfaces. In this paper, instead of the chemically engineered interface, we adopted the morphology engineered interface in V-VI systems to realize an electron-transmitting but phonon-blocking structure using preferential energy carrier scatterings determined by the modulation of geometric factors. The synthetic nanopore in the nanoplates offers superior control of both the pore size and the porosity in the consolidated nanostructured bulk pellets. Such versatility offers an additional degree to improve the thermoelectric properties. The effective multi-frequency phonon scattering along with minimal charge carrier scattering lead to a substantial reduction of lattice thermal conductivity and a slight increase of Seebeck coefficient. Thanks to the existence of pore boundaries, effectively multilayer preferential scatterings were achieved, which involves more phonons scattering than that of charge carriers, more low-energy charge carries scattering than high-energy carries, leading to an improved figure of merit of the V-VI systems.

**TP03.06.26**

**Investigation of Thermoelectric Performance of MoS2 Nanostructure Along with Its Secondary Phase**

Pratisha Gangwar, Sunil Kumar and Neeraj Khare; Physics, Indian Institute of Technology Delhi, New Delhi, India.

Thermoelectric materials have been the subject of intense research from both theoretical and technological point of view due to their ability to directly convert waste heat into the electricity and can provide an alternative approach to deal with the future energy crisis [1]. The energy conversion efficiency of thermoelectric material is evaluated from the figure of merit (zT=S²ρT/κ), a dimensionless quantity, where S is the Seebeck coefficient, ρ is the electrical conductance, T is the absolute temperature and κ (κ = κe+ κp) is the thermal conductance composed of the contributions from electrons (κe) and phonons (κp) [2]. For efficient energy conversion, the figure of merit should be greater than 1. The conventional thermoelectric materials possess low value of zT thus cannot be used for thermoelectric applications [1]. Thus to improve the zT value, materials which possess high Seebeck coefficient and high electrical conductivity or low thermal conductivity are required.

Recently, layered transition metal dichalcogenides (TMDCs) have gained a lot of research attention for thermoelectric applications due to the advantage of low thermal conductivity possessed by these materials [3]. Among TMDCs, molybdenum disulfide (MoS2) has been demonstrated as a good thermoelectric material due to its high value of thermo-EMF (or thermoelectric voltage) and low value of thermal conductivity [3]. But, low electrical conductivity limits its thermoelectric conversion efficiency [4]. So, the challenge is to increase its electrical conductivity without compromising the low thermal conductivity. One of the way is to enhance its electrical conductivity is by incorporating metal nanostructures in the semiconducting host matrix [1].

In the present work, we demonstrate thermoelectric properties of MoS2 by incorporating MoS2, a semi-metallic secondary phase of MoS2. The presence of semi-metallic MoS2 in MoS2 matrix enhances its electrical conductivity. Further, enhancement in Seebeck coefficient is also observed due the filtering of low energy charge carriers. For this study, we have synthesised MoS2 nanosheets (pristine and secondary phase incorporated) via hydrothermal method. By varying the growth time, 16 hours and 36 hours, we are able to get pristine MoS2 (labelled as M36) and MoS2 with secondary phases (labelled as M16). The structural and morphological analysis of as-synthesized MoS2 is performed with X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Furthermore, thermoelectric performance of the MoS2 samples (M16 and M36) is studied and analysed.

**TP03.06.27**

**Effect of In as a Substitute and not a Filler on Thermoelectric Properties of CoSb3 Skutterudites**

Keshav P. Dabral and Satish Vitta; Indian Institute of Technology Bombay, Mumbai, India.

CoSb3 with an open structure which can accumulate several fillers has been extremely studied due to its phonon glass electronic crystal character. In the earlier studies In has been added to CoSb3 as a filler to reduce thermal conductivity due to its large size compared to both Co and Sb. In the present work however its effect on the thermoelectric performance when used as substitute for Sb has been investigated in detail. The substituted alloys, CoₓSbₓ₋ₓInₓ with x=0.5 and 1.5 were synthesised by standard technique and hot pressed at 600°C under a pressure of 60Mpa for 12 minutes into circular pellets. Structure characterization by X-ray diffraction shows that for x<0.5 and 1.0 , the alloys consist of essentially single phase indicating that In has gone into solution as substitute for Sb. The alloy with x=1.5 however shows phase segregation. The skutterudite phase, CoSb3 is present along with CoSb3 and Sb. Hence this alloy was not investigated further. The variation of electrical conductivity with temperature shows a weak metallic behaviour for x<0.5 while that of x=1.0 exhibits a weak semiconducting behaviour. Both the alloys show very weak temperature dependence with conductivity varying between 9×10⁴ and 1.1×10⁷ sm⁻¹ when the temperature increased from 300K to 800K. The Seebeck coefficient of the alloys in the complete temperature range is negative indicating electrons to be the dominating charge carriers. The Seebeck coefficient of x=0.5 alloy is found to be higher varying from 152 µVK⁻¹ to 200 µVK⁻¹ compared to x=1.0 alloy in which it varies from 125 µVK⁻¹ to 175 µVK⁻¹. At ~600K bipolar transport begins in the both alloys clearly showing the presence of low energy charge carriers. The high Seebeck coefficient and electrical conductivity of x<0.5 alloys results in a large power factor of 3.7mWm⁻¹K⁻² at ~650K. The thermal conductivity of both compound x=0.5 and x=1.0 alloys is found to be low in the complete temperature range, 300K to 800K varying between 2.5 Wm⁻¹K⁻² and 3.5 Wm⁻¹K⁻². The thermal conductivity of x=0.5 alloy however is found to be lower than that of x=1 alloys at almost the temperatures. The relatively low thermal conductivity and extremely large power factor of x=0.5 alloy results in a high figure-of-merit of 0.82 at 773K. These results clearly show that low levels of substitution of Sb with In is highly beneficial in increasing the power factor substantially compared to the reduction in the thermal conductivity.

**TP03.06.28**

**Gaussian Process Regression of Electron-Phonon Coupling Matrix Elements with Applications in Thermoelectric Materials Research**

Jeeyoun Kim, Semi Bang and Daehyun Wee; Ewha Womans University , Seoul, Korea (the Republic of).

Electronic transport coefficients in semiconductors can be obtained by solving the semiclassical Boltzmann transport equation within the relaxation time approximation. The main task is the evaluation of the inverse of the electron energy relaxation time induced by the electron-phonon (el-ph) interaction. Here, we investigate a method, the electron-phonon averaged via Gaussian process regression (EPA-GPR) method, of predicting the Seebeck coefficient and electrical conductivity by estimating the electron-phonon coupling. This method results from the combination of the electron-phonon averaged (EPA) method and the Gaussian process regression (GPR) strategy. With the electron-phonon averaged (EPA) method, the momentum-dependent electron-phonon coupling matrix, [gₘₙ(ν,k)q]², is approximated by its energy-dependent equivalent, gₘₙ(ν,εₘ,εₙ)q. gₘₙ(ν,εₘ,εₙ) is modeled as a Gaussian process which is a collection of random variables, any finite number of which can have a joint Gaussian distribution. During the regression, the characteristic length-scale of the covariance function of the Gaussian process can be estimated within the type two maximum likelihood (ML-two) approximation. To reduce the computational cost, we use the KISS-GP (Kernel Interpolation for Scalable Structured Gaussian Processes) method, in which the evaluation of the covariance function is replaced with interpolation on a well-defined grid. The calculation on the grid can exploit its underlying Kronecker-Toeplitz structure to boost the calculation speed. A potential thermoelectric half-Heusler compound, HfCoSb, is considered as a test case. Thermoelectric properties, including the Seebeck coefficient and the electrical conductivity, are estimated. The results of the two different approaches are compared in order to show the advantages of the EPA-GPR method as a practical method for estimating thermoelectric properties of materials.

**TP03.06.29**

**Accelerating Evaluation of Converged Lattice Thermal Conductivity**

Guangzhao Qin and Ming Hu; University of South Carolina, COLUMBIA, South
Designing materials with specific properties is a long-term goal in materials science. High-throughput \textit{ab-initio} materials screening and design is a new and rapidly growing area in computational materials research. The application of high-throughput calculations has recently made formidable progress and led to novel insights in this field. The lattice thermal conductivity (\(\kappa\)) is a crucial physical property of crystalline materials for enormous practical implications, such as electronic cooling, thermoelectricity, phase change memories, and etc. Therefore, the fast evaluation of reliable \(\kappa\) for variety of materials plays a key role in identifying suitable materials for targeted applications. Currently, first-principles based anharmonic lattice dynamics (ALD) method coupled with phonon Boltzmann transport equation (BTE) is one of the most featured methods to obtain the \(\kappa\), which involves calculation of interatomic force constants (IFCs). Especially, the anharmonic IFCs are evaluated based on the third order derivatives of the total energy with respect to the atomic displacements, which requires huge computational costs. However, severe problem arises for choosing an appropriate (usually not large enough) cutoff distance (\(r_{\text{cutoff}}\)) when calculating the anharmonic IFCs. Thus, the high-throughput evaluation of reliable \(\kappa\) remains a challenge due to the large resources costs and time-consuming procedures in calculating the anharmonic IFCs for the convergence test. In this work, based on the analysis of the harmonic (second order) IFCs, we propose a concise strategy to efficiently accelerate the evaluation process of obtaining accurate and converged \(\kappa\) by solving the cutoff distance problem. The proposed strategy is efficient for directly determining when the \(\kappa\) converges with respect to \(r_{\text{cutoff}}\) and how to fast get satisfactorily converged \(\kappa\). With this strategy, we study the divergence problem of thermal conductivity of graphene, a long debate of two-dimensional heat conduction in literature. The feasibility of the method is also confirmed by other systems. In addition, the computing speed with our approach could be one order of magnitude faster compared to the traditional method in most situations, where the \(20^{\text{th}}\) nearest neighbors are considered. The quantitative strategy proposed herein can be a good candidate for fast evaluating the reliable \(\kappa\) and thus provides useful tool for high-throughput materials screening and design with targeted thermal transport properties.
This indicates that coupling of Au-thiol heterojunctions is much stronger than coupling of the ligands to water. Our work facilitates better understanding of heat transfer at atomic scale.

9:00 AM TP03.07.04
Magnetically Driven Heat Transport in Field-Induced Weyl Semimetals
Dung Vu, Koen Vandaele, Nandini Trivedi and Joseph P. Heremans; The Ohio State University, Columbus, Ohio, United States.

Theory predicts\(^1\) that the Fermi arcs in Weyl semimetals (WSM) induce entropy transport driven by circulating electronic currents in a magnetic field. Here, we report the first experimental observation of that theory. Fermi arcs are projections of Weyl nodal crossings in the surface Brillouin zone. This new transport phenomenon has no net charge transport, but a net heat transport that contributes to the magneto-thermal conductivity of the material.

Experimental demonstration of the circulating current in a traditional WSM is difficult since the effect scales with thickness, yet the growth technology for thick, high-quality films of traditional WSMs is not well developed. Bi\(_x\)Sb\(_{1-x}\) alloys with varying Sb concentrations have bands that close at \(k=\pi\) and have a Dirac point at the \(L\)-point of the Brillouin zone\(^2\). In strong magnetic fields, this Dirac point theoretically is expected to split into two field-induced Weyl points. Here we experimentally demonstrate the new, magnetically-driven enhancement of thermal conductivity in bulk Bi\(_x\)Sb\(_{1-x}\). Samples report a strong, positive magneto-thermal conductivity at the Sb concentration and magnetic field where the Weyl points are expected to appear.

This work is supported by the OSU Center for Emergent Materials, an NSF MRSEC, Award Number DMR-1420451.

References

9:15 AM TP03.07.05
Giant Anomalous Nernst Effect Observed in Single Crystal MnBi
Bin He, Stephen Boona, Brian C. Sales\(^2\) and Joseph P. Heremans\(^1\); The Ohio State University, Columbus, Ohio, United States; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

MnBi is a high temperature ferromagnet (\(T_{\text{Curie}}\approx 630\)K) and crystallizes in the HCP structure. Its thermal transport properties have remained uninvestigated. The anisotropic transport properties (including resistivity, thermal conductivity, thermopower and Nernst effect) of two MnBi single crystals are measured and presented here separately from 80K to 300K in magnetic field up to 1.4T along different crystalllographic axis. We observed a giant anomalous Nernst thermopower in both \(\alpha_{xy}\) and \(\alpha_{xy}\) configurations (the first index indicates the direction of the flux, the second of the measured field, the third of the applied magnetic field, \(\alpha=\text{hexagonal axis}\)). The anomalous Nernst thermopower in \(\alpha_{xy}\) configuration decays with temperature while in the \(\alpha_{xy}\) configuration the anomalous Nernst effect strengthens. Anomalous Hall effect is also observed. We suspect the presence of a strong magnon contribution to the anomalous Nernst effect. This can be understood as a self-Spin Seebeck effect, whereby a thermally driven magnon flux in the sample generates a spin polarization of the conduction electrons through magnon-electron scattering. This in turn gives rise to an inverse spin-Hall effects via spin-orbit coupling in the materials itself.

Work supported by the National Science Foundation under Award Number DMR-1420451.

9:30 AM TP03.07.06
Nernst Thermopower in Bi - MnBi Composites
Koen Vandaele, Bin He, Stephen Boona and Joseph P. Heremans; The Ohio State University, Columbus, Ohio, United States.

Magnetic materials in which thermal transport involves the generation of spin fluxes provide new opportunities to improve the thermal-to-electric energy conversion efficiency over that of conventional, electron-based thermoelectrics. In bulk ferromagnetic (FM) metals such as Co, Fe, and Ni, magnon dynamics in the material result in a magnonic contribution to total thermopower, as shown by Watzman et al.\(^1\) In thin-film structures composed of a normal metal (NM) film, such as Pt, deposited on an electrically insulating FM, such as yttrium iron garnet (YIG), a thermally driven spin flux injected from the FM into the NM layer gives rise to inverse spin-Hall voltage in the NM layer.\(^2\) This voltage is perpendicular to the temperature gradient and the applied magnetic field.\(^2\) Although these thin-film structures are not suitable for power generation applications, it was shown by Boona et al.\(^3\) that it is possible to obtain a contribution from the spin-Seebeck effect (SSE) to the Nernst thermopower in bulk nanocomposite structures composed of a NM (Pt) with strong spin-orbit interactions and a FM (Ni). In this work, Bi, which has a large spin-Hall angle and Nernst effect, will be used as a NM and MnBi as the FM. Bulk composites composed of Bi and MnBi needles will be studied specifically in a Nernst geometry to determine the SSE contribution to Nernst thermopower.

References
(2) S. R. Boona, Energy Environ. Sci. 7 (2014)
(3) S. R. Boona et al., Nature Communications 7 (2016)

9:45 AM TP03.07.07
Investigation of Electron Transport via Quantum Mechanical Estimation of Electrical Conductivity in Thermoelectric Materials
Semi Bang\(^1\), Georgy Samsonidze\(^2\), Boris Kozinsky\(^3\) and Daehyun Wae; \(^1\)Environmental Science and Engineering, Ewha Womans University, Seoul, Korea (the Republic of); \(^2\)Research and Technology Center, Robert Bosch LLC, Cambridge, Massachusetts, United States; \(^3\)Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

A quantitatively accurate description of electron transport from first principles would greatly enhance our ability to design new materials or optimize existing materials via prediction of electronic transport properties. In particular, electrical conductivity is a key property determining the performance of many types of bulk materials for energy storage and conversion including thermoelectrics (TE). However, relatively little work has been done on fully ab-initio prediction of electrical conductivity for realistic TE materials. In this study, we perform the validation study of a newly developed computational prediction method of electrical conductivity, i.e., the electron-phonon-averaged (EPA) approximation, in order to verify the feasibility of first-principles screening applications for various realistic and complex TE materials. Regarding target TE materials, we study the pnictogen-substituted ternary skutterudites (PSTSs), which are formed by isoelectronic replacement of pnictogen atoms with group 14 (Ge, Sn) and group 16 (S, Se, Te) elements. PSTSs are considered as the attractive features to be investigated as potential thermoelectric materials. Nevertheless, the rigorous understanding of the chemical substitution effect on transport phenomena of the PSTSs still remains largely unexplored. Therefore, we investigate the effect of pnictogen-substitution on electron transport via estimation of interrelated electronic transport properties in skutterudite compounds. Based on these results, certain guidance for the rational design of next-generation TE materials is also provided.

10:00 AM BREAK
It has been almost three decades since Nanoscale Thermal Science and Engineering became a well-established research field. Various major breakthroughs in fundamental understanding of thermal transport (phonons, photons, and electrons) at the nanoscale have been achieved in these three decades; however, the impact of these fundamental insights has been primarily targeted toward microelectronics and thermoelectrics applications. In this talk we provide examples of other applications such as Lithium ion battery thermal management, building thermal insulation, and high density thermochemical storage where molecular and nanoscale thermal science has a significant role to play.

11:00 AM TP03.08.02

Thermoelectric technology has key benefits and strengths in many terrestrial energy recovery applications. Thermoelectric system cost is a key factor governing final decisions on the use of thermoelectric energy recovery systems in all terrestrial applications; thus cost being just as important as power density or efficiency for the adoption of waste energy recovery (WER) thermoelectric generators (TEG). New integrated cost analysis / thermoelectric analysis approaches have shown key relationships and interdependencies between overall TEG system costs, including TE material costs, manufacturing costs, and specifically heat exchanger costs; and the TE performance design metrics such as TE material properties, TE device design parameters, heat exchanger performance metrics such as hot-side and cold-side conductances and UA values, and hot side heat flux in achieving optimal TEG WER designs. These new approaches have led to a new thermoelectric system economics paradigm that strongly influences TEG cost and performance decisions. While work by Yee et al. and LeBlanc et al. provided foundations for the latest cost scaling analysis / TE performance analysis, this new work takes prior work to new insights and understandings and provides the basis for new thermoelectric system economics. Optimum TEG system cost conditions can now be tied directly to the TE materials, TEG design parameters, and heat exchanger design parameters through critical non-dimensional analysis. The non-dimensional analysis and metrics show the TEG system cost and performance interdependencies and interlinks in one unifying and cohesive relationship. Prior work has shown that the system design that minimizes cost (e.g., the G [$/W$] value) can be close to designs that maximize power, but these design regimes are not necessarily aligned with high system conversion efficiency or high specific power. This paper will explore the key sensitivities and interrelationships between critical cost metrics and critical TE performance and design metrics in the new thermoelectric system economics paradigm, provide quantitative data showing these sensitivities, and their serious implications on TEG system design in terrestrial WER applications. Critical non-dimensional parameter mapping has shown where heat exchanger cost-dominated conditions, TE material or manufacturing cost-dominated conditions, and combinations of cost conditions control and drive the overall TEG cost and performance. This new cost-performance paradigm shows the required pathways and challenges to achieving TEG system costs of $1-$3/Wdec.

11:15 AM TP03.08.03
Optimization of Thermoelectric Power Generators for Low-Grade Heat Recovery Kazuaki Yazawa, Yee Rui Koh and Ali Shakouri; Purdue University, Minneapolis, Minnesota, United States.

The most suitable thermoelectric properties for low-grade heat recovery is very well matched to the material in Peltier devices for general cooling application. This is based on an analytical modeling and optimization with temperature dependent material properties. The analytic model is validated based on experiments with commercially available thermoelectric modules. This highlights the importance of the geometric aspect ratio of the thermoelements which is key for thermal impedance matching with the heat transfer coefficients at both hot and cold contacts. Especially, reduction of thermal conductivity has bigger impact compared to the TE power factor. At the same time, however, relative thermal conductivity of TE material compared to the gap fill material has a big impact on the performance. The latter is often neglected in high temperature applications. The talk will go over the experimental results of TE systems optimized for small temperature differences for various heat transfer conditions. The cases include (a) Heat energy harvesting from inaccessible two parallel water pipelines with 10 cm separation and 10-20 deg-C temperature difference for powering wireless sensors transmitting self-diagnostic information about heating and cooling supplies in datacenters. (b) Reversible body heat recovery and spot heating for winter sport jackets with compact heat exchanger design. In the experiments, power generation is measured at room temperature with water chiller and adjusted with temperature-dependent material properties to determine the performance in real conditions. The power output at the level of 1-100 mW with a 40 mm x 40 mm off-the-shelf module were observed depending on the heat/water flow path. At the optimum design, 1.2 V can be generated with electrical series transmitting self-diagnostic information about heating and cooling supplies in datacenters. (b) Reversible body heat recovery and spot heating for winter sport jackets with compact heat exchanger design. In the experiments, power generation is measured at room temperature with water chiller and adjusted with temperature-dependent material properties to determine the performance in real conditions. The power output at the level of 1-100 mW with a 40 mm x 40 mm off-the-shelf module were observed depending on the heat/water flow path. At the optimum design, 1.2 V can be generated with electrical series connection of two modules each with 127 thermopairs.

11:30 AM TP03.08.04
Experimental Proof of Thermoelectric Charge Generation and Separation within p-i-n Junction TEGs Franziska Maculewicz; Khaled Arzi, Timo Wagner and Roland Schneebeli; 1Institute of Technology for Nanostructure & CENIDE, University of Duisburg-Essen, Duisburg, Germany; 2Components for High Frequency Electronics, University of Duisburg-Essen, Duisburg, Germany.

Common thermoelectric generators are built from unipolar p- and n-legs and use the Seebeck-effect for power generation. In theoretical studies (Span et al.) a p-i-n structure operated parallel to the temperature gradient was proposed. A big advantage of this device concept is beside the conventional thermoelectric effect is the additional ability to harvest energy from thermal excited bipolar carriers in the space charge region (+-region) and their separation in the built-in field of the p-i-n TEG. Here we present for the first time the experimental evidence of thermal excited bipolar carriers in the space charge region and its contribution to the electrical output power of the TEG. Silicon p-i-n TEGs were fabricated by laser sintering of highly doped boron and phosphorus nanoparticles on each side of an intrinsic silicon wafer. $II$-characteristics were measured under different temperature gradients. The hot side was heated to a temperature around 300 °C. The fundamental characteristics of this complex 2-dimension problem, could be explained by a simple lumped equivalent circuit. It is shown that an additional physical mechanism, beside the regular Seebeck-effect is needed to describe the measured behavior. This indicates the present of a second
independent energy conversion process, as predicted by Span et al. This energy which is assigned to the separation of thermally excited bipolar charge carriers within the region can be measured by excluding the contribution from the p- and n-legs. In this experiment the Seebeck-effect which occurs mainly in the p- and n-region is canceled by electrically short circuiting the p- and n-legs of the TEG with a full metallization of the legs. The short-circuited device assures a direct access to the thermally excited bipolar charge carriers in the i-region. The output power of the short-circuited devices kept raising with the hot side temperature, which confirms the mentioned assumption. The extracted electric power from the i-region by bipolar charge separation is compared to the Seebeck-effect of the bare i-region. This comparison underlines again the different nature of both mechanism. Besides that, device simulations are carried out on same structures and achieved a good agreement to the measured data. The generated power dependency on the i-region thickness is currently investigated to maximize the contribution of thermally generated bipolar carriers in the i-region to the p-i-n TEG power output.

11:45 AM TP03.08.05
Ferroelectric Energy Conversion by First Order Phase Transformation in the Small Temperature Difference Regime
Ashley Bucek1, William Nunn2, Bharat Jalali2 and Richard James1; 1Aerospace Engineering and Mechanics, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; 2Chemical Engineering and Materials Science, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Ferroic materials respond to external stimuli by undergoing spontaneous changes in macroscopic behavior via advanced deformation mechanisms such as a reversible phase transformation. This includes ferroelastics or shape memory alloys, ferromagnetics, ferroelectrics, and multiferroics. For instance, ferroelectrics that undergo a reversible phase transformation can alternate between one phase that is a strong ferroelectric and another phase that is non-ferroelectric. The transformation between one phase and the other can be induced through small changes in temperature. This material system is incredibly promising for society-improving technological advances in direct energy conversion from heat to electricity, where “direct” means that the material itself generates the electricity. Furthermore, the ferroelectric heat recovery system is ideal for operation in the “small temperature difference regime,” e.g. solar-thermal sources, waste heat from air conditioners, data centers, or even hand-held electronic devices. We present a thermal energy conversion device that utilizes the first order phase transformations in ferroelectric capacitors. We demonstrate the validity of such a device, present a theoretical framework to model and optimize the circuit parameters, and discuss using phase engineering to achieve extreme cyclic repeatability.

SESSION TP03.09/BM08.09: Joint Session: Thermoelectrics and Organic Polymers Toward Applications in Wearable Devices
Session Chairs: Kedar Hippalgaonkar and Dongyan Xu
Wednesday Afternoon, November 28, 2018
Sheraton, 2nd Floor, Grand Ballroom

1:30 PM *TP03.09.01/BM08.09.01
Ionic Effects in Organic Thermoelectrics
Rachel Segalman, University of California, Santa Barbara, Santa Barbara, California, United States.

Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO2-free conversion of heat to electricity. Molecular materials and hybrid organic-inorganics bring the promise of inexpensive, solution processible, mechanically durable devices potentially suitable for wearable applications. While highly conductive polymers are now commonplace, they generally demonstrate lower thermopower at a given conductivity than inorganic counterparts. Ion conducting materials have previously been demonstrated to have very large Seebeck coefficients, and a major advantage of polymers over inorganics is the high room temperature ionic conductivity. Notably, PEDOT:PSS demonstrates a significant but short-term increase in Seebeck coefficient which is attributed to a large ionic Seebeck contribution. We have recently shown that doping with protic ionic liquids and other proton conductors can be used to control the thermoelectric power factor. In this talk, I will discuss how electrochemical transistor geometries can be used to understand the scaling of thermopower with carrier concentration and to begin to untangle the intertwined ion/electron effects in mixed conductor thermoelectrics. I will also discuss how electrochemistry can be utilized to stabilize the Seebeck enhancement leading to stable improvements to power factor in mixed conductor thermoelectrics.

2:00 PM TP03.09.02/BM08.09.02
Design and Fabrication of Textile-Based Wearable Thermoelectric Devices
Hend M. Elmoughni, Akanksha K. Menon, Shannon Yee and Rylan Wolfe; Georgia Tech, Atlanta, Georgia, United States.

Textile fabrics as substrates for wearable thermoelectric generators (WTEG) are attractive for body heat harvesting. Textile-based WTEGs can be integrated into clothing to convert temperature differences between the human body and ambient into electricity. One target application of the technology is powering body mounted electronics with low energy consumption that ranges from 1μW to 10mW. Transformation of the conventionally rigid thermoelectric devices consisting of p- and n-type inorganic semiconductors into flexible fabrics offers various advantages including: better conformity to the skin which maximizes the temperature difference needed for power generation, light weight structure which does not restrict mobility or comfort, and easy integration of the technology into clothing. Development of WTEGs has been mainly focused on employing additive printing techniques such as screen printing to deposit the thermoelectric material onto the flexible substrate. While this approach has demonstrated great potential, a number of challenges have to be overcome before a fully functioning textile-based WTEG can be realized. Device-level challenges include small fill factors ~0.2 requiring large areas to generate appreciable amounts of power, low fabric thickness that results in small temperature differences, and dominant interconnect and electrical contact resistances for thin-film devices that hamper the power output; these factors need to be considered when designing WTEGs in order to maintain device structure flexibility and high power density. Furthermore, a material-level challenge lies primarily in the development of p- and n-type thermoelectric ink formulations that can be compatible with a cost-effective, scalable fabrication technique without compromising thermoelectric properties. Herein, we present strategies to overcome the aforementioned challenges and fabricate a knitted-base WTEG capable of human body heat harvesting using a through-plane temperature difference. Both the proposed device design and proof-of-concept prototype are presented to demonstrate the feasibility and potential of this technology for low grade heat energy harvesting.

2:15 PM TP03.09.03/BM08.09.03
Towards a Thermoelectric Fabric—3D-Extruded Thermoelectric Threads
Jun Peng1, Ian Witting1, Nicholas Geisendorfer1, Mingyi Wang1, Mingchiang Chang1, Ramille N. Shah1, 2, Jeff J. Snyder1, Matthew Grayson1 and Adam Jakus2; 1Northwestern University, Evanston, Illinois, United States; 2Dimension Ink, Evanston, Illinois, United States.

Thermoelectrics (TE) have the potential for diverse applications in energy harvesting, however the rigid configuration of typical TE modules can be a limiting factor whereas flexible platforms would find much broader use. Here, we realize continuous, flexible thermoelectric threads via three-dimensional
Thermoelectric generators (TEGs) are promising for harvesting waste heat from the environment to power wireless sensor nodes in smart buildings. In this talk, I will share our recent research effort on developing non-flexible micro-TEGs by integrating pulsed electroplating with microfabrication processes. We systematically studied the effects of the pulsed electroplating conditions on the composition, microstructure, and thermoelectric properties of the electroplated Bi2Te3 thin films. Our results show that the thermoelectric figure of merit of the electroplated Bi2Te3 films can be enhanced by increasing the pulse off-to-on ratio, which is mainly due to the reduced thermal conductivity and the increased Seebeck coefficient. A maximum ZT of 0.16 is obtained at the pulse off-to-on ratio of 50 at room temperature. Based on the fundamental materials research, we further developed cross-plane micro-TEGs on a SiO2/Si substrate. The device consists of a total of 127 pairs of n-type Bi2Te3 and p-type Sb2Te3 thermoelectric pillars embedded in a SU-8 matrix. Both thermoelectric pillars and interconnectors are formed by electroplating, which is advantageous because of low parasitic electrical resistances. The micro-TEG we developed demonstrates a maximum power of 3 mW at a temperature difference of 52.5°C, corresponding to a power density as high as 9.2 mW cm⁻². The power density of our TEG is more than two times the highest value reported for the electroplated TEGs in the literature, which can be attributed to the low internal resistance and high packing density of thermoelectric pillars.

With expediting trends in electronic device miniaturization, thermoelectric energy harvesting becomes increasingly valuable, especially in wearable technologies and sensors for the internet-of-things. However, it has been impossible to match the device thermal impedance with the natural heat gradient using the thin-film thermoelectric materials much needed for device miniaturization. This limitation has prevented thermoelectrics from competing as a technology and environmental pollution. It is crucial to develop clean and renewable energy technology for the sustainable development of human society. Targeting at scavenging thermal energy, thermoelectric effect has been utilized to develop thermal energy harvesting technology. Compared to the pyroelectric energy harvester which has little energy output, thermoelectric devices have been widely recognized as more effective and efficient technologies which have been utilized to develop thermal energy harvesting technology. However, it has been impossible to match the device thermal impedance with the natural heat gradient using the thin-film thermoelectric materials much needed for device miniaturization. This limitation has prevented thermoelectrics from competing as a technology.

In this work, we report on a flexible photo-thermoelectric nanogenerator (PTENG) by hybridizing MoS2/PU photothermal layer with tellurium (Te) nanowire based thermoelectric device. The MoS2/PU film which is flexible and transferable exhibits excellent photothermal characteristics due to exceptional surface-area-to-mass ratio of MoS2 nanoclusters. Te nanowire is chosen for the thermoelectric nanogenerator because of its reported outstanding thermoelectric properties, such as low thermal conductivity and a wide temperature range. By integrating the photothermal layer with
thermoelectric device, the PTENG can absorb infrared light to form a temperature difference across the device. With this, a potential difference between two electrodes can be established and used for electrical energy generation. Therefore, the PTENG can generate electricity without a spatial temperature gradient. Furthermore, the PTENG which is flexible and shape-adaptive can demonstrate great practical application of photo-thermoelectric energy harvesting for wearable electronics and implantable electronics.

1.0, 10 and 50 mM doped films showed n-type nature of the films. Interestingly, we found that Seebeck coefficient of 1.0 mM doped film changed to positive, while 10 mM doped film showed stable negative value. From above results, we conclude that the mechanism of the air-stabilization of n-doping is the passivation effect by the formation of o-MeO-DMBI layer onto the surface of SWCNT films. [2] Bao, Z. et al. Nano Lett. 2013, 13, 1890. [1] Nakashima, Y.; Nakashima, N, Fujigaya, T. Synth. Met. 2017. 225. 76.

Concentration of o-MeO-DMBI solution was studied. It is noted that the films were kept under air condition at room temperature to evaluate the air stability. DIPS (Meijo Nano Carbon, EC1.5) was used as SWCNT. SWCNT films were dipped in the 0.01, 0.1, 1.0, 10 and 50 mM ethanol solutions of o-MeO-DMBI for 10 min and dried in vacuum at room temperature for 12 h. The time course of Seebeck coefficient of the SWCNT films doped with various concentration of o-MeO-DMBI solution was studied. It is noted that the films were kept under air condition at room temperature to evaluate the air stability of the o-MeO-DMBI-doped SWCNT films. Positive value of Seebeck coefficient for 0.01 and 0.1 mM doped films indicated p-type, and negative value for 1.0, 10 and 50 mM doped films showed n-type nature of the films. Interestingly, we found that Seebeck coefficient of 1.0 mM doped film changed to positive, while 10 mM doped film showed stable negative value. From above results, we conclude that the mechanism of the air-stabilization of n-doping is the passivation effect by the formation of o-MeO-DMBI layer onto the surface of SWCNT films.


Thermoelectric (TE) conversion is one of the most promising methods for the generation of cost-effective electricity. TE devices have applications in many fields especially microelectronics devices due to their simple device structures. TE generation using Seebeck effect requires both n-type and p-type TE materials for the efficient conversion; however, deterioration of n-type nature due to air oxidation has been the critical issue. Recently, we reported single-walled carbon nanotubes (SWCNT) sheet doped by 2-(2-methoxyphenyl)-1,3-dimethyl-2,3-dihydro-1H-benzimidazole (o-MeO-DMBI) showed n-type property and remarkable air-stability. We chose o-MeO-DMBI because of the following reasons; i) o-MeO-DMBI is stable under atmospheric conditions, ii) the cationic form of o-MeO-DMBI is also stable and, iii) n-doping of the other carbon materials such as fullerene and graphene has already been reported.[2,3] Here, we study the mechanism of the air stability of o-MeO-DMBI-doped SWCNT films by changing the doping level. eDIPS (Meijo Nano Carbon, EC1.5) was used as SWCNT. SWCNT films were dipped in the 0.01, 0.1, 1.0, 10 and 50 mM ethanol solutions of o-MeO-DMBI for 10 min and dried in vacuum at room temperature for 12 h. The time course of Seebeck coefficient of the SWCNT films dipped with various concentration of o-MeO-DMBI solution was studied. It is noted that the films were kept under air condition at room temperature to evaluate the air stability of the o-MeO-DMBI-doped SWCNT films. Positive value of Seebeck coefficient for 0.01 and 0.1 mM doped films indicated p-type, and negative value for 1.0, 10 and 50 mM doped films showed n-type nature of the films. Interestingly, we found that Seebeck coefficient of 1.0 mM doped film changed to positive, while 10 mM doped film showed stable negative value. From above results, we conclude that the mechanism of the air-stabilization of n-doping is the passivation effect by the formation of o-MeO-DMBI layer onto the surface of SWCNT films.
for higher temperature application, reducing conductivity mass for higher mobility or band convergence for dramatic increase in density of states (Pb(Se,Te), Mg(Si,Mn), Bi(Se,T,Te)3). In principle all of these defects can be better controlled by engineering chemical potentials through phase boundaries. Even if the Ni content MnSn (M = Ti, Zr, Hf) Half-Heusler thermoelectrics can be sufficiently altered to make substantial differences in electronic properties. The excess Ni produces impurity states in the band gap that changes the effective band gap and leads to additional electron and phonon scattering.

8:30 AM TP03.10.02 YbSiGe—A Promising Thermoelectric Material with High Power Factor at Room Temperature Sora-At Tanusilp1, Yuji Ohishi1, Hiroaki Muta1, Akinori Nishide2, Jun Hayakawa2 and Ken Kurosaki1,2,4, Osaka University, Osaka, Japan; 3Hitachi, Ltd., Tokyo, Japan; 4University of Fukui, Fukui, Japan; 5JST, PRESTO, Saitama, Japan.

Metal silicide-based thermoelectric (TE) materials have been widely attracted attention, because they are less toxic, low production cost, and high chemical stability. Recently, it has been reported that YbSi1.8 shows high electrical conductivity (σ) accompanied by uncommonly large Seebeck coefficient (S) probably due to intermediate valence mechanism of Yb (Yb2+/Yb3+), leading to high-power factor (σS) 2.2 mW/mK2 at room temperature [6–8]. Here, we demonstrated that Yb(Si1.8Ge0.2) is a more promising TE material. The substitution of Ge on the Si site changes the Yb2+/Yb3+ ratio and transform the phase from the AI2B type (random defects in the Si site) to the ThPd1 type (ordered defects in the Si/Ge site). It is revealed that the x = 0.5, i.e., YbSiGe, is the best composition with the highest power factor 3.6 mW/mK2 at room temperature, which is comparable to or higher than those of conventional TE materials. Furthermore, the lattice thermal conductivity (κ/l) of Yb(Si1.8Ge0.2) is significantly reduced because the substituted Ge acts as scattering centers of heat carrying phonons. The enhanced S and reduced κ/l lead to 80% enhancement in the zT value is 0.13 at room temperature.

8:45 AM TP03.10.03 Creating Zipper-Like van der Waals Gap Discontinuity in Low-Temperature-Processed Nanostructured PbBi2nTe1+3n for Enhanced Phonon Scattering and Improved Thermoelectric Performance Yue Wu and Wei Zheng; Iowa State University, Ames, Iowa, United States.

Nanoengineered materials can embody distinct atomic structures that deviate from the bulk-grain counterpart and induce significantly modified electronic structure and physical/chemical properties. Besides, the phonon structure and thermal properties that can also be potentially modulated due to the modified atomic structure in nanostructured material, however, are seldom investigated. In this presentation, we will discuss a mild approach to fabricate nanostructured PbBi2nTe1+3n using solution-synthesized PbTe-Bi2Te3 nanoheterostructure as a precursor. The as-obtained monoliths have unprecedented atomic structure differing from the bulk counterpart, especially the zipper-like van der Waals gap discontinuity and the random arrangement of septuple-quintuple layers. These structural motifs break the lattice periodicity and coherence of phonon transport, leading to ultra-low thermal conductivity and excellent thermoelectric zT. We anticipate that this strategy can be widely applicable to fabricate existing thermoelectric compounds into their nano forms with unique atomic structures and good performances.

9:00 AM TP03.10.04 Thermoelectric Properties of All-Inorganic Halide Perovskite Nanowires Wooshal Lee; Mechanical Engineering, University of Hawaii at Manoa, Honolulu, Hawaii, United States.

Controlling the flow of thermal energy is crucial to numerous applications ranging from microelectronic devices to energy storage and energy conversion devices. I will present experimental ultralow lattice thermal conductivities of solution-synthesized, single-crystalline all-inorganic halide perovskite nanowires composed of CaPbI3, CsPbBr3, and CsSnI3. I will also discuss mechanisms behind ultralow thermal conductivity values of all-inorganic halide perovskites. Further, I will present a rare combination of ultralow thermal conductivity and high electrical conductivity of CsSnI3, which is a promising candidate for thermoelectric applications.

9:15 AM TP03.10.05 Hyper-Doped Nanocrystalline Silicon Thin Films for Low-Temperature ThermoElectric Harvesting—Energy Filtering and the Role of Hydrogen Dario Narducci, Laura Zuliani, Carlos J. Álvarez, Andrea P.C. Campos, Claude Alfonsi, Marion Descoins, Dominique Mangelinck, Xanthipp Zanni and Ahmed Charal; 1Department Materials Science, University of Milano Bicocca, Milan, Italy; 2Laboratoire IM2NP, CNRS, Aix Marseille Université, Marseille, France; 3Dept. of Aircraft Technology, Technological Educational Institution of Sterea Ellada, Psachna, Greece.

Despite its intrinsic low thermoelectric figure of merit, silicon has found applications in low-temperature thermal microharvesting due to the available know-how for planar manufacturing [1,2]. In recent years, many groups have revived the interest toward enhancing silicon ZT [3]. This can be achieved either by reducing the thermal conductivity of single-crystalline silicon [4] or increasing the power factor (PF) of polycrystalline silicon. Some of the present authors reported in 2010 [5] first evidence about the possibility of enhancing the power factor (PF) of nanocrystalline silicon by a factor 10 through the controlled precipitation of second phases at grain boundaries. Such results were extensively confirmed [6–8], and modeling showed that enhanced PF was mostly related to energy filtering by potential barriers at grain boundaries [9,10]. However, effort to move these results toward production has shown that PF enhancement is more elusive than expected, with a puzzling dependence upon sample size. This communication reports about the analysis of the dependence of PF upon sample size in hyper-doped p-type nanocrystalline Si thin films. Nanocrystalline Si thin films were deposited by PECVD on SiO2 and then ion-implanted with B+ After damage recovery, samples were cut to varied sizes and submitted to annealing for 2 h at 1000 °C in Ar. Their electrical conductivity and Seebeck coefficient were found to depend on the sample size, with a standard PF of 1.3 mW/mK2 in 200-nm wafers that raises to 13.6 mW/mK2 in 5x50 mm2 chips. Analyses by transmission electron microscopy, high-resolution scanning electron microscopy, and atomic probe tomography could prove that the disappearance of PF enhancement in wafer-scale samples was due to the combined effect of B-H complexation and incomplete implantation damage recovery at film surface. These results indicated proper remediation measures, therefore opening the path toward full industrial exploitation of silicon as a high-performance material for heat microharvesting in the low-temperature range. Possible applications of integrated thermoelectric harvesters will be discussed.

References
Al2Fe3Si3 phase forms a narrow band gap near the Fermi level and has shown potential as a thermoelectric material. We demonstrated that fine tuning of phonon scattering improved the power factor at mid temperatures using machine-learning-assisted synthesis [3]. However, a remaining important issue is to develop the anomalously low observed value being in fact due to microstructure, i.e. to grain boundary scattering of phonons due to polycrystallinity, which we model by Casimir scattering (anisotropy and isotopic scattering affect the conductivity at the level of 10% at room temperature). We use the calculated thermal conductivity to estimate $\kappa_T$ for a range of different situations, also including effects of grain boundaries on electrical conductivity and Seebeck effect.

9:00 AM BREAK

10:30 AM TP03.10.08
Internal-Strain Softening Significantly Reduces Thermal Conductivity and Leads to High ThermoElectric Efficiency PbTe—Reconsidering Phonon Scattering Riley C. Hanus1, Matthias T. Agne1, Zhiwei Chen1, Yanzhong Pei1, Peter W. Voorhees1 and G. J. Snyder1; 1Northwestern University, Chicago, Illinois, United States; 2Materials Science and Engineering, Tongji University, Shanghai, China.

The influence of micro/nanostructure on thermal conductivity is a topic of great scientific interest and of particular technological importance to thermoelectrics. The current paradigm of understanding is that structural defects primarily decrease thermal conductivity through phonon scattering where the phonon dispersion (and thus the speeds of sound) are fixed when describing the thermal transport, especially when chemical composition is unchanged. Experimental work on a PbTe model system is presented which shows that the speed of sound significantly decreases in PbTe with increasing internal-strain which completely accounts for the reduction in lattice thermal conductivity without assuming an increase in phonon scattering centers. Furthermore, we experimentally show that internal-strain is linearly related to the materials speed of sound, which provides evidence for the thermodynamic origin of this phenomena. It is also shown that this mechanism is a major part of the reduction in thermal conductivity and the resulting improvement in thermoelectric figure of merit in high efficiency PbTe ($\kappa_T > 1$). This presents new avenues to engineer thermal conductivity, beyond phonon scattering, by modifying the phonon dispersion relation (i.e. speeds of sound and lattice stiffness) with microstructural defects and internal-strain, and shines new light on studies of thermal conductivity in fields of energy materials, microelectronics, and nano-scale heat transfer.

10:45 AM TP03.10.09
Development of Low-Cost and Non-Toxic Al2Fe3Si3 Thermoelectric Material—Experiment, Theoretical Calculation and Machine Learning Prediction Yoshiki Takagiwa1, Yukihiro Isoda1, Masahiro Goto1, Yosikazu Shinohara1, Zhufeng Hou1, Yibin Xu1 and Koji Tsuda2, 3; 1National Institute for Materials Science, Tsukuba, Japan; 2The University of Tokyo, Kashiwa, Japan.

To develop new thermoelectric materials that are low-cost and non-toxic with sufficient power output toward practical applications, in particular, at a low-temperature region below 400 K, we performed materials screening of Al-Fe-Si ternary system using band structure calculations [1,2]. We found that $\tau_1$-Al2Fe3Si3 phase forms a narrow band gap near the Fermi level and has shown potential as a thermoelectric material. We demonstrated that fine tuning of the $\tau_1$ ratio could control its conduction type and enhance power factor without chemical substitutions [2]. Relatively large power factors exceeding 500 $\mu$W/mK$^2$ were obtained for both p- and n-type materials below 400 K, which can be used in such as sensor applications. Recently, we succeeded in an enhancement of power factor at mid temperatures using machine-learning-assisted synthesis [3]. However, remaining important issue is to develop the single phase of Al2Fe3Si3 and optimize the sample composition for better thermoelectric performance. In this presentation, we will review the recent progress of newly developed thermoelectric material Al2Fe3Si3 and discuss how to enhance the power output toward practical usage.


11:00 AM TP03.10.10
High Sn-type Thermoelectric Power Factor and Efficiency in Ba$_2$Sb$_5$ from a Highly Dispersive Band Junsoo Park1, 2, 4, Yi Xia1 and Vidvuds Ozolins5, 6; 1Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California, United States; 2Applied Physics, Yale University, New Haven, Connecticut, United States; 3Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, United States; 4Energy Sciences Institute, Yale University, West Haven, Connecticut, United States.

Using first-principles density-functional theory calculations, we predict the potential for unprecedented $\xi T$ge5$ at 800 K in SnS-type Ba$_2$Sb$_5$. The $\xi T$ value reaches 7$\mu$W/mK$^2$ at 800 K, which is significantly higher than that of other SnS-type materials. Such a high efficiency arises from intrinsically ultralow lattice thermal conductivity coupled with very high power factor reaching 7
mW m$^{-1}$K$^{-1}$, which is higher than that of PbTe. The main reason for such a high $zT$ was low thermal conductivity, i.e., 1.09 W/mK at 923 K. Our developed modeling based on dependent phonon scattering, i.e., coherent phonon scattering, adequately explain extremely low thermal conductivity of SnTe nanocomposites. We found that with same concentration of impurities which scatters phonons, coated grain nanocomposite shows lower thermal conductivity compared with that of nanoparticle nanocomposite.

1:45 PM TP03.10.11

Thin Film Tin Selenide (SnSe) Thermoelectric Generators Exhibiting Ultra Low Thermal Conductivity Matthew R. Burton1, Tianjun Liu2, James McGettrick3, Shahin Mehraban1, Jennifer Baker1, Adam Pocock1, Trystan Watson1, Oliver Fenwick2 and Matt Carnie1; 1Swansea University, Swansea, United Kingdom; 2School of Engineering and Materials Science, Queen Mary University of London, London, United Kingdom.

Tin selenide (SnSe) has attracted much attention in the field of thermoelectrics since the discovery of the record figure of merit ($zT$) of 2.6 ± 0.3 along the $b$-axis of the material. The record $zT$ is attributed to an ultralow thermal conductivity that arises from anharmonicity in bonding. Whilst it is known that nanosstructuring offers the prospect of enhanced thermoelectric performance, there has been minimal studies in the literature to date of the thermoelectric performance of thin films of SnSe. Tin selenide (SnSe) has attracted much attention in the field of thermoelectrics since the discovery of the record figure of merit ($zT$) of 2.6 ± 0.3 along the $b$-axis of the material. The record $zT$ is attributed to an ultralow thermal conductivity that arises from anharmonicity in bonding. Whilst it is known that nanosstructuring offers the prospect of enhanced thermoelectric performance, there has been minimal studies in the literature to date of the thermoelectric performance of thin films of SnSe. In this presentation, we will demonstrate the first known example of a working thin-film SnSe thermoelectric generator [1], fabricated in an extremely simple thermal evaporation method. Seebeck coefficients are comparable to that seen in bulk SnSe, whilst materials characterisation reveals that the microstructure of the SnSe material is of a preferentially orientated porous network of thin film SnSe nanosheets which exhibited an unprecedentedly low thermal conductivity of 0.08 W m$^{-1}$K$^{-1}$ between 375 K and 450 K which can be primarily attributed to the reduction of the lattice component.


1:30 PM TP03.10.12

Copper Iodide-Based Composite Materials for Thermoelectric Application Shiejiang Bai; Institute of Materials Research and Engineering, A*STAR, Singapore, Singapore.

Novel hybrid thermoelectric materials have attracted great attentions for their potential applications for thermal energy conversion and sustainable environment. As an environment-friendly, abundant, economic and semiconducting material with broad band gap values, copper iodide has been systematically investigated in the research areas of photophysics, photochemistry and light-emitting diodes. A recent report demonstrates a promising room temperature thermoelectric performance of ZT = 0.21. We are exploring inorganic-organic thermoelectric composites using molecular materials. In this presentation, a series of copper iodide-based thermoelectric composites with robust pellets and low densities shall be introduced. The fabrication procedure, structures, recyclable electrical conductivities and Seebeck coefficients will be discussed.

SESSION TP03.11: High Temperature Inorganic Thermoelectric Materials

Session Chairs: Jenny Pringle, Jeff Snyder and Dongyan Xu
Thursday, November, November 29, 2018
Sheraton, 3rd Floor, Gardner AB

1:30 PM TP03.11.01

Coherent Phonon Scattering in SnTe Nanocomposite Resulting in High Thermoelectric Performance Junphil Hwang1,2, Jisook Hong1, Mi-Kyung Han2, Ji Hoon Shim3, Sung-Jin Kim2, Ying-Shi Jin2, Hoon Kim2, Jiyoung Kim1, Hwanjoo Park1 and Woohul Kim1; 1School of Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of); 2Department of Chemistry and Nano Science, Ewha Womans University, Seoul, Korea (the Republic of); 3Department of Chemistry, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

We are reporting that coherent phonon scattering can induce severe thermal conductivity reduction while maintaining electrical transport which is ideal for thermoelectric application. SnTe has been drawn attention for last several years to replace Pb containing thermoelectric materials especially PbTe. However, larger thermal conductivity compared with that of PbTe hinders higher thermoelectric performance. We synthesized polycrystalline SnTe where the grain boundaries were coated by nanosized CdTe, SnO2, SnTe particles which were clarified by TEM study. The thermoelectric figure of merit ($zT$) for the SnTe nanocomposites is 2.18 at 923 K which is higher than that of PbTe. The main reason for such a high $zT$ was low thermal conductivity, i.e., 1.09 W/mK at 923 K. Our developed modeling based on dependent phonon scattering, i.e., coherent phonon scattering, adequately explain extremely low thermal conductivity of SnTe nanocomposites. We found that with same concentration of impurities which scatters phonons, coated grain nanocomposite shows lower thermal conductivity compared with that of nanoparticle nanocomposite.

1:45 PM TP03.11.02

Low Cost Scalable Printed Tin Selenide (SnSe) for Thermoelectric Generators Matthew R. Burton, Shahin Mehraban and Matt Carnie; University of Swansea, Swansea, United Kingdom.

Tin selenide (SnSe) sparked much interest in the field of thermoelectrics when Zhao et al.[1] reported an unprecedented ZT of 2.6 ± 0.3 at 923 K along the $b$-axis. This discovery was observed in single crystals formed at high temperature (1223 K) over several hours. Whilst doping SnSe with elements such as Na[2] and Bi[3] have also shown promising thermoelectric performance, these too were shown on single crystals with expensive and lengthy fabrication techniques which are unfavorable for commercial applications. Since the discovery of the record ZT in single crystal SnSe,[1] studies on the thermoelectric performance of polycrystalline SnSe have been reported.[4]–[12] These fabrication techniques presented in the literature, however, require high temperature, lengthy fabrication times and in most cases high pressure. This makes these processes of fabrication unfavorable for commercial development.

In this work we present a cheap, facile and scalable technique, with the aim of producing a commercially viable thermoelectric device. Polycrystalline SnSe
was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

A lack of control over the dopability of thermoelectric materials continues to limit the efficiency of potentially good material systems. Phase boundary mapping has recently been shown to be an effective means of engineering defects in materials such as Mg2Sb, where Mg-rich conditions are required to overcome “killer defects” and achieve n-type behavior. Herein, we demonstrate that defect engineering is critical for efficient doping in a PbTe model system, validating the principles of phase boundary mapping in a material system that does not have a history of difficult dopability. PbTe ingots with increasing levels of n-type iodine dopant were annealed at 700 °C under Pb-rich and Te-rich partial pressures and quenched. Ingots annealed in Pb-rich conditions have degenerate, n-type thermoelectric properties typical of a good thermoelectric material, while the same materials annealed in Te-rich conditions show intrinsic, poorly performing properties and are p-type at lower doping levels. The drastic difference in performance agrees with expectations from a defect model and demonstrates the effectiveness of phase boundary mapping to engineer dopability in PbTe. Using the same experimental technique, it was possible to repeatedly switch between degenerate n-type and non-degenerate p-type conduction in a single material. This behavior corresponds to the subtle change in composition associated with crossing the small phase width of the single-phase region of the phase diagram.

The AgSbTe2 compound is a promising p-type semiconductor. The δ phase, which is stable between about 600 and 550° C, and exists metastable after reducing conditions show intrinsic, poorly performing properties and are p-type at lower doping levels. The drastic difference in performance agrees with expectations from a defect model and demonstrates the effectiveness of phase boundary mapping to engineer dopability in PbTe. Using the same experimental technique, it was possible to repeatedly switch between degenerate n-type and non-degenerate p-type conduction in a single material. This behavior corresponds to the subtle change in composition associated with crossing the small phase width of the single-phase region of the phase diagram.

Research on thermoelectric (TE) materials has experienced a considerable increase in interest within the last years. The design of different microstructures and new classes of materials like complex chalcogenides is considered a promising approach for improving the efficiency of potential TE materials [1]. TE materials directly convert heat into electricity through the Seebeck effect. The conversion efficiency is determined by the dimensionless figure of merit, ZT, which depends on the thermal conductivity κ, electrical conductivity σ, and the Seebeck coefficient S and the temperature T. Attempts to optimize ZT require reducing κ, while maintaining relatively high values of σ and S.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.

was fabricated by low-cost ball milling of the constituent elements. Films were printed in a water-based ink using carboxymethyl cellulose as a binder. The effect of variation of the binder concentrations on properties (including electrical conductivity, Seebeck coefficient and thermal conductivity) were studied. Thermoelectric characterization of the printed polycrystalline SnSe, reveals peak ZT ~0.14 at 760 K, which is comparable to examples in the literature for polycrystalline SnSe.
discuss the impact of this different microstructural features on the performance of our compounds [3].


2:45 PM TP03.11.06
TE Thin-Film Materials from Organic Electronics Xizu Wang; IMRE, Singapore, Singapore.

In the past two decades, materials and thin film structures that were well-known for their applications in organic electronic devices, such as LEDs and solar cells, had found new applications through engineering of their semiconductor properties, nanoscale structures, and designs. In our research, we have found many thin film materials in organic solar cells to be the strong candidates for novel applications in thermoelectric devices. Here we report some high performance thermoelectric thin films based on materials commonly used in organic electronics, including PEDOT:PSS, ITO, P3HT and inorganic-organic MAPbI₃ perovskite crystals. The high electrical conductivity of 2980 S/cm and correspondingly high power factor of 142 µW/mK² are observed in anhydrous, treated PEDOT-PSS thin films. Ultra-high Seebeck coefficient and low thermal conductivity are obtained in a centimeter-sized perovskite single crystal. Furthermore, we discover some newly optimized methods for the enhancement of thermoelectric properties of ITO, P3HT and AZO thin films and devices. Our investigations show that materials discovery and development for thermoelectric applications can be accelerated by re-engineering of materials conventionally used in organic electronics.

**SYMPOSIUM X**

Frontiers of Materials Research
November 26 - November 29, 2018

**Symposium Organizers**
Kristen Brosnan, GE Global Research
David LaVan, National Institute of Standards and Technology
Patrycja Paruch, University of Geneva
Joan Redwing,
Takao Someya, The University of Tokyo

* Invited Paper

**SESSION X.01**
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Grand Ballroom

12:15 PM *X.01.01

Atomically-resolved imaging of materials has become the mainstay of modern materials science, as enabled by advent of aberration corrected scanning transmission electron microscopy (STEM). However, the wealth of quantitative information contained in the fine details of atomic structure or spectra remains largely unexplored. In this talk, I will present the new opportunities enabled by physics-informed big data and machine learning technologies to extract physical information from static and dynamic STEM images, ranging from statistical thermodynamics of alloys to kinetics of solid-state reactions on a single defect level. Synergy of deep learning image analytics and real-time feedback further allows harnessing beam-induced atomic and bond dynamics to enable direct atom-by-atom fabrication. Examples of direct atomic motion over mesoscopic distances, engineered doping at selected lattice site, and assembly of multilitermic structures will be demonstrated. These advances position STEM towards transition from purely imaging tool for atomic-scale laboratory of electronic, phonon, and quantum phenomena in atomically-engineered structures.

**Biography:**
Sergei Kalinin is the director of the Institute for Functional Imaging of Materials (IFIM) and distinguished staff member at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory. He received his MS degree from Moscow State University in 1998 and Ph.D. from the University of Pennsylvania (with Dawn Bonnell) in 2002. His research presently focuses on the applications of big data and artificial intelligence methods in atomically resolved imaging by scanning transmission electron microscopy and scanning probes, as well as mesoscopic studies of electromechanical and transport phenomena via scanning probe microscopy. Sergei has co-authored >600 publications, with a total citation of >25,000 and an h-index of >77. He is a fellow of MRS, APS, IoP, IEEE, Foresight Institute, and AVS; a recipient of the RMS medal for Scanning Probe Microscopy (2015); Presidential Early Career Award for Scientists and Engineers (PECASE) (2009); Burton medal of Microscopy Society of America (2010); 3 R&D100 Awards (2008, 2010, and 2016); and a number of other distinctions.
Recent advances in soft electronics have attracted great attention due in large to its potential applications in personalized bio-integrated healthcare devices. The mechanical mismatch between conventional electronic/optoelectronic devices and soft human tissues/organs often causes various challenges, such as the low signal to noise ratio of biosensors, inflammations and/or excessive immune responses near implanted sites, and discomfort and consequent stress to users. Ultra-flexible and stretchable electronic devices have low system modulus and intrinsic softness, and thereby have potential to solve these issues. Nanomaterials are particularly beneficial in realizing these flexible and stretchable electronics due to their intrinsic ultraflexibility thanks to nanoscale dimensions. Here, our unique strategies in the synthesis of nanomaterials, their seamless integration with electronics, and unconventional biomedical device designs toward implantable and wearable bioelectronics are presented. These implantable and wearable bioelectronic systems combine recent breakthroughs in unconventional soft electronics to address unsolved issues in the clinical medicine.

Biography:
Dae-Hyeong Kim obtained B.S. and M.S. degree in Chemical Engineering from Seoul National University, Korea, in 2000 and 2002, respectively. He received Ph. D. degree in Materials Science and Engineering from University of Illinois at Urbana Champaign in 2009. From 2009 to 2011, he was a post-doctoral research associate at University of Illinois. He joined Seoul National University in 2011 and is currently an associate professor in the School of Chemical and Biological Engineering of Seoul National University. He has published more than 75 papers and 25 international and domestic patents. He has been recognized with several awards including George Smith Award (2009), MRS Graduate Student Award (2009), Green Photonics Award (2011), TR 35 award (2011), Hong Jin-ki Creative Award (2015), SCEJ Award (2016), and Korea Young Scientist Award (2017).

What is Next for Solar PV Technology? Mariana I. Bertoni; Arizona State University, Tempe, Arizona, United States.

The solar PV market is far from slowing down in demand or popularity and in the last seven years we have seen it moved from niche generation to reaching grid parity and becoming a mainstream electricity generation source. The reality of silicon module prices below US$0.4/W and projections of US$0.2/W has fundamentally changed solar R&D.

As we move towards an “electric-powered world” and everything around us starts demanding electricity in a clean and efficient way, new challenges arise. Similar to many consumer applications, solar margins will improve and R&D hurdles centered around aesthetics, customization and functionality will be part of our everyday life. In this talk, I will introduce approaches to achieve high power in small areas and the use of sustainable materials for device manufacturing. I will discuss the importance of understanding the defects that underpin performance under real operating conditions and how can we accelerate discovery and defect engineering to facilitate high-power, portable and reliable devices.

Mariana Bertoni is an assistant professor at Arizona State University and the lead of the Next Generation Modules Testbed at the Quantum Energy and Sustainable Solar Technology Engineering Research Center. She received her BS and MS degree from the Buenos Aires Institute of Technology and her PhD degree in Materials Science from Northwestern University in 2007. She held senior scientist positions at two start-up firms in the photovoltaic industry and her previous postgraduate experience includes a postdoctoral appointment at MIT and a Marie Curie postdoctoral fellowship in Germany.

Biography:
She is a pioneer in correlative X-ray microscopy approaches to engineer defects in solar absorbers. She has received numerous awards, including the Edward C. Henry Award from the American Ceramic Society, a Marie Sklodowska-Curie Fellowship from the EU and a Fulbright Scholarship. She was selected to NAE’s 2017 U.S. Frontiers of Engineering. She has co-founded two companies commercializing technology from her lab.

Bottom-Up Grown Nanowire Quantum Devices Erik P. Bakkers1, 2; 1Department of Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; 2QuTech and Kavli Institute of NanoScience, Delft University of Technology, Delft, Netherlands.

Signatures of Majorana’s have been obtained in devices based on InSb nanowires coupled to a superconductor [1]. Different schemes for uncovering their
unique non-Abelian statistics are proposed, for which a nanowire network assembly is needed. Here, we demonstrate a generic process by which we can design any proposed nanowire network device by manipulating an InP substrate and thereby the nanowire growth position and orientation [2]. Nanowire “hashtag” structures are grown in which phase coherent transport is demonstrated by the Aharonov–Bohm (AB) effect. In addition, we can in-situ grow epitaxial Al islands on the nanowires, resulting high quality interfaces. We employ here self-shadowing structures, such that complete device can be realized by bottom-up grown techniques. With these new devices we have observed a quantized Majorana signal [3].


Biography:
After obtaining his PhD in nanoelectrochemistry at the University of Utrecht, Erik started working at Philips Research in Eindhoven in 2000. He started his own research group, and the team focused on nanowires - lines of material with a width of several tens of nanometers- an area he continues to research, looking at integration into semiconductors in particular. In 2010, his growing interest in fundamental research resulted in Erik joining the Technical University of Eindhoven as well as Delft Technical University as part-time professor in the Quantum Transport group. His current interest is in Quantum Materials, to detect and manipulate Majorana states, and in Hexagonal Silicon, to demonstrate and exploit the predicted direct band gap in this material. He has received the Technical Review award from MIT, VICI grant, ERC CoG, and the Science AAAS Newcomb Cleveland Prize.